

RATIONAL CONDITIONS OF PRODUCING THE ACTIVATED CARBON WITH WELL-DEVELOPED NANOPOROUS STRUCTURE FOR THE TREATMENT OF NATURAL AND WASTE WATERS

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Rational conditions for the activation of coal of a high stage of metamorphism (anthracite) have been determined, which allow the development of a nanoporous structure. Obtained activate carbon with nanoporous structure can be use for the treatment of natural and waste waters have been carried out. The structurally sorptive characteristics and granulometric size composition of obtained samples were determined. It was established that in order to obtain a sorbent with specified properties, it is necessary to introduce oxygen into the reacting mixture at the second stage of anthracite activation and control the activation time. The activation in the first stage was carried out with steam at a temperature of 750–800 °C, and in the second stage – with steam in the presence of air oxygen at 280–300 °C. The rational content of oxygen in the activating mixture is in the range of 2.7–4.4 %, while the specific surface area of activated carbon increases, which corresponds to nano-sized pores and, accordingly, the volume of the adsorption space of coal. The process led to the development of mesoporosity ~ 0.2–0.3 cm³/g, after which the microporous sample of activated carbon was impregnated with a surfactant solution. Thus, the rational conditions of activation are the duration of the process of 1.5 hours in the presence of 4.4 % oxygen in the activating mixture. It is shown that the largest values of the total specific surface area and the specific surface area of mesopores are achieved when using ionic surfactants with alkyl chain length $n = 10–16$ as modifiers. In particular, the use of sodium dodecyl sulfate $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_3\text{Na}$ as a modifier allows to obtain the largest value of the total surface S_{tot} 1030 m²/g and the surface of mesopores S_{me} 334 m²/g. It was established that the activation of modified samples of activated carbon leads to a decrease in the size of granules. The content of fractions with a size of 1.0–2.0 mm and 0.5–1.0 mm is 80–85 %, which are rational for use for water purification from organic compounds.

Keywords: *activating mixture, activation of coal, anthracite, coal modification, rational conditions, surfactant*

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1. Introduction

The consumption of activated carbon (AC) steadily grows in many branches of

industry, and water conditioning and wastewater treatment are among the largest consumers of AC. In developed countries the

production and use of AC for environmental goals is as high as 500 g per man year (Olontsev et al., 2015) or 30 % of the total AC production. At the existing AC production volume of 1.25 million tons, its annual consumption amounts to 5–10% (Mukhin et al.; Global Adsorbents, 2023).

The effective use of activated carbon in the water conditioning and water treatment process stipulates the need to obtain sorbents with prespecified properties that best meet the requirements to the AC rational porous structure. The coal that is mainly microporous coal actually does not sorb from water large organic compounds, such as humic and fulvic acids, dyes, surfactants, water-soluble high-molecular mass compounds.

Therefore, such AC can be ineffective in conditioning of the water from surface sources or in wastewater treatment. Hence, for purposes of water conditioning and water treatment, it is expedient to utilize AC with well-developed nanoporous structure that is optimal in relation to the molecular size of absorbed organic substances. The rational structure of activated carbon intended for the purposes of water conditioning and wastewater treatment must be narrow porous, where the average effective pore radius is found in the near border zone of wide supermicropores and narrow mesopores, while the upper limit of effectively used micropore radii does not exceed 4–5 nm (Grechanik et al., 2017).

The raw materials for AC production involve the use of a wide spectrum of substances with a high content of carbon that satisfy the following requirements: low content of inorganic impurities (low ash content), high density, sufficient content of volatile compounds, and low degradation during storage (Tadda et al., 2016).

The pit coal and especially anthracite and thermoanthracite satisfy the specified requirements in the best way. The above coals feature a well-developed system of pores and the absence of macropores. AC obtained from the specified raw materials are effective sorbents suitable for the treatment of natural and waste waters (Zhilina et al., 2011).

When anthracite is used for a raw material, the carbonization stage in AC production is eliminated, and stages of carbonization and activation are combined. The anthracite activation can be implemented by using chemical additives (Siriwardena et al., 2019). The main purpose of activation is to develop the rational structure of pores in activated carbon. The activation process involves the burning out of internal and peripheral structure of coal particles.

