Polish Journal of Environmental Studies Vol. 6, No. 3 (1997), 5–15

Review

Preparation of Carbon and Carbon-Mineral Adsorbents and their Application in Technique, Environmental Protection and Chemical Analysis

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Received 1 August, 1996
Accepted 12 November, 1996

Abstract:

This reviev describes the methods of preparation of carbon and carbon-mineral adsorbents by carbonization of different organic materials. The methods of carbon preparation were subdivided into two groups: preparation of sorbents on a large industrial scale, and for laboratory (chromatographic and adsorption) purposes. It also demonstrates the specific properties of some carbon adsorbents as well as the possibilities of their utilization for the purposes of environmental protection (sorption of organic pollutants from water wastes) and for analytical purposes especially for gas (GC) and liquid (HPLC) chromatography.

This article also shows some possibilities (e.g. consumed catalysts, sorbents used in food and paper industries, from removal of oil from waste waters, etc.) of preparing different, mainly carbon-mineral adsorbents.

Keywords: carbon adsorbents, carbon-mineral adsorbents, application of carbon adsorbents.

Introduction

Last year saw a rapid increase in the degree of environmental contamination. This relates either to soil and water or to air. At present we are in the course of establishing type and permissible concentration of harmful substances introduced to the environment in the form of combustible gases, wastes, exhaust, etc. Such questions as the removal of formed contamination or toxic pollutants released to the atmosphere or rivers and other aquifers raises significantly lower interest. This means that the total amount of pollutants released to the environment remains unchanged. Special attention must be paid to limiting the amount of pollutants released to the environment such as removal or even recovery of chemical compounds from wastes or gases before their release to the atmosphere or wastewater. This relates mainly to water used in technological processes. It says at present that some methods of recovery of some chemical compounds are uneconomical because the expenses of their recovery exceeds production costs. However, this does not take into account the fact that wastes are released to aquifers from which they derive water for consumption.

This leads to significant increase of the costs of water conditioning or even makes impossible the purification of such water. This is connected directly with additional costs, namely an increase in medical costs due to an increase in morbidity. Moreover, norms related to water quality do not rigorously define the content of different organic substances (e.g. petroleum products, phenols, aromatic and polyaromatic compounds) in water used for municipal purposes. This is connected with some limitation of monitoring these compounds in water due to lack of the appropriate apparatus.

One of the most effective methods of purification of water and waste consists of the sorption of organic pollutants and heavy metals on active carbons. From an economical viewpoint it seems that the simplest way to lower costs of waste purification or water conditioning may consist of replacing expensive active carbons (the cost of filling one filter is ca $ 100,000). Carbosils or similar carbon-mineral adsorbents fulfil all the above requirements and may be utilized for these purposes. Such adsorbents have some specific property, i.e. they combine the elements of polar inorganic sorbents (such as SiO_2, Al_2O_3, etc.) and those of non-polar

carbons and in this connection they show an ability to the sorption of different organic substances as well as of cations and inorganic substances. Moreover, the carbon and mineral components of such adsorbents are permanently connected by adhesion - chemisorption bonds and owing to these adsorbents show good mechanical properties, are more hard than typical active carbons and the carbon component is built in permanently in mineral matrices, therefore difficult to mechanically remove from sorbent surface.

Preparation of Carbon and Carbon-Mineral Adsorbents and Their Utilization in Practice

Carbosils are interesting materials because of their industrial applications. The possibilities of utilizing active carbons are limited because they adsorb mainly hydrophobic substances (hydrocarbons and their nonpolar derivatives) and moreover, they are characterized by poor mechanical properties and combustibility. In contrast, complex adsorbents possess complex sorption properties, are mechanically stable and are characterized by a higher ignition temperature.

One of the first attempts to prepare a complex carbon mineral adsorbent was made by Shilov and Dubinin [1], who saturated birch shavings with glasswater treated with saturated $ZnCl_2$ solution heated to obtain a gel, then carburing its organic components at an elevated temperature. They stated that sorbents prepared in this way show better adsorption ability in comparison to individual adsorbents, assuming the additive properties of complex adsorbents.

Different methods of preparation of carbon-silica adsorbents by incorporation of carbon or carbon black particles are described in a monograph of Neimark, et al. [2].

Another paper [3] describes the methods of preparation of carbon-silica adsorbents consisting in dissolution of saccharose in hydrochloride acid and then mixing this solution with silica acid solution. After coagulation of the zol and its transformation to gel the latter was heated in conditions permitting carbonization of the sugar.

