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ADSORPTION AND STRUCTURAL PROPERTIES OF MINERAL–CARBON SORBENTS

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Abstract

In the present work an attempt was made to obtain mineral–carbon sorbents by thermal decompositon. The mineral matrix for the sorbents (aluminium hydroxide) was based on petrochemical waste stream containing considerable amounts of aluminium chloride. Reference tests were carried out with a model solution prepared with the use of analytical grade $AlCl_3$. Atactic polypropylene and hydrocarbon mixtures obtained in the flotation of petrochemical waste waters were used as carbon-containing raw materials.

The aim of this work was to determine the adsorption and structural characteristics of the complex sorbents and to check the possibility of evaluation of their hydrophobic-hydrophilic properties.

Keywords: hydrophobic–hydrophilic properties, mineral–carbon sorbents, mineral matrix–aluminium hydroxide

Introduction

Adsorption and catalytic processes play a substantial role in many branches of modern technology. Among many applications of adsorption in unit processes its importance in the removal of chemical pollutants from liquid wastes is often appreciated.

Active carbon is an adsorbent which has been applied most frequently for elimination of residues of dyestuffs, detergents, hydrocarbons and other organic compounds, as well as of heavy metal ions. Because of the high price, which is a heavy barrier in application of active carbon in sewage treatment processes, there has been a world-wide tendency of replacing active carbon with mineral–carbon sorbents.

The low price of such sorbents extends the field of their application in various ecology processes, whereas their high mechanical strength, along with the high sorption capacity, comparable with that of active carbon, extends the time of their usage and gives a possibility of repeated regeneration thus improving the economy of the sorption processes. The effectiveness of mineral–carbon sorbents is not inferior to that of many active carbons, and the combination of the carbon and mineral components is of great importance in separation of complex mixtures.

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The degree and the homogeneity of carbonisation of the mineral matrix surface, which is decisive for the competitiveness of these sorbents compared with active carbons, can be controlled by suitable preparation methods [1].

Former works [2–7] were devoted to the investigation of the possibility of using some petrochemical wastes for obtaining mineral–carbon sorbents. The use of waste materials as media for sewage treatment gives both economic profits (saving of chemicals, cheap raw materials) and protection of environment by closing the circuits of some technological streams.

Experimental

Preparation of mineral matrix

The mineral matrix was obtained by precipitating $Al(OH)_3$ from aluminium salts by means of ammonia. The main raw materials used were: a model aluminium chloride solution and an $AlCl_3$-containing waste water from the installation for manufacture of phenol and acetone by the cumene method. The content of aluminium chloride in the waste water, as determined gravimetrically with the use of 8-hydroxyquinoline, varied between 6.25 and 11.88 g dm^{-3}.

In cases where aluminium hydroxide was precipitated from the waste water the variable parameters of the process were: time of ageing of the mother liquor (1–5 h), temperature (20–90°C), and assumed mass of the final product (5 g; 10 g).

An additional variable parameter – the concentration of aluminium chloride (6.25 or 11.8 g dm^{-3}), was applied in cases where pure $AlCl_3$ solutions were used for preparing the mineral matrix.

Adsorption methods were applied for establishing the optimum conditions for precipitating aluminium hydroxide of highly developed porous structure.

The detailed results of the studies of physicochemical parameters of aluminium hydroxide depending on the preparation method were presented previously.

Preparation of mineral–carbon sorbents

The carbon–aluminium sorbents were prepared by thermal decomposition of mixtures composed of a mineral matrix (aluminium hydroxide) and a carbon-containing substance. Atactic polypropylene (APP) and a mixture of hydrocarbons obtained during the flotation of petrochemical waste waters were used as the organic component. APP is a waste product obtained in polymerisation of propylene, where the required isotactic polypropylene is accompanied by 4–10% of unwanted atactic modification.

The hydrocarbon mixture used, further on referred to as the waste skim, is a waste material obtained in the flotation of petrochemical waste waters. It contains mostly organic compounds of different structure including large amounts of aromatic compounds that promote the formation of polycyclic carbon structures occurring typically in sorbent materials.

Sorbent samples were prepared either by mixing the two components (the mineral matrix and the carbon material) or by depositing the carbonaceous substance in the mineral matrix (by including the carbon sorbent particles between the gel particles in the course of the precipitation process). The final stage of the process consisted in carbonization of the mineral–carbon mixture in an inert gas (nitrogen) atmosphere.

