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MINERAL–CARBON SORBENTS BASED ON ALUMINIUM HYDROXIDE AND ATACTIC POLY(PROPYLENE)

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Abstract

The present work is an attempt to use the waste water stream, containing considerable amounts of aluminium chloride, for the manufacture of mineral–carbon sorbents. The use of the waste water has given a possibility of obtaining a suitable mineral matrix of aluminium hydroxide for the sorbents. Atactic poly(propylene) (APP) have been used as the necessary carbon raw material. The modification of aluminium hydroxide was attained by preliminary mixing with the organic component, followed by carbonisation. Optimum conditions for obtaining $Al(OH)_3$ have been determined and the effect of the amount of carbon matter on the properties of the materials obtained has been evaluated. The studies have enabled to trace the changes in the structure and properties of the sorbents obtained.

Keywords: mineral–carbon sorbents, petrochemical wastes, thermal decomposition, waste water treatment

Introduction

Among many materials with sorptive properties binary mixed sorbents have been widely applied. Such sorbents consist of two components: a mineral matrix and a carbon sorbent. The mineral–carbon sorbents are featured by a low cost of manufacture, which promotes their use in practice and application in many ecological projects. The high mechanical stability, as compared with active carbons, increases their working lifetime, and thus also the economy of the sorption processes. Besides, the sorption effectiveness of the mineral–carbon sorbents is not inferior than that of active carbons, and their joint properties are of great importance in separations of complex mixtures [1].

The mineral–carbon sorbents can be manufactured by either mechanical mixing of the two components (a mineral substance and a carbon material), by depositing the carbon substance inside the mineral structure of a gel, e.g. of silica gel, or by carbonisation of an organic matter, previously bound by physical or chemical forces with the surface of a mineral sorbent [2–4].

Studies on the possibility of obtaining mineral–carbon sorbents have been an object of our interest over the last several years. The waste sludge comprises calcium,

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aluminium, and iron salts and hydroxides, as well as hydrocarbons. The studies have shown that an appropriate physicochemical treatment enables to convert the solid wastes into mineral–carbon materials of considerable porosity, suitable for application in the treatment of industrial waste waters [5–8]. The conversion of the waste sludges into materials for treatment of waste waters gives the advantages from the economical viewpoint (economy in chemicals, cheap raw materials) and profits for the environment protection by closing circuits of technological streams.

Experimental

Preparation of mineral matrix

The aluminium hydroxide to be used as the mineral matrix has been precipitated from aluminium salt solutions by means of aqueous ammonia. Waste water from the plant producing phenol and acetone by the cumene method has been used as the main raw material. The content of aluminium chloride in the waste water, as determined gravimetrically with the use of 8-hydroxyquinoline, varied within 6.25–11.88 g dm^3.

A preliminary stage of the studies was to optimise the conditions of precipitating aluminium hydroxide with the view of obtaining a product of well developed mesopore structure. Aluminium hydroxide was precipitated under various conditions including time of ageing in the mother liquor (1, 3 or 5 h) and precipitation temperature (20, 60, 80 or 90°C). The experimental setup consisted of a thermostat, two burettes, mechanical agitator and pH-meter. The rate of the waste water addition was varied depending on aluminium concentration and the assumed theoretical yield of the final product for the process lasting exactly 60 min. The ammonia solution of concentration 1.32 mole dm^{-3} was added to the reaction mixture in amounts necessary to obtain a steady value of pH=7. After the end of precipitation the gel of hydrated alumina was separated from the mother liquor by paper filtering, then washed with distilled water and dried at 105°C. Two series of samples have been obtained, with different assumed theoretical mass (I series – 10 g, II series – 5 g) denoted as $Al(OH)_3$ I and $Al(OH)_3$ II.

Preparation of mineral–carbon sorbents

Mineral–carbon sorbents were prepared by thermal decomposition of a mixture composed of a mineral matrix [$Al(OH)_3$] and atactic poly(propylene) as the carbon component. The organic matter used was a waste product of petrochemical industry.

The obtained samples contained 10, 20, 30 or 50% APP. Both components were heated to 160°C, in order to melt the atactic poly(propylene), and were ground carefully. In order to find the optimum calcination temperature a sample containing 20% APP was heated for 30 min in nitrogen atmosphere at 300, 350 and 450°C. Other samples were pyrolized at 450°C.

The physicochemical characteristics of the obtained samples were determined with the use of thermal analysis, X-ray phase analysis, infrared absorption, low-temperature adsorption of nitrogen, adsorption and desorption of benzene.