Complex adsorbents were prepared by means of similar techniques in which such materials as peat, filtration paper or finely divided carbon were used as starting materials [4-6]. By means of these methods it can obtain the complex adsorbents containing any among carbon and usually characterized by better adsorption properties than each individual component separately.

It has also obtained the adsorbents being the mixtures of hydrophilic alumina gel and hydrophobic carbon. Such adsorbents may be obtained by impregnation of tree shavings with aluminum salts following carbonization at high temperatures. Another version of this method consists of introducing finely divided carbon to alumina gel suspension. To a vigorously mixed solution of aluminum salt, finely divided carbon is added and then such mixture is heated with continuous stirring and ammonia solution is added. This leads to precipitation of aluminum hydroxide, which adsorbs divided carbon particles. The formed precipitate is filtrated, divided and washed in order to remove salt and hydroxide residues and finally dehydrated, which leads to solid adsorbent.

Yermolenko, et al. [8] prepared so-called titanium carbons by saturation of charcoals with titanium tetrachloride followed by hydrolysis with steam and calcination at an elevated temperature. Complex carbon-mineral adsorbents were obtained also by pyrolysis, or chemical bonding of organic substances to the surface of mineral sorbent (SiO_2, Al_2O_3, etc.) in the next stage of this process these substances underwent carbonization. Such a method of preparing complex carbon-mineral adsorbents is widely described in literature. The properties of such sorbents depend largely on the chemical nature of the matrix, its porous structure, and the nature of carbonized substances as well as on the conditions of the process. Therefore, this method creates the possibilities of preparation of carbon adsorbents of very differentiated surface properties. The selection of the type of carbonized substance as well as the mode of realization of pyrolysis process depend on the destination of complex adsorbent. If the final product is destined to technical applications, e.g. as a catalyst, plastic filler or the bed for purification of gases and liquids (where very large amounts of adsorbent are needed), then the starting materials must be cheap and easily available and the technological process must be performed in relatively simple conditions and not very strenuous for the environment. In the case of more subtle destination (e.g. for chromatography, isolation and concentration of trace amounts of the compounds) where small amounts of adsorbents of strictly defined surface properties are used (the above elements are less significant), but in this case there appears the problem of reproducibility of prepared sorbents, their energetical homogeneity and appropriate chemical and physical structure of carbon deposits. For the above reasons significantly two different areas of preparation of complex adsorbents must be distinguished, i.e. for technical (mainly for purification of water) and for analytical purposes preparation of complex adsorbents on technical scale. This problem is solved in two ways. First, in utilization of mineral adsorbents (or catalysts) consumed in different processes of purification during which different substances of organic origin deposited on the surface of such adsorbent (or catalyst) are able to form carbon substances during the thermal treatment of such materials. Food, pulp and paper, petrochemical and other industries represent potential sources of raw materials to production of carbon-mineral adsorbents. The second

method consists of the spread of appropriate substance on mineral sorbent followed by thermal or chemical carbonization.

For example, the technology of purifying wines and juices traditionally uses bentonite clays. In beds of consumed bentonite there are peptides, pectines, tannins, dyes, sugar, organic acids, etc. The content of these substances attains 15-20 % w/w. After appropriate thermal treatment of such consumed clay it can obtain the complex carbon-mineral adsorbents, which may be utilized in water purification technology [9,10]. Similarly, in the food industry utilization of clay sorbents to purify liquid confectionery seems to be very promising [11]. In a cited paper the activated Palygorskite was used for these purposes. After long-time exploitation of this sorbent there remained on its surface the residues of saccharose, the product of its caramelization as well as melamine and other substances capable of carbonization.

Another paper [12] demonstrates the possibilities of utilizing scania bentonite consumed in the process of purification of cane sugar solution. This utilization consists of heating bentonite at 500°C. In this way there was obtained the micro porous carbon-mineral adsorbent characterized by the following parameters: specific surface area S = 130 m^2/g, total pore volume Vp= 0.10 cm/g, predominant pore radius R = 2 - 3 nm.