Preparation of carbon–aluminium sorbents with the use of $AlCl_3$-containing waste waters

In order to obtain sorbent samples of required mass ratios of the two components, with APP used as a source of carbon, both components were weighed and heated together to 160°C in an electric drier. At that temperature the atactic polypropylene passed into a semi-fluid state thus enabling a good mixing of the components. Samples containing 10, 20, 30, 50 mass percent APP were prepared.

In cases where sorbents were prepared with the use of hydrocarbons from petrochemical wastes the two components were mixed together in suitable ratios at room temperature. Samples containing 30, 50, 70, and 90 mass percent of the skim hydrocarbons were obtained.

One sample composed of $Al(OH)_3$+waste skim hydrocarbons was also prepared by co-precipitation of hydroxide in an aqueous-hydrocarbon emulsion obtained by mixing together the skim hydrocarbons with the $AlCl_3$-containing waste water. In this aim a measured volume of the waste water corresponding to the required amount of aluminium hydroxide (10 g) was mixed with 200 cm^3 of the hydrocarbon mixture. The mixture was thermostated at 90°C while adding 1.32 M aq. ammonia. The process of co-precipitation was carried out for 1 h. The final value of pH was 7.0. The precipitate formed was matured for 5 h in the mother liquor, with gentle agitation, then it was filtered and dried at 105°C.

Preparation of carbon–alumina sorbents with the use of analytical grade $AlCl_3$ solution

Sorbents of definite composition containing APP as the organic component were prepared by weighing suitable amounts of the components, mixing and heating to 180°C to melt the atactic polypropylene. The hot components were triturated in a mortar to obtain homogenous systems composed of mineral and carbon components. The obtained samples contained 10, 20, 30 and 90% by mass of APP.

In cases where a mixture of hydrocarbons obtained from flotation of petrochemical wastes was used aluminium hydroxide was precipitated in a medium of aqueous-hydrocarbon emulsion obtained by mixing the petrochemical waste skim with aqueous solution of analytical grade aluminium chloride. The process was carried out under conditions analogous to those applied in the co-precipitation from the petrochemical waste water, but lesser amounts of the waste skim were used: 25, 50 and 100 cm^3.

All the mineral–carbon mixtures prepared were carbonized for 30 min at 450°C in nitrogen atmosphere.

Measurements

The physicochemical properties of the sorbents were studied, as a function of their composition and conditions of preparation, with the use of the following methods: thermal analysis, infrared spectroscopy, X-ray phase analysis, low-temperature nitrogen adsorption, and adsorption of benzene vapours.

The thermogravimetric curves were recorded by means of Derivatograph C produced by MOM Budapest, using 100 mg samples, heating rate 10°C min^{-1}, air atmosphere, and temperature range of 20–1000°C.

The infrared absorption spectra were measured in the wavenumber range 400–4000 cm^{-1} using a Spectrophotometer Specord 75IR produced by Carl-Zeiss-Jena, Germany. The X-ray diffraction patterns were recorded by means of a HZG-4C diffractometer under the following conditions: Cu lamp (voltage 40 kV, current 25 mA); radiation CuK_{α_1}, Ni filter, measuring range 2θ from 10 to 70°; measuring step 0.025 or 0.05°; integration time 25 or 5 s.

The porous structure parameters were determined by the adsorption methods using nitrogen and benzene as adsorbates. The specific surface (S_{BET}) was determined by the method based on the low-temperature adsorption of nitrogen.

For selected samples of initial aluminium hydroxide and carbon–aluminium sorbents benzene adsorption and desorption isotherms were determined in the gas phase. The studies were performed in a standard gravimetric apparatus using quartz spirals of McBain-Bakr type. The adsorption isotherms obtained were used for calculation, by means of a formerly developed computer programme [8], of parameters of the porous structure: the BET specific surface (S_{BET}), the specific surface (S_t) and the volume of micropores (V_{micro}) by De-Boer method, the mesopore surface (S_{mes}) from adsorption and desorption by Kiselov method, and the distribution of mesopore volume and surface by Dollimore–Hill method.

Results and discussion

The results of the studies performed for the samples that have been prepared with a mineral matrices obtained from petrochemical waste water and from analytical grade AlCl_3 have shown that the porosity of the hydroxides obtained depends mainly on precipitation conditions such as the rate and temperature of the process, concentration of aluminium chloride, time of maturation in the mother liquor, and final theoretical mass of the sample. Any change in these parameters leads to changes in porosity of the samples.

Figure 1 shows the changes in porous structure of aluminium hydroxide samples obtained by precipitation of aqueous solutions of analytical grade AlCl_3. The values of S_{BET} were determined from the low-temperature adsorption of nitrogen.

