TITLE: THE INFLUENCE ON GAS-PHASE DIOXIN ADSORPTION FROM PORE PARAMETERS OF ACTIVATED CARBON: CHARACTERISTICS AND EFFICIENCY

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Introduction

With the increasing generation of municipal solid waste (MSW) in China, waste incineration has also rapidly developed to treat MSW. In the past five years, the volume of waste disposed by incineration has grown from 61.76 million tons in 2015 to 121.74 million tons in 2019, which was almost doubled, and the number of factories for waste incineration has also increased from 220 in 2015 to 389 in 2019[1]. Dioxins are a kind of trace pollutants discharged from waste incineration plants, which can be controlled in three stages: before incineration, during incineration and after incineration. Among them, after incineration technology refers to the terminal removal of produced dioxin, which is also the final guarantee of dioxin emission.

The adsorption by activated carbon, one of the after incineration technologies, is the most widely used method for dioxin removal in the flue gas of waste incineration plants[2]. The pore parameters of activated carbon mainly include surface area, pore volume and pore size distribution, which are the key factors affecting dioxin adsorption. According to the pore size, the International Union of Pure and Applied Chemistry (IUPAC) divides the pore size into three categories[3]: micropores less than 2 nm, mesopores between 2-50 nm and macropores larger than 50 nm. At present, only a few and controversial studies discussed the correlation between pore parameters of activated carbon and dioxin adsorption. In this study, based on a system that could produce dioxin stably, an experiment was conducted to research on the adsorption characteristics of three typical activated carbons on gas-phase dioxin and the correlation between their pore parameters and the adsorption efficiency of dioxin.

Materials and methods

Dioxin stock solution, a certain concentration of liquid phase dioxin, was used to produce dioxin carrying flow. Dioxin stock solution is prepared by method USEPA1613 pretreatment of fly ash which was from a waste incineration power plant in China. ^{12}C and ^{37}Cl standard samples were not added in the process. The concentration of dioxin stock solution can be adjusted by concentration or dilution.

Three kinds of commercial activated carbon with different materials were selected in the experiment, which were coal activated carbon, coconut shell & coal activated carbon and wooden activated carbon, respectively. Before the experiment, they were dried at 80 ℃ for 12h and sieved through 100 meshes.

As shown in Figure 1, the experimental device consisted of three parts: dioxin generation, adsorption and tail gas collection. The microdialysis pump CMA 300 (CMA Microdialysis AB, USA) was used as the power unit and the dioxin stock solution in micro injector (0-0.5 ml) was injected into the nebulizer (Meinhard, USA) at the injection rate of 1μl/min. Under the synergistic effect of carrier gas (N_2:O_2 = 9:1, 1L/min), it was sprayed into the quartz tube (200 °C) in the form of atomization, and fully volatilized into the form of gas in the quartz tube. Thus, a gas carrying a certain concentration of dioxins was obtained. The gas then passed through a quartz tube (150 ℃) equipped with an activated carbon column, and the residual dioxin in the tail gas was collected by toluene in the ice bath. The adsorption time of each group was 0.5h, and the amount of activated carbon used was 0.5g. Before the experiment, the experimental device needed to run empty for 6 hours to make the pipe wall reach the adsorption saturation state of dioxin. A set of parallel samples were set for all groups to ensure the repeatability and representativeness of the results.

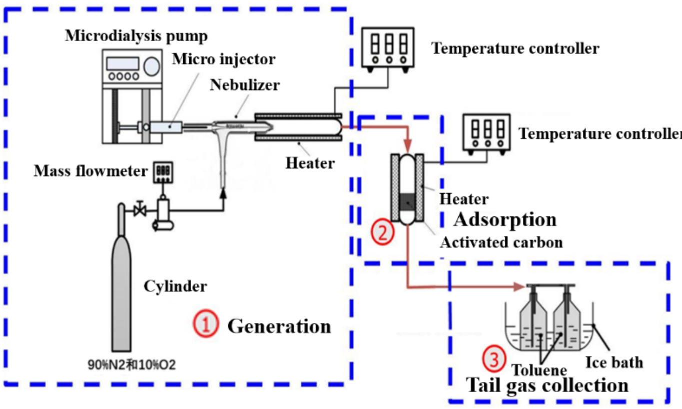

Figure 1. Experimental facilities for adsorption of PCDD/Fs by activated carbon.