As mentioned above, some by-products of the pulp and paper industry may be utilized to produce carbon-mineral adsorbents. This is connected frequently with the problems of environmental protection. For example, Bilitevsky [13] has shown that the utilization of precipitates contained in waste-water of pulp and paper industry in order to prepare of porous carbonizates is reasonable from an economical viewpoint. The carbonizates prepared in this way were characterized by high sorption capacity (~65% sorption per sorbent mass unit) at relatively low specific surface area. In the pulp and paper industry strongly dispersed cellulose fibres pass through the wires of paper producing machines and then to waste-water from which are isolated by means of different chemico-colloidal methods including these in which bentonite clays are used. By thermal treatment of mechanically mixed cellulose fibres and bentonite it can obtain a very effective mixed sorbent. The lack of chemical bonds between the particles of cellulose fibres and clay limits the possibilities of obtaining granulated material. In this connection in order to obtain active carbonizates it recommends adding ca. 20% of mineral impurities (e.g. perlite) and chemical activator (e.g. $ZnCl_2$) to solid wastes of paper industry before carbonization.

There are many papers relating to the preparation of complex sorbents on the basis of active clay occuring in great amounts in many parts of the world, including Poland. Such trends appear to be very promising because they make possible a complex solution of the problem of purification and utilization of the precipitates contained in wastewaters. Strielenko and Tarasewicz [19] have utilized a properly conditioned mass of active clay being a mixture of precipitates originating from settling tanks of I and II degree of purification of wastewaters from pulp and paper factory. Starting mixture was concentrated by introduction of 10% ferrous chloride and 20% lime milk and then dehydrated so that its final hydratation degree was 75 - 80%. Such material contains ~39% of cellulose fibre, 27% of active clay and 34% of mineral compounds. After carbonization of this mixture for 1 hour at 600-700°C they obtained an sorbent containing about 45% carbon.

Other authors [20] have introduced not only active carbon to clay materials but also alumina-silica catalyst or zeolite X. Low prices of carbons as well as the fact that these materials combine the advantages of active carbons and dispersed aluminosilicates create possibilities of their utilization as the materials improving the sedimentation properties of active clay, because their packet structure montmorillonites seem to be interesting materials. Moreover, it is known that glucose and saccharose show an ability to penetrate of interlayer spaces of these materials [21]. In these spaces may be localized also other substances. Introducing large organic cations to interpacket spaces [23] changing properties of this mineral from hydrophilic to hydrophobic. Simultaneously, with the exchange of inorganic cation to organic one the increase of interpacket distances in montmorillonites structure takes place and therefore the sorption of large organic molecules (paraffins, aromatic hydrocarbons) becomes possible.

Appropriate preparation of the sorbents may secure even selective sorption of hydrocarbons. Such advantages have encouraged numerous authors to prepare carbon-mineral adsorbents using montmorillonites. It is assumed that there are the adsorbents in which organic substances introduced between the packets of montmorillonite will form a specific "pillar" after carbonization. Such "column" adsorbents should contain slit pores separated by carbon clusters of different sizes. The data presented in references [24,25] show, hovewer, that the cokes obtained by carbonization of glucose and saccharose fill the interpacket spaces with a continuous layer, thus eliminating them from adsorption processes.

More promising results are presented by Krzyżanowski and Zyla [22], who carbonized glycol, glycerin and polymer in the montmorillonite bed. The pyrolysis was performed at three temperatures, i.e. 450, 500 and 600°C. As follows from results that of their investigations sorption properties of clay materials can be modified choosing an appropriate activating compound and its pyrolysis temperature. The most profitable changes may be obtained when the activating

substance can penetrate the interpacket spaces forming in this way so called interlaminar complexes and when this substance decomposes readily forming a large number of carbonaceous products. Under the experimental conditions used by these authors the best reagent fulfilling these requirements was glycerin.

Much earlier (1979), Loeppert et al. made efforts to obtain column clays with carbon clusters localized in the interpacket spaces. The concept of such adsorbent formation consists of the creation of the complex cations with uncharged organic ligands in the silica interlayer space followed by carbonization of the obtained compounds at 450-550°C. In order to trap the oils leaking from ship waste the carbonized sorbent is often prepared on the basis of clay [27]. The clay is dried, ground and saturated with vegetable oil. The oil penetrates the granule interior to some depth and then the granules are subjected to a two-step thermal treatment: at 160°C for 2 h and then at 220°C until a partly carbonized product is obtained. Utilization of consumed sorbents and other products such as consumed oils constitutes a very serious economic and ecological problem [28,29].

