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MINERAL-CARBON SORBENTS BASED ON POST-DECARBONIZATION LIME AND MIXTURE OF HYDROCARBONS

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An attempt was made to obtain mineral-carbon sorbents from waste products of petrochemical industry: lime from the decarbonization of river water to be used in technology and hydrocarbon wastes obtained in the treatment of industrial waste waters. The sorbents were prepared by thermal decomposition of mixtures of the mineral and carbon components. In order to optimize the preparation conditions, physicochemical studies were performed of both the mineral matrix and the mineral-carbon sorbents. Adsorption measurements involving nitrogen, water, and benzene as adsorbates were used for determining the parameters of porous structure of the obtained materials and their hydrophilic–hydrophobic properties. The properties influencing the sorptive properties of the organic compounds present in the petrochemical wastes were pointed out.

Keywords: *hydrophobic–hydrophilic properties, mineral-carbon sorbents, mixture of hydrocarbons, post-decarbonization lime, waste water treatment*

Introduction

Much attention has been paid for recent years to the so-called mixed systems [1]. These are mixtures of two or more sorbents and have the adsorption and structural properties generally much different from those of the individual components of the mixture. Among them there are so called mineral-carbon sorbents which are two-component materials containing the inorganic mineral matrix and organic material. The essential features of such sorbents are: low unit price, high sorption capacity, comparable with that of active carbons, and high mechanical strength. The joint properties of both the carbon and the inorganic components are of great importance in separation of complex mixtures.

The competitiveness of sorptive properties of the sorbents, as compared with those of active carbons, depends on the degree and homogeneity of carbonation of the mineral matrix, which can be controlled by a proper procedure of deposition.

The mineral-carbon sorbents can be obtained by mechanical mixing of the mineral component with the carbon material or by inclusion of the carbon sorbent inside the mineral structure of the matrix, between the particles of the gel used (e.g. silica) [2–4].

The aim of this work was to study the possibility of obtaining mixed carbonate–carbon sorbents with the use of waste petrochemical materials.

The experimental procedures aimed at determining the optimum composition and optimum conditions of obtaining carbonate-carbon sorbents suitable for removal of organic matter from petrochemical waste waters. Thus, an attempt was made to realize the idea of closing the technological streams by using waste materials for sorbents manufacture.

The sorbent materials were obtained by thermal decomposition of mixtures of post-carbonation lime (the mineral component) with waste hydrocarbons (the organic component).

Experimental

Material and methods

Post-decarbonization lime was used in this work as the mineral matrix of the complex sorbents, and a mixture of hydrocarbons obtained in the flotation of petrochemical waste waters served as the organic component.

The post-decarbonization lime is a waste material obtained in the treatment of river water to be used in the technological process of a refinery-petrochemical plant. In this process, realized in the so-called accelerators, easily hydrolysable heptahydrate iron(II) sulfate is used as a coagulant, and lime milk as a decarbonizing and pH-increasing agent. The technological process for obtaining post-decarbonization lime was developed at the Institute of Chemistry at Warsaw University of Technology, Branch at Płock [5]. This process aiming at a proper treatment of forming muds includes such units as: degassing, sedimentation and filtration. The final product taken from the

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waste water treatment plant, in the form of bright yellow and easily triturable powder was used as the mineral matrix for the complex sorbents.

The organic component of the complex sorbents consisted of waste hydrocarbons collected from the refinery-petrochemical wastes treatment plant. The use was made of a mixture of hydrocarbons collected from flotation of liquid wastes from the petrochemical processes and containing considerable amounts of aromatic hydrocarbons. It has been assumed that the increased content of aromatic compounds can be favourable for obtaining polycyclic carbon structures characteristic for the sorbents. The hydrocarbon mixture used had the form of semi-liquid black matter of high content of aromatic compounds. The loss of mass determined at 105°C was 48.7 mass%.

