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Ozone and Chlorine in Wastewater Disinfection

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Synopsis

In this paper,we compare ozone with chlorine regarding following respects;

(1)Disinfection efficiency

(2)Oxidation power

(3)Effects of secondary effluents treated by ozone or chlorine on aerobic microorganisms.

Both ozone and chlorine are powerfull oxidizing agents. However,those are greatly different from each other in effects of treatment. Ozone is superior to chlorine in oxidation of organics,perfection of disinfection and effects on aerobic microorganisms. On the other hand, chlorine is superior in disinfection of Coliform group bacteria.

Based on these results,it may be concluded that chlorination will be effective in disinfection of effluents which do not contain so much contaminants. However in case of rather highly cotaminated effluents,ozonation will be suitable.

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1. Introduction

Disinfection is the final step in the purification of wastewater. Chlorination has been widely applied for the purpose of disinfection. However, according to the recent works,[1)2)] chlorination produces some kinds of chlorinated compounds, such as chloroholm, chlorinated benzen and so on. This would suggest that the application of chlorination to secondary effluents is harmfull to aquatic lives.

Ozone is being considered as a powerfull oxidizing agent that results in little or no toxity to aquatic lives, and as a possible alternative to chlorine.

Therefore, we compare ozone with chlorine regarding following respects;

(1)Disinfection efficiency

(2)Oxidation power

(3)Effects of secondary effluents treated by ozone or chlorine on aerobic microorganisms in natural streems. From the comparison of these respects, we try to assess the application of ozone and chlorine to wastewater disinfection.

2. Experimental Procedures

The samples are collected from secondary effluents of the municipal sewage plant treated by activated sludge process.

The ozone treatment is carried out by the apparatus shown in Fig.1. The contact column is operated in batchwise. On the other hand, the chlorination is performed as follows. Sodium hypochlorite is added to each test sample by fixed concentration, and the agitation is carried out for 20 minutes. After each treatment the deozonation by aeration and dechlorination by sodium sulfite are conducted. Then, the samples are used for the analysis.

The experiments consist of two steps, Step 1 and Step 2, according to the method of fractionating the components in secondary effluents. In Step 1, the components are divided into two fractions, suspended solids and dissolved matter, by Toyo-Filter No.5c. The average

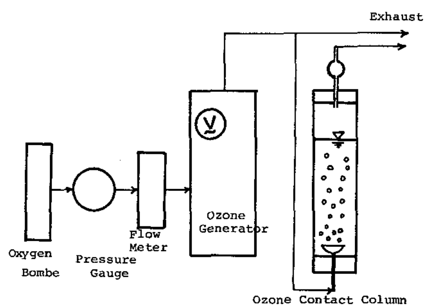

Fig.1 Experimental Apparatus

pore size of this filter is about 1.2μ. The flow chart of Step 1 is shown in Fig.2. In Step 2,dissolved matter is further divided into fractions by means of gel chromatography. The flow chart of Step 2 is shown in Fig.3. The gel used in this study is Sephadex G-15. This gel can fractionate the contaminants of less than 1500 equivalent molecular weight. The conditions of gel chromatography are shown in Table 1.

The water quality items measured are shown in Table 2. The examinations of disinfection,oxidation of contaminants and the effects on aerobic microorganisms in streams are conducted.The examinations of disinfection are performed with the measurements of total colonies and Coliform group bacteria. Regarding the oxidation of contaminants COD_{Cr} is utilized in both steps. In Step 1 the changes of both supended solids and dissolved matter are measured, and in Step 2 the gel chromatogram changes due to each treatment are obtained.

