

DIOXINS REMOVAL CHARACTERISTICS OF ALKALI-LOADED
ACTIVATED CARBON

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Introduction

A primary measure for removing dioxins from a variety of incinerators is still injection of powdered activated carbon(PAC) into exhaustive gas followed by capture of the resultant particulates adsorbing the dioxins through dust collectors.

In the PAC injection, more effective PAC has been desired to achieve highly efficient and cost-effective emission control. Recently, alkali-loaded PAC has been suggested by Miyata et al.¹ as an effective adsorbent capable of reducing total dioxins emission by suppressing catalytic formation of PCDDs/PCDFs on the surface of PAC or fly ash. They found a remarkable inhibition effect with the alkali-loaded PAC in their real field test which was carried out at 240°C. In fact, there has been much observations on the significant formation of PCDDs/PCDFs through the catalytic formation from precursors or de Novo synthesis, in particular, at temperatures of 250 – 600°C^{2,3}. However, since the observations were mostly made at the high temperatures, it still needs to understand the effectiveness and its possible explanation of the alkali-loaded PAC at lower temperatures. Hence, the authors have examined the adsorptive behaviors of the NaOH-loaded PAC over a chlorinated organic compound at 150 °C through a laboratory test and also tested the PAC in a commercial industrial waste incinerator. This article addresses the main results of the laboratory adsorption tests and the field tests.

Materials and Methods

Adsorbents : The as-received and NaOH-loaded PAC(Calgon) were used in the adsorption tests. The alkali loading was done as following ; thirty gram of the PAC was introduced into 60 ml of the aqueous NaOH solutions with different concentrations, and then the slurry was heated with thorough stirring until the wet cake was obtained. The caked PAC was vacuum-dried at 100 °C overnight, and pulverized and sieved under 200 mesh, and then stored in a desiccator until use. The accurate NaOH loading content was analysed by an atomic absorption spectrometer.

Adsorption test : First, a mixture of 50 mg of the PAC and 50mg of small glass beads was placed on the top of glass wool layer inside a quartz column, where the glass beads were used to protect the pressure drop across the column. After being purged with the flow of nitrogen gas for 30 min, the column was heated to a given temperature, that is, 150 °C which was controlled within ± 1 °C. Once the temperature was reached, a mixed flow of the carrier nitrogen and another nitrogen flow containing an adsorbate, 1,2-dichlorobenzene(DCB) vapor was introduced into the column. The total flow rate was 300 ml/min, and the concentration of DCB was fixed at 390 ppm which was produced by bubbling a liquid DCB placed in a temperature-controlled bath at 16 ± 0.5 °C. The concentration of DCB at the outlet was analysed using GC-FID(HP5890) with an interval of one minute.

The steady state adsorption was obtained within 25 min for all the runs. Once the steady state was reached for each run, the nitrogen flow for the DCB bubbling was bypassed to the carrier

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nitrogen flow to observe a desorptive behavior. The desorption was carried out under the nitrogen flow of 300 ml/min at temperatures of 150 °C to 400 °C. During the desorption run, the column was kept at 150 °C for 15 min, and then heated to 200 °C or 400 °C at rates of 5 °C/min and 25 °C/min, respectively.

Field test : To examine the effectiveness of the alkali loading on dioxins removal, the non-treated and alkali-treated PACs were employed in an industrial solid waste incinerator with its capacity of 50 ton/day. The incinerator is equipped with an PAC injection facility followed by fabric filter house (FF) operated at 150 °C. In our injection tests, the PAC was injected into the flue gas at a position of 20 m ahead of the FF with the rate of 50 mg/Nm³ to 200 mg/Nm³. The flue gas samples were simultaneously taken at two points, that is, before the injection of PAC and after the FF. The sampling and analysis of the samples were performed according to the U.S. EPA Methods. The quantitative analysis was done using a HR GC/HR MS (Autospec-Ultima, Micromass).

