

Methods of preparation and properties of mineral-carbon sorbents obtained from coal-tar pitch-polymer compositions

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Abstract The purpose of this study was to determine the possibility of producing hydrophobic mesoporous mineral-carbon sorbents from aluminum hydroxide and coal-tar pitch-polymer compositions by carbonization at 600 °C in an nitrogen atmosphere. The method of homogenization was optimized using different solvents. Blends of aluminum hydroxide and coal-tar pitch with a definite composition or the products of co-precipitation of aluminum hydroxide in the coal-tar pitch-polymer medium were subjected to carbonization process. The hydrophilic–hydrophobic properties were evaluated by adsorption of water vapors. The highest value of BET surface area about 370 m²/g, was achieved for the carbonization product obtained from co-precipitated raw components with 10 wt% coal-tar pitch-polymer compositions.

Keywords Mineral-carbon sorbents · Aluminum hydroxide · Coal-tar pitch-polymer compositions

Introduction

The search for effective and of low cost adsorbents to eliminate present and future developments, to restore polluted environments, and to treat hazardous wastes is a scientific and technological issue of paramount importance. Activated carbons occupy a unique position in the hierarchy of adsorbent materials for cleaning air, gases, water, etc. Analogous porous inorganic materials have also been

investigated and developed for adsorption and separation materials. Examples include natural and synthetic zeolites, clay minerals, and oxides (alumina, ferrites, goethite, and manganese oxide) [1].

Literature references present the possibilities of use of various mineral and carbon substances to produce complex sorbents and hybrid materials. Particularly often used mineral substances of highly developed surface are silica and alumina while among organic substances are both chemical compounds of defined composition like acenaphthene, naphthalene, formaldehyde, alcohols, and mixtures of organic substances, for instance olefins and industrial waste [2–8].

Mineral-carbon sorbents are produced by mechanical mixing of mineral and carbon substances or the deposition of carbon substance in the structure of mineral by inserting carbon precursors between gel particles and then its carbonization. They are competitive both to active carbons and mineral sorbents such as alumina. Moreover, compared to active carbons, they have better mechanical resistance and allow to shape their hydrophobic–hydrophilic surface character [9].

Mineral-carbon sorbents are characterized by certain specific properties compared to that of “classical adsorbents”. Their surface possessing a mosaic character can adsorb both organic and inorganic substances [10]. Equally important is role of chemical groups present on the adsorbent surface because such groups give possibility to polar interactions [11].

Many natural inorganic substances are used to obtain mineral-carbon sorbents [1, 10, 12–15].

Authors [10] used natural Palygorskite as the initial material for production of series mineral-carbon sorbents. These materials were prepared using several procedures: thermal treatment in nitrogen stream on heating at

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20–200 °C for 1 h and 700 °C for 1 h, hydrothermal treatment and treatment in CCl_4 atmosphere under the same conditions as thermal treatment. It was shown that the carbon deposits formed during carbonization process are characterized by high mechanical resistance and relatively uniform distribution at the matrix surface. The Lewis acidic sites (Al^{3+} , Fe^{3+}) and bridging hydroxyls and as Brönsted acid sites at the surface of the mineral matrix play important role upon preparation hybrid adsorbents.

Other authors [15] used organic-modified clays based on montmorillonite by embedding ammonium organic derivatives with different chelating functionalities. These sorbents have good effectivity in removals of heavy metals.

The aim of this article was summary and presentation of important conclusions from several years investigation of possibility of production concerning hydrophobic mesoporous mineral-carbon sorbents from aluminum hydroxide and compositions of coal-tar pitch-polymers. It was known possibility of utilization PET wastes by producing activate carbon [16]. In literature references is not any information's about using polymer-tar pitch compositions as raw materials to produce sorbents. In presented work was investigated methods of preparation alumina-coal-tar pitch-polymer sorbents and also was determined their hydrophilic–hydrophobic properties.

Materials and methods of sample preparation

As carriers of coal pyrolyzate, granulated coal-tar pitch produced by Institute for Chemical Processing of Coal, Zabrze, Poland, pitch-polymer compositions containing up to 50 wt% of poly(ethylene terephthalate) or phenol–formaldehyde resin were used. Highly porous aluminum hydroxide was applied as a mineral matrix. The precursor for the preparation of aluminum hydroxide was aluminum chloride (purified) produced by POCh Gliwice.

Three methods for obtaining alumina-coal-tar pitch-polymer sorbents was applied.

