

Article

Influence of Raw Materials and Technological Factors on the Sorption Properties of Blast-Fuel Coke

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Abstract: The influence of raw material factors (component composition of batches, petrographic characteristics, indicators of proximate and plastometric analyses, granulometric composition) and technological factors (coking period, process temperature) on the sorption properties of the carbonized product (coke) was studied. Based on the research results, it is shown that such characteristics of coke as low humidity and ash, minimal yield of volatile matters, developed pore system and low cost make its use as a sorbent promising and economically justified. The obtained equations for predicting the sorption capacity by alkali and acid and adsorption activity by iodine, taking into account the content of vitrinite and the yield of volatile matters coal batch. They are characterized by high approximation coefficients r (0.912 and 0.927 and 0.937, respectively), so they can be recommended for predicting the indicated indicators.

Keywords: carbon adsorbents; coke sorbent; sorption capacity; adsorption activity; activation



Citation: Miroshnichenko, D.; Shmeltser, K.; Kormer, M.; Sahalai, D.; Pyshyev, S.; Kukhar, O.; Korchak, B.; Chervinsky, T. Influence of Raw Materials and Technological Factors on the Sorption Properties of Blast-Fuel Coke. *ChemEngineering* **2024**, *8*, 30. <https://doi.org/10.3390/chemengineering8020030>

Academic Editors: Vasile Lavric and José P. Coelho

Received: 9 November 2023

Revised: 8 February 2024

Accepted: 26 February 2024

Published: 5 March 2024



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1. Introduction

Carbon adsorbents are widely used in the chemical, petrochemical and biotechnological industries. Activated coal is also necessary for solving environmental problems that have arisen as a result of man-made activities. Treatment with adsorbents is based on physical adsorption and sometimes chemical adsorption can be used. High-molecular-weight porous carbon materials with a developed specific surface area have the ability to effectively and selectively adsorb molecules of substances of various chemical natures from gas, vapor-gas and liquid media. Adsorption methods are characterized by simplicity of apparatus design and relatively low operating costs. Modern technologies for cleaning from organic inclusions include biological, physical, physicochemical, chemical and adsorption methods. The latter are quite effective when using materials with high adsorption activity. In addition, the adsorption method is a relatively simple technological process, unlike chemical and biological methods. The high adsorption capacity of activated carbon is related to its internal porosity and depends on the specific surface area, pore volume, and pore size distribution. Typically, activated carbons are microporous, but the need for meso- and macroporous pores meso- and macroporous pores are necessary because they provide access for the adsorbate to the interior of the carbon particle. Consequently, carbon sorbents are used to purify water from dyes, phenols, various metal ions, and to purify gases. The efficiency of the adsorption process depends on the physicochemical properties of the sorbent (bulk density, specific surface area, pore volume, and mechanical strength) [1–4].

Therefore, the possibility directed influence on the formation of the porous structure carbon sorbents, improvement of their physico-mechanical and adsorption properties, obtaining a product with a given set of characteristics is a promising direction of research.

In the production of various brands activated carbon, one of the determining factors is the raw material, its composition and properties [1]. Traditional raw materials for the production of activated carbons are wood peat, lignite, hard coal, and nut shells and fruit seeds. It is obvious that raw materials derived from plant waste have a significant advantage due to their low cost and environmental friendliness compared to synthetic polymers and natural carbon. The most large-tonnage raw materials for the production of activated carbon are hard and brown coal. The economic feasibility of using a particular raw material is also determined by the availability of natural resources [5,6]. A significant advantage of using an inexpensive carbon-based material as an adsorbent is that it can still be used as a fuel, thus overcoming disposal problem [6]. It is noted in the work that the fine fraction of lignite with a size of 212–425 μm without prior physical and chemical treatment has a high adsorption capacity by methylene blue. Thus, the values of adsorption capacity of two untreated lignite samples calculated using the Langmuir isotherm were 286 and 370 mg/g, which was higher than that of activated carbon based on coconut shell (167 mg/g), but lower than that of activated carbon based on coal (435 mg/g) [7].

The authors of the study [5] also note that the lignite fraction with a size of 1–2 mm without preliminary preparation has a high adsorption capacity for copper ions, which makes this material attractive for use in wastewater treatment processes.

It is also promising to use semi-coke, which is formed during the gasification of low rank coal (LRC) [8]. Semi-coke (SC) has a high carbon content, is usually characterized by low moisture content, minimal yield of volatile matters, low adhesiveness and the presence of micro-, meso- and macropores. The specified characteristics determine its potential as a high-value sorbent, the use of which has both ecological advantages and economic feasibility.

Foreign companies (USA) prefer shiny bituminous coal with the following parameters: yield of volatile matters—from 27–39%, ash content—no more than 3%, minimum ash melting temperature—1370 $^{\circ}\text{C}$, total sulfur content—0.5% [9].

The work [8] notes the possibility of obtaining a conditioned carbon sorbent from Donetsk coal rank D in the presence of stages of thermal oxidation, carbonization and activation in a stationary layer. At the same time, the possibility of obtaining carbon sorbents using a simplified technology (without the stage of thermal oxidation) in chamber layer furnaces with the use of a retort to activate carbonizate was revealed. Also, as a raw material base for the production of activated coal in Ukraine, coal of ranks D and DG from the mines «Trudivska» and «Luhanska» was proposed. The adsorbents obtained from this coal are suitable for cleaning oil-emulsion wastewater, for adsorption of surface-active substances from wastewater, and clarification of sugar solutions. In addition, studies have shown the possibility of using adsorbents obtained from this coal for the purification of wastewater from petroleum products.

Drozyk I.D. notes that activated carbon from Donetsk low rank coal is characterized by high adsorption activity in relation to substances soluble in carbon tetrachloride, petroleum products, phenol, toluene, as well as copper ions, which ensures high efficiency of the use of these sorbents in industrial wastewater treatment processes [9].

In laboratory conditions, the possibility of obtaining activated carbon from gas coal of Western Donbas with an increased content of chlorine and sodium compounds (salted coal) has been proven. Such sorbents were effective in the adsorption of phenol from dilute aqueous solutions [9].

In the production of activated carbon, carbon-containing raw materials are first subjected to carbonization—heating to high temperatures without access to air. The obtained carbonized product is activated during steam treatment at a high temperature of 800–1000 $^{\circ}\text{C}$, as a result, a sorbent with a specific pore structure is obtained, which determines high adsorption properties.

The quality of the sorbent determines both the sorption capacity the active surface and the nature of the porosity. The literature reflects a number of judgments about the nature of the development the porous structure in activated carbon. Thus, the microporous structure of activated carbon is related to certain states of the graphite body, and the transition and macroporosity depend on the nature of the source material and the conditions for obtaining the sorbent. In order to obtain a sorbent with developed transitional porosity, it must be developed in the process of carbonization [10].

The process forming the porosity of raw coal during thermal decomposition depends on many factors, which include: the yield of volatile matters, the composition of the released gas, the temperature regime of carbonization, etc. There is no criterion that would allow to predict in advance the porosity of raw coal depending on the properties of the raw material and the heat treatment mode. This leads to the need for experimental selection of optimal processing conditions [11].

As is known, the structure of the substance and the porosity of the coke depend on the characteristics of the original coal (yield of volatile matters) and the thermal regime and speed of coking [11–19].

There is also a general trend that indicates that the minimum porosity corresponds to the optimum of the vitrinite reflectance index R_{0max} and the maximum strength of coke after reaction with CO_2 . Concentration of vitrinite significantly affects the formation of porosity. The porosity of coke increases after the reaction with CO_2 , which leads to a weakening of its structure. This increase in porosity depends on the degree of metamorphism of the coal and the microtexture of the coke. The loss of coke strength after the reaction is higher with a higher content of coal of low stages of metamorphism in the batch [14].

