

## EVALUATION OF THE PARAMETERS OF THE ADSORPTION ISOTHERM OF HIGHLY TOXIC VAPOR ORGANIC SUBSTANCES ON ACTIVATED CHARCOAL CLOTH

*The adsorption of benzene, as a reference vapor, on activated charcoal cloth (ACC) at 23°C was measured by the chromatographic method. It was found that the Dubinin–Radushkevich (DR) equation represents the relationship between the adsorbed volume and the adsorption potential quite well and that it may be used for calculating the ACC structural constant and adsorption space. Since these two parameters are fundamental for a particular carbon and independent of the vapor adsorbed, it was possible to calculate the adsorption of 3,3-dimethylbutoxy-(2)-methyl-phosphorylfluoride (soman, (GD)) and bis-(2-chlorethyl)-thioether (S-mustard, (HD)).*

Activated charcoal cloth (activation by the gas phase of pyrolysed viscose rayon) has a high affinity (i.e., large adsorption capacity) for vapors of many organic compounds. The most important adsorption properties of activated carbons are based on their microporous structures [1]. The presence of micropores in a carbonaceous adsorbent substantially changes its sorption properties in comparison to a non-porous one. A major advantage of the use of activated charcoal cloth for adsorbing contaminant vapor from moving air streams is its relative non-specificity. A potential disadvantage is that the experimental determination of its efficiency requires measuring of the kinetic adsorption capacity  $W_e$  (g/g), for each combination of activated charcoal cloth and vapor as contaminant. However, the adsorption theory provides an easier means of predicting the performances of such materials for various vapors [2,3]. The results presented in this paper show how existing theory may be used, firstly, to characterize an activated charcoal cloth with benzene as a reference vapor, and then, to predict, from that data, the adsorption capacity of some highly toxic organic vapors.

### THEORETICAL BACKGROUND

The initial work on predicting the equilibrium vapor adsorption performance of an activated carbon, based on the physical properties of the adsorbants, was proposed by Dubinin [4]. In this work the adsorption parameters of carbon were characterized for an arbitrarily chosen reference vapor by using isotherm adsorption data, and then the carbon structural constant  $k$  ( $\text{mol}^2/\text{kJ}^2$ ) and maximum adsorption space  $W_0$  ( $\text{cm}^3/\text{g}$ ) were calculated by Dubinin's equation. Namely, these two parameters are the values which can be used for the characterization of particular carbon materials. They are

independent of the adsorbed vapor, enabling the calculation of the adsorption of other vapors on carbon at any relative pressure by using the Dubinin–Radushkevich (DR) equation [3,4]. The adsorption space  $W_v$  ( $\text{cm}^3/\text{g}$ ) present in carbon to adsorb the vapor of interest can be determined from the DR equation:

$$W_v = W_0 \cdot \exp \left[ -\frac{k}{\beta^2} \left( R \cdot T \cdot \ln \frac{P_0}{P} \right)^2 \right] \quad (1)$$

where

$R = 8.314 \text{ J/mol}\cdot\text{K}$  – is the gas constant;

$T, \text{K}$  – the temperature,

$\beta$  – the affinity coefficient that permits comparison of the adsorption potential of the test adsorbate to a reference adsorbate (for the reference vapor  $\beta=1$ );

$P_0$  – the saturated vapor pressure of the adsorbate at the test temperature;

$P$  – the equilibrium vapor pressure of the adsorbate.

The adsorption space of carbon for a vapor is related to the weight of vapor adsorbed per unit weight of carbon by the relationship:

$$W_v \cdot \rho = W_e \quad (2)$$

This relationship uses the concept of volume pore filling [5] which states that an adsorbed vapor fills the pore into which it is adsorbed as if it is in the liquid phase.

Three different methods can be used to calculate the theoretical affinity coefficients [6]. For non-polar and weakly polar adsorbates, the work of Dubinin and co-workers has shown that the affinity coefficient can be expressed as the ratio of the molar volumes of the test adsorbate,  $V$ , and reference adsorbate,  $V_r$ :

$$\beta = \frac{V}{V_r} \quad (3)$$

where:

$$V = \frac{M}{\rho} \quad (4)$$

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$M$  – is the molar mass of the adsorbate, g/mol,  
 $\rho$  – the density of the adsorbate, g/cm<sup>3</sup>.

