Memoirs of the School of Engineering, Okayama University Vol. 14-1, November 1979

Ozonation of Organic Substances from View Points of Wastewater Treatment

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(Received October 31, 1979)

Synopsis

In this paper, ozonation of organic substances which are found in wastewater is discussed regarding following respects; (1)removal ratios of COD(Cr) and TOC, (2)removal properties, and (3)oxidation products.

The main results are summarized as follows.

(1)Ozonation quickly removes proteins and amino acids, but mildly polysaccharides and n-saturated carboxylic acids.

(2)The initial removal of COD(Cr) or TOC is quite rapid, but, as the reaction continues, it slows down so drastically that one may suspect that it has completed.

(3)Starch and albumine are decomposed to the smaller molecular compounds.

(4)The COD(Cr)/TOC ratio of each substance which is chosen in this study decreases. This means that ozonation results in the formation of oxygenated fragments of the original molecule—occurs by bond fission or partial oxidation.

(5)Proteins are indispensable components in frothing because they are surface active. They are removed by not only oxidation but also foaming, however, the removal by foaming is not so large.

1. Introduction

Ozone has been used for odor control, disinfection, iron and manga-

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nese removal, and color reduction[1, 2, 3, 4]. In temporary, interest in ozonation is directed toward water quality exchange of wastewater[5]. Ozone is a powerful oxidizing agent, but can't oxidize all contaminants in wastewater to carbon dioxide and water. Main effects of ozonation of wastewater are water quality exchange or partial oxidation of the contaminants such as decomposition of suspended solids and the higher molecular substances. These effects extend the capabilities of intermediate treatment plants.

For the purpose of the understanding and evaluation of these effects, the investigations of ozonation of the substances contained in wastewater are necessary. Unfortunately, very few studies have been made into ozonation of organic substances in aqueous media in the organic chemistry of ozone.

Therefore, in this study the organic substances which seems to be contained are chosen and investigated. The results of experiments are discussed from the following view points of wastewater treatment.

(1)Removal ratios of COD(Cr) and TOC,
(2)Removal properties,
(3)Oxidation products.

These discussions will provide a useful theoretical background for the application of ozone to wastewater treatment.

2. Experimental procedures

Examined organic substances were chosen from following view points;

(1)Biodegradable or not,
(2)Soluble or not,
(3)Hydrophilic or not,
(4)High molecular or not,
(5)Saturated or not.

The ozonation was carried out by the apparatus shown in Fig.1. The contact column was constructed from acrylic cylinder(100 × 5 cm in diam) and operated in batchwise. Ozone was generated from oxygen. The flow rate of ozonated pure oxygen was

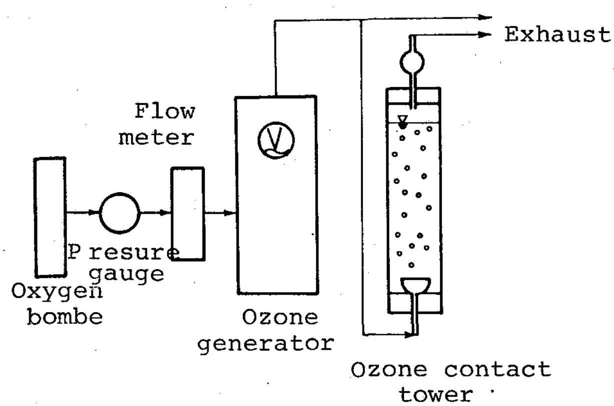


Fig.1 Experimental apparatus

1.0 l/min. Ozone concentration was about 73 mg/l, and this value was maximum under these conditions.

As pH of wastewater is buffered near nuetrality by carbonates and phosphates and, further, pH effects on treatment efficiency, phosphates buffer solutions (KH_2PO_4-Na_2HPO_4) were used in oder to dissolve or suspend tested substances. The temperature of the solution during ozonation was 20±1°C.

The concentrations of tested substances were 150mg/l except the case of the foaming test. The contact time with ozone was 40 minutes or 80 minutes. The samplings were conducted at fixed intervals. The samples withdrawn were aerated by air in oder to purge dissolved ozone, and then they were analyzed.