The investigation was carried out in two stages. In the first stage the physicochemical transformations of the mineral matrix (post-decarbonization lime) were studied as a function of calcination parameters such as temperature (150, 350, 450, 500, 600 or 900°C), time (0.5 or 1 h) and gas atmosphere (nitrogen or air). The second part was devoted to optimization of the process of obtaining complex mineral-carbon sorbents from waste hydrocarbons and post-decarbonization lime. A number of compositions were prepared with different contents of the organic component and the mineral matrix. The starting mixture was obtained by weighing-up and mixing suitable amounts of the two components with subsequent homogenization. The homogenous mixtures were placed in a tubular furnace preheated to a suitable temperature and were then carbonized for a predetermined time. The essential carbonization parameters: temperature 450°C, nitrogen atmosphere, and calcination time 0.5 h were a result of former studies on manufacture of mineral-carbon sorbents [6–8].

The samples of the post-carbonization lime, products of its calcination, and mineral-carbon sorbents were studied by thermal analysis, X-ray diffraction analysis, adsorption and desorpion of benzene and water vapours, and low-temperature adsorption of nitrogen.

The IR spectra were recorded for tablets with KBr within the wavenumber 4000–400 cm^{-1} by means of a Genesis II FTIR spectrophotometer (produced by Mattson) provided with a computer-controlled Fourier transformation.

The X-ray diffraction patterns were recorded by means of a HZG-4C diffractometer with a Cu lamp, within the 2θ degree 5–60°.

The thermogravimetric studies were carried out with the use of a computer-controlled thermoanalyzer SDT 2960 TA Instruments. The samples of mass 20 mg were heated with a rate of 10 K min^{-1} within a temperature 20–1000°C.

Adsorption and desorption isotherms of benzene vapours and water were determined by the gravimetric method using a vacuum apparatus of McBain–Bacr type. The calculations of BET specific surface (S_{BET}), specific surface (S_t), micropore volume (V_{micro}) by the de Boer's method, mesopore surface area (S_{mes}) from the adsorption and desorption parts of the isotherms by the Kiselev method, and distribution of the mesopore volume and surface by Dollimore–Hill method (ΣS, ΣV) were performed using the formerly developed computer programme 'Isotherms' [9, 10].

Results and discussion

Investigation of mineral matrix

The physicochemical studies of the mineral matrix (post-decarbonization lime) have shown that it consists mainly of calcite, which is the crystal form of calcium carbonate. This was evidenced by both the X-ray phase analysis and by IR absorption spectra (Fig. 1). The presence of carbonates in the samples is confirmed by the presence of absorption bands in the spectra within the wavenumbers 2500, 1790, 700 and 875 cm^{-1} [11–13]. The estimated content of calcite in the material studied, as determined by thermogravimetric studies, was about 72 mass%. It is not excluded that calcite is accompanied by some amorphous components such as oxides or hydroxides of magnesium, iron, or calcium. The composition of the products of calcination at temperatures within 150–500°C was similar to that of the initial lime. Increase of calcination temperature within this region results in increasing sample dehydration and decomposition of metal hydroxides, which becomes almost complete at 600°C. A substantial difference has been found in the results obtained for lime samples calcined at 900°C (Fig. 1). At this temperature calcite was found to undergo a thermal dissociation to produce calcium oxide. The sample contained also some portlandite due to the hydration of CaO.

The analysis of the parameters of porous structure determined from adsorption of benzene vapours for pure components of post-decarbonization lime (Table 1) indicates that both calcium hydroxide and calcium carbonate have low sorption capacities. Their specific surface is from 1 to 2 $m^2 g^{-1}$. The adsorption of benzene vapours on iron(III) hydroxide is also small, although much higher than that on $Ca(OH)_2$ and $CaCO_3$ (S_{BET}=6.6 $m^2 g^{-1}$).

