DISCHARGED PATTERNS AND FORMATION MECHANISM OF PCDDs/PCDFs IN PULP AND PAPER FACILITIES

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ABSTRACT

The one of the pulp manufacture facility was selected as surveying facility to examine the discharged amount and generation mechanism of dioxins except for bleaching stage wastewater. In recovery and finishing process, 2,3,7,8-TCDF, OCDD and OCDF were mainly detected, and the ratio of PCDDs and PCDFs were surveyed 76:24 and 62:38. In catch basin, The OCDD, 1,2,3,7,8-PeCDD and 1,2,3,4,7,8-HxCDD as the concentration of 2,3,7,8-substitute isomer were discharged which is known as the typical emission pattern of pulp & paper manufacture facility, and the 1,2,3,7,8-PeCDD and 1,2,3,4,7,8-HxCDD was discharged more than 90% in toxic equivalent concentration. Also, the OCDD and 2,3,7,8-TCDF for 2,3,7,8-isomer concentration, and 1,2,3,7,8-PeCDD and 2,3,7,8-TCDF as toxic equivalent concentration were discharged in effluent. The detected PCDDs/PCDFs concentration were surveyed 0.2266 ng-TEQ/ℓ for influent and 0.0377 ng-TEQ/ℓ for effluent.

INTRODUCTION

Chlorinated organics such as PCDDs/PCDFs, PCBs, and pesticides and so on. are a class of compounds, which have highly toxic and quite persistent in the environment[1,2]. Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs) are formed during incomplete combustion and released as unknown by-products of industrial process [3]. The PCDDs/PCDFs related to the chlorine bleaching of pulp. The PCDDs/ PCDFs are two series of planar tricyclic aromatic compounds. The PCDDs/PCDFs were first identified as accidental by products in the production of pentachlorophenol, PCBs and certain chlorophenoxy herbicides[4,5,6]. Also, these groups of compounds were associated with the chlorine bleaching of wood pulp, which suggested by Sandermann in 1974[7]. Therefore to properly assess the environmental impact of pulp and paper industry, the discharged patterns and formation mechanism in pulp manufacturer facility have been performed in this study. The 12 samples and laboratory blank were analyzed to examine, and these samples had included recovery process, finishing process, influent and effluent

EXPERIMENTAL METHODS

The analytical condition, expression of analytical result and detection limits was represented in previous papers[8]. The analytical procedure of liquid sample showed in Figure 1. The sample collected in the process.

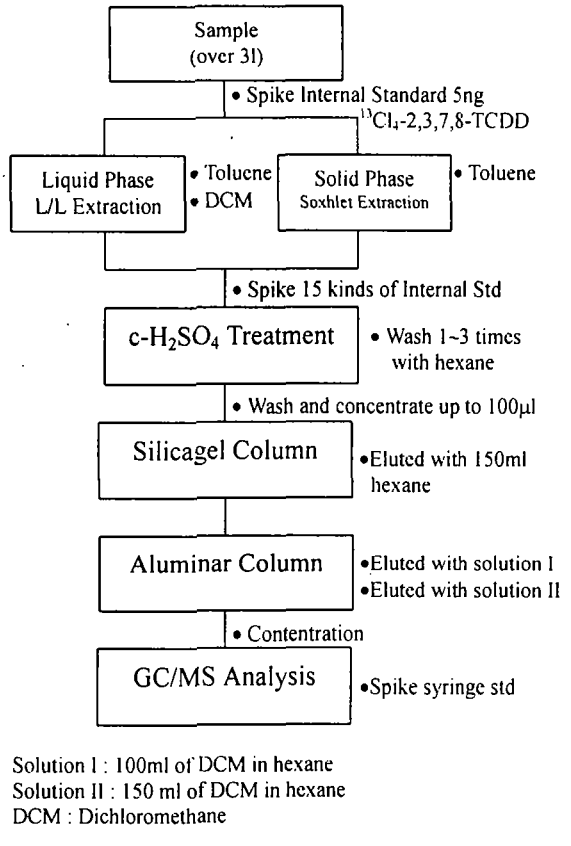

Figure 1. Flowchart of Liquid Sample Analysis

RESULTS AND DISSCUSION:

The wastewater samples of recovery, finishing, influent and effluent process were collected to analyze the discharged patterns and examine the PCDDs/PCDFs formation mechanism. The bleaching stage was discussed in previous paper[8].

Discharged Patterns of PCDDs/PCDFs : The discharged wastewater in pulp and paper industry can be divided into acidic wastewater from bleaching stage and alkali wastewater from other process. The produced wastewater in recovery process after stream process concluded the washing and evaporating, and the alkali wastewater contained the lignin, which separated from stream process. The finishing process is to remove the impurity from bleached pulp, and the waste has also alkali character. In influent, the wastewater mixed the acid wastewater, which came from bleaching stage and alkali wastewater. The analytical result showed in Table 1 and 2.