The significance of the problem may be illustrated by the fact that, e.g. in the USA, the amounts of consumed clays being the wastes from different industrial processes were 50,000 tons per year (in 80's). The clays consumed in the processes of contact purification of edible and technical oils might be thermally treated and the obtained carbonized and hydrophobized adsorbent could be applied as an element of protective screens in slime chambers [30] or as ion-exchangers [31]. The method of application of bleaching earths consumed in the process of purification of edible oils [32] to be used as carbon-mineral adsorbents, e.g. in the processes of adsorption of dyes and surface active agents after the appropriate thermal treatment was patented.

Hydrolyzed lignins [33], petroleum asphaltenes [34] or the wastes formed during agricultural product processing [35] are also an important group of potential raw materials to produce carbon-mineral adsorbents. There is also a great interest in application of local raw materials to produce mineral-carbon adsorbents for environmental purification. In the region of Saint Cross Mountains an attempt was made to use activated basalt waste and clay slate for the sorption of heavy metals and petroleum products from natural waters.

Adsorbents for Laboratory Purposes

One of the first attempts to prepare carbon-silica adsorbents for chromatographic purposes is presented in [37-39]. On the surface of hydroxylated silica gel there were chemisorbed aliphatic and aromatic alcohols which were then carburized. In this way there were obtained the complex carbon-mineral adsorbents containing a few percent of carbon bonded with the silica surface. Such adsorbents were called carbosils [40]. In the initial period of investigations these materials were tested as the packings of chromatographic columns for gas chromatography [40] e.g. for separation of components of liquefied petroleum gas as well as for high performance liquid chromatography [41-44] either in the normal or in the reversed phase system.

Carbosil packings were also tested but without success in the polymer separation by size exclusion chromatography [41].

Because the prepared carbosils are characterized by strong adsorption ability and greatly heterogenous surface the attempt was made to modify their chromatographic properties by spreading different liquid stationary phases such as DC-550 silicon oil [45] or polyethylene glycol on their surface [46]. The surface functional groups of carbosils originating either from the silica matrix or from the carbon deposits were modified by means of the reaction with silanes (hexamethyldisilazane - HMDS or trimethylchlorosilane - TMCS) [47].

The papers of Bebris et al. [48,49] and Guiochon et al. [50,51] propose other ways of preparation of such adsorbents. Benzene vapors were passed over the stationary layer of thermally resistant silica at 850-900°C. In such conditions benzene decomposed, forming pyrocarbon on the surface of inorganic matrix. Coverage density of the matrix with pyrocarbon was 1.3-6.7 mg/m.

In the respect of adsorption characteristics carbon-silica adsorbent prepared in this way and containing about 7 mg/m of carbon is comparable to the thermally graphitized carbon black while in the respect of geometrical and energetical homogeneity it is much poorer. Poor adhesion of carbon spread in this way on the silica surface makes formation of a uniform modifying film impossible. The surface of such carbosils is in fact mosaic: its properties are intermediate between those of silica gel and carbon adsorbents. Complex adsorbents obtained by these authors were used mainly as the packing of the columns for HPLC for separation of aromatic hydrocarbons in the reverse phase system.

From the studies of Rudenko et al. [52] it results that appreciable deposition of carboneous substance on the silica surface during the pyrolysis of benzene is observed at 700°C, and in the conditions applied by Bebris et al. [48] the degree of conversion of benzene to carbon was about 20%. The references cited in [52] represent a rich source of the data relating to the mechanisms of formation of carbon deposits on the adsorbent and catalyst surface from the substances of different chemical nature. The method proposed by Bebris et al. [48] was used but without success for hardening mechanically poor graphitized carbon blacks used for HPLC purposes [53,54].

The intermediate processes and intermediate products formed during the pyrolysis of a given compound can play a very important role in the creation of carbosil properties. The most important processes accompanying pyrolysis are:

a) chemisorption of the chemical compounds deposited on the surface of modified silica before their pyrolysis;

b) formation of the compounds of higher molecular weight as a result of the mutual chemical reaction between different substances spread physically on the solid surface. There is usually a mixture of different compounds containing functional groups and capable of polymerization. For example, alcohols react with the silanol groups or the siloxane bridges [55] of silica surfaces forming surface esters. The alcohols (or surface esters) dehydrated at an elevated temperature form olefins [56], which undergo conversion and form more complex compounds.

The effect of pyrolysis of various alcohols on the properties of the obtained carbosils was investigated [37-39, 57-68]. The reactions were performed under static (in autoclave [37-39, 57-63]) and dynamic conditions. The latter case made use of a rotary reactor constructed especially for these purposes [60,69]. In each case there were obtained the adsorbents containing relatively small quantities of deposit carbon (a few % of w/w) not securing the complete coverage of the silica surface with carbon. Therefore, a search for substances which would permit deposition of sufficient amounts of carbon on the silica surface under the pyrolysis moderate conditions was made. The reason was also to escape from strong sintering of modified adsorbent skeletons.