Thermogravimetric curves (TG, DTG and DTA) were recorded by means of derivatograph C (MOM, Budapest) on heating up to 1000°C with a rate of 10°C min^{-1} in air atmosphere.

Besides, some experiments were performed with treatment of petrochemical waste waters with the use of the initial aluminium hydroxide and the coal–alumina sorbents obtained. The tests were performed in a single stage, using various amounts (0.25–1 g of the sorbent) per dm^3 of the waste water, as well as in a 2-stage process using 0.5 g of the sorbent per dm^3 of the wastes.

Discussion of results

No substantial difference has been found in the infrared absorption spectra (e.g. one shown in Fig. 1) obtained for $Al(OH)_3$ I samples obtained by precipitating from the waste waters under the different conditions (temperature, ageing time) applied.

When analysing the quantitative differences between the samples tested some relationships can be noticed based on the height of the peak in the absorption band about 1420 cm^{-1} as being due to boehmite. $Al(OH)_3$ I samples obtained at various times of maturing exhibit an insignificant decrease of boehmite content at increased time of resing in the mother liquor, irrespective of temperature applied. It is possible

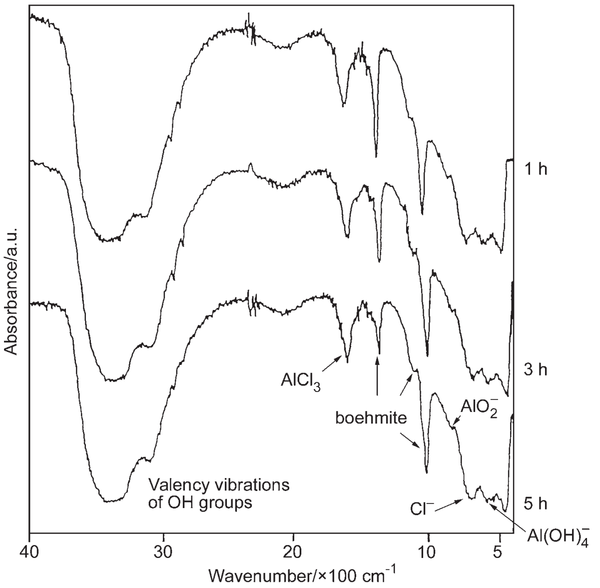

Fig. 1 Infrared absorption spectra of samples of aluminium hydroxide $Al(OH)_3$ I obtained under the following conditions: temperature 90°C, time of ageing in the mother liquor: 1, 3 or 5 h

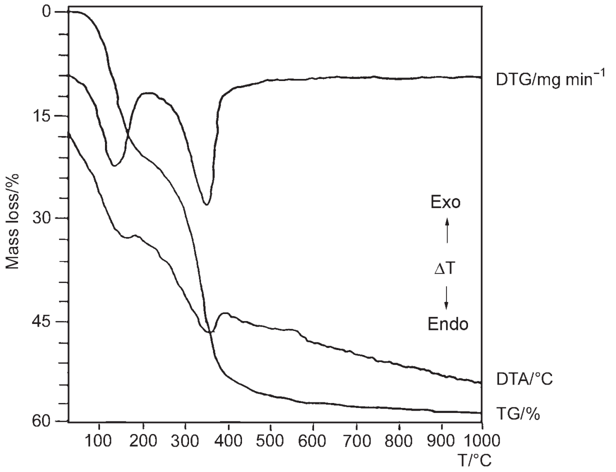

Fig. 2 Thermogravimetric curves of a sample of Al(OH)$_3$ I obtained under following conditions: temperature 20°C, time of ageing in the mother liquor 1 h

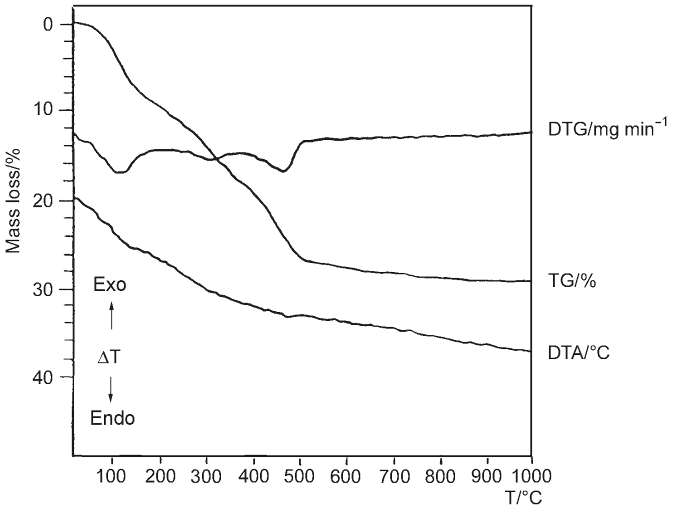

Fig. 3 Thermogravimetric curves of a sample of Al(OH)$_3$ I obtained under following conditions: temperature 90°C, time of ageing in the mother liquor 5 h

to conclude, that the higher rate of precipitating Al(OH)$_3$ samples results in a slight decrease of boehmite content with increasing time of maturing, irrespectively of the process temperature.