More precisely, the affinity coefficient can be calculated from the ratio of the molar parachore of the test adsorbate,  $\Omega$  and of some reference adsorbate,  $\Omega_r$ :

$$\beta = \frac{\Omega}{\Omega_r} \quad (5)$$

where

$$\Omega = \frac{M \cdot \gamma^4}{\rho} \quad (6)$$

$\gamma$  – is the surface tension of the adsorbate, g/s<sup>2</sup>.

For polar adsorbates, Reucroft et al. suggested that the ratio of the electronic polarizations of the test adsorbate,  $P_e$  and reference adsorbate,  $(P_e)_r$ , could be used to calculate the affinity coefficient:

$$\beta = \frac{P_e}{(P_e)_r} \quad (7)$$

where

$$P_e = \frac{(n^2 - 1) \cdot M}{(n^2 + 2) \cdot \rho} \quad (8)$$

$n$  – is the refractive index of the liquid at the sodium D wavelength.

Jonas and Rehrman were applied predicted techniques of measuring equilibrium vapor adsorption under dynamic (or kinetic) conditions [7]. They showed that a well-packed bed of activated carbon granules exhibited an adsorption capacity very close to its equilibrium adsorption value, which was also confirmed by the results of some other published experimental investigations [8].

The kinetic adsorption capacity,  $W_e$  of some vapor, at a certain vapor concentration and flow rate can be calculated from the straight line relationship of the breakthrough time vs. the carbon bed mass, according to the modified Wheeler equation [9]:

$$t_b = \frac{W_e}{C_0 \cdot Q} \cdot \left( W + \frac{\rho_B Q}{k_v} \cdot \ln \frac{p}{1-p} \right) \quad (9)$$

where:

$t_b$  – is the breakthrough time, min;

$W_e$  – kinetic adsorption capacity, g/g;

$p = C/C_0$ ,

$C$  – the contaminant concentration in the adsorbent bed, mg/dm<sup>3</sup>;

$C_0$  – contaminant concentration at the inlet, mg/dm<sup>3</sup>;

$W$  – the mass of carbon adsorbent, g;

$\rho_B$  – the packed bed density, g/cm<sup>3</sup>;

$k_v$  – the pseudo-first-order rate constant, min<sup>-1</sup>; and

$Q$  – the volumetric flow rate, dm<sup>3</sup>/min.

The equilibrium solid-phase concentration  $W_{eq}$  can be calculated from the mass-balance equation [10] when the time-dependent transmission  $C/C_0$  is experimentally measured:

$$W_{eq} \cdot L \cdot \frac{1-\varepsilon}{\varepsilon} + C_0 \cdot L = u \cdot C_0 \cdot \int_0^\infty \left( 1 - \frac{C}{C_0} \right) \cdot dt \quad (10)$$

where:

$\varepsilon$  – the carbon bed void fraction;

$L$  – the length of the bed, dm,

$U$  – the superficial gas (vapor) velocity, dm/s, and

$C$  – the vapor concentration leaving the adsorbent bed, mg/dm<sup>3</sup>.

## MATERIALS

The vapors used as adsorbates in these investigations were: benzene as the reference vapor, p.a. grade, from E. Merck, Germany, 3,3-dimethyl-butoxy-(2)-methyl-phosphorylfluorid (GD, > 90%) and bis-(2-chlorethyl)-thioether (HD, > 96%) synthesised in our laboratory. The pertinent physical properties of these compounds and calculated values of the affinity coefficients are shown in Table 1.

Table 1. Physical properties of the used adsorbates [11–13]

	Benzene	GD	HD
Mol. wt, g/mol	78.1	182.2	159.1
Density, $\rho_{23^\circ\text{C}}$ , g/cm <sup>3</sup>	0.8761	1.026	1.274
Max. vapor conc, $C_{s,23^\circ\text{C}}$ , mg/dm <sup>3</sup>	364.8	3.376	0.776
Index of refraction, $n_{D,25^\circ\text{C}}$	1.4958	1.4080	1.5313
Surface tension, $\nu_{20^\circ\text{C}}$ , g/s <sup>2</sup>	29.02	26.03	41.25
Affinity coefficient, $\beta$			
Eqns. (3 and 4)	1	1,990	1,398
Eqns. (5 and 6)	1	1,936	1,535
Eqns. (7 and 8)	1	1,678	1,481

The activated charcoal cloth (ACC) adsorbent used for testing was CNF 1500–50 grade manufactured by Tyobo Co., Ltd., Osaka, Japan with a specific surface area of 1350 g/m<sup>2</sup> (determined by the BET method).