The analysis of the results shows that the formation of highly porous precipitates is promoted by increasing the process temperature (during both the precipitation and the maturation) and increase of the precipitation rate at low concentrations of the salt solution. Low temperature promotes the coagulation and compression of the gel

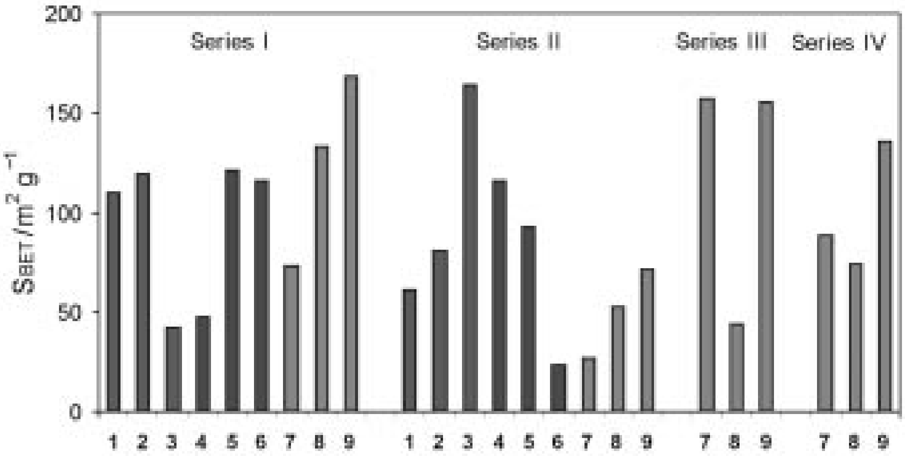

Fig. 1 Effect of conditions of precipitating aluminium hydroxide from aluminium chloride on its porous structure. The samples were obtained under the following conditions of temperature and time of ageing: 1 – 60°C, 1 h, 2 – 60°C, 3 h, 3 – 60°C, 5 h, 4 – 80°C, 1 h, 5 – 80°C, 3 h, 6 – 80°C, 5 h, 7 – 90°C, 1 h, 8 – 90°C, 3 h, 9 – 90°C, 5 h
Series I – theoretical mass 10 g, aluminium chloride concentration 6.25 g dm^{-3}, duration of precipitation 60 min;
Series II – theoretical mass 5 g, aluminium chloride concentration 6.25 g dm^{-3}, duration of precipitation 60 min;
Series III – theoretical mass 10 g, aluminium chloride concentration 6.25 g dm^{-3}, duration of precipitation 30 min;
Series IV – theoretical mass 10 g, aluminium chloride concentration 11.88 g dm^{-3}, duration of precipitation 60 min

formed with simultaneous entrapping water molecules inside the solid structure. X-ray diffraction, infrared spectroscopy, and thermal analysis studies have shown that the hydroxide gels formed are amorphous or have both amorphous and crystalline structure that includes bemite. The changes in the porous structure depended strongly on the crystallographic structure of the samples. High specific surface was characteristic of amorphous hydroxides with low contents of crystalline oxyhydroxide phase. $Al(OH)_3$ samples with the highest specific surface were obtained at 90°C, with maturation time 5 h, for aluminium chloride concentration 6.25 g cm^{-3} and precipitation rate 9.2 cm^3 min^{-1}. Such samples were used in further studies as mineral matrix for the composite sorbents.

Studies of the surface structure of mineral–carbon sorbents

The chemical structure of the adsorbent surfaces influences the adsorption capacity substantially. Various functional groups present on the adsorbent surface determine its hydrophilic-hydrophobic properties, which result in different orientation of the benzene molecules adsorbed. The vertical orientation is the most probable for the polar surface of aluminium oxide, whereas the horizontal orientation of benzene molecules in the adsorption layer is characteristic of carbon sorbents, e.g. for active carbon.

In the case of mineral–carbon sorbents the main factor, decisive for the development of porous structure, sorption capacity, and orientation of benzene molecules adsorbed is, in addition to the affinity of adsorbate to the sorbent tested, also the homogeneity of the initial mixture of the organic and mineral components before the carbonization. This factor is decisive for the uniform coverage of the adsorbent surface with the carbon pyrolysis products thus promoting the horizontal disposition of benzene molecules.

An insufficient coverage of the alumina surface with carbon substance owing to e.g. insufficient amount of this substance used in the preparation of the sorbent may result in the occurrence of hydrophilic spots on the surface that partly orient benzene molecules in vertical positions and, in consequence, to a mixed nature of the benzene adsorption. A higher content of the carbon pyrolysate gives a better coverage of the mineral matrix surface, which renders it more hydrophobic and leads to a horizontal orientation of benzene molecules. The existence of different orientations of benzene molecules adsorbed is confirmed by the results of comparative analysis of adsorption of nitrogen and benzene.