To eliminate the burning out of geometrical surface of coal during its activation and to develop its nanoporous structure, it is necessary to modify the activation process and intensify the penetration of oxidizer in depth of the porous structure of coal. In accordance with paper (Orenbakh et al., 1973), the activation of preactivated carbon takes place in both the internal diffusion and intermediate regions.

The role of secondary activation consists in making the existing pores accessible. In this respect it is promising to use the impregnation of proactivated coal with organic substances of predominantly surfactant nature.

Besides the Rebinder effect that causes the appearance of additional structure defects in the texture of coal, the molecules of surfactants having a hydrocarbon chain diffuse depthward into the micro- and supermicroporous structure and can play the

role of “Bickford’s fuse” that facilitates the access of the oxidizer into coal pores.

The AC density, total pore volume and prevailing development of nanoporous structure of pore space most likely depends on such parameters as duration of the two-stage activation process involving the use of a modifier, modifier type, and the amount of oxygen in vapor-gas mixture.

Obtaining activated carbon with a developed nanoporous structure from anthracite for treatment large organic compounds from water, such as humic and fulvic acids, dyes, surface-active substances, water-soluble high-molecular compounds, is relevant.

Thus, the purpose of this study was to provide a scientific substantiation and determination of rational activation conditions for the development of predominantly nanoporous structure of high-grade (anthracite) intended for water purification.

To achieve the set goal, the following tasks must be solved:

- to establish rational conditions for the activation of anthracite to obtain a sorbent with a given nanoporous structure (activation time, activator composition, and oxygen content in the activating mixture);

- to choose a surfactant, the use of which will allow obtaining a nanoporous structure during the activation of anthracite;

- to investigate the structural and sorption properties of the obtained sorbents;

- to determine the fraction of micropores and mesoporous space by iodine number and methylene blue number, respectively;

- to check the efficiency of the obtained sorbents according to the iodine value and the degree of extraction of the methylene blue dye.

2. Materials and methods

The anthracite from the Donetsk Basin (Ukraine) with ash-content of no more than 8 % was selected as a basis for producing sorbents with well-developed nanoporous structure. Anthracite is a high-grade metamorphic coal, i.e., the coal with carbon content above 86 %. The granulometric size composition of the activation working mixture was no less than 0.5 mm and no more than 2.0 mm.

Anthracite has a specific microporous structure and represents a glasslike substance pierced with a small number of crevices. The accessible porosity of anthracite is negligible and lies within the limits 0.005–0.02 cm³/g. At the same time, its total porosity is about 0.1 cm³/g. It is obvious that a larger part of internal volume is linked with an external surface or connected with it by pores of diameter less than 0.5 nm. For the development of the coal texture and the maximum opening of internal porosity it is sufficient to perform a single-stage activation up to combustion loss (coal loss) of 40–50 % that makes it possible to achieve the level of boundary adsorptive pore volume as high as 0.3–0.35 cm³/g, however, this is mostly microporous space. For the development of nanoporous structure the microporous anthracite was impregnated with a solution of organic substances, mostly surface-active that are presented in Table 1 at the concentration below the critical concentration of micelle formation (CCM) (Definition of CMC, 1979).

Structure-sorptive properties of obtained coal samples were tested by the methods of low-temperature nitrogen sorption at 77 K using the Quantachrome Autosorb Automated Gas Sorption System (NOVA Quantachrome 4200e, USA) and adsorption of

n-chloroaniline from the aqueous solution by using a two-beam spectrophotometer (Unico 4802, USA) (wavelength 237 nm and tray length of 1 cm).

In addition, the sample characteristics of sorbents were estimated by measuring the standard indicators for rapid assessment of adsorptive capacity of coal, i.e., iodine index and the methylene blue number. As is known (Kinle et al., 1984; ASTM Designation, 1994; DIN 53241-1, 1995), the iodine index

characterizes the content of pores having the size < 2 nm. Iodine index shows the amount of iodine that can be adsorbed from the diluted iodine solution by 1 g of sorbent. The equilibrium concentration of iodine solution must be close to 0.02N. It is assumed that under the specified conditions the monolayer iodine adsorption takes place. If residual concentrations are obtained in the interval 0.03–0.07N, a correction coefficient is used.

