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# Removal of PCDD/Fs from Flue Gas by a Fixed-Bed Activated Carbon Filter in a Hazardous Waste Incinerator

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The adsorption of polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs) by activated carbon (AC) was examined in a fixed-bed AC unit in a hazardous waste incinerator (IZAYDAS) in Turkey. Results showed that the removal efficiencies of PCDD/Fs decrease as the chlorination level increases, which was explained by the difference in gas/particle partitioning of the compounds. Since dioxins are tightly adsorbed by activated carbon, other flue gas constituents showed no clear effect on the dioxin removal. Adsorption kinetics indicated that the adsorption of volatile congeners and homologues fits well with Henry's law, possibly due to the higher gaseous fractions, while the correlation was lower for lowly volatile ones. PCDD/F congeners and homologues had a concentration value up to which no adsorption occurred, which could be attributed to the insufficient contact times at the low concentrations.

## Introduction

Carbon has been used for many years for the removal of vapor-phase organics in low concentrations from industrial waste gas streams. Data from waste incinerators in Europe have shown that dioxins, furans, and other semi-volatile products of incomplete combustion (PICs) at parts per billion (ppb) or lower concentrations can be effectively removed from the combustion gases by carbon. Adsorption of organic compounds on carbon is a function of many parameters including properties of the sorbent and the gases to be removed, concentration of other adsorbable gases and vapors, operating temperature, and residence time (1–4).

Two different methods of contacting gas with carbon adsorbent have been used. In fixed-bed (or passive) mode of operation, the gas flows through a bed (or series of beds) of solid adsorbent. Sufficient adsorbent is provided so that the operation can continue for a long time, from several hours to 1 yr or more, before the bed becomes saturated. The second mode of operation, which is commonly used for cleanup of flue gas, involves injecting a small amount of solid adsorbent into the flowing gas, providing sufficient contact time for the efficient use of the carbon, and then separating the adsorbent before discharging the gas up the stack. Each method has some advantages and drawbacks.

For example, the carbon injection process has the advantage of causing less pressure drop than a fixed-bed process, but the use of the adsorbent is less efficient (3, 5, 6). Both methods are widely used on municipal waste combustors and hazardous waste incinerators. The main objective of employing activated carbon (AC) units in waste incinerators is the removal of PCDD/Fs. Since AC adsorbs gaseous dioxins, the gas/particle partitioning of PCDD/Fs through the air pollution control equipments (APCE) should also be taken into consideration. Partitioning of PCDD/Fs between gas and particle phases depends mainly on the temperature and saturation vapor pressure of the compound besides other factors such as solid–surface area in the gas volume, mass amount of the compound at monomolecular surface covering, etc. (7). A highly chlorinated congener has a lower vapor pressure as compared to a lower chlorinated congener and has a higher tendency to condense on particles (8). As the vapor pressure of dioxin congeners decreases with increasing chlorination, the percentage of particle-bound dioxins and the removal efficiency of each dioxin congener in an AC unit will be different. Generally lower chlorinated dioxins with higher gaseous fractions are removed by carbon adsorption more efficiently than the highly chlorinated ones (9).

IZAYDAS, the first hazardous waste incinerator of Turkey, started to operate in 1997 in the Izmit region, the most polluted area in Turkey. The capacity of the plant is 35 000 t/yr. The facility has a two-stage combustion system consisting of a rotary kiln that is 12 m in length and 4.2 m in diameter; with combustion temperatures in the range of 950–1050 °C and a retention time of 2–2.5 h for solids. The vertical post-combustion chamber is 12 m in height and 4.1 m in diameter. This chamber incinerates the gases produced from the rotary kiln, vapors from the ash quench chamber, and some liquid wastes. It has a retention time of about 2 s at 1150–1250 °C, thus ensuring the complete destruction of hazardous organic compounds. The original air pollution control system of the plant consisted of an electrostatic precipitator (ESP) and dual wet scrubbers (a venturi scrubber and a lime scrubber) in series. However, operation of the incinerator created a large public debate on the atmospheric emissions of PCDD/Fs. Therefore, an additional fixed-bed AC unit was installed downstream of wet scrubbers in 1999, although PCDD/F emissions were measured below the European limit in several trial burns (10). Figure 1 shows the flow diagram of post-combustion units with associated temperature profiles and retention times. This paper presents the results and assessment of dioxin tests conducted at the AC unit between 2000 and 2002 to observe its dioxin removal efficiency.

