ADSORPTION OF BENZENE AND PYRIDINE VAPORS BY VARIOUS CARBON ADSORBENTS

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Abstract: For the first time with the help of express-method we compare adsorption of benzene and pyridine vapors by carbon adsorbents (CA) that differ in raw materials, methods of production and textural characteristics. With the BET and Aranovich (AR) equations we define the interval of relative pressure, in which the adsorption of studied components is described by suggested models of polymolecular adsorption, and calculated general characteristics of adsorption. A comparative analysis of these equations shows that adsorption isotherms of benzene vapors should be described with the Aranocich model and pyridine vapors with the BET model. It is stated that the adsorption of both benzene and pyridine is characterized by the low energy constant C that means weak adsorption localization on a carbon surface and difficulty with exact determination of monolayer capacity. We stated that with benzene adsorption by CA and pyridine adsorption by lignite sorbent the area taken by adsorbate molecule exceeds molecule's own size. Such action is typical for realized specific sorbent-sorbate interaction which is expected by molecular structure of adsorbates and surface state of adsorbents and is proved by the amount of calculated adsorption heat. It is stated that pyridine molecules when adsorbed are oriented in parallel to the adsorbent surface and for benzene molecules such reaction exists only for granular carbon adsorbents. Random orientation of benzene molecules when adsorbed by granular CA can be connected with overall attraction-repulsion effect of π-electron system of benzene and polar groups on the adsorbent surface. We define the exponent of the Dubinin-Astakhov equation using the theory of volume filling of micropores (TVFM), calculate the limiting adsorption volume and size of pores occupied by components. We state that both benzene and pyridine adsorption proceeds similarly in available at size micro- and mesopores of adsorbents. Differences in adsorption behavior of benzene and pyridine with a filled monolayer are probably connected with peculiarities of molecule structure of pyridine which has an additional potential center of adsorption that is an unshared electron pair of nitrogen.

Keywords: vapor adsorption, carbon adsorbents, pyridine, benzene

INTRODUCTION

Isotherms of adsorption-desorption of vapors and gases allow to estimate characteristics of adsorbent structure. To define monolayer specific surface and capacity we traditionally use the BET polymolecular adsorption theory that describes the process of sorbent-sorbate interaction with the help of the following equation [1]:

$$a = a_m \frac{C \cdot X}{(1-X) \cdot \left[1 + (C-1) \cdot X\right]},$$

where is an equilibrium vapor adsorption; a_m is a capacity of a filled monolayer; X is a relative pressure (P/P_0); C is a constant of an adsorbent-adsorbate interaction. But there are some restrictions to this equation, among them are narrow relative pressure range ($0.05 < P/P_0 < 0.35$) of linear dependence observance, absence of surface heterogeneity and specific sorbent-sorbate interaction [1, 2].

Some drawbacks of the BET theory were taken into account in the Aranovich model [2, 3] whose equation

(thermodynamically more correct) allows to describe isotherms within the range of relative pressures up to 0.7–0.8 [2, 3]:

$$a = a_m \frac{C \cdot X}{(1-X)^{0.5} \cdot (1 + C \cdot X)}.$$

These equations were derived for the case of gase adsorption on nonporous adsorbents that is why if an adsorbent has a big number of micropores then calculated values of the total surface area can greatly differ from the real value [2] that is why this parameter can be estimated only conditionally.

For studies on characteristics of porous structure of adsorbents most frequently as an adsorbate nitrogen is used for which we can clearly differentiate processes of monolayer filling and the following polymolecular layer formation [2]. But in the case of the following sorbent usage for adsorption of aromatic organic compounds it is better to use benzene as a test adsorbate because its conditions of adsorption and molecule size are close to practical problems [4].

To estimate porosity we use the Dubinin-Radushkevich equation (the model of TVFM) or its modified versions (the Dubinin-Astakhov equation, the Dubinin-Stoekli equation and others) [3, 5]:

$$a = \frac{W_0}{V_M} \exp\left[-\left(\frac{RT}{\beta E} \ln \frac{1}{X}\right)^2\right],$$

where X is a relative pressure; V_M is a molar volume, cm^3/mole; W_0 is a limiting volume of adsorption space, cm^3/g; E is characteristic energy of adsorption, J/mole; β is an affinity coefficient.