The water quality items measured were COD(Cr) (Standard Methods) and TOC(TOC analyzer). The decomposition of albumine and starch were examined by gel chromatography. The gel used in this study was Sephadex G-15. This gel can fractionate the substances of less than 1500 equivalent molecular weight. The

Table 1 Conditions of gel chromatography

Gel bed volume	1055 ml
Gel bed diameter	4 cm
Elution	K_2SO_4 (8.4×10^{-3}mol/l)
Flow rate	2.1 ml/min
Sample amount applied	40 ml
Fraction volume	20 ml

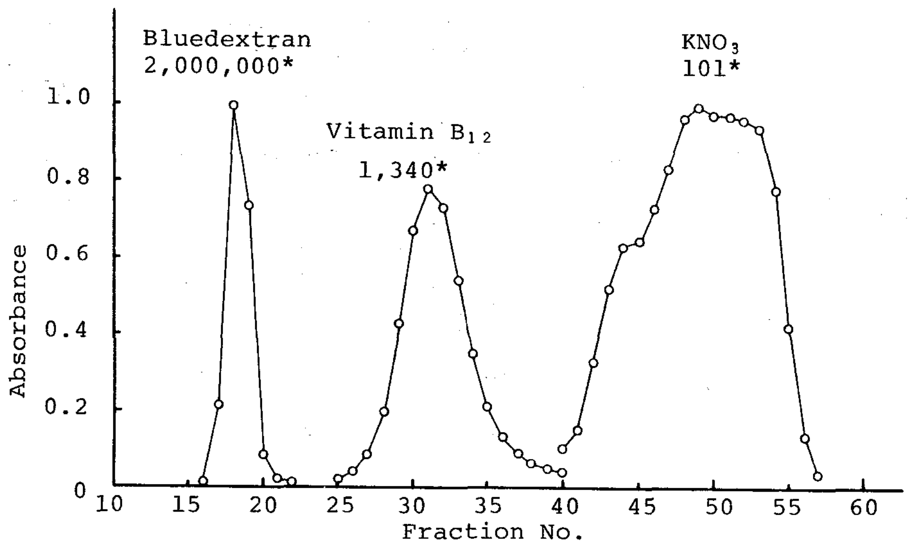


Fig.2 Gel chromatograms of typical standard substances

* Molecular weight

conditions of gel chromatography are shown in Table 1. The gel chromatograms of standard substances are shown in Fig.2.

3. Results and discussions

3—1. Removal ratios of COD(Cr) and TOC

Table 2 shows the removal ratios of COD(Cr) and TOC for ozonation

Table 2 COD(Cr) and TOC Removal

	Name	Property	COD(Cr)	TOC
Carbohydrate	Glucose	Monosaccharide	75%	34%
	Lactose	Disaccharide	77%	33%
	Raffinose	Trisaccharide	69%	45%
	Cellulose	Polysaccharide Insoluble	52%	59%
	Starch	Polysaccharide Insoluble	59%	55%
Amino acid	α-Alanine	α-Amino acid	69%	42%
	Arginine	α-Amino acid	73%	25%
	Monosodium glutamate	α-Amino acid	73%	51%
	Aspartic acid	α-Amino acid	89%	33%
Protein	Albumine	Simple protein Surface active	62%	41%
	Polypeptone	Derived protein Surface active	78%	46%
	Urease	Simple protein Insoluble	92%	67%
	Casein	Phosphoprotein Insoluble	68%	31%
Carboxylic acid	Sodium oleate	Unsaturated fatty acid	69%	9%
	Sodium palmitate	n-Saturated fatty acid Insoluble	90%	86%
	Citric acid	Hydroxy tri-carboxylic acid	66%	64%
	Acetic acid	n-Saturated fatty acid	N.D.	N.D.
	Benzoic acid	Aromatic acid	80%	63%
	Fumaric acid	Unsaturated dicarboxylic acid	74%	62%

of 40 minutes. In most cases, COD(Cr) is removed to more than 60 per cent, but in some cases less than 60 per cent. Among the latter, cellulose, starch, and acetic acid are contained. Especially, acetic acid does not seem to be removed by not only oxidation but also other mechanisms.