Results and discussion

The low-temperature nitrogen adsorption method was used to measure the surface area, pore volume and pore size distribution of activated carbon. The low temperature nitrogen adsorption isotherms of the three activated carbons are shown in Figure 2. According to the classification of IUPAC, the nitrogen adsorption isotherm of coal activated carbon belonged to type I, with a microporous structure. The nitrogen adsorption isotherms of coconut shell & coal activated carbon and wooden activated carbon belonged to type IV, and both activated carbons had a certain number of mesopores. The pore structure parameters of three activated carbons are summarized in Table 1. Among them, the wooden activated carbon had the most abundant pore structure, with a total BET surface area of 1315 m^2/g and a total pore volume of 1.26 cm^3/g, while the coal activated carbon had the least pore structure parameters, with a total BET surface area of 858 m^2/g and a total pore volume of 0.51 cm^3/g. Although the total BET surface area of coconut shell & coal activated carbon was smaller than that of wooden activated carbon, the micropore structure of coconut shell & coal activated carbon was the most abundant among these three activated carbons, with the micropore surface area and micropore volume of 654 m^2/g and 0.35 cm^3/g, respectively.

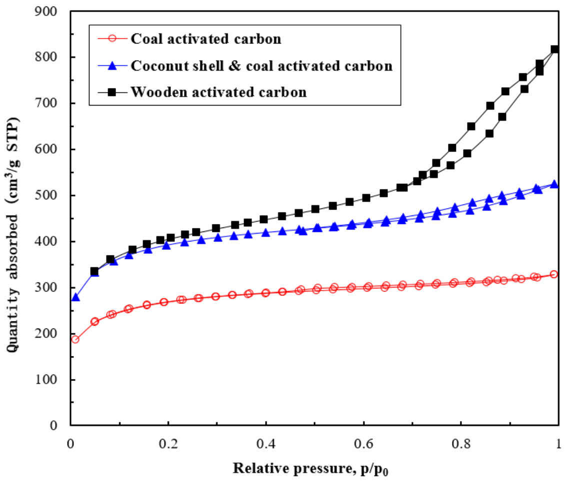

Figure 2. Nitrogen adsorption isotherm of activated carbon at low temperature (77 K).

Table 1. Pore structure parameters of activated carbon.

	BET Surface area m^2/g	**Micropore surface area m^2/g**	**Mesopore surface area m^2/g**	**Total pore volume cm^3/g**	**Micropore volume cm^3/g**	**Mesopore volume cm^3/g**	**Average pore diameter nm**
Coal AC	858	409	450	0.51	0.22	0.29	2.30
Coconut shell & coal AC	1245	654	590	0.81	0.35	0.46	2.60
Wooden AC	1315	582	732	1.26	0.30	0.85	4.60

The total mass concentration of 17 toxic isomers of initial dioxin was 94.4 ng/Nm^3, and the total toxic equivalent (TEQ) concentration was 6.27 ng $I\text{-}TEQ/Nm^3$. Table 2 summarized the changes of total mass concentration and I-TEQ of 17 toxic dioxins before and after adsorption by three kinds of activated carbon. In the case of the same initial dioxin concentration, wooden activated carbon had the highest removal efficiency of dioxins, and the adsorption efficiencies of total mass concentration and I-TEQ were 98.7% and 98.2% respectively, while the total mass concentration adsorption efficiencies of coal activated carbon and coconut shell & coal activated carbon were 93.0% and 91.8% respectively, and the I-TEQ adsorption efficiencies were 92.4% and 92.1% respectively.

Table 2. Variation of 17 toxic dioxins mass concentration and TEQ concentration.

	Mass concentration (ng/Nm^3)	**η_m (%)**	**I-TEQ concentration (ng $I\text{-}TEQ/Nm^3$)**	**η_{TEQ} (%)**
Initial dioxin	94.4±3.02	/	6.27±0.41	/
Coal AC	6.57±0.07	93.0	0.48±0.02	92.4
Coconut shell & coal AC	7.70±0.08	91.8	0.49±0.02	92.1
Wooden AC	1.26±0.05	98.7	0.11±0.01	98.2

Figure 3 shows the change of dioxin adsorption efficiency with chlorination level. Compared with high-chlorinated dioxins, the three activated carbons had lower adsorption efficiency for low-chlorinated dioxins, which was consistent with the research results of Chang[4], because at the same temperature, the saturated vapor pressure of dioxin homologues would decrease with the increase of chlorination level, and it would be easier to be adsorbed on the surface of porous materials such as activated carbon. Among the three kinds of activated carbon, coconut shell & coal activated carbon had the lowest adsorption capacity for dioxins, so its adsorption selectivity for dioxins with different chlorination levels was also the most obvious. The adsorption efficiency of PCDDs and PCDFs by the three activated carbons was shown in Table 3. Among them, coal activated carbon and coconut shell & coal activated carbon had higher adsorption efficiency for PCDDs than PCDFs. Hung[5] et al. Also obtained a similar research result, which was attributed to the lower saturated vapor pressure of PCDDs compared with PCDFs at the same chlorination level.

