Study of the structure and morphology of carbon sorbents

I Yu Zykov, Y N Dudnikova, N I Fedorova, Z R Ismagilov and E S Mihaylova

Federal Research Center of Coal and Coal Chemistry, Siberian Branch of Russian Academy of Science,
18 Sovetskiy Ave., 650000, Kemerovo, Russia
E-mail: zyak.kot@mail.ru

Abstract. The paper presents the results of a study of the morphology of carbon sorbents from Kuzbass coal. Carbon sorbents were obtained by chemical activation of the initial coal with potassium hydroxide at a temperature of 800 °C and a KOH/coal ratio of 1 g/g. It was shown that alkaline activation has no significant effect on the ash content of the obtained carbon sorbents. The elemental composition of the obtained carbon sorbents practically does not differ and remains constant when the elemental composition of the initial coal changes. The morphology of the surface of the initial coal and sorbents was studied by the SEM method, and the different nature of the surface of carbon sorbents based on coal was shown. For carbon sorbents from bituminous coals of low stages of metamorphism, a spongy structure is characteristic, for carbon sorbents from bituminous coals of high stages, it is layered. The physicochemical characteristics of carbon sorbents were determined. A study was carried out for the content of total and water-soluble iron for the amount of water-soluble ash.

1. Introduction
Understanding the field of application of carbon sorbents is inextricably linked both with knowledge of their sorption properties in relation to various chemical substances, and their physicochemical properties. Carbon sorbents were obtained from coal of four grades of various degrees of metamorphism. The original coals were classified as long-flame "LF", gas "G", weakly caking "WC", lean "L", and the method of alkaline activation with potassium hydroxide was used as a method for obtaining sorbents. The method of alkaline activation allows one to obtain a developed specific surface area of sorbents from various grades of coal [1-5], and potassium hydroxide is the most effective alkali in this method of activation [6]. In [7], the sorption characteristics of the obtained sorbents in relation to organic pollutants were investigated. However, further introduction of carbon sorbents requires a more detailed study of not only sorption, but also their physicochemical properties.

The aim of this work is to study the structure, morphology of carbon sorbents and study the physicochemical characteristics of sorbents obtained by alkaline activation from coals of varying degrees of metamorphism.

2. Experimental

2.1. Preparation of carbon sorbents
Carbon sorbents were obtained by the alkaline activation method; the method of obtaining sorbents from [1, 8] was chosen as the basis of the method. When obtaining sorbents, low-ash coal with a particle size of 0.2-0.5 mm was used, and potassium hydroxide powder was used as an alkaline reagent. The mixing of coal and alkali was carried out at a mass ratio of alkali/coal \( R_{KOH} = 1 \) g/g. A detailed description of the process of obtaining carbon sorbents from coal of Kuzbass is given in [7].

2.2. Characteristics of carbon and sorbents
For analytical studies, samples with a particle size of less than 0.2 mm were prepared from the initial coal of each grade, as well as sorbents derived from them. Characteristics studies were carried out in accordance with the standards ISO 602–74, 562–74 (technical analysis) and ISO 625–75 (elemental composition). The values of the characteristics of the initial coals and the obtained sorbents are presented in Tables 1 and 2.

| Grade | Initial coal | Carbon sorbent |
|-------|--------------|----------------|
|       | \( W_\infty, % \) | \( V_{daf}, % \) | \( W_\infty, % \) | \( V_{daf}, % \) | \( A_d, % \) |
| «LF»  | 4.5          | 43.3           | 1.2           | 1.8           | 5.4   |
| «G»   | 2.2          | 43.3           | 1.7           | 9.0           | 6.8   |
| «WC»  | 1.9          | 19.5           | 1.6           | 4.7           | 6.2   |
| «L»   | 0.5          | 14.1           | 2.3           | 7.4           | 6.8   |