Comparing COD(Cr) with TOC removals in Table 2, TOC removals are smaller than COD(Cr) in most cases. Especially, in the cases of glucose, lactose, arginine, aspartic acid, casein and sodium oleate, the ratios of TOC removal to COD(Cr) removal are from one-seventh to half. On the other hand, in the cases of citric acid and polysaccharides, the ratios are nearly equal to unity. From the facts described above, it is concluded that COD(Cr) reductions of most substances are generally large, but that TOC reductions remarkably change according to the properties of substances.

In Figure 3, 4, 5 and 6 are shown the COD(Cr) and TOC reduction curves. Two character-

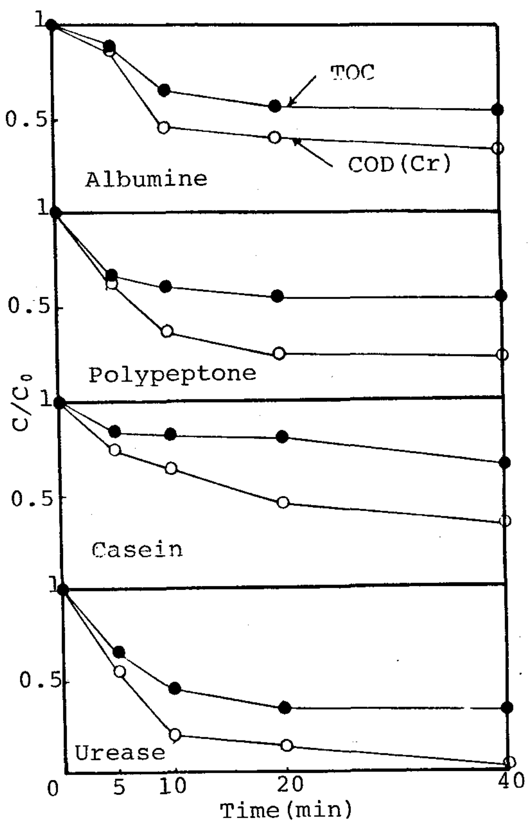


Fig.4 Ozonation of proteins

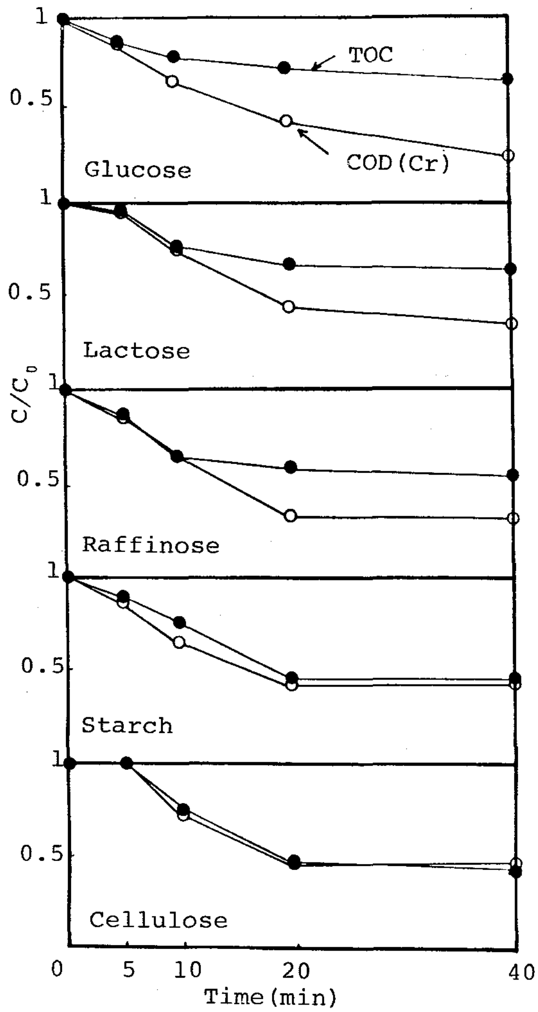


Fig.3 Ozonation of carbohydrates

istics are evident. The initial COD(Cr) and TOC reduction curves are steep, but, as the treatment continues, they slow down. The initial COD(Cr) reduction rates of amino acids and proteins are far greater than those of polysaccharides and citric acid. As the ozone concentration of a practical application is far lower than in these experiments, it is assumed that some substances are little oxidized in such a case. Within the limits of these results, reaction rates are great in amino acids and proteins, but small in polysaccharides and n-saturated carboxylic acids.

