EXPERIMENTAL STUDY ON CYCLONE AND PACKED SCRUBBERS FOR CAPTURING PCBS AND PCDD/FS

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Introduction

Since 1966, Polychlorinated biphenyls (PCBs) were recognized as adverse persistent contaminants. Over ten thousand tons of PCBs were manufactured in China from 1966 to 1975. Main compounds are trichlorodiphenyl and pentachlorobiphenyl, applied as transformer oil and capacitor oil. Since 1979, PCBs usage was already forbidden including in electrical devices, however, the previous amount of PCBs have threatened to the environment and human health.

Thermal desorption is one of common technologies to remediate PCBs contaminated sites[1]. The typical thermal desorption consists of two steps: (1) heating the contaminated material to volatize the organic contaminants and (2) treating the exhaust gas stream by Air Pollution Control Devices (APCDs) to avoid secondary pollution[2]. Cyclone and wet scrubber are the useful APCDs to catch and separate organic pollutants from flue gas. Some published work also concentrates the formation and emission during this process, monitoring PCDD/Fs concentration at inlet and outlet of wet scrubber[3-14]. Wet scrubber can get remarkable remove efficiency for heavier loads of dust and particle-bound PCDD/DF[15], while in some case, wet scrubbers could become a potential PCDD/Fs source because of the adsorption/desorption of PCDD/Fs in plastic packed materials and other plastic assembly[3-7,9-11]. To enhance the PCDD/Fs adsorption/absorption, Some new Polypropylenes were also developed[8]. Until now, few researches about PCBs and PCDD/Fs concentrations in the inlets and outlets of cyclone and packed scrubbers were conducted.

Materials and methods

PCBs contaminated soil was collected from one of waste transformer conservation points in Shaoxin City, China. Large scale soil was contaminated because of PCBs oil leakage from waste transformer. The raw soil was dried by air in a hood and sieved through 250 um screen. Some physicochemical properties were analyzed, including soil texture, water content, chlorine content, PH value, organic content and porosity.

Fig 1 shows the sketch figure of setup system. PCBs contaminated soil was heated in a laboratory-scale horizontal quartz tube furnace, nitrogen was used as carrier gas to sweep PCBs vapor. For each experiment, 10 gram was heated at 500 ºC for 50 minutes at Nitrogen flow of 4 Nm3/h.The flue gas cleaning system consists of a cyclone and two packed scrubbers. The diameter of cyclone is 60 mm, the diameter of tower 1 and tower 2 is 108 mm and 88 mm, respectively. For avoiding corrosion, all packed materials in both two packed scrubbers are made of stainless steel. The water flow for tower 1 and tower 2 was 30 L/h and 60 L/h. There were 3 sampling points (SA, SB and SC) located in the flue gas cleaning system as shown in Fig.1. The sampling time for all samples was 50 minutes with 0.05 m3/h flow.

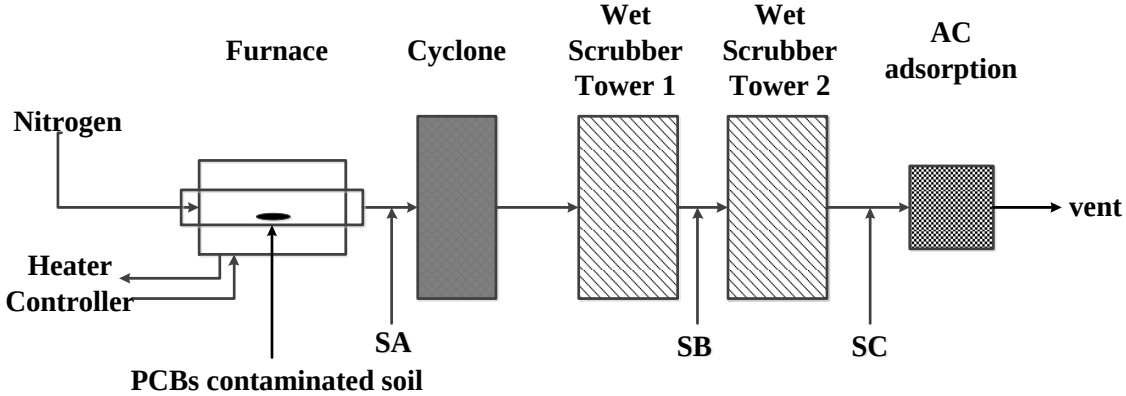

Fig.1 Diagram of the experimental reaction system

The PCBs gas samples collected and the treated soil were pre-treated by Soxhlet extraction, rotary evaporation, solvent exchange and volume extraction respectively. Then the pre-treated samples was sequentially purified with multi-silica gel column and Florisil column, the detailed method of pre-treatment and purification was conducted as EPA 1668 method. Finally, the PCBs solution was analyzed by HRGC/HRMS (JEOL JMS-800D, Japan) with a DB-5MS column (60m×0.25mm×0.25μm), and 209 PCBs isomers from mono-chlorinated to deco-chlorinated PCBs were detected, the detailed operation conditions of PCBs analyzer were depicted by Chen et al[16].