First method depended on carrying out coal-tar pitch in semi-liquid state by heating up in sand baths and mixing in suitable proportions with mineral matrix.

The next methods were based on the use of the suitable solvent, which dissolves coal-tar pitch entirely. It was chosen two substances dissolving pitch in the high degree: chloroform and *N*-methylpyrrolidone. In the case of second solvent it was possibility to apply method of co-precipitation aluminum hydroxide in environmental of coal-tar pitch polymer compositions. All samples were carbonized in nitrogen atmosphere in an electric tube furnace in 600 °C for 3 h.

In order to use modified pitches for the production of mineral-carbon sorbents, actions aimed at the preparation of products of their modification having very high

softening points, high coke number and high fluidity were undertaken.

Thermal properties of products of carbonization coal-tar pitches modified with phenol–formaldehyde resin and poly (ethylene terephthalate), containing 10–50% of polymeric additive, were studied.

Carbonization was carried out in two stages in nitrogen atmosphere. The first stage of initial carbonization was conducted by heating the sample to the temperature of 520 °C with the temperature increase rate of 5 °C/min, holding in this temperature for 1 h and then cooling. The second, main stage of carbonization was carried out by heating the sample to the temperature of 520 °C with the heating rate of 15 °C/min and then to 850 °C (final temperature was maintained for 1 h) with the rate of 5 °C/min.

Experimental methods

In this study thermal properties of products of carbonization coal-tar pitches modified with phenol–formaldehyde resin and poly (ethylene terephthalate), containing 10–50% of polymeric additive, were studied. Thermal properties were studied using Netzsch Maia F3 scanning differential calorimeter (DSC). DSC studies allowed to examine the behavior of pitch and pitch-polymer compositions after carbonization in temperatures from -30 °C do 530 °C, with the heating ratio of 3°/min.

In order to evaluate the structural properties of the samples of mineral matrix and mineral-carbon sorbents, adsorption studies were carried out in a vacuum glass apparatus. Measurements of water vapors at 20 °C by McBain–Bakr gravimetric method was carried out. These investigations was compared with presented earlier [19] nitrogen adsorption at -196 °C by volumetric method and adsorption of benzene vapors. Samples were outgases at 100 °C (heating rate 1 °C/min).

With the use of “Izotermy” [17] computer software, the calculations of specific surface by BET method (S_{BET}) and distributions of pore via effective radii was conducted.

Selection of optimal ratio of components for obtaining compositions coal-tar-pitch polymer as carbon pyrolyzate

In DSC curves it was observed only one effect connected with desorption of water (Fig. 1). The highest amount of water is determined for carbonization products of composition containing 50 wt% of PET. It indicates big sorption capacity for this samples. On the Figs. 2, 3 it was shown temperature of water desorption determined on the base DSC for carbonization product of coal-tar pitch-PF and PET compositions. The highest temperature of desorption water was observed also for sample containing 50 wt% of

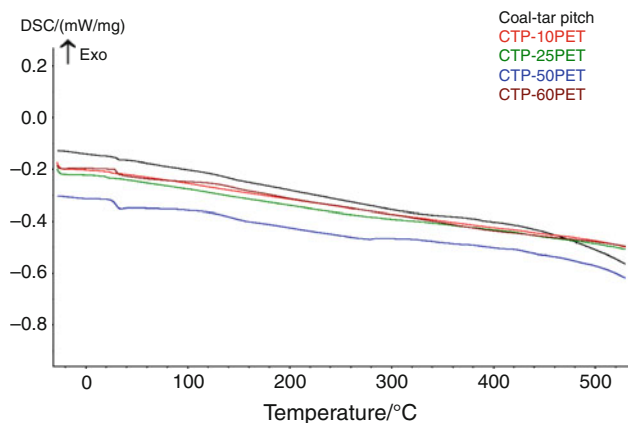


Fig. 1 DSC curves of carbonization product obtained from coal-tar pitch-PET compositions

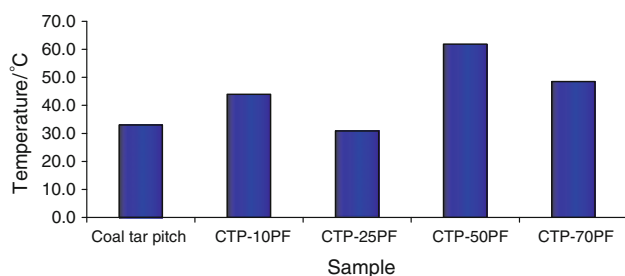


Fig. 2 Temperature of water desorption determine on the base DSC for carbonization product of coal-tar pitch-PF compositions