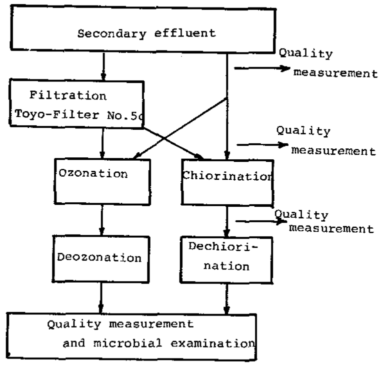

Fig.2 Flow chart of Step 1

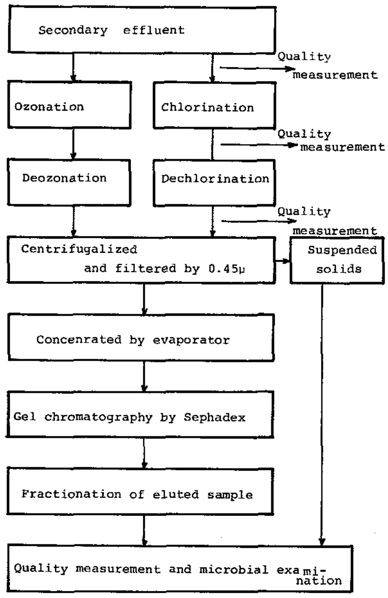

Fig.3 Flow chart of Step 2

Table 2 Water quality items

Ozone concentration	Standard Methods,13th edition Iodometric method
Residual chlorine concentration	Sewage Examination Methods established by Japan Sewage Works Association,Orthotolidine method
Total colonies	Sewage Examination Methods
Coliform group bacteria	Sewage Examination Methods
COD_{cr}	Standard Methods,13th edition
BOD	Sewage Examination Methods
TOC	TOC Analyzer

Table 1 Condition of gel chromatography

Gel bed volume	1,055 ml
Gel bed diameter	4 cm
Gel bed length	84 cm
Elution	Ion strength 0.025 K_2SO_4 $(8.4\cdot10^{-3}Mol/l)$
Flow velocity	2.1ml/min
Sample amount applied	100 ml (sample collection) 40 ml (gel chromatogram)
Fraction volume	20 ml

The microbial examinations are carried out to investigate the effects of effluents treated by ozone or chlorine on aerobic microbes in natural streams. These examinations are consist of two series. These are the examinations of microbial growth and biodegradability. They are performed according to following procedures.

(1)On microbial growth

This detection method has been developed by Inoue,et al.[3],designated as"the precise toxic detection method"using a kind of microbes in natural streams which are able to utilize acetic acid as substrate. Hereafter, we call this kind of microbes as "acetic acid bacteria".

The reasons why this method is adopted are as follows. Acetic acid bacteria play impotant parts in selfpurification mechanisms in natural streams. Therefore, the effects of treated effluents on selfpurification can be evaluated.

The culture medium is composed by ammonium acetate 10g/l and each solution 10ml/l which is added in the dilution solution of BOD test. The medium is pored by 10ml into each piece of petridish sterilized. Then,the testing sample of 10ml and the river water of 1ml,which is taken from the river receiving the municipal sewage effluent and cultivated with ammonium acetate solution under an aerobic condition,are added. Acetic acid bacteria decompose ammonium acetate and grow in the dark at 36c°. The growth of acetic acid bacteria is measured by the decrease of dissolved TOC.

(2)On biodegradability

Investing the biodegradability of organics produced by each treatment is indispensable to accounting for the action of the organics in natural streams. As no suitable indicator of biodegradability has been developed,the ratio of BOD/initial COD_{Cr} is adopted. BOD is measured at fixed intervals.

3. Results and Discussions

3.1 Disinfection Efficiency

The disinfection efficiency by oxidizing agents is effected by the existence of organics,because oxidizing agents are consumed by organics. Here,we discuss the effects of suspended solids on the disinfection efficiency.

In the experiments,the numbers of Coliform group bacteria and total colonies,which can grow on desoxycholate medium and nutrient agar medium respectively,are counted.

