

Processing of Lignites into Effective Sorbents for Solving Environmental Problems and Improving the Quality of Life

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Abstract—The paper shows the possibility of processing of lignites of Kuzbass (Tisulskoye coalfield) into effective carbon sorbents. The sorbents are obtained at the different ratio of KOH/coal – 0.25g/g; 0.5g/g; 1g/g; 2g/g. The correlation of the porous structure and sorption activity of carbon sorbents with the amount of alkali used at obtaining the sorbent was determined.

Keywords— carbon sorbent, lignite, carbonization, alkaline activation, porous structure, adsorption, quality of life

I. INTRODUCTION

The ecological problem concerning pollution water resources of the planet does not lose its relevance. High rates of industry and motor transport development lead to a growing of the surface water pollution [1-3]. The quality of some natural water sources is unacceptable for their use not only for food purposes, but also for technical use. There can be dangerous organic substances, heavy metals, radionuclides in quantities considerably exceeding maximum permissible concentrations in water. Such water is low-quality water and must be cleaned.

The use of carbon sorbents, as the main substance for the sorption purification or as a stage of the complex water purification process, is topical [4]. There are various schemes for obtaining carbon sorbents, which include preparation of a feedstock, carbonization and activation of the carbonizate by gas (water vapor and / or carbon dioxide). In addition, besides gas during activation, various chemical reagents are used in the stages of carbonization and raw materials preparation. A variety of plant raw materials (different types of wood, shells of various nuts, remains of stems and seed shells), products of processing of carbon-containing substances (plastics, rubber, oil) and coal are used as a raw material for the carbon sorbents production [5-7]. The specific surface area of carbon sorbents, including those

obtained from lignite according to traditional schemes is about 600 m²/g [8].

In the papers [9-11] it was shown that alkaline activation (thermolysis in the presence of alkali) of different nature coals leads to the formation of a developed porous structure of carbon sorbents. Using sapropelite coals it is possible to obtain sorbents with a specific surface area up to 1200 m²/g [9]. Potassium hydroxide is the most effective alkali in the reaction of alkaline carbon activation [12]. It is also known in the literature that it is possible to obtain high-porous sorbents from anthracites (the specific surface area can reach 3000 m²/g) however, this result is only possible if a large KOH/coal weight ratio of 4/1 g/g is used [13]. Such a large amount of alkali generates a number of economic problems associated with the activating alkali cost and environmental problems associated with the necessity to remove a large amount of alkali from the product and then to decontaminate it.

For producing carbon sorbents it can be use a brown low metamorphic grade coal – a relatively cheap and available raw material [14, 15]. The high volatile matter and the presence of large amounts of oxygen containing groups make this coal effective for alkaline activation [11]. These features of lignites will allow us to use a small amount of alkali during activation, thereby increasing the environmental friendliness of the obtaining carbon sorbents technology.

Thus, it is possible to obtain carbon sorbents by the alkaline activation method with high values of the porous structure characteristics for solving ecological problems and absorption of impurities from water.

II. EXPERIMENTAL

Coal characteristic

The lignite of Kaychaksky mine of Tisulsky coalfield, located in Kemerovo region was used in the work. A sample

of coal with a particle size 0.2-0.5 mm was prepared by successive grinding and quartering from the initial coal and dried in air. For analytical analysis, an analytical sample with a particle size less than 0.2 mm was prepared from the coal sample. The analysis of the coal characteristics was carried out in accordance with standards ISO 602-74, 562-74 (technical analysis) and ISO 625-75 (elemental composition) and are presented in Table 1.

TABLE I. THE CHARACTERISTIC OF THE COAL OF TISULSKOYE COALFIELD

Technical analysis characteristic, %			Elemental composition, % per daf			Atomic ratio	
W^a	A^d	V^{daf}	C	H	(O+N+S)	H/C	O/C
11.5	10.4	46.7	70.4	4.4	25.2	0.75	0.27

According to the results of the technical analysis, it can be seen that the initial coal is characterized by a high ash content (10.4%) and humidity (11.5%), a high content of heteroatoms (25.2% per daf). Sulfur content analysis was carried out according to GOST 8606-93. It was found that there is no sulfur content in the organic mass of coal.

