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Adsorption Behavior of Dioxin Model Compounds on Activated Carbon in Supercritical Carbon Dioxide

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Abstract. Removal of toxic substances such as dioxins and PCBs in the environmental matrices such as fly ash and soil is becoming important. We have been developing combined process of extraction with supercritical carbon dioxide, concentration by adsorption, and then destruction by supercritical water oxidation as a national project (NEDO/Energy Conservation Center). In the extraction—adsorption process, dioxins contained in solid samples can be transferred and concentrated into adsorbent. Then, the adsorbent containing dioxins is completely destructed by supercritical water oxidation. For supercritical CO_2 extraction and supercritical water oxidation, efficiencies of more than 99% were achieved. In this work, we studied the adsorption of model compounds of dioxins onto activated carbon in supercritical carbon dioxide to obtain the design data for the process. The adsorption behavior of dioxins model compounds was measured by impulse or step response technique in supercritical CO_2 in the pressure range of 10–40 MPa at 323 K. As the model compounds, we used benzene, monochlorobenzene, dichlorobenzene, biphenyl, and anthracene to evaluate the effect molecular weight and the presence of chlorine in the molecule. By using the step response technique, we obtained the amount adsorbed on activated carbon. Adsorption decreased as molecular weight increased, but was not affected by pressure. The adsorbed amount was not significantly influenced by the pressure. This result suggests that these components can be effectively adsorbed on activated carbon in supercritical CO_2. We have also measured impulse response to evaluate the adsorption equilibrium constant. Analysis based on the molecular shape and the size is applied to evaluate the adsorption behavior.

Keywords: dioxin, supercritical carbon dioxide, step response, impulse response

1. Introduction

Removal of toxic substances such as dioxins and PCBs in the environmental matrices such as fly ash and soil is becoming important. The extraction of these toxic substances has been achieved conventionally by using organic solvent. In the analytical process, dioxins are leached from solid samples by toluene in a Soxhlet extractor. Supercritical fluid technology may be suitable for environmental application because of environmentally friendly solvent such as carbon dioxide or water. Supercritical water was applied as an extraction solvent or reaction media for oxidative decomposition (Hashimoto et al., 2004). When supercritical water oxidation is applied directly to environmental samples (Sako et al., 1997), huge amount of solid materials must be supplied to high pressure and high temperature reactor. Thus the process could not be economically feasible. Supercritical carbon dioxide is also used to extract dioxins from solid matrix (Windal et al., 2000).

We have been developing combined process of extraction with supercritical carbon dioxide, concentration by adsorption, and then destruction by supercritical water oxidation. In the extraction—adsorption process,

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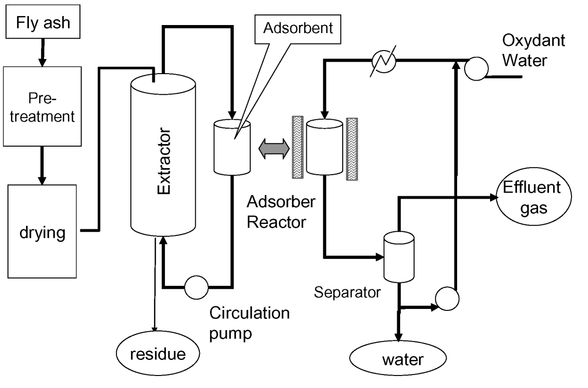

Figure 1. Combined process of supercritical CO_2 extraction, adsorption, and supercritical water oxidation.

dioxins contained in solid samples can be transferred and concentrated into adsorbent. Then, the adsorbent containing dioxins is completely destructed by supercritical water oxidation. The process outline is shown in Fig. 1. As a national project (NEDO/Energy Conservation Center) we have been developing the process for the treatment of fly ash or soil containing dioxins (Goto and Kawajiri, 2002; Kawajiri et al., 1999, 2000, 2001).

In this work, we studied the adsorption of model compounds of dioxins onto activated carbon in supercritical carbon dioxide to obtain the design data for the process. We have also measured impulse response to evaluate the adsorption equilibrium constant. Analysis based on the molecular shape and the size is applied to evaluate the adsorption behavior.

