УДК 661.183.123: 661.183.2

V.Yu. Korovin, Yu.G. Shestak, A.M. Valyaev

FRACTAL CHARACTERISTICS OF ACRYLONITRILE-DIVINYLBENZENE COPOLYMER AND SCAN CARBONACEOUS SORBENT

M.S. Polyakov Institute of Geotechnical Mechanics, National Academy of Sciences of Ukraine, Dnipro

The paper deals with the measurement of fractal dimension for the acrylonitrile — divinyl benzene copolymer prepared with alkylate petrol and CCl_4 pore formers, copolymer carbonizate and SCAN carbonaceous sorbent based on the mercury porosimetry results and using fractal analysis. It is found that copolymer has meso- and macroporous structure, which parameters have been determined by synthesis conditions. The pore space surface and volume of the copolymer have a multi-fractal structure. The number of pore radius ranges, for which the self-similarity of the pore space surface and volume is maintained, is from 1 to 4. Fractal dimension change within the range of 2.03 ± 0.002 to 3.04 ± 0.11 for the surface and within the range of 1.95 ± 0.13 to 2.99 ± 0.002 for the volume of pore space. It is shown that 33.05 to 90.21% of the surface and 6.38 to 87.84% of the volume for pore space have fractal properties depending upon copolymer synthesis conditions. The changes of fractal properties in the course of copolymer carbonization and activation are defined. Multi-fractal structures are formed in the pore space surface and in the volume of carbonizate and carbonaceous sorbent. An increase of the pore radius ranges, where self-similarity is maintained, is also observed.

Keywords: acrylonitrile-divinyl benzene copolymer, carbonizate, carbonaceous sorbent, porous characteristics, fractal properties.

Nowadays, fractal theory is increasingly applied for studying various physical and chemical processes [1] including formation of porous structure in materials and their properties [2]. To determine fractal characteristics, physical and physical-chemical techniques are applied including mercury porosimetry, which was previously used to measure fractal dimensions for the pore space surface [3] and volume [4] for different porous materials.

Polyacrylonitrile-based polymers are widely applied in various industries. The greatest scientific and practical interest is due to their usage as a precursor while manufacturing carbon fibers, where acrylic acid nitrile (acrylonitrile, AAN) is among the components. Copolymer based on AAN and divinyl benzene (DVB) prepared using pore formers serves as a porous matrix during manufacturing carboxylic cation exchangers. Authors proposed [5] a method for producing macroporous cation exchanger based on AAN and methylmethacrylate with technical-grade DVB (9 wt.% to 12 wt.%) in the presence of alkylated petrol (AP) pore former with volumetric fraction approx. 40 vol.% of the total monomer volume.

Previously [6], we studied regulations of producing SCAN carbonaceous sorbent during heat treatment of AAN-DVB copolymer (DVB weight

fraction was 10% and 20%) while using the pore former comprising AP (volumetric fraction was 5% and 10%) and carbon tetrachloride (volumetric fraction was 90% and 110%) of the total volume of monomers. Using mercury porosimetry and low-temperature nitrogen adsorption, formation of SCAN porous structure was studied [6]. It was shown that the sorbent obtained had a well-developed meso-and macropore system, which properties were defined by synthesis conditions of the original copolymer. The matrix structure was studies for SKN and SCAN carbonaceous sorbents using ¹³C NMR method [7]; donor — acceptor properties of their surface were investigated [7–9] by ³¹P NMR spectroscopy using tributyl phosphate (TBP) as a probe.

Sorption properties of SCAN-40 carbonaceous sorbent, which was produced using acrylonitrile-divinylbenzene copolymer (DVB weight fraction was 15%) and AP pore former (volumetric fraction was 40%), were studied relatively bilirubin, albumin, creatinine, and vitamin B12 as compared with sorption properties of SKN-1K hemosorbent as well as for removing large associates from biological fluids [10,11]. The possibility was studied to use SCAN carbonaceous sorbent for carbon dioxide adsorption [12]. It was shown that SCAN might be used as a carrier for impregnated resins based on

organophosphorus compounds for selective metal extraction and separation. Thus, the impregnated resin based on SCAN-30 and different-radical phosphine oxide may be used in processing high-level radioactive wastes [13].

In this paper, measurement of fractal characteristics is described for acrylonitrile-divinyl benzene copolymer prepared in the presence of AP and CCl₄ pore makers as well as its carbonizate and SCAN-30 carbonaceous sorbent (commercial prototype). The measurement was carried out by fractal analysis using mercury porosimetry results.

