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Effect of Activated Carbon Preliminary Thermal Treatment on the Adsorption Extraction of Aniline and Phenol

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Abstract

An effect was studied concerning the preliminary heating of activated carbon at the temperature of 250 °C on the porosity parameters of the adsorbent and the state of its surface. A comparative analysis was performed for the adsorption extraction of aniline and phenol from aqueous solutions by initial and pre-heated samples of the adsorbent. It was demonstrated that the thermal treatment of activated carbon causes an increase in the adsorption level of aniline and exerts almost no effect on the adsorption of phenol.

Key words: preliminary heated activated carbon, adsorption, aniline, phenol

INTRODUCTION

It is known that the adsorption level depends not only on the porosity parameters of an adsorbent, but also on the state of its surface. When porous carbon adsorbents are used it is recommended to heat them preliminary up to the temperature ranging within 105–300 °C in order to remove gaseous substances and water vapour absorbed in the course of its storage [1]. However, the authors of [2] noted that the carbon surface is capable of chemisorbing oxygen within the mentioned temperature range to form unstable surface compounds such as C_xO_y . The acidity of the latter depends on the heating conditions (the temperature values lower than 110 °C results in the formation of presumably basic compounds, whereas the heating temperature higher than 200 °C results in the formation of preferably acidic compounds).

The preliminary heating of activated carbon species (AC) causes a considerable increase in the adsorption level from the aqueous solutions of ϵ -caprolactam and pyridine [3, 4] those can interact specifically with oxygen-containing functional surface groups (OFSG) of the carbon surface.

We studied the effect of the thermal treatment of activated carbon on the adsorption of aniline and phenol from aqueous solutions. The molecules of aromatic compounds under investigation also have the functional group capable of interaction with different types of OFSG on the carbon surface.

OBJECTS AND METHODS OF INVESTIGATION

As the object of investigation, we chose AG-OV-1 activated carbon (Sorbent OJSC, Perm) which is preliminarily sifted, washed with distilled water in order to remove dust and dried then in air (sample I). Further, a part of coal was subjected to thermal treatment at 250 °C during 5 h in air (sample II).

The specific surface area (S), the volume of micro- and mesopores (V) were determined by means of low-temperature nitrogen adsorption on a Sorbtometer M surface area analyzer (Institute of Catalysis, SB RAS, Novosibirsk).

IR spectra of diffuse reflectance (IR DR) were registered on a Perkin-Elmer System 2000 FTIR spectrophotometer. The spectra obtained were subjected to the Kubelka-Munk transfor-

mation with the help of IRDM software package. The differential spectrum for sample II we obtained by subtracting the spectrum of sample I from the initial spectrum of sample II.

The composition of the organic part of the AC was investigated by means of elemental analysis. The sulphur content was determined by means of SC-432 elemental analyzer (LECO), the content of carbon, hydrogen and nitrogen was determined using CHN-1000 elemental analyzer (LECO). The oxygen content was calculated from the difference in the total amount of organic matter and total the content of elements C, H and N.

The oxygen content in the "active" form was calculated as the sum of the oxygen content in the form of carboxyl, phenolic and carbonyl groups, whereas that in the "inactive" form was found as the difference between the total oxygen amount and number of "active" oxygen. The amount of carbonyl groups was determined from the reaction with hydroxylamine hydrochloride, the amount of carboxylic and phenolic groups were determined by means of potentiometric titration according to Boehm [5, 6].

The adsorption of organic compounds was studied under static conditions using model solutions at a ratio between the adsorbent weighed portion and the volume of the solution under investigation equal to 1 : 100, with the concentration of components ranging within 0.5–50.0 mmol/dm³. The determination of aniline concentration was carried out basing on the intrinsic absorption of the solutions at 230 nm, whereas the concentration of phenol was determined according to the reaction of forming a coloured compound with 4-aminoantipyrine [7] exhibiting the absorption band at 490 nm, with the help of a SF-46 spectrophotometer using the technique of absolute calibration.

The value of the excess Gibbs adsorption was calculated from formula

$$\Gamma = \frac{(C - C_{\text{eq}})V}{m} \quad (1)$$

Here Γ is the excess Gibbs adsorption, mmol/g; C , C_{eq} are the initial and equilibrium concentration of a component under determination, respectively, mmol/dm³; V is the volume of the solution under investigation, dm³; m is the mass of the weighed portion of adsorbent.

