

# Dioxins and Furans Adsorption on Activated Carbon under Simulated Flue Gas Conditions Using Chloroaromatic Species as Models

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## Abstract

In this study, Carbon G209, a coconut based activated carbon, particle size fraction 1.18 - 1.7 mm supplied by Pica, Vierzon, France was used to investigate adsorption dynamics of polychlorinated dibenzo-p-dioxins and dibenzofurans species, extremely toxic compounds generated in low concentration in post combustion gases. The adsorption of these toxic compounds were analyzed using model species to understand their barrier to diffusion on the activated carbon, which may affect its removal and performance on carbon filters in real situations. Adsorption studies were carried out under conditions of very low concentration and temperatures up to 453 K, which simulate those found in dioxin and furans abatement systems. The extreme toxicity and very low volatility prevent detail study of their adsorption characteristic, and therefore, chloroaromatic model dioxins comprising Chlorobenzene, 2-chlorotoulene, 1,3-dichlorobenzene and 2-chloroanole have been used. These toxic organic compounds was effectively removed by G209 activated carbon as both hydrophilic functionalities and hydrophobic graphene layers are present in the material acting as primary adsorption sites for hydroxyl groups and hydrocarbons respectively

**Keywords:** *Dioxins, Furans, Flue Gas, Chloroaromatic, Activated carbon, Adsorption.*

## 1. Introduction

Activated carbons are cheap and effective adsorbent used to capture harmful environmental species formed in flue gas systems and combustions zones of incinerators.[1] The large internal surface area associated with these materials is attributed to an expansive system of ultramicropores, which provide enhanced adsorption capabilities under flue gas conditions of high temperature and low concentration.[2-4] The adsorption kinetics of flue gas systems and combustions zones of incinerators conditions could help determines the abatement efficiency of an activated carbon filter, as the thermodynamics dioxin concentrations in flue gases are far from equilibrium in the real situation. [2-4]

The polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are classes of aromatic compounds that form in low concentrations when

chlorine species are present in post combustion gases. [5] These gases are complex mixtures of gases and particles with both homogeneous and heterogeneous formation and decomposition mechanisms.[6-8] The homogeneous formation mechanism involves reactions of many precursors such as chlorobenzenes, and chlorophenols in the temperature range 400-800 oC. Heterogeneous reactions mechanisms occur in the temperature range 200-400 oC. The complexity of dioxin formation in combustion systems has led to the use of quantum chemical calculations, modeling reaction mechanisms, and adsorption of precursor species on surfaces to understand the relationship of PCCD/PCDF formation to operational conditions. [8-11] The dioxin and furan species are amongst the most toxic species released from combustion processes to the environmental for municipal waste incinerators, although emissions of these species are very low, they are extremely toxic and tend to accumulate in biosystems. [6-7] Therefore emissions must be controlled in order to minimize the environmental impact of combustion processes. [7] It is important to note that chloroaromatic species and their precursors result in the formation of Polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran from post combustion flue gases.[6-7] Therefore, pore structure and surface chemistry characteristics are important for optimizing adsorbents the for the dioxins and furans species removal from combustion flue gases. Hence, in order to understand the mechanism of adsorption of these chloroaromatic species on activated carbons, realistic simulation of the conditions under which they are adsorbed in the emission abatement system is essential for investigation of the factors that control the adsorption of process.

This study was to investigate the adsorption characteristics of the models for dioxins and furans within the temperature range used for realistic adsorption systems in order to establish the importance of the specific structural characteristics of the porosity in determining the thermodynamics and kinetics of adsorption. The extreme toxicity of these environmental unfriendly species prevents direct study of their adsorption characteristics on porous materials. Therefore, chlorobenzene, 1, 3-

dichlorobenzene, and related species were selected as model compounds with similar structural characteristics and low toxicity to be used as precursors in dioxin formation to replicate the dioxin adsorption. The study will help in understanding the role of adsorptive structural factors and interactions with carbon surfaces to establish an improved understanding of the adsorption process from which the influence on dioxin adsorption on porous carbons may be inferred. Studies were carried out at temperature range of 313K – 423K as species may be removed from flue gases by adsorption on activated carbon at this temperature range.

## 2. Experimental

### 2.1 Materials Used

Carbon G209, a coconut based activated carbon, particle size fraction 1.18 - 1.7 mm supplied by Pica, Vierzon, France.

Model dioxin adsorptives used are chlorobenzene (99 %), 2-chlorotoluene (99 %), 1,3 dichlorobenzene (99 %), and 2-chloroanisole (99%) supplied by Sigma Aldrich.