Preparation of carbon sorbents

The preparation of carbon sorbents was carried out by thermolysis of coal in the presence of potassium hydroxide according to the method described in the papers [9, 10]. The coal with a particle size of 0.2-0.5 mm was impregnated for 24 hours with a potassium hydroxide solution. The amount of potassium hydroxide was taken thus that the mass ratio of KOH/coal (R_{KOH}) was - 0.25g/g; 0.5g/g; 1g/g; 2g/g. Then the mixture was dried in a drying oven at 105 ± 5 °C. Thermolysis was carried out in closed crucibles in a muffle furnace. The heating process consisted of two stages: an increase in temperature at a rate of 7-9 °C / min up to 800 °C and isothermal exposition for 1 hour. Further crucibles were removed and placed in a desiccator for rapid cooling. The sintered carbonized residues were crushed to particle size <1 mm, then successively washed from the alkali with distilled water, 0.1 N hydrochloric acid and further with distilled water until neutral reaction. The washed carbon sorbents were dried to constant weight in a drying oven at 105 ± 5 °C. The resulting carbon sorbents are an inhomogeneous powder consisting of different sizes particles, therefore sorbents 0.2-0.5 mm in size have been prepared for the investigation of texture and sorption characteristics.

Microphotographs of the surface areas of the sorbents were obtained with the JEOL JSM – 6390 LV electron microscope (Figure 1).

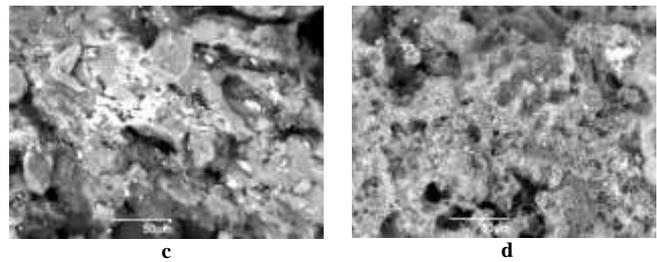
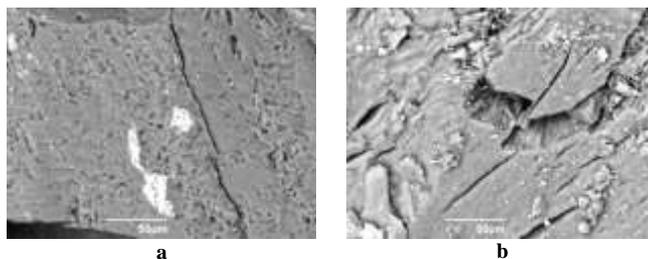


Fig. 1. Microphotographs of the surface of carbon sorbents obtained from the coal of Tisulskoye coalfield at different KOH/coal mass ratios (R_{KOH}) (a – without alkali; b – $R_{KOH} = 0.5g/g$; c – $R_{KOH} = 1g/g$; d – $R_{KOH} = 2g/g$)

The photographs show the evolution of the surface with an increase in the alkali amount upon the activation. In carbonizate obtained without alkali (Fig. 1a), the surface is almost flat with insignificant pits. When potassium hydroxide use, the sorbents surface begins to become more complicated, first cracks appear at $R_{KOH} = 0.5g/g$ (Fig 1b), as R_{KOH} increases to 1g/g, large cracks develop with a spongy wall structure (Fig 1c), and at $R_{KOH} = 2g/g$, almost the whole surface of the sorbent is spongy with round holes of different pore size (Fig. 1d).