The specific surface of initial post-decarbonization lime is much higher than that of its potential components. It may be due to the role of its other components, such as hydroxides. In the process of decarbonization and coagulation of Vistula water by means of

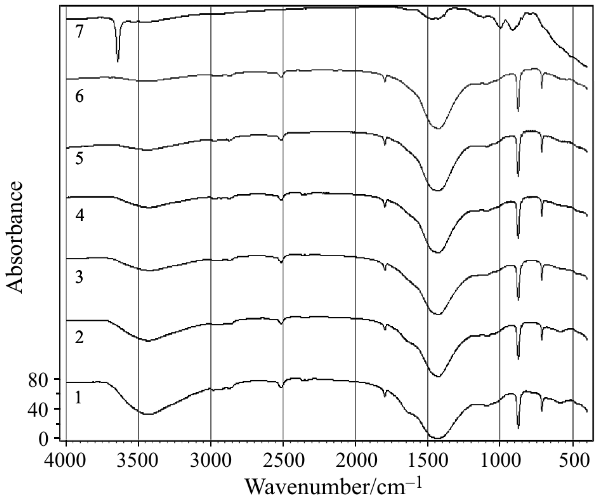

Fig. 1 Infrared absorption spectra of post-decarbonization lime and its calcination products: 1 – initial lime, 2 – lime (150°C nitrogen/0.5 h), 3 – lime (350°C/nitrogen/0.5 h), 4 – lime (450°C/nitrogen/0.5 h), 5 – lime (500°C/nitrogen/0.5 h), 6 – lime (600°C/nitrogen/0.5 h), 7 – lime (900°C/nitrogen/0.5 h)

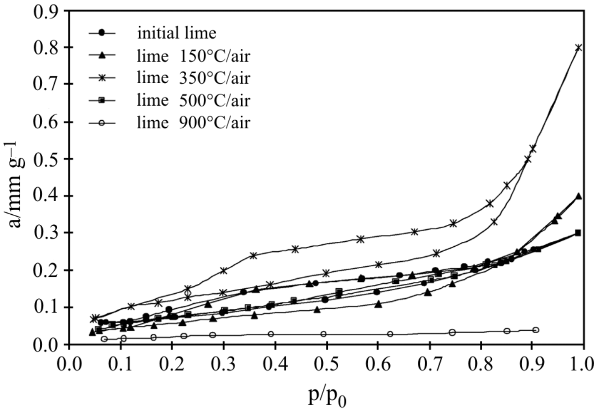

Fig. 2 Adsorption and desorption isotherms of benzene vapours of post-decarbonization lime and its decarbonization products

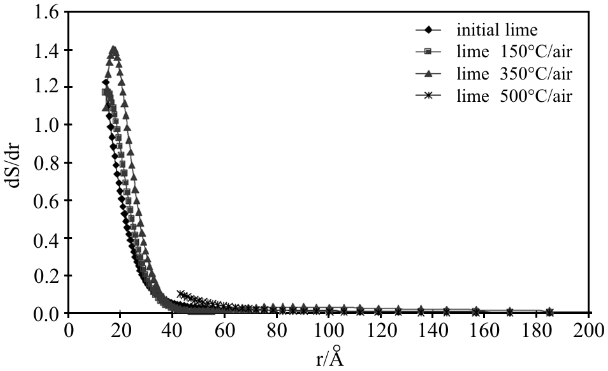

Fig. 3 Pore surface as a function of effective radius for post-carbonization lime and its calcination products

$FeSO_4{\cdot}7H_2O$ and $Ca(OH)_2$ the process of $CaCO_3$ formation is accompanied by the precipitation of hydroxides of different solubility products.

The hydroxide formed at higher pH values is deposited on colloidal particles of hydroxides of smaller solubility products. The hydroxides formed are deposited on the surface of calcium carbonate giving a new porous structure. The possibility of occurrence of hydroxides as potential admixtures of post-decarbonization lime was confirmed in the course of thermogravimetric studies [14, 15]. They have probably amorphous or finely crystalline structures. Heating a post-decarbonization lime at 350°C for 1 h in air atmosphere improves its sorptive capacity for benzene vapours and increases the specific surface.

The thermal analysis of the products of calcination at that temperature may be due to partial thermal dissociation of the hydroxides included in the crystal structure of calcite. Further heating at 500°C leads to a slow reduction of the sorptive properties of the product owing to the processes recrystallization, sintering and shrinking of the crystalline phase of calcite. The product obtained by heating for 1 h at 900°C in air exhibits practically complete disappearance of the sorptive capacity as evidenced by the shape of the adsorption isotherm, characteristic for the advantage of macropores in the sample (Fig. 2) and small specific surface.