Nitrogen molecule has a low sitting surface (0.16 nm^2) as compared with that of benzene (0.25 nm^2 in vertical orientation and 0.40 nm^2 in horizontal orientation). For this reason the sorption surface and the sorption capacity determined from nitrogen adsorption measurements are more conclusive.

In the case of hydrophobic surfaces that favour the planar placement of benzene molecules the value of specific surface should not be higher than the S_{BET} found from the adsorption of nitrogen. Any increase of the value of $S_{\mathrm{BET\ (planar)}}$ with respect to the value of surface determined on the basis of nitrogen adsorption may be accounted for mixed orientation of benzene molecules in the pores of the material studied.

Table 1 Values of specific surface as calculated by the BET method for $Al(OH)_3$ and $Al(OH)_3$+APP samples prepared from the waste water containing $AlCl_3$, obtained in the studies of benzene and nitrogen adsorption. (calcination conditions: temp. 450°C, duration 0.5 h, nitrogen atmosphere)

Sample	S_{BET} C_6H_6/m^2 g^{-1}		S_{BET} N_2/ m^2 g^{-1}
	Planar orientation	Vertical orientation	
Initial $Al(OH)_3$	234.7	146.7	174.7
Calcined $Al(OH)_3$	226.2	141.5	211.3
$Al(OH)_3$+10% APP	183.3	114.5	214.1
$Al(OH)_3$+20% APP	264.1	165.0	223.7
$Al(OH)_3$+30% APP	224.7	140.4	222.9
$Al(OH)_3$+50% APP	192.1	120.1	199.4

The results obtained from nitrogen and benzene adsorption on the samples obtained with a matrix precipitated from the petrochemical waste water have shown that the samples prepared with a mixture with atactic polypropylene adsorb considerable quantities of benzene vapours and they are characterised by high values of specific surface in the range of 183.3–264.1 $m^2 g^{-1}$ (at horizontal orientation of benzene molecules adsorbed on the surface) (Table 1).

The specific surface of aluminium hydroxide is slightly higher than that of the products of its calcination under the conditions 450°C/nitrogen/0.5 h. Addition of up to 10% by mass of APP results in a further decrease of S_{BET}. The sorption capacity rises abruptly for 20% by mass addition of APP (264.1 $m^2 g^{-1}$), but further increase of APP in the systems results in a decrease of their benzene sorption capacity. The content of the carbon pyrolysate in the samples, as determined by thermal analysis, varies within 2–5% by mass depending on the initial amount of APP used.

An analysis of the results of nitrogen adsorption shows a slightly different nature of qualitative changes of S_{BET}. In the case of nitrogen adsorption the $Al(OH)_3$ sample calcined under the conditions 450°C/nitrogen/0.5 h gives S_{BET} values higher than that of initial $Al(OH)_3$. Probably the process of dehydration of aluminium hydroxide leads to the formation of narrow-necked pores with a limited access for benzene molecules. Similarly, as in the case of benzene adsorption, the highest value of surface area is attained for 20% addition of APP. Greater additions of atactic polypropylene result in a decrease of specific surface, although the decrease is not as abrupt as in the case of benzene adsorption.

The values of S_{BET} obtained for benzene adsorption, with the assumption of a planar orientation of the adsorbate are higher than those obtained from nitrogen adsorption, whereas the assumption of the vertical orientation gives lower values of S_{BET} as compared with the values obtained from nitrogen adsorption. These observations lead to the conclusion that the nature of adsorption of benzene molecules on the sorbents studied is mixed: partly planar and partly vertical. The partly naked surface of the mineral matrix changes the orientation of benzene molecules in the adsorption layer. One may assume, therefore, that the coverage of the obtained samples with carbon pyrolysate in not uniform.

In the case of the samples prepared with the use of a mixture of hydrocarbons obtained from flotation of petrochemical wastes the values of specific surface calculated with the assumption of a planar orientation of benzene molecules vary within 210.9–267.9 $m^2 g^{-1}$ and do not depend on the method of preparation. Comparison of the obtained results with the values of S_{BET} obtained from the adsorption of nitrogen shows that the effect of increasing amount of the hydrocarbon waste skim is similar for all the samples studied (Table 2).