Results and Discussion

Adsorptive and desorptive behaviors of the NaOH-loaded PAC

Table 1 summarizes the changes in the adsorptive capacity of DCB at 150 °C with the NaOH loading varied from 0 to 9 wt%. The capacity is noticeably enhanced as the NaOH loading increases, showing a maximum at around 5% of the NaOH loading. On the other hand, we can see the effect of the NaOH loading on the desorptive behavior of the PAC in Table 2. With the non-loaded PAC, the whole adsorbed DCB is almost completely desorbed during the heating from 150 °C to 200 °C, while with the NaOH-loaded PAC the desorbed amounts become greatly lower compared with the adsorbed amounts even at the higher desorption temperature of 400 °C. The results demonstrating an occurrence of stronger adsorption may indicate a creation of more favorable sites for the DCB adsorption with the addition of NaOH. From the above observations,

Table 1. Comparison of DCB adsorption capacity at 150 °C of NaOH-loaded PAC

NaOH loading (wt%)	Adsorption capacity (mg of DCB/g of PAC)	Increase in adsorption capacity
0.0	93	-
1.0	110	18
2.8	114	23
4.7	118	27
8.7	117	26

it is expected that the alkali loading may lead to more effective adsorptive removal of the precursor compounds and/or PCDDs/PCDFs in the flue gas.

Table 2. Comparison of DCB desorption at different temperatures with NaOH-loaded PAC

NaOH loading (wt%)	Desorbed % at 150 °C	Desorbed % at 150 °C to 200 °C	Desorbed % at 150 °C to 400 °C
0.0	78	21	-
1.0	68	14	-
2.8	65	13	28
4.7	60	15	23
8.7	53	14	24

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Effect of the NaOH loading on dioxins removal efficiency

Several PAC injection tests were carried out in the industrial waste incinerator to examine the effects of the NaOH loading on the PCDDs/PCDFs removal efficiency.

Table 3 summarizes the inlet and outlet PCDDs/PCDFs concentrations of the FF in I-TEQ values with the varied injection rates from 0 to 200 mg/Nm³ of the two PACs, that is, the non-treated and 5% NaOH-loaded PAC. With no PAC injection, the concentration decreases from 12.21 ng I-TEQ/Nm³ to 1.65 ng I-TEQ/Nm³, which is only due to the FF. With the PAC injection, the concentration is sharply reduced until the injection rate increases to 100 mg/Nm³ and it is gradually leveled off at higher rate, as shown in Fig 1. More interestingly, it is obvious that the NaOH-loaded PAC injection leads to noticeable additional reductions in the outlet concentration by comparing with those of the non-treated PAC injection at the same rates.

Table 3. Inlet and outlet PCDDs/PCDFs concentrations of FF in I-TEQ values
(unit : ng I-TEQ/Nm³ at 12% O₂)

	Injection rates (mg/Nm ³)							
	0		50		100		200	
	inlet	outlet	inlet	outlet	inlet	outlet	inlet	outlet
Non-treated PAC	12.21	1.65	15.81	0.37	10.40	0.14	2.79	0.07
5% NaOH-loaded PAC			11.45	0.13	9.08	0.03	-	-

At this moment, a clear explanation on the enhanced efficiency with the NaOH loading could not be given because of our lack of knowledge about the catalytic interaction of our fly ash in the presence of precursors or the de Novo synthesis. However, considering the results on the adsorptive/desorptive characteristics with the NaOH loading, in particular, at somewhat low temperature, it is concluded that the alkali treatment may lead to more effective adsorptive removal of the precursor compounds and/or the PCDDs/PCDFs, probably by generating highly interactive surface sites favorable for the kinetically fast adsorption necessary in the PAC injection.

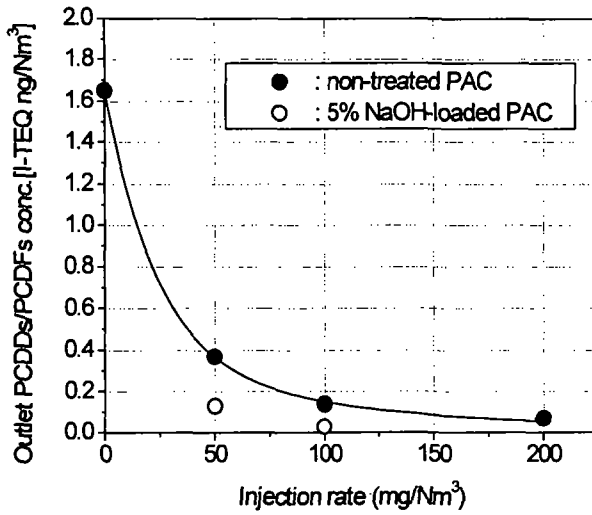


Fig. 1. Reduction of outlet PCDDs/PCDFs concentrations with varied injection rates of PACs.

References

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