Porous characteristics of AAN-DVB copolymer

The study was carried out using AAN-DVB copolymer containing cross-linking agent with weight fraction 5% to 25%. Pore former comprised alkylated petrol (volumetric fraction was from 0% to 40%) and carbon tetrachloride (volumetric fraction was from 0% to 110%) of the total volume of monomers.

Porous structure of samples was characterized by mercury porosimetry. Pore specific surface area (S) and total volume (V) was measured using Carlo Erba series 2000 mercury porosimeter. Average effective pore radius was calculated by the formula:

$$r = \frac{2V}{S} \cdot 10^3,$$

where V is pore volume by mercury, $cm^3 \cdot g^{-1};\ S$ is

specific pore area by mercury, m²·g⁻¹.

To plot programs, the software product developed in Delphi environment was used. Table 1 contains the values of total volume, specific area and average effective radius of pores for AAN-DVB copolymer prepared under different conditions.

It is evident from Table 1 that total pore volume of AAN-DVB copolymer is within the range (0.54 to 1.4) cm³·g⁻¹, specific pore area – (15.82 to 117.01) m²·g⁻¹, and average effective pore radius is (15.8 to 98.4) nm depending upon the ratio of cross-linking agent and pore former.

As an example, Fig. 1 illustrates integral and differential curves of the pore volume distribution by radius for AAN-DVB samples with cross-linking degree (weight fraction are 5%, 10%, 15% and 25%) and almost the same content of pore former.

The figure illustrates that copolymer samples had mainly meso- and macroporous structure. Prevailing pore radius for sample No. 1 was within 90 nm to 300 nm, sample No. 12-30 nm to 150 nm, sample No. 18-20 nm to 200 nm, sample No. 23-4 nm to 120 nm. Increase of cross-linking degree resulted in formation of smaller pores and increasing the range of prevailing pore radius.

Fig. 2 shows the dependence of pore total volume and specific area for AAN–DVB copolymer upon the content of CCl_4 (60% to 100%) and AP (0% to 40%) at constant content of cross-linking agent 10%.

Table 1
Porous characteristics of AAN-DVB copolymer

Copolymer composition Total pore volume, Specific pore area, Average effective Sample DVB, %|CCl4, %|AP, % $cm^3 \cdot g^{-1}$ $m^2 \cdot g^{-1}$ pore radius, nm 100 10 0.85 38.98 43.6 5 2 10 70.83 60 10 0.66 18.6 3 70 10 22.7 10 0.65 57.36 4 10 80 0 0.54 67.98 15.8 0.79 5 10 80 40 39.02 40.6 6 10 80 20 0.92 27.34 67.2 7 10 80 10 0.69 43.38 32.0 8 59.68 10 90 10 0.83 27.8 9 10 100 0 0.93 95.7 19.4 10 10 100 40 1.05 33.11 63.4 41.76 11 10 20 0.86 41.2 100 12 43.15 37.5 10 100 10 0.81 13 15 0 30 0.55 55.49 19.9 14 15 0 50 0.76 75.2 20.3 15 15 0 80 1.20 62.5 38.4 50 50 98.4 16 15 0.78 15.82 17 15 100 10 1.03 78.53 26.2 45.16 18 15 100 7.5 1.10 48.7 19 20 90 5 1.03 70.9 29.1 90 20 20 10 1.40 94.81 29.5 21 20 110 5 1.20 84.23 28.5 22 20 110 10 1.36 58.01 46.9 23 25 100 10 1.07 117.01 18.3