The aim of this research is to study adsorption of benzene and pyridine vapors by carbon materials that differ in raw material, method of production and characteristics of porous structure, to choose an equation of polymolecular adsorption describing adsorption equilibrium, to calculate general parameters of adsorption of organic compounds with the usage of polymolecular adsorption models and the theory of volume filling of micropores.

MATERIALS AND METHODS

Used benzene and pyridine were purified according to the method in [6].

Activated charcoal of brands AG-OV-1 and AG-5 (OJSC "Sorbent", Perm) and activated semi-coke of brands Purolat-Standart (LLC "Ters", Shakhty) and ABG (CJSC "Carbonika F", Krasnoyarsk) were used as adsorbents. Basic characteristics of adsorbents are given in Table 1.

$$Y_{DA} = \ln a = \ln\left(W_0/V_M\right) - D\left[\ln\left(1/X\right)\right]^n, \quad (3)$$

where $D = (RT/\beta E)^n$.

Adsorption heat of the first adsorbate layer (ΔQ) was calculated by the formula (4) for the BET model and (5) for the Aranovich model:

$$\Delta Q = RT \ln C, \quad (4)$$

$$\Delta Q = RT \ln\left(C \rho_l/\rho_v + 1\right), \quad (5)$$

where ρ_l and ρ_v are densities of liquid adsorbate and its saturated vapor accordingly, g/cm^3.

Average area occupied by adsorbate molecule in a filled monolayer (ω_m, nm^2) was calculated by

$$\omega_m = \frac{S_{BET}}{a_m N_A},$$

where S_{BET} is a surface area of activated charcoal, m^2/g; a_m is an adsorption capacity of a saturated monolayer, mole/g, N_A is Avogadro's number.

Half-width of slit-shaped micropores (χ, nm) occupied by a component was calculated with the usage of dependence [2]:

$$\chi = \frac{12 \cdot 10^3 \cdot \beta}{E}.$$

RESULTS AND DISCUSSION

Obtained adsorption isotherms of benzene and pyridine on granular CA (Fig. 1) refer to the first I type (it is peculiar to microporous adsorbents) according to

Table 1. Characteristics of carbon adsorbents [7]

Brand of AC		AG-OV-1	AG-5	Purolat-Standart	ABG
raw material		coal	coal	anthracite	lignite
carbonization /activation		two-step	two-step	one-step	one-step
granulation		granular	granular	crushed	crushed
S_{BET}, m^2/g		682	925	311	412
V_{micro}, cm^3/g		0.218	0.465	0.07	0.02
V_{meso}, cm^3/g		0.241	0.135	–	0.24
$n_{surface\ group}$, mmol-eq/g	acid	0.32	0.36	0.24	0.19
	basic	0.48	0.47	0.12	0.92

Carbon adsorbents were preliminarily heated at a temperature 110 ± 5°C to remove all gases and water vapors absorbed at shelf time.

Adsorption of benzene and pyridine vapors was conducted by express-method [8] at 25 ± 1°C, exposure time was 24 hours, error of relative pressure determination was not higher than 2% and error of adsorption amount was not higher than 6–9%.

Basic parameters of the adsorption of organic substances were calculated with the use of linearized BET (1), Aranovich (2) and Dubinin-Astakhov (3) equations:

$$Y_{BET} = \frac{X}{a(1-X)} = \frac{1}{a_m C} + \frac{C-1}{a_m C} X, \quad (1)$$

$$Y_{AP} = \frac{X}{a(1-X)^{0.5}} = \frac{1}{a_m C} + \frac{X}{a_m C}, \quad (2)$$

the Brunauer classification [1], the form of adsorption isotherms of pyridine by broken CA refers to the II type (mainly macroporous adsorbents).

Linearized forms of adsorption isotherms of the studied adsorbates on adsorbents AG-5 and ABG obtained with the usage of Eq. (1) and (2), correlation coefficients (R^2), and linear dependence region are on Fig. 2.

