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Brominated Phenol Production from the Chlorination of Wastewater Containing Bromide Ions

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Chlorine oxides (chlorine gas, sodium hypochlorite, and calcium hypochlorite) are used as disinfectants for potable water, wastewater and cooling water. When treating of water with these compounds, brominated and chlorinated organic products are known to be formed (Bean et al. 1978; Quimby et al. 1980). On regard to brominated phenols, the formation of 2,4,6-tribromophenol from the chlorination of water containing bromide ions and phenol takes place (Sweetman et al. 1980). Bean et al. (1980) have also reported the production of brominated phenols, i.e., bromodichlorophenol, dibromochlorophenol and tribromophenol, from the chlorination of natural water under simulated biofouling control conditions.

Brominated phenols such as bromodichlorophenol, dibromochlorophenol and 2,4,6-tribromophenol along with chlorinated phenols have been detected in the river sediment collected in Osaka, Japan, but in very low concentration (Watanabe, unpublished data). We found that these phenols in sediments were formed primarily by the chlorination of wastewater. This study presents a discussion of brominated phenol production from the chlorination of wastewater.

MATERIALS AND METHODS

Non-chlorinated wastewater samples were obtained from a sewage-treatment plant in Osaka, Japan. Calcium hypochlorite was used to chlorinated the samples, with potassium bromide as the source of bromide ions. Most of the halogenated phenols used in this study as reference substances were obtained from commercial sources. 2-Bromo-4,6-dichlorophenol was kindly provided by Dr. T. Sohma (Takeda Yakuhin Kogyo Co. Ltd., Japan). Another bromodichlorophenol, 4-bromo-2,6-dichlorophenol (estimated), was prepared from 2,6-dichlorophenol by bromination. Two isomers of dibromochlorophenol, 2,4-dibromo-6-chlorophenol (estimated) and 2,6-dibromo-4-chlorophenol (estimated), were also prepared from 4-bromo-2-chlorophenol and 2-bromo-4-chlorophenol, respectively, by bromination.

A JEOL JMS DX-300 mass spectrometer connected to a Hewlett Packard 5710A gas chromatograph, a JEOL JMS 3500 data system and a column (2 mm x 1.5 m) of 2%-DEGS were used for determination of the halogenated phenols under the following conditions: column temperature, 200°C; gas (He) flow rate, 30 ml/min.; electron impact ionization voltage, 70 eV; ion source temperature, 220°C. A capillary column (0.31 mm x 25 m) of crosslinked 5% phenyl methyl silicon was also used for confirmation of the halogenated phenols in this GC/MS system at a column temperature from 100 to 210°C (8°C/min.) and a gas (He) flow rate of 1 ml/min. A Varian 2100 gas chromatograph equipped with an electron capture detector (^{63}Ni) and a column (2 mm x 1.8 m) of 2% OV-17 was used for the determination of pentabromophenol at a column temperature of 200°C and a gas (N_2) flow rate of 40 ml/min.

Five liters of wastewater were placed in 10 liters glass bottle followed by the addition of chlorine and bromide ions, as shown in Table 1. The contents were then mixed to initiate the reaction. No adjustment was made for pH. The reaction was made to stop after 24 hours by adding an excess of sodium thiosulfate to decompose the remaining chlorine. The reaction products were extracted using a mixture of hexane and diethyl ether (2:1) at a pH from 2 to 3 after removing non-polar substances by washing with hexane at a pH from 10 to 11. Halogenated phenols in the extract were determined by mass fragmentography, using a GC/MS. Pentabromophenol was determined by gas chromatography after ethylation of the extract with ethylbromide according to the method described by Miyazaki et al. (1981).

Table 1. Chlorination conditions of wastewater

Sample	Cl added[1] (ppm)	Br^- added[2] (ppm)	Reaction time (hr.)	pH[3]
I	0	0	0	7.4
II	20	0	24	7.6
III	100	0	24	7.5
IV	100	10	24	7.5

[1]Chlorination by calcium hypochlorite.
[2]Bromide spiked with potassium bromide.
[3]pH values obtained at the start of the reaction.

RESULTS AND DISCUSSION

Figure 1 shows the mass fragmentograms of halogenated phenol standards and the extract of Sample IV. Halogenated phenols

