

THE EFFECTS OF MOLECULAR SIZE AND PACKING ON THE ADSORPTION OF AROMATIC COMPOUNDS ONTO ACTIVATED CARBONS

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Introduction

In liquid phase adsorption, it is established that the adsorption capacity of an activated carbon depends on the following factors. First, it is the nature of the adsorbent such as its pore structure, ash content and functional groups. Second, the nature of the adsorbate e.g. its pK_a , functional group present, polarity, molecular weight and size. Finally, the solution conditions, referring to the solution pH, ionic strength and the adsorbate concentration [1]. In this work, the effects of molecular size and packing are reported.

Experimental

The chemicals, benzoic acid (BA), p-nitrophenol (PNP), p-cresol (PC), Salicylic acid (SA) and nitrobenzene (NB) were supplied by Merck. The activated Carbon, F100 was obtained from Calgon Corporation.

The adsorption experiments were carried out by placing 45mg of the activated carbon into 50 ml of the solution containing different concentrations of the adsorbates. Solution pH conditions were lowered using dilute solution of HCl. All solutions were then left in Thermostat shaking bath for 4 days at 301 K to reach equilibrium. After reaching equilibrium conditions, the residual concentrations of the solutes were then measured spectrophotometrically, using Jasco-V550 spectrophotometer.

Results and Discussion

The literature shows discrepancies in the reported values of the area covered by simple aromatic compounds. Müller et al. [2] used an average value of 0.35 nm^2 per aromatic molecule. While for one phenol molecule, areas of 0.437 and 0.499 have also been reported [3,4].

In our work, using the Cerius2 (Molecular Simulations Incorporated San Diego USA) we determined the area of each adsorbate molecule in the XY (flat face), XZ, and the

YZ plains. These three plains are defined as follows. The XY plain is on the plain of the paper, X corresponding to the longest side and Y to the shortest side. On the other hand, Z corresponds to the axis out of the plain of the paper. The area of the molecules in the XY plain would translate into the minimum possible number of molecules packed on the surface and the other two would translate into the maximum possible numbers. The calculated areas in all plains of the molecules are shown in Table 1.

All adsorption experiments were carried out in solution at pH of 2, where all adsorbates were in molecular forms. All experimental isotherms are observed to fit into the homogenous Langmuir Equation (Eq. 1) reasonably well, as shown by the isotherms of NB and BA in Figure 1.

$$\frac{q}{Q_{\max}} = \frac{K_1 C_{\text{eq}}}{1 + K_1 C_{\text{eq}}} \quad (1)$$

where q_e is the adsorbed amount, C_{eq} is the equilibrium liquid phase concentration (mmols l^{-1}), Q_{\max} Maximum adsorption capacity of the carbon (mmols g^{-1}) and K_1 Langmuir constant (mmol l^{-1})

The packing manner of the sorbate molecules can be examined by investigating the variations of the calculated Q_{\max} values with the molecular areas of the solutes in all three plains (Figure 2a,b and c). Figure 2a shows that there is no relationship between Q_{\max} and the molecular areas in the XY plain. This indicates that most likely the solute molecules are not arranged face-down on the carbon surface. In the case of the molecular areas in the XZ plain, however, Q_{\max} is observed to decrease linearly (Figure 2b). This indicates that the packing is most likely edge to face (sorbate-carbon). However, knowledge of the edge areas of the sorbates does lead to simple determination of the maximum possible adsorption capacity, since it can not be assumed that all molecules would sit on the carbon surface at exactly 90° . This is illustrated in Figure 2c. This Figure shows that Q_{\max} decreases drastically with an increase in the calculated areas in the YZ plain. In other words, as the molecules stand 'taller' on the surface, the values of Q_{\max} decrease more rapidly. This could only happen if the

sorbate molecules are tilted on the surface. Other factors, affecting the adsorption of the molecular form of simple aromatic compounds are discussed in details elsewhere [5].

Conclusions

This work shows that the area covered by the adsorbate molecules can be used to explain the part of the observed adsorption characteristics of aromatic compounds onto activated carbons in their molecular form. Furthermore, the packing manner is most likely edge-to-face- with various tilt angles.