## ADSORPTION APPARATUS

The adsorption apparatus is shown in Figure 1.

The apparatus consists of three functionally discrete sections: the first is for specific vapor generation; the second, for measuring vapor adsorption by the charcoal cloth bed; and the third is for vapor detection in the outlet gas phase from the charcoal cloth bed.

The organic vapors were generated using Dynacalibrator™ instrument, Model 340–50–XTC from VICI Metronics 2991 CA, USA., by applying the controlled flow of dry nitrogen (99.9999 %) over a commercial capillary diffusion tube "D" (DT) (capillary bore diameter  $d=5$  mm and diffusion path  $L=2.2$  cm). The temperature chamber of the Dynacalibrator has a proportional temperature controller with  $\pm 0.5^\circ\text{C}$  set

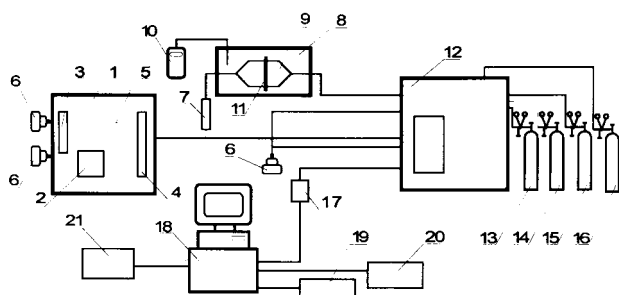


Figure 1. Vapor generation/activated charcoal cloth (ACC) adsorption system: 1 - Dynacalibrator; 2 - Chamber for thermostating the diffusion tube; 3, 4 and 7 - Flowmeters; 5 - Switch for changing the vapor flow from one to another; 6 - Canister; 8 - Chamber for thermostating the sample holder; 9 - Sample holder; 10 - Thermometer; 11 - Sample; 12 - GC; 13-16 - Air, hydrogen and nitrogen cylinders for GC; 17 - Interface; 18 - Computer; 19 - Keyboard; 20 - Printer; 21 - Plotter.

point accuracy and permits the selection of temperature from any of the four possible calibrated ranges: 25 to 50°C, 45 to 70°C, 65 to 90°C and 85 to 110°C. Dry nitrogen (> 99,9999 %) from an external source was used as the carrier gas. The vapor, prepared in the generation sections was divided into two streams; one passed through an adsorbent bed and went into the detector of the GC, while the other flowed directly to the detector of the GC for measurement of the inlet vapor concentrations.

The adsorption section of the apparatus consists of an ACC bed in a stainless steel holder thermostated in an air chamber with a heatband (Tems 2; 1,1 m in length; power of 44 W; from Heraeus, Germany).

The apparatus was constructed primarily with stainless steel tubing (small sections contained copper tubing). A liquid leak detector was used to test for leakage in the apparatus. All the valves were made of stainless steel. The flow rate was regulated by fine metering valves.

The gas chromatograph (GC) Hewlett-Packard, HP 5890A with a FID detector was used in the detection

section of the apparatus, enabling measurement of the inlet and outlet vapor concentrations. The GC was equipped with a stainless steel column (SE 30). The measured concentrations were recorded on a HP Thin Jet Terminal.

## PROCEDURE

The ACC was dried in an oven at 120°C and stored in a desiccator before use. The adsorbent beds were prepared by putting from one to five weighted layers of ACC in a cylindrical sample holder, with an inside cross-sectional area of 10 cm<sup>2</sup>, and then exposed to the prepared vapor concentration of some desired volumetric flow rate at 23°C. The bulk density of the packing of the adsorbent was 0.15 g/cm<sup>3</sup>. Vapor samples were injected into the GC column every 7-8 min for benzene (retention time; r.t.=0.9 min) and 37 min for GD (r.t.=1.35 min) and HD (r.t.=1.175 min), using a heated gas sampling valve (GSV) with ten port configurations and two loops (0.5 cm<sup>3</sup>). The GSV, therefore, enables the sampling of inlet vapor and vapor passed through the charcoal bed. The ratio of the concentrations at the outlet and inlet of the bed was monitored as a function of time. The breakthrough time,  $t_b$ , was measured in minutes when the vapor concentrations at the outlet stream from the bed reached 1% of the inlet concentration ( $C_b/C_o = 0,01$ ).