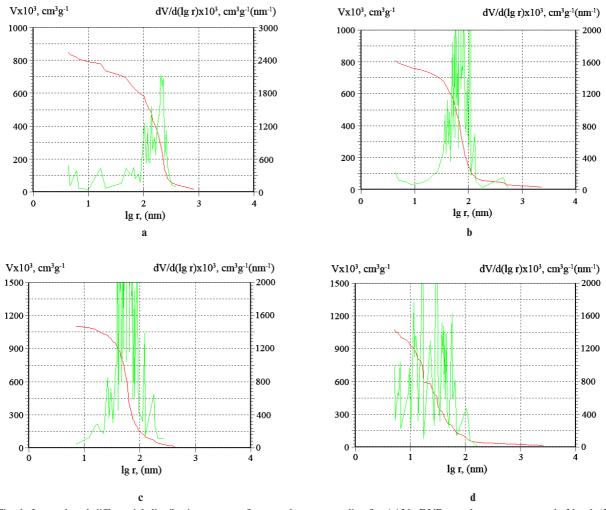


Fig. 1. Integral and differential distribution curves of pore volume per radius for AAN-DVB copolymers: a - sample No. 1 (5% DVB, 100% CCl₄, 10% AP); b - sample No. 12 (10% DVB, 100% CCl₄, 10% AP); c - sample No. 18 (15% DVB, 100% CCl₄, 7.5% AP); d - sample No. 23 (25% DVB, 100% CCl₄, 10% AP)

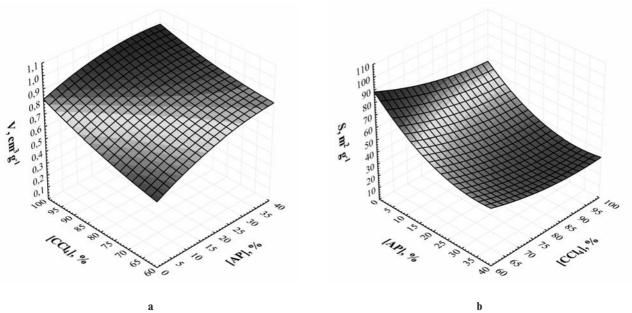


Fig. 2. Dependence of pore total volume (a) and specific area (b) upon CCl₄ and AP content at permanent cross-linking degree (10% DVB)

The data obtained showed that increase of AP content in the reaction mixture resulted in ascending both pore total volume and specific area while increase of CCl₄ amount ended in the increase of total pore volume and insignificant decrease of their specific area. The data showed that pore formation in AAN–DVB copolymer complies with the same regularities obtained for the styrene-divinyl benzene system with non-solvating pore formers and tributyl phosphate [14].

Fractal dimensions of AAN-DVB copolymer

Fractal dimension of the pore space surface and volume was calculated using exponential function $V(r) \sim r^{E-d_E}$, where d_E is fractal dimension of the surface (d_f) or volume (d_V) of pore space, E-topological dimension (2 is for surface, 3 is for volume). Fractal dimension of the pore space surface

 (d_f) and volume (d_v) was defined based on the mercury porosimetry data by selecting linear sections in the lnV(r) versus ln(r) plots, where $d_{f,V}$ value was within the range $2 < d_{f,V} < 3$; and the root mean square deviation (R^2) was the highest. This approach was implemented to define d_f in [3] and d_V in [4]. We also used it when calculating fractal properties of TVEX-TBP matrix [14].

Tables 2 and 3 illustrate the ranges of pore radius in AAN–DVB copolymer, where fractal properties are maintained, fractal dimensions of the pore space surface (d_f) and volume (d_V) as well as the fraction (n_f , n_V) and total fraction (Σn_f , Σn_V) of pore surface and volume with self-similarity.

As it may be seen from the data obtained, multifractality of the pore space surface remained for all AAN-DVB samples. The number of pore radius