### 2.2 Static Adsorption Measurements

The adsorption mechanism of chloroaromatic species on activated carbons were investigated using the Intelligent Gravimetric Analyzer (IGA), at Wolfson Carbon Reduction Laboratories, Newcastle University; supplied by Hiden Isochema Ltd., Warrington, UK. The system is an ultra-high vacuum (UHV) system and allows measurement of isotherms and accurate determination of the adsorption and desorption kinetic profiles for each pressure step. The system consists of a fully computer controlled microbalance, pressure admit system and temperature regulation system. The mass was recorded using a computer-controlled microbalance and the temperature and pressure was computer controlled. The microbalance has a long-term stability of  $\pm 1 \mu\text{g}$  with a weighing resolution of  $0.2 \mu\text{g}$ . The carbon sample ( $100 \pm 1 \text{ mg}$ ) was outgassed to a constant weight, at  $< 10^{-6} \text{ Pa}$ , at 393 K. For model dioxin adsorption the liquid used to generate the vapour was degassed fully by repeated evacuation and vapour generation equilibration cycles. Three pressure transducers control the admitted gas/vapour pressure. The transducers have individual pressure ranges of 0-0.2 kPa, 0-10 kPa and 0-0.1 MPa. In order to prevent disruption of the microbalance, during the pressure increment/decrement, the gas/vapour admittance time was set to ~30 seconds. As a result, there are minimal changes in pressure, during the mass relaxation process, compared with the adsorption kinetics. The pressure set point accuracy was achieved to 0.02 % of the range employed. The set pressure value was maintained by

computer control during the course of the experiment. The sample temperature was recorded using a thermocouple located close to the sample. For high temperature adsorption of model dioxins measurements, carried out between 353 K - 453 K, a high temperature furnace was used, which controlled the target temperature within  $\pm 0.1 \text{ K}$ . The mass increase was monitored as a function of time, with approach to equilibrium monitored by a computer algorithm. The real-time processing uses non-linear least squares regression analysis to determine estimates of kinetic parameters during the adsorption/desorption process. Once equilibrium was reached the vapour pressure was subsequently increased to the next designated pressure value and uptake was monitored until equilibrium at this new pressure was established. The equilibrium uptake value was determined as being 99.9 % of the predicted value, calculated in real time using the mass uptake profile. The weight uptake profiles for each pressure step were used to calculate kinetic parameters for adsorption using an appropriate kinetic model.

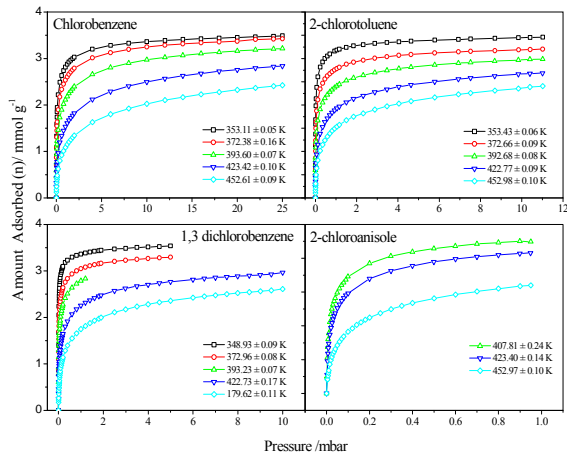
Saturated vapour pressures were calculated using the Antoine equation: [12]

$$\log p^0 = A - \frac{B}{T + C} \quad (1)$$

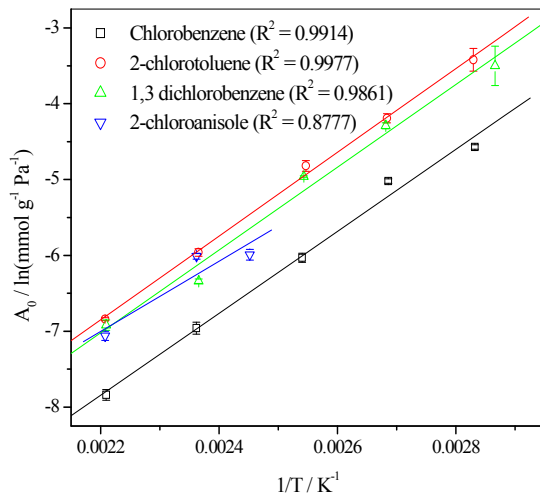
Where  $p^0$  is the saturated vapour pressure (Torr), T is the temperature (K), and A, B, and C are adsorbate dependent constants. The parameters used for each adsorptive are as follows: carbon dioxide (77 – 303 K) (A) 7.81024, (B) 995.705, (C) 293.475; nitrogen (75 – 373 K) (A) 6.49457, (B), 255.68, (C) 266.550 [12]; chlorobenzene (227.8 – 632.3 K ) (A) 7.18342, (B) 1574.53, (C) 234.229; 2-chlorotoluene (280.6 – 660 K) (A) 7.18144, (B) 1645.900, (C) 223.563; [13] 1,3 dichlorobenzene (353 – 446 K) (A) 7.0401 (B) 1607.15 (C) 213.38; and 2-chloroanisole (388 – 459 K ) (A) 7.12136 (B) 1655.80 (C) 188.77. [12]