## Experimental Section

**Description of the AC Unit.** Flue gases leaving the wet scrubbers at 60–65 °C are generally supersaturated with water vapor (about 22–24% (v/v) at normal conditions, corresponding to relative humidities (RH) between 110 and 130%); therefore, a condensation process is required before the AC. High humidity can negatively affect the adsorption of a carbon bed by filling up the pores in the carbon particles with condensed water. The extent to which the RH of the gas must be reduced in order to prevent this depends on the gas temperature (e.g., 80% RH would be satisfactory at 77 °C and about 50% RH at 57 °C) (3). Condensation occurs in the condensation chamber, which is combined with the AC unit, by a sudden decrease in the velocity of the flue gas and contact with the cold metallic surfaces. A volume of 72 m<sup>3</sup> is provided for condensation, corresponding to a retention time of 6.5–9 s for the actual gas flow rates of 30 000–40 000 m<sup>3</sup>/h. A total

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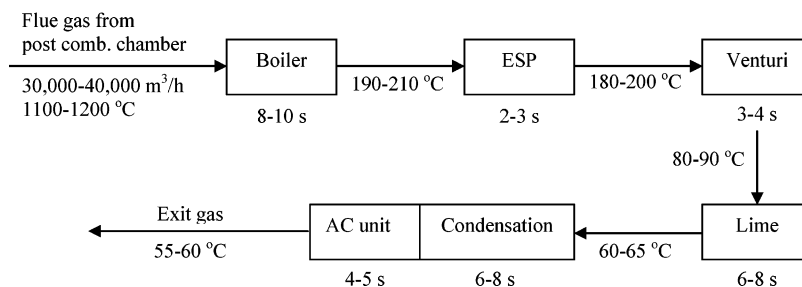


FIGURE 1. Flow diagram of post-combustion units with associated temperature profiles and retention times in the plant.

of 1.5–2 m cubes of condensed water are collected per hour from the condensation, reducing the RH to about saturation levels. The activated carbon unit includes five AC columns (in parallel) in a large cylindrical tank on the condensation chamber, providing direct passage to inside of the AC columns. Each column consists of two cylinders (one within the other, 1.8 and 0.6 m in diameter, 4 m in height) with perforated lateral surfaces. The space between the cylinders is filled with activated carbon (DioxSorb BXB, Jacobi, Sweden), providing a bed depth of 0.6 m. The activated carbon has a BET surface area of 1000 m<sup>2</sup>/g with weakly basic nature and a particle size range between 4 and 6 mm. Gases move from the inside to the outside by coming into contact with the activated carbon for 4–5 s.

**Sampling and Analyses.** Flue gas samples were taken from two sampling points (before and after the combined condensation and AC unit) simultaneously at five different dates between 2000 and 2002. PCDD/F sampling, cleanup, and quantification were conducted in accordance with current European Standard Protocols (11). Isokinetic flue gas sampling was performed by the filter–condenser method with a sampling train consisting of a quartz fiber filtration media, in line with a cooling device, glass cartridges, and Zambelli isokinetic sampler. Glass cartridges packed with XAD-2 Amberlite resin and supported by a polyurethane foam (PUF) plug were used to collect PCDD/Fs after condensation of the moisture in the gas. Sampling time was about 8–10 h in each test, resulting in sampling volumes of about 10–15 m<sup>3</sup> of flue gas. Following extraction and chromatographic cleanup, PCDD/F analysis of sample extracts was conducted by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) after 48-h toluene extraction in a certified laboratory (Dr. Wessling Laboratory, Germany). Samples were spiked with <sup>13</sup>C<sub>12</sub>-labeled 2,3,7,8-substituted PCDD/F internal standards, and recovery ratios were reported as 75–90%. Toxic equivalents as 2,3,7,8-TCDD (TEQ) were calculated by using international toxicity equivalency factors (I-TEF). Other results related to the flue gas composition represent the average values of on-line measurements in the exit flue gas during the sampling period.

## Results and Discussion

**PCDD/F Removal Efficiencies of Activated Carbon.** Table 1 summarizes the operational conditions and the flue gas composition results obtained from the plant data for the five sampling periods, while Table 2 shows the results of the tests. Total PCDD/F concentrations in the flue gas at the inlet of the activated carbon unit were in the range of 720–2656 pg/Nm<sup>3</sup> (15–96 pg TEQ/Nm<sup>3</sup>). After the AC, these values were reduced to 258–934 pg/Nm<sup>3</sup> (6–37 pg TEQ/Nm<sup>3</sup>) after the AC unit, corresponding to dioxin removal rates of 40–69% (57% on average) on total PCDD/F and of 42–84% (58% on average) on the TEQ basis.

It should be noted that dioxin concentrations after the wet scrubbers (i.e., before the AC) did not exceed the European standard of 0.1 ng TEQ/Nm<sup>3</sup> in all tests. Therefore, a further decrease of 50–60% by the AC unit guarantees that

TABLE 1. Operational Conditions and Flue Gas Compositions in Samplings

parameter	range <sup>a</sup>
Waste loading (kg/d)	52 200–78 400
rotary kiln temp (°C)	923–1140
post-combustion chamber temp (°C)	959–1102
flue gas composition	
flow rate (dry, Nm <sup>3</sup> /h)	20 200–22 900
O <sub>2</sub> (%)	8.06–9.40
CO <sub>2</sub> (%)	6.74–8.75
H <sub>2</sub> O (%)	16.6–19.6
CO (mg/Nm <sup>3</sup> )	0.88–8.05
HCl (mg/Nm <sup>3</sup> )	0.09–0.32
HF (mg/Nm <sup>3</sup> )	0.20–0.25
NO <sub>x</sub> (mg/Nm <sup>3</sup> )	99.8–127
SO <sub>2</sub> (mg/Nm <sup>3</sup> )	0.22–7.71
org. C (mg/Nm <sup>3</sup> )	0.01–0.13
particles (mg/Nm <sup>3</sup> )	0.82–1.19