Table 1. Surfactants for modifying the active anthracite

Substance	Chemical formula	Molecular weight	Number of alkyl carbon atoms
Sodium dodecyl sulfate (NaDDS)	$\text{CH}_3(\text{CH}_2)_{11}\text{SO}_3^-\text{Na}^+$	288	12
Sodium oleate (NaO)	$\text{C}_{17}\text{H}_{33}\text{COO}^-\text{Na}^+$	304	17
Sodium tetradecyl sulfate (NaTDS)	$\text{C}_{14}\text{H}_{29}\text{SO}_3^-\text{Na}^+$	316	14
Sodium hexadecyl benzosulphonate (NaHDBS)	$\text{C}_{16}\text{H}_{33}\text{C}_6\text{H}_4\text{OSO}_3^-\text{Na}^+$	420	16
Sodium dibutyl naphthalene sulphonate (NaDBNS)	$\text{C}_{10}\text{H}_5(\text{C}_4\text{H}_9)_2\text{OSO}_3^-\text{Na}^+$	358	18
Sodium nonylphenol ethoxylate (NaNPE)	$\text{C}_9\text{H}_{19}\text{C}_6\text{H}_4\text{O}(\text{C}_2\text{H}_4\text{O})_{10}\text{OH}$	676	29
Tetradecylpyridinium bromide (TDPBr)	$\text{C}_{14}\text{H}_{29}\text{C}_5\text{H}_5\text{N}^+\text{Br}^-$	356	14

The iodine index is calculated as follows:

$$\text{iodine}(\text{index}) = \frac{x}{m} \cdot D$$

where $\frac{x}{m}$ is the amount of iodine in milligramm that is sorbed by 1 g of activated carbon; D is the correction coefficient (obtained from the graph).

The methylene blue number is related to the quantity of mesopores (Raposo et al., 2009; Rafatullah et al., 2010; Yan et al., 2009).

In this study the quantity of methylene blue extracted from its aqueous solution per AC mass unit was assessed by measuring the adsorption isotherms and employing the Langmuir model for estimating the experimental data (Koganovsky et al., 1990). The Langmuir theory is intended for the assessment of monolayer adsorption on the homogeneous surface when the attraction forces between the adsorbate molecules and their mobility on the surface are neglected.

The Langmuir isotherm equation has the form:

$$a = a_m \frac{C}{C + b},$$

where b is the constant for the given adsorbent-adsorbate pair that depends on the adsorption energy and temperature; a_m is the capacity of monolayer.

The linearized form of Langmuir equation can be presented as

$$\frac{C}{a} = \frac{1}{a_\infty b} + \frac{1}{a_\infty} C,$$

where a_∞ is the boundary amount of adsorbed substance.

Since the linear form of Langmuir equation is a straight-line equation, the constants of this equation are determined by the inclination of the line in the coordinate system and the ordinate intercept. The experimental determination of a_∞ makes it possible to calculate the adsorbent specific surface area S :

$$S = a_\infty \cdot N_A \cdot \omega,$$

where N_A is Avogadro's constant; ω is the area per one molecule of adsorbate in monomolecular layer (planting site of molecule).

The working fraction of crushed anthracite was activated in the fluidized layer furnace by using steam, the mixture of steam with oxygen and the mixture of steam with products of combustion of gaseous fuel as an activator (Klymenko et al., 2013; Grechanik et al., 2013). The temperature of activation by steam was 750–800 °C, while the temperature of activation by steam in the presence of air oxygen was 280–300 °C. This process was conducted till the development of mesoporosity of ~0.2–0.3 cm³/g. Next, a microporous AC sample was impregnated with the surfactant solution. The process of additional activation was performed in the same way as at the first stage by varying the activation duration, composition of activator and its oxygen content. All tests were repeated at least five times, and the final results represent the average values for all indicators. Table 2 presents data regarding the effect of the nature of impregnation substance on the change of total surface area (S_{tot}) and the surface area of mesopores (S_{me}) that are estimated based on the iodine index and the methylene blue number, respectively.

Table 2. The effect of the nature of impregnation substance on the development of mesoporosity of modified anthracites (activator is steam)

Sample No.	Impregnation substance	S_{tot} , m ² /g	S_{me} , m ² /g
1*	None	281	6,5
2**	None	643	68
3	NaO	324	41
4	NaDDS	1030	334
5	NaTDS	874	153
6	NaHDBS	477	92
7	NaDBNS	508	101
8	NaNPE	772	53
9	TDPBr	756	87

*Sample 1 is the initial nonactivated anthracite; **samples 2–9 are of the activated microporous modified anthracite.

