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Full-scale study of removal effect on Cyclops of zooplankton with chlorine dioxide

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Abstract: Cyclops of zooplankton propagated excessively in eutrophic water body and could not be effectively inactivated by the conventional disinfections process like chlorination due to its stronger resistance to oxidation. In this paper, a full-scale study of chlorine dioxide preoxidation cooperating with routine clarification process for Cyclops removal was conducted in a waterworks. The experimental results were compared with that of the existing prechlorination process in several aspects: including the Cyclops removal efficiencies of water samples taken from the outlets of sedimentation tank and sand filter and the security of drinking water and so on. The results showed that chlorine dioxide might be more effective to inactivate Cyclops than chlorine and Cyclops could be thoroughly removed from water by pre-dosing chlorine dioxide process. The GC-MS examination and Ames test further showed that the sort and amount of organic substance in the treated water by chlorine dioxide preoxidation were evidently less than that of prechlorination and the mutagenicity of drinking water treated by pre-dosing chlorine dioxide was substantially reduced compared with prechlorination.

Keywords: Cyclops of zooplankton; chlorine dioxide; chlorine; preoxidation; water treatment

Introduction

Cyclops of zooplankton excessively propagated in eutrophic water reservoir or fresh lake as source of urban water supply, which brought several researchers to take an active interest in (Cui, 2002). Cyclops could not be effectively inactivated by the conventional disinfections such as chlorination due to its stronger resistance to oxidation. In addition, the motility of Cyclops made it easily penetrate sand filter into the clean water tank in waterworks even municipal service pipe. Adult Cyclops with body length of one to several millimeters, may be caught by naked eye to bring consumers unsanitary sense and may become disease transmission medium as the host of pathogenic parasite, like schistosome or eelworm, to threaten human health. For example, Guineaworm disease still affected a large number of people in rural areas in tropical countries and Olajide *et al*. (Olajide, 1987) pointed out that this disease could be effectively controlled by killing the intermediate host Cyclops. The references showed that present study to settle the danger to drinking water security of zooplankton was little and limited in conventional water treatment process. Lupi *et al*. (Lupi, 1994) showed that flocculation and sand filtration processes were insufficient to remove zooplankton normally present in surface water and nematodes and water flea might occur in treated water. Bernhardt *et al*. (Bernhardt, 1989) pointed out that the inactivation of zooplankton was necessary to eliminate zooplankton in water treatment process and rotifer abundance would be reduced from 20—300 ind./L to 0—5 ind./L in drinking water by oxidation with 2.5—3 mg/L of chlorine for 20 min. Mitcham *et al*. (Mitcham, 1983) found that ammonia-chlorine was more effective against Copepoda (Cyclops) but less effective against Cladocera (Daphnia and Bosmina). At present, most waterworks killed or inactivated Cyclops by prechlorination and removed it thoroughly from water by subsequent water treatment process. Although with a proven removal of Cyclops, prechlorination would reduce the drinking water security for increasing the halomethane content in treated water. So it was essential to explore a more effective and safe removal technique.

In this paper, a full-scale study of chlorine dioxide preoxidation cooperating with routine clarification process for Cyclops removal was conducted in Binxian Waterworks of Harbin. The removal efficiency of Cyclops by pre-dosing chlorine dioxide in water treatment process was comprehensively compared with that of the conventional prechlorination process. The results showed that chlorine dioxide preoxidation was an excellent substitute for the conventional pre-dosing chlorine process. Hence this provided a valuable basis for the further investigation on Cyclops removal from water treatment process.

1 Materials and methods

1.1 Site description

Binxian Waterworks locating in Heilongjiang Province used a eutrophic reservoir as water source, in which the amount of Cyclops has sharply increased due to eutrophication. The annual variations of the number of Cyclops in the raw water are shown in Fig.1. At present, the waterworks removed Cyclops by prechlorination with dosage of 3.0 mg chlorine/L, in this condition 80% of Cyclops was removed from water after filtration. The full-scale experimental investigation intended to replace liquid chlorine-by-chlorine dioxide for Cyclops removal. The water treatment process adopted in the waterworks is shown in Fig.2. During the study, the water quality indexes were as follows: average water temperature 19℃, turbidity 13 NTU, COD_{Mn} 5.68 mg/

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L, pH 7.3, algae density 2.61×10^6 ind./L, and Cyclops density 24 ind./L.

