CARBON ADSORBENTS MADE FROM PETROLEUM ASPHALTITE SEMICOKE

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Petroleum asphaltite semicoke added to the batch makes it possible to synthesize adsorbents with important sorption capacity and selectivity in extraction of silver from multicomponent polymetallic solutions with the existing industrial scheme.

A stable trend toward using active carbons as adsorbents for extracting precious metals is being observed in our country and abroad [1]. A specific feature of silver-containing ores is an extremely low silver content and the complexity of the component composition determines the necessity of using relatively voluminous and selective

Table 1

Indexes	Asphaltite	Semicoke* from asphaltite
Group composition, wt. %		
oils	12.6	–
resins	8	–
asphaltenes	79.4	–
Heteroatom content, %		
S	5.45	5.67
N	0.86	1.3
O (by difference)	2.04	5.03
C:H (atomic)	1.02	2.18
Note. *60% yield of semicoke.		

adsorbents for extracting silver from them. Readily available and economically suitable feedstock is necessary for obtaining such adsorbents.

It was shown in [2-4] that adsorbents made from petroleum asphaltites and products of their chemical transformations have higher adsorption characteristics than domestic and foreign industrial adsorbents. We report the manufacture and investigation of adsorbents made with asphaltite semicoke.

A sample of asphaltite (Table 1) underwent semicoking in a ZK-1 industrial delayed coking unit. The process was conducted for 10 h at 500-550°C with a temperature elevation rate of 50-60°/h. At the end of the process, the asphaltite was held for 1 h at the same temperature. The yield of products was, wt. %: 55-60% semicoke, 34-40% gas, and 3-5% condensate.

As a result of semicoking, the C:H ratio increased by two times. As indicated in [2-4], the asphaltenes obtained in heat treatment of oils and resins contain fewer heteroatoms, are more aromatized, and have an ordered structure in comparison to native asphaltenes.

The adsorbents were molded from a batch obtained by mixing previously ground asphaltite semicoke with 10% total shale phenols – a mixture of alkylresorcinols, 37% wood resin, and the dust fraction (0.1 mm particles $\leq$ 1%) of lean dug coal for 4-6 min in a two-paddle mixer at 60-70°C.

The ash content of the latter was 7.09%, the moisture content was 1.25%, and the volatiles content was 13.2%. The batch obtained was granulated, then carbonized in carbon dioxide medium while heating from 200 to 800°C and activated in steam at 800-900°C.

A significant amount of volatiles (4-7%) was liberated during carbonization, and the yield of carbon residue was 70-74%. The mechanical strength and density of the adsorbents did not change up to high degrees of combustion loss (Table 2).

Experimental isotherms of adsorption of benzene vapors at 20°C on a vacuum microbalance were made to characterize the pore structure and they were used to calculate the pore parameters of the adsorbents [5]. The isotherms were processed with the Kiselev method to calculate the specific micro- and mesopores volumes [6]. The parameters of the microporous structure were calculated with Dubinin's theory of volume filling [7].

Table 2

Indexes	Adsorbent with degree of combustion loss, %		
	0	56 (Sample 1)	70 (Sample 2)
C:H (atomic)	5.52	7.35	7.95
Content, wt. %			
heteroatoms	8.7	12.56	12.9
ash	3.4	5.8	8.5
Density, g/cm^3	0.77	0.5	0.41
Total pore volume, cm^3/g	0.26	0.71	1.13
Volume, cm^3/cm^3			
micropores	0.01	0.14	0.22
mesopores	0.04	0.14	0.2
macropores	0.21	0.29	0.32
Specific surface area of mesopores, m^2/g	–	105	167