Al(OH)$_3$ samples obtained by precipitation at 20°C, as well as the sample Al(OH)$_3$ I 60°C/5 h had a polymeric structure, containing considerable amounts of combined water. All they were hard and difficult to crumble. This observation has been confirmed by thermal studies (Fig. 2). Thermal decomposition of these samples proceeded in two steps. The samples lost 21% of their mass in the first stage at 20–180°C, and 36% of the mass in the second stage at 250–400°C. The loss of mass observed in the heating is much higher than the theoretical loss calculated for the conversion of $Al(OH)_3$ to oxide, amounting to 34.6%. Other samples exhibited a smaller loss of mass, amounting to 30–36% (Fig. 3).

It has been found that S_{BET} surface of the aluminium hydroxide samples obtained at 80 and 90°C increases with increasing time of maturing. It has also been observed, that the samples obtained at 90°C give the highest values of S_{BET}. The processes of increase of porosity were associated with the transformation of the crystal structure. The content of the crystalline phase (boehmite) is rather small and it does grow less with increasing time of ageing.

In the case of series II, a polymeric structure of aluminium hydroxide (hard and difficult to crumble) at 60°C and time of resing in the mother liquor – 1 h has been obtained. For remaining samples $Al(OH)_3$ II/60°C the surface area does not change with increasing time of maturing. The surface area of samples prepared at 80 and 90°C (series II) decreased with increasing time of maturing in the mother liquor, and simultaneously increasing contents of boehmite is observed.

The highest values of specific surface were observed in $Al(OH)_3$ samples of series I, prepared at 90°C with curing time 5 h and assumed mass 10 g. S_{BET} values obtained for three samples prepared under these conditions are similar to each other and range within 160.6–198.0 $m^2\ g^{-1}$. The samples denoted as $Al(OH)_3$ I 90°C/5 h have been used as the mineral matrix in the synthesis of the carbon–alumina sorbents.

The optimum carbonization temperature has been established based on the studies of composition of the starting $Al(OH)_3$ with 20% by mass of APP.

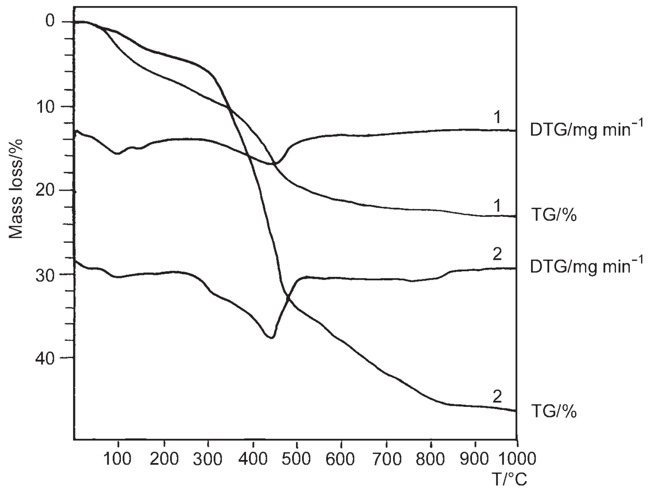

Fig. 4 Thermogravimetric curves of a sample: 1 – $Al(OH)_3$ I/90°C/5 h, carbonized under the conditions: 300°C/nitrogen/30 min; 2 – $Al(OH)_3$ I/90°C/5 h mixed with 20% mass APP, carbonized under the conditions: 300°C/nitrogen/30 min

The thermogravimetric analysis of aluminium hydroxide calcined for 30 min at 300°C in nitrogen atmosphere has shown that the dehydration process is not completed under these conditions (Fig. 4, curve 1). The decompositions proceed in two stages. In the 1st step (at temperatures below 150°C) the adsorbed water (6%) is evaporated. The 2nd stage, characteristic by mass loss amounting to 16.8%, corresponds to dehydration of the sample to give aluminium oxide. The decomposition is complete at 500°C. In the case of aluminium hydroxide mixed with atactic polypropylene (Fig. 4, curve 2) the content of water is smaller (3% by mass), and the process of aluminium hydroxide dehydration in the 2nd stage is accompanied by combustion of the polymer (mass loss 23% by mass). At higher temperatures (500–800°C) further amounts of tarry substances are burnt with mass loss ranging 9.2% by mass. Apparently, the presence of APP inhibits also the dehydration of aluminium hydroxide. It is evidenced by smaller mass loss during the carbonization of samples containing APP (8.1% by mass) as compared with aluminium hydroxide alone (19.0%). The lower sorptive properties of the obtained carbonization product may also be accounted for the smaller quantity the adsorbed water than that observed for pure $Al(OH)_3$.