The quantification of PCBs content was assured by adding internal standards mixture, purification standards mixture, and injection standards mixture before Soxhlet extraction, purification and analysis process respectively. Data analysis demonstrated that, the recovery rates of each internal standard were between 30% and 128%, which were in accordance with the recovery standard of 25% to 150%; the recovery rates of each purification standard were between 56% and 124%, which were also in accordance with the purification standard of 30% to 135%.

Results and Discussion

Table 1 shows the PCBs concentration in raw soil and thermal desorption soil. Hepta- and higher chlorinated PCBs homologues totally account for less than 1% of PCBs amount, so the analysis and discussion concerned on the lower chlorinated species. TrCB and TeCB predominate the homologues of PCBs, the amounts of TrCB and TeCB account for 30.0% and 52.4% of total PCBs in raw Soil, and 53.4% and 33.9% in thermal desorption soil respectively. After 50 minutes heating, total PCBs decrease about 82.1%. This remove efficiency is not high enough, partly because of short heating time and low heating temperature.

Table.1 PCBs concentration in raw soil and thermal desorption soil

	Raw soil(mg/kg)	Thermal Desorption soil(mg/kg)	Remove efficiency
MoCB	4.2	0.5	88.9%
DiCB	280.4	128	54.4%
TiCB	3537.7	672.7	81.0%
TeCB	2779	426.6	84.7%
PeCB	352.8	27.2	92.3%
HeCB	36.5	2.1	94.2%
sum	6990.6	1257.1	82.1%

Table 2 shows the PCBs concentrations in SA, SB and SC. Hepta- and higher chlorinated PCBs homologues totally account for less than 1% of PCBs amount, so the analysis and discussion concerned on the lower chlorinated species. TrCB and TeCB predominate the homologues of PCBs, the amount of TrCB and TeCB account for more than 84.0% in all three samples. Generally, PCBs homologues with more chlorines decrease more in Tower 2 except for DiCB, and PCBs homologues with more chlorines decrease more after cyclone and wet scrubbers.

Table.2 PCBs concentration and remove efficiencies in SA, SB and SC

	PCB concentration (μg/m3)			Remove efficiency		
	SA(=a)	SB(=b)	SC (=c)	b-a	c-b	c-a
MoCB	6.81	1.8	1.39	73.5%	22.7%	79.5%
DiCB	82.08	29.26	16.75	64.4%	42.8%	79.6%
TrCB	321.36	128.77	77.49	59.9%	39.8%	75.9%
TeCB	210.51	50.7	27.41	75.9%	45.9%	87.0%
PeCB	11.58	2.69	1	76.8%	62.9%	91.4%
HeCB	0.72	0.23	0.06	68.5%	74.4%	91.9%
sum	633.2	213.5	124.1	66.3%	41.90%	80.40%

Table 3 shows the Dioxin-Like PCBs concentration in SA, SB and SC. The concentrations of Dioxin-Like PCBs are 2.95 μg/m3, 1.73μg/m3 and 0.24 μg/m3 in SA, SB and SC respectively. PCB 126# increases 38.5% after cyclone and Tower 1. It shows that Tower 2 perform well in removing the Dioxin-Like PCBs. The homologue profiles of Dioxin-Like PCBs change little. All PCBs congeners get a similar remove efficiency after cyclone and wet scrubbers.

Table.3 Congeners profiles and remove efficiencies of Dioxin-Like PCBs in SA, SB and SC

	PCB concentration (μg/m3)			remove efficiency			TEQ of PCBs(pg W-TEQ/m3)		
	SA(=a)	SB(=b)	SC (=c)	b-a	c-b	c-a	SA	SB	SC
81#	0.073	0.0549	0.0088	24.9%	84.0%	88.0%	21.9	16.47	2.64
77#	1.8053	1.1239	0.1518	37.7%	86.5%	91.6%	180.53	112.39	15.18
123#	0.0748	0.0146	0.0039	80.5%	73.1%	94.8%	2.244	0.438	0.117
114#	0.1068	0.0466	0.0084	56.4%	82.0%	92.2%	3.204	1.398	0.252
105#	0.8269	0.4535	0.0644	45.2%	85.8%	92.2%	24.807	13.605	1.932
126#	0.0072	0.01	0.0009	-38.5%	90.8%	87.2%	720	1000	90
167#	0.0094	0.0037	0.0005	60.4%	85.5%	94.2%	0.282	0.111	0.015
156#	0.0159	0.0131	0.0012	17.7%	90.6%	92.2%	0.477	0.393	0.036
157#	0.0046	0.0031	0.0005	32.7%	83.8%	89.1%	0.138	0.093	0.015
169#	ND	ND	ND	-	-	-	-	-	-
189#	ND	ND	ND	-	-	-	-	-	-
118#	0.0261	0.0099	0.0011	62.0%	88.7%	95.7%	0.783	0.297	0.033
sum	2.95	1.7333	0.2415	41.20%	86.10%	91.80%	954.4	1145.2	110.2

TEQ of PCBs were calculated base on WHO 2005 TEF. After Cyclone and tower 1, the TEQ increases from 954.4 pg TEQ/m3 to 1145.2 pg TEQ/m3. And after two-stage Scrubbers, the TEQ decrease to 110.2 pg TEQ/m3. PCB 126# and PCB 77# are the main contributors of the TEQ, which are 94.4%, 97.1% and 95.4% respectively. PCB 126#, which has the highest TEF of Dioxin-Like PCBs, increases from 0.007 μg/m3 to 0.010 μg/m3, and causes TEQ increasing .