Calculations showed (Fig. 1, Table 2) that relative pressure region, in which with high correlation degree experimental data are described by polymolecular adsorption models, is rather narrow and in this case benzene adsorption is better described by the Aranovich model and pyridine adsorption by the BET model (Fig. 1). Expected expansion of P/P_0, in which experimental data are described, in case of passing from the BET to the Aranovich model does not occur: for pyridine they almost coincide or become narrower, for benzene a considerable increase (up to $P/P_0 \approx 0.62$) is observed only for Pulorat-Standart (Table 2). Similar

behavior was observed in the case of adsorption of water vapors on soot with high oxygen surface compounds [9] and was explained by water clusters formation.

Low values of the coefficient C (Table 2) show absence of precise localization of adsorbates on a carbon surface and difficulties of division of monolayer and polymolecular layers formation processes [1]. Amount of calculated adsorption heat (ΔQ) allows to think that by adsorption of both benzene and pyridine additional specific sorbent-sorbate interaction is possible (π-π – stacking and dipole-dipole for pyridine).

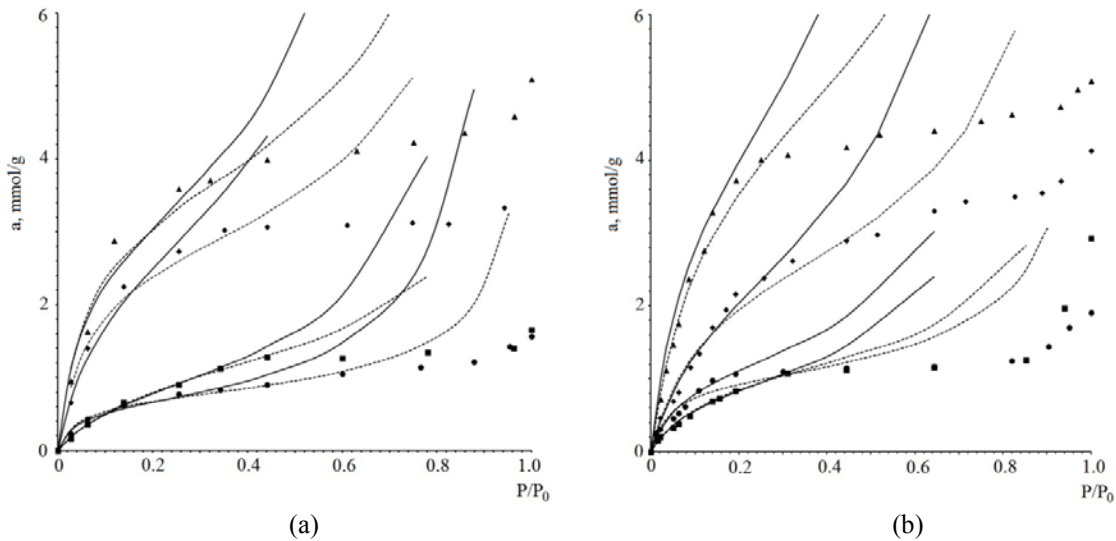(a)   (b)