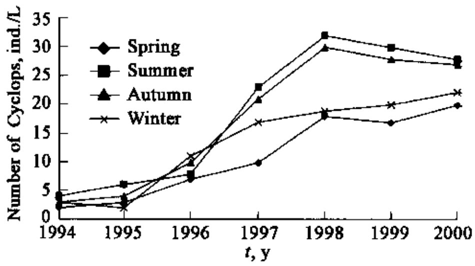

Fig.1 Annual variations of the number of Cyclops in raw water

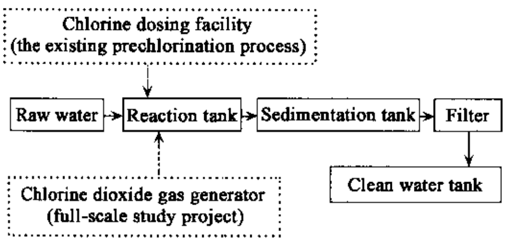

Fig.2 Flow chart of full-scale study of two preoxidation processes

1.2 Experimental equipment

The chlorine dioxide gas generator, manufactured by ourselves. Componential analysis of chlorine dioxide gas is listed in Tablet 1; QP5050A type gas chromatograph-mass spectrometer. Shimadzu Instruments Factory; TA100 and TA98 strains without metabolic activation S9, attained from Harbin Medical University.

Table 1 Componential analysis of chlorine dioxide gas

Chemical composition	Chlorine dioxide	Chlorine	Chlorite	Chlorate
Percentage composition, %	82.3	10.4	5.2	2.1

1.3 Methods

Cyclops was determined by microscopic count method, by which the changes of Cyclops number between raw water and treated water from sedimentation tank and sand filter were investigated.

Chlorine dioxide was generated by mixing hydrochloric acid solution (23% weight) and sodium chlorite solution (25% weight) in a weight ratio of 1∶1, so exceeding about 300% of the stoichiometric acid demand, in order to improve the efficiency and to obtain a lower Cl_2, ClO_2^- and ClO_3^- production. Componential analysis of chlorine dioxide was measured by iodimetry.

Raw water and treated water by chlorine dioxide or chlorine preoxidation were sampled by 250 L for each respectively. Organic substances in water samples were enriched with macroporous resin and then were eluted with about 60 ml of carbinol. The carbinol samples containing organic substances were concentrated to about 1 ml with K-D concentrator. The concentrated samples were examined in duplicate with gas chromatograph-mass spectrometer(GC-MS) and tested by Ames test procedure using TA100 and TA98 strains without metabolic activation S9 at increasing doses of concentration(corresponding to 1, 3, 5 and 7 L of equivalent volume per plate).

2 Results and discussions

2.1 The removal effect of dosage of ClO_2 on Cyclops

The oxidant, chlorine dioxide, was added into reaction tank together with coagulant, 15 mg/L of $AlCl_3$, and chlorine dioxide dosage ranged from 0 to 1.0 mg/L during the full-scale study. The results are shown in Fig.3. As can be seen, the removal effects were strengthened gradually with the increase of the dose of ClO_2. 100% of removal effect in treated water from sand filter may be attained by 1.0 mg/L of ClO_2. In addition, 10% and 40% of removal rate may be attained by sedimentation and filtration process respectively under no chlorine dioxide dosing condition.