Table 2 Values of specific surface calculated by the BET method for the samples of $Al(OH)_3$ and $Al(OH)_3$+hydrocarbon waste 'skim', prepared from the $AlCl_3$-containing waste water, obtained in the studies of benzene and nitrogen adsorption (calcination conditions: temp. 450°C, duration 0.5 h, nitrogen atmosphere)

Sample	S_{BET} C_6H_6/m^2 g^{-1}		S_{BET} N_2/ m^2 g^{-1}
	Planar orientation	Vertical orientation	
Initial $Al(OH)_3$	234.7	146.7	174.7
Calcined $Al(OH)_3$	226.2	141.5	211.3
$Al(OH)_3$ co-precipitated from an aqueous emulsion of waste hydrocarbon 'skim'	236.2	147.6	270.1
$Al(OH)_3$+30% of 'hydrocarbon skim'	267.9	167.5	269.3
$Al(OH)_3$+50% of 'hydrocarbon skim'	240.6	150.4	251.2
$Al(OH)_3$+70% of 'hydrocarbon skim'	210.9	131.8	217.4

The values of $S_{BET\ planar}$ are, in all cases, lower than those found from the nitrogen adsorption. The probable reason is that the adsorption on the samples tested proceeds mainly with planar disposition of the adsorbate molecules. The change of orientation of benzene molecules in the adsorption layer is due to different surface structure as compared with the sorbents obtained from APP: the higher content of carbon-containing matter (8.5–16% by mass) gives a uniform coverage of the mineral matrix (aluminium oxide) surface.

A highly developed specific surface was found for the sample obtained by calcination of aluminium hydroxide precipitated in aqueous emulsion of waste hydrocarbon 'skim'. The co-precipitation method applied enables to obtain mineral-carbon matrices that are uniform in the phase of precipitation and this fact is decisive for the adsorption properties of the carbonisation product.

Table 3 Specific surface values calculated by the BET method for $Al(OH)_3$ and $Al(OH)_3$+APP samples prepared from solutions of analytical grade $AlCl_3$ basing on the results of benzene and nitrogen adsorption (calcination conditions: temp. 450°C, duration 0.5 h, nitrogen atmosphere)

Sample	SBET C_6H_6/m^2 g^{-1}		S_{BET} N_2/ m^2 g^{-1}
	Planar orientation	Vertical orientation	
Initial $Al(OH)_3$	200.9	125.6	168.5
Calcined $Al(OH)_3$	258.4	161.5	196.9
$Al(OH)_3$+10% APP	263.4	164.6	257.2
$Al(OH)_3$+20% APP	256.9	160.6	246.9
$Al(OH)_3$+30% APP	262.2	163.9	255.6
$Al(OH)_3$+90% APP	180.4	112.7	176.4

Also the samples obtained with a mineral matrix precipitated from solutions of analytical grade $AlCl_3$ adsorb considerable quantities of benzene vapours and they are characterised with high values of specific surface ranging 150.1–263.4 $m^2 g^{-1}$ (with an assumption of planar orientation of benzene molecules adsorbed, Table 3).

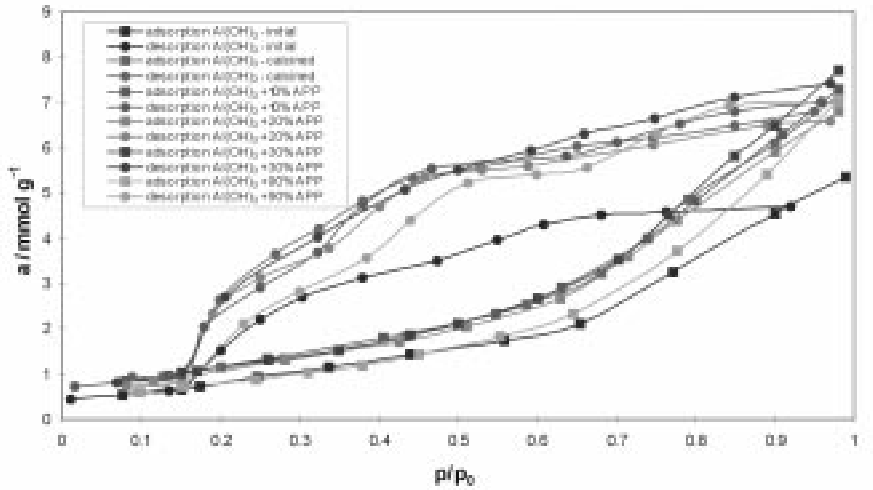

Fig. 2 Adsorption and desorption isotherms for benzene vapours on samples of mineral–carbon sorbents obtained from $AlCl_3$ solution and APP carbonised under the conditions: 450°C/nitrogen/30 min