<sup>a</sup> Range of average values for each sampling.

the dioxin emissions are lower than the regulated limit, although the removal efficiencies were low as compared to those given in the literature (3–6). This could be attributed to the very high moisture content of the flue gas, varying between 16 and 20% (v/v) at normal conditions (corresponding to the relative humidities at about saturation level). Water can reduce adsorption if the RH is higher than 60% by adsorbing onto activated carbon and competing with the organic compounds for adsorption sites. Since the solubility of PCDD/Fs in water is very low, adsorption of water will result in a decrease in their removal efficiency (3, 4). Retention time could also play a role because contact times about 4–5 s may not be long enough for an efficient removal of dioxins in such low inlet concentrations. Further modifications providing more efficient condensation or collection of ultrafine particles prior to the AC column could result in higher PCDD/F removal efficiencies.

Figures 2 and 3 illustrate the distribution of 17 TEF-valued PCDD/F congeners and PCDD/F homologues before and after the AC unit. The distribution of the congeners and homologues is nearly the same as the previous measurements reported in Bakoglu et al. (10). PCDF compounds constituted 84% of the total dioxin concentration on average (87% on TEQ basis), and 2,3,4,7,8-PeCDF had the highest contribution (50%) to the total dioxin TEQ.

In assessing the removal of PCDD/F congeners and homologues by carbon adsorption, the differences in their physical and chemical properties should be considered. Dioxin distribution between solid and vapor phases in the flue gas is related to the vapor pressure of the congener. In certain conditions at a given temperature, it is a linear function of the saturation vapor pressure (7). Generally lower chlorinated congeners with higher vapor pressures have higher gaseous fractions at a specific temperature as compared to the highly chlorinated ones. Since activated carbon can effectively remove gas-phase dioxins and it is ineffective

TABLE 2. Flue Gas PCDD/F Concentrations (in pg/Nm<sup>3</sup>, Corrected to 11% O<sub>2</sub>) Measured in the Tests

	test no.									
	1-inlet <sup>a</sup>	1-outlet	2-inlet	2-outlet	3-inlet	3-outlet	4-inlet	4-outlet	5-inlet	5-outlet
Congener										
2,3,7,8-TCDD	1.280	0.440	0.589	0.186	0.216	0.155	0.299	0.254	3.501	0.749
1,2,3,7,8-PeCDD	5.489	2.749	6.918	1.153	1.357	0.756	2.073	1.460	15.262	5.140
1,2,3,4,7,8-HxCDD	1.648	1.130	5.018	0.961	1.519	0.805	2.047	1.439	7.059	3.371
1,2,3,6,7,8-HxCDD	2.850	2.427	14.017	1.985	3.771	1.796	5.629	3.632	11.338	5.494
1,2,3,7,8,9-HxCDD	1.436	1.356	4.612	1.089	2.043	0.929	2.900	1.850	6.784	3.371
1,2,3,4,6,7,8-HpCDD	3.262	3.665	15.78	4.355	11.90	5.265	18.00	10.83	20.49	11.57
OCDD	2.872	3.915	18.86	7.108	20.58	8.672	24.82	18.37	16.25	11.49
2,3,7,8-TCDF	26.11	8.412	13.23	3.394	2.903	1.672	4.094	2.741	66.31	15.69
1,2,3,7,8-PeCDF	26.32	14.98	33.86	4.803	5.260	2.106	7.079	4.249	68.42	24.81
2,3,4,7,8-PeCDF	35.00	19.29	62.50	9.798	12.72	5.637	19.11	10.55	90.61	32.88
1,2,3,4,7,8-HxCDF	24.35	19.39	54.25	5.059	13.09	5.699	19.70	11.51	95.05	45.14
1,2,3,6,7,8-HxCDF	24.14	19.97	55.34	6.916	14.07	5.699	19.53	10.83	93.91	44.54
2,3,4,6,7,8-HxCDF	14.11	12.47	34.83	7.236	24.84	7.991	34.97	16.93	56.10	28.51
1,2,3,7,8,9-HxCDF	1.358	1.035	2.269	0.320 <sup>b</sup>	1.085	0.310	1.535	0.343	5.171	2.706
1,2,3,4,6,7,8-HpCDF	26.33	26.31	28.52	21.71	109.2	31.47	128.5	66.68	150.0	81.94
1,2,3,4,7,8,9-HpCDF	1.548	1.511	5.668	2.049	9.802	1.734	8.188	4.112	9.942	5.557
OCDF	4.821	6.485	17.29	8.581	157.8	11.77	41.37	20.08	19.37	14.49
ΣTEF-valued congeners	202.9	145.5	373.5	86.7	392.2	92.46	339.9	185.9	735.5	337.4
TEQ	32.76	19.08	55.99	8.766	15.22	6.240	21.68	12.00	95.87	36.90
Homologues										
TCDD	36.92	12.21	30.83	11.59	14.67	9.725	22.69	17.27	88.91	20.08
PeCDD	33.43	17.10	60.01	14.66	20.20	10.41	30.28	21.66	90.07	30.95
HxCDD	21.90	19.89	76.76	20.36	36.59	19.20	59.45	39.82	96.12	46.66
HpCDD	6.435	7.187	26.09	8.389	22.07	10.902	35.48	22.34	38.30	22.12
OCDD	2.872	3.915	18.86	7.108	20.58	8.672	24.82	18.37	16.25	11.49
TCDF	307.7	115.1	146.8	53.28	53.50	32.52	82.91	58.11	856.9	186.7
PeCDF	249.5	126.1	280.8	77.42	116.2	53.46	158.2	90.39	646.0	214.2
HxCDF	141.1	125.2	218.9	58.27	137.7	61.02	218.7	128.3	607.5	281.0
HpCDF	32.85	33.09	64.02	28.50	140.6	40.14	163.0	82.78	196.6	106.6
OCDF	4.821	6.485	17.29	8.581	157.8	11.77	41.37	20.08	19.37	14.49
ΣCDD	101.6	60.301	212.6	62.12	114.1	58.91	172.7	119.4	329.6	131.3
ΣCDF	735.9	405.9	727.8	226.1	605.8	198.9	664.2	379.7	2326	802.9
ΣCDD/F	837.5	466.2	940.3	288.2	719.9	257.8	836.9	499.1	2656	934.2