Table 4 shows PCDD/Fs concentrations in SA, SB and SC. After Cyclone and tower 1, PCDD/Fs concentration increases from 5489.5 pg/m3 to 11429.7 pg/m3. And after cyclone and wet scrubbers, the PCDD/Fs concentration decreases to 3783.4pg TEQ/m3. It is observed that the homologue profiles change considerably. The concentrations of PCDDs change a little in all 3 points, while PCDFs, especially 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF, change a lot in these points. The concentrations of PCDFs are 3764.3 pg/m3, 9818.4 pg/m3 and 2030.2 pg/m3 respectively.

Table.4 The profiles of PCDD/Fs concentration in SA, SB and SC

	PCDD/Fs concentration (pg/m3)			Variation ratio			TEQ of PCDD/Fs(pg I-TEQ/m3)		
	SA(=a)	SB(=b)	SC (=c)	=b/a	=c/b	=c/a	SA	SB	SC
2378-TCDD	82.5	142.7	151	1.73	1.06	1.83	82.5	142.7	151.0
12378-PeCDD	114.2	116.7	306.3	1.02	2.62	2.68	57.1	58.4	153.2
123478-HxCDD	85.5	142.3	73.7	1.66	0.52	0.86	8.6	14.2	7.4
123678-HxCDD	109.8	149.3	114.8	1.36	0.77	1.05	11.0	14.9	11.5
123789-HxCDD	172.5	78.1	173	0.45	2.21	1	17.3	7.8	17.3
1234678-HpCDD	445	268.8	310.2	0.6	1.15	0.7	4.5	2.7	3.1
OCDD	715.7	713.3	624.3	1	0.88	0.87	0.7	0.7	0.6
2378-TCDF	1281.3	4797.7	284.2	3.74	0.06	0.22	128.1	479.8	28.4

12378-PeCDF	475	1778.3	70	3.74	0.04	0.15	23.8	88.9	3.5
23478-PeCDF	274.7	1504.5	274.5	5.48	0.18	1	137.4	752.3	137.3
123478-HxCDF	181.5	269.4	217.8	1.48	0.81	1.2	18.2	26.9	21.8
123678-HxCDF	295.3	341.7	288.3	1.16	0.84	0.98	29.5	34.2	28.8
123789-HxCDF	87.6	249.7	109.8	2.85	0.44	1.25	8.8	25.0	11.0
234678-HxCDF	272	192.3	165.5	0.71	0.86	0.61	27.2	19.2	16.6
1234678-HpCDF	464.5	371.2	369.3	0.8	0.99	0.8	4.6	3.7	3.7
1234789-HpCDF	184.9	220.9	45.8	1.19	0.21	0.25	1.8	2.2	0.5
OCDF	247.4	92.8	205	0.37	2.21	0.83	0.2	0.1	0.2
PCDD	1725.2	1611.3	1753.2	0.93	1.09	1.02	181.5	241.4	344.0
PCDF	3764.3	9818.4	2030.2	2.61	0.21	0.54	379.6	1432.3	251.7
PCDD/Fs	5489.5	11429.7	3783.4	2.08	0.33	0.69	561.2	1673.7	595.7

The TEQs of PCDD/Fs are 561.2 pg TEQ/m3, 1673.7 pg TEQ/m3 and 595.7 pg TEQ/m3 in SA, SB and SC respectively. The cyclone and Tower 1 perform badly in removing PCDD/Fs, especially for PCDF. After cyclone and Tower 1, The TEQ of PCDF increases about 2 times. It is observed that the TEQ of PCDD/Fs increases after cyclone and wet scrubbers.

Conclusions

1. Cyclone and two stages wet scrubber towers could effectively remove total PCBs and Dioxin-like PCBs in gas, achieving the PCBs remove rates 80.4% for the former and 91.8% for the latter.
2. PCDD concentrations did not change within measurement accuracy in gas downstream the cyclone and two stages wet scrubbers, while PCDF, especially 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF, increased a lot in gas downstream the tower 1, causing a TEQ of PCDD/Fs increasing of 198%. In gas downstream the tower 2, PCDF concentration dropped sharply, which indicated wet scrubber could be useful in removing of PCDD/Fs in appropriate situations.

Acknowledgements

This research work was financially supported by the National High Technology Research and Development Program of China (No.2009AA061304) and Major State Basic Research Development Program of China (973 Program) (No.2011CB201500).

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