

FORMATION AND SOURCES I -POSTER

OCCURRENCE AND FORMATION MECHANISM OF PCDDs/PCDFs IN CHLORINE BLEACHING OF WOOD PULP

SUN KYOUNG SHIN, SEONG KI JANG, YOUNG HEE CHUNG

National Instituted of Environmental Research, Sudokwon Landfill 2-1 Environmental Complex
Kyunseodong, Seogu, Incheon 404-170, Korea

ABSTRACT

The one of the pulp manufacture facility was selected as surveying facilities to examine the discharged rate and generation mechanism of dioxin in bleaching stage wastewater. The analytical method was established in the wastewater and the sample was collected and analyzed.

The outlet concentration of bleaching stage was increased 5 times for 2,3,7,8-TCDF and 7 times for OCDD, and the discharged ratio between PCDFs and PCDDs was surveyed about 2:3. The 2,3,7,8-TCDF and 2,3,7,8-TCDD were mainly detected in acid wastewater of bleaching stage that is known as the typical discharged patterns of chlorine bleaching stage.

INTRODUCTION

Polychlorinated dibenzofurane(PCDFs) and polychlorinated dibenzo-p-dioxin(PCDDs) are well known to toxic compounds and environmentally persistent[1~2]. These groups of compounds were associated with the chlorine bleaching of wood pulp[3~6], and the industry has influential factors such as economic influence and environmental impact in many countries. Therefore, to properly assess the environmental impact of pulp and paper industry, the emission patterns and formation mechanism in pulp bleaching stage have been developed. To do this, the analytical method was developed and the samples were analyzed using high resolution gas chromatography/high resolution mass spectrometry(HRGC/HRMS). This methods have been applied the 18 samples and laboratory blank. These samples have included a variety of bleaching liquors, which contained inlet and outlet of bleaching stage, recovery process, finishing process, influent and effluent. These analytical methods have been applied to a large number of wastewater samples to examine the discharged patterns and formation mechanisms in wastewater samples.

In this study, the discharge patterns and PCDDs/PCDFs formation mechanism were examined by analyzing the inlet and outlet of pulp bleaching stages.

EXPERIMENTAL METHODS

Instrumental Analysis : The analytical condition represented in Table 1. The expression of analytical results were represented in Table 2. The detection limits of each isomer was surveyed variously. The detection limits were surveyed 0.5~10 pg/l for tetra-/penta-, 0.2~25pg/l for hexa-/hepta- and 0.5~50 for octa-PCDDs/PCDFs. The 0.005 ng-TEQ/l was detected in blank sample as shown in Table 2, therefore the sample, which detected less than 0.005 ng-TEQ/l, was regarded as Not Detected.

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Table 1. GC/MS Analytical Conditions of PCDDs/PCSFs

	PCDDs/PCDFs
GC/MS	VG Co., Autospec Ultima
Injector Temp.	250°C
Column	DB-5MS(60m× 0.32mm ID× 3.0 μ m) 150°C(1min)→ 210°C(10°C/min, 8min)→ 235°C(3°C/min, 8min) → 310°C (6°C/min, 20min)
Carrier Gas	He, 2.5ml/min
Injecton Port	Splitless
Ionization Type	EI
Ion Source Voltage	36eV
Ion Source Temp.	260°C
Resolution	10,000
Monitoring	SIM, 5 Function

Table 2. Detection Limits of International Official methods.

Method (Matrix, Sample Amount, Concentrated Amount)	Tetra- Penta-	Hexa- Hepta-	Octa-
EPA 8290(Water, 1l , 20 μ l)	10 pg/l	25 pg/l	50 pg/l
EPA 8290(Soils, Sediment, Pulp, Ash, Tissue, 10g, 20 μ l)	1 pg/g	2.5 pg/g	5 pg/g
Japan(Wastewater, 4l)	0.5 pg/l	1 pg/l	2.5 pg/l
Japan(Water, 20l)	0.1 pg/l	0.2 pg/l	0.5 pg/l
This Study	1pg/l	2pg/l	5pg/l

Sampling and sample Analysis : The samples were collected three times in the inlet and outlet of bleaching pulp stage. The collected samples were analyzed in previous paper[7]. The procedure of each pretreatment step was considered in laboratory scale and established based on the experimental data, which applied to real environmental sample. The internal standard recoveries of 2,3,7,8-substituted isomers were obtained between 85% and 89%, which was satisfied the EPA method(40~135%), JIS method(50~120%) and Korean official method(50~120%).

RESULTS AND DISCUSSION

Dicharged Characteristics in Bleaching Stage : The bleaching process could be divided into 5 steps containing the chlorine bleaching stages and 3 steps containing the chlorine and oxygen bleaching stages, and the wastewater produced by chlorine bleaching steps called acidic wastewater. Table 3 and Table 4 showed the analytical results of inlet and outlet bleaching process. Table 3 represented the inlet of bleaching stage, which called stream process. OCDD and PCDF mainly detected in stream process.