Fractal dimensions of the pore space surface for AAN-DVB copolymers

Table 2

Sample	Pore radius range, nm	Fractal dimension d_f	RMS deviation R ²	Fraction of total surface n_f , %	Total fraction Σn_f	
1	4.4–48.1	2.07±0.005	0.97	75.22	, ,	
	59.0–123.0	2.32±0.02	0.97	8.10	89.18	
	130.1–196.6	3.0±0.05	0.98	5.86		
2	4.4–12.5	2.17±0.01	0.98	40.48		
	12.9–26.9	2.58±0.02	0.99	30.77	71.25	
	6.1-30.9	2.17±0.004	0.99	60.91	74.71	
3	38.1–57.4	2.90±0.06	0.98	13.80		
4	5.2–17.2	2.3±0.022	0.95	61.73	65.05	
4	35.7-803.7	2.5±0.06	0.94	3.32	65.05	
	5.2-23.5	2.06±0.005	0.96	43.89	(2.00	
5	32.5-56.6	2.43±0.018	0.98	18.19	62.08	
	5.3-43.7	2.04±0.005	0.92	49.35		
6	52.9–95.0	2.4±0.02	0.95	20.33	80.54	
	127.0-268.4	2.9±0.07	0.94	10.86		
7	5.1-17.9	2.1±0.007	0.97	40.42	(7.65	
7	22.3–39.3	2.6±0.04	0.94	27.23	67.65	
8	6.1–30.9	2.12±0.005	0.98	47.74	47.74	
9	3.8-18.0	2.21±0.006	0.99	75.26	00.21	
9	18.6–53.6	2.35±0.01	0.93	14.95	90.21	
	5.5-11.8	2.04±0.007	0.96	35.90	89.57	
10	15.4–34.1	2.11±0.003	0.99	22.35		
10	36.0–105.1	2.26±0.009	0.98	22.62		
	108.1–933.9	2.34±0.008	0.99	8.71		
11	5.5-69.2	2.03±0.002	0.97	30.89	35.13	
11	77.8–193.6	2.18±0.01	0.97	4.24	33.13	
12	4.3-26.4	2.06±0.003	0.99	51.49	71.06	
12	34.4–59.3	2.60±0.03	0.98	19.57		
12	4.9–26.0	2.19±0.02	0.92	70.05	70.44	
13	31.1–40.8	3.04±0.11	0.96	8.39	78.44	
16	10.1-51.9	2.03±0.007	0.92	22.73	44.73	
	63.0–108.1	2.38±0.03	0.96	20.97		
	165.4–2318.0	2.41±0.01	0.99	1.03		
17	5.8-17.7	2.11±0.01	0.95	33.05	33.05	
18	7.0–30.0	2.07±0.01	0.89	28.93	62.31	
	36.3–58.6	3.02±0.05	0.95	33.39		
23	5.1–12.2	2.21±0.008	0.98	43.59	43.59	

ranges, where self-similarity was maintained, was 1 to 4 depending upon synthesis conditions of the copolymer thus testifying the trend to "fill" the whole pore space. Total fraction of pores Sn_f with the self-similarity of the pore space surface was within 33.05% to 90.21% with an average value 64.35% and tended to increase with increasing cross-linking degree and to insignificantly decrease with increasing AP content.

According to the data obtained, the pore space volume of AAN-DVB copolymers had multi-fractal properties similar to the pore space surface. The number of pore radius ranges, where self-similarity was maintained, was 1 to 4 depending upon synthesis conditions of copolymer. Fractal dimension of the

pore space volume varied from 1.95 ± 0.13 to 2.99 ± 0.002 . Total fraction of pores Σn_v with self-similarity maintenance was 6.38% to 87.84% with an average value 48.52%. Total fraction of pores, where self-similarity was maintained for the pore space volume, tended to increase with the increase of cross-linking degree and AP content.

Porous and fractal properties of the carbonizate of AAN-DVB copolymer and SCAN carbonaceous sorbent

The effect of carbonization and activation on the change of porous and fractal properties was studied relatively to preparation of a pilot sample of SCAN-30 carbonaceous sorbent. Sample No. 13

Table 3 Fractal dimensions of the pore space volume for AAN-DVB copolymer

Sample	Pore radius range,	Fractal dimension	RMS deviation R ²	Fraction of total volume	Total fraction	
	nm	$ m d_{V}$		11V, 70	$\Sigma n_{\rm V}$, %	
1	6.6-87.3	2.31±0.03	0.98	8.33		
	103.2–226.3	1.96±0.01	0.99	45.0	78.33	
	244.0-315.9	2.63±0.05	0.95	25.0		
2	42.2–128.5	2.95±0.02	0.89	6.38	6.38	
3	43.2–62.8	2.35±0.03	0.98	19.57	19.57	
	8.7–12.8	2.26±0.012	0.99	5.26		
4	24.2-41.1	2.62±0.05	0.92	18.42	31.57	
	44.2-803.5	2.98±0.006	0.90	7.89		
5	5.4–32.5	1.93±0.07	0.98	10.71	35.71	
3	78.7–109.9	2.13±0.08	0.92	25.0	33./1	
6	11.0-43.7	2.18±0.09	0.95	7.69	22.21	
O	183.6–9010.2	2.93±0.004	0.95	24.62	32.31	
	9.9–22.3	1.93±0.06	0.98	8.16		
7	45.6–56.7	2.02±0.03	0.99	14.29	44.90	
/	58.2–99.4	2.7±0.02	0.96	12.24	44.89	
	118.6–10255.1	2.98±0.001	0.98	10.20		
	8.0-32.4	2.3±0.03	0.98	16.95	45.76	
8	61.6–89.0	2.15±0.05	0.95	25.42		
	94.1–123.8	2.87±0.01	0.98	3.90		
	6.8–26.7	2.04±0.02	0.99	28.79	81.82	
9	33.1–177.1	2.54±0.007	0.99	46.97		
	226.3-1859.7	2.98±0.007	0.86	6.06		
10	5.9-134.3	1.97±0.02	0.98	41.89	07.04	
10	148.1–3363.1	2.78±0.005	0.99	45.95	87.84	
	7.9–51.2	2.74±0.04	0.90	4.92	80.33	
11	69.2–598.4	2.24±0.01	0.98	62.30		
	718.9–2648.9	2.89±0.007	0.98	13.11		
10	6.4–34.4	2.16±0.04	0.99	12.28	28.07	
12	92.6-178.4	2.72±0.04	0.84	15.79		
13	5.5-37.4	2.22±0.06	0.94	38.46	38.46	
16	33.2-63.0	1.95±0.13	0.98	3.64		
16	165.4–2318.0	2.99±0.002	0.96	3.64	7.28	
17	54.5-81.3	2.24±0.08	0.90	21.92	27.40	
17	112.8–304.4	2.95±0.008	0.92	5.48	27.40	
18	63.5-80.7	1.99±0.06	0.96	16.67	28.20	
	89.3–125.7	2.75±0.02	0.93	8.97		
	179.7–212.8	2.85±0.03	0.94	2.56		
23	17.4–49.8	2.37±0.03	0.95	35.53	50.00	
	56.7–163.2	2.85±0.01	0.93	14.47	50.00	