As shown in Table 1, the discharged 2,3,7,8-substituted isomers in recovery and finishing process were mainly detected 2,3,7,8-TCDF, OCDD and OCDF, and the ratio of PCDFs and PCDDs is about 3:1. Especially, 2,3,7,8-TCDF accounted for 67% and 48%.

But, the discharged isomers in influent were detected OCDD, 1,2,3,7,8-PeCDD and 1,2,3,4,7,8-HxCDD, and 1,2,3,7,8-PeCDD accounted for 81% in TEQ. Therefore, the tendency of discharged patterns between process wastewater and influent were surveyed differently due to the influent contained alkali and acidic wastewater. Also, the alkali wastewater contained 1,2,3,7,8-PeCDD and 1,2,3,4,7,8-HxCDD, and the acid wastewater mainly discharged 2,3,7,8-TCDD/TCDF. The detected concentration were 0.0514 ng-TEQ/l for acidic wastewater and 0.2266 ng-TEQ/l for alkali wastewater. This result was the same as previous reported research[7], which the alkali waste water discharged 30~40% of PCDDs/PCDFs comparing the acidic wastewater discharged 10% of PCDDs/PCDFs.

Formation Mechanism of PCDDs/PCDFs : The alkali wastewater in stream process and influent wastewater analyzed to examine the dioxin formation mechanism. The discharged concentrations were recalculated to $[\text{influent}]_{conc} - [\text{alkali}]_{conc}$. OCDD, 1,2,3,7,8-PeCDD and

1,2,3,4,7,8-HxCDD mainly detected.

This result agreed with Sweden researcher's result[7], which 1,2,3,7,8-PeCDD formed in the step of alkali extraction steps. The result also occurred the condensation, chlorination and dechlorination of 2,3,5-, 2,4,5-, 2,4,6-trichlorophenol, tetrachlorophenol and pentachlorophenol by heating of alkali condition. Figure 2 and 3 showed the chromatogram of PeCDD and HxCDD in inlet and outlet process.

Table 1. Discharged Distribution of 2,3,7,8-Substituted Isomers in wastewater

2,3,7,8-Substituted Isomer(Unit : ng/ℓ)	Recovery		Finishing		Influent		Effluent	
	Conc.	%	Conc.	%	Conc.	%	Conc.	%
2,3,7,8-TCDF	0.3365	66.75	0.1806	47.58	0.0063	0.19	0.0975	16.16
1,2,3,7,8-PeCDF	0.0026	0.51	0.0040	1.06	0.0048	0.15	0.0000	0.00
2,3,4,7,8-PeCDF	0.0040	0.80	0.0000	0.00	0.0076	0.23	0.0000	0.00
1,2,3,4,7,8-HxCDF	0.0044	0.87	0.0045	1.18	0.0040	0.12	0.0000	0.00
1,2,3,6,7,8-HxCDF	0.0029	0.57	0.0054	1.43	0.0067	0.20	0.0107	1.84
2,3,4,6,7,8-HxCDF	0.0037	0.74	0.0048	1.26	0.0078	0.24	0.0171	2.92
1,2,3,7,8,9-HxCDF	0.0030	0.60	0.0106	2.78	0.0150	0.45	0.0247	4.22
1,2,3,4,6,7,8-HpCDF	0.0072	1.44	0.0068	1.80	0.0082	0.25	0.0175	3.00
1,2,3,4,7,8,9-HpCDF	0.0027	0.53	0.0029	0.76	0.0123	0.37	0.0276	4.73
OCDF	0.0149	2.95	0.0145	3.84	0.0363	1.10	0.0269	4.61
2,3,7,8-TCDD	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0035	0.61
1,2,3,7,8-PeCDD	0.0125	2.47	0.0000	0.00	0.3698	11.20	0.0241	4.12
1,2,3,4,7,8-HxCDD	0.0069	1.37	0.0063	1.68	0.2781	8.42	0.0283	4.84
1,2,3,6,7,8-HxCDD	0.0050	0.99	0.0044	1.17	0.0134	0.41	0.0165	2.83
1,2,3,7,8,9-HxCDD	0.0057	1.14	0.0055	1.45	0.0118	0.36	0.0161	2.77
1,2,3,4,6,7,8-HpCDD	0.0062	1.24	0.0071	1.88	0.0541	1.64	0.0291	4.98
OCDD	0.0858	17.01	0.1219	32.14	2.4659	74.67	0.2448	41.87
Total	0.5041	100	0.3795	100	3.3026	100	0.5848	100
Internal Std. Recovery	98.7		88.4		86.8		90.8	