In work [19] data are given that the micropore surface of coke from the coal fraction enriched with vitrinite (coke from vitrinite) is significantly lower than coke from the fraction enriched with inertinite (coke from inertinite), which is related to the surface area of micropores, which increases almost linearly with an increase in the content macerals of the inertinite group in coal. The degree orderliness of the coke structure depends on the maceral composition and the rank of the original coal. Thus, coke from vitrinite has a higher degree of order of the L_c structure than coke obtained from inertinite. with an increased content of inertinite in the initial batch, the microporosity of the coke will increase and, accordingly, the reactivity will increase due to the increase in the reaction surface. Coke from inertinite has lower L_c values than coke from vitrinite, due to the lesser ordering of its carbon structure.

One of the significant advantages of activated carbon is the possibility of improving its properties by modifying it with various metals. This makes it possible to obtain sorbents for extracting certain types of substances [7]. Thus, in works [20] it is noted that the efficiency of removing chromium ions from wastewater reaches 95% when using a carbon-containing sorbent, which is a heterogeneous composite of zero-valent iron and activated carbon.

The positive experience of improving the characteristics of sorbents when they are modified with alkaline earth metals (Ba, Ca, Mg) is also illustrated by research results [7,21].

The authors [22] presented the results of using a carbon sorbent based on cellulose obtained from waste paper and modified with particles of iron oxide and graphene oxide for solid-phase extraction of antibiotics.

Pyrolysis of a mixture lignite with poplar leaves in a ratio of 3:2 in a nitrogen atmosphere and subsequent activation modification of the obtained coal with solutions zinc chloride and iron chloride in the reactor makes it possible to obtain a carbon sorbent with a high adsorption capacity for removing lead and cadmium ions [23].

The work [8] analyzed the experience using activated anthracite produced in Ukraine, obtained from anthracites with a different structure of the porous space by modifying the surface with metal ions and salts, as an ammonia absorber. Moreover, it is shown that when using different methods of modification, a high absorption capacity coal from the gas phase and solutions was achieved with relatively small amounts of the activating additive.

Two stages of raw material processing (carbonization + activation) and ensures the formation of the required structural and physicochemical properties of the product. Among the practical methods of activation of carbon-containing materials, the following options can be distinguished [6,23,24]: chemical activation (treatment with acids—HCl, H₃PO₄ or alkalis—KOH, NaOH); physical activation (hot steam treatment). Chemical activation methods of carbon-containing materials are widely used to produce carbon-containing materials. Chemical methods allow to obtain adsorbents with strictly specified parameters of porous structure and high adsorption properties. Some chemical activators—alkali metal hydroxides, inorganic acids—contribute to the development of the porous structure of carbon-containing materials in the process of thermolysis. The interest in alkaline activation of carbonaceous raw materials is also related to the fact that with the fact that the materials obtained in this way have a highly developed microporous structure. Such carbon-containing materials can compete with carbon materials, the methods of whose methods are much more complicated technologically and economically unprofitable.

Interaction with oxidizing reagents, such as H₂O₂, O₃, and KMnO₄, is also a promising method of activation [6,24]. According to [25], in the process of such modification, the material acquires high hydrophilicity due to an increase in the number of acidic functional groups.

For the coke fraction with a size of 2–5 mm, the authors [3] indicate that steam activation at a temperature of up to 850 °C with a process duration of 120 min is optimal. At the same time, the average value of the specific surface increases eight times compared to the raw material. Thus, it was established that the obtained activated carbon has a porous structure consisting of meso- and macropores, and the value of the specific surface is ~301 m²/g. The obtained sorbent is characterized by a high sorption capacity for removing phenol (74.94 mg/g) and methylene blue (145 mg/g) from aqueous solutions, and when it is used to clean tap water, the content of calcium, sulfates and hydrocarbons decreases and the total mineralization.

In [26], the authors present the results of positive experience using coke for the adsorption of gold ions from a cyanide solution. Preparation of gold-bearing ore includes crushing, grinding, pelletizing using a pelletizing additive (mainly Portland cement), and sintering. The resulting pellets of 15–30 mm in size are sent for heap leaching. Gold leaching is carried out with the use of solvent reagents (mainly alkaline solutions of NaCN 1.2–1.5 g·L⁻¹ at pH 10–11.5 are used). The concentration of Au (I) extracted from the productive solutions depends on a number of factors:—permeability of the reagent into the leached material, its porosity, composition of the solvent reagent, the structure of the leached ore materials (gold-bearing minerals and porous ore bodies cut by cracks, etc.), the form of gold in them (free, bound, dispersed, etc.). Then follows the processing of the obtained solutions by sorption methods (on ion exchange resins or activated carbons) for the separation of metals. The process is accompanied by regeneration of adsorbents and eluate with separation of cathode precipitate containing gold. Gold is also extracted from the eluates by cementation on electronegative metals. To increase the degree of gold recovery, it is important to find an effective and inexpensive sorbent [27–37]. In the research [36] adsorbent was obtained by activating the coke fraction with a size of 2–5 mm with superheated steam at 850 °C for 30 min. The qualitative characteristics of the new coke adsorbent are as follows: ash content 4.5%; adsorption activity remove to iodine 52%; specific surface, 600 m²/g, a porous structure is developed, in which round or oval-shaped pores with a cross-sectional size of up to 20 mm are mostly present, and the total pore volume is 0.4 cm³/g. Elemental composition according to X-ray spectral analysis, %: C-92.1; O-6.18; Na-0.13; Mg-0.14; Al-0.3; Si-0.25; S-0.45; Ca-0.28; Fe-0.18. Coke sorbent was tested for the extraction of gold from 200 dm³ of a 0.06% solution of sodium cyanide NaCN containing, mg/dm³: 2.6 Au, 0.42 Ag, 490 Cu. The total amount of noble metals (Au + Ag) adsorbed from the solution was 99.99%, while gold ions were 94%. The maximum adsorption capacity of coke sorbent for gold reached 2900 g/t.

Work [28–38] illustrates the results of using the method of low-temperature chemical treatment of shale semi-coke for its activation, which provides an increase in the surface area by 6–11 times compared to untreated material. Thus, using acid (HCl) and alkali (KOH) treatment, the surface area of semi-coke samples was increased from 15 m²/g (pyrolyzed semi-coke) to more than 150 m²/g after washing the samples with hydrochloric acid. According to research data, double treatment with hydrochloric acid HCl was the most effective, which provides a sorbent with a high adsorption capacity, which exceeds coal-based analogues (1 g of carbon present in chemically activated semi-coke can adsorb approximately 120 mg of SO₂ gas at 40 °C).

The purpose of this work is to research the sorption properties of cokes and assess the possibility of using them as adsorbents. As can be seen from the review, one of the sources of raw materials for the production of coal sorbents is low-metamorphosed high volatile coal, the resources of which are sufficient in Ukraine. This coal in a very limited volume is used in the batch for coking in the production of metallurgical coke, so the possibility of its qualified use for the production of sorbents is promising. The coking is essentially a process of carbonization of coal raw materials. Thus, the analyze the influence of raw material factors (composition of batches, petrographic characteristics, indicators of proximate and plastometric analyses, granulometric composition) and carbonization conditions (coking period, process temperature) on the sorption properties of the carbonized product is actuality task.

2. Materials and Methods

In this work, coal batches of different component composition were used for research (Table 1), their main characteristics and technological properties are presented in Tables 2 and 3. The conditions of coking of the specified coal charges are illustrated by the data in Table 4.

Table 1. Composition of coal batches.

Blend	Batch Component (Coal Ranks), %						PS	KS
	G1	G2	GZhP	GZh	Zh	K		
1	-	-	6	44	6	16	13	15
2	-	10	3	33	15	2	14	23
3	-	-	20	43	10	9	9	9
4	30	25	4	10	4	27	-	-
5	34	23	5	-	10	28	-	-
6	24	29	10	-	7	30	-	-
7	35	8	5	23	-	29	-	-
8	35	8	5	23	-	29	-	-
9	-	35	-	35	-	30	-	-
10	-	31	-	12	-	57	-	-
11	-	31	-	12	-	57	-	-
12	-	72	-	-	-	28	-	-
13	-	45	-	-	-	55	-	-
14	-	43	-	-	-	57	-	-
15	26	46	-	-	-	28	-	-

Sampling of coal concentrates and coal batch was carried out manually from the surface of the stopped conveyor using a device (frame). A frame was installed on the conveyor belt, which was two parallel walls vertically located at a distance that was at least two sizes of the maximum piece.