As can be seen from Table 2, the largest values of Stot and Sme were achieved while using ionic surfactants with alkyl chain length $n = 10-16$ as modifiers.

3. Results and discussion

The smallest effect on the development of nanoporous structure was achieved while using sodium oleate as a modifier. This can be stipulated by the fact that sodium oleate is practically insoluble in water and forms a colloidal emulsion therein, drops of which due to adhesion are concentrated on the

external surface of activated carbon and inhibit the penetration of activated agent deep inside the porous structure. As a result, we obtain the following series in terms of the efficiency of modifier substance for the development of mesoporosity of samples of activated carbon: NaDDS > NaTDS > NaDBNS > NaHDBS > TDPBr > NaNPE > lack of modifier > NaO.

The next set of tests involved the investigation of the change of granulometric size composition of AC samples depending on the activation period (Table 3).

Table 3. Variation of the granulometric composition of activated carbon samples depending on the time of activation and the composition of activating mixture

Sample	Time of activation, hour	Composition of mixture	Content of fraction, %				
			Size of fraction, mm				
			> 2.0	1.0–2.0	0.5–1.0	0.25–0.5	< 0.25
1	3	steam	0.3	92.8	4.6	1.7	0.6
2	2	steam	0	49.7	33.9	16.2	0.2
3	1.5	steam + oxygen 1.0 %	0	48.8	33.7	17.1	0.4
4	2	steam + oxygen 1.0 %	0	44.4	36.1	19.0	0.5
5	2	steam + oxygen 2.0 %	0.4	49.8	35.1	14.2	0.5

Sample 1 was not impregnated using the surfactant (SAS) solution, samples 2–5 were impregnated using the sodium tetradecyl sulfate (NaTDS) solution. The conditions of sample processing differ depending on the time of activation and the composition of activating mixture.

As can be seen from Table 3, the amount of 1.0–2.0 mm size fraction does not change practically during the activation of modified coal under different regimes, however, it decreases twofold in comparison with the amount of fraction of unmodified sample.

The share of fractions having the size of 0.5–1.0 mm and 0.25–0.5 mm increases as compared to the unmodified sample, and the activation regime hardly affects this share.

Thus, the activation of AC modified samples leads to the reduction of pellet size. However, the total content of fractions having the size of 1.0–2.0 mm and 0.5–1.0 mm that are most suitable for application in water purification filters is fairly high (80–85%).

The variation of the methylene blue adsorption level on different AC samples depending on the activation parameters and the size of AC pellets is shown in Fig. 1.

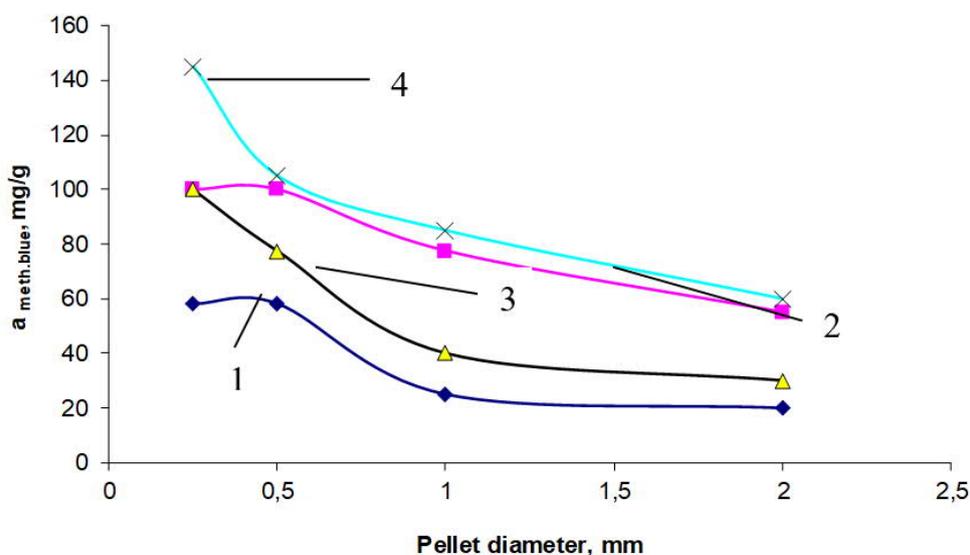


Fig. 1. The impact of parameters of activation and size of activated carbon pellets on the methylene blue adsorption efficiency: without impregnation (1), impregnation without addition of oxygen (2), impregnation plus 1% oxygen (3) and impregnation plus 2% oxygen (4)

As could be expected, the reduced size of pellets leads to an increase of adsorption value that is stipulated by increased kinetic parameters of smaller size pellets (Pan et al., 2017).