<sup>a</sup> Inlet and outlet concentrations measured in flue gas before and after the combined condensation and AC unit, respectively. <sup>b</sup> Detection limits were between 0.1 and 0.7 pg/Nm<sup>3</sup> and between 1 and 2 pg/Nm<sup>3</sup> for the congeners and homologues, respectively. The concentrations measured below the detection limits were accepted as half of the corresponding detection limit, and they are shown in italics in the table.

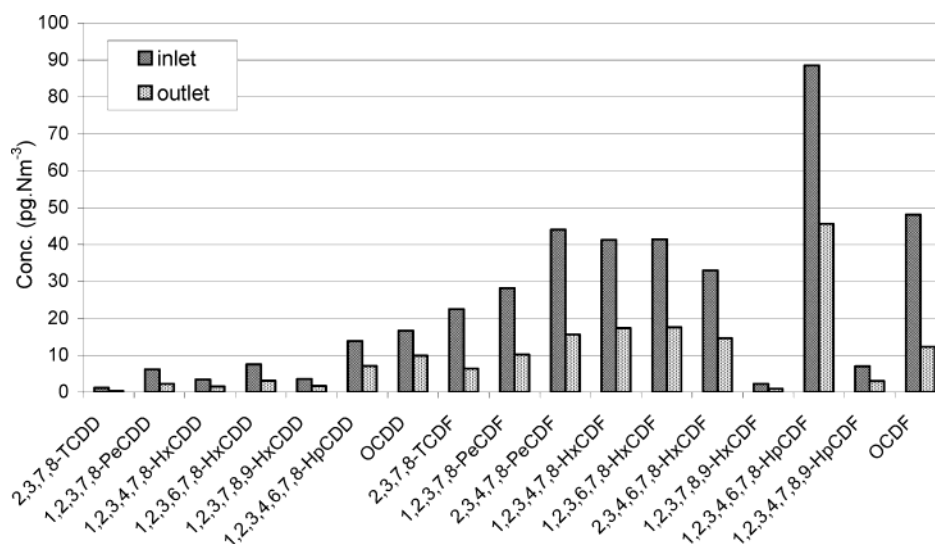


FIGURE 2. Average flue gas concentrations of TEF-valued PCDD/F congeners at the inlet and the outlet of the AC unit.

in removing particle-bound dioxins, the partitioning of these compounds plays a significant role. Smolka and Schmidt (7) presented a theoretical and experimental study on the partitioning of PCDD/Fs in the flue gas at low temperatures before and after an AC filter. They reported that the gaseous fraction was higher before the AC unit ( $T = 65^\circ\text{C}$ ) and that the gaseous fraction increased as the vapor pressure in-

creases, in compliance with theoretical results showing higher gas/particle ratios for lower chlorinated PCDD/Fs. The average gas/particle ratio at  $65^\circ\text{C}$  in a flue gas with a low particulate matter content was calculated as approximately 50 for lower chlorinated PCDD/Fs, while it was about 0.1 for highly chlorinated ones. However, there was a preponderance of PCDD/F on the solid in the same unit after the AC; meaning