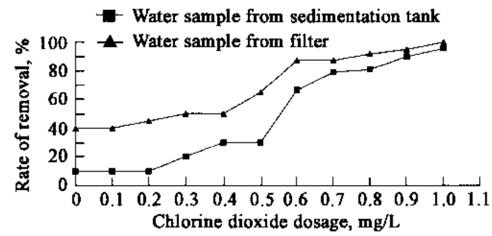

Fig.3 Comparison of removal effect on Cyclops in two different processes

The removal of Cyclops in water treatment process was the results of oxidizing inactivation by chlorine dioxide cooperating with clarification process. The removal rate of Cyclops were 10% and 40% respectively by sedimentation and filtration with no chlorine dioxide dosing, which showed that Cyclops could be partially removed from water by single clarification process. The vitality of Cyclops in raw water was found to be distinct, namely, the activity of larve and senile Cyclops were obviously weaker than that of mature Cyclops. So a part of weaker Cyclops may deposit together with the flock formed in flocculation process or be captured by sand filter. But the removal effect on Cyclops by single clarification process was finite because Cyclops with stronger vitality still might penetrate sand filter and the further removal of it needed depend on the inactivation of oxidant preoxidation. The removal rate of Cyclops was no obviously increased under condition of lower chlorine dioxide dosage(< 0.5 mg/L), which showed that mature Cyclops could not be effectively inactivated with lower dose of chlorine dioxide due to its stronger resistance to oxidation and here the clarification process still could not capture this part of Cyclops. So to inactivate or weaken Cyclops with adequate available chlorine dioxide is key to remove Cyclops completely from water treatment system. More and more Cyclops could be inactivated or its vitality could be greatly weakened with the increase of ClO_2 dosing, which, similar to larve and senile Cyclops, was effectively removed from water by subsequent clarification process. The experimental results showed that the conventional clarification processes, sedimentation and filtration, play an important role in removing Cyclops but the inactivation of Cyclops by preoxidation with adequate available oxidant is essential to ensure drinking water security. Cyclops can be thoroughly removed from water by the cooperation of oxidant preoxidation and clarification process.

2.2 Comparison of removal effects of two preoxidation

processes

According to the above experimental results, 100% of Cyclops could be removed from treated water by 1.0 mg/L of ClO_2. At present, Binxian Waterworks removed Cyclops by prechlorination process with 3 mg/L of chlorine, by which a fair removal rate was attained. So during the full-scale study, the removal effect on Cyclops by chlorine dioxide preoxidation with 1.0 mg/L of ClO_2 was compared with the existing prechlorination process with 3.0 mg/L of chlorine. The results are shown in Fig.4. As can be seen, the removal effect of chlorine dioxide preoxidation was better than that of prechlorination. For instance, Cyclops was thoroughly removed from water body by filtration with chlorine dioxide, whereas only 80% of removal effect was attained with chlorine.

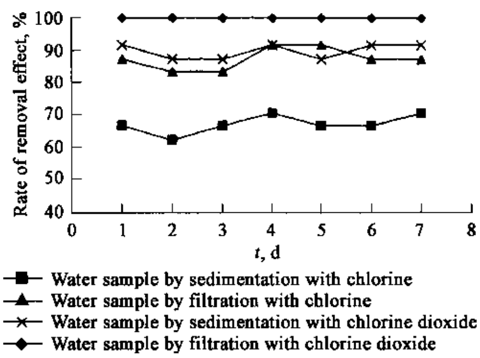

Fig.4 Comparison of removal effect on Cyclops in two different processes

Mature Cyclops hardly was removed from water by sedimentation unless it was effectively inactivated by oxidation with oxidant. The removal result of sedimentation tank showed that Cyclops inactivation of chlorine dioxide was superior to that of chlorine. For example, 90% of removal rate in treated water after sedimentation was attained by chlorine dioxide preoxidation, but for prechlorination, only 65% was attained. The distinct difference in Cyclops inactivation efficiency of two preoxidation processes may be the results of the body structure of Cyclops and the different performance of oxidant in oxidizing cellular tissue. Contrasted to common bacteria or virus, Cyclops has a special surface structure consisting of seven layers cell tissue such as bottom membrane, epithelium, calcific layer, etc. The body surface provides Cyclops stronger protection against oxidation. Cyclops can not 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 and not to participate in the activities of the oxidation-reduction system. So higher oxidizability of oxidant is key to thoroughly inactivate Cyclops. For chlorine in ClO_2, oxidation number is expressed as +4. According to counting, it contains 263% of available chlorine, i.e. oxidizability of ClO_2 is about 2.5 times as high as that of chlorine (Huang, 1997). So the ability of chlorine dioxide to oxidize Cyclops body structure is more effective than that of chlorine. In addition, after dissolving in water, 100% of ClO_2 exists in molecular state not reacting with water molecular like chlorine, which makes ClO_2 contact Cyclops surface easily and permeate it through into body inner to destroy inner cellular protein as to inactivate cyclops. The above advantages of chlorine dioxide not only result in a better inactivation of Cyclops but also a lower required amount of it than chlorine.