The mesopore surface values obtained from the distribution by Dollimore–Hill and Kiselev's methods are in accordance with S_{BET} values (Table 1). The mathematic models used in the case of de Boer's method did not reveal the presence of micropores in the samples studied.

The distribution of mesopore surface as a function of effective radii (Fig. 3) was determined by the Dollimore–Hill's method with assumption of the model of cylindrical pores, open from both sides, for quartz as the adsorption layer. It has been found that the pores of radii within 15–20 Å contribute the most to the porosity of the samples. The increase of the pore volume and surface of the sample calcined at 350°C is due to the insignificant increase of their effective radii up to 20 Å.

It has been shown in former papers [6–8] that the chemical structure of the surface of sorbents has a substantial effect on their sorptive capacity. The hydrophilic–hydrophobic properties depend on the surface functional groups which are decisive for the different orientation of benzene molecules sorbed and for the degree of their packing in the adsorption layer. The different orientation of the adsorbed benzene molecules may be proved by the comparative analysis of adsorption of nitrogen and benzene. The nitrogen molecule (inert gas) has a small seating surface (0.16 nm^2) as

Table 1 Porous structure parameters of post-decarbonization lime, its calcination products and its pure components determined from the sorption isotherms of benzene vapours

Sample	Specific surface (nitrogen)	Specific surface (benzene)		Surface (de Boer method)	Surface of mesopores (Kisielov method)			Dollimore–Hill's method	
	S_{BET}/ $m^2 g^{-1}$	$S_{BET(planar)}$/ $m^2 g^{-1}$	$S_{BET(vertical)}$/ $m^2 g^{-1}$	S_t/ $m^2 g^{-1}$	S_{mes} adsorption/ $m^2 g^{-1}$	S_{mes} desorption/ $m^2 g^{-1}$	S_{AVR} / $m^2 g^{-1}$	ΣS/ $m^2 g^{-1}$	ΣV/ $cm^3 g^{-1}$
$CaCO_3$	–	1.2	0.8	1.6					
$Fe(OH)_3$	–	6.6	4.1	7.7					
$Ca(OH)_2$	–	2.0	1.3	2.1					
initial lime	15.0	15.2	9.4	12.7	9.8	12.5	11.2	11.9	0.02
lime 150°C	13.1	13.6	8.5	17.9	10.3	16.4	13.4	14.3	0.03
lime 350°C	22.6	25.1	16.4	35.5	16.2	28.9	22.6	21.7	0.07
lime 450°C	18.1								
lime 500°C	17.4	17.3	10.8	21.6	4.2	4.7	4.5	5.3	0.02
lime 600°C	13.9								
lime 900°C	7.3	4.8	3.0	6.3	–	–	–	–	–

Table 2 Porous structure parameters of selected samples of carbonate-coal sorbents obtained from post-decarbonization lime and waste hydrocarbons, as determined with the use of nitrogen, water and benzene as the adsorbates

Content of hydrocarbons in initial mixture	Specific surface (water)	Specific surface (nitrogen)	Specific surface (benzene)		Surface (de Boer method)	Surface of mesopores (Kisielov method)		Dollimore–Hill's method	
	S_{BET}/ $m^2 g^{-1}$	S_{BET}/ $m^2 g^{-1}$	$S_{BET(planar)}$/ $m^2 g^{-1}$	$S_{BET(vertical)}$/ $m^2 g^{-1}$	S_t/ $m^2 g^{-1}$	S_{mes} adsorption/ $m^2 g^{-1}$	S_{mes} desorption/ $m^2 g^{-1}$	ΣS/ $m^2 g^{-1}$	ΣV/ $cm^3 g^{-1}$
initial lime	94.30	15.0	15.2	9.4	12.7	9.8	12.5	11.9	0.020
10%	–	17.4	8.2	5.1	12.9	14.1	21.9	22.2	0.084
20%	28.20	18.0	–	–	–	–	–	–	–
30%	10.00	15.0	17.3	10.8	14.9	12.9	18.2	16.8	0.044
70%	–	25.3	19.0	11.9	18.9	10.2	29.5	25.5	0.041
90%	–	38.2	23.7	14.8	33.9	21.6	21.3	19.5	0.070
95%	7.63	56.0	–	–	–	–	–	–	–