The frame was immersed in the coal raw material to the transport surface perpendicular to the flow direction. The selected sample was delivered to the coal testing room for further preparation for the test. The preparation included successive operations of grinding, reduction, and separation of the sample. Equipment and tools for sample preparation met the requirements of State standard of Ukraine 4096–2002: “Brown coal, hard coal, anthracite,

combustible shale and coal briquettes. Methods of sample selection and preparation for laboratory tests" [29].

Table 2. Proximate, plastometric and petrographic analyses of coal batches.

Blend	Proximate Analysis, %					Plastometric Parameters, mm		Petrographic Characteristics, %	
	W _t ^r	A _t ^d	S _t ^d	V ^d	V ^{daf}	x	y	Mean Vitrinite Reflection Coefficient, R _o , %	Contents of Vitrinite, V _t , %
1	9.9 ± 0.5	8.5 ± 0.2	0.51 ± 0.05	27.2 ± 0.3	29.7 ± 0.3	39 ± 3	14 ± 1	1 ± 0.02	71.6 ± 5
2	8.6 ± 0.5	8.7 ± 0.2	0.96 ± 0.05	27.4 ± 0.3	30 ± 0.3	36 ± 3	17 ± 1	1.01 ± 0.03	74.9 ± 5
3	9.1 ± 0.5	9.7 ± 0.2	0.56 ± 0.05	29 ± 0.3	31.9 ± 0.3	35 ± 3	18 ± 1	0.95 ± 0.02	71.6 ± 5
4	10 ± 0.5	11.3 ± 0.2	1.59 ± 0.05	31.1 ± 0.3	35.1 ± 0.3	43 ± 3	12 ± 1	0.86 ± 0.02	77 ± 5
5	10 ± 0.5	12 ± 0.2	1.54 ± 0.05	30.8 ± 0.3	35 ± 0.3	41 ± 3	13 ± 1	0.91 ± 0.02	86.8 ± 4
6	7.8 ± 0.5	11.1 ± 0.2	1.47 ± 0.05	30.3 ± 0.3	34.1 ± 0.3	40 ± 3	15 ± 1	0.85 ± 0.02	81.7 ± 4
7	8.2 ± 0.5	12 ± 0.2	1.82 ± 0.05	31.5 ± 0.3	35.8 ± 0.3	42 ± 3	14 ± 1	0.83 ± 0.02	84.6 ± 4
8	8.5 ± 0.5	10.3 ± 0.2	1.62 ± 0.05	31.3 ± 0.3	34.9 ± 0.3	41 ± 3	15 ± 1	0.83 ± 0.02	78.7 ± 5
9	9.1 ± 0.5	10.2 ± 0.2	1.9 ± 0.05	31 ± 0.3	34.5 ± 0.3	36 ± 3	18 ± 1	0.87 ± 0.02	77.2 ± 5
10	8.8 ± 0.5	7.8 ± 0.2	1.17 ± 0.05	30.2 ± 0.3	32.8 ± 0.3	35 ± 3	16 ± 1	1 ± 0.02	87 ± 4
11	8.6 ± 0.5	7.4 ± 0.2	1.24 ± 0.05	30.5 ± 0.3	32.9 ± 0.3	32 ± 3	16 ± 1	0.97 ± 0.02	86.1 ± 4
12	8 ± 0.5	9.7 ± 0.2	1.6 ± 0.05	31.8 ± 0.3	35.3 ± 0.3	38 ± 3	13 ± 1	0.88 ± 0.02	79 ± 5
13	9.2 ± 0.5	8.1 ± 0.2	1.16 ± 0.05	28.6 ± 0.3	31.1 ± 0.3	39 ± 3	18 ± 1	0.95 ± 0.02	73.1 ± 5
14	8.2 ± 0.5	8.4 ± 0.2	1 ± 0.05	28.1 ± 0.3	30.7 ± 0.3	35 ± 3	14 ± 1	1 ± 0.02	82 ± 4
15	9.4 ± 0.5	9.2 ± 0.2	1.48 ± 0.05	34.2 ± 0.3	37 ± 0.3	44 ± 3	14 ± 1	0.83 ± 0.02	80.1 ± 5

Table 3. Granulometric composition of coal batches.

Blend	Granulometric Composition (%) by Class (mm)						
	10	10–6	6–3	3–1	1–0.5	0–0.5	0–3
1	1.6	7.1	10.4	29.9	17.3	33.7	80.9
2	1.5	6.9	11	29.7	16.4	34.5	80.6
3	2	7.6	11.7	28.9	17.8	32	78.7
4	1.9	6.7	10.8	29.8	17.4	33.4	80.6
5	1.6	7.1	11.4	29.6	17.7	32.6	79.9
6	1.5	7.1	10.4	29.5	18.6	32.9	81
7	1.7	7.3	11.9	29.8	16.8	32.5	79.1
8	1.7	7.6	12	30.1	16.8	31.8	78.7
9	1.6	7.6	11.4	29	16.9	33.5	79.4
10	1.1	6.2	9.5	30.2	17.9	35.1	83.2
11	1.4	7.3	8.1	29.9	19.2	34.1	83.2
12	1.9	8.4	11.3	30	17.8	30.6	78.4
13	0.9	6.9	9.1	28.6	20	34.5	83.1
14	2.1	7.1	9.2	29.9	18.9	32.8	81.6
15	1.9	8.4	11.3	30.4	17.2	30.8	78.4

Table 4. Coking conditions of coal batches.

Blend	Coking Period, Hours	Temperatures in Control Verticals, °C	
		Machine Side	Coke Side
1	23.46	1230	1265
2	19.69	1220	1260
3	58.74	1100	1160
4	28.11	1160	1180
5	21.05	1200	1240
6	17.56	1200	1230
7	36.8	1150	1170
8	37.06	1150	1170
9	20.3	1210	1250
10	18.41	1250	1270
11	18.9	1240	1275
12	30.68	1150	1170
13	24.58	1200	1240
14	22.55	1230	1265
15	31.14	1150	1170

The coal batch sample was poured onto the sampling table and sifted through a sieve with cell sizes of 3 mm. Grains that did not pass through the sieve were crushed and sieved again until the entire sample passed through the sieve. Next, the sample was thoroughly

mixed with the shoveling method, which consists of placing the sample on the table, then scooping it evenly around the perimeter with scoops, pouring it into one point, and taking it to the center to form a cone. The operation was repeated three times with a change in the location of the cone. Then, the sample was reduced by the quartering method in the following order:

The cone obtained after mixing was leveled so that the upper part was in the shape of a circle with a uniform thickness of the layer. The center of the circle had to coincide with the center of the cone;

The circle was divided into four parts using a cross;

Two diametrically opposite parts were discarded, and the remaining parts were combined; the reduction operation was repeated until the weight was at least 2 kg;

In order to prevent an error, two opposite parts were rejected at each subsequent operation. Next, the sample was divided into four parts with the help of a cross to determine the quality parameters of the coal raw material.

To determine the characteristics of coal raw materials, standardized methods were used:

- State standard of Ukraine 4096–2002 “Brown coal, hard coal, anthracite, combustible shale and coal briquettes. Methods of sample selection and preparation for laboratory tests” [29];
- ISO 1171-97 “Solid mineral fuels. Methods for determination of ash” [30];
- ISO 589-81 “Hard coal—Determination of total moisture” [31];
- ISO 7404-3-84 “Methods for the petrographic analysis of bituminous coal and anthracite—Part 3: Method of determining maceral group composition” [32];
- ISO 7404-5-85 “Methods for the petrographic analysis of coals—Part 5: Method of determining microscopically the reflectance of vitrinite” [33];
- State standard of Ukraine 7722:2015 “Hard coal. Method of Determining Plastometric Characteristics” [34].

