

EFFECTS OF ACTIVE CARBON SURFACE CHEMISTRY ON *para*CHLOROPHENOL ADSORPTION

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Introduction

Active carbons used for environmental clean-up applications are frequently required to adsorb organic species from aqueous solution. Phenolic compounds have been much studied in this respect. It has often been assumed that the mechanism of adsorption is by polar interaction between the phenolic -OH and anionic oxide groups present on the carbon surface [1] and that therefore surface oxidation increases adsorptivity. In current work we are studying the effects of carbon surface chemistry on the adsorption of *parachlorophenol* (PCP) from aqueous solution in order to clarify the mechanism(s) of the interactions of this molecule at energetically heterogeneous carbon surfaces. Here we present preliminary results from our work.

Experimental

Five wood based, phosphoric acid activated commercial carbons (*Westvaco Ltd.*) have been studied. Porosity has been characterised from nitrogen adsorption data measured at 77 K. Surface chemistry has been probed using X-ray photoelectron spectroscopy (XPS) and the polarity of the carbons has been assessed by water adsorption at 293 K. The Cu II adsorption characteristics of these carbons are described elsewhere [2]. The kinetics of PCP adsorption at 298 K have been followed by equilibrating 1g of each carbon with 1000 cm³ of 20 m.mol/l PCP in a stirred system and analysing 0.5 cm³ aliquots at intervals by UV/Visible spectroscopy. Initially, aliquots were taken at 2 minute intervals up to 12 minutes, thereafter 5 minute interval times were used.

Results and Discussion

Structural data for the five carbons are given in Table 1. C46 has the highest micropore volume and C45, C47, C48 and C49 have similar micropore volumes. It can be seen that C48 contains about 25% more mesoporosity than the others.

Table 1. Structural Characteristics from N₂ adsorption

| Carbon | C45 | C46 | C47 | C48 | C49 |
|--------------------|------|------|------|------|------|
| V _{micro} | 0.20 | 0.30 | 0.21 | 0.20 | 0.22 |
| V _{meso} | 1.06 | 1.04 | 1.03 | 1.26 | 1.01 |
| V _{total} | 1.26 | 1.35 | 1.24 | 1.46 | 1.24 |

Figure 1 shows the kinetic data for PCP adsorption by each carbon. There is a clear anti-correlation between the levels of surface oxygen recorded by XPS (Table 2) and (i) the times taken to reach maximum uptake and (ii) the maximum uptake values. Thus for these systems it appears that increasing the oxygen content/structural polarity of the carbons causes a decrease in PCP adsorptivity. This appears to be consistent with the dominant adsorption force for this molecule being dispersion in character with the most likely orientation of the molecule being flat with the benzene ring of the PCP parallel to the rings of the graphene structure of the carbon. The adsorption force would therefore arise from the dispersion interaction of the π electrons in the respective aromatic systems. Decreases in dispersion energy with increasing polarity for carbon surfaces have been observed in previous work [3], and domination of the polar interaction of the -OH group by the dispersion interaction of methyl groups for an homologous series of

alcohols from the vapour phase has also been reported previously [4]. The latter was characterised by an increase in the type I character of the resulting isotherms as the alkyl chain length increased from methanol to butan-1-ol (i.e. as the dispersion interaction became stronger). The adsorption of PCP from this aqueous system appears also to be dominated by non-specific interactions. The effects of porosity are not clear at present. Similarly, the mesoporosity of C48 may be factor contributing to its high PCP adsorptivity. These aspects are currently being investigated.

Table 2 also contains nitrogen BET surface area data and PCP saturation areas derived from the plateau regions in Figure 1. The latter have been calculated assuming a geometric area of 71.4 \AA^2 for the PCP molecule adsorbed flat onto the surface. No correction has been attempted for distortion due to adsorption forces. In the case of C45, C47 and C48, the PCP area is larger than the corresponding BET area. It is generally accepted that the BET equation overestimates the true internal area of microporous solids by incorporation of adsorption which occurs by the volume filling mechanism(s), and it therefore appears that the plateau regions for these 3 carbons represent adsorption beyond the formation of a single monolayer. It is not currently known if this is accompanied by a change in orientation of the adsorbed molecules.

Table 2. BET surface areas PCP saturation areas and Oxygen levels

| | BET (m^2/g) | PCP sat m^2/g | Oxygen (atomic %) |
|-----|----------------------------------|----------------------------------|----------------------|
| C48 | 2079 | 2458 | 1.8 |
| C47 | 1611 | 1924 | 5.8 |
| C46 | 2016 | 1907 | 8.0 |
| C45 | 1615 | 1670 | 8.6 |
| C49 | 1704 | 1442 | 8.6 |

Conclusions

The adsorption of PCP from aqueous solution appears to be adversely affected by increases in the surface polarity of wood based carbons. This is consistent with non-specific adsorption by dispersion interactions of the π electrons of the PCP and graphene aromatic structure. Assuming a planar orientation at the graphene surface, the saturation uptakes for three of the carbons are above the nominal BET surface areas which indicates that, in those instances, multilayer adsorption may be occurring.

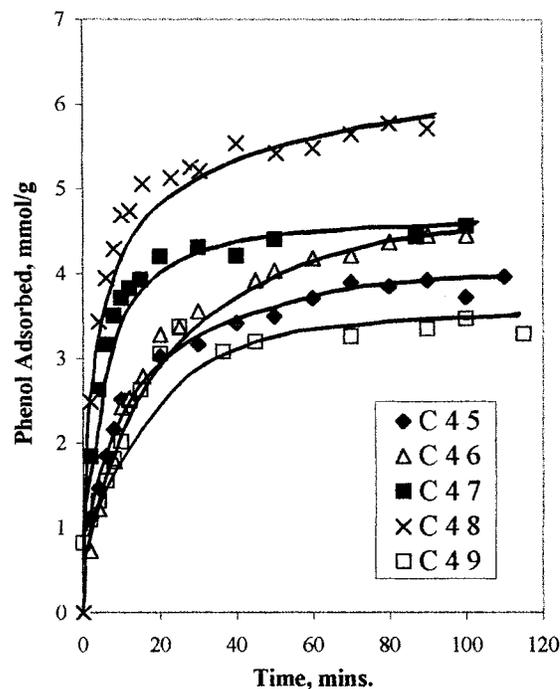


Figure 1: para-Chlorophenol Uptake versus time

References

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