

CHARACTERISTICS OF DIOXINS REMOVAL BY COAGULATION AND SEDIMENTATION PROCESS

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Introduction

In order to prolong the service life of landfill sites, incineration of waste has been promoted to reduce the volume of dumped waste in Japan. Incineration of waste is one of the main causes of dioxin emission¹ and then, leachate from landfill sites, mainly dumped incineration residue, contains dioxins². Moreover, the regulation for dioxins in water was enforced in January, 2000, in Japan. For dioxin treatment, some methods like an advanced oxidation process³ as decomposition technology or an ultrafiltration process⁴ as removal technology have been developed. On the other hand, as the solubility of dioxins is so low, it is said that the most of dioxins in leachate are insoluble⁵ and can be removed only by removing suspended solids. For the SS removal, the coagulation and sedimentation process or the sand filter process are effective methods. However, the sufficient of study on the characteristics of dioxin removal by the coagulation and sedimentation process has not been done.

The objective of this paper is to investigate the characteristics of dioxins removal by the coagulation and sedimentation process.

Methods and Materials

A jar tester by using a 500mL beaker was used in this study and the experimental conditions are as follows:

1. Preparation of sample: Surrogates, Dioxins, Kaolin and Humic Acid dose
2. Mixing: 120r.p.m. (3mins)
3. Coagulation: 30r.p.m. (10-60mins)
4. Settlement: 60mins

Coagulant: PAC (poly aluminum chloride)

The pH value in this study was controlled at around 7.0 by dosing NaOH and HCl. 10 mL for surrogate substances and 3-6 L for dioxins and after 60mins settlement, were sampled for analysis. For surrogate substances analysis, after internal standards were added to the samples, and the pH adjusted to 4.0 in order to increase extraction efficiency, and 1mL of toluene was dosed, and then, the samples were shaken for 15mins. The toluene phase was extracted by using a Pasteur pipette after separating by a cyclone separator. An aliquot of the extract was injected into a gas chromatograph (GC) and detected by a mass spectrometer. For dioxins, the samples were filtered through a glass fiber filter. The filter was extracted for 16 hours using toluene in a Soxhlet extractor, and the filtrate was extracted with methylene chloride. The methylene chloride extract was concentrated by a rotary evaporator and combined with the Soxhlet extract prior to cleanup. The extracts were cleaned up using a silica gel adsorption and were concentrated to near dryness. Immediately prior to injection, internal standards were added to each extract, and an aliquot of extract was injected into the GC. Dioxins were separated by the GC (Silica capillary column) and detected by a high-resolution mass spectrometer.

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Properties of dioxins and dioxins' surrogates

In this study, we investigate the characteristics of dioxins' surrogates removed by the coagulation and sedimentation process as well as that of dioxins, and compared these characteristics.

Table 1 shows properties of dioxins and dioxins' surrogates which were examined in this study. Solubility and vapor pressure of both dioxins and dioxins' surrogates increase in accordance with the increase of the chlorine number. The experimental conditions and results dosing 9 of surrogate substances, MCBZ, o-CP, o-CT, o-DCBZ, 1,2,4-TCBZ, 2,4-DCP, 1,2,3-TCBZ, PCBZ and HCBZ, to leachate are shown in Table 2. The concentrations of CPs and MCBZ in treated water were higher than in raw water because of obstructions. Regarding the other surrogate substances, the removal ratio ranged from 16% to 88% in RUN1-1, from 8.0% to 92% in RUN1-2 and from 5.0% to 96% in RUN1-3, and the removal ratio of low solubility was higher than that of high solubility. In this study, a detection limit for surrogate analysis was 0.01mg/L. So it would be adequate to make examinations around 1mg/L in surrogate concentration. As a result of the experiments by dosing 9 surrogate substances, considering each solubility and the detection limit for analysis, we used PCBZ for dioxins surrogate in the following experiments.