Both Fig.4 and Fig.5 show the typical results of total colonies treated by ozone or chlorine. Fig.4 shows the results of the secondary effluent and Fig.5 shows that of the filtrate. From both figures it is evident that there are not so great differences in disinfection efficiency at less than 10mg/l of chlorine dosage or ozone consumption,and that the number of colonies decreases to the level of less than 100 counts per ml. On the other hand,the performances at more than 10mg/l are different from each other. As for ozonation the number of colonies decreases to zero rapidly,whereas as for chlorination it is apparent that there is a certain limit of bactericidal efficiency.

The effect of suspended solids on the bactericidal efficiency is as follows. In ozonation,the disinfection efficiency is affected by the existence of suspended solids. In case of samples without suspended solids,no colonies detected at the ozone consumption of less than 20 mg/l,but in case with suspended

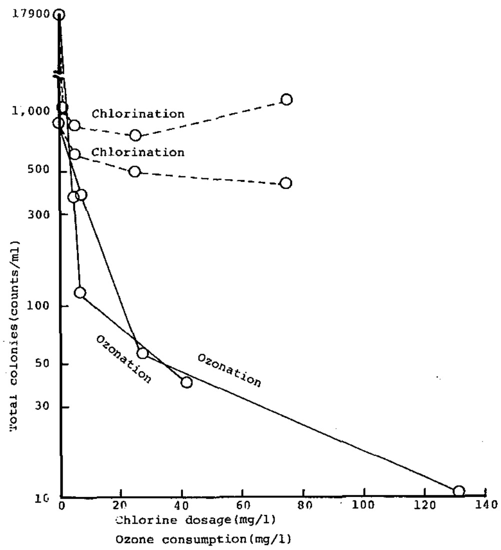

Fig.4 Disinfection of secondary effluent

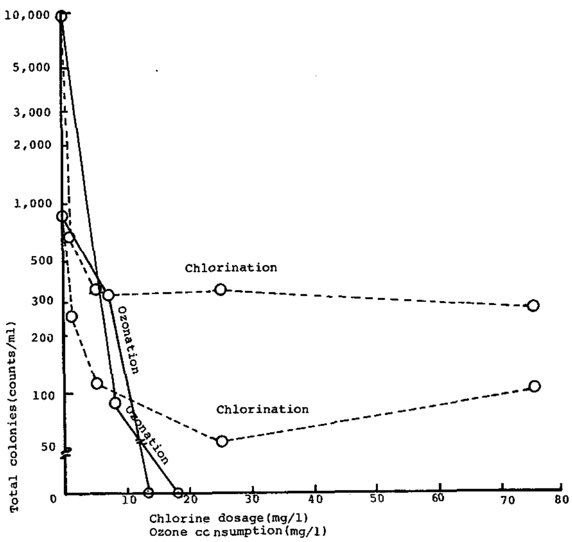

Fig.5 Disinfection of filtrate

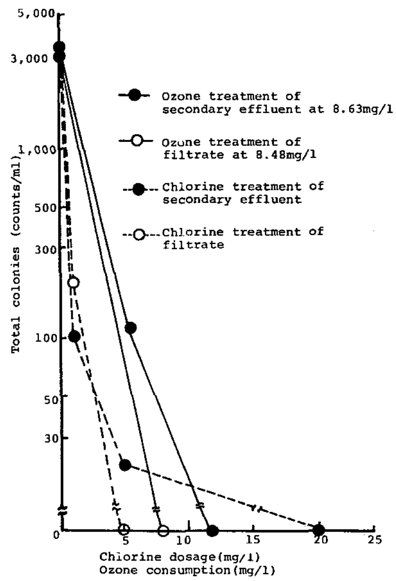

Fig.6 Disinfection of Coliform group bacteria

solids a few colonies are detected at more than 100mg/l. On the other hand,in the chlorination the efficiency is scarcely affected. These facts show that ozone is more powerfull a sterilizer than chlorine,and that in ozonation it is effective to remove suspended solids.