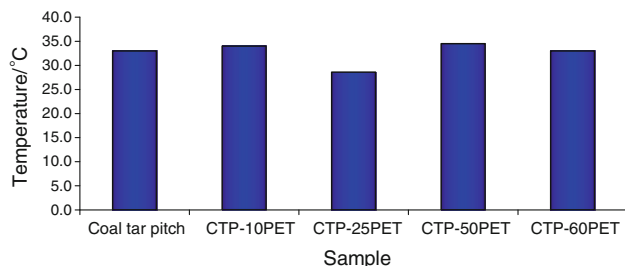


Fig. 3 Temperature of water desorption determine on the base DSC for carbonization product of coal-tar pitch-PET compositions

polymers. Compositions with 50 wt% additions of polymers were chosen for preparations of mineral-carbon sorbents.

Investigations of optimal method for obtaining alumina-carbon sorbents

In the initial investigations it was determined optimal conditions of carbonization process—temperature 600 °C, nitrogen atmosphere and time 3 h [18]. They enable on the one hand deeper carbonization carbonaceous substances and on the other hand do not cause in significant degree degradation of mineral matrix surface. Obtained in

mentioned above conditions specific surface area of carbon pyrolyzate from coal-tar pitch was 30 m²/g (Fig. 4). In the case of usage of low temperatures and shorter time of carbonization samples of carbon pyrolyzate with development of specific surface area (but not higher than 10 m²/g) was obtained.

Specific surface of aluminum hydroxide determined on the basis of low-temperature nitrogen adsorption was into the range of 170–180 m²/g, while the surface of alumina obtained during calcinations in 600 °C aluminum hydroxide is ca. 200 m²/g (Fig. 4). The development of specific surface is caused by dehydration of aluminum hydroxide. Dehydration of mineral matrix during carbonization of mineral-carbon mixture is also beneficial for the development of the final product's surface.

The main problem encountered in the investigations was appointment of method for preparation of preliminary mineral-carbon mixture, the substratum of carbonization process. For this purpose three methods were applied.

First method depended on carrying out coal-tar pitch in semi-liquid state by heating up in sand baths and mixing in suitable proportions with mineral matrix. This method was problematical because of necessity to use too large amounts of coal-tar pitch substance in relation to mineral matrix, necessary to obtain a homogeneous mixture. The carbonization product obtained by this method exhibits low specific surface area, about 25 m²/g (Fig. 4). It is caused by too large amount of carbon pyrolyzate in creating the porous structure. It cannot also be excluded that the processes the dehydration of mineral matrix (aluminum hydroxide) slowed down through carbon pyrolyzate layer. Moreover, the very well developed surface area of mineral matrix causes, during homogenization process, adsorption of light oil fractions from pitch, which makes impossible the obtainment of homogeneous mixture.

The next two methods were based on the use of the suitable solvent, which dissolves coal-tar pitch entirely. In the study such different solvents as: toluene, *N*-methylpyrrolidone, methanol, chloroform, phenol, acetone, and *n*-hexane were applied. During the selection, it was important to find a substance which has simultaneously hydrophobic properties, enabling dissolution of coal-tar pitch, and properties which make possible mixing up the solvent coal-tar pitch system in water.

Two substances were chosen dissolving pitch in the high degree: chloroform and *N*-methylpyrrolidone. Chloroform is characterized by relatively low boiling temperature, about 62 °C, which is essential from the point of view of possibility of its removal from the system by evaporation, after mechanical mixing with mineral matrix. However, limited solubility in water, about 8 g/100 cm³, is a defect of this solvent. Due to this, chloroform was used only in the method of mechanical mixing of components in a solution.

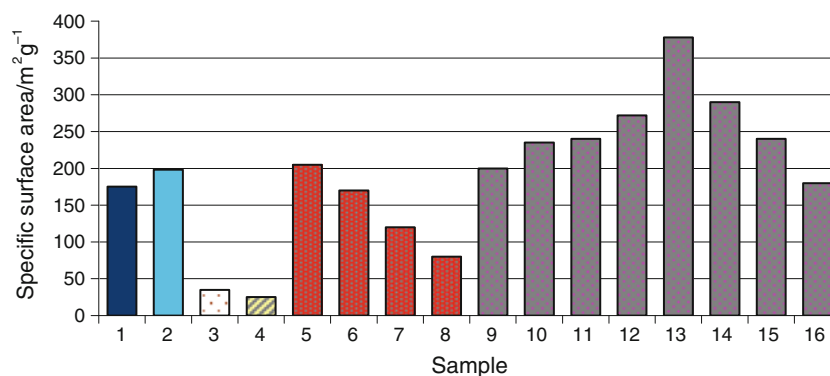


Fig. 4 BET surface area for mineral-carbon sorbents obtained using different methods of homogenization of raw materials. **1** raw aluminum hydroxide. **2** aluminum hydroxide after calcinations under conditions: 600 °C/3 h. **3** coal-tar pitch carbonized under conditions: 600 °C/3 h. **4** sorbent obtained by the method of mixing components