The papers [67,68] describe carburization of α-phenylethylalcohol and p-chlorotoluene initially leading to the formation of intermediate products (alkoxytoluene with simultaneous liberation of HCl) and then to carbosil containing over 13% carbon. The products of aromatic alcohols pyrolysis provide in the same conditions greater amounts of carbon deposited on the silica surface than aliphatic alcohols containing the same number of carbon atoms. Carbosils prepared by carbonization of the mixture of the same alcohols possess intermediate properties [57,60].

Chemisorption of alcohols on silanol (≡Si-OH) and siloxane (≡Si-O-Si≡) may occur at low temperatures [55]. An increase in temperature liberates olefins, which can undergo condensation with aromatic compounds, forming coke. This takes place in the case of pyrolysis of aliphatic and aromatic alcohols. Alkoxytoluene formed during the process of pyrolysis of the mixture of α-phenylalcohol and p-chlorotoluene is bonded more strongly with the silica surface than the starting components because of higher molecular weight. Such a stage i.e. strong adsorption, plays a very important role in the formation of greater amounts of coke on the solid catalysts and promotes good adhesion of the carbon deposit to the surface of the mineral matrix [71].

An excellent method from the viewpoint of the reaction mechanism and the consequences resulting from it is described in [72]. This paper presents carbonization of acenaphtene on the silica surface. The characteristic feature of this process results from the fact that even at a low temperature (~200°C) this substance (as well as acenaphtylene) undergoes polymerization, leading to formation of a substance of high molecular weight. These substances interact strongly with the silica surface and are less mobile. Thus, a larger amount of the substance remains on the solid surface than in the gas phase when the equilibrium state is being established. For this reason a high degree of conversion of acenaphtene to carboneous substances is obtained (90%) compared to a few or anywhere from ten to twenty % in the case of alcohol pyrolysis [57, 58, 67, 68, 73] depending on the type of alcohol and on carbonization conditions. Benzene and hexane show significantly lower degrees of conversion [67].

Another noteworthly reaction includes decomposition of methylene-chloride on the surface of the mineral adsorbent:

$$CH_2Cl_2 = C + 2HCl \qquad (1)$$

This reaction was occasionally used by Grobb [81] and Zoccolillo and Liberti to cover the internal surfaces of capillary columns with pyrolytic carbon [82]. Extensive experimental material is contained in Gierak's dissertation. Readiness of carboneous substance formation in the above reaction results from the stoichiometry of this reaction as well as from a high energy of HCl formation. However, this does not mean that all chloro-derivatives of organic compounds in which the ratios of hydrogen to halogen equal 1 : 1 (e.g. in the case of CH_2Cl_2) form carbon deposits readily. For example, the attempt to decompose 1,3,5-trichlorobenzene $C_6H_3Cl_3$ on silica gel at 900°C have not been successful. During the investigations carbon-mineral adsorbents of different carbon deposit contents (1.0-70% w/w) and different specific surface areas 40-400 m^2/g) were obtained. The prepared carbosils were characterized by very good mechanical properties (high hardness and very good adhesion of carbon deposits); therefore, the attempts of their use as column packings for HPLC were made. Unfortunately the results comparable to those for the standard HPLC packings such as RP-18 or RP-8 were not obtained. In order to improve structural and surface properties of the complex adsorbents obtained by pyrolysis of methylene chloride, they were subjected to different reactions and processes of physico-chemical treatment such as:

- hydrogen treatment or heating at an elevated temperature in the inert gas atmosphere;
- silanization with hexamethyldisilazane HMDS and trichlorosilane TMCS [47];
- activation with steam at 800-900°C [85];

The above processes of modification permitted changes not only in structural parameters of carbosils but also their hydrophilic-hydrophobic properties.

Using the possibility of carbosils surface and structural properties, it was attempted to apply them in environmental analysis to isolation and concentration of trace amounts of organic substances from water and air. For these purposes the solid phase, extraction (SPE) method is usually applied [85-88], which permits enrichment with (with a good yield) trihalomethanes (THM), phenols and their chloro- and nitro- derivatives. Carbosils are also used as the packing of adsorption columns for collecting vapors of organic substances (e.g. gasoline, organic solvents) from air by the thermodesorption method [85].