Experimental results and discussion

Experiments using PCBZ

Table 3 shows the experimental conditions by dosing PCBZ to tap water and Fig. 1 shows its results.

The treatment results of PCBZ, ranging from 0.3mg/L to 10mg/L in raw water, indicated that it was removed below 0.83mg/L, its solubility, by dosing more than 10 mg/L of PAC. Raw water containing 3.5 mg/L of PCBZ was treated to from 0.29mg/L of 100mg/L PAC dosage in RUN2-4 to 1.27mg/L of 1mg/L PAC dosage in RUN2-1. This indicates that the removal ratio increases in proportion to the increase of PAC dosage. When the PAC dosage was the same, such as 1mg/L in RUN2-1, 0.3mg/L of PCBZ was removed down to 0.15mg/L and 10mg/L of PCBZ was removed down to 1.44mg/L, and it showed that raw water containing a low concentration of PCBZ was treated more than raw water with a high concentration of PCBZ. PCBZ in treated water, however, ranged only from 0.26mg/L to 0.31mg/L except the RUN2-4 contained 0.3mg/L of PCBZ in raw water. Then we examined whether applying the coagulation and sedimentation treatment two or more times would influence its removal ratio. Table 4 and Fig.3 show the experimental conditions and results. 1.5mg/L of PCBZ was removed from 0.16mg/L to 0.28mg/L, the removal ratio ranged from 84% to 93% by treatment twice, whereas PCBZ was removed from 0.32mg/L to 0.45mg/L, the removal ratio ranging 70% to 79% by one treatment. This indicates that the removal ratio increases as the number of coagulation and sedimentation treatments increase.

The experimental results using leachate from landfill sites mainly with dumped incineration residue was shown in Table 5. 0.3mg/L of PCBZ was treated to 0.21mg/L, and 2.3mg/L of PCBZ was treated to 0.4mg/L. The removal ratio was 30% and 83%, respectively. The more the concentration of PCBZ increases, the higher the removal ratio, and PCBZ was removed below its solubility even though the treated water only ranged from 0.21mg/L to 0.4mg/L in concentration. This result was quite similar to experiments using tap water. The above results showed PCBZ in tap water and leachate was removed down to its solubility by dosing a certain concentration of coagulant because not only insoluble matter but also so solubility is removed by the adsorption of coagulants.

Experiments by using dioxins

In order to investigate the characteristics of dioxins removal by the coagulation and sedimentation process, dioxins extracted from fly ash were added to tap water and leachate.

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Table 1 Properties (at 25°C) of DNx and DNx' Surrogates

Compound	Vapor pressure		Solubility	Compound	Vapor pressure(25°C)		Solubility
	Pa	Pa(1iquid)	ng/L		Pa	f @ L	
2,3,7,8-TCDF	2.00E-07	1.18E-04	19,300	Mono chlorobenzene	1.665	293,000	
1,2,3,4,7-PCDF	8.80E-08	4.23E-06	118,000	1,4 dichlorobenzene	197	91,100	
1,2,3,4,7,8-HCDF	5.10E-09	1.45E-06	4,420	1,2 dichlorobenzene	269	123,000	
1,2,3,4,6,7,8-HPCDF	7.50E-10	1.77E-07	2,400	1,2,3-trichlorobenzene	17.3	12,200	
OCDF	1.10E-10	9.53E-07	0.074	1,2,4-trichlorobenzene	45.3	45,300	
2,3,7,8-TCDF	2.00E-06	1.99E-04	419,000	1,2,4,5-tetrachlorobenzene	0.72	2,160	
1,2,4,7,8-PCDF	3.50E-07	1.72E-05	236,000	1,2,4-dichlorobenzene	133(98.6)	830	
1,2,3,4,7,8-HCDF	3.20E-08	3.08E-06	8,250	Hexachlorobenzene	0.00145	6.2	
1,2,3,4,6,7,8-HPCDF	3.50E-08	3.61E-06	17,700	1,4 chlorophenol	230(20)	28,500,000	
1,2,3,4,6,7,8-HPCDF	4.70E-09	5.74E-07	1,350	2,4-dichlorophenol	133(53)	5,000	
1,2,3,4,4,7,8,9-HPCDF	6.20E-09	5.39E-07	1,160	1,4 chlorotoluene	360(20)	89,000	
OCDF	5.00E-10	1.01E-07	1.160	p-nitrophenol	0.0032(20)	12,400	
				B phenyl	133(20)	20	
				D phenyl ether	2.7(20)	20	