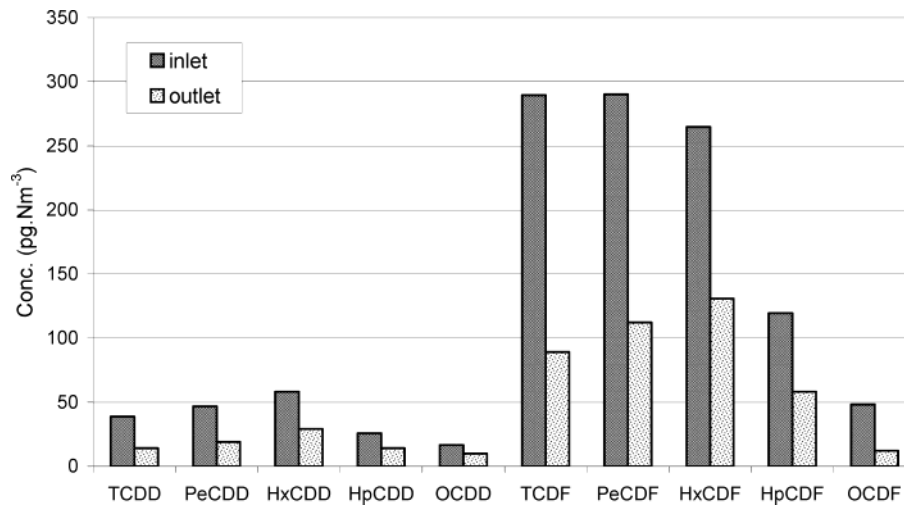


FIGURE 3. Average flue gas concentrations of PCDD/F homologues at the inlet and the outlet of the AC unit.

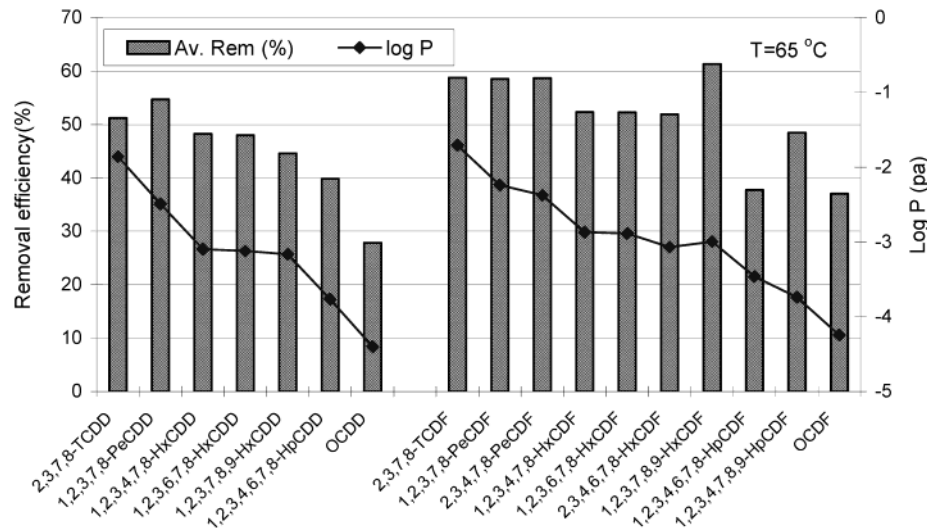


FIGURE 4. Average removal efficiencies of TEF-valued PCDD/F congeners.

that highly volatile congeners were adsorbed comparatively more strongly than lower volatile ones ( $T = 100\text{ }^{\circ}\text{C}$ ; see Figures 3 and 4 in ref 7). Cains and Eduljee (12) obtained similar results by comparing the simultaneous PCDD/F concentrations in stack emissions and ESP fly ash. The fraction of PCDD/Fs entrained as a vapor in a stack gas in an ESP was about 0.20 for TCDD/Fs, while it was reduced to 0.07 for OCDD/Fs. A more recent study by Chang et al. (9) agrees with these data by reporting higher removal efficiencies for lower chlorinated PCDD/F congeners (with higher vapor pressures) by carbon adsorption. Figures 4 and 5 show the average removal efficiencies of the five tests for PCDD/F congeners and homologues, respectively, and their relationship with the vapor pressures ( $\log P$ ) at  $65\text{ }^{\circ}\text{C}$ .

Figures 4 and 5 show that as the chlorination level of dioxin congeners and homologues increases, the removal efficiency of PCDD/F by carbon adsorption decreases. These results are consistent with previous studies attributing the decrease of removal efficiency with increasing chlorination to the partitioning between solid and vapor phases. The particulate matter concentrations in the flue gas are generally between 0 and  $2\text{ mg/Nm}^3$  and do not change significantly before and after the AC unit. Since the flue gas passes through two pollution control stages (ESP and dual wet scrubbers) before the AC, the particles that could not be removed by these units consist of very fine fractions. Actually ESP is not efficient in removing the fine particles, and most of them are

removed in the dual wet scrubbers. As Chang et al. (9) states, the removal efficiency of common APCEs for particles with small diameters (especially with diameters of  $0.1\text{--}1\text{ }\mu\text{m}$ ) is relatively low. It is likely that the particles escaping the dual wet scrubbers could have such ultrafine fractions. On the other hand, most of the volatile and semi-volatile pollutants including dioxins were reported to be adsorbed on such small particles due to the high surface area/volume ratios (13, 14). Such high enrichment on the fine particles could also be related to the two-stage combustion system of the plant. Niessen (15) reported that staged combustion systems exhibit fine particle enrichment with the combustion hearth temperature being more important than the gas exit temperature.