3—2. Removal properties

Fig.3 shows the resuts of carbohydrates. These curves demonstrate that COD(Cr) removals of cellulose and starch stop after ozonation for 20 minutes, and that in the other carbo-

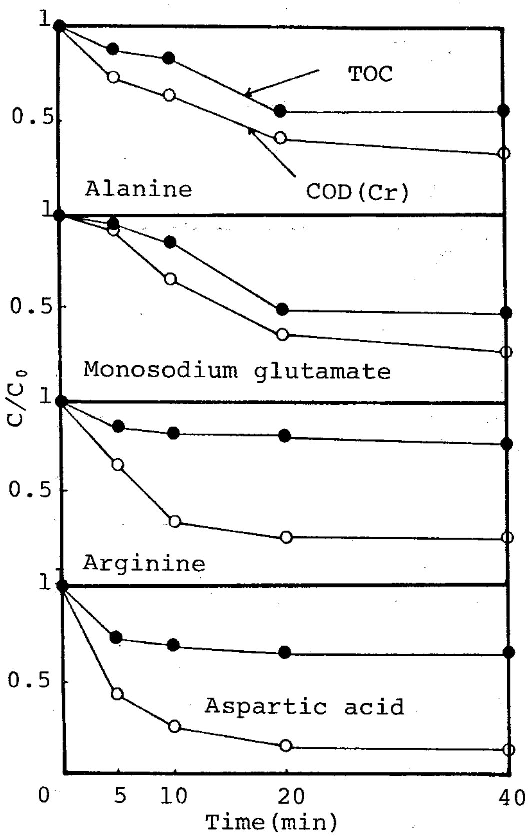


Fig.5 Ozonation of amino acids

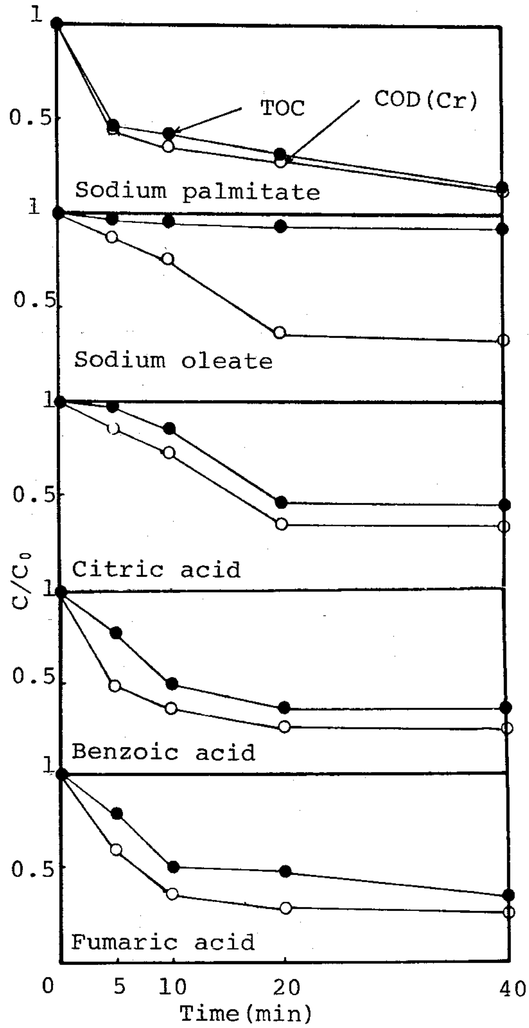


Fig.6 Ozonation of carboxylic acids

hydrates the similar tendency is also observed. Ozonation of carbohydrates seem to yield compounds resisting further oxidation by ozone.

Fig.4 shows the results of proteins. However, the initial reduction rates of proteins are rapid, all of reductions are not owing to oxidation. As urease and casein are insoluble, they are removed by floatation. On the other hand, as the soluble proteins are surface active they are removed by not only oxidation but also foaming.However, as Fig.7 removal by foaming is not so large.

The results of amino acids are shown in Fig.5. The initial rates of amino acids are rapid as well as proteins. No clear difference is found amoung amino acids.