2. Process Outline

(1) *Pre-treatment*: The sample was treated in 2N-hydrochloric acids in order to remove alkaline component that covers the surface of the fly ash particle. As a result of acid treatment, the specific surface area increased about 10 times.
(2) *Supercritical carbon dioxide extraction*: Semi-batch flow extractor where samples were packed in the extractor vessel was used. The extracted dioxins were adsorbed onto activated carbon in an adsorber vessel. The extraction pressure was changed from 10 to 60 MPa. The extraction efficiency for PCDD isomers remarkably increased with the increase in pressure. At the pressure of 60 MPa, the extraction efficiency attained 99.8%. Similar results were obtained for PCDFs and co-PCBs. The extraction efficiency for these isomers also reached over 99%.
(3) *Concentration of dioxins in adsorbent*: Dioxins extracted with supercritical carbon dioxide were concentrated in adsorbent in adsorber vessel. Activated carbon was used as an adsorbent.
(4) *Supercritical water oxidation (SCWO) of dioxins in fly ash*: For the destruction of dioxins adsorbed in activated carbon, we preliminary carried out the SCWO of dioxins in the fly ash. The destruction efficiency of dioxins was about 99% at 673 K and over 99.99% at the temperature higher than 773 K.

3. Experiments

Chemical structures of dioxins including polychlorodibenzodioxins (PCDDs), polychlorodibenzofurans (PCDFs), and coplanar PCB (co-PCB) are shown in Fig. 2. There are many isomers for PCDDs and PCDFs. Since it is difficult to use pure compounds of these materials because of toxicity, we have used model compounds having similar structure. As the model compounds, we used benzene, monochlorobenzene, dichlorobenzene, biphenyl, anthracene, anthraquinone, and anthrone to evaluate the effect molecular weight and the presence of chlorine in the molecule as shown in Fig. 3.

The adsorption behavior of dioxins model compounds was measured by an impulse response technique in supercritical CO_2 in the pressure range of 10–40 MPa. By using a step response technique, we evaluate the adsorption capacity of the model

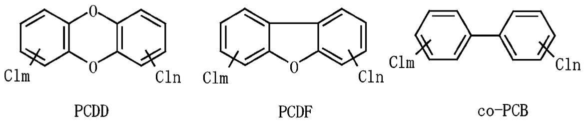

Figure 2. Structures of dioxins and co-PCB.

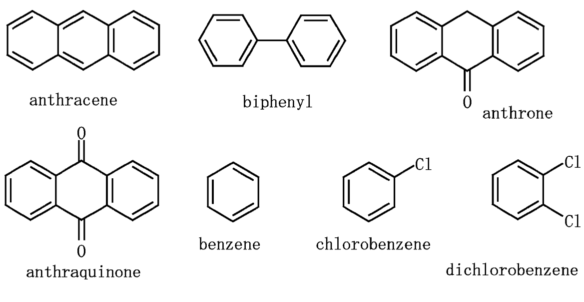

Figure 3. Model compounds dioxins used in this work.

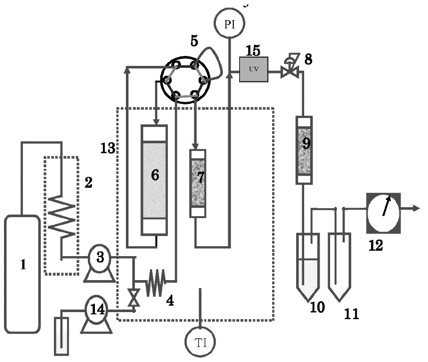

Figure 4. Experimental apparatus for the measurement of adsorbed amount on activated carbon. (1: CO_2 cylinder, 2: cooling coil, 3: high pressure pump, 4: mixing device, 5: six-port valve, 6: dissolution column, 7: adsorption column, 8: back-pressure regulator, 9: activated carbon trap, 10: toluene trap, 11: trap, 12, gas meter, 13: thermostatted bath, 14: solvent pump, 15: UV detector).