Aluminium oxide obtained by calcination of $Al(OH)_3$ at 450°C exhibits a highly increased S_{BET}. Atactic polypropylene introduced to the system in amounts of 10–30% by mass gives a further slight increase of the sorption capacity. Numerical data listed in Table 3 are confirmed by the course of adsorption and desorption of benzene vapours shown as example in Fig. 2. The isotherms for the samples of calcined $Al(OH)_3$ and for those containing 10–30% by mass of APP do not exhibit appreciable differences in either shape or position in the range of relative pressures from 0 to 1. This fact may be accounted for similar pore size of the samples studied. The wide hysteresis loops may be accounted for a considerable porosity of the materials and predominance of mesopores in the formation of their structure. No increase of adsorption of benzene vapours has been observed in the lower range (below 0.1) of relative pressures which may be accounted for the absence or a negligible amount of micropores.

Lower sorption capacities have been observed in the samples containing 90% additions of APP and those co-precipitated in aqueous emulsions of the waste hydrocarbon skim (Table 4). An analysis of the course of adsorption isotherms does not evidence any surface reconstruction of the samples by formation of pores differing in the size. The lower sorption capacities are probably due to a decrease of the mesopore surface.

The S_{BET} values obtained from benzene adsorption with the assumption of planar orientation of benzene molecules are in a very good accordance with S_{BET} values found from nitrogen adsorption measurements (Table 3). One may assume, therefore, that within the whole range of APP additions (10–90% by mass) be adsorption of benzene proceeds under conditions of planar orientation. It results probably from the uniform coverage of the matrix surface with the carbon pyrolysate and from its hydrophobic properties. It should be noted, however, that like in the samples prepared from waste aluminium chloride the content of the carbon pyrolysate varies within narrow limits (0.1–3.4% by mass). The contents of the carbon substances in the composite sorbents are not decisive for their sorption capacities. The decisive factor is, in this case, the homogeneity of the initial mixture of mineral and organic component subjected to the carbonization which determines the uniform coverage of the mineral matrix. A homogenous mixture was obtained in this case by preliminary trituration of the mineral and carbon components at an increased temperature.

The process of benzene adsorption proceeds in a different way on the surface of $Al(OH)_3$ samples precipitated from aqueous solutions of analytical grade $AlCl_3$ in aqueous emulsion of the waste hydrocarbon skim (Table 4).

Table 4 Values of specific surface calculated by the BET method for the samples of $Al(OH)_3$ and $Al(OH)_3$+waste hydrocarbon ‘skim’, prepared from aqueous solutions of analytical grade $AlCl_3$ found in the studies of benzene and nitrogen adsorption (calcination conditions: temp. 450°C, duration 0.5 h, nitrogen atmosphere)

Sample	S_{BET} C_6H_6/m^2 g^{-1}		S_{BET} N_2/ m^2 g^{-1}
	Planar orientation	Vertical orientation	
Initial $Al(OH)_3$	200.9	125.6	168.5
Calcined $Al(OH)_3$	258.4	161.5	196.9
$Al(OH)_3$+25 mL of hydrocarbon skim	191.7	119.8	126.4
$Al(OH)_3$+100 mL of hydrocarbon skim	150.1	93.8	131.5

In all cases the values of $S_{BET\ (planar)}$ were higher than those determined from nitrogen adsorption. The partial vertical orientation of benzene molecules observed in this case was probably due to insufficient coverage of aluminium oxide surface with carbon pyrolysate resulted from too small amount of carbon substances introduced in the precipitation stage.

The isotherms of benzene vapour adsorption and desorption obtained for all the samples prepared were used for calculating the parameters of the porous structure. Examples of the results are shown in Table 5. The results enable to state that the calculation models applied give a consistent image of changes in the porous structure of aluminium hydroxide samples modified with organic substances, both those prepared by precipitation from the waste water and those precipitated from the precursor solution. The samples were characterised with a small number of micropores and a highly developed mesopore surface.