Fig.6 shows the results of carboxylic acids. Sodium oleate and fumaric acid, which have a c-c double bond, are rapidly oxidized as well as benzoic acid. But COD(Cr) removal rates remarkably slow down after ozonation for 20 minutes. Acetic acid,citric acid and sodium palmitate are saturated compounds, but they are removed except acetic acid. citric acid is removed by oxidation and sodium palmitate by floatation.

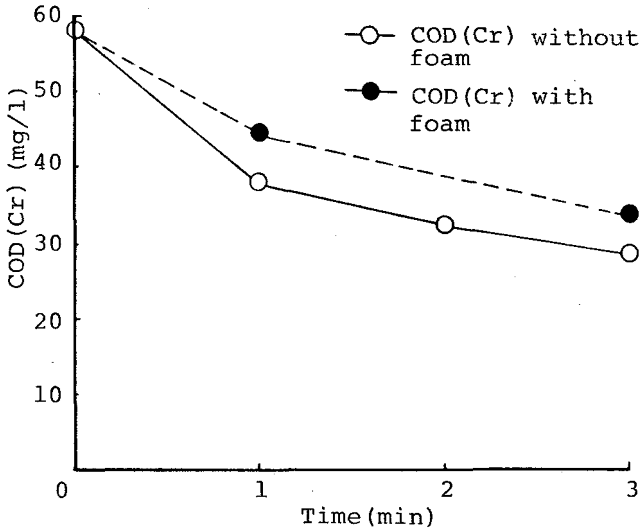


Fig.7 Removal by foaming for albumine

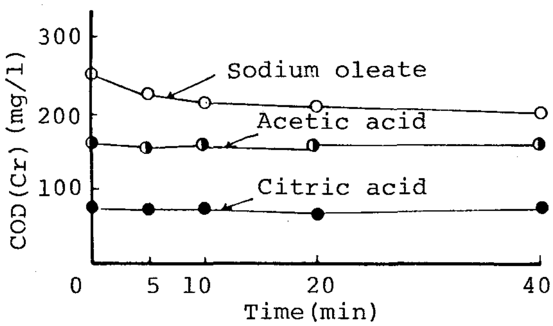


Fig.8 Aeration of carboxylic acids by oxygen

If volatile compounds are yielded, removal by stripping may take place. Unstable compounds may be removed by autoxidation. Therefore, stripping and autoxidation are examined concerning carboxylic acids. Fig.8 shows the results of aerating the carboxylic acids. COD(Cr) of sodium oleate only reduces slightly. It might be assmed that this reduction is casused by foaming or autoxidation as acetic acid and citric acid do not change. However, it is far smaller than that by ozonation.