## RESULTS AND DISCUSSION

The experimental values of the vapor breakthrough time  $t_b = t_{1\%}$  as a function of the activated charcoal cloth (ACC) bed mass,  $W$  (0.065 to 0.200 g), for benzene as a reference vapor with concentrations ranging from 1.7 to 33 mg/dm<sup>3</sup> and flowrates of vapor from 0.028 to 0.15 dm<sup>3</sup>/min (corresponding to gas superficial velocities from 2.8 to 15 cm/min) were obtained and subjected to linear regression analysis, in accordance to Wheeler's equation (9). The results of these analyses are shown in Table 2 together with the correlation coefficients which are higher from 0.984, indicating a high degree of confidence of the derived relationship  $t_{1\%} = f(W)$

Table 2. Regression equations of benzene 1% breakthrough times for ACC and adsorption parameters derived from the experimental time-weight curves

$C_0$		$P_r^*$	$Q$ dm <sup>3</sup> /min	$t_{1\%} = \frac{W_e}{C_0 \cdot Q} \cdot \left( W + \frac{p_B \cdot Q}{k_v} \cdot \ln \frac{p}{1-p} \right)$	$r$	$W_e$ g <sub>6H6</sub> /g <sub>ACC</sub>
mg/dm <sup>3</sup>	$\sigma, \%$					
30.32	2,8	0.0831	0.100	$t_{\%} = 142.65 \cdot W - 4.29$	0.999	0.433
33.81	0,9	0.0927	0.035	$t_{\%} = 389.10 \cdot W - 12.24$	1.000	0.460
6.22	1,1	0.0170	0.100	$t_{\%} = 503.28 \cdot W - 16.75$	0.999	0.313
1.71	1,4	0.0047	0.100	$t_{\%} = 1082.81 \cdot W - 38.84$	0.999	0.185
14.24	2,5	0.0390	0.150	$t_{\%} = 180.37 \cdot W - 6.05$	0.984	0.385
14.37	1,1	0.0394	0.050	$t_{\%} = 468.13 \cdot W - 13.42$	0.990	0.336
14.24	2.5	0.0390	0.028	$t_{\%} = 925.93 \cdot W - 29.81$	1.000	0.374

$$*P_r = \frac{P_0}{P_r} \cong \frac{C_0}{C_s}; C_{s,25^\circ\text{C}} = 364.8 \text{ mg/dm}^3$$

The  $W_e$  values may be calculated from the slopes of the regression equations (Table 2), knowing the values of  $C_0$  and  $Q$  and the relationship  $W_e/C_0 \propto Q$ , which are also given in Table 2.

Assuming that the kinetic adsorption capacity closely approximates the equilibrium capacity value at the same relative pressure and temperature, in accordance to the DR equation (1), the experimental values of  $W_e$  as a function of  $A = R \cdot T \cdot \ln(1/P_r)$ , (from Table 2) were calculated by equation (11):

$$\ln W_r = 1,9555 - 6,18 \cdot 10^{-3} \cdot \left( R \cdot T \cdot \ln \frac{1}{P_r} \right)^2 \quad (r=0,985) \quad (11)$$

The characteristic properties of ACC, derived from equation (11), were the maximum adsorption space  $W_0 = 0,629 \text{ cm}^3/\text{g}$  (obtained from the y-axis intercept), and the structural constant  $k = 6.18 \cdot 10^{-3} \text{ [kJ/mol]}^{-2}$  (obtained from the slope).

The parameters of the adsorption isotherms of highly toxic organic vapors, GD and HD on ACC, were determined by evaluating the values of the maximum adsorption capacity ( $p_i \cdot W_0$ ) in  $\text{g}/\text{cm}^3$ , where  $i = \text{GD, HD}$ , and the affinity coefficient  $\beta_i$ , by means of equations (3–8) (the data from Table 1 are shown in Table 3). The calculation was done by using the parameters of the DR adsorption isotherm of benzene as the reference vapor.