Fig.6 shows the results of Coliform group bacteria. Not only ozone but also chlorine sterilizes Coliform group bacteria to zero at the ozone consumption or chlorine dosage of less than 20mg/l. Judging from this,Coliform group seem to be sterilized more easily than total colonies. Ozone consumption or chlorine dosage seems to increase somewhat owing to the existence of suspended solids. In comparison with ozone consumption and chlorine dosage needed to destroy the organisms to the level 20 organisms per ml, ozone seems to be consumed by 3–5 mg/l,whereas chlorine is needed to dose by 1–3mg/l. In disinfection of Coliform group chlorine seems to be more effective than ozone.

The results on the disinfection efficiency will be summarized as follows. Ozone is superior in the perfectness of sterilization to chlorine,whereas chlorine is more effective in Coliform group.

3.2 Comparison of Oxidation Power

3.2.1 Changes of Suspended Solids and Dissolved Matter

Fig.7 shows the typical changes of suspended solids and dissolved matter by ozonation or chlorination. From this figure,it is apparent that the suspended solids are broken down by both oxidizing agents.The decrement trend in ozonation is steeper than that of chlorination. On the other hand,the dissolved matters increase at first,and then decrease with the consumption or dosage. This would sugest that the suspended solids are broken down into the dissolved matters, and that the dissolved matters futher oxidized to inorganic compounds. The decrement of both fractions,suspended solids and dissolved matters,is more in ozonation than in chlorination. Ozone would oxidize contaminants in secondary effluents more powerfully than chlorine.

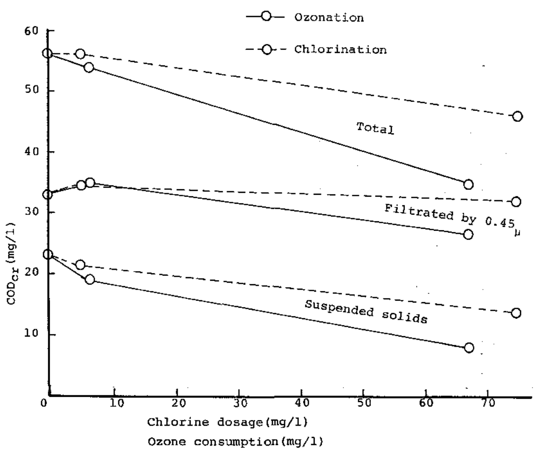

Fig.7 Changes of suspended solids

3.2.2 Change of Gel Chromatogram

The change of gel chromatogram is measured by using Sephadex G-15. The gel chromatograms of three compounds, Blue dextran, Vitamin B_{12} and KNO_3, are shown in Fig.8. The molecular weights of these compounds are shown too.

Fig.9 shows the gel chromatogram of the secondary effluent feeded to each treatment.

Fig.10 and Fig.11 show the results of the ozonation, and Fig.12 and Fig.13 show those of the chlorination.