in raised temperature. **5–8** sorbents obtained by the method of mixing components in chloroform, content of coal-tar pitch: 4, 9, 16, and 33 wt%. **9–16** sorbents obtained by the methods of co-precipitation, content of coal-tar pitch-polymer compositions: 0.5, 1, 5, 8, 10, 12, and 20 wt%

Mineral-carbon sorbents obtained after carbonization process of mixture of mineral matrix and dissolved in chloroform coal-tar pitch were characterized by higher value of specific surface area, in the range from 80 to 205 m²/g, in comparison to sorbents obtained by the method of mechanical mixing of substrates. (Fig. 4).

The next selected solvent, *N*-methylpyrrolidone, is characterized by high solubility in water, and simultaneously high boiling temperature (202 °C). It makes impossible of its application in mechanical mixing methods, because of uncontrolled decomposition of mineral matrix in the temperature conditions that are necessary to removing the residue of solvent. However, high solubility in water makes possible the application of co-precipitation method. It was found that this method was optimal to obtain alumina-coal-tar pitch-polymer sorbents from the point of view their high specific surface area (Fig. 4) and hydrophobization of mineral matrix area.

Given amount of pitch (or pitch-polymer composition containing 50% polymers) in adequate mass ratio with aluminum hydroxide, was dissolved in 200 cm³ of *N*-methylpyrrolidone. Such mixture was placed in a thermostat heated at 100 °C, and 0.5 M aluminum chloride and 1.5 M ammonia aqueous solutions were dosed into the mixture at constant rate. After finishing the dosing the mixture was annealed in 100 °C for 1 h, after which it was cooled to room temperature and separated on paper filter. Obtained precipitate was dried in a laboratory drier at 100 °C and then it was subjected to carbonization [9].

It is important to see that specific surface area of alone carbon pyrolyzate obtained in the used conditions is very small (about 30 m²/g) in comparison of mineral-carbon sorbents. The present of catalytical centers on the surface of mineral matrix play mainly role in development of porous structure of carbonization products [10].

Low-temperature nitrogen adsorption studies of the samples obtained by co-precipitation of aluminum hydroxide in the environment of coal-tar pitch-polymer compositions and carbonization indicate the increase of surface for the concentration of pitch from 0.5 to 10% in the initial mixture. The highest value of specific surface ca. 370 m²/g had the sample containing 10% of pitch-poly (ethylene terephthalate) or pitch-phenol-formaldehyde resin compositions (Fig. 4). It has to be noted that specific surface of obtained sorbents is significantly higher compared to the initial mineral matrix calcinated in the same conditions, which proves that the obtained product has new, different porous structure. Further increase of pitch content in the initial mixture results in the overtaking of the structure building role by carbon pyrolyzate, which results in the reduction of specific surface [19].

Calculated values of S_{BET} specific surface with the assumption of horizontal orientation of benzene indicate that with increasing content of carbon pitch compared to mineral matrix, specific surface of obtained sorbents increases. The highest value of S_{BET} specific surface, have the samples containing initially 10% of pitch-polymer compositions [18, 19].

Based on earlier determined adsorption of benzene isotherms [19] it was calculated in this study pore size distributions via effective radii for investigated sorbents (Fig. 5).

For the samples of alumina-coal-tar pitch-polymer, there is a dominance of about 17 Å radii, and they exhibit monodisperse distribution of pore surface (Fig. 5). It indicates that independently on using coal-tar pitch—compositions as raw carbonaceous substances, the result is mineral-carbon sorbents with defined mesoporous surface.