The corresponding DR adsorption isotherms of GD and HD vapors were experimentally determined from the breakthrough curves of these vapors. The relationship between  $W_{eq}$  and  $C$  was determined first from the experimentally obtained breakthrough curves by applying the mass-balance equation (10), and then the DR adsorption isotherm equation (1) was analyzed.

The experimental breakthrough curves for GD vapor through the layers of ACC bed with a mass,  $W$ , from 0.064 to 0.130 g, at  $23 \pm 1^\circ\text{C}$ , were determined at the concentration  $C_0 = 0.561 \text{ mg}/\text{dm}^3$  ( $\sigma = 1.7\%$ ;  $P_r = 0.166$ ), and for volumetric flowrates of vapor from 0.05 to  $0.10 \text{ dm}^3/\text{min}$  (corresponding to superficial velocities of 5 to  $10 \text{ cm}/\text{min}$ ). The obtained DR adsorption isotherm for GD on ACC is shown in Figure 2 and the regression line was fitted by equation (12).

$$\ln W_{eq, \text{GD}} = 1.983 - 2.801 \cdot 10^{-3} \cdot A^2 \quad (r = 0.927) \quad (12)$$

The maximum adsorption capacity ( $W_{0eq, \text{GD}, \text{exp}} = 3.315 \text{ mmol}_{\text{GD}}/\text{g}_{\text{ACC}} = 0.604 \text{ g}_{\text{GD}}/\text{g}_{\text{ACC}}$ ) was determined from the intercept (equation 12) which is 5.9% lower than the evaluated value ( $3.522 \text{ mmol}_{\text{GD}}/\text{g}_{\text{ACC}}$ ; Table 3).

The experimental value of the affinity coefficient of GD vapor was calculated from the square root of the ratio of the slopes of the experimentally determined DR adsorption isotherms of benzene and GD. Namely, such calculation enable determination of the dependence of the slope of the DR adsorption isotherm on the coefficient affinity, and  $\beta = 1$  for benzene as a reference vapor. Obtained  $\beta_{\text{GD}, \text{exp}} = 1.4854$  was compared with calculated values (Table 1). It was found

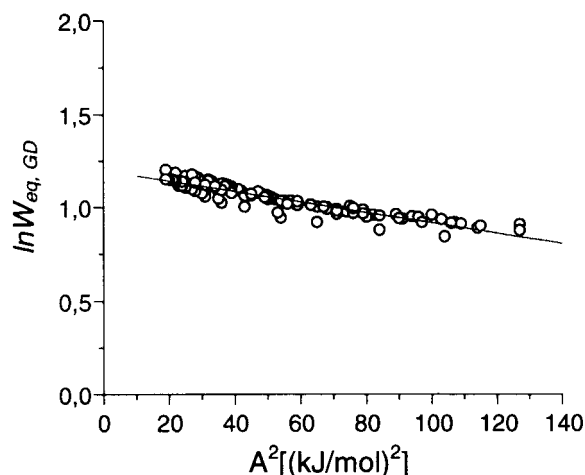


Figure 2. DR adsorption isotherms of GD on ACC

that the experimentally determined value is only 11.5% lower than that calculated from the ratio of the electronic polarization of GD and benzene as a reference vapor ( $\beta_{\text{GD}, \text{EP}} = 1.678$ ).

The experimental breakthrough curves of HD vapor through a layer of ACC bed at  $23 \pm 2^\circ\text{C}$  were determined at the concentration  $C_0 = 0.188 \text{ mg}/\text{dm}^3$  ( $P_r = 0.242$ ) and flow rates 0.10 and  $0.15 \text{ dm}^3/\text{min}$  (corresponding to the superficial velocities 10 and  $15 \text{ cm}/\text{min}$ ). The obtained DR adsorption isotherms of HD on ACC are shown in Figure 3 and the data fitted by equation (13).

$$\ln W_{eq, \text{HD}} = 1.6092 - 3.340 \cdot 10^{-3} \cdot A^2 \quad (r=0.970) \quad (13)$$

The maximum adsorption capacity  $W_{0eq, \text{HD}, \text{exp}} = 4.999 \text{ mmol}_{\text{HD}}/\text{g}_{\text{ACC}} = 0.795 \text{ g}_{\text{HD}}/\text{g}_{\text{ACC}}$  was determined from the intercept (equation 13), which is only 0.8% lower than the evaluated value ( $5.040 \text{ mmol}_{\text{HD}}/\text{g}_{\text{ACC}}$ ; Table 3).

