

STUDY OF THE HYSTERESIS ON THE ADSORPTION OF VOC'S IN ACTIVATED CARBON

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Introduction

Adsorption and desorption isotherms for ketone, ethyl acetate and ethanol at various temperatures are presented.

They exhibit hysteresis which persists to very low pressures and vary with the initial load and temperature, i.e., they depend on the system history. To understand how this adsorbent would behave when used to separate residual quantities of Volatile Organic Compounds (VOC's) from air, pressure cycles were imposed and the adsorption isotherms of the activated carbon measured.

The paper presents a discussion on the causes of this abnormal behaviour and on its implications on adsorption column design and operation.

Experimental

Adsorption and desorption isotherms were measured by the volumetric method.

Results and Discussion

Low pressure hysteresis

Four adsorption and desorption isotherms of ethyl acetate on activated carbon at 80 C - in each one fresh activated carbon was used - are shown in figure 1. They display hysteresis that persists down to very low pressures.

This behaviour, displayed also, but in a smaller scale, by ethanol and ketone, is mentioned by a few authors. They studied systems that exhibit Type I isotherms and attributed the hysteresis to the difficulty of the sorbate molecules to pass through constrictions with similar dimensions.

Forty years ago Arnell and McDermott [1] explained this behaviour considering that the adsorbate molecules promote the swelling and the distortion of the structure of the adsorbent, by prising apart weak junctions of the matrix of the solid. So they can open up cavities that were previously not accessible.

The fact that the distortion is not perfectly reversible and some molecules can not escape from the cavities is responsible, according to the same authors, for the existence of the hysteresis.

This basic explanation has been accepted and developed by other authors [2-4].

Adsorption-desorption cycles

Systems with this abnormal behavior deserve some attention when applied in industrial gas separation. When the regeneration of the adsorbent is performed by reducing the pressure, as for example in Pressure Swing Adsorption (PSA) units, it is imperative to understand how the adsorbent will behave. Therefore we measured adsorption-desorption cycles between fixed minimum and maximum pressures. One example is shown in figures 2.

It is clearly shown that after some cycles, usually five are enough, the adsorption/desorption isotherms become almost coincident and at that point the adsorption isotherm is different from the first adsorption and desorption isotherms.

After a considerable number of tests it seems that the limiting adsorption isotherm is dependent on the minimum and maximum pressures used. In other words, it seems that there is a dependence on the system history or a memory effect.

We verified that the experiments where the adsorbent reaches a higher capacity were performed with a very low minimum cycle pressure (near 2mbar) and/or a very high maximum pressure, close to the vapor pressure. In both cases the limiting curves are almost coincident and thus we have only one adsorption isotherm.

Another important point to predict the operating conditions of an adsorption column is to understand how the system will react when, after reaching the limiting adsorption isotherm, one increases the minimum and/or decreases the maximum pressure of the cycles. Such a study was done and fortunately we verified that a unique adsorption isotherm is reached.

Conclusions

1. The adsorption-desorption behaviour presented in this paper is coherent with the explanation given first by Arnell and McDermott and later developed by other investigators. The smaller molecules (ethanol and ketone) show less hysteresis than ethil acetate. This supports the idea that the relationship between the size of the molecules and the dimensions of the pores is the main reason for the existence of this type of hysteresis.
2. In this system it is possible to eliminate all the constrictions that make it difficult for the sorbate molecules to pass through the smaller pores by performing adsorption-desorption cycles with very low minimum pressures and/or very high maximum pressures. McEnaney [2] showed that the stresses in carbons induced by adsorption are of the same order of magnitude as experimental bulk fracture strengths and so it is possible to open the constrictions with many adsorption-desorption cycles.
3. Thus adsorption column design and the operating conditions should be based on the limiting adsorption isotherm since only a few number of cycles are necessary to reach that state. If the equilibrium adsorption conditions used were based on the first adsorption isotherm a subcapacity of the adsorbent would be considered. On the other hand this phenomenon indicates some regeneration difficulties.
4. In industrial adsorption processes it is expected that the time between adsorption steps is much smaller than the carbon matrix relaxation time constant (assuming reversibility). Thus the limiting adsorption isotherm should be used for this purpose.

