

CHROMATOGRAPHIC DETERMINATION OF REGENERATION EFFECTS OF ACTIVE CARBON BY SUPERCRITICAL EXTRACTION WITH CARBON DIOXIDE

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Introduction

Technologies using supercritical fluids have received widespread attention recently. One of their applications is regeneration of active carbons loaded with pesticides [1], phenol [2], ethyl acetate, toluene, benzene [3,4] polyaromatic hydrocarbons and polychlorinated benzenes [5] using CO₂ as supercritical fluid. During the regeneration of adsorbents loaded with ethyl acetate and toluene Tau and Liou observed that the regeneration with supercritical CO₂ was more effective than the steam regeneration method [4]. The advantages of supercritical regeneration were the lower energy consumption and the lesser carbon loss compared with the thermal regeneration process [5].

Effectiveness of the mentioned regeneration was only estimated on the adsorptive capacities of adsorbent bed [3,4]. Hence, we have made an attempt to estimate the regenerability of active carbon (loaded with *tert*-butylbenzene - tBB) and qualify the usefulness of inverse gas chromatography for rapid testing of changes an adsorbent micropore structure before and after regeneration with supercritical CO₂.

Experimental

The commercial active carbon AG-5 prepared from hard coal at Hajnówka's Factory of Dry Wood Distillation, Poland (denoted as V) and samples obtained from it as a result of double ash-discharging (by Korver's method [6], denoted as AD) and oxidizing (with concentrated HNO₃) after double ash-discharging (denoted as O) were used in our research. All carbon samples have the sieve fraction of 0.40 - 1.25 mm.

The changes of micropore structure during the mentioned processes were determined on the ground of nitrogen adsorption isotherm at 77 K.

The active carbon samples characterized in such way were loaded with tBB (0.87g tBB / 5g active carbon).

Supercritical fluid extraction of the samples loaded with tBB was carried out at 323 K under 15 MPa in extraction apparatus with 10 cm³ extraction cell by dynamic method.

The chromatographic investigations were carried out by means of a gas chromatograph UNICAM type 610 with on-line Unicam 4880 Chromatography Data Handling System which was started simultaneously when injecting.

Results and Discussion

The total ash (mineral impurities) quantities in the V, AD and O carbon samples were 21.55, 0.11 and 0.08 %, respectively. The contents of ash components were determined by means of analytical system which contained scanning microscope CamScan S4/80DV and X-ray spectrometer with energy dispersion LINK 10AN/85S.

The Dubinin-Radushkevich (DR) equation characteristic parameters were calculated on the ground of N₂ adsorption isotherm at 77 K, assuming the slit-like model of micropores [7] (see Tab. 1). It is noteworthy that the largest change in micropore structure appeared after double ash-discharging process, and oxidizing after the double ash-discharging caused the decrease of the W₀ and S_{mi} values. It was probably connected with limiting of access to micropores for N₂ molecules by surface functional groups containing oxygen.

Table 1. Parameters of DR equation of active carbon samples: V - virgin, AD - ash-discharged and O - oxidized after ash discharging calculated on the ground of N₂ isotherms at 77 K.

Parameter	Carbon adsorbent		
	V	AD	O
W ₀ [cm ³ /g]	0.43	0.61	0.56
x ₀ [nm]	0.73	0.82	0.82
S _{mi} [m ² /g]	590	730	680
x ₀ E ₀ [nmkJmol ⁻¹]	12.69	12.80	12.80

For the description of the micropore structure of the tested adsorbents on the ground of chromatographically determined adsorption isotherm of propane at 303 K (see Fig.1), the slit-like model of micropores was also assumed.

The C₃H₈ adsorption isotherms described the tested adsorption systems to 2.5·10⁻⁴ relative pressure of adsorbate. The characteristic curves for all the tested adsorption are listed in Table 2.

