

KINETICS OF METHANOL VAPOR ADSORPTION AND DESORPTION ON AN ACTIVATED CARBON

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Introduction

Activated carbon filters have many practical applications in the removal of toxic organic material from air streams. Activated carbons have both hydrophilic and hydrophobic sites, the former acting as primary adsorption sites for hydroxyl groups and the latter as sites for hydrocarbon adsorption. Isotherms are a function of the distribution of adsorption sites, pore structure and vapor pressure. Adsorption kinetics are vital for carbon bed performance analysis [1-3]. Here we report the adsorption characteristics of methanol vapor which may be adsorbed on both the hydrophobic and hydrophilic sites of activated carbon.

Experimental

Adsorption of methanol on BAX950, wood-based active carbon, was studied using an 'Intelligent Gravimetric Analyser' (IGA) from Hiden Analytical Ltd. 100 ± 1 mg, of carbon was outgassed until it reached constant weight (at $\sim 10^{-6}$ Pa). Vapor isotherms were obtained at temperatures in the range 288-313 K by setting pressure steps between vacuum and $p/p^\circ = 0.97$. Subsequent adsorption kinetics were determined using vapor uptake for each relative pressure step.

Kinetic Model

The kinetics of methanol adsorption on BAX950 can be modeled by the linear driving force (L.D.F.) mass transfer model:

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

where M_t is the uptake at time t , M_e is the equilibrium uptake, t is the time (s) and k is the rate constant (s^{-1}), hence a plot of $\ln(1 - M_t/M_e)$ versus time will be linear with a gradient equal to the rate constant.

Results and Discussion

Dubinin-Radushkevich plots of the type II isotherms (Figure 1) were initially linear but deviated at high

pressures ($p/p^\circ > 0.02$, pore volume $> 0.04 \text{ cm}^3 \text{ g}^{-1}$). Isothermic heats of adsorption decrease as surface coverage increases and range between 39-52 kJ mol^{-1} , with a limiting value of $\sim 56 \text{ kJ mol}^{-1}$ at zero surface coverage compared to the enthalpy of vaporization of 37.5 kJ mol^{-1} .

The kinetics follow a linear driving force mass transfer (LDF) model regardless of position on the isotherm (Figure 2). The rate increases to a maximum at $p/p^\circ \sim 0.02$, then decreases steadily, with surface coverage. This maximum occurs at the same p/p° as the deviation in the D-R plots, due to a barrier which decreases the rate. Activation energies and corresponding pre-exponential (A) terms were calculated. The highest activation energies (Figure 3) were obtained at low p/p° and it is apparent there is good correlation between $\ln(A)$ and the activation energy indicative of a compensation effect. The activation energies cover the range upto $\sim 40 \text{ kJ mol}^{-1}$, with an initially large value for the activation energy due to molecular sieving, after which a steady decrease in activation energy is observed. Rate constant increases with p/p° suggesting up to $p/p^\circ = 0.02$, after this point the rate decreases steadily indicating conditions for adsorption become increasingly difficult. Kinetics for desorption follow the same mass transfer model as the adsorption process. Rate constant increases as p/p° decreases suggesting conditions become progressively more favorable for desorption. A peak was observed at $p/p^\circ = 0.02$, after which the rate constant decreases indicating increasing difficulty for desorption. Adsorption and desorption rate constants were similar except at low p/p° . This difference at low pressure may be ascribed to difficulty in desorption from ultramicroporosity.

Conclusions

The kinetics follow a LDF rate law for $> 90\%$ of the sorption process for pressure increments over $p/p^\circ \sim 0-0.97$. Rate of adsorption varies with position on the isotherm and hence the mechanism of the adsorption process. Below $p/p^\circ \sim 0.04$ the rate constant increases with increasing surface coverage. Slowest rates correspond to the high p/p° region of the isotherm and fastest adsorption rates correspond to the region $p/p^\circ \sim 0.04$. Rate constants obtained for the desorption process show a reverse trend to adsorption. The adsorption and desorption isotherms do not exhibit a significant amount of hysteresis. Adsorption

activation energy is at a maximum at low p/p^0 where diffusion into highest energy sites in the microporosity occurs and is, in effect, molecular sieving. The dynamics of methanol vapor adsorption provide an insight into the kinetic requirements of an activated carbon filter for the removal of VOCs from the atmosphere at very low concentrations.