Porous structure

Investigation of the porous structure of sorbents (specific surface – S_{BET} , m^2/g , total pore volume – V_{Σ} , sm^3/g , volume of mesopores – V_{me} , sm^3/g and micropores – V_{mi} , sm^3/g) was carried out with the ASAP-2020 analyzer. The porous structure characteristics of the sorbents was calculated by the analysis of nitrogen adsorption-desorption isotherms at 77 K in the region of equilibrium relative pressures of nitrogen vapors from 10^{-3} до 0.995 p/p₀. Before the measurements the sorbent samples were evacuated at 200 °C for 12 hours and a residual pressure $5 \cdot 10^{-3}$ mm Hg for complete removal of adsorbed impurities

The Brunauer-Emmett-Teller model (BET) was used to determine the specific surface area of the sorbents, the t-plot method with the Harkins-Jura equation was used to calculate the volume of micropores, the volume of mesopores was calculated by the Barrett-Joyner-Halenda method (BJH). These methods make possibility to calculate characteristics of the porous structure of carbon sorbents obtained on the native coals basis [16].

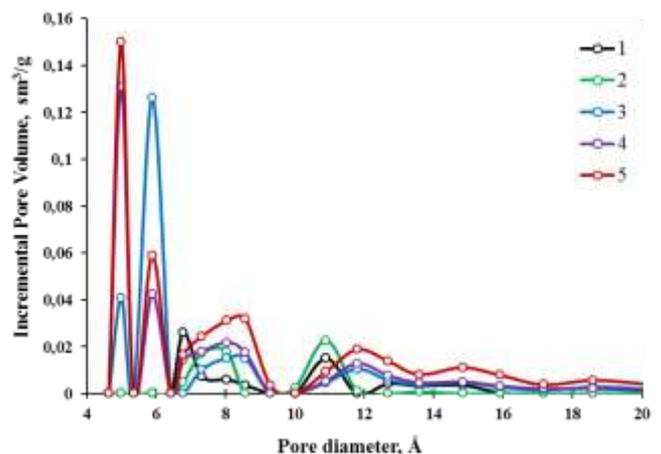


Fig. 2. Micropore size distribution (DFT method) of carbon sorbents obtained from the coal of Tisulskoye coalfield at different KOH/coal mass ratios (R_{KOH}) (1 – without alkali; 2 – $R_{KOH} = 0.25g/g$; 3 – $R_{KOH} = 0.5g/g$; 4 – $R_{KOH} = 1g/g$; 5 – $R_{KOH} = 2g/g$)

Using the software of the ASAP-2020 analyzer, a pore volume distribution (Incremental Pore Volume, sm^3/g) was constructed by DFT method for micropores with a diameter $<20 \text{ \AA}$ (by definition, $d = 2 \text{ nm}$ is the upper limit of the width of micropores).

The sorbent obtained without of potassium hydroxide (Fig. 2, curve 1) is characterized by a bimodal distribution of the micropores volume with peaks at pore diameters of 6.8 \AA and 10.8 \AA .

The distribution of the micropores volume for the sorbent obtained at the ratio $R_{\text{KOH}} = 0.25\text{g/g}$ is also characterized by two maxima (Fig. 2, curve 2), as for carbonizate without alkali: the first maximum expands and shifts from 6.8 \AA toward larger pore radii; the second maximum becomes higher than that in carbonizate without alkali and has the same position.

For the sorbent obtained by using KOH with the ratio $R_{\text{KOH}} = 0.5\text{g/g}$ (Fig. 2, curve 3) the distribution maxima observed for carbonizate without alkali are broadened and shifted towards an increase in the pore diameter (d) from 6.8 \AA to 8 \AA and from 10.8 \AA to 11.8 \AA , two additional modes with maxima at 5 \AA and 5.9 \AA appear on the distribution.