From the comparison of S_{BET} values calculated on the basis of benzene vapors adsorption assuming horizontal

Fig. 5 Pore surface distribution curves related to effective radii for the sample of alumina-coal-tar pitch-polymer compositions

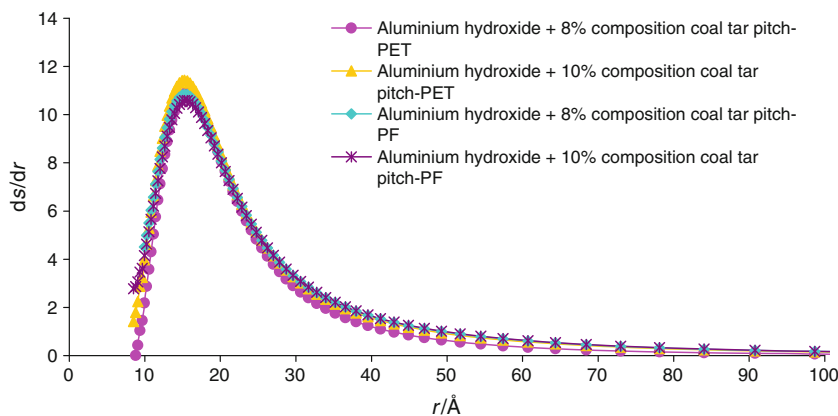
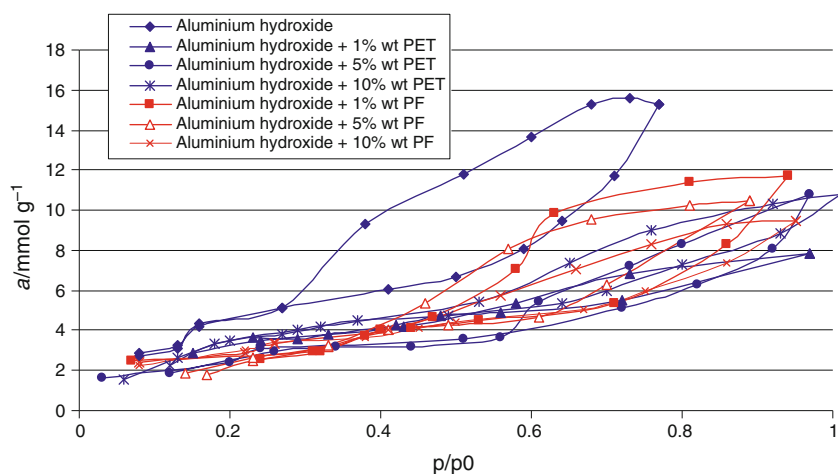


Fig. 6 Isotherms of water adsorption and desorption for samples alumina-coal-tar pitch-polymer sorbents



and vertical orientations of benzene molecules and S_{BET} determined from the low-temperature nitrogen adsorption it can be concluded that the sample of initial aluminum hydroxide contains high amounts of surface hydrophilic centers preventing horizontal orientation of benzene molecules in the adsorption layer. The samples containing initially introduced compositions of coal-tar pitch-polymer had the surface uniformly covered with carbon pyrolyzate, which is testified by decreased value of S_{BET} (horizontal), compared to S_{BET} calculated from nitrogen adsorption [18, 19].

For confirming this thesis adsorptions and desorptions isotherms of water vapors were determined for investigated materials (Fig. 6).

Wide hysteresis loops for benzene vapors adsorptions and desorption isotherms indicate that the porous structure on the surface of samples is well developed, including pores of irregular shapes. The higher position and wider hysteresis loop has isotherm for aluminum hydroxide. It confirms high interactions between material and adsorbed molecules. The shape of isotherms for all studies samples, initial matrix, and sorbents alike is similar, which indicates that the deposition of carbon pyrolyzate on the surface of

mineral substances does not change significantly the structure of pores obtained materials.

Obtained isotherm can be classified, according to IUPAC nomenclature, to the H2 type. It meets the case of pores