The changes in porosity of the samples were connected mainly with the developed structure of mesopores. All changes in the values of specific surface were con-

Table 5 Pore surface and volume calculated by De Boer'a (A), Dubinin–Radushkewich (B), Kiselew (C), and Dollimore–Hill (D) methods for mineral–carbon sorbents obtained from $AlCl_3$ solution (calcination conditions: temp. 450°C, duration 0.5 h, nitrogen atmosphere)

Sample	A		B	C		D	
	S_t/m^2 g^{-1}	V_{micro}/cm^3 g^{-1}	V_{micro}/cm^3 g^{-1}	Adsorption S_{mez}/m^2 g^{-1}	Desorption S_{mez}/m^2 g^{-1}	Adsorption ΣS/m^2 g^{-1}	Adsorption ΣV/cm^3 g^{-1}
Initial $Al(OH)_3$	209.4	0.005	0.007	173.1	392.4	151.5	0.451
Calcined $Al(OH)_3$	277.8	0.018	0.066	216.3	569.0	176.9	0.605
$Al(OH)_3$+10% APP	298.3	0.015	0.059	227.3	549.3	194.2	0.618
$Al(OH)_3$+20% APP	292.5	0.009	0.062	217.3	553.6	195.6	0.583
$Al(OH)_3$+30% APP	275.7	0.019	0.067	225.8	543.6	192.1	0.653
$Al(OH)_3$+90% APP	199.3	0.011	0.019	187.2	531.9	155.7	0.622
$Al(OH)_3$+25 mL of hydrocarbon skim	235.1	–	0.036	124.9	263.7	115.3	0.286
$Al(OH)_3$+100 mL of hydrocarbon skim	181.3	–	0.039	109.1	208.5	94.3	0.336

nected with a decrease or an increase of S_{mes} value, and the qualitative estimation was almost independent of the calculation method applied (Kisielew's or Dollimore–Hill's method).

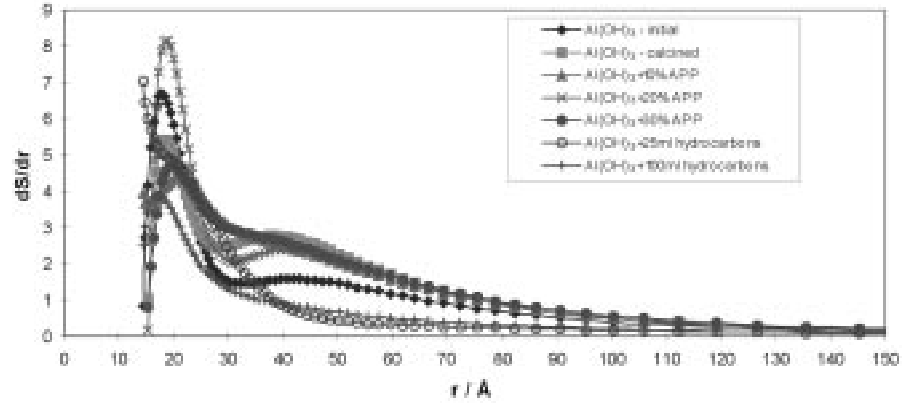

Fig. 3 Distribution of pore volumes as a function of effective radius for mineral–carbon samples obtained from aluminium hydroxide precipitated from aqueous solution of analytical grade $AlCl_3$ and carbonised under the following conditions: 450°C/nitrogen/0.5 h

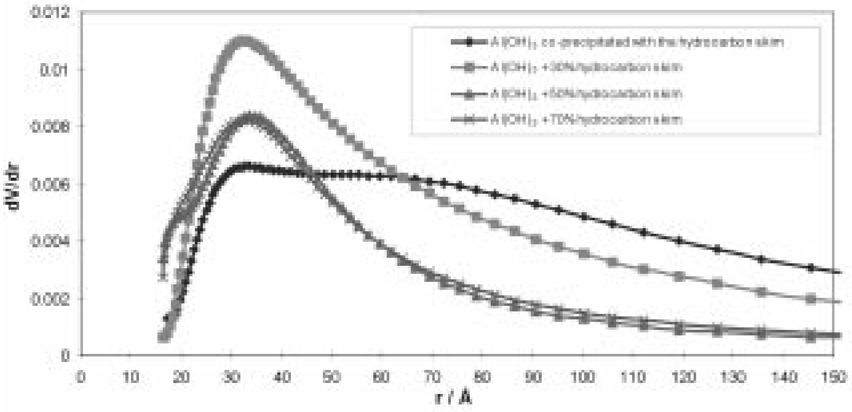

Fig. 4 Distribution of pore volumes as a function of effective radius for mineral–carbon sorbent samples obtained from aluminium hydroxide precipitated from waste water and waste hydrocarbon skim, subjected to carbonising at the following conditions: 450°C/nitrogen/0.5 h

Substantial discrepancies in the values of mesopore surface occur in calculations based on the adsorption and the desorption branches of the isotherms. They result from the remarkable irreversibility of the adsorption isotherm (broad hysteresis loop) which confirms the developed surface porosity with considerable contribution of pores of irregular shape. S_{mes} calculated from the adsorption isotherms seem to be more reliable owing to their better resemblance to the values of the specific surface. For this reason the determination of the distribution of pore surface and volume has been based on the adsorption branches of the isotherms, with use being made of the model of on-side open cylindrical pores.