(15% DVB, 0% CCl₄, 30% AP) of AAN-DVB copolymer was taken as a source. Copolymer was thermally treated in inert environment in a rotating furnace; carbonizate was activated by water steam in a fluid-bed furnace [15]. Porous characteristics of prepared samples are stated in Table 4 and Fig. 3.

Table 4
Porous characteristics of AAN-DVB copolymer,
carbonization product on its basis and SCAN-30
carbonaceous sorbent

Sample	Total pore volume, cm ³ ·g ⁻¹	Specific pore area, m ² ·g ⁻¹	Average effective pore radius, nm
13	0.55	55.49	19.9
Carbonizate	0.42	57.03	14.6
SCAN-30	0.59	79.0	14.9

During the initial copolymer carbonization, total pore volume and average effective pore radius decreased within (0.55 to 0.42) cm³·g⁻¹ and within (19.9 to 14.6) nm correspondingly; at the same time, specific pore area insignificantly increased from 55.49 m²·g⁻¹ to 57.03 m²·g⁻¹. During activation, total pore volume and specific pore area increased to 0.59 cm³·g⁻¹ and 79.0 m²·g⁻¹. Pore prevailing radius was within (3.7 to 10) nm and (20 to 90) nm for carbonizate and (3.7 to 20) nm and (30 to 200) nm for carbonaceous sorbent.

We have also obtained the similar results for pilot sample of SCAN-40 sorbent [11,15], where

total pore volume increased during its production from 0.62 cm³·g⁻¹ (AAN-DVB copolymer) to 0.49 cm³·g⁻¹ (carbonizate) and 0.64 cm³·g⁻¹ (SCAN-40). At the same time, sorption volume of pores measured by benzene increased from 0.15 cm³·g⁻¹ (carbonizate) to 0.46 cm³·g⁻¹ (SCAN-40) due to formation of micropores. Pore prevailing radius for carbonaceous sorbent was (25 to 150) nm.

Tables 5 and 6 contain fractal dimensions of the pore space surface and volume for AAN-DVB copolymer, carbonizate and SCAN carbonaceous sorbent.

During copolymer carbonization, the range of pore radius with maintaining self-similarity of the pore space surface increased from 40.84 nm to 53.66 nm; at the same time, total fraction Σn_f was almost the same. Activation resulted in formation of multifractal structure, increasing pore range (up to 170 nm) with maintaining fractal properties; and Σn_f attained 96%.

Carbonization resulted in the increase of the pore radius range, where self-similarity of the pore space volume maintained, from 37 nm to 76 nm and formation of multi-fractal structure; it was the same as for the fractal dimension of the pore space surface. At the same time, total fraction Σn_V was almost the same and equaled to 37% to 38%. Activation process resulted in the further expansion of pore radius with maintaining fractal properties up to 215 nm; in this case, total fraction attained ~70%.