The data in Fig. 1 also demonstrate a significant value of oxygen in the activating mixture. Table 4 presents data that illustrate the impact of oxygen content in the mixture on the variation of AC structural parameters.

As can be seen from the above data, the most rational content of oxygen in the activating mixture lies in the interval 2.7–4.4 % that leads to an increase of the value of AC specific surface area, which falls upon the nanosized pores and, accordingly, upon the volume of AC adsorptive space.

Table 5 illustrates the impact of activation time on the change of the value of methylene blue adsorption at AC samples.

The coal samples saturated with the substance for modification were activated by steam with addition of oxygen. The time

interval of activation was in the range of 1–3 hours.

The tests were conducted for two types of samples: the grain fraction with 0.5–2.0 mm coal grain size and the dustlike fraction with particle size < 0.25 mm. The above data were obtained after triple repetition of test.

Table 4. The impact of the oxygen amount in activating mixture on the development of mesoporosity of modified anthracite

Oxygen content, %	S_{BET}	S_{me}	V_a	V_{me}
	m^2/g		cm^3/g	
0.0	910	49.2	0.35	0.06
1.0	981	50.4	0.45	0.07
2.0	945	107.3	0.50	0.14
2.7	1050	323	0.51	0.17
3.2	952	284.3	0.53	0.17
4.4	950	354	0.53	0.16
6.0	972	208	0.55	0.17

As can be seen from Table 5, the activation process should be expediently conducted during 1.5 h. Further increase of activation duration degrades the adsorptive properties of AC because it results in the reduced efficiency of the development of sorbent mesoporosity.

Table 6 presents the comparative data regarding the impact of the presence of oxygen in the activating mixture and the surfactant modification before the second stage of activation on the structural AC parameters.

Table 5. *The impact of the AC sample activation time on the value of methylene blue adsorption*

Activation duration, hour	Methylene blue adsorption, mg/g	
	Fraction of 0.5–2.0 mm	Fraction < 0.25 mm
1.0	100–120	180–184
1.25	80–90	200–215
1.5	60–65	151–168
1.67	54–60	140–150
1.75	52–57	120–137
1.83	50–55	100–107
2.0	44–50	84–99
2.5	40–45	70–74
3.0	45–49	50–60