As shown based on the distribution curves (Figs 3 and 4) the contribution of the pores with the radius of 20–30 Å has the highest contribution to the porosity of the samples prepared from APP and waste hydrocarbon skim. Only the sorbent prepared by co-precipitation in aqueous emulsion of the waste hydrocarbon skim exhibits an increase of the share of the volume of mesopores from the range of 30–80 Å. All the other samples did not show any substantial change of the pore size. They were characterised with a monodisperse distribution curve irrespective of the preparation method applied.

Conclusions

- The experimental studies performed have shown that materials of good sorption properties can be obtained using either pure aluminium chloride or a liquid waste containing aluminium chloride for preparation of a mineral matrix of $Al(OH)_3$ and organic substances such as atactic polypropylene or a mixture of hydrocarbons obtained from flotation of petrochemical waste waters.
- Optimum conditions were developed for laboratory scale preparation of aluminium hydroxide from waste waters containing $AlCl_3$. $Al(OH)_3$ was precipitated with ammonia solutions under strictly controlled conditions. The most favourable conditions comprised separate dosage of the reagents (waste water or the precursor solution) using: waste water dosage rate 6.8 $cm^3\ min^{-1}$, dosage rate of ammonia solution (conc. 1.32 mol dm^{-3}) enabling to maintain a constant pH of about 7, temperature 90°C, duration of the precipitation process 1 h, and time of maturation of the precipitate 5 h.

  All the obtained samples were characterised with a high specific surface within the range of 160.6–200.9 $m^2\ g^{-1}$.
- Optimum preparation conditions and optimum composition were established for the carbon–aluminium sorbents. The obtained aluminium hydroxide samples were used as the mineral component, and waste atactic polypropylene or a hydrocarbon skim obtained during flotation of petrochemical waste waters were used as the organic component. The procedure for preparation of mineral–carbon sorbents consisted in thermal decomposition of $Al(OH)_3$ mixtures with the organic substances. The sorption properties of the obtained materials depend on the contents of the carbon substance, degree of coverage of the mineral matrix with the carbon pyrolysate, and conditions of the carbonisation process. Active sorbents were obtained by carbonisation under the following conditions: temperature 450°C, nitrogen atmosphere, heating time 30 min. The optimum content of the carbon component in the initial mixture was:

– 20% by mass and 30% by mass for sorbents obtained with addition of APP,
– 30% by mass and 50% by mass for sorbents obtained with addition of the hydrocarbon waste skim.

A high sorption capacity was found for the sorbent obtained by co-precipitation of aluminium hydroxide from the petrochemical waste water in an aqueous emulsion of hydrocarbon waste skim (S_{BET}=270.1 m^2 g^{-1}).

- Comparative analysis of the specific surface determined from the adsorption of nitrogen and benzene may be an efficient method for determining the homogeneity of mineral–carbon materials.

  A possibility of various orientations of benzene molecules in the adsorption layer has been postulated. In the case of sorbents based on aluminium hydroxide precipitated from the petrochemical waste water mixed with APP a mixed orientation (planar and vertical) of benzene molecules is probably a predominating form. The vertical orientation is characteristic for the polar surface of aluminium oxide, thus it might be accounted for not complete coverage of the carrier surface with the carbon pyrolysate. A different relationship was found in the case of samples based on aluminium hydroxide precipitated from the precursor solutions. The similar results of S_{BET} obtained from the nitrogen and benzene adsorptions with assumption of planar orientation of benzene molecules was probably due to the hydrophobic nature of the matrix surface. A decisive factor of procedure in this case consisted in preliminary trituration of the components heated at 180°C.

  A horizontal orientation of benzene molecules in the adsorption layer was found for the sorbents prepared with the use of the hydrocarbon waste skim, except the samples obtained by co-precipitation of $Al(OH)_3$ from aluminium chloride solution in aqueous emulsion of the hydrocarbon waste skim. A higher content of the organic substance may give a more uniform coverage of the mineral matrix.

  The obtained samples were characterised by a mesopore structure with predominating pore radius of 20–30 Å. Only the sorbent obtained by co-precipitation in aqueous emulsion of the hydrocarbon waste skim had a higher content of mesopores from the range of 30–80 Å.

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