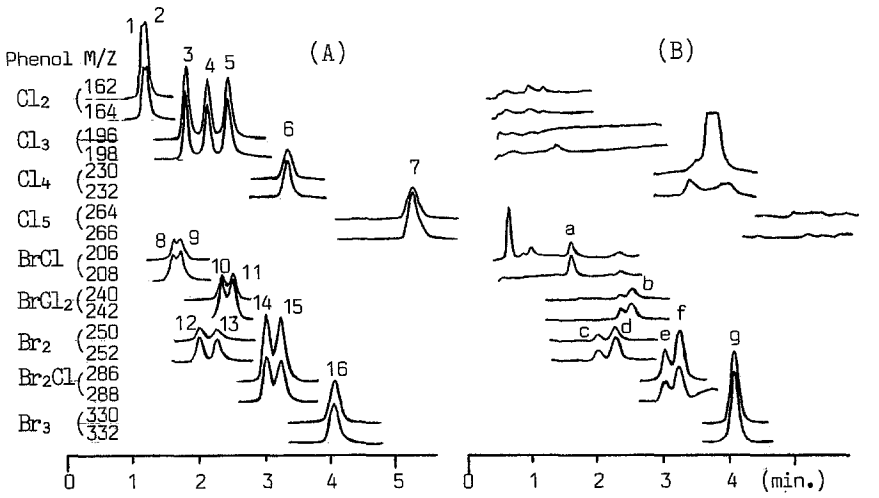

Figure 1. Mass fragmentograms of (A). halogenated phenol standards and (B). an extract of Sample IV (1: 2,6-dichlorophenol, 2: 2,4-dichlorophenol, 3: 2,4,6-trichlorophenol, 4: 2,4,5-trichlorophenol, 5: 2,3,6-trichlorophenol, 6: 2,3,4,6-tetrachlorophenol, 7; pentachlorophenol, 8: 2-bromo-4-chlorophenol, 9: 4-bromo-2-chlorophenol, 10: 2-bromo-4,6-dichlorophenol, 11: 4-bromo-2,6-dichlorophenol (estimated), 12: 2,6-dibromophenol, 13: 2,4-dibromophenol, 14: 2,6-dibromo-4-chlorophenol (estimated), 15: 2,4-dibromo-6-chlorophenol (estimated), 16: 2,4,6-tribromophenol). A column of 2% DEGS was used.

from this sample were 2-bromo-4-chlorophenol (peak a), 4-bromo-2,6-dichlorophenol (peak b), 2,6-dibromophenol (peak c), 2,4-dibromophenol (peak d), 2,6-dibromo-4-chlorophenol (peak e), 2,4-dibromo-6-chlorophenol (peak f), and 2,4,6-tribromophenol (peak g), as shown in this figure. After ethylation, these brominated phenols found were further confirmed by comparing of the retention time and ratio of the fragment ion peaks of the sample extract with those of the standards on the mass chromatography, using a capillary column.

Table 2 shows the resulting concentrations of halogenated phenols in chlorinated wastewater. In sample I, the control, some chlorinated phenols such as dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol, were found at relatively higher concentrations. 2,6-Dibromophenol and 2,4,6-tribromophenol were also found in this sample, though the concentration of these two compounds was quite low. The concentration of the halogenated phenols found in Sample II treated with 20 ppm of chlorine was lower than that in Sample I except for 2,4,6-trichlorophenol. It was found that only 2,4,6-trichlorophenol was formed, and that the other halogenated phenols were slightly decomposed by chlorination at the experimental conditions. No halogenated phenol was found in Sample III treated with 100 ppm of chlorine. All the halogenated phenols

Table 2. Levels of halogenated phenols (in ng/l) in chlorinated wastewater

Phenol	Sample			
	I	II	III	IV
Dichlorophenol [1]	98.1	80.8	nd[2]	nd[2]
2,4,6-Trichlorophenol	18.2	21.6	"	"
2,4,5-Trichlorophenol	nd[2]	nd[2]	"	"
2,3,6-Trichlorophenol	"	"	"	"
2,3,4,6-Tetrachlorophenol	8.9	7.2	"	"
Pentachlorophenol	20.3	14.7	"	"
2-Bromo-4-Chlorophenol	nd[2]	nd[2]	"	6.3
4-Bromo-2-chlorophenol	"	"	"	nd[2]
2-Bromo-4,6-dichlorophenol	"	"	"	"
4-Bromo-2,6-dichlorophenol (estimated)	"	"	"	1.8
2,6-Dibromophenol	1.9	"	"	3.0
2,4-Dibromophenol	nd[2]	"	"	8.6
2,6-Dibromo-4-chlorophenol (estimated)	"	"	"	9.0
2,4-Dibromo-6-chlorophenol (estimated)	"	"	"	16.7
2,4,6-Tribromophenol	3.2	2.9		71.1
Pentabromophenol	nd[2]	nd[2]	"	nd[2]

[1]The main compound was 2,4-dichlorophenol.
[2]nd: not detected, <1.0 ng/l.

were apparently decomposed by this chlorination.

However, seven brominated phenols were found in Sample IV treated with 100 ppm of chlorine in the presence of 10 ppm of bromide ions, as shown in Table 2. The concentration of these brominated phenols was much higher than that in the control. Therefore, it is clear that these brominated phenols were formed by the chlorination of wastewater containing bromide ions. The production of brominated organics in water chlorination may possibly have been due to hypobromous acid formed from bromide ions through the action of chlorine (Morris 1978). 2,4,6-Tribromophenol was the main product, followed by dibromochlorophenols in this experiment. No production of brominated phenols in Sample II and III took place due to the extremely low level of bromide ions in these samples.

The results obtained in the present experiment indicate that brominated phenols are possibly formed through chlorination of wastewater. Also, the production of brominated phenols along with chlorinated phenols through the chlorination of natural water was reported by Bean et al. (1980), as described above. The formation of brominated phenols in the chlorination of sea water used as coolant at power plants is also expected, because of the high level of bromide ions in sea water, about 65 ppm. Consequently, environmental pollution by brominated phenols formed in the chlorination of water is suspected. Indeed,

the pollution of river sediment by brominated phenols has been recognized, as described above (Watanabe, unpublished data). It has been also recognized that pollution of marine fish and shellfish is caused by brominated anisoles produced from the decomposition of brominated phenols through a microbiological methylation in the environment (Miyazaki et al. 1981; Watanabe et al. 1983).

Therefore, brominated phenols present in the environment should be carefully controlled when using chlorine oxides as water disinfectant. An investigation of the biological and toxicological effects should also be carried out on these compounds.

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