References

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Table 1. Some important Properties of the solutes

Solute	Molecular Area (\AA^2 /molecule)		
	XY	XZ	YZ
P-Cresol	41.6	26.1	18
p-Nitrophenol	46	25.1	16.7
Benzoic Acid	43.7	24.6	16.9
Nitrobenzene	42.2	22.8	16.6
Salicylic Acid	46.5	26.7	20.7

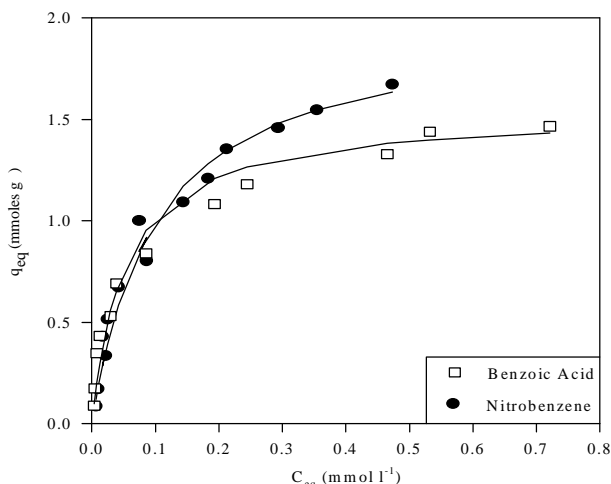


Figure 1 Adsorption isotherms of NB and BA. Solid line is the fitted Langmuir model

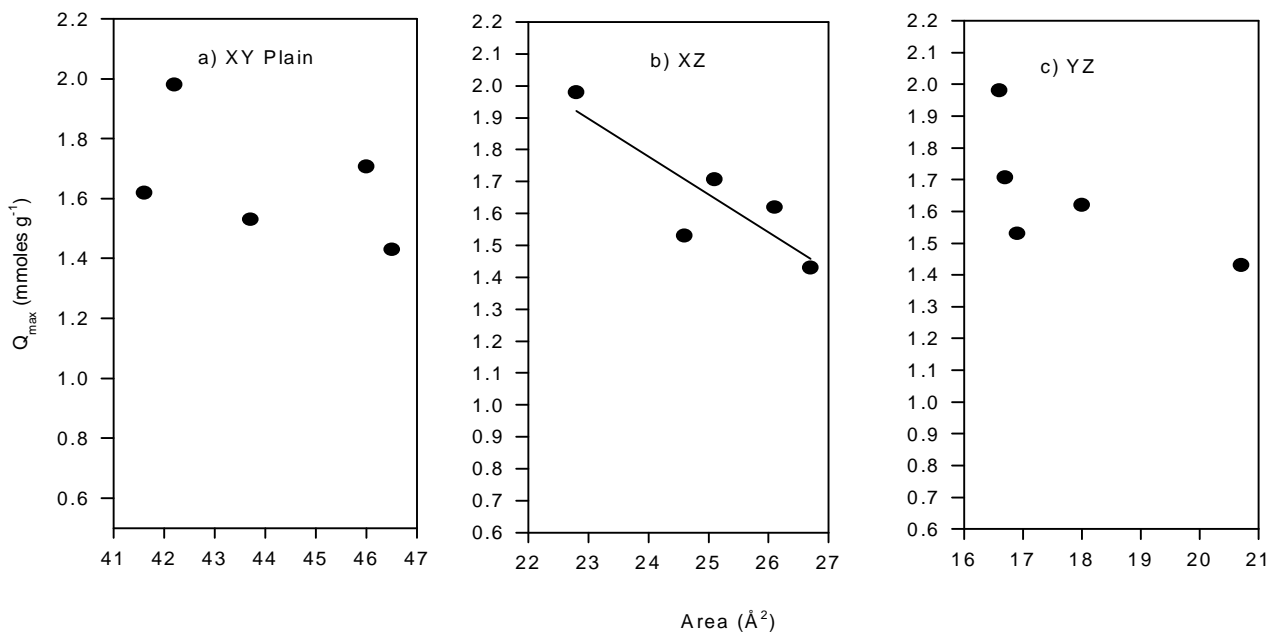


Figure 2. Variation of Q_{max} , with the molecular areas in all three plains