2.3 Influence of preoxidation on organic substances and mutagenicity

The GC-MS examination and Ames test were carried out with raw water sample and two treated water samples by preoxidation in order to value the security of drinking water. The GC-MS examination results are shown in Fig.5 to Fig.7 and Table 2. The Ames test results are shown in Fig. 8 and Fig.9.

2.3.1 GC-MS examination

Compared with that in raw water (Table 2), the amount of halogenated hydrocarbon in treated water by prechlorination increased to 13 species and 5 species were increased in the total amount of organic substance. As can be seen in Fig.6, the amount of organic species occurring in retention time between 20 min and 30 min accounted for 44.4% of total amount. Moreover, the intensity of spectrum peak was stronger and the area of peak was bigger in whole scanning area than that of the water sample by chlorine dioxide preoxidation.

Table 2 Analysis of GC-MS results of three water samples

Organic species	Raw water		Treated water by preoxidation			
			Chlorine		Chlorine dioxide	
	Amount	Peak area	Amount	Peak area	Amount	Peak area
Paraffin	22	50052134	19	83418846	14	38552821
Olefin	4	3703129	0	0	1	722801
Halogenated hydrocarbon	2	5619919	13	65706374	3	24916046
Arene	2	6571797	3	5218775	3	58537881
Heterocyclic compound	2	7668507	1	1626622	1	775786
Nitrogen compound	11	64235860	4	26415371	1	36663305
Benzene	7	236040538	5	108419603	6	134638566
Alcohol, aldehyde, etc.	21	386596361	31	333345213	12	81050299
Total	71	760488245	76	624150804	41	323173412

The amount of organic substance decreased to 41 species by chlorine dioxide preoxidation, which was equal to 57.5% of that in raw water (Fig.5). 85.4% of species were low boiling point and micromolecule organic substances, which occurred in retention time before 20 min. In addition, the number of halogenated hydrocarbon was only 3 species in treated water by chlorine dioxide preoxidation.

The total amount of organic substance by chlorine dioxide preoxidation was decreased to 41 species from 71 species of raw water, which was only about at half level of that by prechlorination, 76 species. Especially, the matters harmful to people's health, halogenated hydrocarbon, were only 3 species in treated water by chlorine dioxide preoxidation compared with 13 species of prechlorination. In addition, most of matters produced by chlorine dioxide preoxidation were low boiling point and micromolecule organic substances such as paraffin and alcohol etc., which almost accounted for 85.4% of total amount. But for prechlorination, about 55% of matters were macromolecule organic compounds with high boiling point such as halogenated hydrocarbon. The different reaction mechanisms of organic substances reacting with chlorine dioxide and chlorine caused diverse results in GC-MS examination. The free radical oxidation reaction happens when chlorine dioxide reacting with organic substances and the macromolecule organic compounds are oxidized into oxocompounds and micromolecule substances, in which some volatile compounds, even CO_2 and HO_2, are formed (Benjamin, 1986). Moreover, the stronger oxidizability of chlorine dioxide may easily oxidize organic substance to such products with low boiling point and minor molecular weight, which have short retention time in graphic of GC-MS examination. The electrophilic substitution reaction when chlorine oxidizing organic substance results in the formation of more mutagenic halogenated hydrocarbon such as trichloromethane, which belong to high boiling point and macromolecule organic compounds with long retention time (Reckhow, 1990; Langvik, 1994). In addition, much intermediate products such as aldehyde may be produced during chlorination due to no thoroughly oxidizing organic substances with chlorine, which results in the total amount of organic substance by prechlorination is more than that treated by chlorine dioxide preoxidation. So it can be said that the drinking water quality by chlorine dioxide preoxidation is better than that by prechlorination.