3–3. Oxidation products

Here, ozonolisis products are examined by the ratios of COD(Cr)/

Fig.9 Change curves of COD(Cr)/TOC for proteins

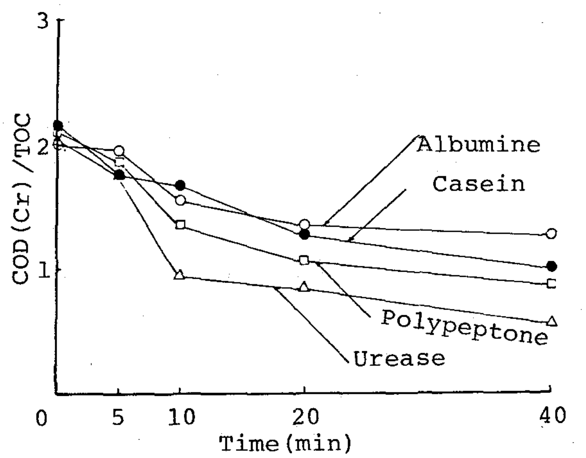


Fig.10 Change curves of COD(Cr)/TOC for carbohydrates

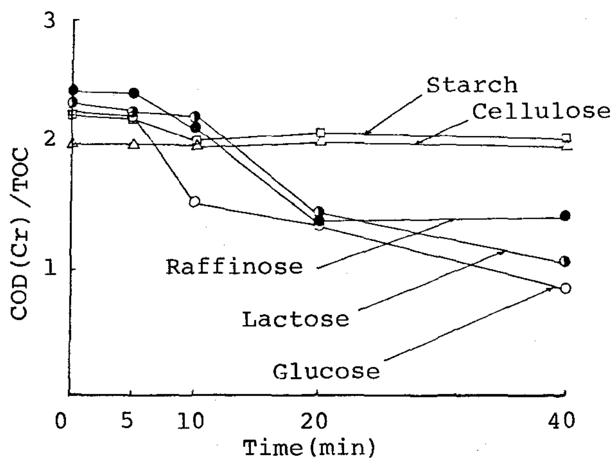
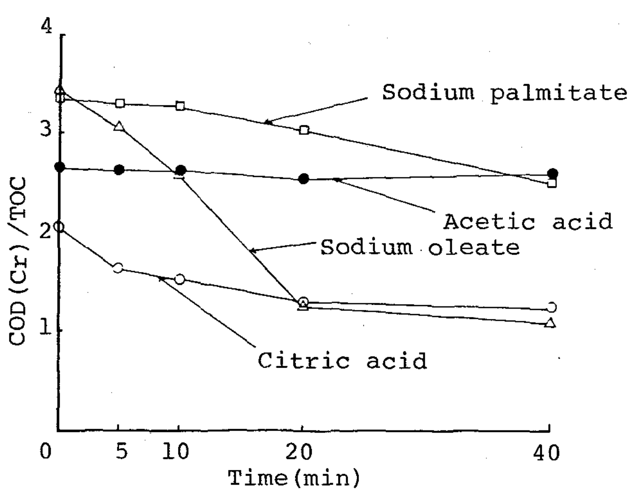


Fig.11 Change curves of COD(Cr)/TOC for carboxylic acids



TOC and gel chromatograms. It can be considered that COD(Cr)/TOC represents an oxidation level. For example, COD(Cr)/TOC of CH_4, CH_3OH, CH_2O, HCOOH and CO_2 are 5.3, 4.0, 2.7, 1.3 and 0 respectively if COD(Cr) is equal to a theoretical oxygen demand. The smaller value represents the higher oxidation level. The change curves of COD(Cr)/TOC due to ozonation are shown in Figure 9, 10, 11 and 12.

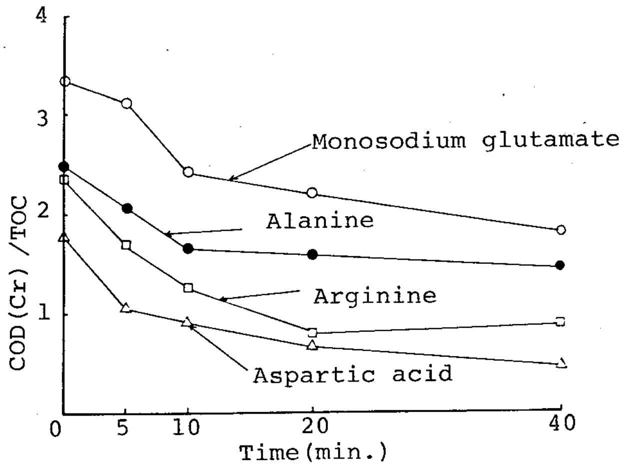


Fig.12 Change curves of COD(Cr)/TOC for amino acids

The ratios remarkably decrease except cellulose, starch and acetic acid. At ozonation for 40 minutes, the values become from one to two.

Fig.13 shows the ratios of a theoretical oxygen demand to TOC in carboxylic acids. The theoretical oxygen demand is not always equal to COD(Cr), but the theoretical oxygen demands of carboxylic acids are nearil equal to unity. Therefore, Fig.13 is considered to represent COD(Cr)/TOC against molecular weight. Ozonolysis products are similar to the smaller molecular n-saturated carboxylic acids in the respects of the ratios of COD(Cr)/TOC and resistance to ozonlysis. Criegee ozonolysis mechanism suggests that one of the main ozonolysis products in aqueous media is a carboxylic acid[6].