Table 1. Technical analysis of initial coals and sorbents obtained by alkaline activation

| Grade | Elemental composition, % per daf | Atomic ratio | Elemental composition, % per daf | Atomic ratio |
|-------|---------------------------------|--------------|---------------------------------|--------------|
| «LF»  | 80.2 5.6 14.2                   | 0.84/0.13    | 83.5 0.40 6.1                   | 0.05/0.05    |
| «G»   | 81.8 5.6 12.6                   | 0.82/0.12    | 87.3 0.45 6.1                   | 0.06/0.05    |
| «WC»  | 87.5 4.5 8.0                    | 0.82/0.07    | 82.6 0.55 6.1                   | 0.09/0.05    |
| «L»   | 90.3 4.1 5.6                    | 0.45/0.05    | 84.3 0.62 6.1                   | 0.08/0.05    |

Table 2. Elemental composition of initial coals and sorbents based on them

Technical analysis data indicate not high ash content of the original bituminous coals (3.1-8.4%). After alkaline activation and washing with hydrochloric acid to remove unreacted potassium hydroxide, the ash content of the obtained sorbents decreases. However, for "G" grade coal, the resulting sorbent has an ash content of 9%, such an increase can be associated with the origin of this coal and the presence of hardly soluble ash-forming elements in it.

The yield of volatile sorbents obtained practically does not differ and amounts to 67%. Such values indicate an incomplete stage of coke structuring at temperatures of 800-820 °C [9], which, in turn, is necessary for highly porous carbon materials.

The elemental composition of the obtained carbon sorbents differs significantly from the initial coals, but practically does not differ for various carbon sorbents. The amount of carbon in the sorbents is close to 94.0% and heteroatoms to 6.2%, regardless of the origin of the original coal. Despite practically the same elemental composition, the obtained sorbents have different specific surface area determined by the method of work [10], for example, the specific surface of the sorbent from coal "LF" (1770 m²/g) [7] is 1.85 times larger than the surface of the sorbent from coal "L" (960 m²/g) [7].
2.3. Surface morphology
The study of the surface morphology of the samples of coals and sorbents based on them was carried out on a JEOL JSM-6390 LV scanning electron microscope located at the Center for Collective Use of the Federal Research Center of CCC SB RAS, micrographs were obtained in reflected and secondary electrons.

Figures 1-4 show electronic photographs of initial coals of grades "LF", "G", "WC", "L" and carbon sorbents obtained by the method of alkaline activation. Figure 5 shows micrographs of the surface of carbon sorbents at magnification.

**Figure 1.** Micrographs of the initial coal of the "LF" grade (a) and carbon sorbents obtained by activation with potassium hydroxide (R_{KOH} = 1 g/g) (b)

**Figure 2.** Micrographs of the initial coal of the "G" grade (a) and carbon sorbents obtained by activation with potassium hydroxide (R_{KOH} = 1 g/g) (b)
Figure 3. Micrographs of the original coal of the "WC" grade (a) and carbon sorbents obtained by activation with potassium hydroxide ($R_{\text{KOH}} = 1 \text{ g/g}$) (b)

Figure 4. Micrographs of the initial grade L coal (a) and carbon sorbents obtained by activation with potassium hydroxide ($R_{\text{KOH}} = 1 \text{ g/g}$) (b)
Images of the surface of LF coal and a sorbent based on it, obtained using the method of scanning electron microscopy, are shown in Figures 1a and 1b, respectively. As a result of activation with potassium hydroxide, the surface of the coal acquires a spongy appearance (Figure 1b). In some cases, a developed porous system is observed only on individual faces of a particle, while others are characterized by a low surface concentration of pores. This feature can be explained by the layered structure of the initial coal particles. At higher magnification, it becomes possible to see macropores on the surface (Figure 5a). The pore outlet to the surface has a round or oval shape with sizes up to 1 micron. During high-temperature activation processes, the organic matter of coal is partially melted with the release of volatiles and subsequent graphitization, which causes a round and oval appearance of the pores. Also visible on the surface are dark spots associated with pores near the surface without direct exit.