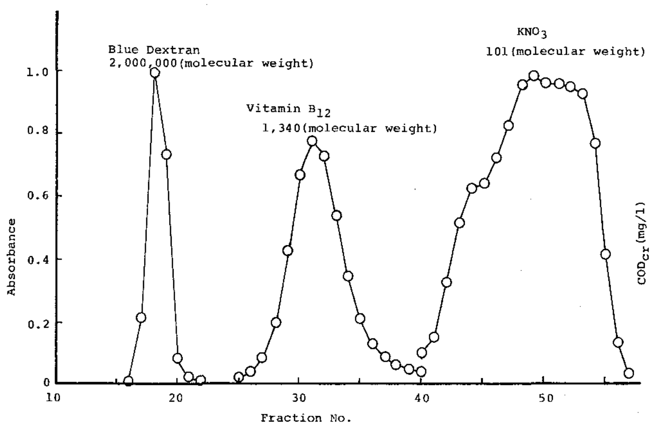

Fig.8 Gel chromatograms of standard substances

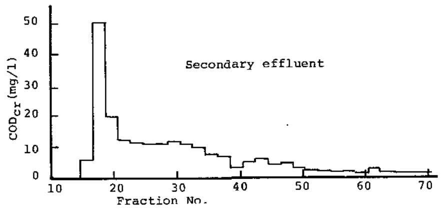

Fig.9 Secondary effluent

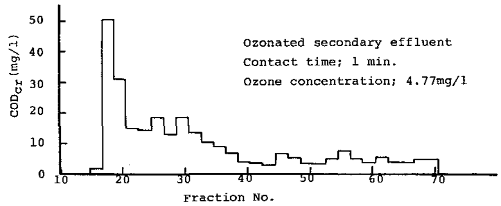

Fig.10 Ozonation for 1 minute

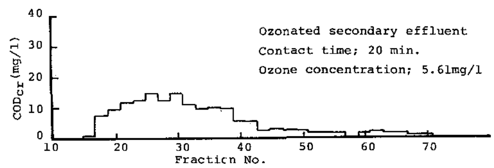

Fig.11 Ozonation for 20 minutes

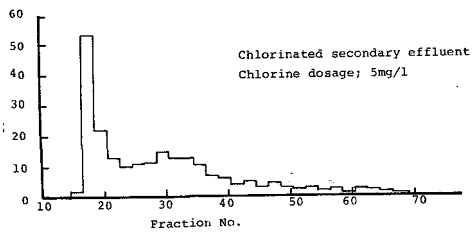

Fig.12 Chlorination at 5 mg/l

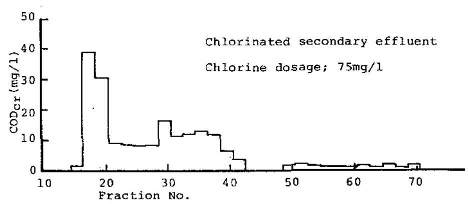

Fig.13 Chlorination at 75 mg/l

From Fig.9–11, it is evident that the peak of the higher molecular compounds, the fractions of No.16 to 20, diminishes by ozone treatment of 20 minutes.

According to former experiments[4], suspended solids are decomposed into the higher molecular compounds, and then further into the lower molecular compounds. The higher molecular compounds are oxidized into the lower molecular compounds. These results are shown in Fig.14 and Fig.15. It would seem that these phenomena occur in this case.

On the other hand, in chlorination the gel chromatogram hardly changes even at 75 mg/l. However, the following phenomena were ob-