compounds on activated carbon. Since most of the compounds are strongly adsorbed on the activated carbon, it was difficult to measure the equilibrium behavior on activated carbon. Thus, to evaluate adsorption equilibrium constant, we used ODS silica for the impulse response measurement

The impulse response measurement was carried out with an apparatus consisting of adsorption column packed with activated carbon or ODS silica, high pressure pump to supply supercritical carbon dioxide, feeding system, and on-line UV detector. To measure the adsorption capacity on activated carbon, solutes were injected discretely by high pressure pump until the solutes appeared in the effluent of the column when the adsorbent was saturated. For the impulse response measurement, we used a sample saturator where solutes were dissolved in supercritical fluid phase and small amount of the solute was injected.

A schematic diagram of the experimental apparatus is shown in Fig. 4. Carbon dioxide from a cylinder with a siphon attachment (Uchimura Sanso Ltd.) was passed through a cooled line and compressed to operation pressure by a high pressure pump with a recycle line equipped with a back-pressure regulator. The compressed CO_2 was passed through a heat exchanger to reach the desired temperature. The solute in the effluent from the adsorption column was monitored by on-line UV detector (292 nm, Jasco, UV-970). The flow rate of supercritical fluid was controlled by a metering valve and the measured by a rotameter and dry gas meter.

For the impulse response measurement on ODS silica, the sample was charged into a saturation column prior to the experiment. A very low flow rate was set in the saturator to ensure the carbon dioxide eluting from the saturator was saturated with the sample at the given condition. A 10 μL pulse of sample dissolved in supercritical carbon dioxide was injected by switching the six-port valve through a sample loop. When entrainer (modifier) was used, another high pressure pump was used to mix the entrainer into carbon dioxide line.

The adsorbent used was activated carbon (Wako Co. Ltd.) and ODS silica (particle diameter 30–50 μm, pore size 70 Å, GL Science Co. Ltd.). The properties of the packed column are: pore diameter: 75 Å specific surface area: 500 m^2/g, pore volume: 0.80 ml/g, bed voidage: 0.471, particle porosity: 0.265. As an modifier, methanol was used in 1 and 5%. The pressures used were 15, 20, 25, and 30 MPa. The temperatures used were 313, 323, and 333 K.

4. Results and Discussion

4.1. Breakthrough Analysis on Activated Carbon

Figure 5 shows the influence of pressure on the adsorbed amount of solutes, benzene, monochlorobenzene, dichlorobenzene, biphenyl, and anthracene at the temperature of 323 K. With increase in the pressure adsorbed amount decreased. This is owing to the increase in fluid density with pressure. Since adsorption of these compounds on activated carbon may be almost

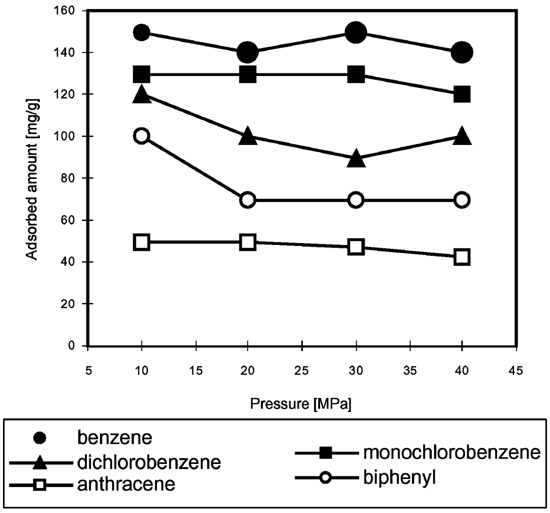

Figure 5. Effect of pressure on the adsorbed amount on activated carbon at 323 K.