A photo of coke sorbent is presented in Figure 1.



Figure 1. Coke sorbent.

The characteristics of the obtained cokes (indicators of proximate analysis, physico-mechanical properties, thermo-mechanical properties) are presented in Tables 5 and 6 and were determined according to the following standard methods:

- State standard of Ukraine ISO 579-2002 “Coke-Determination of total moisture” [35];
- ISO 556-80 “Coke (greater than 20 mm in size)-Determination of mechanical strength” [36];
- ISO 18894:2006 “Coke-Determination of coke reactivity index (CRI) and coke strength after reaction (CSR)” [37];

- ISO 728-81 “Coke (nominal top size greater than 20 mm)-Size analysis” [38].

Table 5. Proximate analysis of coke.

Blend	W_t^r	Proximate Analysis, %		V_{daf}
		A^d	S_t^d	
1	2.7 ± 0.5	11.8 ± 0.2	0.51 ± 0.05	0.2 ± 0.2
2	4 ± 0.5	11.7 ± 0.2	0.86 ± 0.05	0.29 ± 0.2
3	4.5 ± 0.5	14 ± 0.2	0.62 ± 0.05	0.19 ± 0.2
4	5.4 ± 0.5	17.1 ± 0.2	1.5 ± 0.05	0.45 ± 0.2
5	4.4 ± 0.5	13.7 ± 0.2	1.32 ± 0.05	0.24 ± 0.2
6	4.3 ± 0.5	15.5 ± 0.2	1.46 ± 0.05	0.32 ± 0.2
7	4.9 ± 0.5	14.8 ± 0.2	1.51 ± 0.05	0.29 ± 0.2
8	5.8 ± 0.5	15 ± 0.2	1.45 ± 0.05	0.2 ± 0.2
9	4.7 ± 0.5	14.8 ± 0.2	1.97 ± 0.05	0.46 ± 0.2
10	3.7 ± 0.5	11.3 ± 0.2	1.2 ± 0.05	0.26 ± 0.2
11	2.5 ± 0.5	10.7 ± 0.2	1.24 ± 0.05	0.65 ± 0.2
12	5.1 ± 0.5	13.2 ± 0.2	1.56 ± 0.05	0.35 ± 0.2
13	3.3 ± 0.5	11.4 ± 0.2	1.1 ± 0.05	0.12 ± 0.2
14	3 ± 0.5	11.2 ± 0.2	1.01 ± 0.05	0.12 ± 0.2
15	7.7 ± 0.5	14.3 ± 0.2	1.4 ± 0.05	0.36 ± 0.2

Table 6. Granulometric composition, mechanical strength and thermochemical properties (CRI/CSR) of cokes.

Blend	Granulometric Composition (%)					Thermochemical Properties, %		Mechanical Strength, %	
	>80	80–60	60–40	40–25	<25	CRI	CSR	M ₂₅	M ₁₀
1	6.5	31.2	38.3	18.8	5.2	34.3 ± 3	49.5 ± 3.5	87.4 ± 3	8 ± 1
2	10.9	33.5	35.7	11.7	8.2	41.7 ± 3.5	34.4 ± 3.5	85.4 ± 3	9.5 ± 1
3	11.5	35.7	33.7	11	8.1	41.9 ± 3.5	37 ± 3.5	84.6 ± 3	9.6 ± 1
4	15.1	35.9	29.5	10.7	8.8	51.5 ± 3.5	23.8 ± 3.5	83 ± 3	9.9 ± 1
5	11	35.1	34	11.5	8.4	54.9 ± 3.5	20.2 ± 3.5	83.3 ± 3	9.8 ± 1
6	10	33.3	36.1	11.7	8.9	53.9 ± 3.5	20.2 ± 3.5	83.2 ± 3	9.8 ± 1
7	10.9	29.6	33.8	16.7	9	56 ± 3.5	21 ± 3.5	78.8 ± 3	9.9 ± 1
8	11.2	29.5	32.8	17.5	9	52 ± 3.5	24 ± 3.5	78.8 ± 3	10 ± 1
9	10.9	30.2	32.6	17.4	8.9	49.3 ± 3.5	31.1 ± 3.5	81.3 ± 3	9.4 ± 1
10	9.7	33.5	33	18.1	5.7	41.3 ± 3.5	42.6 ± 3.5	86.6 ± 3	8 ± 1
11	8.8	32.7	33.8	19	5.7	43 ± 3.5	40.7 ± 3.5	86 ± 3	8.2 ± 1
12	14.8	31.2	31.6	13.4	9	54.4 ± 3.5	28.5 ± 3.5	81.3 ± 3	9.6 ± 1
13	12.8	37	33.9	10.6	5.7	43.8 ± 3.5	40.4 ± 3.5	86.2 ± 3	8.2 ± 1
14	12.5	37.3	33.7	10.7	5.8	43.4 ± 3.5	40.8 ± 3.5	86.5 ± 3	8.2 ± 1
15	13.5	31.7	32.5	13.6	8.7	53.3 ± 3.5	27.9 ± 3.5	82 ± 3	9.6 ± 1

To determine the sorption capacity remove to acid (A_{acid}), 0.5 g of coke was placed in a conical flask with a volume of 250 cm³, 50 cm³ of 0.1 N hydrochloric acid solution was added, closed with a stopper and shaken manually every minute for 60 min. After settling the solution, an aliquot of 10 cm³ of the solution was taken with a pipette, placed in a conical flask and titrated with a 0.1 N sodium hydroxide solution in the presence of the phenolphthalein indicator until the appearance of color. The sorption capacity by acid, mg-eq/g, was calculated by the formula:

$$A_{acid} = \frac{(V_1 - V_2) \cdot 1.33 \cdot K}{m} \quad (1)$$

$$K = \frac{100}{(100 - W_a)} \quad (2)$$

where V_1 is the volume of 0.1 N sodium hydroxide solution used for the titration of 10 cm³ of hydrochloric acid solution, cm³; V_2 —volume of 0.1 N sodium hydroxide solution, spent on titration of 10 cm³ of hydrochloric acid solution, after treatment with coal, cm³; 1.33—correction factor; m —weight of coke weight, g.

To determine the sorption capacity remove to alkali (A_{alkali}), 0.5 g of coke was weighed, placed in a conical flask with a volume of 250 cm³, 50 cm³ of 0.1 N sodium hydroxide solution was added, closed with a stopper and shaken manually every minute for 60 min. After settling the solution, 10 cm³ of the solution was taken with a pipette, placed in a conical flask and titrated with a 0.1 N hydrochloric acid solution in the presence of the phenolphthalein indicator until the color disappeared. The sorption capacity by alkali, mg-eq/g, was calculated according to the formula:

$$A_{\text{alkali}} = \frac{(V_1 - V_2) \cdot 1.15 \cdot K}{m} \quad (3)$$

where V_1 is the volume of 0.1 N hydrochloric acid solution spent on titration of 10 cm³ of sodium hydroxide solution, cm³; V_2 —volume of 0.1 N hydrochloric acid solution, spent on titration of 10 cm³ of sodium hydroxide solution, after treatment with coke, cm³; 1.15—correction factor; K is calculated according to Formula (2); m is the weight of coke, g.