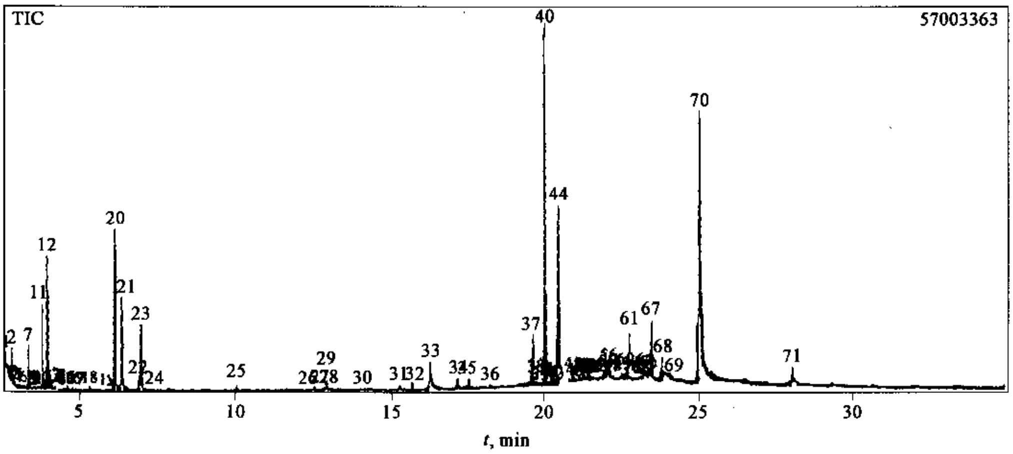

Fig.5 Graphic of total organic ions of raw water

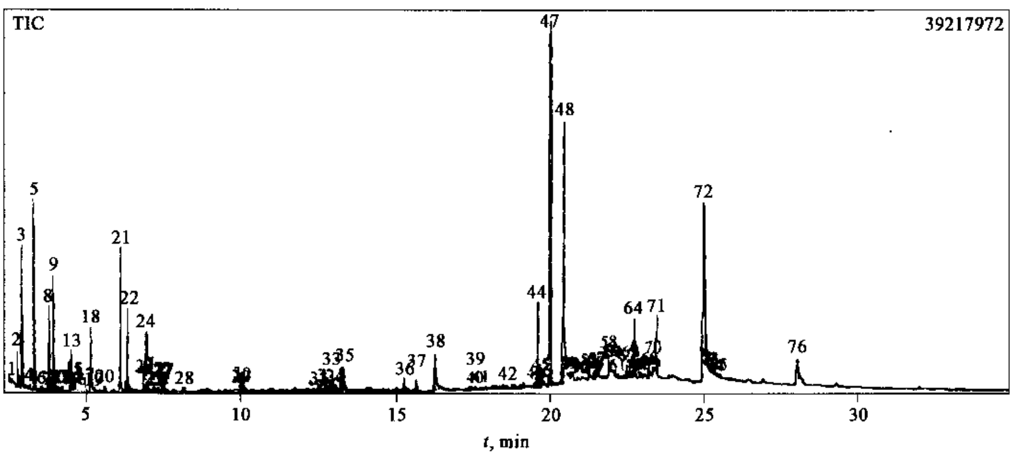

Fig.6 Graphic of total organic ions of water sample by prechlorination

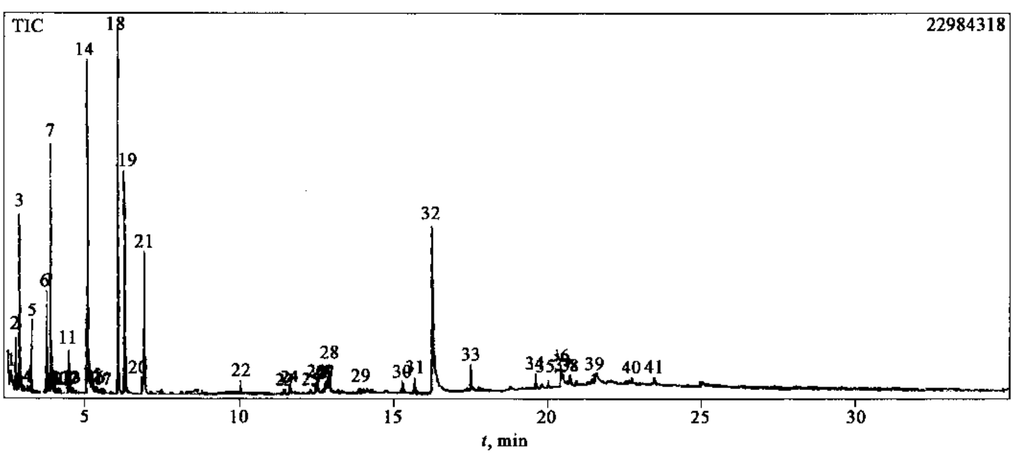

Fig.7 Graphic of total organic ions of water sample by chlorine dioxide preoxidation

2.3.2 The Ames test

The mutagenicity of concentrated water samples before and after preoxidation was expressed as *MR* value (rate of mutagenicity). The result with *MR* value greater than 2 was considered as having mutagenic activity. The results of Ames test are shown in Fig.8 and 9. As can be seen, the results of raw water have not behaved mutagenic activity under any dose condition and the *MR* value of water sample by prechlorination was higher than that by chlorine dioxide preoxidation at the same doses.

As is well known, TA98 strain is used to detect frame-shift point mutations and TA100 strain is applied to detect base pair substitution mutations. Cl_2-treated water showed mutagenicity with TA98 strain ($MR = 2.54$) and TA100 strain ($MR = 2.23$) at lower doses (5 L equivalent/plate), whereas ClO_2-treated water might have a lower mutagenic activity detectable only at the highest doses (7 L equivalent/plate), in which the *MR* value with TA98 and TA100 were 2.1 and 2.07 respectively. 13 species of halogentated compounds are formed during prechlorination due to electrophilic substitution reaction between chlorine and organic substances and the special chemical active group of them, halogen with stronger electrophonic effect, reinforces molecule polarity as to easily react with biologic enzyme system, during which the mutagenic action is attained by a series of chemical reactions such as DNA base substitution etc. (Langvik, 1994). Whereas less halogentated compounds (only one species) are formed during chlorine dioxide preoxidation due to different reaction mechanism, oxidation-reduction reaction not electrophilic substitution reaction, so that mutagenicity of ClO_2-treated water is obviously lower than that of Cl_2-treated. In addition, the mutagenicity of ClO_2-treated water occurs at the doses of 7 L equivalent/plate, which is alien to some previous Ames test results (Fiessinger, 1991; Huang, 1998). The reason may be caused by impurities special chlorine in chlorine dioxide gas produced by generator (Table 1). As can be seen, the amount of chlorine accounts for 10.4% of the total chlorine dioxide content, which may result in the mutagenic activity analogous to the result of prechloriation. This can be improved by enhancing chlorine dioxide gas purity with advanced generator.