compared with that of benzene molecule (0.25 nm^2 in the vertical orientation and 0.40 nm^2 in the planar orientation). For this reason, if the surface structure is favourable for the planar orientation of benzene molecule, the specific surface $S_{\mathrm{BET(planar)}}$ should be smaller or equal to the S_{BET} value determined from the adsorption of nitrogen. Excessive values of $S_{\mathrm{BET(planar)}}$ with respect to the specific surface values determined from nitrogen adsorption may be accounted for the decrease of the surface accessible for seating of benzene molecules, which can be a result of the change in orientation of its molecules in the adsorption layer.

The similarity of results obtained in specific surface determination of post-decarbonization lime and its calcination products (Table 1), based on adsorption isotherms of benzene and nitrogen, may be considered as a proof of planar orientation of benzene molecules in the adsorption layer. The orientation does not change with the increasing of calcination temperature within 150–900°C. The chemical structure of benzene molecule enables to suppose that its behaviour as the adsorbate is controlled by the interaction of the labile π electrons. The non-dispersive phase interactions are probably responsive for the formation of coordination bonds between Ca and benzene and for the planar orientation of the adsorbate molecules.

The analysis of the obtained results enables to state that, from the viewpoint of using the post-decarbonization lime as a matrix for mineral-carbon sorbents the optimum carbonization temperature lies in the range of 350–450°C.

Investigation of mineral-carbon sorbents

Thermal analysis of the calcination products of mixtures of post-decarbonization lime with various amounts of waste hydrocarbons shows that the thermal decomposition proceeds in three stages. The carbonization of the mineral-carbon mixtures resulted in a partial dissociation of metal hydroxides present in the post-decarbonization lime and in a pyrolysis of the organic matter.

The process of heating the samples in temperature range 20–1000°C (Fig. 4) shows that physically adsorbed water evaporates at temperatures up to 200°C. The carbon pyrolysate is burned within 300–650°C (the maximum of the process is observed on the DTG curve at about 430°C), and thermal dissociation of carbonates proceeds above 650°C. The content of carbon pyrolysate in the samples varied within 1 to 20 mass%.

The adsorption and desorption isotherms of benzene vapours shown in Fig. 5 indicate that the samples used have essentially mesoporous structure with rather small pore radii, as evidenced by narrow hysteresis loop and abrupt increase of adsorption at p/p_0 values not lower than above 0.7.

The specific surface of the materials studied, as well as the mesopore surface area and volume, increase with increasing amount of the organic substance, up to 23.7 m^2 g^{-1} (with assumption of planar