Images of coal grade "G" used to obtain the sorbent and the carbon sorbent itself are shown in Figure 2. The surface of the sorbent in the process of alkaline activation acquires a spongy structure (Figure 2b). The formation of pores on different faces is not uniform due to the layered structure of the original coal. In the process of gas evolution during heating and destruction of the organic mass of coal under the action of potassium hydroxide, the formation of pores of various diameters occurs (Figure 2b). At greater magnification, the surface of the carbon sorbent obtained from coal grade "G" can be examined in detail (Figure 5b). Pores with a diameter of less than 0.5 mm are visible on the surface; these pores are mainly located in groups of several pieces, creating a system of pores with different diameters. Apparently, the process of gas evolution during the preparation of the sorbent proceeded uniformly and as a result of which some bridges in the coal structure were preserved. Dark spots of closed pores are visible on the surface of the carbon sorbent made of G grade coal (Figure 2b).

Figure 3 shows images of WC grade coal and carbon sorbent obtained on its basis. The particles of the original coal "WC", shown in Figure 3a, differ from the particles of other coals by their relatively sharp and even edges. The side faces of some of the particles of "WC" coal (Figure 3a) are formed by a stack of graphite-like layers, which indicates a layered structure of coal. Alkaline activation of "WC" coal with the formation of a sorbent leads to a violation of the smooth structure of the particles of the original coal. Figure 3b shows particles of a carbon sorbent, whose faces are represented by open graphite-like planes, smooth planes of the initial coal (Figure 3a) are practically absent. An increase in the magnification of the surface of the carbon sorbent from coal "WC" gives a more detailed idea of its defects (Figure 5c). The main surface defects are cracks. Round pores typical for carbon sorbents from LF and G coals. In the sorbent based on coal "WC" is not observed.

Micrographs of "L" grade coal and sorbent obtained from it by activation with potassium hydroxide are shown in Figure 4. Uneven chips are present in the "L" coal particles, and the layered structure of coal can be seen on the side faces (Fig. 4a). Figure 4b shows an electron micrograph of a carbon sorbent fired from "L" grade coal. There is no significant change in the appearance of the particles in
comparison with the original coal (in contrast to the sorbents described above). Upon activation of coal "L", a local process of defect formation is observed on the side faces of the particles (Figure 4b), however, the low yield of volatiles of the initial coal and a high degree of graphitization do not allow obtaining a sufficiently developed defect structure. An enlarged image of the surface, shown in Figure 5d, shows the build-up of the mineral component, as well as the presence of cracks and minor defects in the layered structure.

3. Physicochemical characteristics

It is known that important characteristics of active carbons used as adsorbents for the purification of liquid media are their physicochemical properties. These mainly include the content of total ash (usually 2-15%), water-soluble ash (usually 0.2-3.0%), total iron in terms of Fe\textsuperscript{3+} (usually 0.30-0.64%), water-soluble iron compounds (usually absence) [11].

Determination of the total ash content in carbon sorbents was carried out in accordance with GOST 12596-67 “Active coals. Method for determining the mass fraction of ash”. The essence of the method consists in ashing a sample in a muffle furnace, calcining the ash residue to constant weight at a temperature of 800 ± 25 °C, and weighing the residue.

Determination of water-soluble ash in carbon sorbents was carried out according to the method described in GOST 4453-74 “Powdered active clarifying wood coal. Technical conditions”. The essence of the method is to determine the weight of the dry residue after evaporation of the solution obtained by boiling the test sorbent in distilled water.

Determination of the total iron content in carbon sorbents was carried out in accordance with GOST 4453-74 “Active wood powder clarifying coal. Specifications” by sulfosalicylic method.

Determination of water-soluble iron in carbon sorbents was carried out according to the method described in GOST 4453-74 “Powdered active clarifying wood coal. Technical conditions”. The essence of the method lies in the qualitative determination of iron by adding potassium hexacyanoferrate (III) to the acidified solution obtained after boiling the sorbent sample.

The main indicators of the physicochemical properties of the studied carbon materials are shown in Table 3. The data presented show that the studied sorption materials have a fairly low ash content not exceeding 15%.