Table 3. Evaluated parameters of the DR adsorption isotherms for GD and HD on ACC

i	$W_{0i} = W_0 \cdot p_i$		$k_{0i} = k_0/\beta_i^2, (\text{kJ}/\text{mol})^{-2}$		
	$\text{g}/\text{g}_{\text{ACC}}$	$\text{mmol}/\text{g}_{\text{ACC}}$	$\beta_{i, \text{MZ}}^*$	$\beta_{i, \text{MP}}^*$	$\beta_{i, \text{EP}}^*$
GD	0.645	3.522	$1.561 \cdot 10^{-3}$	$1.648 \cdot 10^{-3}$	$2.194 \cdot 10^{-3}$
HD	0.801	5.040	$3.162 \cdot 10^{-3}$	$2.623 \cdot 10^{-3}$	$2.818 \cdot 10^{-3}$

\*Table 1

The experimental value of the affinity coefficient of HD vapor was calculated using the same procedure described above for GD vapor. The obtained value of  $\beta_{\text{HD}, \text{exp}} = 1.3603$  was compared with the calculated one (Table 1) indicating that the best agreement (differences less than 2.7%) is obtained for the calculation based on the ratio of molar volumes of HD and benzene as a reference vapor ( $\beta_{\text{HD}, \text{MV}} = 1.398$ ).

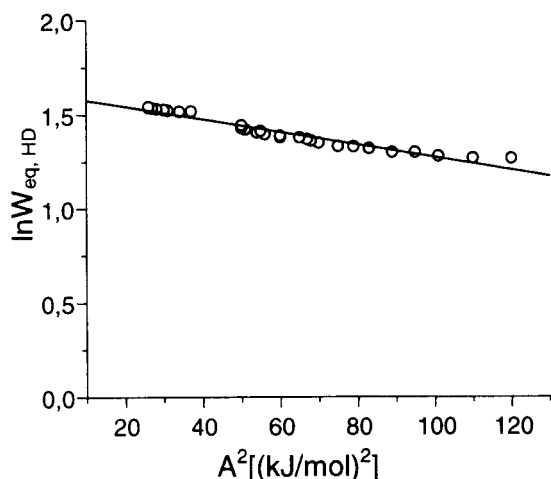


Figure 3. DR adsorption isotherms of HD on ACC

## CONCLUSIONS

Determination of the adsorption characteristics of an activated charcoal cloth (CNF 1500-50 grade; made by Tyobo Co., Japan) was performed under dynamic conditions and by using benzene as a reference vapor. These data enabled determination of the parameters of the DR adsorption isotherms of soman (GD) and S-mustard (HD). The maximal adsorption capacity was calculated and experimentally determined from the corresponding isotherms for these substances; obtained data showed that 5.9% difference exists in the case of GD and only 0.8% for HD. The best fitting of isotherm slope could be predicted if  $\beta$ , the affinity coefficient is determined by the method based on the ratio of electronic polarization for GD and a reference vapor (benzene), and by the method of the ratio of molar volume for HD and a reference vapor (benzene).

## SUMMARY

PROCENA PARAMETARA ADSORPCIONIH IZOTERMI VISOKOTOKSIČNIH ORGANSKIH PARA NA UGLJENIČNOM ADSORBENTU KORIŠĆENJEM BENZENA KAO REFERENTNE SUPSTANCE

(Naučni rad)

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Poznato je da aktivni ugljevi pokazuju veliki afinitet za adsorpciju para mnogih organskih jedinjenja kao i relativnu nespecificnost pri adsorbovanju para kontaminanta iz pokretne struje u dinamičkim uslovima. Jedna od osnovnih karakteristika koju je potrebno eksperimentalno odrediti za svaku kombinaciju aktivni ugaj (adsorbent)-adsorbat je kinetički adsorpcioni kapacitet  $W_e$  (g/g), što je kod korišćenja visokotoksičnih i teško isparljivih organskih para povezano sa znatnim eksperimentalnim teškoćama.