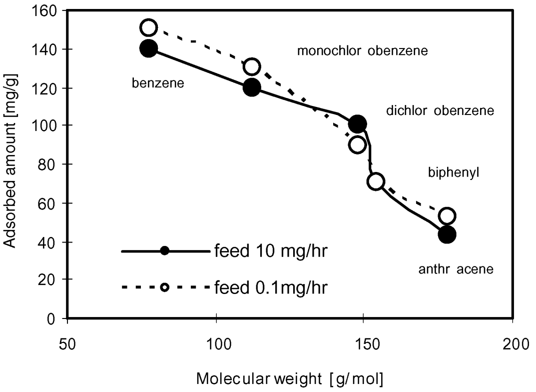

Figure 6. Effect of feeding rate of solute on adsorbed amount plotted as a function of molecular weight of solutes.

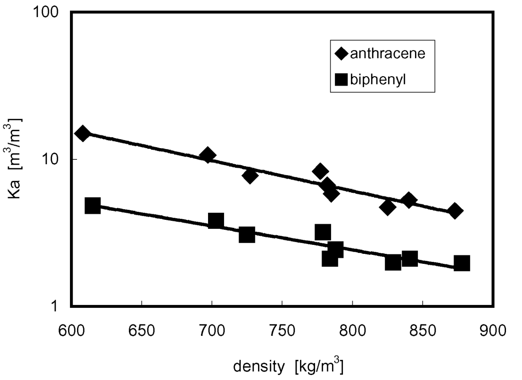

Figure 7. Adsorption equilibrium constant on ODS silica in pure carbon dioxide.

irreversible, the effect of pressure on the adsorption amount was small. Adsorbed amount for the solutes used in this work was the following order. benzene > monochlorobenzene > dichlorobenzene > biphenyl > anthracene.

Figure 6 shows the effect of feeding rate of solutes on the adsorbed amount. The solutes are fed to the adsorption column at the 0.1 mg/hr and 10 mg/hr. There is no significant effect of the feeding rate as shown in Fig. 6, indicating that the adsorbed amount is equivalent to the adsorption capacity of the solute on the activated carbon. The adsorbed amount is plotted as a function of molecular weight in Fig. 6. The adsorbed amount decreased with increase in the molecular weight of the solute regardless of chlorine content in the molecule.

4.2. Impulse Response on ODS Silica

From the impulse response of solutes on ODS silica, moment analysis was applied to evaluate adsorption behavior. Adsorption equilibrium constant, Ka was calculated from the first moment of the peak of the response.

Figure 7 shows the adsorption equilibrium constant for anthracene and biphenyl measure at various pressures and temperatures. Fluid density of supercritical carbon dioxide was estimated at a given temperature and pressure. As shown in our previous paper (Goto et al., 1996; Sato et al., 1998), adsorption equilibrium constants were estimated to give a straight line on a semi-log plot of log (Ka) versus fluid density, as shown in Fig. 7, independent of pressure and temperature.

As a carrier fluid, pure carbon dioxide was used. Among four components, anthracene and biphenyl were chromatographically eluted and the adsorption equilibrium constant was evaluated. However, the eluted peak of anthraquinone and anthrone were not observed because they were adsorbed strongly on the adsorbent.

To reduce adsorption strength of solutes, methanol was added to carbon dioxide as an entrainer or modifier.

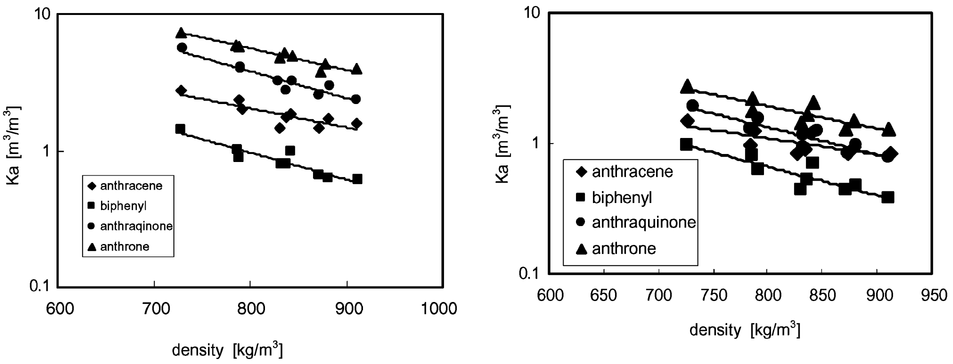

Figure 8. Adsorption equilibrium constant on ODS silica in carbon dioxide with 1% methanol (left) and 5% methanol (right).