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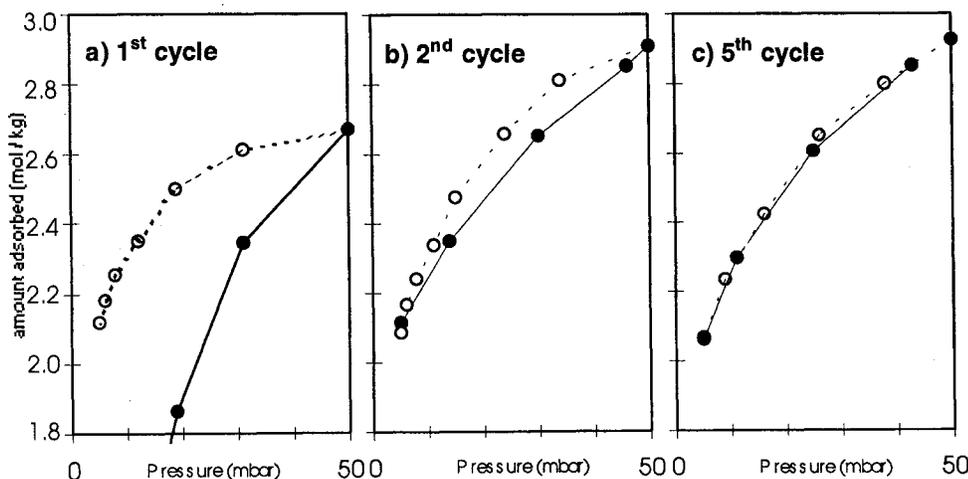


Figure 2. Ethil acetate adsorption-desorption cycles at 80 C on activated carbon; ● adsorption, ○ desorption. Cycles were performed with a minimum pressure of 5mbar and a maximum pressure of 50mbar.

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References

1. Arnell, J.C. and McDermott, H.L., in *Proceedings of the Second International Congress on Surface Activity*, Butterworths, London, 1957. II, p. 113.
2. McEnaney, B., *J. Chem. Soc. Faraday Trans.*, 1974, 70, 84.
3. Bailey, A., Cadenhead, D.A., Davies, D.H., Everett, D.H. and Miles, A.J., *Trans. Faraday Soc.*, 1971, 67, 231.
4. Koresh, J.E., *J. Chem. Soc. Faraday Trans.*, 1993, 89, 935.

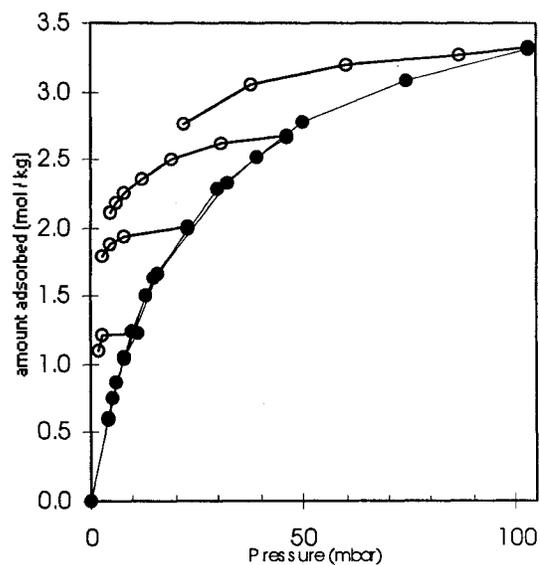


Figure 1. Ethil acetate isotherms at 80 C; ● adsorption, ○ desorption. Each desorption branch corresponds to a different starting pressure.