U ovom radu je adsorpcioni kapacitet aktivnog uglja određen primenom Dubinin-Radushkevich (D-R) jednačine, a na osnovu podataka o ravnotežnoj adsorpciji referentne pare, što omogućava da se odredi maksimalna adsorpciona zapremina  $W_0$  (cm<sup>3</sup>/g) i strukturna konstanta  $k$  (kJ/mol)<sup>-2</sup>, koja je u vezi sa karakterističnom energijom adsorpcije  $E$  ( $k = E^{-2}$ ).

## REFERENCES

- [1] H. Juntgen, New Application for Carbonaceous Adsorbents. *Carbon*. **15** (1977) 273-283.
- [2] E. B. Sansone, L. A. Jonas, Prediction of Activated Carbon Performance for Carcinogenic Vapor. *Am. Ind. Hyg. Assoc. J.* **42** (1984) 688-691.
- [3] P. I. Reucroft, W. I. Simpson, L. A. Jonas, Sorption Properties of Activated Carbon. *J. Phys. Chem.* **75** (1971) 3526-3531.
- [4] M. M. Dubinin, Physical Adsorption of Gases and Vapors in Micropores. *Prog. Surf. Membr. Sci.* **9** (1975) 1-70.
- [5] B. P. Bering, M. M. Dubinin, V. V. Serpinsky, Theory of Volume Filling for Vapor Adsorption. *J. Colloid Interface Sci.* **21** (1966) 378-393.
- [6] K. E. Noll, D. Wang, T. Shen, Comparison of Three Methods to Predict Adsorption Isotherms for Organic Vapors from Similar Polarity and Nonsimilar Polarity Reference Vapors. *Carbon*. **27** (2) (1989) 239-245
- [7] L. A. Jonas, J. A. Rehrmann, Predictive Equations in Gas Adsorption Kinetics. *Carbon*. **11** (1973) 59-64.
- [8] J. I. Bastić, D. U. Skala, Parameter Prediction of Adsorption Isotherms of Highly Toxic Vapor Organic Substances Using Carbon Adsorbent and Benzene as a Reference Compound, II Symposium on Chemistry and the Environment, Vrnjacka Banja, Serbia, June 1993.
- [9] Y.H. Yoon, J. H. Nelson, Application of Gas Adsorption Kinetics I. A Theoretical Model for Respirator Cartridge Service Life. *Am. Ind. Hyg. Assoc. J.* **45** (8) (1984) 509-516.
- [10] J. C. Huang, R. Madey, Application of Potential Theory to Adsorption of Binary Mixtures on Activated Carbon. **20** (2) (1982) 118-120.
- [11] Kratkaja hemiceskaja enciklopedija, 1 (A-E), GNI, Sovjetskaja Enciklopedija, Moskva (1961).
- [12] J. H. Perry, Chemical Engineers Handbook, 5 ed., Mc Graw-Hill, New York (1973).
- [13] A. Vankovsky, T. M. Horidi, V. Dolezal: Theoreticky razbor rychlosti odmoredni nekterych bol proudeni horkych vyfurovych plynu. Proceedings VAAZ, paper B, 1 (1979) 92-98.

Ključne reči: Adsorpcija • Adsorpciona izoterma • Aktivni ugaj • Toksične pare •  
Key words: Adsorption • Adsorption isotherm • Activated charcoal • Toxic vapor •

S obzirom da su parametri D–R jednačine,  $W_0$  i  $k$ , karakteristični za odgovarajući adsorbent i ne zavise od adsorbovane pare, to je primenom ove jednačine moguće proceniti i adsorpciju drugih para organskih jedinjenja na istom adsorbentu, pri bilo kom relativnom pritisku, ukoliko se uspešno proceni koeficijent afiniteta koji je karakteristika prirode adsorpcione interakcije.

Za izračunavanje koeficijenta afiniteta ( $\beta$ ) koriste se različite metode koje se zasnivaju na odgovarajućim odnosima 1) molskih zapremina; 2) molarnih parahora i 3) elektronskih polarizacija, adsorbata od interesa i referentnog adsorbata. Ukoliko referentna supstanca ima približno istu polarnost kao adsorbat koji se ispituje ne bi trebalo da postoji razlika u pogledu primenjene metode za procenu koeficijenta afiniteta.