To determine the adsorption activity, remove to iodine, 1 g of coke was transferred to a conical flask with a volume of 250 cm³, 100 cm³ of a solution of iodine in potassium iodide was added, closed with a stopper and shaken manually every minute for 30 min. After settling the solution, 10 cm³ of the solution was taken with a pipette, transferred to a conical flask and titrated with a 0.1 N solution of sodium thiosulfate. At the end of titration, 3–5 drops of starch solution were added and titrated until the blue color disappeared. At the same time, the initial content of iodine in the solution was determined; for this, 10 cm³ of a solution of iodine in potassium iodide was placed in a conical flask and titrated with a 0.1 N sodium thiosulfate solution, adding a starch solution at the end of the titration. The adsorption activity by iodine was calculated according to the formula:

$$F_{\text{iodine}} = \frac{(V_1 - V_2) \cdot 0.0127 \cdot 100 \cdot 100}{10 \cdot m} \cdot K \quad (4)$$

where V_1 is the volume of sodium thiosulfate solution with a concentration of 0.1 mol/dm³ (0.1 N), spent on titration of 10 cm³ of iodine solution in potassium iodide, cm³; V_2 —volume of sodium thiosulfate solution with a concentration of 0.1 mol/dm³ (0.1 N), spent on titration of 10 cm³ of iodine solution in potassium iodide, after treatment with coke, cm³; 0.0127—the mass of iodine corresponding to 1 cm³ of sodium thiosulfate solution with a concentration of 0.1 mol/dm³ (0.1 N), g; 100—volume of solution of iodine in potassium iodide, taken for illumination with coke, cm³; K was calculated according to Formula (2), m is the weight of coke, g.

To determine the adsorption activity to remove methylene blue 0.15 g of the methylene blue indicator was taken into a volumetric flask with a volume of 1000 cm³ and dissolved in 200 cm³ of hot distilled water, then the solution was cooled, brought up to the mark with distilled water (a working solution with a mass concentration of 150 mg/dm³ for analysis was obtained). To construct a graduation graph, comparison solutions were prepared: 0.5 was injected into 10 volumetric flasks with a volume of 100 cm³ each; 1.0; 2.0; 3.0; 4.0; 5.0; 6.0; 7.0; 8.0; 9.0 cm³ of a working solution of methylene blue with a mass concentration of 150 mg/dm³, after which the volume was brought up to the mark with water at a temperature of 20 ± 2 °C. The resulting solutions contain 1 dm³, respectively, 0.75; 1.50; 3.00; 4.50; 6.00; 7.50; 9.00; 10.50; 12.00; 13.50 mg/dm³ methylene blue solution. The optical density of the prepared comparison solutions was measured on a photoelectrocolorimeter. Colorimeter is an optical instrument for measuring the concentration of substances in solutions. The principle of operation of the colorimeter is based on the property of colored solutions to absorb light passing through them more strongly, the higher the concentration of the coloring substance in them. In this case we using a light filter with a wavelength of λ from 390 to 410 nm in cuvettes with a light-absorbing layer thickness of 10 mm. Distilled water was used as a control solution. According to the obtained data, a graduation graph

of the dependence of the optical density on the mass concentration of the comparison solution was constructed. For analysis, a coke weight was transferred to a conical flask with a volume of 100 cm³, 25 cm³ of methylene blue solution with a mass concentration of 1500 mg/dm³ was added, closed with a stopper and shaken on a liquid shaker for 20 min. After shaking, the coke slurry was poured into centrifuge tubes and centrifuged for 15 min. Carefully remove 1 cm³ of the clarified solution with a pipette and transfer it to a volumetric flask with a volume of 100 cm³. The solution in the flask was diluted to the mark with distilled water. The optical density of the solution after dilution should be from 0.2 to 0.8 optical units. In this case, the dilution factor will be equal to 100. The residual mass concentration of the methylene blue solution in the diluted solution was found based on the obtained value of the optical density, using the graduation graph. The adsorption activity of coal according to the indicator in milligrams per 1 g of product was calculated according to the formula:

$$F_{mb} = \frac{(C_1 - C_2 \cdot K) \cdot 0.025}{m} \quad (5)$$

where C_1 is the mass concentration of the initial solution of the indicator, 1500 mg/dm³; C_2 —mass concentration of the solution after contact with coke, mg/dm³; K —dilution factor of the solution, 100; 0.025—the volume of the indicator solution taken for illumination, dm³; m —weight of coke weight, g.

The statistical analysis of the results and the development of mathematical dependencies were performed using the licensed computer program Microsoft Excel (state the version number 2012 (13530.20264)).

3. Results

The results of studying the sorption characteristics of coke are presented in Table 7.

Table 7. Quality indicators of coke as a sorbent.

Blend	Sorption Capacity A, mg-eq/g		Adsorption Activity F	
	By Acid	By Alkali	By Iodine, %	By Methylene Blue, mg/g
1	1.07 ± 0.5	1.94 ± 0.5	12.1 ± 0.5	30.8 ± 0.5
2	0.94 ± 0.5	3.15 ± 0.5	12.1 ± 0.5	33.8 ± 0.5
3	1.07 ± 0.5	2.2 ± 0.5	12.34 ± 0.5	32.2 ± 0.5
4	1.24 ± 0.5	3.9 ± 0.5	14.73 ± 0.5	33 ± 0.5
5	1.2 ± 0.5	3.44 ± 0.5	13.53 ± 0.5	32.6 ± 0.5
6	1.18 ± 0.5	3.29 ± 0.5	13.54 ± 0.5	32.5 ± 0.5
7	1.27 ± 0.5	3.38 ± 0.5	13.78 ± 0.5	32.8 ± 0.5
8	1.2 ± 0.5	2.9 ± 0.5	13.11 ± 0.5	31.8 ± 0.5
9	1.22 ± 0.5	3.6 ± 0.5	13.38 ± 0.5	32.8 ± 0.5
10	1.2 ± 0.5	3.69 ± 0.5	13.55 ± 0.5	32.5 ± 0.5
11	0.27 ± 0.5	0.34 ± 0.5	14.53 ± 0.5	33.6 ± 0.5
12	1.17 ± 0.5	3.59 ± 0.5	13.56 ± 0.5	32.5 ± 0.5
13	1.04 ± 0.5	1.79 ± 0.5	11.94 ± 0.5	31.9 ± 0.5
14	1.48 ± 0.5	1.16 ± 0.5	4.49 ± 0.5	32 ± 0.5
15	1.24 ± 0.5	3.73 ± 0.5	13.66 ± 0.5	33.8 ± 0.5

Studying the relationship between the properties of carbon-containing raw ± 0.5 materials and the sorption characteristics of coke (carbonized residue), we obtained the following dependencies (Figures 2–13).

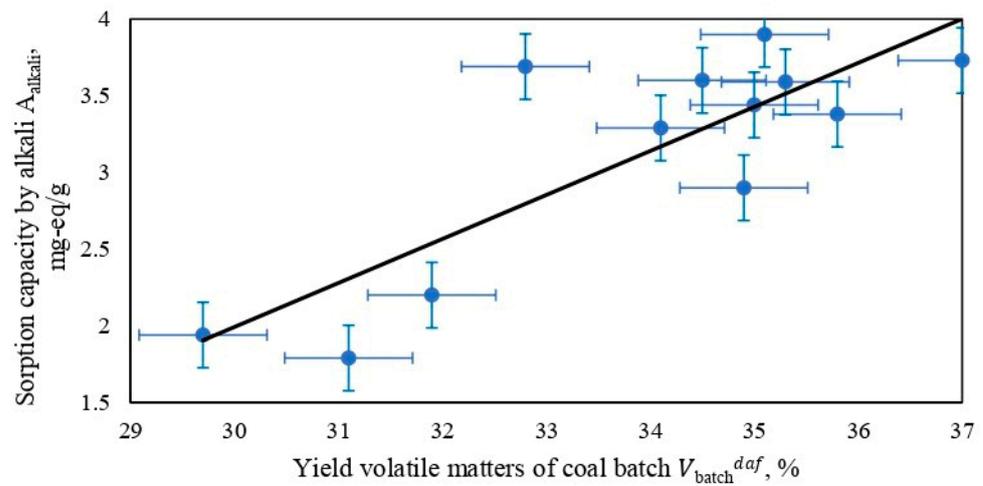


Figure 2. Dependence of the sorption capacity by alkali on the yield volatile matters of coal batch.

