ADSORPTION STUDIES OF TOXIC CHLORINATED AROMATIC SPECIES ON ACTIVE CARBONS

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Introduction
Active carbons are used for the removal of a wide range of species from flue gases. Dioxin and furan species are amongst the most toxic species released from combustion processes. These species may be removed from flue gases by adsorption on active carbons at temperature in the range 423-473K. The adsorption characteristics of chloro- and dichlorobenzene species on active carbons can be used as models for the extremely toxic dioxin species. In this paper adsorption isotherms of chlorinated aromatic compounds as models for toxic species are presented for temperatures in the range 313-453K. The results are discussed in terms of the structure of the adsorptive in relation to the pore structure of the adsorbent.

Experimental
Carbon BAX950, a wood-based activated carbon used in this study was obtained from Westvaco Corporation, Virginia, U.S.A. An active carbon was prepared from Longannet char by activation in carbon dioxide at 1073K. Chlorobenzene and 1,3-dichlorobenzene with purity of 99.9% was supplied by SIGMA-Aldrich Co. Adsorption studies were carried out using an Intelligent Gravimetric Analyser (IGA) supplied by Hiden Analytical Ltd. This apparatus allows isotherms and the corresponding kinetics of adsorption to be determined for the individual pressure steps.

Results and Discussion
The adsorption isotherms for chlorobenzene on carbon BAX950 over the temperature range 313-453K are shown in Figure 1. The isotherms are classified as Type I but have a finite slope at high relative pressure. The amount adsorbed decreased systematically with increasing temperature. The total pore volume obtained from the amount adsorbed at 313K was 0.84 cm³g⁻¹, which is consistent with the total pore volume, 0.83 cm³g⁻¹, obtained from nitrogen adsorption at 77K. The isotherms of 1,3-dichlorobenzene adsorption on BAX950 are similar in shape to chlorobenzene, at same temperature. Comparison of the isotherms on a P/P⁰ basis (see figure 2) shows that the isotherms cross over each other and the adsorption of 1,3-dichlorobenzene is larger than chlorobenzene at low relative pressure.

The chlorobenzene adsorption isotherm on Longannet char sample over the temperature range 313-453K are typical Type I isotherms and decrease systematically with increasing temperature. The isosteric enthalpies of chlorobenzene adsorption on Longannet char and BAX950 were 43kJmol⁻¹ and 37kJmol⁻¹, respectively, calculated using van’t Hoff isochore when amount adsorbed was 1.0 mmolg⁻¹. This compares with the enthalpy of vaporisation of 35.19kJmol⁻¹. A comparison on isotherms for chlorobenzene adsorption on Longannet char and BAX950 at 413K are shown in Figure 3. Longannet char is a microporous activated carbon, whereas carbon BAX950 has an extensive meso- and macroporous structure in addition to a microporous structure. The D-R graphs of log (n) against (RT)²log₂(p₀/p) show slight curvature at high relative pressure (see Figure 4). The micropore volume of Longannet char obtained from the D-R equation for chlorobenzene adsorption at 313K was 0.164 cm³g⁻¹. This is slightly lower than the micropore volume (0.196 cm³g⁻¹) obtained from CO₂ adsorption at 273K. This suggests that there is some exclusion of chlorobenzene from part of the microporous structure.

The adsorption kinetics followed the Linear Driving Force (LDF) model which is described by the equation:

$$\frac{M_t}{M_e} = 1 - e^{-kt}$$

where Mₜ is the uptake at time t, Mₑ is the equilibrium uptake, t is the time(s) and k is the rate constant(s⁻¹). The rate constants for chlorobenzene and 1,3-dichlorobenzene adsorption on BAX950 at 423K are shown in Figure 5. Chlorobenzene adsorption rate constants are faster than 1,3-dichlorobenzene, which has a larger molecular size.

Conclusion
This study shows that the relationships between adsorption characteristics and temperature are complex and depend on the porous and adsorptive structure. These results demonstrate that adsorption studies of models for dioxin and furan can be studied at temperatures within the range used for commercial adsorption systems.
References


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