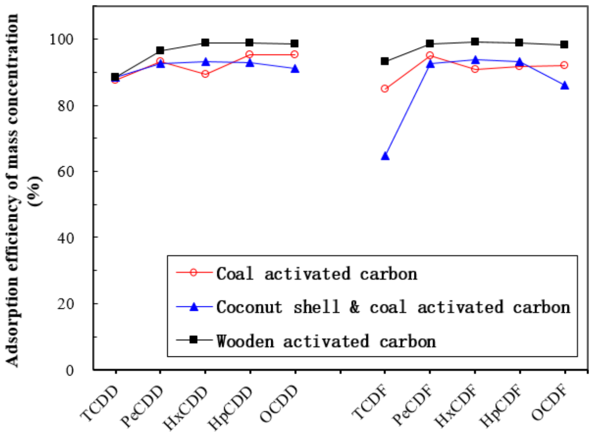

Figure 3. Variation of dioxins adsorption efficiency with the chlorination level.

Table 3. Mass concentration adsorption efficiency of PCDDs and PCDFs by three activated carbons.

	Coal AC	Coconut shell & coal AC	Wooden AC
PCDDs	94.6%	91.9%	98.7%
PCDFs	91.8%	91.8%	98.7%

Table 4 shows the correlation between pore parameters of activated carbon and I-TEQ adsorption efficiency of dioxins. The six pore parameters and the I-TEQ adsorption efficiency are ranked as follows:
Mesoporous volume > Total pore volume > Mesoporous surface area > BET surface area > > Microporous surface area > Microporous volume
When the pore size of activated carbon was larger than 2 nm, the correlation between the pore volume of activated carbon and the adsorption efficiency of dioxin was better than the BET surface area of activated carbon. The adsorption efficiency of dioxin increased with the increase of pore volume of activated carbon, which was similar to Zhou[6]'s research. The richness of mesoporous structure was the key to determin the adsorption performance of activated carbon for dioxins. The correlation coefficients of mesoporous pore volume and mesoporous surface area with the adsorption efficiency of dioxins were all above 0.85. Gu[7] believed that when the ratio of pore diameter of adsorbent to molecular diameter of adsorbate was 1.7 ~ 3.0, the utilization rate of adsorbent was the highest. When the adsorbent needed to be regenerated, the ratio was 3.0 ~ 6.0 or higher. Nagano[8] calculated that the long axis of 2,3,7,8-TCDD was 1.3688 nm, the short axis was 0.7348 nm, and the thickness was 0.35 nm. Based on this data, the optimal pore size range for activated carbon to adsorb dioxins was calculated to be 2.3 ~4.1 nm, and for regenerated activated carbon, the optimal pore size range was 4.1~8.2 nm. The results showed that the optimal range of the pore size for activated carbon adsorbing dioxins belonged to mesoporous structure, which is consistent with the conclusion of this paper.

Table 4. Correlation between pore parameters of activated carbon and I-TEQ adsorption efficiency of dioxins.

	BET Surface area	Micropore surface area	Mesopore surface area	Total pore volume	Micropore volume	Mesopore volume	η_{TEQ}
BET Surface area	1						
Micropore surface area	0.908	1					

Mesopore surface area	0.928	0.686	1				
Total pore volume	0.880	0.600	0.994	1			
Micropore volume	0.861	0.995	0.608	0.515	1		
Mesopore volume	0.823	0.510	0.976	0.994	0.420	1	
η_{TEQ}	0.592	0.201	0.851	0.904	0.100	0.945	1

Iodine value is often used to evaluate the adsorption performance of activated carbon in practical applications. Table 5 shows the iodine value of three activated carbons. Among them, coconut shell & coal activated carbon with the most abundant microporous structure had the highest iodine adsorption value, but its dioxin adsorption efficiency was the lowest among the three activated carbons. This is because the molecular size of iodine is about 0.6 nm, which indicates the richness degree of the more than 1 nm microporous structure of activated carbon, so it is not suitable for evaluating the adsorption capacity of activated carbon for dioxin.

Table 5. Iodine value and I-TEQ adsorption efficiency of activated carbon

	Coal AC	**Coconut shell & coal AC**	**Wooden AC**
Iodine value (mg/g)	1021	1367	1047
η_{TEQ} (%)	92.4	92.1	98.2

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