TABLE 1

Parameters of the substances under investigation

Adsorbates	V_m , cm ³ /mol	M , g/mol	S_0 , nm ² [9]	C_s , [10] mol/dm ³	β
C ₆ H ₅ OH	87.96	94.113	0.440	0.8628	1.09
C ₆ H ₅ NH ₂	91.14	93.128	0.416	0.3912	1.13

The adsorption characteristics of the AC were estimated using the equation of Dubinin–Radushkevich:

$$\Gamma = \frac{W_0}{V_m} \exp \left[- \left(\frac{RT \ln (C_s / C_{\text{eq}})}{E\beta} \right)^2 \right] \quad (2)$$

Here W_0 is the maximum volume of the adsorption space, cm³/g; V_m is the molar volume of adsorbate, cm³/mol; E is the characteristic energy of adsorption, kJ/mol; β is the coefficient of affinity; C_s , C_{eq} are the concentration values for saturated and equilibrium solutions, respectively, mol/dm³. We also used by the BET equation [8]:

$$\Gamma = \Gamma_m \frac{K}{(1 - C_{\text{eq}}/C_s) [1 + (K + 1)C_{\text{eq}}/C_s]} C_{\text{eq}}/C_s \quad (3)$$

Here Γ_m is the adsorption capacity for saturated monolayer, mol/g; K is the constant in the equation of multilayer adsorption.

The heat of adsorption (Q) with covering the monolayer (in J/mol) was calculated according to formula

$$-Q = RT \ln (K + 1) \quad (4)$$

Here K is the constant in the equation of multilayer adsorption (see eq. (3)).

The specific surface area for the adsorbent filled with adsorbate (S_a), was calculated from the formula

$$S_a = S_0 \Gamma_m N_A \quad (5)$$

where S_0 is the projected area for the adsorbate molecules, m²; Γ_m is the adsorption capacity of saturated monolayer, mol/g; N_A is the Avogadro constant, mol⁻¹.

Some of the parameters used in the calculation for the organic substances are listed in Table 1.

RESULTS AND DISCUSSION

The comparative analysis of the results of determining the specific surface area, the vol-

TABLE 2
Parameters of carbon sorbent samples I and II

Parameters	I	II
S_{BET} , m ² /g	682	619
S_{micro} , m ² /g	369	433
V_{S} , cm ³ /g	0.46	0.42
V_{micro} , cm ³ /g	0.22	0.27
V_{mezo} , cm ³ /g	0.24	0.15
Content of elements,* %:		
C ^{daf}	96.54	92.98
H ^{daf}	0.62	0.56
N ^{daf}	1.16	1.15
S ^d	0.26	0.27
O ^{daf} _{tot}	1.68	5.31
O ^{daf} _{act}	1.67	1.98
n_{OFSG} , mmol-eq/g		
-OH	0.21	0.36
-COOH:		
strongly acidic	0.03	0.06
weakly acidic	0.08	0.05
>C=O	2.29	2.32

Notes. 1. S_{BET} is the total surface area; S_{micro} is specific surface area of micropores; V_{S} is total pore volume; V_{micro} , V_{mezo} are the volumes of micro- and mesopores, respectively. 2. d, daf – values calculated for dry and dry ash-free coal, respectively.

ume of micro- and mesopores for initial (I) and preliminary heated (II) samples demonstrated that the porosity parameters of the AC changed insignificantly (Table 2). As the result of heating, one could observe somewhat decreasing the total surface area and total pore volume, whereas the specific surface area and micropore volume exhibit an increase.

The analysis of DRIFTS data (Fig. 1) indicates that the heat treatment at 250 °C results in an increase in the quantity of the quinoid carbonyl groups (stretching vibration >C=O bond at 1630–1710 cm⁻¹) on the surface of the AC. The intensity of the absorption bands at 1500–1600 cm⁻¹ (within this region, there are demonstrated vibrations of conjugate -C=C-, >C=O groups; >COO⁻ and R-O-R' groups, where R and R' are phenyl or vinyl radicals) and the bands at 1250–1100 cm⁻¹ (-C-O-stretching vibrations in alcohols and ethers) [11].