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

2,3,7,8-Substituted Isomer(ng-TEQ/ℓ)	Recovery		Finishing		Influent		Effluent	
	Conc.*	%	Conc.*	%	Conc.*	%	Conc.*	%
2,3,7,8-TCDF	0.0337	74.05	0.0018	79.49	0.0006	0.28	0.0098	25.84
1,2,3,7,8-PeCDF	0.0001	0.29	0.0002	0.88	0.0002	0.11	0.0000	0.00
2,3,4,7,8-PeCDF	0.0020	4.42	0.0000	0.00	0.0380	1.69	0.0000	0.00
1,2,3,4,7,8-HxCDF	0.0004	0.97	0.0005	1.98	0.0004	0.18	0.0000	0.00
1,2,3,6,7,8-HxCDF	0.0003	0.64	0.0005	2.38	0.0007	0.30	0.0011	2.84
2,3,4,6,7,8-HxCDF	0.0004	0.81	0.0005	2.11	0.0008	0.34	0.0017	4.53
1,2,3,7,8,9-HxCDF	0.0003	0.66	0.0011	4.67	0.0015	0.66	0.0025	6.55
1,2,3,4,6,7,8-HpCDF	0.0001	0.15	0.0001	0.31	0.0001	0.04	0.0002	0.48
1,2,3,4,7,8,9-HpCDF	3.0×10^{-5}	0.04	0.0000	0.13	0.0001	0.05	0.0003	0.74
OCDF	1.0×10^{-5}	0.02	0.0000	0.04	0.0000	0.02	0.0000	0.08
2,3,7,8-TCDD	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0036	9.41
1,2,3,7,8-PeCDD	0.0062	13.73	0.0000	0.00	0.1849	81.62	0.0121	31.96
1,2,3,4,7,8-HxCDD	0.0007	1.52	0.0006	2.82	0.0278	12.27	0.0028	7.50
1,2,3,6,7,8-HxCDD	0.0005	1.10	0.0004	1.94	0.0013	0.60	0.0017	4.37
1,2,3,7,8,9-HxCDD	0.0006	1.25	0.0006	2.42	0.0018	0.52	0.0016	4.29
1,2,3,4,6,7,8-HpCDD	0.0001	0.13	0.0001	0.31	0.0005	0.24	0.0003	0.77
OCDD	0.0001	0.20	0.0001	0.53	0.0025	1.09	0.0002	0.64
Conc.(ng-TEQ/ℓ)	0.0422	100	0.0227	100	0.2266	100	0.0377	100
Internal Std. Recovery	98.7		88.4		86.8		90.8	

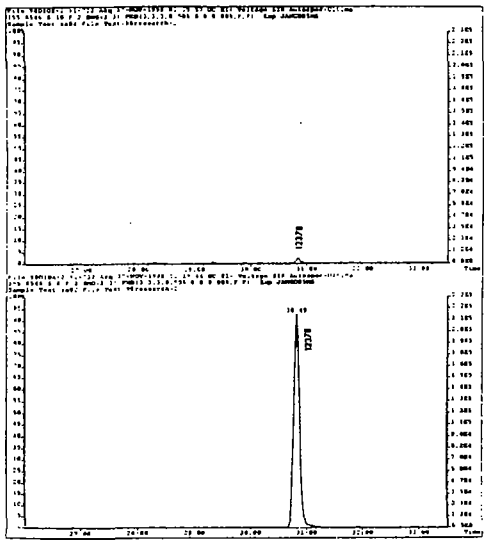

Figure 2. PeCDDs Chromatogram
(Up : Outlet of stream stage, Down : influent)

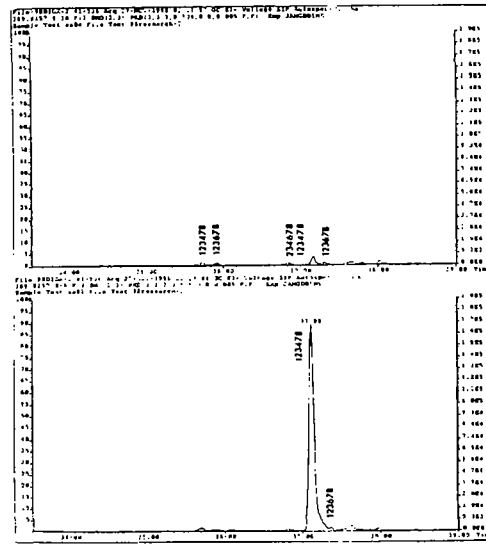

Figure 3. HxCDDs Chromatogram
(Up : Outlet of stream stage, Down : influent)