The results obtained show particularities in

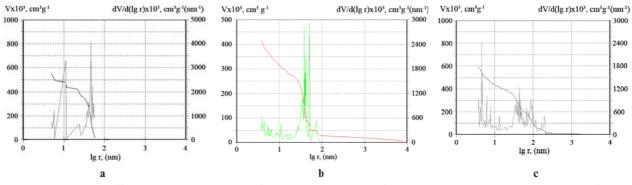


Fig. 3. Integral and differential distribution curves of pore volume per radius for AAN-DVB copolymer (a), carbonizate (b) and SCAN-30 carbonaceous sorbent (c)

Table 5 Fractal dimensions of the pore space surface

Sample	Pore radius range, nm	Fractal dimension $d_{\rm f}$	RMS deviation R ²	Fraction of total surface n _f , %	Total fraction Σn_f , %
13	4.9–26.0	2.19±0.02	0.92	70.05	78.44
	31.1-40.8	3.04±0.11	0.96	8.39	/8.44
Carbonizate	3.8-53.7	2.24±0.003	0.99	81.45	81.45
SCAN-30	3.7–29.9	2.23±0.005	0.97	85.34	
	31.9-80.9	2.84±0.01	0.99	10.50	96.12
	122.9–169.6	3.04±0.08	0.98	0.29	

Fractal dimensions of the pore space volume

Sample	Pore radius range,	Fractal dimension	RMS deviation R ²	Fraction of total volume	Total fraction
	nm	$ m d_{ m V}$	Л	$n_{\rm V}, \%$	Σn_{V} , %
13	5.5-37.4	2.22±0.06	0.94	38.46	38.46
Carbonizate	6.3–12.1	2.05±0.02	0.99	12.82	
	13.4–27.7	2.57±0.01	0.98	11.97	36.76
	43.3–75.7	2.77±0.03	0.82	11.97	
SCAN-30	9.1–29.9	2.61±0.006	0.99	15.49	
	31.9–117.1	2.49±0.012	0.97	46.48	69.72
	122.9–214.8	2.86±0.015	0.92	7.75	

changing in porous structure of AAN-DVB copolymer and its fractal characteristics depending on synthesis conditions and effect of heat treatment during carbonization and activation. They may be used during preparation of synthetic carbonaceous sorbents with preset physical and chemical characteristics.

REFERENCES

- 1. *Mandelbrot B.B.* The Fractal Geometry of Nature. W.H. Freeman and Comp., San-Francisco, 1982. 459 p.
- 2. Fraktaly v geomekhanike / Bulat A.F., Dyrda V.I., Zvyagilskyi E.L. et al. Naukova dumka, Kiev, 2007. 390 p.
- 3. *Mosolov A.B., Dinariev O.Yu*. Fraktaly, skeily i geometriya poristykh materialov // Zhurnal teoreticheskoy fiziki. − 1988. − Vol.58. − № 2. − P.233-238.
- 4. Yongfu Xu. Calculation of unsaturated hydraulic conductivity using a fractal model for the pore-size distribution / Computers and Geotechnics. -2004. $-N_{\odot}$ 31. -P.549-557.
- 5. Patent RF, № 2326130. Sposob polucheniya karboksilnogo kationita / An En Dok, Ledovskikh G.I., Balanovskiy N.V., Zorina A.I., Roschin, Balashova G.L., Senkov V.A. 2008.
- 6. Formirovaniye poristoy structury sinteticheskogo azonsoderzhaschego uglerodnogo sorbenta SKAN / Platonov V.A., Merkulov V.A., Korovin V.Yu., Randarevich S.B. // Khimicheskaya Technologiya. $-1991.-N_0$ 6. -P.56-60.
- 7. Hemosorbents with controllable mesoporous and macroporous structure and investigation of them by the MMR (C-13, P-31) method / Kuzovov Y., Korovin V., Myasnikov V., Merkulov V., Randarevich S. // International Journal of Artificial Organs. 1987. Vol.11. No 6. P.504.
- 8. NMR-study of hemosorbent surface properties / Korovin V.Yu., Randarevich S.B., Platonov V.A., Merkulov V.A. // International Journal of Artificial Organs. 1990. Vol.13. No 9. P.574.