The content of water-soluble ash (A\textsubscript{ws.}) for all obtained sorbents is less than 3.0%. For a carbon sorbent made of LF grade coal, the value is minimal and is less than 0.6%; for sorbents made from coals "G" and "WC" - about 1%. In all samples of the studied carbon sorbents, the numerical values of water-soluble ash are less than 1/3 of the values of the total ash.

| Coal grade | S\textsubscript{BET} [7], m\textsuperscript{2}/g | Total ash A\textsubscript{d}, % | Water-soluble ash A\textsubscript{ws.}, % | Iron content Fe\textsuperscript{3+}, % | Water-soluble iron |
|------------|------------------|-----------------|-----------------|-----------------|----------------|
| «LF»       | 1770              | 1.8             | 0.5             | 0.01            | Present        |
| «G»        | 1730              | 9.0             | 1.1             | 0.24            | Present        |
| «WC»       | 1320              | 4.7             | 1.4             | 0.11            | Present        |
| «L»        | 960               | 7.4             | 2.6             | 0.01            | Present        |

The total iron content in the studied carbon sorbents is rather low and does not exceed 0.64%. The minimum amount of this component (0.01%) is determined in the carbon material made of coals of grades "LF" and "L", in the sorbent made of coal of grade "G" the iron content is maximum and is 0.24%. It should be noted that against the general background of a rather low content of total iron in all samples of the studied carbon sorbents, the presence of water-soluble forms of iron, both bivalent and trivalent, was revealed. Thus, the measured values of physical and chemical characteristics make
it possible to recommend the obtained carbon sorbents for the purification of aqueous media from harmful chemical compounds.

4. Conclusion
By the method of alkaline activation with potassium hydroxide at a KOH/coal ratio of 1 g/g and a temperature of 800 °C, carbon sorbents were obtained from coals of grades "LF", "G", "WC", "L".

The technical characteristics and elemental composition of the obtained carbon sorbents have been investigated. It has been shown that the alkaline activation method described in the work does not significantly affect the ash content of the obtained carbon sorbents, and, therefore, to obtain low-ash sorbents, it is necessary to use low-ash coal grades without hardly soluble ash-forming elements. The elemental composition of the obtained carbon sorbents practically does not differ and remains constant when the elemental composition of the initial coals changes.

The morphology of the surface of the initial coal and sorbents was investigated by the SEM method. The different nature of the surface of carbon sorbents based on coal is shown. For sorbents from coals of low stages of metamorphism, a spongy structure is characteristic, for carbon sorbents from coals of high stages, it is layered.

The physicochemical characteristics of the sorbents have been determined. Water-soluble iron was found, however, the total iron contains less than 0.24%, and water-soluble ash less than 2.6%. The values of the physicochemical characteristics of the obtained sorbents make it possible to recommend them for water purification.

Acknowledgments
The work was carried out within the framework of the state assignment of the Federal Research Center of Coal and Coal Chemistry SB RAS (project AAAA-A17-117041910151-9).

When performing the work, the equipment of the Center for Collective Use of the Federal Research Center of Coal and Coal Chemistry SB RAS was used.

References
[1] Zykov I Yu et al 2017 Chemistry for Sustainable Development 25(6) 621-5
[2] Kozlov A P и др 2018 Вестник Кузбасского государственного технического университета 3(127) 93-101
[3] Kozlov A P et al 2018 Bulletin of the Kuzbass State Technical University 3 (127) 93-101
[4] Nikitin A P et al 2018 Coke and Chemistry 12 4-10
[5] Kozlov A P et al 2017 Bulletin of the Kuzbass State Technical University 4 (122) 170-6
[6] Marsh H and Yan S Denis 1984 Carbon 22(26) 603-11
[7] Zvekov A A et al. 2019 Cokе and Chemistry 6 22-7
[8] Manina T S, Fedorova N I and Ismagilov Z R 2016 Coke and Chemistry 59(7) 260-3
[9] Fedorova N I and Tryasunov B G 2014 Bulletin of the Kuzbass State Technical University 4 (104) 93-7
[10] Kozlov AP et al 2017 Bulletin of the Kuzbass State Technical University 6 (124) 197-204
[11] Mukhin VM and Klushin VN 2012 Production and Use of Carbon Adsorbents (Moscow: Russian Chemical-Technological University named after D.I.Mendeleev) 308 p