**Effect of Flue Gas Composition on AC Removal of PCDD/Fs.** Flue gas from waste incineration processes contains many pollutants that can compete for available adsorption sites. These include organic products of incomplete combustion (PICs), volatile metallic compounds, acid gases, and moisture. PICs having relatively weak adsorption and high concentration tend to have poor removal if there is insufficient carbon. Acid gases such as sulfur dioxide and hydrogen chloride can also be adsorbed by some types of carbon, but these are not expected to influence PIC removal due to the lower adsorption potential of these gases. Industrial experience has shown that chlorinated dioxins and furans are tightly adsorbed on the first fraction of the bed with breakthrough times in deep beds of many years. For evaluation of the effect of flue gas

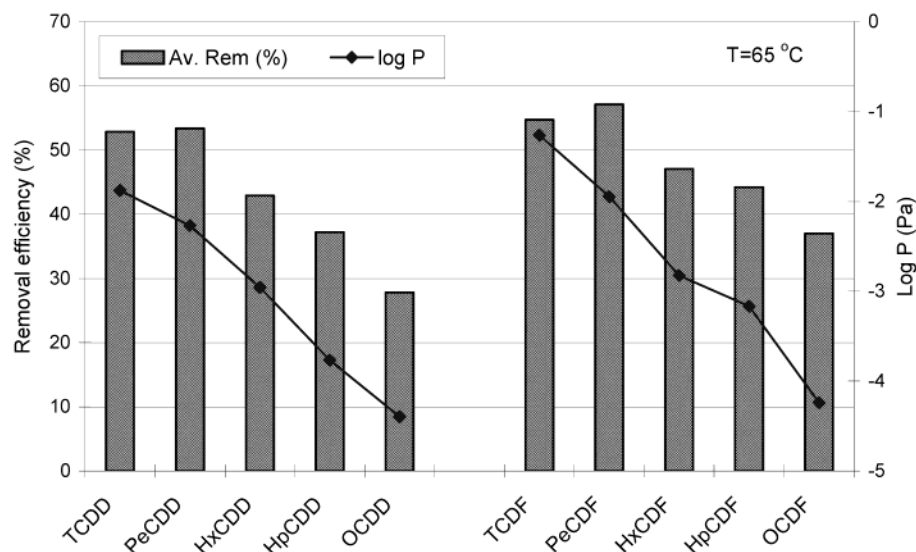


FIGURE 5. Average removal efficiencies of PCDD/F homologues.

composition on AC dioxin removal, the results of on-line measurements in the exit flue gas were used. Some additional measurements of the combustion gases were made before and after the AC unit during the sampling. PCDD/F removal efficiencies showed negative correlations with  $\text{SO}_2$  ( $R^2 = 0.51$ ),  $\text{NO}_x$  ( $R^2 = 0.65$ ), and  $\text{HCl}$  ( $R^2 = 0.64$ ) suggesting that these gases could have an effect on the PCDD/F adsorptive capacity. In the measurements of combustion gases,  $\text{SO}_2$  and  $\text{NO}_x$  concentrations were reduced by 50–60% and 5–10%, respectively, through AC.  $\text{SO}_2$  adsorbed on the activated carbon reacts catalytically with oxygen to produce  $\text{SO}_3$ , which with the gas moisture forms sulfuric acid. The sulfuric acid continues to absorb water, resulting in a decrease in the adsorptive capacity of carbon material. A similar effect could be considered for hydrogen chloride. Moreover, it has a different equilibrium isotherm than the organic compounds. Experimental data for  $\text{HCl}$  adsorption suggests that, under humid conditions, nearly twice as much  $\text{HCl}$  is adsorbed as would be expected from water solubility considerations. As a result of these acidic effects, the AC material is getting wet (3, 16). Since the RH of the flue gas is high (70–80%) in the AC unit at IZAYDAS, the decrease in the removal efficiency could be attributed to the increase of  $\text{SO}_2$  and  $\text{HCl}$  concentrations. However, they have lower adsorption potentials, and the lime scrubber removes most of the  $\text{SO}_2$  and  $\text{HCl}$  in the flue gas, as can be seen from the low concentration ranges in Table 1. Moreover, the correlation coefficients are not high; therefore, additional studies are necessary to confirm their possible relationship with the PCDD/F adsorption capacity.

**Adsorption Kinetics.** The models related to the adsorption of organic vapors by carbon and other microporous adsorbents are generally based on the Polanyi potential theory of adsorption as developed by Dubinin and co-workers. These models relate the driving force for adsorption to the ratio of the equilibrium (i.e., in exhaust gas from treatment) partial pressure to the saturation vapor pressure, which is expressed by the well-known Dubinin–Radushkevich (D–R) relationship (3, 4, 17–21). However, in low concentrations, the D–R relationship will overpredict the adsorbed amount, which was well-illustrated by Rordorf (22). A criterion attributed to Dubinin (3) is that the D–R relationship should hold for “relative pressure” (i.e., partial pressure/vapor pressure) values above  $10^{-6}$ . For values below  $10^{-6}$  to 0, a linear relationship (i.e., Henry’s law) could be applied. However, in the given conditions, the vapor fractions of PCDD/Fs should be known first to determine the relative pressures.