- 9. ³¹P NMR study of organic phosphorus compounds complexing with the surfaces of porous materials / Randarevich S.V., Korovin V.Yu., Platonov V.A., Merkulov V.A., Trachevskij V.V. // Spektroskopiya koordinatsionnykh soedineniy: V Vsesoyuznjye soveschanie" Tezisy dokladov [5. All-union conference on spectroscopy of coordination compounds. Short note]. Krasnodar, 1988. P.103.
- 10. *Macroporous* nitrogen-containing carbonaceous hemosorbent SCAN / Korovin V.Yu., Randarevich S.B., Platonov V.A., Merkulov V.A. // International Journal of Artificial Organs. $-1990. \text{Vol.} 13. \text{N}_{2} 9. \text{P.575}.$
- 11. *Comparative* assessment of structural and sorption properties of SCAN carbonaceous hemo- and enterosorbent / Platonov V.A., Korovin V.Yu., Merkulov V.A., Nikolaev V.G., Barkova V.V. // Efferentnye metody v medicine: Tez. dokl. Vseros. Nauch. Conf. Moscow. 1992. P.161-163.
- 12. Korovin V.Yu., Barkova V.V., Platonov V.A. Adosrption of carbon dioxide by nitrogen-containing synthetic carbon adsorbents SKN and SKAN // Russian Journal of Applied Chemistry. -1994. -Vol.67. -No.2. -P.237-240.
- 13. Solid extractants and impregnates on polymer and carbonaceous basis containing calixarene complexing agents for radionuclide recovery / Korovin Yu.F., Pogorelov Yu.M., Korovin V.Yu., Shestak Yu.G., Kalchenko V.I., Drapailo A.B. // Nedelya ecologa. Ekologicheskiye problemy gorno-metallurgicheskich regionov. Progressivnye informatsionnye i technicheskiye resheniya: Tez. dokl. Mezhdunar. Nauch. Simp. Dneprodzerzhinsk. 2010. P.150-151.
- 14. Korovin V.Yu., Shestak Yu.G., Valyaev A.M. Poristye kharakteristiki I fractalnye svoistva matricy TVEX-TBF // Voprosy khimii i khimicheskoi tekhnologii. 2014. Vol.4 (97). P.51-58
- 15. *Highly-porous* hemo- and enterosorption material based on SCAN synthetic nitrogen-containing sorbent / Platonov V.A., Korovin V.Yu., Makhorin K.E., Golovchenko V.A., Merkulov V.A., Randarevich S.B., Barkova V.V. // Tez. dokl. III Mezhdunarodnoy konferencii po problemam mediciny katastrof. Kiev. 1991. Vol.II. P.53-54.

Received 16.12.2016

FRACTAL CHARACTERISTICS OF ACRYLONITRILE-DIVINYL BENZENE COPOLYMER AND SCAN CARBONACEOUS SORBENT

V.Yu. Korovin, Yu.G. Shestak, A.M. Valyaev
N. Polyakov Institute of Geotechnical Mechanics, National
Academy of Sciences of Ukraine, Dnipro, Ukraine

The paper deals with the measurement of fractal dimension for the acrylonitrile - divinyl benzene copolymer prepared with alkylate petrol and CCl4 pore formers, copolymer carbonizate and SCAN carbonaceous sorbent based on the mercury porosimetry results and using fractal analysis. It is found that copolymer has meso- and macroporous structure, which parameters have been determined by synthesis conditions. The pore space surface and volume of the copolymer have a multi-fractal structure. The number of pore radius ranges, for which the self-similarity of the pore space surface and volume is maintained, is from 1 to 4. Fractal dimension change within the range of 2.03±0.002 to 3.04±0.11 for the surface and within the range of 1.95 ± 0.13 to 2.99 ± 0.002 for the volume of pore space. It is shown that 33.05 to 90.21% of the surface and 6.38 to 87.84% of the volume for pore space have fractal properties depending upon copolymer synthesis conditions. The changes of fractal properties in the course of copolymer carbonization and activation are defined. Multi-fractal structures are formed in the pore space surface and in the volume of carbonizate and carbonaceous sorbent. An increase of the pore radius ranges, where self-similarity is maintained, is also observed.

Keywords: acrylonitrile-divinyl benzene copolymer; carbonizate; carbonaceous sorbent; porous characteristics; fractal properties.