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Table 3. Discharged Distribution of 2,3,7,8-Substituted Isomers in Bleaching Stage

2,3,7,8-Substituted Isomer	Inlet		Outlet	
	Conc.(ng/l)	%	Conc (ng/l)	%
2,3,7,8-TCDF	0.0322	19.55	0.1580	12.95
1,2,3,7,8-PeCDF	0.0000	0.00	0.0203	1.66
2,3,4,7,8-PeCDF	0.0000	0.00	0.0000	0.00
1,2,3,4,7,8-HxCDF	0.0049	2.96	0.0251	2.06
1,2,3,6,7,8-HxCDF	0.0028	1.72	0.0253	2.08
2,3,4,6,7,8-HxCDF	0.0036	2.16	0.0392	3.22
1,2,3,7,8,9-HxCDF	0.0037	2.24	0.0572	4.70
1,2,3,4,6,7,8-HpCDF	0.0041	2.48	0.0301	2.47
1,2,3,4,7,8,9-HpCDF	0.0041	2.50	0.0366	3.01
OCDF	0.0091	5.51	0.0811	6.65
2,3,7,8-TCDD	0.0000	0.00	0.0072	0.59
1,2,3,7,8-PeCDD	0.0034	2.05	0.0000	0.00
1,2,3,4,7,8-HxCDD	0.0073	4.42	0.0414	3.39
1,2,3,6,7,8-HxCDD	0.0000	0.00	0.0259	2.12
1,2,3,7,8,9-HxCDD	0.0044	2.68	0.0401	3.29
1,2,3,4,6,7,8-HpCDD	0.0059	3.60	0.0575	4.71
OCDD	0.0794	48.15	0.5745	47.11
Total	0.1649	100.00	1.2919	100.00
Internal Std. Recovery	85.09		88.84	

The PCDDs/PCDFs discharged 2:3 in inlet and outlet of this process. In outlet of bleaching stage, the concentration of 2,3,7,8-substituted isomers increased except for 1,2,3,7,8-PeCDD. Especially, the concentration of 2,3,7,8-TCDF was increased 5 times from 0.3220ng/l to 0.1580ng/, and this isomer formed in the process of chlorine bleaching. The toxic equivalent concentration was calculated using the TEF values, and the TEQ value represented 0.0078

ng-TEQ/l for inlet and 0.0514 ng-TEQ/l for outlet of bleaching stage. Also, the 2,3,7,8-TCDF, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8 HxCDD and 1,2,3,4,7,8-HxCDF were detected in inlet of bleaching stage, and 2,3,7,8-TCDD, 2,3,7,8-TCDF and 1,2,3,4,7,8-HxCDD were detected in outlet of bleaching. The concentration of 2,3,7,8-TCDF and 2,3,7,8-TCDD in outlet of bleaching stage were increased, therefore these isomer produced in chlorine bleaching process. This result is the same as other country research [10].

PCDDs/PCDFs Formation Mechanism : The concentration of OCDD and 2,3,7,8-TCDF remarkably increased in chlorine bleaching process. The OCDD might be produced the condensation of pentachlorophenol or condensation and addition of di-, tri- and tetrachlorophenol. The 2,3,7,8-TCDD and TCDF might be produced the condensation or structural rearrangement of chlorophenols and chlorination of dibenzo-p-dioxin and dibenzofurane.

The concentration of 1,2,3,7,8-PeCDF decreased in this process. These phenomena could be explained the transition from this compound to low chlorinated compounds, which occurred the dechlorination followed by hydrogenation, and rearrangement of chlorine substituted position between congeners[11]. Also, 2,3,7,8-TCDF accounted for 29%, and 2,3,7,8-TCDD accounted for 15% of total detected PCDDs/PCDFs.

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Table 4. Discharged Distribution of 2,3,7,8-Substituted Isomers (TEQ) in Bleaching Stage

2,3,7,8-Substituted Isomer	Inlet		Outlet	
	Conc. (ng-TEQ/ℓ)	%	Conc. (ng-TEQ/ℓ)	%
2,3,7,8-TCDF	0.0032	41.23	0.0158	30.74
1,2,3,7,8-PeCDF	0.0000	0.00	0.0010	1.96
2,3,4,7,8-PeCDF	0.0000	0.00	0.0000	0.00
1,2,3,4,7,8-HxCDF	0.0005	6.27	0.0025	4.88
1,2,3,6,7,8-HxCDF	0.0003	3.59	0.0026	5.12
2,3,4,6,7,8-HxCDF	0.0004	4.61	0.0039	7.63
1,2,3,7,8,9-HxCDF	0.0004	4.74	0.0057	11.15
1,2,3,4,6,7,8-HpCDF	4.0×10^{-5}	0.51	0.0003	0.58
1,2,3,4,7,8,9-HpCDF	4.0×10^{-5}	0.51	0.0004	0.72
OCDF	1.0×10^{-5}	0.13	8.0×10^{-5}	0.16
2,3,7,8-TCDD	0.0000	0.00	0.0072	13.95
1,2,3,7,8-PeCDD	0.0017	21.64	0.0000	0.00
1,2,3,4,7,8-HxCDD	0.0007	9.35	0.0041	8.05
1,2,3,6,7,8-HxCDD	0.0000	0.00	0.0026	5.04
1,2,3,7,8,9-HxCDD	0.0004	5.63	0.0040	7.80
1,2,3,4,6,7,8-HpCDD	6.0×10^{-5}	0.77	0.0006	1.11
OCDD	8.0×10^{-5}	1.02	0.0006	1.11
Total	0.0078	100.00	0.0514	100.0

These results had some difference of other country's study which results were reported the 2,3,7,8-TCDD/TCDF occupied almost 100%, but the result could be agreed that tetra-PCDD/PCDF were mainly detected in wastewater of bleaching stage.

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ORGANOHALOGEN COMPOUNDS