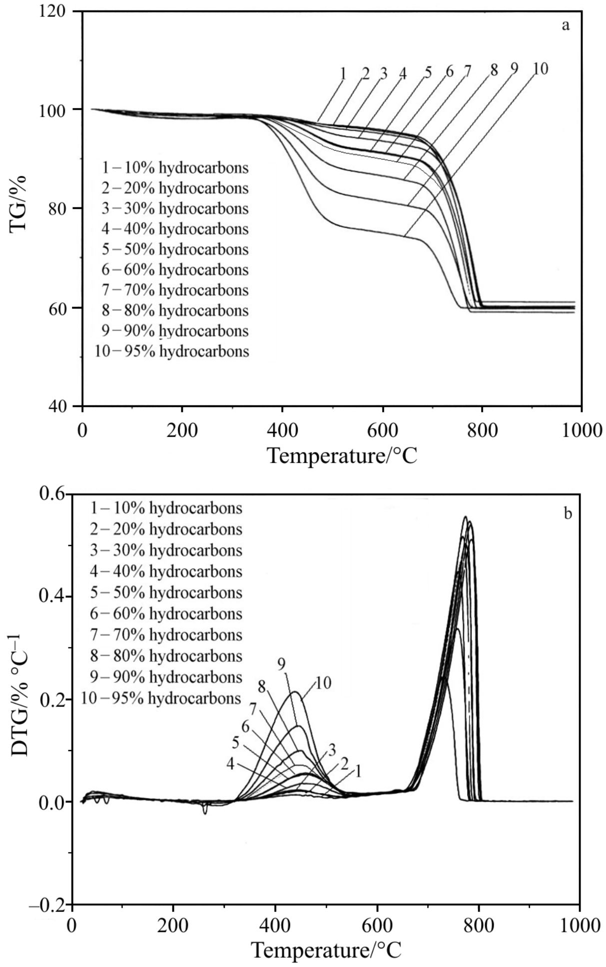

Fig. 4 a – TG and b – DTG curves obtained for samples of carbonate-coal sorbents

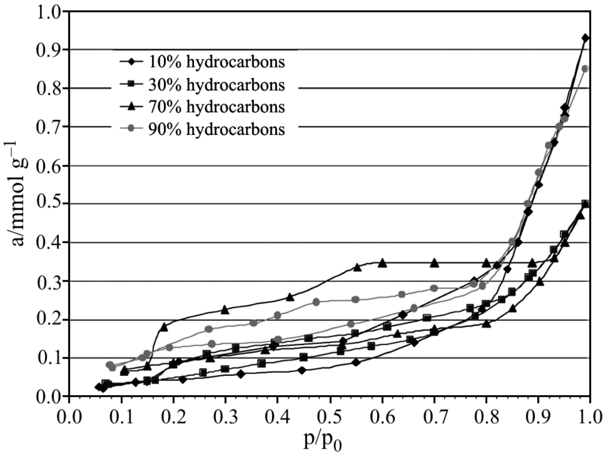

Fig. 5 Adsorption and desorption isotherms of benzene vapours on carbonate-coal sorbents

orientation of benzene molecules, as shown in Table 2). This relation is due to the increasing amount of the carbon pyrolysate deposited on the surface of the mineral matrix.

Figure 6 presents the distribution of mesopore surface area and volume as a function of the effective radii. The calculations were carried out, with assumption of the model of cylindrical pores open from both ends, from the desorption parts of the isotherms. The assumption of such a pore shape enabled obtaining the mesopore surface areas closest to the values of $S_{\mathrm{BET(planar)}}$ and S_{T} – calculated by de Boer's method.

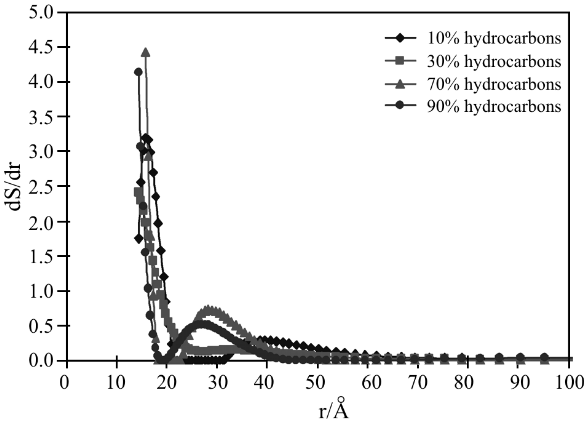

Fig. 6 Distribution of pore surface area *vs*. effective pore radii in carbonizate samples obtained from post-decarbonization lime and waste hydrocarbons

The obtained diagrams show that the sample containing 30 mass% of hydrocarbons has a monodispersive distribution of the pores (maximum values of pore surface area and volume for pore radii within 15–20 Å).

The monodispersive distribution of pore surface area and volume is a feature of the inital post-decarbonization lime and of its calcination products (Fig. 3). One may assume that the samples containing up to 30% of organic matter are not homogenous, and their surface is not fully coated with carbon pyrolysate. In such samples the naked parts of the mineral matrix are of primary importance for their porosity.