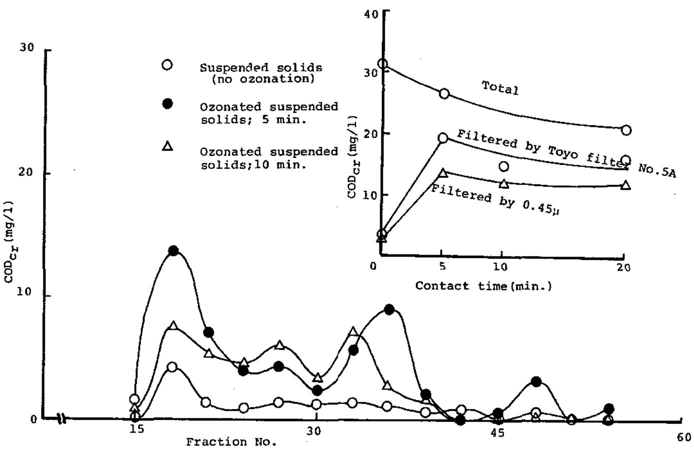

Fig.14 Ozonation of suspended solids

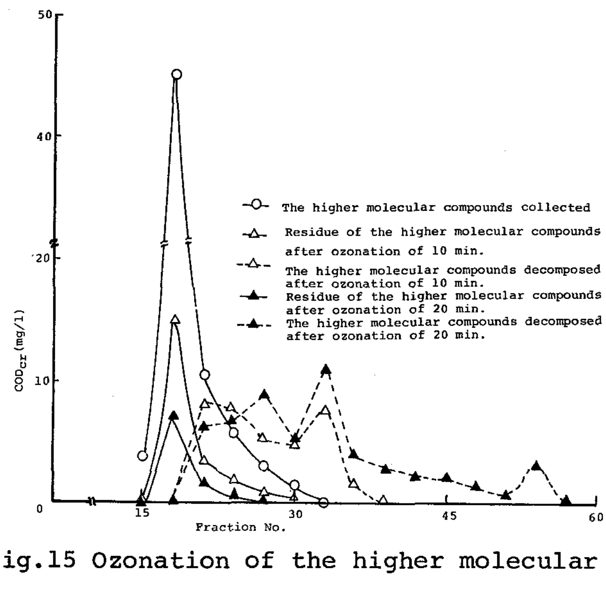

Fig.15 Ozonation of the higher molecular compounds

served. first substances eluted nearby fraction No.46 in the secondary effluent disappeared after chlorination, secondly the white turbidity was observed in the fractions of No.35—38 when COD_{Cr} was measured. The reasons of these phenomena are still unknown.

As above-mentioned, concerning the oxidation of the contaminants in secondary effluents ozone is more effective than chlorine.

3.3 Effects of the Secondary Effluents Treated by Ozone or Chlorine on Aerobic Microorganisms in Natural Streams

3.3.1 Effects on growth of Microorganisms

After the cultivated media in pieces of petridish are filtered by Milli-pore Filter of 0.45μ in oder to remove the microorganisms, TOC of the filtrates are measured. The decrease of TOC means the growth of microorganisms.

Fig.16 and Fig.17 show the typical results of the secondary effluent and its filtrate respectively. Both figures contain the control tests in which the distilled water is added instead of the sample. The growth rate of the control test is the lowest in each figure. On the

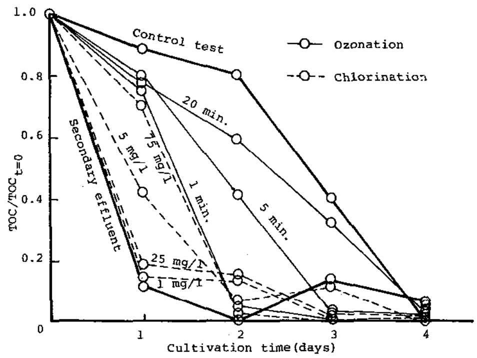

Fig.16 Secondary effluent

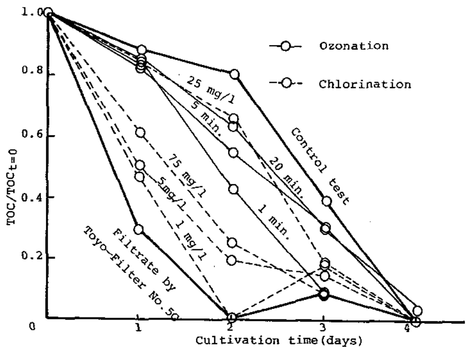

Fig.17 Filtrate

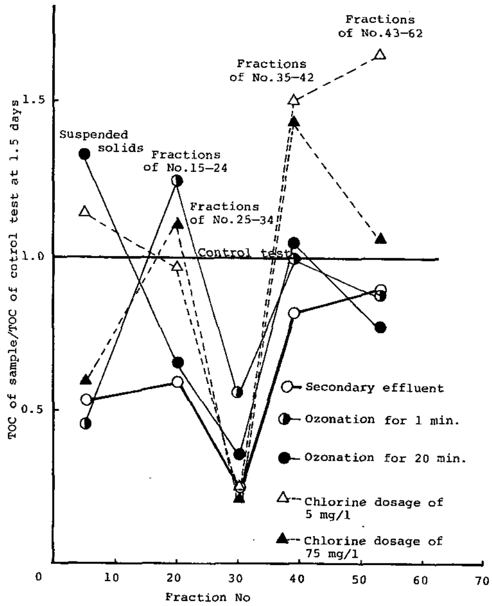

Fig.18 Comparison of each fraction

other hand, the rate for the secondary effluent or its filtrate is the most rapid in each case. These facts sugest that the secondary effluent and its filtrate contain certain compounds promoting the growth of aerobic microorganisms in natural streams.