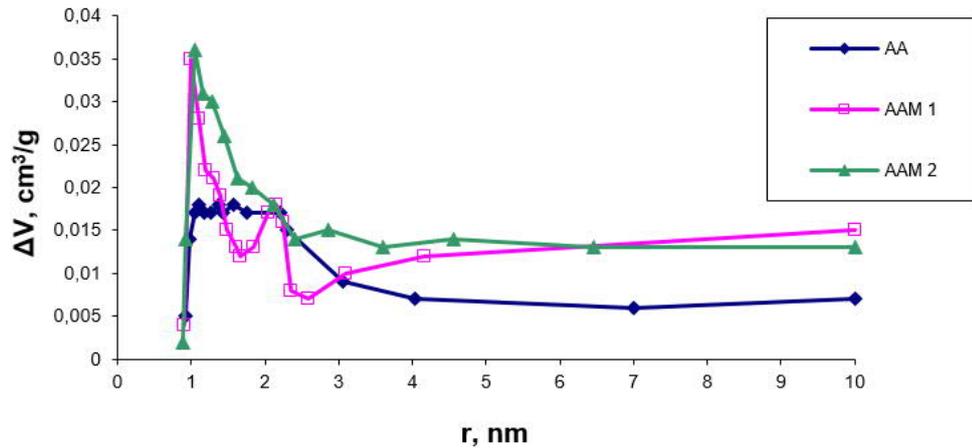
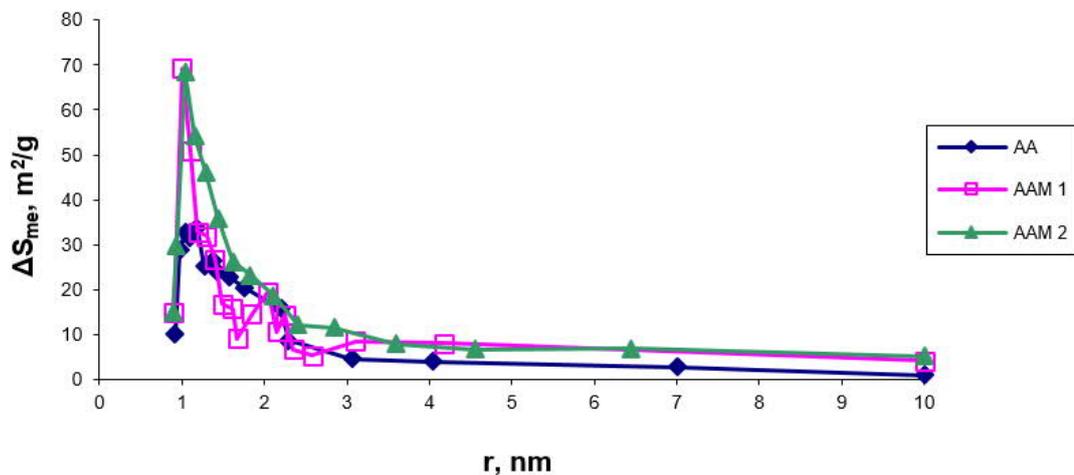
Figures 2 and 3 illustrate changes of the values of specific adsorption AC volume ΔV on the surface of mesopores ΔS_{me} depending on the distribution of pores in terms of their size in the interval 1.0–10.0 nm. For this set of tests, we used coal samples that conventionally were designated as follows: AA is the anthracite activated without addition of oxygen and without modification by sodium dodecyl sulphate; AAM 1 is the sample after the secondary stage of activation of the modified AA sample with addition of 4.4 % of oxygen to the activating mixture; and AAM 2 is the sample under the same conditions but with the amount of oxygen in mixture equal to 2.7 %.

As can be seen from the data in Table 6 and Fig. 2, the best activation conditions imply the presence of 4.4% of oxygen in the activating mixture due to the larger development of nanosized porous structure and smaller number of large pores in the interval 4.5–10.0 nm.

It is well-known that the ignition temperature of adsorbed organic substances is 70–100 °C below the ignition point of coal (Radic et al., 2017). As the activating agent comes into contact with the coal surface where the modifier is adsorbed, the thermal disintegration of modifier and the temperature rise of the surface occur due to a lower ignition temperature.

Table 6. The impact of coal activation conditions on the change of AC pore radii

AC	$S_{\text{BET}}, \text{m}^2/\text{g}$	Sme in the interval of pore radii, m^2/g				$\Sigma S_{\text{me}}, \text{m}^2/\text{g}$	$V_a, \text{cm}^3/\text{g}$
		1.0–1.5	1.5–2.0	2.5–4.5	4.5–10.0		
		nm					
AA	805	155	44	9	–	208	0.26
AAM 1	950	228	93	21	3	354	0.35
AAM 2	1050	205	80	26	12	323	038

**Fig. 2.** Differential curve of the variation of specific adsorption volume in the interval 1.0–10.0 nm depending on the oxygen amount in the activating mixture**Fig. 3.** Differential curve of the variation of mesopore surface area in the interval 1.0–10.0 nm depending on the oxygen amount in the activating mixture

This is stipulated by the fact that amorphous carbon, which is formed owing to the sorbate disintegration on activated carbon, enters into the oxidation reaction first because of its higher reactive power. Hence, it results in an easier access of the oxidizer to the

internal structure of coal. In this case, the carbon sorbent interacts with both, the components of activating gas phase and the products of desorption and destruction of sorbate.

The burning out of the internal surface of sorbent occurs due to the formation of the flow of combustible vapors sufficient for coal ignition. In our view, the dependence of the modifier efficiency for the proper behavior of the activation process on its chemical nature is stipulated by the following reasons. It is well-known (Potekhin et al., 2007) that the thermal destruction of organic substance begins with the opening of one of chemical bonds of molecule. The weakest links are carbon-carbon ones. The average value of dissociation energy of such links is equal to 340 kJ/mol (the dissociation energy of carbon-hydrogen link is equal to 415 kJ/mol, and that of carbon-oxygen link amounts to 720 kJ/mol). The presence of side chains, heteroatoms and aromatic rings essentially affect the strength of links between carbon atoms (Combustion, destruction and stabilization of polymers, 2007).

