PREPARATION OF MESOPOROUS CARBON ON ADSORBENTS FOR ADSORPTION OF EXPLOSIVE NITRO-COMPOUNDS FROM THE AQUEOUS SOLUTION

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Introduction

Analytical chemistry (chromatography, electrochemistry, isolation and concentration of trace amounts of the substances, etc.) is at present one of the most important branches in which the carbon materials of different porosity are used [1]. Particularly interesting and important from the viewpoint of adsorption (analytical) practice are the method of preparation of mesoporous carbon adsorbents not containing micropores and characterized by relatively high pore volume, high mechanical resistance as well as by energetical and structural homogenity. As it is known commercially available adsorbents donot satisfy these requirements. This paper there are presented some possibilities of preparation of such adsorbents using simple technical ways. Usefulness of prepared carbons in the analytical practice for isolation and concentration of trace amounts of explosive substances contained in water is shown.

Experimental

The initial active coke was obtained from the Wood Dry Distillation Works in Hajnówka (Poland). The surface contamination with mineral matter was removed from the commercial active coke by washing with a mixture of HCl and methanol [2]. The catalytic gasification of the initial active coke was carried out as described previously [3]. A sample of gassified coke was impregnated with 3 % of Ca (II) in the way presented in [4]. Activation was carried out in the quartz fluid reactor with pure steam at 800^{0}C. The burn off was 74 %. In this way the adsorbent labelled as ADO was obtained. The methylene chloride was pyrolysed (500^{0}C, 15 min, in the nitrogen stream) on the surface of this carbon in a special rotary reactor [5]. In this way the carbon adsorbent labelled as AD was obtained. This adsorbent contained 29% w/w of the carbon deposit. The parameters of porous structure of the adsorbents were determined from the analysis of low-temperature (77 K) isotherms. Fig.1 presents the above isotherms for the initial coke as well as for ADO and AD adsorbents.

The usefulness of the prepared adsorbents for adsorption of selected explosive nitro-compounds was investigated by the solid-phase extraction (SPE) method [6]. Two commercially available SPE cartridges packed with different carbon materials (Hypercarb from Hypersil, UK and Envicarb from Supelco, USA) were used as reference sorbents. All used cartridges had the same volume (3 ml) and were packed with the same mass of sorbents - 100 mg. The dimethylformamide (DMFA) solvent used was of HPLC grade. Standards of explosives: octogen (HMX), hexogen (RDX), 2,4,6-trinitrotoluen (TNT), dipicrylamine (hexyl) and hexanitrodinitrobenzyl (HNDB) were obtained mainly from Promochem (Poland). HPLC analyses were performed on the LC-51 ternary gradient system (Bruker, Germany) with UV detection at 225 nm.

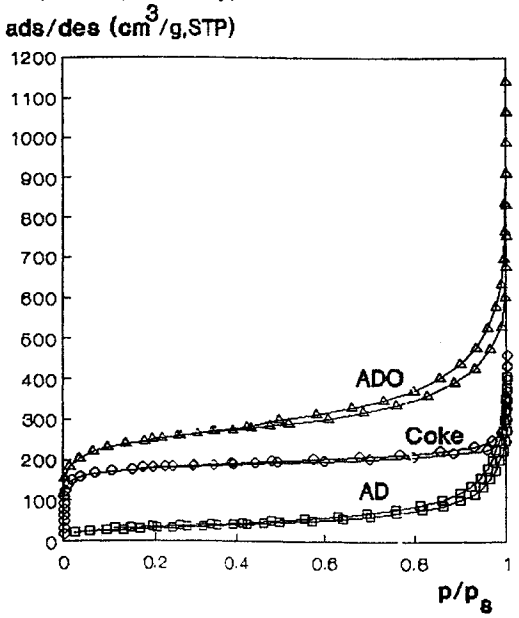

Figure 1. Adsorption/desorption isotherms of nitrogen on the surface of initial coke and ADO and AD carbon adsorbents synthetized on its basis.

Results

In Refs. [4-7] it is shown that the use of calcium catalyst in the steam gasification of carbon adsorbents permits to increase the total pore volume of these adsorbents as well as to develop their mesoporous structure.

Unfortunately these changes are usually accompanied by deterioration of mechanical strength which is required (sometimes it must be very high as e.g. in HPLC) in many practical applications. In paper [8] it was pointed out that carbon deposits obtained by pyrolysis of CH_2Cl_2 are characterized by unusually high mechanical resistance, required in many adsorption processes. At the same time the pyrolysis reaction occurs under moderate conditions. It could be expected therefore that by a proper combination of the method of development of mesoporosity in carbon materials with the method of spreading carbon deposits of exceptionally high hardness (causing the increase of mechanical strength of the modified material) on the surface of different adsorbents the carbon adsorbent satisfying all requirements would be obtained. This problem was the main subject of our investigations.

Table 1. Characteristics of porous structure of the investigated adsorbents.

Carbon	S_{BET} m^2/g	V_p cm^3/g	R Å	V_{micro} cm^3/g	$D_{particle}$ μm.
Coke	636	0.40	12.9	0.28	100-200
ADO	911	0.92	20.0	0.38	100-200
AD	111	0.36	65.1	0.05	100-200
Envicarb	100	-		-	40-60
Hypercarb	120	0.70		-	30-40

From the data presented in Table 1 it is can be seen that the partial catalytical gasification of starting coke with water vapour (steam) causes over twofold increase of pore volume V_p, mean pore radius R and specific surface area S_{BET}. Carburization of the surface of this adsorbent under appropriate conditions by the product of pyrolysis of CH_2Cl_2 has caused several-fold decrease of S_{BET} (which is now comparable to those of Hypercarb and Envicarb) and the increase of R. The pore volume V_p decreases too, but in comparison to the starting coke the changes of these parameters are rather small.

Table 2 presents the comparison of the results of concentration of trace amounts of nitro-compounds on the prepared adsorbents and the same results obtained for Hypercarb and Envicarb. From the analysis of the data listed in this table, it follows: the worst results of concentrations (strong adsorption, weak desorption) were obtained for the starting coke. Development of the mesoporous structure followed by modification of the surface with the product of CH_2Cl_2 pyrolysis (blocking of micropores, adsorbent AD) improves significantly its properties its application for concentration of nitro-compounds is concerned.

It can be stated readily that the recoveries obtained for AD carbon are comparable to those obtained for Hypercarb and Envicarb. It is important, that the way of preparation of AD adsorbent is simple from the technical viewpoint. In addition the carburization of partially gasified coke (ADO) restitutes and even increases its starting mechanical resistance. It is known that steam gasification always leads to deterioration of mechanical properties of carbon adsorbents.

Table 2. Comparison of the recoveries of nitro-compounds from the studied carbon adsorbents by DMFA as a solvent.

Substance	Adsorbent			
	Recovery in %			
	Coke	AD	Envicarb	Hypercarb
HMX	60	104	105	110
RDX	65	95	58	44
TNT	0	57	43	48
HEXYL	40	101	95	96
HNDB	34	95	102	99

Conclusions

A simple method of preparation of mesoporous carbon adsorbents practically not containing mesopores was presented. The usefulness of the prepared adsorbents for isolation and concentration of the trace amounts of explosive nitro-compounds in water was demonstrated. It was stated that in the above respects this adsorbent is comparable to the commercial carbon adsorbents such as Hypersil and Envicarb.

Acknowledgments

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