Compareing the effects of the chlorination on the growth with those of the ozonation, it is recognized that the chlorination does not have so much effect and has the results very close with the secondary effluent or its filtrate. On the contrary, the ozonation has a great effect and the rate of the samples treated by ozone decreases according to the degree of the treatment to the same level as that of control tests.

Comparing between Fig.16 and Fig.17, it is noted that the existence of suspended solids somewhat promote the growth of microbes. This suggests that not only suspended solids but also the products by ozonation or chlorination of them promote the growth.

In the next place, we discuss the effects of fractions obtained by gel chromatography on the growth of microorganisms. The compounds contained in the secondary effluent are divided into 5 fractions. They are suspended solids and the groups of fraction No.15–24, fraction No.25–34, fraction No.35–42 and fraction No.43–62.

Fig.18 shows TOC of samples / TOC of the control test at 1.5 days. In this figure, the growth rate is the greater, the smaller is the ratio. The points under the line of the control test show that the growth of microbes is promoted by the samples. Whereas the points over the line show that the growth is retarded. From this figure, it is evident that in the secondary effluent the growth rates of the group of fraction No.25–34 and suspended solids are the geater. This suggests that the compounds promoting the growth exist mainly in these fractions. The rate of this group decreases by ozone treatment, whereas by chlorination that scarcely changes.

In the groups of fraction No.35–42 and fraction No.43–62, it seems that the rate of samples treated by chlorine decreases. This suggests the compounds retarding the growth such as chlorinated benzen are produced.

The matters above-mentioned are summarized as follows. Ozone decomposes the compounds promoting the growth. Consequently, the growth rate decrease. On the other hand, chlorine does not decompose them. Therefore,the growth rate scarcely changes in chlorination. However, certain compounds retarding the growth seem to be produced.

3.3.2 Effects on Biodegradability of ORganic Compounds

The biodegradability of the effluent treated by ozone or chlorine is estimated based on the ratio of BOD/COD_{Cr}.

The results of the secondary effluent are shown in Fig.19. From this figure, it will be noted that the increase trend of the ratio in each treatment along with incuvation time are obviously different from each other. In case of ozonation, the ratios look to become greater than that of the raw effluent, whereas in chlorination the ratios seem to become smaller.

These facts suggest that the biodegradability increases in ozonation, and that it decreases in chlorination along with increase of dosage.

The results of the effluent filtered by Toyo Filter No.5C are shown in Fig.20. In this figure, the trend above-mentioned is not distinct. The difference between Fig.19 and Fig.20 suggests that the products by oxidation of suspended solids greatly effect on the biodegradability.

In the next place, we dicuss the effects of each group of fractions obtained by gel chromatography on the biodegradability. Table 3 shows