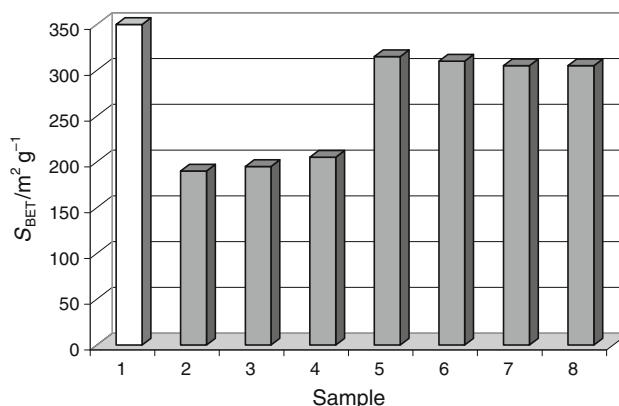
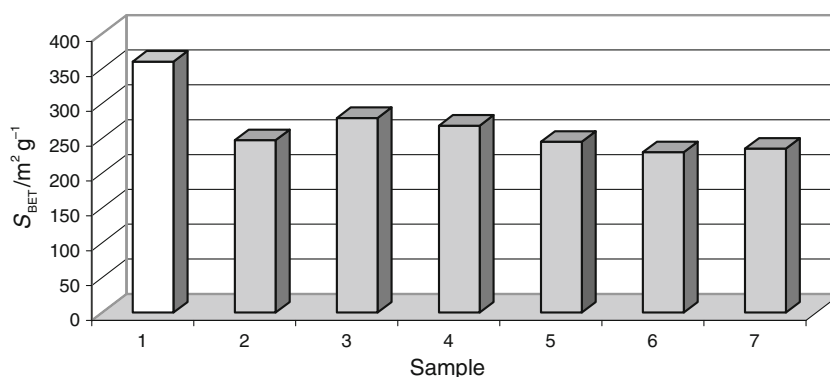


Fig. 7 Specific surface area determined on the base of isotherm of water vapors. **1** aluminum hydroxide after calcinations in 600 °C/3 h. **2–8** sorbents obtained by co-precipitation with the initial concentration of 50% pitch + 50% poly(ethylene terephthalate) of: 0.5, 1, 5, 10, 12, 15, and 20 wt%

Fig. 8 Specific surface area determined on the base of isotherm of water vapors. **1** aluminum hydroxide after calcinations in 600 °C/3 h. **2–7** sorbents obtained by co-precipitation with the initial concentration of 50% pitch + 50% PF of: 1, 5, 10, 12, and 15 wt%



graphically described as an “ink-well” and spherical pores with open endings and significant contractions.

The results of this study allow to ascertain that applied calculation models lead to a concordant picture of changes of the porous structure of carbonizates obtained from aluminum hydroxide with an organic substances. No micropores were found in the samples.

Calculated on the base adsorption of water specific surface area can indicate that these samples are characterized by uniform coverage of surface with hydrophobic carbon pyrolyzate.

It was found that the highest value of S_{BET} is characterized for sample of aluminum hydroxide (about 350 m^2/g) Figs. 7, 8. It belongs to notice that specific surface area determined for alumina by low nitrogen adsorption is about 200 m^2/g . It indicates strong hydrophilic properties of this material. Mineral matrix covered with carbon pyrolyzates give smaller development of porous structure determined by water adsorption. It is a effect of hydrofobization of surface of mineral matrix.

Summary

It was found that properties of mentioned sorbents depend strongly on method of mixing mineral and carbon components, amount of organic substances in initial mineral-carbon mixture, kind of organic substances, proportions of coal-tar pitch—polymer compositions and conditions of carbonization process. These conclusions were agreed with reference [10].

Optimal method for obtaining alumina-coal-tar pitch-polymer adsorbents is co-precipitation of a mineral matrix in an environment of carbonaceous substances. The method causes the incorporation of pitch particles into crystalline structure of aluminum gel and proved to be the best to prepare, during the process of carbonization, a sorbent of much more developed mesoporous structure. Distinct synergism of interaction between mineral and organic component is well visible in this case. The process of infiltration of organic substance particles into porous

structure of formed gel particles assures the covering of matrix surface with thin, homogeneous layer of carbon pyrolyzate. Carbonizates prepared by this method with the use of 10% of pitch-poly(ethylene terephthalate) or pitch-phenol–formaldehyde resin compositions have the highest values of specific surface (ca. 370 m^2/g) and well developed mesoporous structure.

Thermo analytical methods, in particularly DSC, can be useful to determine sorption ability of carbonizates obtained from coal-tar pitch-polymer compositions. Among others on this base it was found that the optimal additive to organic substances is 50 wt% of polymer.

Obtained results of water adsorption in connection with earlier investigations of nitrogen and benzene adsorption show that the sorbents are characterized uniform coverage of mineral matrix by carbon pyrolyzate and hydrophobic properties. It is important form point of view of using mineral-carbon sorbents in the processes of hydrocarbon polluted wastewaters purification, which was tested in the article [19].

Carbonization process of coal-tar pitch-polymer compositions on the surface of aluminum hydroxide is probably catalytical processes by cooperation of active centers (cations Al^{3+}) of mineral matrix. It can indicate low surface area of coal-tar pitch carbonization product in compare of surface of finally sorbents.

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