Figure 8 (left) shows the adsorption equilibrium constant in supercritical carbon dioxide with 1% methanol. In this case chromatographic peaks of antraquinone and anthrone were also observed. The strength of adsorption decreases as anthrone > anthraquinone > anthracene > biphenyl. Comparing with the results in Fig. 8 (right), the adsorption equilibrium constant for anthracene and biphenyl decreased by addition of methanol.

The methanol content in carbon dioxide was increased to 5%. The adsorption equilibrium constants decreased further by increasing methanol from 1 to 5%.

5. Conclusion

By using the step response technique, we obtained the amount adsorbed on activated carbon. With increase in the molecular weight, the adsorption amount decreased. The adsorbed amount was not significantly influenced by the pressure. This result suggests that these components can be effectively adsorbed on activated carbon in supercritical carbon dioxide.

Adsorption equilibrium constants on ODS silica were evaluated. The adsorption equilibrium constants laid on a straight line on semi-log plot against fluid density. Addition of methanol reduced the adsorption equilibrium constants.

Acknowledgment

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References

Goto, M., M. Sato, S. Kawajiri, and T. Hirose, "Impulse Response Analysis for Adsorption of Ethyl Acetate on Activated Carbon in Supercritical Carbon Dioxide," *Sep. Sci. Tech.*, **31**, 1649–1661 (1996).

Goto, M. and S. Kawajiri, "Removal and Destruction of Dioxins from Fly Ash by a Combined Process of Supercritical CO_2 Extraction and SCWO," *Proc. SuperGreen*, 57–60, (2002).

Hartonen, K., S. Bowadt, S.B. Hawthorne, and M.-L. Riekkola, "Supercritical Fluid Extraction with Solid-Phase Trapping of Chlorinated and Brominated Pollutants from Sediment Samples," *J. Chromatogr., A*, **774**, 229–242 (1997).

Hashimoto, S., K. Watanabe, K. Nose, and M. Morita, "Remediation of Soil Contaminated with Dioxins by Supercritical Water Extraction," *Chemosphere*, **54**, 89–96 (2004).

Kawajiri, S., M. Goto, and T. Hirose, "Extraction of the Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Municipal Incinerator Fly Ash with Supercritical Carbon Dioxide," *Organohalogen Compounds*, **40**, 153–155 (1999).

Kawajiri, S., M. Goto, and T. Hirose, "Extraction of Dioxins from Municipal Incinerator Fly Ash with Supercritical CO2 in Comparison with Soxhlet Extraction," *Organohalogen Compounds*, **45**, 101–104 (2000).

Kawajiri, S., M. Goto, A. Kodama, and T. Hirose, "Extraction of Toxic-Organo Halogenated Compounds from Fly Ash with $SCCO_2$," *High Pressure Chemical Engineering*, 1–5 (2001).

Sako, T., T. Sukgeta, K. Otake, M. Sato, M. Tsugumi, T. Hiaki, and M. Hongo, "Decomposition of Dioxins in Fly Ash with Supercritical Water Oxidation," *J. Chem. Eng. Japan*, **30**, 744–747 (1997).

Sato, M., M. Goto, A. Kodama, and T. Hirose, "Chromatographic Analysis of Limonene and Linalool on Silica Gel in Supercritical Carbon Dioxide," *Sep. Sci. Tech.*, **33**, 1283–1301 (1998).

Windal, I., D.J. Miller, E. De Pauw, and S.B. Hawthorne, "Supercritical Fluid Extraction and Accelerated Solvent Extraction of Dioxins from High- and Low-Carbon Fly Ash," *Anal. Chem.*, **72**, 3916–3921 (2000).