References

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Acknowledgments

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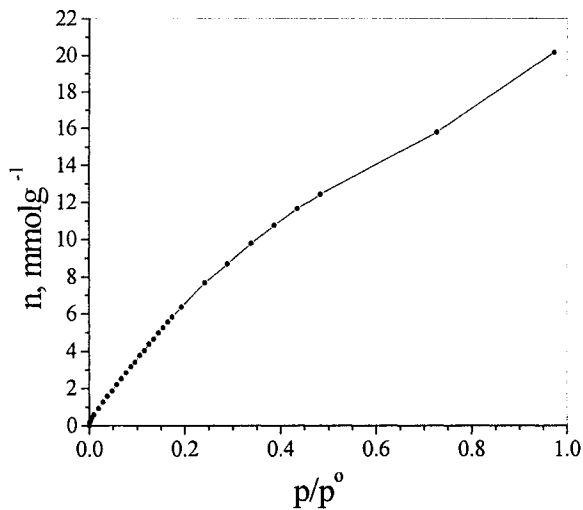


Figure 1. Adsorption isotherm for methanol on BAX950, at 293 K.

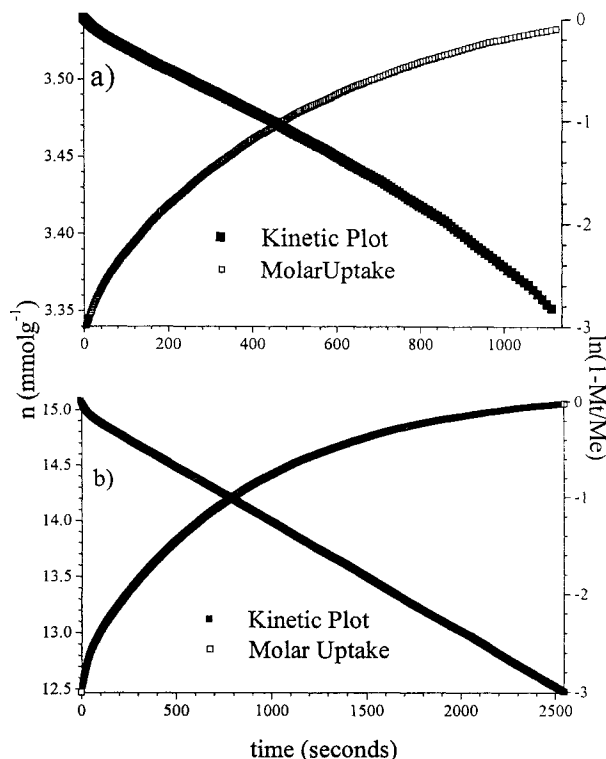


Figure 2. LDF fit for methanol adsorption on BAX950 at 298 K, $p/p^0 =$ a) 0.0973–0.1070 and b) 0.4864–0.7296

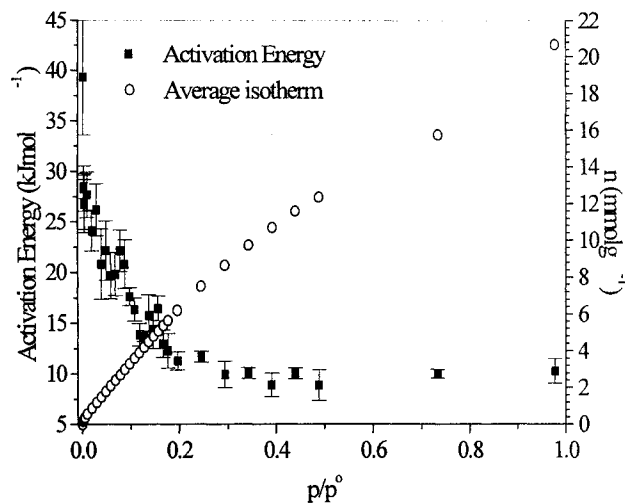


Figure 3. Activation energies for methanol adsorption on BAX950 (288 - 313 K).