Fig. 1. Adsorption isotherms of benzene (a) and pyridine (b) vapors by carbon adsorbents AG-OV-1(♦), AG-5 (▲), Purolat-Standart (●) and ABG (■): experimental (markers) and calculated by BET (solid line) and Aranovich (dotted line) equations.
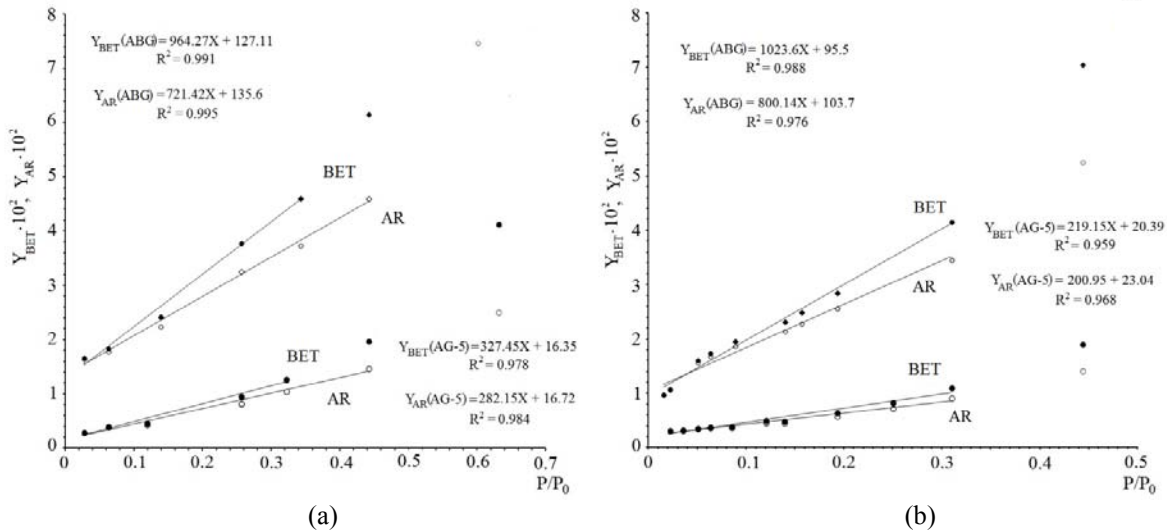

(a)   (b)

Fig. 2. Adsorption isotherms of benzene (a) and pyridine (b) vapors by carbon adsorbents AG-5 (●, ○) and ABG (♦, ◊) in a linear form of BET and Aranovich equations.

Table 2. Parameters of benzene (PhH) and pyridine (Py) adsorption calculated by BET and Aranovich equations

Parameter	Sorbate	AG-OV-1		AG-5		Purolat-Standart		ABG	
		BET	AR	BET	AR	BET	AR	BET	AR
R^2	PhH	0.981	0.983	0.978	0.984	0.981	0.993	0.984	0.990
	Py	0.960	0.966	0.959	0.968	0.952	0.968	0.988	0.976
application up to	PhH	0.22	0.36	0.32	0.46	0.22	0.62	0.32	0.46
	Py	0.25	0.20	0.34	0.34	0.20	0.16	0.38	0.37
a_m, mmol/g	PhH	2.66	2.77	2.91	3.54	0.61	0.74	0.92	1.39
	Py	2.29	2.73	4.12	4.98	1.10	1.16	0.89	1.25
C	PhH	12.03	16.70	21.02	16.88	27.52	22.71	8.59	5.32
	Py	9.39	8.57	13.72	8.72	15.98	16.73	11.72	7.71
ΔQ, kJ/mol	PhH	6.06	8.80	7.42	8.83	8.08	9.53	5.24	6.15
	Py	5.46	10.16	6.38	10.31	6.75	11.78	6.00	9.11
ω_m, nm^2	PhH	0.42	0.41	0.53	0.43	0.85	0.70	0.76	0.51
	Py	0.48	0.41	0.37	0.31	0.47	0.44	0.78	0.56

Average area occupied by adsorbate molecule (ω_m) in the case of adsorption on granular CA is comparable with elementary area of molecules (0.40–0.44 nm^2 and 0.38–0.42 for pyridine [1, 10]), and it implies a close-packed molecule arrangement. A greater amount of ω_m for benzene absorbed by broken CA and pyridine absorbed by ABG is probably connected with high contribution of specific interaction [1].

We should note a big difference between a_m calculated by the Eq. (4) and (5) for AG-5 and ABG (Table 2). It can be explained by a higher surface heterogeneity of these sorbents and, as follows, by higher errors of monolayer capacity evaluation. The first of these CA is characterized by narrow micropores together with high oxygen surface compounds (prevalently carboxyl groups) [7], the second has the highest total content of polar surface groups (Table 1).

According to the calculation of average statistic thickness of an adsorption monolayer (t-curve) with adsorption on granular CA benzene is oriented in parallel to the surface (layer thickness is 0.38–0.42 nm, molecule thickness is 0.37 nm [1]), at the same time with adosption on broken CA orientation is random (layer thickness 0.46–0.68 nm, molecule diameter 0.71–0.75 nm). Pyridine is oriented in parallel to the surface on all studied adsorbents (layer thickness is 0.36–0.42 nm).