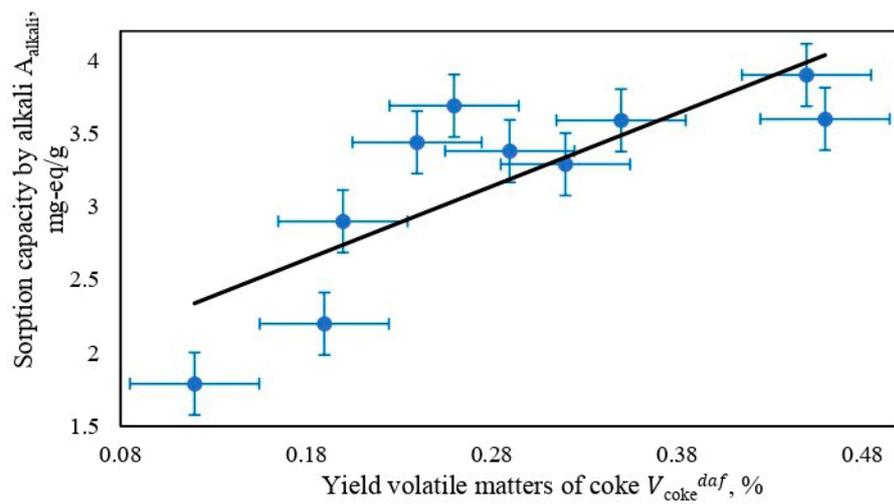


Figure 3. Dependence of the sorption capacity by alkali on the yield volatile matters of coke.

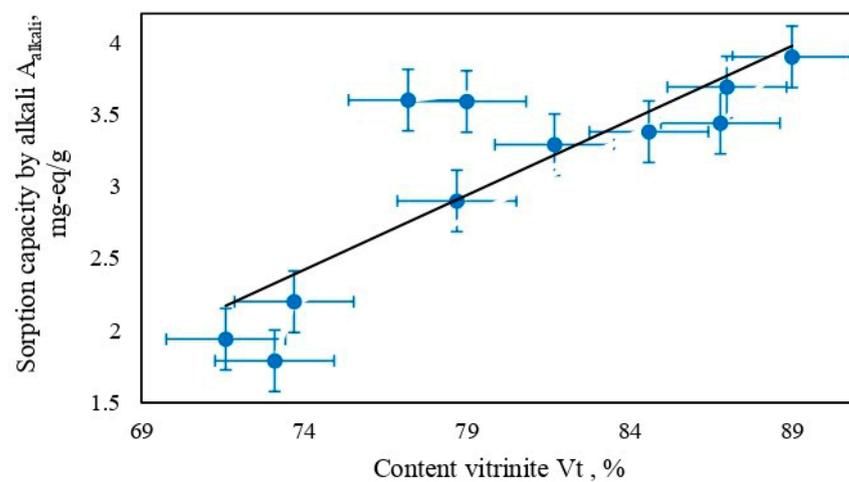


Figure 4. Dependence of the sorption capacity by alkali on the content vitrinite.

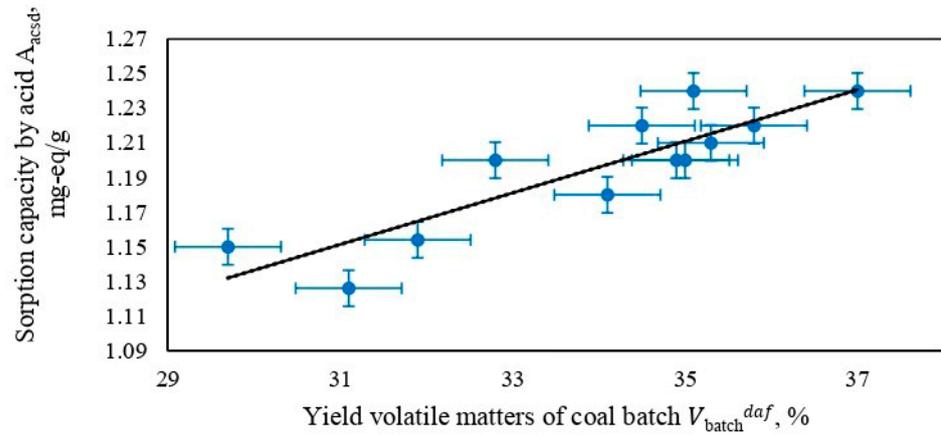


Figure 5. Dependence of the sorption capacity by acid on the yield volatile matters of coal batch.

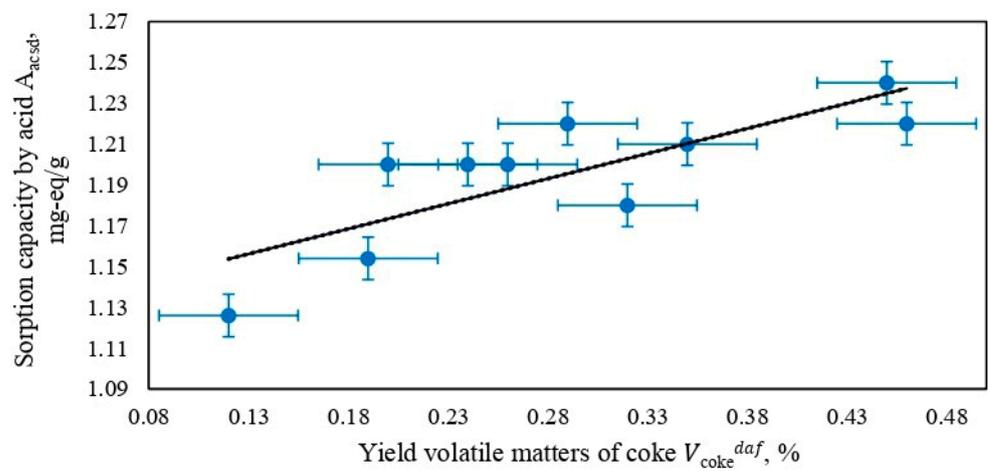


Figure 6. Dependence of the sorption capacity by acid on the yield volatile matters of coke.

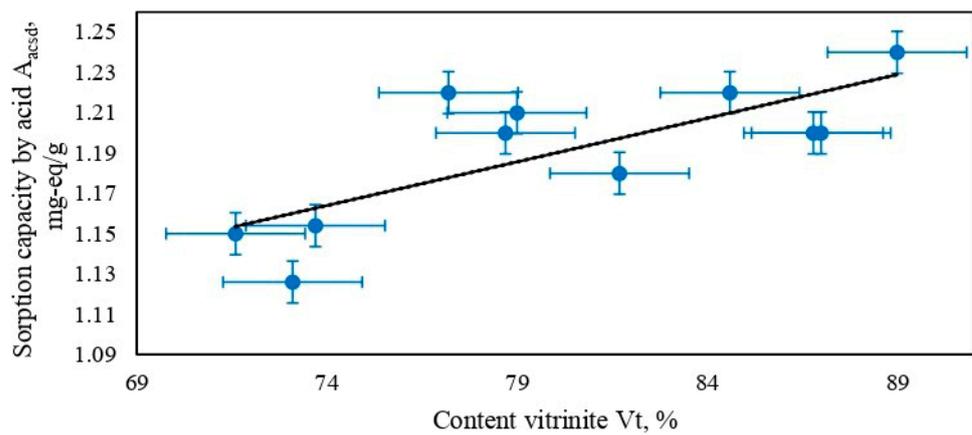


Figure 7. Dependence of the sorption capacity by acid on the content vitrinite.