### 3. Results and Discussion

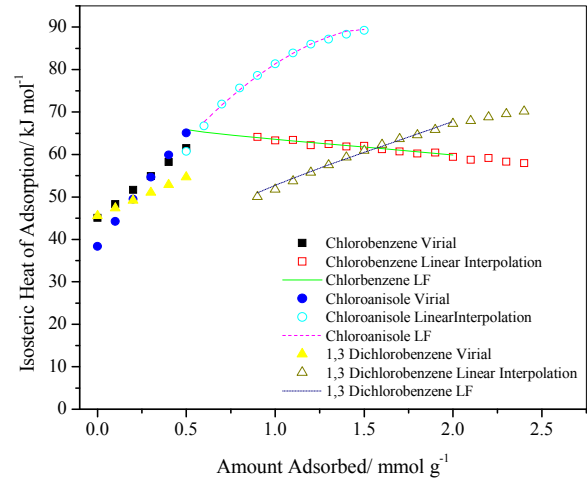
**Figure 1:** Adsorption isotherms for chlorobenzene, chlorotoluene, 1,3 dichlorobenzene, and 2-chloroanisole on pressure (mbar) against temperature range: 353.43 K – 452.98 K on G209 activated carbon.



**Figure 2:** Graphs of  $A_0$  vs.  $1/T$  for adsorption of chlorobenzene, 2-chlorotoluene, 1,3 dichlorobenzene, and 2-chloroanisole on G209 activated carbon.



**Figure 3:** Isothermic heats of adsorption for chlorobenzene, 2-chloroanisole, and 1,3 dichlorobenzene on G209 activated carbon



**Figure 4:** The variation of  $\Delta H_{\ddagger}^{\ddagger} / E_a$  with amount adsorbed for chlorobenzene, 2-chlorotoluene, 1,3 dichlorobenzene, and 2-chloroanisole on G209 activated carbon

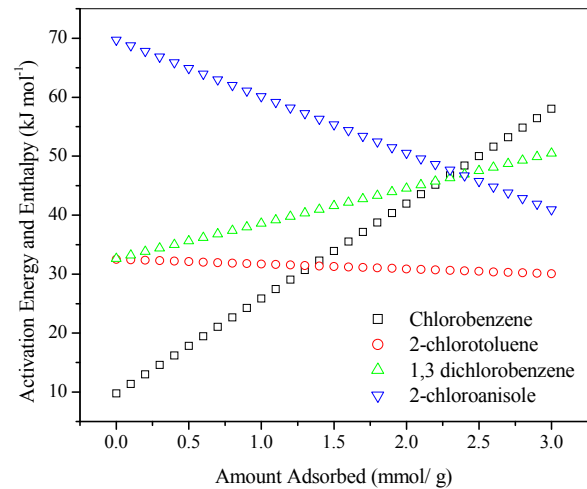


Figure 1 show the adsorption isotherms for chlorobenzene, 2-chlorotoluene, 1,3 dichlorobenzene, and 2-chloroanisole on G209 over the temperature range 353 K – 453 K. The isotherms are very similar with small differences being, in part, due to lower adsorbate density with increasing temperature. The temperature range 353 K – 453 K is similar to those used for dioxin abatement using activated carbon injection in flue gases. All isotherms obtained are Type I in the IUPAC classification scheme. [14] The

amount adsorbed decreases with increasing temperature, which is consistent with a physisorption mechanism.

The adsorption of planar chlorobenzene, 2-chlorotoluene, and 1, 3 dichlorobenzene on G209 over the temperature range 353 – 453 K showed that activation energy at zero surface coverage was significantly lower than the enthalpy of adsorption at zero surface coverage. The adsorption of non-planar 2-chloroanisole on G209 showed opposite trend, as the kinetic barrier is larger than the enthalpy of adsorption, at zero surface coverage. Hence, the probability of desorbing back into the gas phase is high and the mechanism of diffusion must be through constrictions in the porosity.

The results of the adsorption of planar molecules indicate that kinetic barrier was associated with a surface diffusion process, which is consistent with a site to site hopping mechanism, rather than diffusion through constrictions in the porosity. This involves hopping between neighbouring physisorption potential wells via an activated transition state. Therefore, the kinetic barrier reflects the amount of energy required to move from the bottom of the potential well to the activated complex. The adsorption of non-planar molecules (2-chloroanisole) is controlled by diffusion through constrictions in the porosity. Desorption into gas phase occurs is low and the molecule takes the lower energy path of diffusing across the surface. The molecules desorb into the gas phase higher and the large kinetic barrier is attributed to increased diffusion resistance in the micropores due to the rotating methoxy substituent.