TABLE 3. Slopes ( $m$ ),  $x$ -intercepts ( $x$ -int.) and Correlation Coefficients ( $R^2$ ) for C-adsorbed versus C-inlet Graphs of Dioxin Congeners and Homologues

	$m$	$x$ -int.	$R^2$
<b>Congeners</b>			
2,3,7,8-TCDD	0.825	0.18	0.998
1,2,3,7,8-PeCDD	0.713	0.65	0.963
1,2,3,4,7,8-HxCDD	0.673	0.61	0.861
1,2,3,6,7,8-HxCDD	0.907	2.60	0.902
1,2,3,7,8,9-HxCDD	0.651	0.74 (1.40) <sup>a</sup>	0.831 (0.885)
1,2,3,4,6,7,8-HpCDD	0.559	1.80 (3.35)	0.726 (0.823)
OCDD	0.495	3.02 (3.46)	0.583 (0.656)
2,3,7,8-TCDF	0.780	1.83	0.998
1,2,3,7,8-PeCDF	0.673	1.43	0.933
2,3,4,7,8-PeCDF	0.737	5.50	0.923
1,2,3,4,7,8-HxCDF	0.619	2.63	0.805
1,2,3,6,7,8-HxCDF	0.621	3.03	0.816
2,3,4,6,7,8-HxCDF	0.578	1.24 (11.5)	0.713 (0.849)
1,2,3,7,8,9-HxCDF	0.444	-0.75 (0.86) <sup>b</sup>	0.733 (0.817)
1,2,3,4,6,7,8-HpCDF	0.592	15.8 (25.1)	0.870 (0.934)
1,2,3,4,7,8,9-HpCDF	0.703	1.29	0.750
OCDF	0.988	11.7	0.993
<b>Homologues</b>			
TCDD	0.890	11.1	0.988
PeCDD	0.791	11.6	0.950
HxCDD	0.702	16.9	0.828
HpCDD	0.493	2.37 (6.45)	0.727 (0.859)
OCDD	0.495	3.02 (3.46)	0.583 (0.656)
TCDF	0.817	44.1	0.997
PeCDF	0.721	43.5	0.979
HxCDF	0.579	33.3 (117)	0.902 (0.918)
HpCDF	0.563	10.8 (32.5)	0.835 (0.923)
OCDF	0.988	11.7	0.993

<sup>a</sup> Italics numbers in parentheses represent the values for logarithmic curve. <sup>b</sup> The concentration of 1,2,3,7,8,9-HxCDD in the flue gas after the AC column was below the detection limit in three tests. It was assumed that the concentration is half of the corresponding detection limit.

Smolka and Schmidt (7) showed that  $\text{P}_{4,5}\text{CDD/F}$  compounds have an average vapor fraction of 95% at 65 °C in a flue gas with low particulate matter content, while it decreases to 75%, 40%, and 10% for  $\text{HxCDD/Fs}$ ,  $\text{HpCDD/Fs}$ , and  $\text{OCDD/Fs}$ , respectively. Accepting that  $\text{P}_{4,5}\text{CDD/Fs}$  are completely in gas phase in our tests, their relative pressures were determined to be between  $10^{-9}$  and  $10^{-7}$  (i.e., in the Henry’s law range). Taking into consideration that the chlorinated dioxins have a high adsorption potential and breakthrough times of many years, we can neglect the decrease of