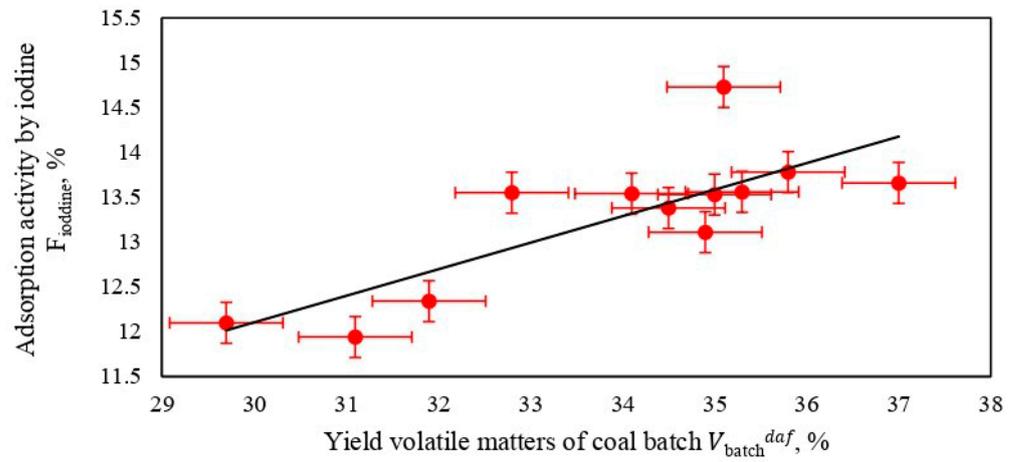


Figure 8. Dependence of the adsorption activity by iodine on the yield volatile matters of coal batch.

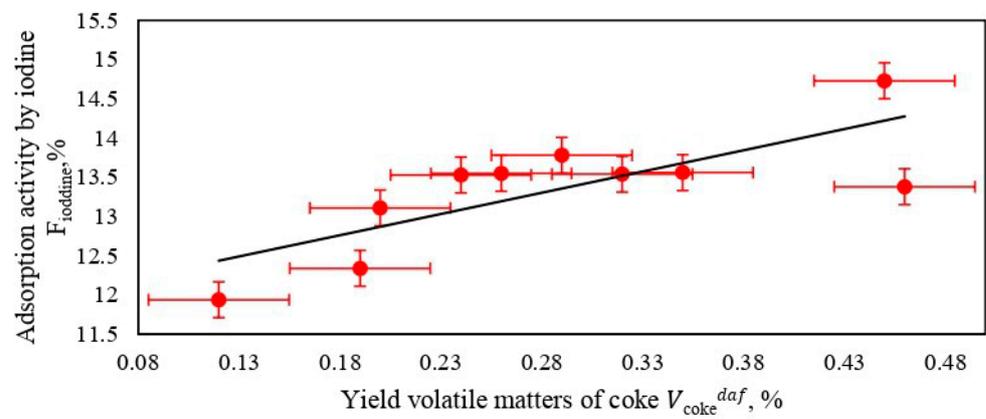


Figure 9. Dependence of the adsorption activity by iodine on the yield volatile matters of coke.

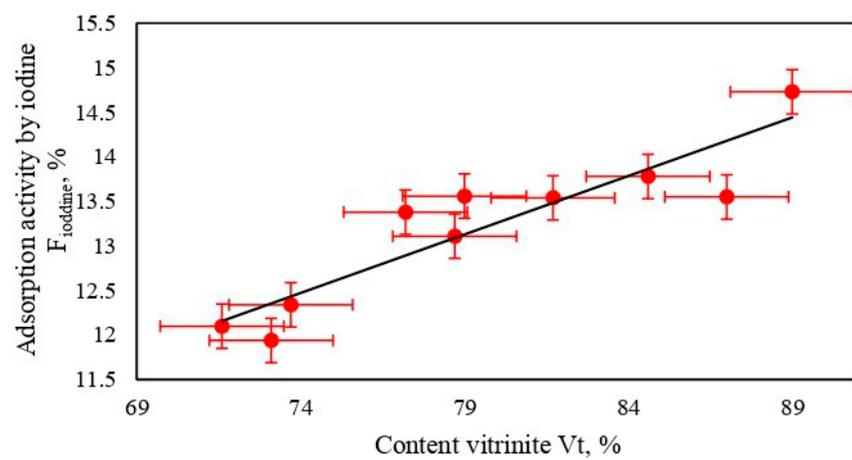


Figure 10. Dependence of the adsorption activity by iodine on the content vitrinite.

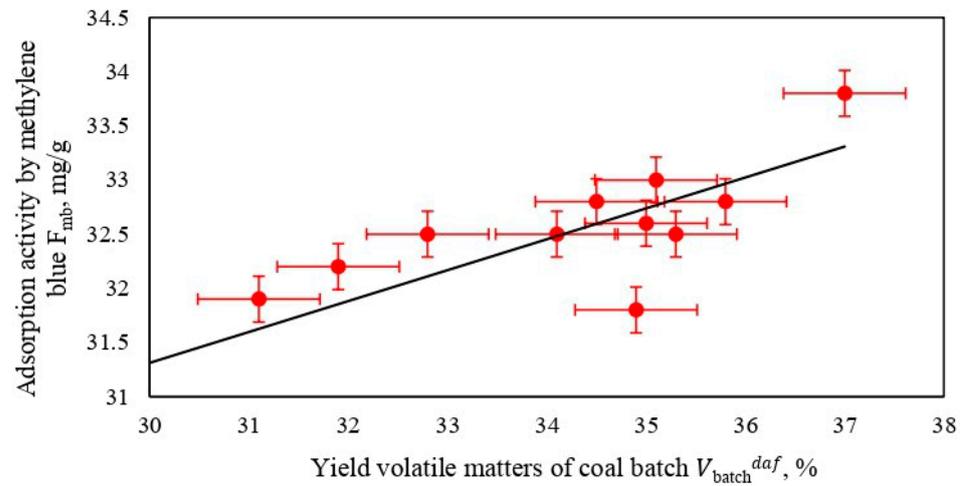


Figure 11. Dependence of the adsorption activity by methylene blue on the yield volatile matters of coal batch.

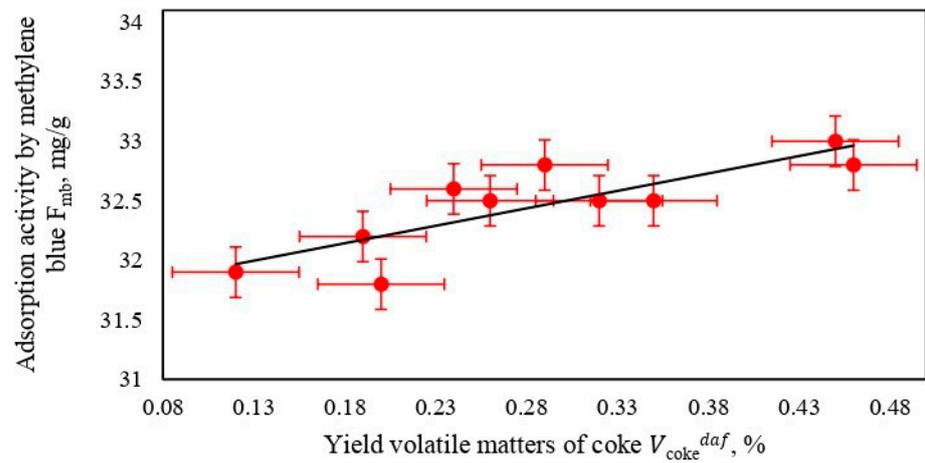


Figure 12. Dependence of the adsorption activity by methylene blue on the yield volatile matters of coke.

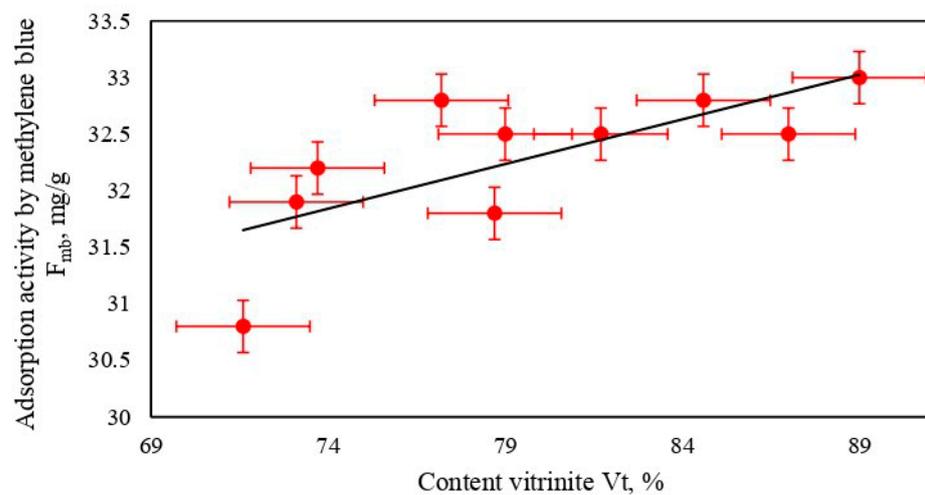


Figure 13. Dependence of the adsorption activity by methylene blue on the content vitrinite.