Figure 7 shows an increase in the enthalpy of activation with enthalpy of adsorption as the size of the adsorbate increases. Hence, as the dispersion potential increases between the carbon surface and the adsorbate, due to an increase in electron density associated with molecules of increasing molecular mass, the enthalpy of activation changes proportionally. Hence, the enthalpy of activation changes proportionally with the enthalpy of adsorption. As the acidity of the carbon surface increases the enthalpy of adsorption and enthalpy of activation at zero surface coverage decrease. This is due to the electron withdrawing acidic oxygen groups reducing the dispersive adsorption potential by decreasing the  $\pi$  electron density in the graphene layers. [15]

#### 4. Conclusions

The reduction of dioxins and furans at low concentrations in air is a generic problem. Adsorption on G209 activated carbon adsorbents appears to be the major area for development in recovery technology; for a complete understanding of the removal processes from flue gas. Result obtained showed that surface diffusion is the rate

limiting step for the diffusion of chlorobenzene, 2-chlorotoluene, and 1,3 dichlorobenzene model compounds with similar structural characteristics to dioxins and furans. The isosteric enthalpy of adsorption is significantly larger than the kinetic barrier at zero surface coverage, hence the probability that the adsorbed molecule will desorb back into the gas phase is low. The kinetics of planar and non-planar chloroaromatic species is very similar at low relative pressure because the rate determining step is the diffusion through the narrowest available porosity.

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#### References

- [1] Brunauer, S. *The Adsorption of Gases and Vapours*; Oxford University Press: London, UK, 1943.
- [2] Chen, Y.; Yang, R. T. "Surface and mesoporous diffusion with multilayer adsorption", *Carbon*, 36, 1998, 1525-1537.
- [3] Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *The Molecular Theory of Gases and Liquids*; Wiley, 1966
- [4] Zwietering, P.; Krevelen, D. W. V. "The effect of thermal treatment on the surface area of coal", *Fuel*, 1954, 33, 331
- [5] Olie, K.; Vermeulen, P. L.; Hutzinger, O., "Chlorodibenzo-p-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in the Netherlands", *Chemosphere*, 6, (8), 1977, 455-459.
- [6] Karasek, F. W.; Dickson, L. C., "Model Studies of Polychlorinated Dibenzo-Para-Dioxin Formation during Municipal Refuse Incineration". *Science*, 237, 4816, 1987, 754-756.
- [7] Altarawneh, M.; Dlugogorski, B. Z.; Kennedy, E. M.; Mackie, J. C., "Mechanisms for formation, chlorination, dechlorination and destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs)". *Progress in Energy and Combustion Science*, 35, 3, 2009, 245-274.
- [8] McKay, G., "Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: review". *Chemical Engineering Journal*, 86, 3, 2002, 343-368.
- [9] Khachatryan, L.; Asatryan, R.; Dellinger, B., "An elementary reaction kinetic model of the gas-phase formation of polychlorinated dibenzofurans from chlorinated phenols". *Journal of Physical Chemistry A*, 108, 44, 2004, 9567-9572.
- [10] Altarawneh, M.; Dlugogorski, B. Z.; Kennedy, E. M.; Mackie, J. C., "Quantum chemical investigation of formation of polychlorodibenzo-p-dioxins and dibenzofurans from oxidation and pyrolysis of 2-chlorophenol". *J. Phys. Chem. A* 111, 13, 2007, 2563-2573.

- [11] Lomnicki, S.; Dellinger, B., "A detailed mechanism of the surface-mediated formation of PCDD/F from the oxidation of 2-chlorophenol on a CuO/silica surface". *Journal of Physical Chemistry A*, 107, 22, 2003, 4387-4395.
- [12] Lange's Handbook of Chemistry; 15th ed.; McGraw-Hill: New York, 1999.
- [13] Yaws, C. L.; Narasimhan, P. K.; Gabbula, C., Yaws' Handbook of Antoine Coefficients for Vapor Pressure (2nd Electronic Edition), Knovel.
- [14] Rouquerol, J.; Avnir, D.; Fairbridge, C. W.; Everett, D. H.; Haynes, J. H.; Pernicone, N.; Ramsay, J. D. F.; Sing, K. S. W.; Unger, K. K., "Recommendations for the characterization of porous solids". *Pure and Applied Chemistry*. 66, (8), 1994, 1739-1758.
- [15] Ruegg, H.; Sigg, A., "Dioxin Removal in a Wet Scrubber and Dry Particulate Remover", *Chemosphere*. 25, (1-2), 1992, 143-148.