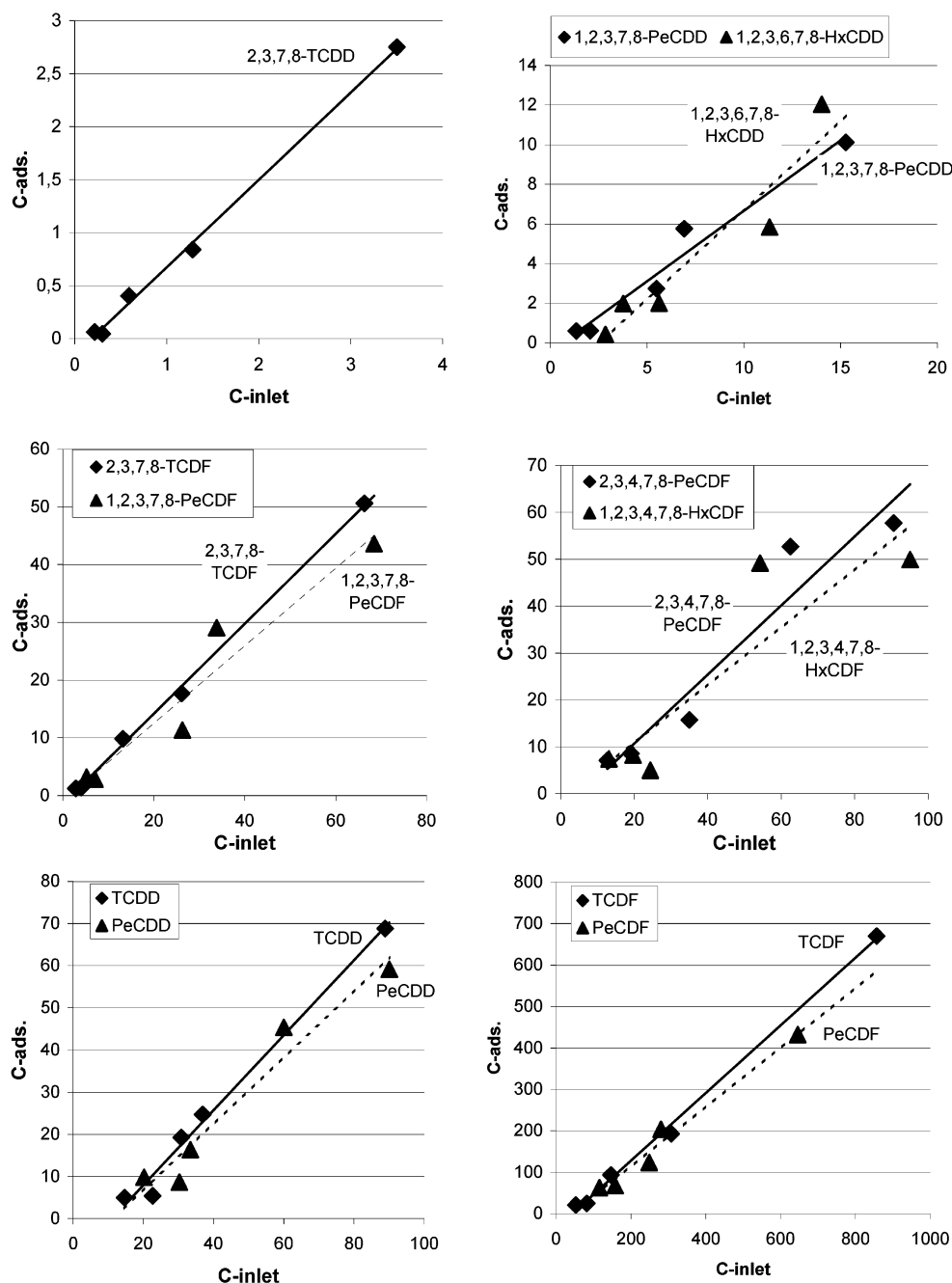


FIGURE 6. Graphs of adsorbed concentrations ( $C_{\text{ads}}$ ,  $\text{pg}/\text{Nm}^3$ ) vs inlet concentrations ( $C_{\text{inlet}}$ ,  $\text{pg}/\text{Nm}^3$ ) for some dioxin congeners and homologues.

adsorption capacity of the AC column during its operation for 3 yr. Assuming that the dioxin compounds are adsorbed homogeneously through the column and that the amount of the adsorbent is constant for all tests, the graph of the concentration removed by activated carbon ( $C_{\text{adsorbed}}$ ) versus inlet concentrations ( $C_{\text{inlet}}$ ) could be drawn to examine the validity of Henry's law for dioxin compounds. Figure 6 shows the graphs for these dioxin congeners and homologues.

Figure 6 shows that there is a good linear relation between inlet and adsorbed concentrations, corresponding to the Henry's law range. Additionally, other congeners and homologues produced similar graphs but with lower correlation coefficients. The slopes,  $x$ -intercepts, and correlation coefficients of the congeners and homologues are given in Table 3.

Figure 6 (and high  $R^2$  values in Table 3) shows that the adsorption of the lower chlorinated dioxin compounds fits

well with Henry's law. The correlation coefficients for a linear relation decrease as the chlorination level increases, possibly due to the increase in particle-bound fraction or possible effects of condensation. Since highly chlorinated PCDD/Fs with high melting points and low vapor pressures could be found in water in the form of heterogeneous crystals, they could be removed by condensation in larger amounts as compared to the lower chlorinated ones. Another interesting point is that all the congeners and the homologues had a positive  $x$ -intercept, which shows a concentration below which no adsorption was observed. These values correspond to 10–35% and 0–24% of the average inlet concentrations of dioxin and furan congeners, respectively, while it was between 9 and 29% for the homologues. This suggests that the dioxin compounds might be completely bound on the particles at certain low concentrations (by a process probably controlled by the available particle surface area) or that

contact times of about 4–5 s are not long enough for the adsorption of these compounds by AC in such low concentrations in the given conditions. Detailed studies on the behavior of the PCDD/Fs in low concentrations and the distribution of them between different particle sizes in the flue gas would be helpful to enlighten this subject. The slope of the line represents C-adsorbed/C-inlet (i.e., the adsorbed fraction of the inlet concentration after the beginning point of the adsorption ( $x_{\text{int}}$ )). They generally followed the same trend with the average removal efficiencies given in Figures 3 and 4, but some surprising results were observed also. These were the high removed fractions of 1,2,3,6,7,8-HxCDD, 1,2,3,4,7,8,9-HpCDF, and OCDF, which showed the slopes of 0.91, 0.70, and 0.99, respectively. Finally, it should be noted that some negative removal efficiencies were observed for the congeners of 1,2,3,4,6,7,8-HpCDD (–12.3%), OCDD (–36.3%), and OCDF (–34.5%) and for the homologues of HpCDD (–11.7%) and HpCDF (–0.7%) in test 1 (see Table 2). Since all of these highly chlorinated compounds have higher particle-bound fractions, the increase of them in the AC exit gas could be attributed to the entrainment of PCDD/F-containing particles in the AC unit by the flue gas flowing through the AC bed.

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