Limiting adsorption volume (W_0) of benzene and pyridine and also characteristic energy of their adsorption (E) on CA was calculated by the Eq. (3). In advance we evaluated exponent n in the Dubinin-Astakhov equation. Obtained data and correlation coefficients (R^2) are presented in Table 3.

Comparison of theoretically calculated isotherms with experimental data showed (Fig. 4, Table 3) that pyridine absorption by CA except for AG-5 is described by the equation with n = 2 (takes the form of the Dubinin-Radushkevich equation). In the case of adsorption of both components by AG-5 and of pyridine by AG-OV-1 exponent n tends to 3, i.e. adsorbate molecule partially loses more than two degrees of freedom [11]. It is typical for adsorption in pores comparable to the diameter of an adsorbate molecule or in pores containing active polar centers [5, 11]. Benzene adsorption on Purolat-Standart is better described by the equation where n = 1 (corresponds to the adsorption in meso- and macropores) [5, 11].
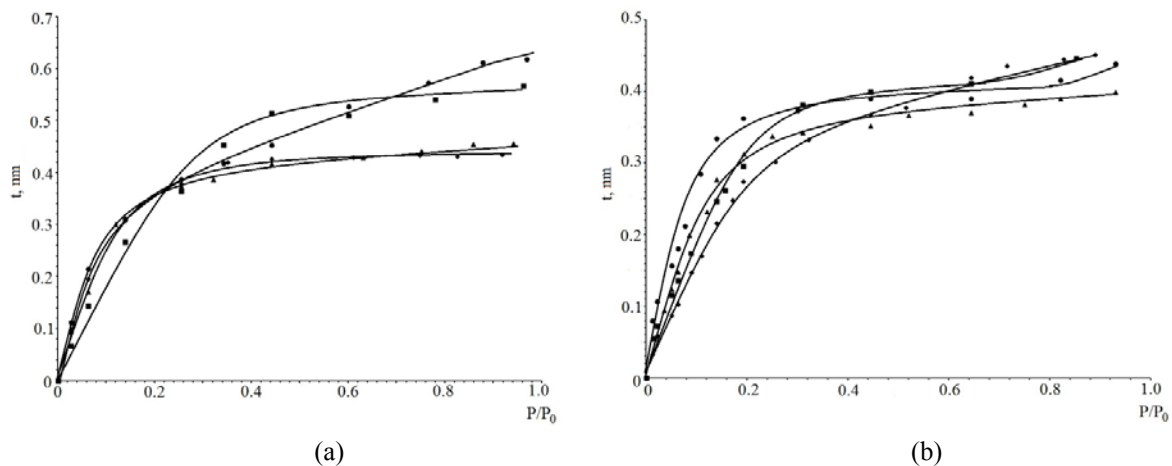

Fig. 3. t-curves of adsorption of benzene (a) and pyridine (b) vapors by carbon adsorbents AG-OV-1 (♦), AG-5 (▲), Purolat-Standart (●) and ABG (■).
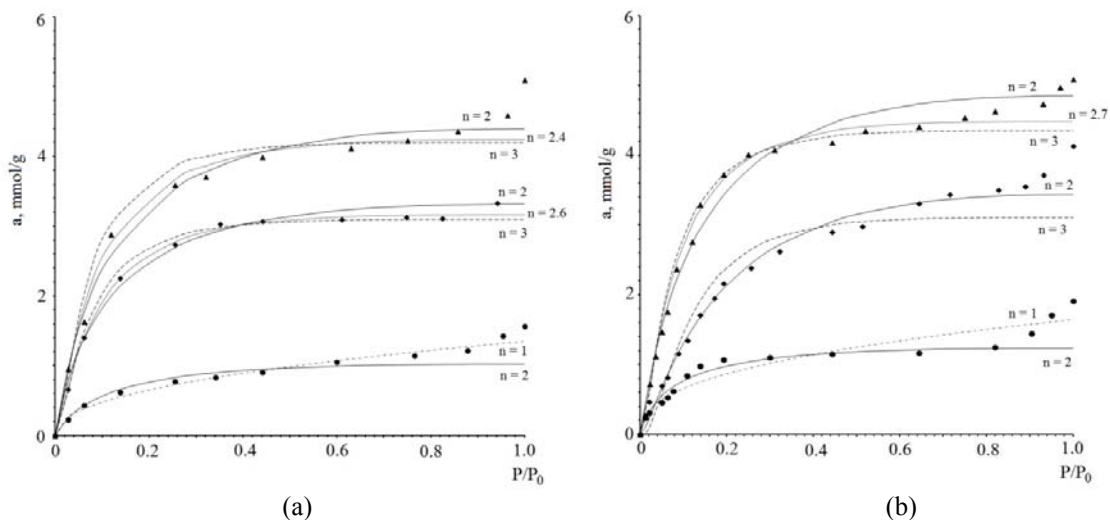