Similar trends appear for sorbents obtained at $R_{\text{KOH}} = 1\text{g/g}$ and $R_{\text{KOH}} = 2\text{g/g}$. For the sorbent obtained at $R_{\text{KOH}} = 1\text{g/g}$ (Fig. 2, curve 4), the positions of the maxima shift from $d = 6.8 \text{ \AA}$ to $d = 8 \text{ \AA}$ and from $d = 10.8 \text{ \AA}$ to $d = 11.8 \text{ \AA}$ as well as for the sorbent obtained at $R_{\text{KOH}} = 0.5\text{g/g}$.

For sorbents obtained at $R_{\text{KOH}} = 2\text{g/g}$ (Fig. 2, curve 5), the maximum is shifted from 6.8 \AA to 8.5 \AA , which is more significant than for sorbents obtained at $R_{\text{KOH}} = 0.5\text{g/g}$ and $R_{\text{KOH}} = 1\text{g/g}$, but the shift of the maximum from 10.8 \AA to 11.8 \AA does not change. In addition, for the sorbent obtained at $R_{\text{KOH}} = 2\text{g/g}$ the pore volume determined by the height of the distribution curves is larger.

In the region of small pore diameters, for all R_{KOH} , two different maxima appear at $d = 5 \text{ \AA}$ and $d = 5.9 \text{ \AA}$, the position of which does not depend on R_{KOH} . The height of these maxima varies: pores 5 \AA in diameter are most characteristic for sorbents with $R_{\text{KOH}} = 2\text{g/g}$, and pores with a diameter of 5.9 \AA are most characteristic for sorbents with $R_{\text{KOH}} = 0.5\text{g/g}$.

Static adsorption

The adsorption activity of carbon sorbents was measured by static sorption of phenol ($A_F, \text{mg / g}$), iodine ($A_I, \text{mg / g}$) and methylene blue ($A_M, \text{mg / g}$) from aqueous solutions. Measurement of sorption activity by iodine was carried out by titration of iodine, left after sorption, by sodium thiosulfate (GOST 6217-74). Measurement of sorption activity by methylene blue was carried out according to GOST 4453-74, measuring the concentration of the remaining dye after sorption in the solution on a spectrophotometer at the absorption band. Measurement of the sorption activity for phenol aqueous solution was carried out on the spectrophotometer using an indicator.

The results of measurements of adsorption activity and porosity characteristics of sorbents are presented in Table 2.

TABLE II. CHARACTERISTICS OF THE SORBENTS OBTAINED FROM THE COAL OF TISULSKOYE COALFIELD AT DIFFERENT KOH/COAL MASS RATIOS (R_{KOH})

N_{b}	$R_{\text{KOH}}, \text{g/g}$	$S_{\text{BET}}, \text{m}^2/\text{g}$	$V_{\Sigma}, \text{sm}^3/\text{g}$	$V_{\text{mi}}, \text{sm}^3/\text{g}$	$V_{\text{me}}, \text{sm}^3/\text{g}$	$A_I, \text{mg/g}$	$A_F, \text{mg/g}$	$A_M, \text{mg/g}$
1	0	215	0.10	0.070	0.006	71	9	9
2	0.25	265	0.10	0.090	0.006	174	40	21
3	0.5	760	0.39	0.250	0.120	450	125	30
4	1	910	0.49	0.295	0.195	510	180	90
5	2	1210	0.56	0.400	0.100	1040	250	205

III. RESULTS AND DISCUSSION

Table 2 shows the characteristics of the carbon sorbents porous structure (S_{BET} - specific surface area, V_{Σ} - total pore volume, V_{mi} - micropores volume, V_{me} - mesopores volume), as well as their sorption activities of iodine (A_I), phenol (A_F) and methylene blue (A_M) from aqueous solutions. An analysis of the data shows that an increase in the amount of potassium hydroxide introduced during thermolysis of the Tisulskoye field lignite leads to an increase in all texture and adsorption characteristics of the sorbents. However, the growth of most characteristics from the amount of introduced alkali is not linear.