Table 2 Experimental conditions and results

Coagulant	100mg/L (PAC)								
	RUN-1			RUN-2			RUN-3		
	Raw	Treated	Removal	Raw	Treated	Removal	Raw	Treated	Removal
MHZ	0.5	1.4	-	1.0	1.6	-	2.0	2.3	-
1,2-DCBZ	0.5	0.42	16.0	1.0	0.92	8.0	2.0	2.1	-
1,2,3-TCBZ	0.5	0.31	38.0	1.0	0.63	37.0	2.0	1.4	30.0
1,2,4-TCBZ	0.5	0.42	16.0	1.0	0.88	12.0	2.0	1.9	5.0
PCBZ	0.5	0.27	46.0	1.0	0.35	65.0	2.0	0.47	76.5
HCBZ	0.5	0.061	87.8	1.0	0.079	92.1	2.0	0.09	95.5
f-PCP	0.5	0.58	-	1.0	1.2	-	2.0	2.4	-
1,2-DOP	0.5	0.56	-	1.0	1.2	-	2.0	2.1	-
f-ICT	0.5	0.47	6.0	1.0	1.4	-	2.0	2.3	-

Table 3 Experimental conditions

PCBZ Concentration	RUN-1			RUN-2			RUN-3			RUN-4			RUN-5			RUN-6		
	PAC Dosage						PAC						Kaolin					
mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
0.3	1	3	10	100														
0.5	1	3	10	100	10	100	50	100										
0.8	1	3	10	100	10	100	50	100										
1.5	1	3	10	100	10	100	50	100										
2.5	1	3	10	100	10	100	50	100										
3.5	1	3	10	100	10	100	50	100										
5	1	3	10	100	10	100												
10	1	3	10	100	10	100												
15					10	100												
24					10	100												

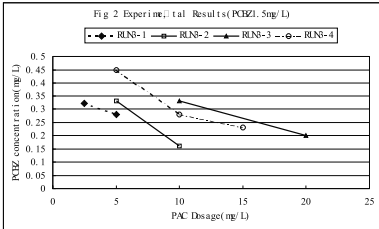


Table 4 Experimental conditions and results

RUN	PS/PCBZ	step		PAC	Treated
		mg/L	mg/L		
RUN-1	1.5	1	2.5	0.32	
		2	2.5	0.28	
RUN-2	1.5	1	5.0	0.33	
		2	5.0	0.16	
RUN-3	1.5	1	10	0.33	
		2	10	0.20	
RUN-4	1.5	1	5.0	0.45	
		2	5.0	0.28	
		3	5.0	0.23	

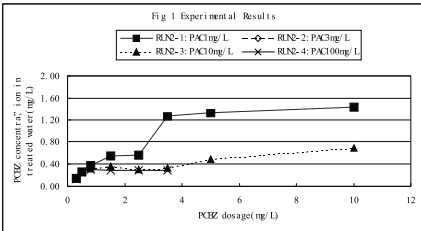


Table 5 Experimental conditions and results

PCBZ	PAC dosage	Treated	Removal
0.3	100	0.21	30
0.5	100	0.22	56
0.8	100	0.30	63
1.3	100	0.32	75
2.3	100	0.40	83