Thus, with the rise of the number of carbon atoms in a molecule and, correspondingly, the molecular weight, the energy consumption for its thermal destruction increases, and the ignition temperature of the modifier increases (for example, the difference between the ignition temperatures of ethane and butane amounts to ~50 °C). As can be seen from Table 1, the resultant (obtained by the authors) set of modifiers demonstrates the dependence of their efficiency on the number of carbon atoms in a molecule and its molecular weight.

The impact of activation temperature in the presence of ambient oxygen, in our view, is related to the following circumstances. During the carbonization of various type sorbates on activated carbon, a large part of organic admixtures disintegrates at 200–350 °C, while at 400 °C, about a half of all adsorbate decomposes. The main amount

of gaseous products of disintegration of organic sorbate (CO, CO₂, CH₄ and others) is released during heating to 350–600 °C. The thermal destruction of organic sorbate terminates at 700–800 °C. The condensation and coking of many compounds are accompanied by vigorous gas release in the conditions of very high viscosity that leads to the blowing away of sorbate, an increase of its volume with formation of jamming at inputs into coal pores (San, 2003).

For preventing this phenomenon and intensifying the supply of the oxidizer deep inside the micropore, it is expedient at this stage of process to use the activating gas mixture containing oxygen. In the temperature range of 400–800 °C, the reaction of carbon with oxygen most likely proceeds through the dissociation of O₂ molecule on the carbon surface (with small energy of activation $E_1 > 0$). The formed oxygen atoms are chemisorbed with formation of covalent link $=C=O$ (activation energy of chemisorption $E_2 = 770$ kJ/mol, while the activation energy of escape of CO₂ from the surface $E_3 = 337$ kJ/mol). Since $E_1 + E_2 > E_3$, it is clear that oxygen departs from the carbon surface only in the form of CO or CO₂.

The reaction of carbon with oxygen is accompanied by a large thermal effect that leads to a strong heating of surface. At low environmental temperatures, small oxygen concentrations, and small velocities of gas flow, we can observe the process that yields a mixture of CO and CO₂, the speed of which depends heavily on temperature. At high oxygen concentrations, high velocities of gas flow, and high temperature, the process can be observed, the speed of which practically does not depend on the environmental temperature and is proportional to the velocity of gas flow. In this case, the CO content in

products sharply increases. As was shown in paper (Frank-Kamenetsky, 1987), these two different thermal regimes of the behavior of reaction of coal with oxygen represent oxidation and burning. The transition from oxidation regime to burning occurs by jump under conditions close to coal ignition conditions.

The continuous transition from the oxidation regime to burning is not possible. A sharp rise of CO content in gases during the transition from the oxidation regime to the burning is naturally explained by a stepwise increase of temperature near the surface and by local heating.

In the process of intensifying the activation of anthracite impregnated with SAS, it is important to maintain those critical conditions that prevent the transition from oxidation regime to the burning regime. The investigations presented in paper (Combustion, destruction and stabilization of polymers, 2007) show that the critical conditions are observed at the oxygen concentration of 2.5 % and they disappear only at 0.8 %. Therefore, in order to intensify the process of burning out of carbonized residue of modifier (amorphous carbon), the oxygen regime in the process of activation must be maintained under the investigated conditions.

A significant part in the coal activation process plays an introduction of steam (water vapor) into the activating mixture. Water molecule is strongly polar unlike non-polar molecules of oxygen and carbon dioxide gas. The effective size of its molecule is 0.269 nm, while the sizes of the latter two are 0.332 nm and 0.290 nm, respectively. Water vapor at the same temperature has the smallest viscosity, the highest diffusion coefficient equal to 0.198 cm²/s (0.139 and 0.173 cm²/s for

CO₂ and O₂, respectively) and very maximum velocity of molecule motion. Hence, it is water molecules that possess properties enabling them to penetrate into coal micropores better than the others. Water molecules are sorbed on the coal surface and dissociate into chemisorbed oxygen and easily desorbed hydrogen. At 750–950 °C, the sorption of another water molecule is required along with chemisorbed oxygen atom and further desorption of molecules of hydrogen and carbon dioxide.