From above mentioned, ozonolysis products are assumed to contain the smaller molecular n-saturated

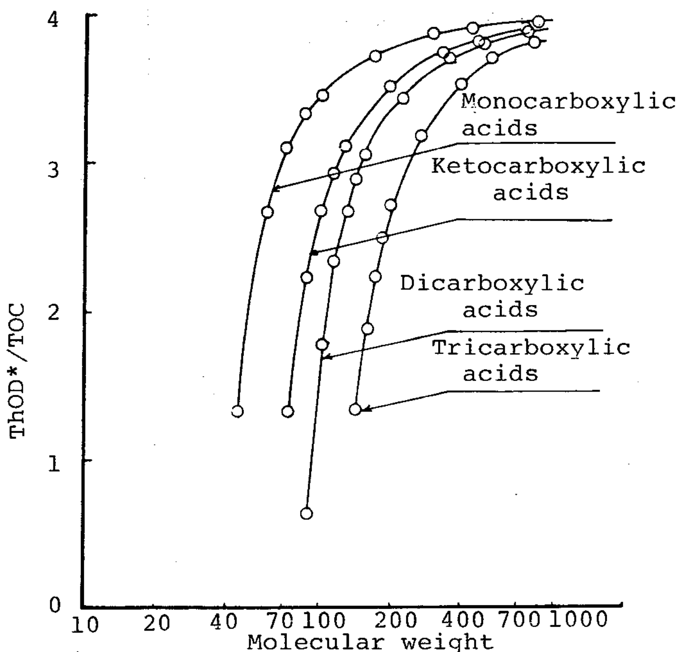


Fig. 13 ThOD*/TOC of carboxylic acids

* Theoretical oxygen demand

carboxylic acids.

The ozonolysis products of albumine and starch are examined by using gel chromatography. The change of starch is shown in Figure 14, 15 and 16. The gel chromatogram before ozonation was not obtained as starch is not soluble at a normal temperature. In ozonation for 10 minutes ozo-

Fig.14 Ozonation of starch for 10 minutes

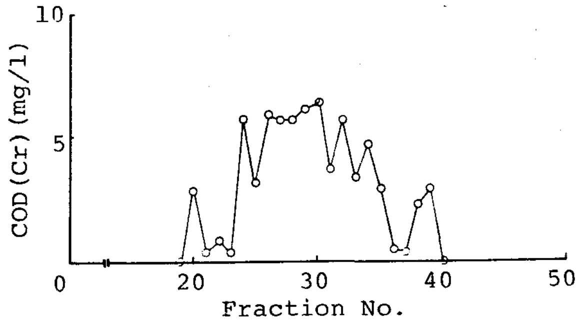


Fig.15 Ozonation of starch for 20 minutes

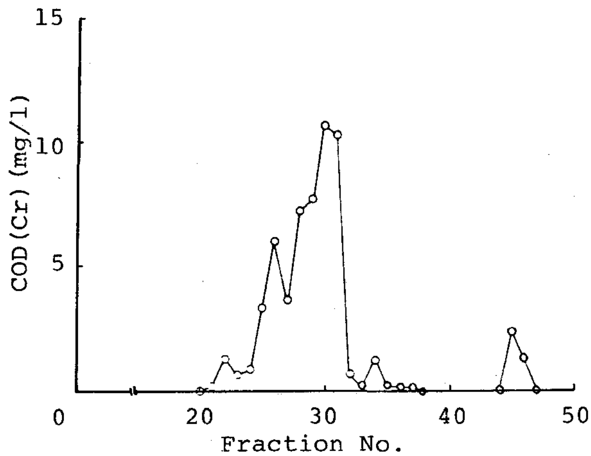
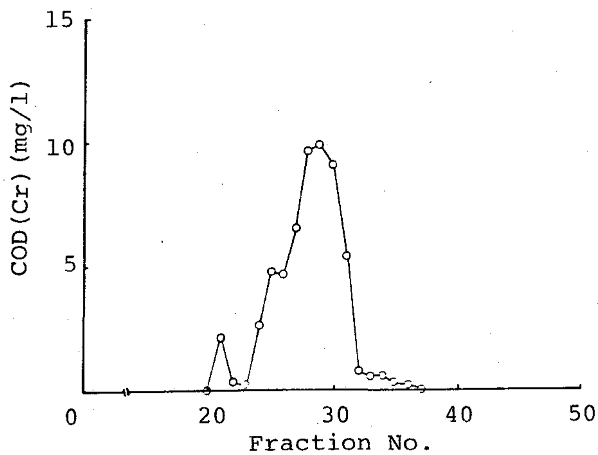


Fig.16 Ozonation of starch for 40 minutes



nolysis products are fractionated from the 24th fraction to the 35th fraction. The compounds fractionated near the 30th fraction increase as the ozonation continues. From above mentioned,starch is decomposed to the smaller molecular weight compounds.