Table 7 Analytical data

RUN	Leachate		Effluent of Sedimentation Tank		Removal
	pg-THQ L	pg/L	pg-THQ L	pg/L	
1	17.1	1,090	1.42	221	92
	(3.1)	(200)	(0.52)	(91)	83
2	8.1	680	2.9	204	64
	(2.2)	(140)	(1.8)	(140)	18

(): DNx concentration in Solubility

Table 6 Experimental conditions and results

RUN	DNx Concentration		Step	PAC	Kaolin	Humic acid	Treated Water		Removal
	pg-THQ L	pg/L					pg-THQ L	pg/L	
RUN-1	16	320	1	20	-	-	6.4	110	66
			2	20	-	-	2.6	57	82
RUN-2	16	320	-	40	-	-	6.7	90	72
			-	20	100	-	6.2	155	97
RUN-3	250	6,147	-	20	-	-	8.2	206	97
RUN-4	250	6,147	-	20	-	100	-	-	-
RUN-1	7.4	240	1	100	-	-	ND	ND	-
			2	100	-	-	ND	ND	-

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Table 6 shows the experimental conditions and results.

16pg-TEQ/L of dioxins in tap water were removed down to 6.4pg-TEQ/L by dosing 20mg/L of PAC and 6.7pg-TEQ/L by dosing 40mg/L of PAC. However, it was removed to 2.6pg-TEQ/L by two coagulation and sedimentation treatments dosed 40mg/L (20mg/L+20mg/L) of PAC totally. The removal ratio increased from 66% to 82% by treatment two times. Each dioxin isomer was also removed below its solubility. These results were the same as with the experiments by PCBZ. Moreover, by dosing Kaolin or Humic acid with PAC, 250pg-TEQ/L of dioxins were removed down to 6.2pg-TEQ/L and 8.2pg-TEQ/L, respectively. Both removal ratios were 97%. In the study by using leachate, 7.4pg-TEQ/L of dioxins was removed below its detection limit. This result assumed that by adsorbed dioxins to suspended matters, dioxins were removed not only by coagulation directly but also with this suspended matter.

These results were also confirmed at a commercial plant. Table 7 shows the analytical data of dioxins at the commercial plant with mainly dumped incineration residue. At this plant, 8.1pg-TEQ/L and 17.1pg-TEQ/L of dioxins in leachate were treated to 1.42pg-TEQ/L and 2.9pg-TEQ/L in the effluent of the sedimentation tank. 92% and 64% of the total dioxins were removed by the coagulation and sedimentation process. In RUN1, 3.1pg-TEQ/L of dioxins in solubility was removed down to 0.52pg-TEQ/L, and in RUN2, 2.2pg-TEQ/L of dioxins in solubility was also removed down to 1.8pg-TEQ/L. The removal ratios were 83% and 18%. This result proved that dioxins in solubility as well as insoluble dioxins could be removed by the coagulation and sedimentation process.

There is research data at 16 commercial plants that dioxins in leachate ranged from 0.0006pg-TEQ/L to 16pg-TEQ/L⁶, and from this study, dioxins in leachate almost met this range of concentration. Therefore, dioxins in leachate would range from 10pg-TEQ/L to 20pg-TEQ/L generally and can be removed below the latest effluent standards of concentration by the coagulation and sedimentation process.

Conclusions

- 1) PCBZ as a surrogate for dioxins can be removed below its solubility by the coagulation and sedimentation process, and the removal ratio increases by treatment two and more times.
- 2) Dioxins can also be removed down to their solubility by the coagulation and sedimentation process, the same as PCBZ and the removal ratio ranged from 66% to 97%.
- 3) PCBZ behaves like dioxins in the process of coagulation and sedimentation. Therefore, by the experiment with PCBZ, we can confirm the characteristics of dioxin removal.
- 4) By the treatment of coagulation and sedimentation, dioxins in leachate were removed to under 10pg-TEQ/L which is equal to or less than the effluent standards in Japan. The removal ratio was 64% and 92% at the commercial plants

Reference

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