The dissociation rate of water vapor on the surface of carbon in the presence of oxygen is several times as high as the rate in the absence of oxygen. It causes the localization of process at individual active sites of coal surface that results in increasing the size of pores. This process can be stopped only by reducing the temperature to 700–750 °C depending on the oxygen concentration.

4. Conclusions

Thus, for obtaining the sorbent with the specified properties at the second stage of anthracite activation, it is necessary to combine several factors in an optimal way: coal modification, the introduction of oxygen into reacting mixture, and the activation duration.

It has been established that the reduction of the number of carbon atoms in a molecule of surfactants-modifiers enhances the efficiency of obtaining the activated carbon with well-developed nanoporous structure.

A series was obtained according to the effectiveness of the modifier substance for the development of mesoporosity of activated carbon samples: DDSNa > TDSNa >

DBNSNa > GDBSNa > TDPBr > NFENa > lack of modifier > ONa.

The activation of modified AC samples leads to the reduction of the size of its pellets, however the total content of fractions of sizes 0.5–1.0 mm and 1.0–2.0 mm amounts to 80 % – 85% that is the most expedient for use in water-purifying filters. It has been shown that the rational content of oxygen in activating mixture amounts to 2.7–4.4%. The activation process can be expediently conducted during 1.5 h under the selected conditions.

Activated carbon with well-developed nanoporous structure is effective sorbent to remove from water large organic compound, such as humic and fulvic acids, dyes, surfactants, water-soluble high-molecular mass substances. Therefore, such activated carbon can be used for drinking water production from surface sources and wastewater treatment.

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РАЦІОНАЛЬНІ УМОВИ ОДЕРЖАННЯ АКТИВНОГО ВУГІЛЛЯ З РОЗВИНЕНОЮ НАНОПОРИСТОЮ СТРУКТУРОЮ ДЛЯ ОЧИЩЕННЯ ПРИРОДНИХ ТА СТІЧНИХ ВОД

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Проведено наукове обґрунтування і визначення раціональних умов активації для розвитку нанопористої структури вугілля високої стадії метаморфізму (антрациту), призначеного для очищення природних та стічних вод. Визначено структурно-сорбційні характеристики та гранулометричний склад одержаних зразків. Встановлено, що для отримання сорбенту із заданими властивостями необхідно на другій стадії активації антрациту вводити у реагуючу суміш кисень та контролювати час активації. Активацію на першій стадії проводили водяною парою за температури 750–800 °С, а на другій стадії – парою за наявності кисню повітря за 280–300 °С. Раціональний вміст кисню в активуючій суміші знаходиться в межах 2,7–4,4 %, при цьому збільшується величина питомої поверхні активованого вугілля, яка припадає на нанорозмірні пори і відповідно на об'єм адсорбційного простору вугілля. Процес вели до розвитку мезопористості ~ 0,2–0,3 см³/г, після чого мікропористий зразок активованого вугілля просочували розчином поверхнево-активної речовини. Таким чином, раціональними умовами активації є тривалість процесу 1,5 год за наявності у активуючій суміші 4,4 % кисню. Показано, що найбільших величин загальної питомої поверхні і питомої поверхні мезопор досягнуто при використанні як модифікаторів іонних поверхнево-активних речовин з довжиною алкільного ланцюга n = 10–16. Зокрема, використання як модифікатора додецилсульфату натрію CH₃(CH₂)₁₁SO₃Na дозволяє отримати найбільшу величину загальної поверхні S_{заг} 1030 м²/г та поверхні мезопор S_{ме} 334 м²/г. Встановлено, що активація модифікованих зразків активованого вугілля призводить до зменшення розмірів гранул. Вміст фракцій з розміром 1,0–2,0 і 0,5–1,0 мм складає 80–85 %, які є раціональними для використання у фільтрах для очищення води від великих органічних сполук, таких як гумінові та фульвокислоти, барвники, поверхнево-активні речовини та водорозчинні високомолекулярні сполуки.

Ключові слова: активація вугілля, активуюча суміш, антрацит, модифікація вугілля, поверхнево-активна речовина, раціональні умови