Carbon sorbent obtained without alkali is characterized by small values of texture characteristics and has a specific surface area (S_{BET}) of $215 \text{ m}^2/\text{g}$. Nevertheless, there is almost no sorption from all the solutions studied, which indicates a low sorbent activity without alkaline activation.

When a small amount of KOH is added ($R_{\text{KOH}} = 0.25\text{g/g}$) the growth of the specific surface area is not high (23% increase) but adsorption characteristics increases by more than 2 times compared to the sorbent without KOH addition.

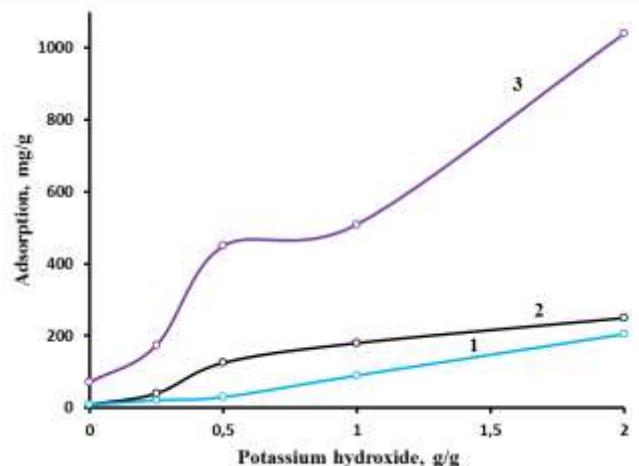


Fig. 3. Dependence of adsorption activities ($A, \text{mg/g}$) from KOH/coal mass ratios towards to aqueous solutions of iodine (3), phenol (2) and methylene blue (1) for sorbents obtained from the coal of Tisulskoye coalfield

If the ratio $R_{\text{KOH}} = 0.5\text{g/g}$ is used, there is a significant increase the specific surface area, the pore volume and sorption characteristics (Fig. 3). The least increase of sorption from the aqueous solution is observed for the methylene blue. The linear dependence of the adsorption activity of iodine deviates at the $R_{\text{KOH}} = 0.5\text{g/g}$ point, which may be due to the effective sorption of iodine in the pores

with a diameter of 5.9 Å (Fig. 2, curve 3) for this carbon sorbent.

Obtaining sorbents from lignite at $R_{\text{KOH}} = 1\text{g/g}$ leads to an increase in the sorbent texture characteristics and an increase in sorption by methylene blue. At this ratio the maximum mesopores volume is observed. However, the increase of pores and sorption characteristics is not as significant for the mass ratio $R_{\text{KOH}} = 0.5\text{g/g}$.

The sorbent obtained at $R_{\text{KOH}} = 2\text{g/g}$ have a special place. On the one hand, the use of a large amount of alkali during thermolysis increases the values of all textural and adsorption characteristics (the greatest increase is observed for the sorption of iodine from the aqueous solution); on the other hand, a large amount of alkali complicates the process of purification of the finished sorbent.

The use of a large amount of alkali suitable for obtaining sorbents with the highest characteristics, however the most practical value is the use of KOH/coal mass ratio not more than 1g/g.

IV. CONCLUSIONS

The using of Tisul lignite and the alkaline activation method leads to obtaining effective carbon sorbents for purifying of water from organic pollutants.

An increase of the KOH/coal ratio leads to the development of the porous structure of the carbon sorbent and an increase in the sorption of organic substances - iodine, phenol and methylene blue.

The porous structure of all carbon sorbents is characterized by the predominance of microporous.

The greatest increase in texture and sorption characteristics is observed for the case of increasing of the KOH/coal ratio from 0.25 to 0.5 g/g.

ACKNOWLEDGMENT

The work was carried out with the financial support of the Ministry of Education and Science of Russia within the framework of the agreement RFMEFI61317X0079.

The work was carried out with the equipment of the Analytical center of FRC CCC SB RAS.

The authors are grateful to S.A. Sozinov for microphotographs.

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