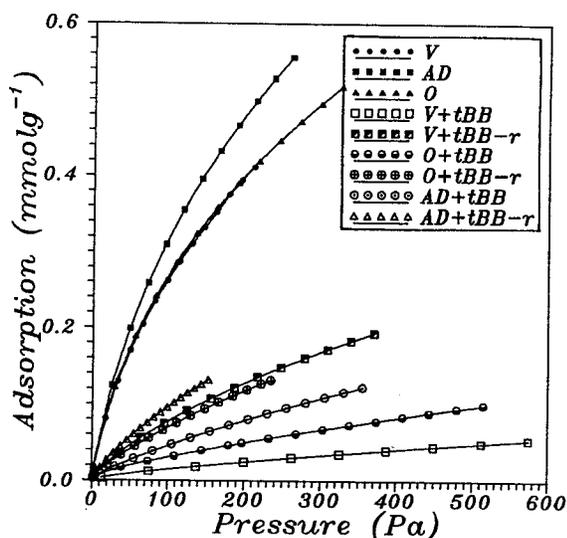


Figure 1. Chromatographically determined adsorption isotherms of propane at 303 K on the tested samples of active carbon before and after modification, loaded with tBB and after regeneration with supercritical CO₂ (denoted as r).

Table 2. Parameters of the tested carbon adsorbents before and after modification, loaded with tBB and after regeneration with supercritical CO₂ calculated from chromatographically determined adsorption isotherms of propane at 303 K.

Carbon adsorbent	Characteristic parameters of pore structure of the tested adsorbents			
	W ₀ [cm ³ /g]	x ₀ [nm]	S _{mi} [m ² /g]	x ₀ E ₀ [nmkJ/mol]
V	0.79	0.58	1370	12.33
V+tBB	0.23	0.74	310	12.65
V+tBB-r	0.61	0.67	900	12.60
AD	1.03	0.58	1775	12.30
AD+tBB	0.22	0.65	340	12.87
AD+tBB-r	0.63	0.66	960	12.56
O	0.72	0.54	1335	12.15
O+tBB	0.31	0.70	440	12.65
O+tBB-r	0.59	0.68	860	12.61

Taking into account the W₀ values for non-loaded and loaded active carbon samples one may say that the samples system were type B according to Rand's classification [8]. The values of the DR equation V and O

were regenerable at approx of 80 %, and for the AD sample of 60 %. The difference between the characteristic energy of adsorption for the propane adsorption on the carbons before and after regeneration process is rather low, but there is a considerable difference for the geometrical surface area S_{mi} of slit-like micropores. The average magnitude of the x₀E₀ product is equal 12.52 nmkJ/mol.

Conclusions

The examination of the results for the systems studied reveals the following:

The isotherms obtained for the systems studied were convex with respect to the pressure axis which indicated that the adsorbate-adsorbent interactions had a dominant influence on the initial progress of propane adsorption.

In spite of fundamental influence of diffusion on the establishing speed of the dynamic adsorption equilibrium in adsorbents beds and using the active carbons samples with developed micropore structure the reproducible adsorption isotherms of propane can be determined.

Susceptibility to supercritical fluid regeneration with CO₂ of carbon adsorbents loaded with *tert*-butylbenzene decreased with the increase of micropore structure participation in the total pore structure. Ash-discharged sample has proved to be the most difficult to regenerate by this method.

Acknowledgments

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References

- DeFilippi, R.P., Krukoni, V.J., Robey, R.J., and Modell, M., *Supercritical Fluid Regeneration of Activated Carbon for Adsorption of Pesticides*, EPA Report, U.S. GPO, Washington, DC, 1980.
- Sutikno, T. and Himmelstein, K.J., *Ind. Eng. Chem. Fundam.*, 1983, 22, 420.
- Tan, C.S. and Liou, D.C., *Ind. Eng. Chem. Res.*, 1988, 27, 988.
- Tan, C.S. and Liou, D.C., *Ind. Eng. Chem. Res.*, 1989, 28, 1222.
- Madras, G., Erkey, C. and Akgerman, A., *Ind. Eng. Chem. Res.*, 1993, 32, 1163.
- Korver, J.A., *Chemisch Weekblad*, 1950, 46, 301.
- Stoeckli, H.F., Kraehenbuehl, F., Ballerini, L. and DeBernardini, S., *Carbon*, 1989, 27, 125.
- Rand, B., *J. Colloid Interface Sci.*, 1976, 56, 337.