Adsorbents of the type of graphitized carbon blacks were and are still attractive for chromatographic and other analytical purposes. They are characterized by well defined and homogeneous topography of adsorption centers [90]. Unfortunately, they are also characterized by poor mechanical properties (fragility), which significantly limits their practical use and the graphitization process is performed at very high temperatures (~3000°C) and in an oxygen-free or reductive atmosphere. It is evident that any carbon-mineral adsorbent will not sustain the treatment in such conditions. However, Gierak et al. [91-93] have shown that complex carbon mineral adsorbents characterized by a highly ordered structure of carbon deposits even in very moderate conditions (350-700°C) can be obtained. In order to prepare such sorbents the process of catalytical decomposition of hydrocarbons on the metal catalyst [94] spread on the surface of silica gel (e.g. decomposition of n-butane on the nickel catalyst, removed after completion of the carburization process) is used. In this way, it can deposit even 90% of carbon characterized by the graphite-like structure.

Mechanical properties of such structures depend on the mechanism of carbonization process. Carbon deposits described in [91-93] are characterized by a poor mechanical structure but at the same time they show good chromatographic properties similar to those of graphitized carbon blacks. Using gas chromatography the aqueous solutions of light aliphatic alcohols, ketones as well as the components of liquid petroleum gas (light aliphatic hydrocarbons) can be effectively separated on these adsorbents.

Deposition of pyrocarbon on the residual active centers of the supports of liquid stationary phases was used to decrease sorption and catalytic activities of these supports [95]. Diatomaceous support Cellite 545 was treated preliminarily with the phenol-formaldehyde solution and then, after removal of the solvent, the substance deposited on the surface was subjected to pyrolysis at 1200°C in the inert atmosphere. In this way the support of elevated mechanical resistance and inert in the adsorption processes was obtained.

An interesting, but rather limited, method of carbon-mineral adsorbents preparation has been proposed by Russian researchers. The method consists of preparing complex sorbents by chlorination of transition metal (IV-VI groups) carbides such as TiC, HfC, VC, NbC, TaC, Cr_3C_2, Mo_2C, WC, W_2C CaC_2, SiC, etc. [96-100]. The possibilities of carbon deposits preparation by decomposition of carbides in the reaction with metal chlorides (KCl, NaCl,$CaCl_2$, etc.) have also been demonstrated by American scientists [101, 102]. Carbon adsorbents of such types may be formed as by-products in so called nonferrous metal metallurgy during the preparation of pure transition metals from their carbides. Therefore, the production of these sorbents may also be justified by economical reasons. By thermal decomposition of the carbides of the above-mentioned metals at 500-1300°C, depending on the conditions of the process, the carbons of graphite-like structure or amorphous carbons not causing X-ray diffraction during the roentgen diffractometric analysis can be obtained [101-105].

Carbon adsorbents prepared in the above way are characterized by large pore volume and without micropores [100], which is very profitable in the case of carbon adsorbents. Of the above mentioned carbides calcium carbide [95, 101, 102], titanium carbide [97, 100] and silicium carbide [98] are most extensively discussed in literature. Preparation of carbon adsorbents (e.g. by decomposition of titanium carbide) is relatively complex and can be presented by the following reaction:

$$TiC+2Cl_2=TiCl_4+C \qquad (2)$$

The above reactions are performed at 500-1300°C, which enables control of the obtained carbon deposits' structural properties. According to the authors they can be used as model adsorbents for adsorption of impurities from air and water as well as for chromatographic purposes.

Other methods of carbon adsorbents preparation are based on catalytic processes. The literature on carbonization of catalysts and adsorbents is very extensive and will not be discussed here in detail. The main question is finding a source of new materials for preparation of carbon adsorbents and their application. The most important observation as follows from the literature is the existence of different forms of carbon deposits as well as ways of their formation and possibilities of mutual transformations of different types of carbon depending on the external conditions and type of catalyst and raw material. This suggests a possibility

of existence of various types of complex adsorbents differing either in physical or in chemical properties. Therefore not all adsorbents show advantageous morphology of carbon deposits.