The results of elemental analysis allow one to conclude that there is absorption by active charcoal observed in the course of heating the

oxygen and decreasing the fraction of carbon at the expense of this process (see Table 2). The determination of the number of “active” OFSG demonstrated that in the course of the heat treatment not only the absorption of oxygen occurs, but also a partial transformation of already existing functional groups is observed. Thus, the quantity of phenolic and strongly acidic carboxylic groups increases, whereas the quantity of weakly acidic groups decreases.

The amount of carbonyl groups remains almost unchanged. The comparison of data concerning the content of the “total” and “active” oxygen indicates that the main changing the surface state occurs due to the formation of “inactive” OFSG (those usually are considered to be quinoid and ether groups), which is in a good agreement with the data of DR IR spectroscopy.

Adsorption isotherms for activated carbon species under investigation studied are demonstrated in Fig. 2. The analysis of the adsorption isotherms and of the calculated adsorption parameters demonstrated that the heat treatment of this type exerts almost no effect on the adsorption of phenol (all changes being within the limits of experimental error), whereas the adsorption level with respect to aniline exhibits an increase. The adsorption heat value (Q) indicates that there is specific interaction between the molecules of organic substances

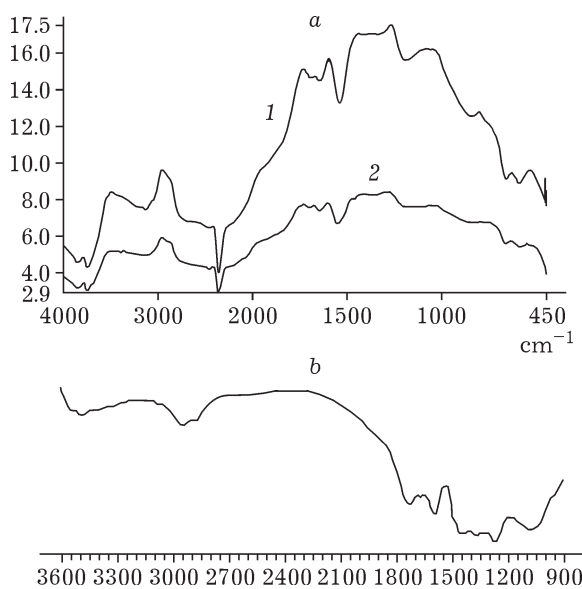


Fig. 1. DRIFT spectra of AG-OV-1 activated carbon: a – initial, b – differential for sample II; 1, 2 – samples I, II, respectively.

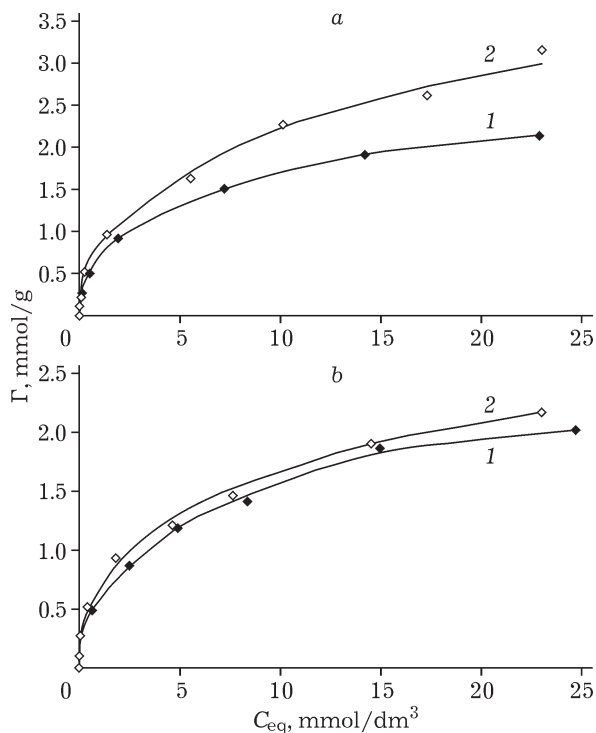


Fig. 2. Adsorption isotherms for aniline (a) and phenol (b) for the samples of activated carbon: 1, 2 – samples I, II, respectively.

under investigation and the surface groups. The comparison between the calculated value of the limiting adsorption volume (W_o) with respect to aniline (Table 3) with the porosity parameters for sample II (see Table 2) allows one to suggest that in this case there takes place not only volumetric filling of micropores, but also that of mesopores.