Moguće je primeniti D–R jednačinu pri analizi adsorpcije para organskih jedinjenja pod dinamičkim uslovima protoka ili pri tzv. kinetičkim uslovima. Kinetički adsorpcioni kapacitet adsorbenta ( $W_e$ ) pri određenoj koncentraciji referentne pare  $C_0$  ( $\text{mg}/\text{dm}^3$ ), moguće je izračunati iz Wheeler–ove jednačine, na osnovu nagiba linearne zavisnosti između vremena pri kome dolazi do određenog probijanja para adsorbata ( $t_b$ , min) i mase adsorpcionog sloja  $W_t$  (g). U ovom radu su ispitivanja izvedena sa sorpcionom ugljeničnom tkaninom (SUT), japanske proizvodnje (Tyobo) i benzena kao referentne supstance (p.a., MERCK). Od visokotoksičnih organskih para odabrani su bis–(2–hloretil)–tioetar (iperit, HD) kao predstavnik plikavaca i 3,3–dimetilbutoksi–(2)–metil–fosforilfluorid (soman, GD), kao predstavnik nervnih visokotoksičnih organofosforinih jedinjenja.

Određivanje krive proboja, tj. zavisnosti redukovane koncentracije  $C/C_0$  od vremena  $t$ , odnosno definisanje karakterističnog vremena pri kome dolazi do 1% probijanja ( $t_b = t_{1\%}$ ) izvedeno je sa aparaturom koja je sastavljena od tri funkcionalna dela, potrebnih za: 1) generaciju para adsorbata; 2) ekspoziciju adsorbenta parama određene koncentracije adsorbata pri definisanom protoku nosećeg gasa, i 3) detekciju sadržaja organskog jedinjenja u izlaznoj i ulaznoj struji nosećeg gasa (GC analiza) u funkciji vremena. Kao noseći gas u svim ispitivanjima korišćen je suv azot.

U skladu sa D–R jednačinom, sa benzenom kao referentnim adsorbatom određena je maksimalna raspoloživa adsorpciona zapremina ( $W_0 = 0.629 \text{ cm}^3/\text{g SUT}$ ) i energija adsorpcije  $E = 12.72 \text{ kJ/mol}$ . Odgovarajuće vrednosti maksimalno raspoloživog adsorpcionog kapaciteta u odnosu na soman (GD), odnosno iperit (HD) izračunate su iz odgovarajućih kriva proboja ovih para i iznose  $3.315 \text{ mmol/g}$  za soman, odnosno  $4.999 \text{ mmol/g}$  za iperit, a vrednost specifične strukturne konstante adsorbenta ( $k$ ) u slučaju somana iznosi  $k = 2.801 \times 10^{-3} (\text{mol}/\text{kJ})^2$  odnosno iperita  $k = 3.340 \times 10^{-3} (\text{mol}/\text{kJ})^2$ .

Eksperimentalni podaci su poslužili kao osnova za verifikaciju mogućnosti da se proceni nagib D–R adsorpcione izoterme GD i HD, na osnovu podataka za  $k$  – kontantu referentne supstance (benzen) uz izračunavanje koeficijenta afiniteta ( $\beta$ ) na osnovu fizičkih karakteristika adsorbata, s obzirom da je  $k_i = k_r/\beta_i^2$  (gde je  $i = \text{HD, GD}$ ;  $r = \text{benzen}$ ). Utvrđeno je da  $\beta_i$  zavisi od primenjene metode za izračunavanje i da se adsorpciona izoterma najbolje može proceniti na osnovu odnosa elektronskih polarizacija (kod somana), odnosno na osnovu odnosa molskih zapremina (iperit). Optimalna procenjena vrednost adsorpcionog kapaciteta SUT–a za soman je  $3.522 \text{ mmolGD/g}$ , što je 6.4% više od eksperimentalno određene ( $3.315$ ), a za iperit  $5.040 \text{ mmol HD/g}$ , što je 0.8% više od eksperimentalno utvrđene vrednosti ( $4.999$ ).