The gel chromatograms of albumine are shown in Figure 17, 18 and 19. Before ozonation, albumine elute near the the 20th fraction. The peak found before ozonation decreases rapidly as ozonation continues. Comparing Figure 18 with 19, it seems that albumine is decomposed to the fractions near the 30th fraction through the fractions from the 20th to the 25th frraction.

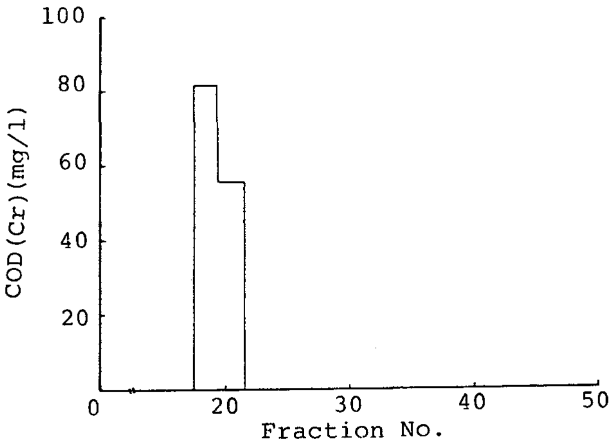


Fig.17 Albumine before ozonation

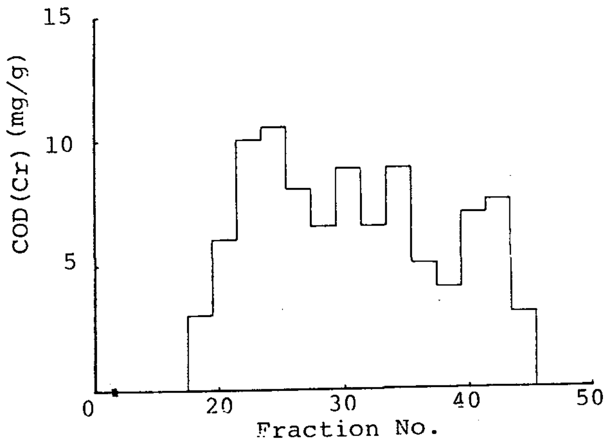


Fig.18 Ozonation of albumine for 10 minutes

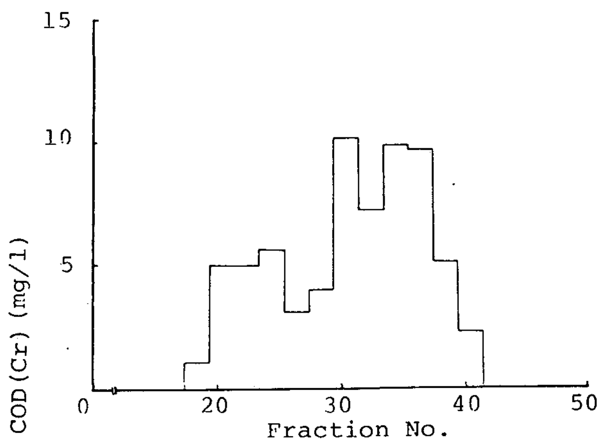


Fig.19 Ozonation of albumine for 20 minutes

4.Conclusions

Main results are summarized as follows.

(1)Ozonation quickly removes proteins and amino acids, but mildly polysaccharides and n-saturated carboxylic acids.

(2)The initial removals of COD(Cr) and TOC are quite rapid, but, as the reaction continues, it slows down .

(3)Starch and albumine are decomposed to the smaller molecular compounds.

(4)The COD(Cr)/TOC ratio of each compound which is chosen in this study decreases. This means that ozonation results in the formation of oxygenated fragments of original molecule—occurs by bond fission or partial oxidation.

(5)Proteins are indispensable components in frothing because they are surface active. They are removed by not only oxidation but also foaming, however, the foaming effect is not so large.

The auther is deeply indepted to Yuji Yasuda, Mitsubishi Heavy Industries LTD., for his considerable assistance with the accomplishment of the experiment.

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