The temperature 450°C has been accepted for all the other samples as the one that guarantees to obtain carbon–alumina pyrolysates of the desired properties.

S_{BET} values obtained from the measurement of benzene adsorption are higher in all cases than those obtained from measurement of nitrogen adsorption. On the other hand, assumption of vertical orientation of benzene molecules on the sample surface makes S_{BET} values too small as compared with the value obtained from the adsorption of nitrogen (Table 1).

Table 1 Specific surface of mineral-carbon sorbents obtained in the studies of adsorption of benzene (A) and nitrogen (B)

Sample	A		B
	S_{BET} (planar)/ $m^2 g^{-1}$	S_{BET} (upright)/ $m^2 g^{-1}$	S_{BET}/ $m^2 g^{-1}$
$Al(OH)_3$ 90°C/5 h	234.7	146.7	174.7
$Al(OH)_3$ 90°C/5 h calcined: 450°C/nitrogen/30 min	226.2	141.4	211.3
$Al(OH)_3$ 90°C/5 h+10% APP calcined: 450°C/ nitrogen /30 min	183.3	114.5	214.1
$Al(OH)_3$ 90°C/5 h+ 20% APP calcined: 450°C/nitrogen/30 min	264.1	165.0	223.7
$Al(OH)_3$ 90°C/5 h+30% APP calcined: 450°C/nitrogen/30 min	224.7	140.4	222.9
$Al(OH)_3$ 90°C/5h+50% APP calcined: 450°C/nitrogen/30 min	192.1	120.1	199.4

The cause of these discrepancies may arise from the different orientation of benzene molecules on the surface of the sorbent. The surface occupied by a benzene molecule lying flat on the surface is 0.40 nm^2, whereas that occupied by a vertically 'standing' molecule only 0.25 nm^2. The nature of surface of aluminium hydroxide and products of its calcination with APP may promote the vertical stacking of benzene molecules.

The adsorption of benzene on the surface of the sorbents studied probably has a mixed character, probably owing to the non-uniform coverage of the carrier surface by the carbon pyrolysate. In the case of nitrogen the surface of 'sitting' cannot change as drastically as may be in the case of benzene. The quantitative nature of changes of S_{BET} (nitrogen) and S_{BET} (benzene) is also slightly different, but in both cases maximum values were obtained aluminium hydroxide sample containing 20% addition of APP, calcined for 30 min in nitrogen at 450°C: S_{BET} (benzene)=264.1 m^2 g^{-1}, S_{BET} (nitrogen)=223.7 m^2 g^{-1}.

Based on the distribution curves of mesopore surface and volume, as determined in the studies of benzene adsorption (Fig. 5) it has been concluded that the porosity of the samples depends mainly on the contribution of pores of internal radius 20 Å. In the case of the samples $Al(OH)_3$+10% and 50% APP a slight shift of the dS/dr and dV/dr curves to the zone of pores of internal radius 15–20 Å was observed. A decrease of the volume of pores 40–60 Å was observed in samples containing 30 and 50% additions of APP has been observed.