Fig. 4. Adsorption isotherms of benzene (a) and pyridine (b) vapors calculated by the Dubinin-Astakhov equation with different values of n; experimental points for carbon adsorbents AG-OV-1 (♦), AG-5 (▲) and Purolat-Standart (●) are on theoretical curves.

Table 3. Parameters of benzene (PhH) and Pyridine (Py) adsorption calculated by Dubinin-Astakhov equation

Parameter	AG-OV-1		AG-5		Purolat-Standart		ABG	
Sorbate	PhH	Py	PhH	Py	PhH	Py	PhH	Py
R^2	0.999	0.995	0.986	0.988	0.970	0.970	0.981	0.978
n	2.6	2.0	2.4	2.7	1.0	2.0	2.0	2.0
W_0, cm^3/g	0.28	0.28	0.38	0.36	0.12	0.10	0.11	0.10
E, kJ/mole	5.55	5.67	7.32	7.18	5.39	8.09	6.02	6.98
χ, nm	2.16	2.39	1.64	1.79	2.23	1.68	1.99	1.94

Comparison of calculated value W_0 (Table 3) with value of CA pores (Table 1) showed that both components, when absorbed on AG-OV-1, fill available in size micro- and mesopores ($W_0 > V_{micro}$), and on AG-5 they fill available micropores ($W_0 < V_{micro}$). In the case of broken CA we can only formally talk about volume filling of available micro- and mesopores because Purolat-Standart is mainly a macroporous adsorbent and ABG has a small amount of micropores. Values of adsorption characteristic energy and half-width of slit-like pores (χ) confirm assumptions on adsorbate localization in available in size micro- and mesopores.

CONCLUSION

Conducted research showed that benzene and pyridine adsorption on studied adsorbents is described by the equations of polymolecular adsorption in a narrow range of relative pressure and in this case it is characterized by low energetic constant value (C is not higher than 28). It does not enable us to determine accurately characteristics of a formed monolayer for adsorbents with micropores (granular) and meso- and macropores (crushed). In the latter case such behavior is explained by the surface heterogeneity because of high oxygen surface compounds. As a result, pyridine and benzene adsorption is a complete process of attraction – repulsion between active centers of adsorbate molecules (π-electron aromatic system and an unshared electron pair of nitrogen for pyridine) and adsorbent surface groups. Random orientation of benzene molecules when absorbed by broken CA and difference in adsorption behavior of benzene and pyridine (molecules are of similar size) when monolayer is filled are also connected with it.

Benzene and pyridine volume filling happens not only in micropores but also in mesopores. In this case a big amount of oxygen surface compounds (and possibility of the specific sorbent-sorbate interaction) is realized in increase of n from 2 to 3 in the Dubinin-Astakhov equation when both components are absorbed by AG-5. Proximity of calculated amount of benzene and pyridine limiting adsorption volume presupposes similar mechanism of pore filling with these components. Differences in adsorption behavior of these components at a time of monolayer filling are probably connected with peculiarities of molecule structure of pyridine which in comparison with benzene has additional potential adsorption center, i.e. an unshared electron pair of nitrogen.

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