REFERENCES

- 1. Mandelbrot B.B., *The fractal geometry of nature.* W.H. Freeman and Comp., San-Francisco, 1982. 459 p.
- 2. Bulat A.F., Dyrda V.I., Zvyagilskyi E.L., *Fraktaly v geomekhanike* [Fractals in geomechanics]. Naukova Dumka, Kiev, 2007. 390 p. (*in Russian*).
- 3. Mosolov A.B., Dinariev O.Yu. Fraktaly, skeily i geometriya poristykh materialov [Fractals, scales and porous material geometry]. *Zhurnal Teoreticheskoi Fiziki*, 1988, vol. 58, no. 2, pp. 233-238. (*in Russian*).
- 4. Xu Y. Calculation of unsaturated hydraulic conductivity using a fractal model for the pore-size distribution. *Computers and Geotechnics*, 2004, no. 31, pp. 549-557.
- 5. Dok A.E., Ledovskikh G.I., Balanovskiy N.V., Zorina A.I., Roschin, Balashova G.L., Senkov V.A., *Sposob polucheniya karboksilnogo kationita* [Process for obtaining carboxylic cationite]. Patent RF, no. 2326130, 2008. (*in Russian*).
- 6. Platonov V.A., Merkulov V.A., Korovin V.Yu., Randarevich S.B. Formirovaniye poristoi structury sinteticheskogo azotsoderzhaschego uglerodnogo sorbenta SKAN [Formation of porous structure for SCAN synthetic nitrogen-containing carbonaceous sorbent]. *Khimicheskaya Technologiya*, 1991, no. 6, pp. 56-60. (*in Russian*).

- 7. Kuzovov Y., Korovin V., Myasnikov V., Merkulov V., Randarevich S. Hemosorbents with controllable mesoporous and macroporous structure and investigation of them by the MMR (C-13, P-31) method. *International Journal of Artificial Organs*, 1987, vol. 11, no. 6, p. 504.
- 8. Korovin V.Yu., Randarevich S.B., Platonov V.A., Merkulov V.A. NMR-study of hemosorbent surface properties. *International Journal of Artificial Organs*, 1990, vol. 13, no. 9, p. 574.
- 9. Randarevich S.V., Korovin V.Yu., Platonov V.A., Merkulov V.A., Trachevskij V.V., ³¹P NMR study of organic phosphorus compounds complexing with the surfaces of porous materials. *Proceedings of the soviet conference on spectroscopy of coordination compounds*. USSR, Krasnodar, 1988, p. 103.
- 10. Korovin V.Yu., Randarevich S.B., Platonov V.A., Merkulov V.A. Macroporous nitrogen-containing carbonaceous hemosorbent SCAN. *International Journal of Artificial Organs*, 1990, vol. 13, no. 9, p. 575.
- 11. Platonov V.A., Korovin V.Yu., Merkulov V.A., Ni-kolaev V.G., Barkova V.V. Comparative assessment of structural and sorption properties of SCAN carbonaceous hemo- and enterosorbent. *Proceedings of the Russian scientific conference «Efferent Techniques in Medicine»*. Russia, Moscow, 1992, pp. 161-163
- 12. Korovin V.Yu., Barkova V.V., Platonov V.A. Adsorption of carbon dioxide by nitrogen-containing synthetic carbon adsorbents SKN and SKAN. *Russian Journal of Applied Chemistry*, 1994, vol. 67, no. 2, pp. 237-240.
- 13. Korovin Yu.F., Pogorelov Yu.M., Korovin V.Yu., Shestak Yu.G., Kalchenko V.I., Drapailo A.B., Solid extractants and impregnates on polymer and carbonaceous basis containing calixarene complexing agents for radionuclide recovery. *Proceedings of the International Scientific Symposium «Ecologist's week-2010. Environmental problems of mining-metallurgical regions. Progressive information and technological solutions»*. Ukraine, Dneprodzerzhinsk, 2010, pp. 150-151. (in Ukrainian).
- 14. Korovin V.Yu., Shestak Yu.G., Valyaev A.M. Poristye kharakteristiki i fraktalnye svoistva matritsy TVEX-TBF [Porous characteristics and fractal properties of TVEX-TBP matrix]. *Voprosy khimii i khimicheskoi tekhnologii*, 2014, vol. 4, pp. 51-58. (*in Russian*).
- 15. Platonov V.A., Korovin V.Yu., Makhorin K.E., Golovchenko V.A., Merkulov V.A., Randarevich S.B., Barkova V.V. Highly-porous hemo- and enterosorption material based on SCAN synthetic nitrogen-containing sorbent. *Abstracts of the III International Conference on emergency medicine problems*. Ukraine, Kiev, 1991, vol. II, pp. 53-54.