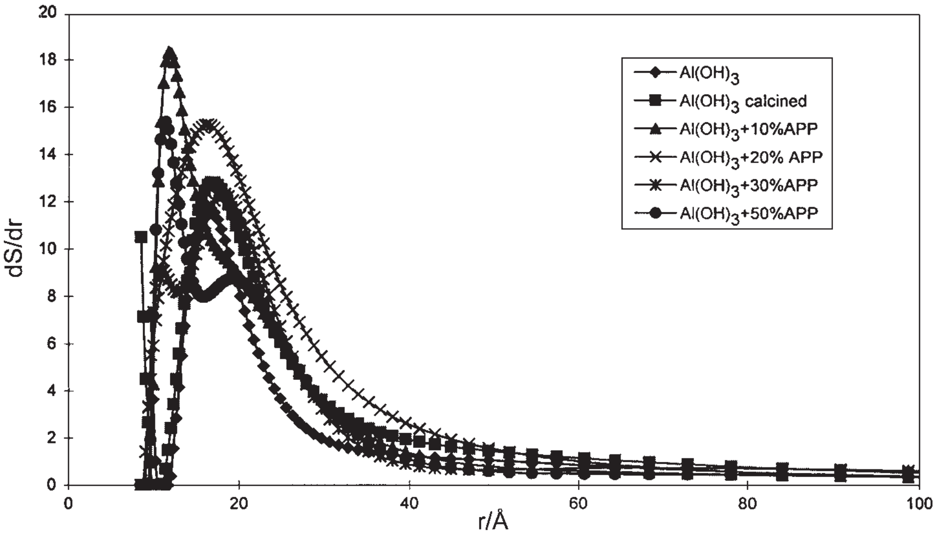

Fig. 5 Pore surface distribution according to the pore effective radius for aluminium hydroxide and mineral carbon sorbents obtained on the base of atactic poly(propylene) under the conditions: 450°C/nitrogen/30 min

Experiments with the treatment of petrochemical waste waters polluted to a high degree with organic compounds have shown a high activity of the sorbents obtained. The chemical oxygen demand decreased by 22, the content of ether extract was reduced by 48%, and the turbidity was reduced by a factor of 6. The degree of elimination of impurities in waste waters depends on the porous structure of the sorbents used. An analysis of distribution of mesopore surface and volume as a function of their effective radii has shown that the structure of the sorbants depends mainly on the pores of internal radius 20–30 Å. Such pores are capable of sorbing the molecules of benzene (sitting surface 0.40 nm^2) and aliphatic hydrocarbons of carbon chain length not exceeding the pore diameter (the C–C bond length is 1.54 Å). It has also been observed that the degree of COD reduction is higher than that of the ether extract, thus providing a proof of improved adsorption of aromatic compounds.

Conclusions

Complex analysis of the results obtained in the studies performed enables to make the following conclusions:

1. The experimental studies and tests performed have shown the feasibility of using the acid waste waters from the Acetone and Phenol Plant for manufacture of a mineral matrix for complex sorbents. The method proposed enables, on the one hand, to deactivate the wastes by elimination of aluminium chloride and, on the other hand, to obtain a valuable semi-product $Al(OH)_3$ for the synthesis of active sorbents, which can be used for the treatment of industrial waste waters polluted with organic compounds. This is an implementation of the idea of closing the technological streams.

2. The conditions of laboratory manufacture of aluminium hydroxide from waste waters containing $AlCl_3$ have been optimized. $Al(OH)_3$ has been precipitated with aqueous ammonia under precisely controlled conditions. Optimum results were obtained with separate batching of the reactants (waste and ammonia waters) under the following conditions: waste water dosing rate: 6.8 cm^3 min^{-1}, aqueous ammonia (concentration 1.32 mole dm^{-3}) dosing rate appropriate to keep constant pH of about 7, reaction temperature: 90°C, time of precipitation: 1 h, time of ageing the precipitate 5 h.

The specific surface of the samples obtained was within 160.6–198.0 m^2 g^{-1}.

3. A number of research methods involved in the studies have enabled to set optimum manufacture conditions and composition of the carbon–alumina sorbents. Alminium hydroxide was used as the mineral component, and waste atactic poly(propylene) was used as the organic component. The procedure of preparing the mineral–carbon sorbents consisted in thermal decomposition of mixtures of $Al(OH)_3$ with the organic substance. The sorptive properties of the materials obtained have been found to depend on the initial contents of the carbon component, the degree of coverage of the mineral matrix with the products of pyrolysis, and the conditions of the carbonization process. Active sorbents were obtained with carbonization temperature 450°C, nitrogen atmosphere, time of carbonization 30 min. Optimum content of the carbon component (APP) in the starting mixture was: 20% by mass (S_{BET}=223.7 m^2 g^{-1}) and 30% by mass (S_{BET}=222.9 m^2 g^{-1}).

4. The studies of benzene vapours adsorption on the carbon-aluminium sorbents have shown that these materials are endowed with high sorption capacity. Comparative analysis of the sorption of nitrogen and benzene has shown that the benzene molecules can have different orientations in the adsorption layer. In the case of the APP

sorbents mixed orientation (planar and vertical) is very probable. The vertical orientation is characteristic of the polar alumina surface, which is likely to suggest an incomplete coverage of the carrier's surface by the carbon pyrolysate. The samples obtained had mesopore structures with prevailing pore size of 20–30 Å.

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