The graphical dependencies shown in Figures 2–13 are described by the corresponding mathematical equations. The obtained mathematical equations and their statistical estimates are shown in Table 8.

Table 8. Mathematical equations.

N ^o	Mathematical Equations	Figure	Statistical Assessment Coefficient of Determination R ²
(6)	$A_{alkali} = 0.287 \cdot V_{batch}^{daf} - 6.6197$	Figure 2	0.684
(7)	$A_{alkali} = 4.9896 \cdot V_{coke}^{daf} + 1.741$	Figure 3	0.6462
(8)	$A_{alkali} = 0.1036 \cdot Vt - 5.2491$	Figure 4	0.7054
(9)	$A_{acid} = 0.149 \cdot V_{batch}^{daf} + 0.6897$	Figure 5	0.7744
(10)	$A_{acid} = 0.2458 \cdot V_{coke}^{daf} + 1.1242$	Figure 6	0.6451
(11)	$A_{acid} = 0.0043 \cdot Vt - 0.8435$	Figure 7	0.5713
(12)	$F_{iodine} = 0.296 \cdot V_{batch}^{daf} + 3.2239$	Figure 8	0.6349
(13)	$F_{iodine} = 5.408 \cdot V_{coke}^{daf} + 11.788$	Figure 9	0.6025
(14)	$F_{iodine} = 0.1313 \cdot Vt + 2.7563$	Figure 10	0.8344
(15)	$F_{mb} = 0.2853 \cdot V_{batch}^{daf} + 22.753$	Figure 11	0.6876
(16)	$F_{mb} = 2.9279 \cdot V_{coke}^{daf} + 31.617$	Figure 12	0.6873
(17)	$F_{mb} = 0.0789 \cdot Vt + 26.002$	Figure 13	0.5286

Based on the processing of experimental data using the methods of mathematical statistics, regression equations were obtained, which are presented in Table 9.

Table 9. Regression equations.

N ^o	Equations	Statistical Assessment Coefficient of Determination R ²
(18)	$A_{alkali} = 0.1848 \cdot V_{batch}^{daf} + 0.062 \cdot Vt - 8.1163$	0.832
(19)	$A_{acid} = 0.0225 \cdot V_{batch}^{daf} + 0.005 \cdot Vt + 0.01$	0.859
(20)	$F_{iodine} = 0.155 \cdot V_{batch}^{daf} + 0.085 \cdot Vt + 1.166$	0.879
(21)	$F_{mb} = 0.26 \cdot V_{batch}^{daf} + 0.015 \cdot Vt + 22.38$	0.697

4. Discussion

The obtained dependencies are linear. Thus, the adsorption characteristics of coke depend on the yield of volatile matters (from the batch and coke), which characterizes the structural features of the carbon-containing material and affects the formation of its porosity. The influence of vitrinite content is also significant.

It was established that a 1% increase in the yield of volatile matters of coal batch contributes to an increase in the sorption capacity by alkali A_{alkali} on 0.287%, the sorption capacity by acid A_{acid} on 0.149%, the adsorption activity index by iodine F_{iodine} on 0.296%, and the adsorption activity by methylene blue F_{mb} on 0.2853%.

An increase in the content of vitrinite leads to an increase in the sorption capacity by alkali A_{alkali} on 0.1036%, the sorption capacity by acid A_{acid} on 0.0043%, the adsorption activity by iodine F_{iodine} on 0.1313%, and the adsorption activity by methylene blue F_{mb} on 0.0789%. An increase in the yield of volatile matters of coke by 1% leads to an increase in the index of sorption capacity by alkali A_{alkali} on 4.9896%, sorption capacity by acid A_{acid} on 0.2458%, index of adsorption activity by iodine F_{iodine} on 5.408%, and adsorption activity by methylene blue F_{mb} on 2.9279%.

The analysis of equations and their statistical evaluation indicates that the investigated relationships are characterized by high values of determination coefficients R^2 (0.5286–0.8344), which makes it possible to predict the sorption capacity on the adsorption coke activity.

The equations for predicting the sorption capacity remove to alkali and acid and adsorption activity remove to iodine taking into account the content of vitrinite and the yield of volatile matters of coal batch (Equations (18)–(20)) are characterized by high coefficient of determination R^2 (0.832 and 0.859 and 0.879, respectively), so they can be recommended for forecasting of these indicators.

The obtained conclusions regarding the relationship between the sorption characteristics of coke from the release of volatile substances and the content of vitrinite are consistent with the results of works [2,3,6,24].

The authors of the article [3] also studied the adsorption properties of the fine fraction of coke with a size of 2–5 mm and proved the prospects of its use for the production of effective carbon sorbents.

But it should be noted that the industrial use of coke and semi-coke as an adsorbent is expedient after the process of its activation, which allows to form a porous structure, significantly increase the surface area, indicators of sorption capacity and adsorption activity. The activation option should be technologically feasible and economically justified, ensuring the formation of the required porosity of the material, but not increasing its cost.

5. Conclusions

The influence of raw materials (composition of batches, petrographic characteristics, indicators of proximate, plastometric analysis, granulometric composition) and technological factors (coking period, process temperature) on the sorption properties of the carbonized product (coke) was studied. Based on the research results, it is shown that such characteristics of coke as low humidity and ash, minimal yield of volatile matters, developed pore system and low cost make its use as a sorbent promising and economically justified. In this work we used standardized methods of studying the technological properties of coal and batches (determination of granulometric composition, proximate and petrographic analyses), as well as special methods for determining the sorption capacity (by alkali and acid) and adsorption activity (by iodine and methylene blue). The study of the quality characteristics of coke was carried out using physico-mechanical and thermochemical methods of studying standardized parameters: particle size composition, indice of crushability (M_{25}), indice of resistance of coke abrasion (M_{10}), coke reactivity index (CRI), coke strength after reaction (CSR). Mathematical statistics methods were used to analyze the influence of raw material factors on the characteristics of coke sorbent.

The conducted research made it possible to establish the dependence of the sorption characteristics of coke on the structural features and nature of coal raw materials (yield of volatile matters, vitrinite content) and the structure and degree of readiness of coke (yield of volatile matters coke).

The practical value of the research lies in the fact that the obtained regression equations for predicting the sorption capacity remove to alkali and acid (A_{alkali} , A_{acid}) and the adsorption activity remove to iodine F_{iodine} taking into account the content of vitrinite and the yield of volatile matters of the coal batch are statistically significant, characterized by high coefficient of determination R^2 (0.832 and 0.859 and 0.879, respectively), so they can be recommended for forecasting the indicated indicators, as well as for selecting coal-containing raw materials (optimizing the composition of coal blends) for the production of sorbents.

Further research will be aimed at developing an effective and economically feasible technology for the activation of the studied cokes, which will allow to manage their quality and obtain a product with specified sorption characteristics.

Author Contributions: Conceptualization, D.M., B.K., S.P. and K.S.; methodology, D.M., B.K. and T.C.; investigation, K.S.; data curation, D.M., S.P.; writing—original draft preparation, K.S., D.S., O.K.,

T.C. and M.K.; writing—review and editing, M.K. and S.P.; visualization, D.S. and O.K.; supervision, D.M.; project administration, D.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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