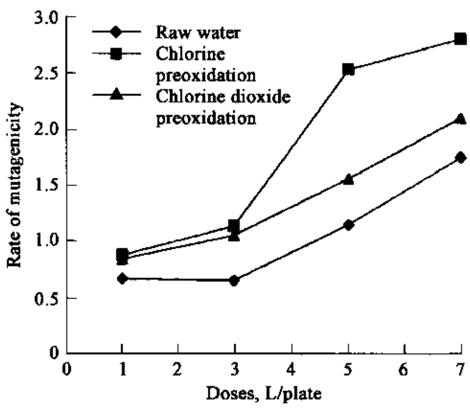

Fig.8 Changes of TA98-S9 dose-response relationship

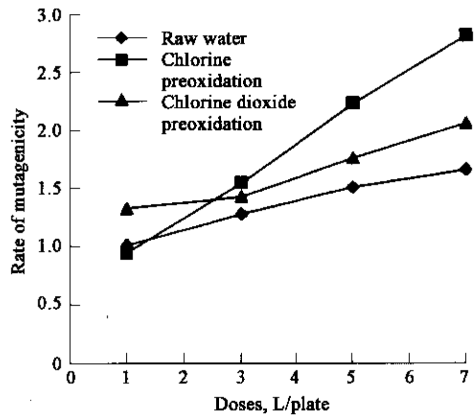

Fig.9 Changes of TA100-S9 dose-response relationship

3 Conclusions

Chlorine dioxide preoxidation possesses very favorable inactivation effect on Cyclops. Cyclops can be effectively removed from water body by chlorine dioxide preoxidation cooperating with the conventional clarification process, i.e. flocculation, sedimentation and filtration. The existing process of prechlorination can not attain the same removal effect as chlorine dioxide.

The GC-MS examination and Ames test further showed that the sort and amount of organic substances in treated water by chlorine dioxide preoxidation are evidently less than that of prechlorination, and the mutagenicity of drinking water is highly reduced. The advantage of chlorine dioxide disinfection may be further improved by enhancing chlorine dioxide gas purity.

References:

Benjamin W, Lukins Jr, Mark H G, 1986. Using chlorine dioxide for trihalomethane control[J]. AWWA, (786): 88—93.

Bernhardt H, Lusse B, 1989. Elimination of zooplankton by flocculation and filtration[J]. Aqua AQUAAA, 38(1): 23—31.

Cui F Y, Lin T, Ma F, 2002. The excess propagation and research on ecological control of the water flea of zooplankton in raw water[J]. Journal of HIT; 34 (3): 399—403.

Fiessinger F, 1991. Advantages and disadvantages of chemical oxidation and disinfection of ozone and chlorine dioxide [J]. Science of the Total Environment, (18): 245—246.

Huang J L, Wang L, Ren N Q, 1997. Disinfection effect of chlorine dioxide on viruses, algae and animal plankton in water[J]. Water Res, 31(3): 455—460.

Huang J L, Li B X, 1998. Comparison of the mutagenicity of drinking water with chlorine dioxide and chlorine disinfections[J]. Environment Chem, 17(4): 34—38.

Kouame Y, Haas C N, 1991. Inactivation of *E. coli* by combined action of free chlorine and monochlorine[J]. Water Res, 25(9): 1027—1032.

Langvik V, Holmbom B, 1994. Formation of mutagentic organic byproducts and aox by chlorination of fractions of humic water[J]. Water Re, 28(3): 553—557.

Liu D M, Cui F Y, Lin T *et al*., 2004. Preliminary study of biological control of cyclops of zooplankton in drinking water source [J]. Journal of Harbin Institute of Technology(New series), 11(2): 184—190.

Lupi E, Ricci V, Burrini D, 1994. Occurrence of nematodes in surface water used in a drinking water plant [J]. Journal of Water Supply Research Technology, 43(3): 107—112.

Lupi E, Ricci V, Burrini D, 1994. Occurrence of nematodes in surface water used in a drinking water plant [J]. Journal of Water Supply Research Technology, 43(3): 107—112.

Mitcham R P, Shelley M W, Wheadon C M, 1983. Free chlorine versus ammonic-chlorine: disinfection, trihalomethane formation, and zooplankton removal[J]. Journal of the American Water Works Association, 75(4): 196—198.

Olajide I, Sridhar M K, 1987. Guineaworm control in an endemic area in Western Nigeria[J]. Aqua AQUAAA, 6: 333—339.

Reckhow D A, Singer P C, Malcolm R L, 1990. Chlorination of humic materials: byproduct formation and chemical interpretations[J]. Environment Science Technology, 24(11): 1655—1664.

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