The tendency to form coke on metal oxides is observed mainly for unsaturated hydrocarbons [112]. The method of purification of aromatic hydrocarbons from unsaturated impurities is based on exceptionally high chemical stability of the former [113-115]. The principle of this method is based on the fact that aromatic hydrocarbons isolated by extraction from reforming catalysts and containing some amounts of unsaturated impurities (to 0.35%), are passed through the bed of granulated aluminosilicate adsorbents (prepared on the basis of appropriately activated natural clays). Unsaturated hydrocarbons polymerize on the acidic centers and then undergo condensation, resulting in coke formation, while aromatic compounds (mainly benzene, toluene and xylenes) remain practically unchanged after perculation purification. Similarly, in the process of purification of aromatic hydrocarbons obtained in the catalytical processes of reforming and hydrocracking-hydrodeacrylation the adsorbents prepared from natural palygorskite montmorillonite clays can operate continuously, e.g. for 1 year [116]. During this period over 8-10% w/w coke is deposited on the sorbent surface, which leads to its strong deactivation. Although methods of thermooxidative regeneration of such sorbents exist [118], the consumed materials are usually discarded at the waste dump, and the adsorber is filled again with a new sorbent. These examples indicate on the one hand, the type of the substances which should be selected for carbonization and, on the other, the source of potential carbon-mineral adsorbents. Taking this fact into account, the Novosibirsk researchers [115] have worked out a method of carbon adsorbents preparation consisting in carburization of aluminoxide surface with the products of divinyl pyrolysis. It was stated [120] that the coke deposits mainly in the form of particles (3 nm) on the whole accessible kinetic surface of Al_2O_3. When the total content of coke is 18-22%, then 25-30% total amount of the coke is localized in the macropores of 10 μm size, 15-20% in the pores of 25-200 nm and 45-50% w/w - in the pores of < 200 nm [121].

Much attention has been paid [121] both to the methods of catalytic cracking and regeneration of catalysts, especially of those containing expensive zeolites. This regeneration must be carried out in such a way that the catalyst will not lose its activity during many technological cycles. For this reason, short-cycle stages of catalyst operation are used, including introduction of special impurities capable of sulphur binding, using ion-exchange resins for catalyst demetanization, etc. This allows us to attain stable operational parameters of zeolites-containing catalysts during many cycles. However, insufficient mechanical resistance may cause, in the circulating stream of the catalyst, spills of its granules of a relatively large cross-section. The effective work of a technological device is possible when the content of spills in the catalyst bed does not exceed 1.5%. For this reason, some part of carbonized material is directed to the separator removing the catalyst spills of 1.5-2.0 mm size [122], introducing the new catalyst in the stream at the same time. Daily consumption of such catalyst amounts to 400 tons in the USA [116].

In industry less expensive semi-synthetic sorbents prepared from natural silicates instead of expensive zeolite containing catalysts are used especially for the cracking of hydrocarbons. Owing to this more often exchange of consumed catalyst becomes profitable [123], because the consumed catalyst may be used further as a carbon-mineral adsorbent.

Several sources of carbonized sorbents and catalysts preparation have been indicated. Consumed catalysts of steam reforming of hydrocarbons, hydrogenation and dehydrogenation of hydrocarbons [106], hydrogenolysis [109], methanolization [110]. Fisher-Troopsh synthesis [111, 112] as well as the catalyst consumed in the processes of purification of paraffins from unsaturated impurities, deep adsorption drying of propylene and other unsaturated hydrocarbons [124] drying the propylene gas are potential raw materials for carbon-mineral sorbents preparation. In the last case [128] on the surface of aluminosilicates, bauxites and natural zeolites are sorbed strongly heavy fractions of condensate, which undergo catalytic changes during thermal regeneration, forming a coke layer on the surface. This process is especially visible when natural gas contains some impurities of unsaturated compounds. It is evident that the process of carbonization may be used deliberately for some purposes. The examples of such application are given in Ref. [91-93]. The complex sorbents prepared in this way may become inexpensive fillers of the filters used for trapping different pollutants of water and air, thus to prevent them from getting into the environment and improving its state. Complex adsorbents seem to be inexpensive and effective sorbents competing with expensive and difficult to prepare active carbons.

The sorbents prepared by carbonization of different polymers constitute a distinct group of carbon adsorbents. The process of preparation of such adsorbents usually consists of thermal pyrolysis of chosen synthetic resins, sometimes especially prepared before carbonization [129-135]. The first papers on polymers carbonization describe preparation of special porous carbons (including molecular sieves) obtained by carburization of polyvinylidene chlorides (PVDC) [135, 136]. This type of adsorbents is used for separation of stable gas mixtures (e.g. CO, CO_2, N_2, CH_4, etc.), components of liquified gases, and trace amounts of different organic substances included in water. The fact that water is

eluted before methane and other hydrocarbons on such adsorbents is used here.