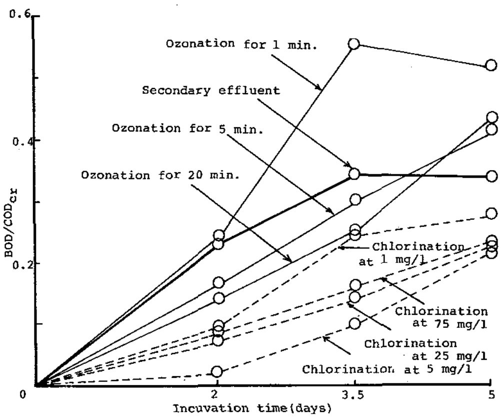

Fig.19 BOD/COD_{Cr} of secondary effluent

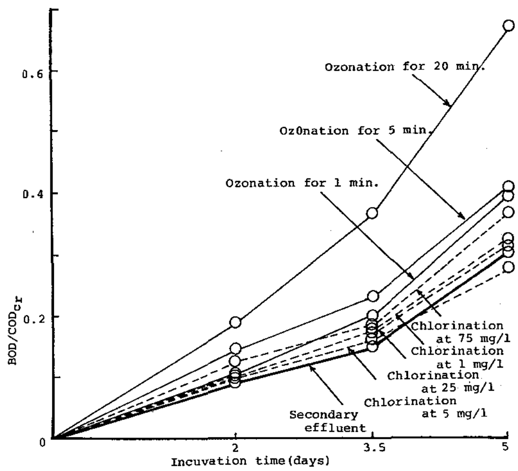

Fig.20 BOD/COD_{Cr} of filtrate

	Secondary effluent	Ozonation for 1min.	Ozonation for 20 min.	Chlorination at 5 mg/l	Chlorination at 75 mg/l
Suspended solids	0.68	0.63	0.60	0.50	0.33
Fraction No. 15–24	0.13	0.13	0.20	0.12	0.16
Fraction No. 25–34	0.74	0.51	0.46	0.75	0.24
Fraction No. 35–42	0.87	0.59	0.91	0.61	0.71
Fraction No. 43–61	0.57*	0.76*	1.9*	1.2*	1.4*

* As BOD values are small, these values are effected by the endogenous respiration of microorganisms.

Table 3 BOD_5/COD_{Cr} of each fraction the results of the biodegradability. From Table 3 it will be noted that in chlorination the biodegradability of suspended solids and the group of fraction No.25–34 drops. On the contrary, in ozonation that of suspended solids hardly decreases. Besides the decrease in the group of fraction No.25–34 is smaller than in chlorination. These facts seem to cause the difference of the biodegradability changes in each treatment.

4. Conclusions

In this study, we compared ozone with chlorine regarding; (1)disinfection efficiency; (2)oxidation power; and (3)effects of secondary effluents disinfected by ozone or chlorine on aerobic microorganisms in natural streams. The main results will be summarized as follows.

(1)Regarding the disinfection of Coliform group bacteria, the dosage of chlorine is less amount than ozone consumption. However, on the sterilization of total colonies chlorine can not completely sterilize even if high dosage is applied, whereas ozone can sterilize easily. In ozonation, not only disinfection but also removal of organic compouds takes place at the same time. Consequently, the more amounts of ozone are consumed. From this fact, ozonation would be applied where both disinfection and removal of organic compounds are in view.

(2)Ozone remarkably decomposes suspended solids and the higher molecular compounds. Consequently, the gel chromatograms remarkably change in ozonation. On the other hand, chlorine hardly decomposes suspended solids and the higher molecular compounds. Consequently, the gel chromatgrams scarcely change.

(3)Certain compounds which promote the growth of aerobic microorganisms in natural streams are contained in secondary effluents, specially, in suspended solids and the group of fraction No.25–34. These compounds seem to be easily decomposed by ozone, but hardly by chlorine. Consequently, the rates of the microbial growth are as following order; secondary effluent > effluent treated by chlorine > effluent treated by ozone > sample of control test.

(4)The biodegradability of effluents increases in ozonation, but decreases in chlorination. This difference is mainly caused by the difference of the quality changes of suspended solids and the group of fraction No.25–34.

Based on these results, we may conclude as follows. Chlorination is effective where contaminants are not contained so much and the removal of them is not aimed at. On the contrary, ozonation is suitable from the points of safety on microorganisms in waters receiving effluents and removal of organic compounds where contaminants are highly contained and not only disinfection but also removal of contaminants is aimed at.

Acknowledgement

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