Table 3

Sorption time, h	Sorption capacity, mg/g							Ag selectivity coefficient, %
	Au	Ag	Cu	Zn	Ni	Co	total	
Adsorbent								
Sample 1 (see Table 2)								
2	0.7	0.32	5.5	0	0	0.05	6.57	5.25
4	0.31	0.42	8.5	0	0	0.10	9.33	4.5
8	0.42	0.55	14.5	11.5	0	0.25	27.22	2.02
12	0.6	0.68	23	18	0	0.3	42.58	1.6
24	0.96	0.84	23	20	0	0.3	45.1	1.87
48	1.08	1.06	23	24	0.03	0.36	49.53	2.1
72	1.25	1.11	25.5	27	0.03	0.4	55.29	2.1
96	1.51	1.17	28.5	29.5	0.05	0.44	61.17	1.91
120	1.64	1.29	28.5	35.5	0.05	0.44	67.42	1.91
Sample 2 (see Table 2)								
2	0.17	0.36	5.5	4	0	0	10.03	3.49
4	0.32	0.52	9.5	7.5	0	0.05	17.89	2.9
8	0.58	0.77	9.5	16	0.2	0.3	27.35	2.81
12	0.76	0.84	12.5	22.5	0.24	0.35	37.19	2.25
24	1.13	0.95	13	24.5	0.27	0.35	40.2	2.3
48	1.13	0.97	16	24.5	0.27	0.35	43.22	2.2
72	1.5	1.07	16.5	26	0.27	0.39	45.73	2.2
96	1.66	1.08	16.5	28.5	0.3	0.3	51.83	2.2
120	1.86	1.77	16.8	29	0.33	0.32	50.08	3.55
SKT*								
120	1.58	0.83	24.5	17.5	0.06	0.45	44.92	1.85
Norit**								
120	1.46	0.86	19	44	0.4	0.6	66.32	1.29
Futamura**								
120	1.97	1.22	26.5	33.5	0.18	0.5	63.87	1.91

Note.   *Domestic

**Foreign.

Using semicoke makes it possible to use an important amount of petroleum feedstock for making the adsorbents. Addition of shale phenols causes development of a microporous structure [8]. An important advantage of asphaltite semicoke adsorbents is the low ash content. A characteristic feature is the significant development

of a mesoporous structure, which is not observed when asphaltites themselves and feedstock of another type are used.

The microporosity and sorption characteristics increase with an increase in the degree of activation (combustion loss). The high heteroatom content in the adsorbents obtained ensured their high surface polarity.

Solutions of complex salt composition, mg/dm^3: 0.01 Au, 0.9 Ag, 63.2 Cu, 55.8 Zn, 0.48 Ni, 0.33 Co, obtained from a gold mining plant were used to study* the sorption characteristics. The content of metals in the solutions was determined by atomic-absorption spectrophotometry on a Perkin – Elmer Mod. 503 instrument.

The sorption characteristics of the adsorbents were evaluated by the method of constant concentrations of the salt composition (changing the solution) [9]. The selectivity coefficient with respect to silver was determined as the mass fraction of silver absorbed by the adsorbent to the sum of all metals sorbed in the form of cyanide complexes (Table 3).

The experiments showed that in the presence of all metals listed, the adsorbents were more rapidly saturated with dicyanoaurates, even at an extremely low content of them in the initial solution. The sorption rate of dicyanoargentate was also very high. The kinetic activity of the silver complex is probably based on the smaller size of the silver ion. According to the data in Table 3, adsorbents with the optimum ratio of pore volumes of different types and the highest heteroatom content exhibited the highest selectivity for silver.

The high sorption capacity and selectivity of the semicoke adsorbents are due to a specific feature of the initial feedstock. The unordered structure of semicokes, the important content of heterorganic compounds and metals of variable valence (especially vanadium and nickel) cause the formation of functional groups during high-temperature self-catalyzed oxidation of functional groups with no special oxidation stage.

Functional groups can be formed due to the stable radicals initially present in the feedstock; the radicals formed during splitting of alkyl substituents; the reactive sites formed during dehydrogenation of alicyclic fragments; the unsubstituted and spatially accessible positions in aromatic and heterocyclic rings. It is necessary to consider the presence of easily oxidized sulfur-containing fragments capable of forming strongly and weakly acid groups in oxidation.

As a result of oxidation of nitrogen-containing cyclic compounds in the overall highly condensed system, the adsorbents acquire the properties of weak amphoteric ion exchangers. The static exchange capacity of the is 0.1-0.4 meq/g. The oxygen-containing acid and basic nitrogen-containing functional groups with unshared electron pairs participate in the overall system of conjugation of the p-electron cloud of the graphite-like aromatic plates by intensifying the micropore adsorption field.

The adsorbents obtained with asphaltite semicoke are thus characterized by better sorption capacity and selectivity in extraction of silver from solutions of complex salt composition in comparison to the best industrial adsorbents – domestic SKT and foreign Norit and Futamura.

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