Carburization of other polymers (especially styrene, vinyl and phenyl-formaldehyde derivatives) leads to the formation of carbon adsorbents of glassy structure (glassy carbon). Such carbons are characterized by excellent mechanical properties, two-dimensional ordering crystallographic structure and surface properties similar to those of graphitized carbon blacks, i.e. they show the tendency for non-specific interactions with most polar organic substances. Moreover, if the process is carried out under controlled conditions such adsorbents in a form of spherical particles can be obtained [132], which is very useful, especially for optimal packing of such adsorbents in chromatographic and adsorption columns as well the efficiency of effectivity of chromatographic processes.

In order to prepare carbon adsorbents of defined porous structure the authors [134-137] used the so-called replica technique. This technique consists of spreading polymers on the surface of some sorbents (e.g. silica sorbents of appropriate porosity) followed by thermal carbonization of polymers and finally removal of silica matrix by leaking with alkali or hydrofluoric acid. In this way, the carbon sorbents of glassy structure and strongly developed porous structure were obtained. They have the specific surface area and chromatographic properties similar to those of the graphitized carbon blacks but better mechanical properties. They were used as the packings of GC and HPLC chromatographic columns for separation of phenols, methylbenzenes, polar monofunctional derivatives of benzene, amino and other compounds (HPLC) [135, 136].

Another method of polymer carbonization was used by Zwier and Burke [138]. Instead of high temperature treatment they used the electrochemical reduction of Teflon (polytetrafluoroethane PTFE) by means of lithium amalgamate. In this way they obtained the carbon adsorbents of very strong adsorption properties and high specific surface area (1400 m^2/g). These adsorbents were subjected to different chemical modifications through surface reactions with chlorosilanes or Grignard reagents after previous chlorination of the carbon surface. This allowed to reduce significantly adsorption properties of these sorbents and then to use them as HPLC packings for separation of aromatic substances.

Paper [126] presents the possibility of spherical carbon adsorbents preparation from consumed ion-exchange resins. This paper describes the pyrolysis of cation-exchange resins such as DOWEX, WOFATITE or ZEOLITE (containing the sulfone group) which resulted in the carbon sorbents of a relatively low specific surface area. For this reason before the application these sorbent were subjected to activation with steam at 800-900°C, sometimes using the catalysts to control the gasification process. This procedure allows to obtain the carbon sorbents of a specific surface area of 1200 m^2/g and pore volume 0.75 cm^3/g. These sorbents were used for preconcentration of various dispersed organic substances from water and air by means of solid-phase extraction (SPE) or thermodesorption method (TD).

Exceptional properties of carbons prepared by carbonization of polymers enable their application in many fields where they cannot be replaced by any other adsorbents. Sentek et al. [136] have described the method of carbonization of different organic polymers and application of the obtained synthetic spherical carbon adsorbents for blood hemoperfusion, i.e. sorption of the toxins directly from the patient's blood. The sorbents used for such purposes must satisfy many very rigorous requirements, i.e. they must be bio compatible with blood, have good mechanical properties (cannot be dusted or crumbled), good sorption properties and spherical shape, because of contact with blood and possibilities of its coagulation on the sharp edges and corners of sorbent grains. Spherical carbon adsorbents prepared by carbonization of polymers satisfy such requirements.

Conclusion

A detailed discusion of all methods of carbon and similar sorbents preparation as well as their application in technology and laboratories constitutes an extensive subject and the author of this review is aware that many important questions related to carbon adsorbents have been omitted. An effort has been made to treat these questions as extensively as possible and for this reason this article reports significant amounts (tons) of carbonized catalysts being the industrial wastes or small (grams or even micrograms) amounts used in analytical laboratories and medicine, e.g. for blood hemoperfusion. I have concentrated mainly on the carbon application in analyses as well as on environmental protection.

Dr Philip L.Walker wrote earlier about the carbon adsorbents that "carbon is truly an old but new material...". I think that this sentence is a guide for investigations of many research workers because carbon adsorbents were the first ones used by people. New and new interesting properties which make them one of most universal and at the same time unique adsorbents are being discovered. I think that chemistry of carbon always represents a current field of investigation, creating possibilities for new discoveries.

Acknowledgement

Financial support by the State Committee for Scientific Research. Project No.3 TO9A 03611.

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