The value of increase in the limiting adsorption volume for phenol amounted to about 3 %, whereas for aniline this value was equal to about 40 %. The adsorption capacity value for saturated monolayer (Γ_m) for phenol ranges within

TABLE 3
Adsorption parameters for the samples of activated carbon

Samples	W_o , cm ³ /g	E , kJ/mol	Γ_m , mmol/g	$-Q$, kJ/mol	S_a , m ² /g
<i>Phenol</i>					
I	0.226	14.75	0.93	19.76	234
II	0.232	15.34	1.02	20.41	255
<i>Aniline</i>					
I	0.240	11.85	1.02	17.65	255
II	0.329	11.12	1.78	17.32	294

10 %, whereas for aniline it varies within the range of more than 70 % (see Table 3).

Since changing the characteristics of porous AC in the course of heating the adsorbent is insignificant, the increase in the aniline adsorption level could mainly be caused by an increased content of OFSG at the surface of thermally oxidized adsorbent, whose total amount calculated for elemental oxygen (O_{tot}^{daf}) demonstrates a three-fold increase. Thereby, the increase in the adsorption level is possible due to specific interaction between the sorbent and the sorbate, which is confirmed by considerable changing the monolayer capacity with respect to aniline. Taking into account the structure of aniline, one could assume that this interaction occurs mainly due to the formation of hydrogen bonds between the amino group of aniline and acid type OFSG on carbon surface (phenolic and carboxylic groups), whose number increases by approximately 50 %.

CONCLUSION

As the result of the studies performed we established that the preheating of the active carbon almost does not cause any change in its porosity characteristics, however this procedure results in an increase in the amount of superficial oxygen-containing functional groups on the surface of the AC. Changing the state of the surface occurs mainly due to the “inactive” oxygen (the formation of quinoid and ether groups). In this case, the amount of “active” oxygen in the form of phenolic and strongly acidic carboxylic groups increases, too. The preliminary thermal treatment of the activated carbon results in increasing the adsorption level with respect to aniline and exerts almost no effect on the adsorption of phenol. Increasing the adsorption level, to all appearance, could be connected with increasing the fraction of aniline adsorbed via specific interaction. The latter is connected with an increase in the amount of acidic type OFSG on the carbon surface.

REFERENCES

- Smirnov A. D., *Sorbtsionnaya Ochistka Vody*, Khimiya, Leningrad, 1982, pp. 28–32.

- 2 Tarkovskaya I. A., *Okislenny Ugol'*, Nauk. Dumka, Kiev, 1981.
- 3 Yustratov V. P., Krasnova T. A., Astrakova T. V., *Khim. Tekhnol. Vody*, 20, 4 (1998) 23.
- 4 Krasnova T. A., Belyaeva O. V., Kirsanov M. P., Shishlyannikova N. Yu., *Zh. Fiz. Khim.*, 78, 8 (2004) 1531.
- 5 Cheronis N. D., Ma G. S., *Mikro- i Polimikrometody Organicheskogo Funktsionalnogo Analiza*, Khimiya, Moscow, 1973, pp. 463–465.
- 6 Boehm H. P., *Carbon*, 40 (2002) 145.
- 7 Lurie Yu. Yu., *Analiticheskaya Khimiya Promyshlennykh Stochnykh Vod*, Khimiya, Moscow, 1984, pp. 374–377.
- 8 Koganovskiy A. M., Klimenko N. A., Levchenko L. M., Roda I. G., *Adsorbtsiya Organicheskikh Veshchestv iz Vody*, Khimiya, Leningrad, 1990.
- 9 Keltsev N. V., *Osnovy Adsorbtsionnoy Tekhniki*, Khimiya, 1984.
- 10 *Novy Spravochnik Khimika i Tekhnologa. Khimicheskoye Ravnovesiye. Svoystva Rastvorov*, ANO NPO "Professional", St. Petersburg, 2004, pp. 427–430.
- 11 Pretsch E., P. Buhlmann P., Affolter S., *Structure Determination of Organic Compounds. Tables of Spectra Data*, Springer-Verlag, Berlin, 2000.