The pore surface area distribution shows that in the samples containing more than 30 mass% of organic matter initially added, the carbonization process gives sorbents of quite different porous structure. The bimodal nature is reflected by the presence of two maxima on the curve of pore surface area *vs*. pore dimensions. The pore radius decreases down to 15 Å and new pores with the radius about 30 Å are produced. These processes are strongly related to the carbonization of organic matter on the calcite surface. The carbon pyrolysate particles penetrate into the matrix mesopores thus reducing their dimensions. At the same time, the depositing pyrolysate undergoes condensation and cyclization of hydrocarbon molecules creating its own porous structure characterized with other physical parameters and geometry.

The comparison of the values of specific surface determined from adsorption of benzene vapours and low-temperature adsorption of nitrogen (Table 2) shows that the new pores formed after the deposition of carbon pyrolysate on the matrix surface are less readily accessible for the large benzene molecules. As a consequence, the specific surface determined from the adsorption of nitrogen is higher than the $S_{\mathrm{BET(planar)}}$ and $S_{\mathrm{BET(vertical)}}$ obtained from the adsorption of benzene. The most probable cause of this discrepancy seems to be due to the pore structure (narrow neck bottle shapes). The effect of nature of the surface on its affinity to the adsorbate seems to be less probable. The hydrophobic carbon pyrolysate should increase the affinity of the surface to the hydrocarbon molecules as this fact determines the increase of sorptive properties with respect to organic compounds present in the liquid wastes.

The studies of water vapour adsorption have confirmed the observations concerning the structural properties of the obtained sorbents. The surface of the mineral matrix, consisting mainly of $CaCO_3$, is strongly hydrophilic, and this property decreases drastically with increasing content of the carbon pyrolysate. The specific surface determined from water vapour adsorption is the largest for pure mineral matrix and is more than 6 times as high as S_{BET} determined from the adsorption of nitrogen (Table 2). The dense packing of water molecules on the surface is due to increased concentration of active sites, which in this case are probably oxygen atoms. Quite different situation is observed for the sample containing 95% addition of hydrocarbons: the specific surface determined from water adsorption is more than 7 times as low as the S_{BET} determined from nitrogen adsorption. This fact provides a confirmation of the former conclusion on increasing hydrophobic properties of the surface with increasing amount carbon pyrolysate spread on the mineral matrix surface.

It has been shown [16] that high specific surface and increased hydrophobic properties are decisive for the very good adsorpiton capacity for adsorbing hydrocarbons from petrochemical waste waters. A particular activity in the reduction of impurities in liquid wastes was observed in carbonate-coal sorbent containing 90% addition of a hydrocarbon mixture to post-decarbonization lime. The use of such a sorbent sample for treatment of a waste water enabled reducing the ChemOD by 86% and reducing the content of organic compounds extractable by petroleum ether by 96%.

Conclusions

Waste materials from petrochemical industry such as post-decarbonization lime and mixtures of hydrocarbons from flotation of petrochemical waste waters can be used for the production of mineral-carbon sorbents by means of the carbonization process.

The use of mineral-carbon sorbents in the treatment of waste waters contaminated with organic compounds contributes to the realization of the idea of closing technologic streams.

The physicochemical parameters of the mineral matrix depending on its structure and chemical composition are decisive for the porous structure of the mineral-carbon sorbents.

In cases, in which a macroporous matrix is used for obtaining the complex sorbents, the carbonous substances especially added in considerable amounts take the structure-forming role.

Appropriate proportions of the mineral and organic components, as well as suitable parameters of the carbonization process, are important factors influencing the physicochemical properties of the mineral-carbon sorbents obtained. In the cases of the waste materials used the optimum carbonization conditions were: temperature 450°C, time 30 min, inert gas (nitrogen) atmosphere.

A higher content of the carbon pyrolysate on surface of the post-decarbonization lime exhibit particularly high developed specific surface, hydrophobic properties and high activity in the treatment of petrochemical waste waters contaminated with organic compounds.

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