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Original Contribution

INVESTIGATION OF THE POSSIBILITIES FOR PREPARING A NEW TYPE OF CARBON SORBENT BY MODIFYING ACTIVATED CARBON WITH LYOPHILIZED PLASMA PROTEINS

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SUMMARY

PURPOSE: The aim is to study the influence of supported blood phase on the porous texture of activated carbon and the strength of its bonding with the carbon surface, thus evaluating the possibilities of the proposed novel method for preparing sorbents by depositing lyophilized plasma proteins on active charcoals. METHODS: A new method is presented for supporting lyophilized plasma proteins on the surface of activated carbon, whereupon the characterization of the samples has been carried out by the method of low-temperature adsorption of nitrogen (77.4 K) prior to and after the thermal treatment of the samples. RESULTS: A new type of sorbent has been prepared and characterized in view of its texture. CONCLUSIONS: The obtained new material is characterized by comparatively uniform distribution of the lyophilized plasma proteins deposited on the surface, which ensures effective contact and interaction on the inter-phase boundary surface between the blood phase and the vapours of the toxic compounds during sorption.

Key words: new type sorbent, modifying activated carbon, supported blood phase

INTRODUCTION

The growing threat of terrorist actions during the last years, that could possibly include even weapons of mass destruction, imposes widening of the scope of investigations focused on the defence of the population and neutralizing various toxic compounds, potentially applicable for terrorist attacks. On the other hand the experience of the industrialised countries shows that in parallel with the development of production technologies, the risk of accidents in the chemical industry has not disappeared, but it is only restricted within some acceptable limits [1].

At the moment the most reliable defence of the population in the case of terrorist actions using chemical methods as well as in the case of industrial accidents is ensured by different types of filtering gas masks, whose principle of operation is based on the adsorption of the toxic vapours in the air by activated carbon (or some other carbonaceous materials) impregnated with various metal oxide components [2].

Not long ago a new type of sorbent was proposed for protection from the vapours of toxic compounds based on blood products [3-9]. Data were reported in a number of publications on the values of static sorption capacity of blood products in regard to vapours of benzene and its derivatives [10], the vapours of halogenated hydrocarbons [11] and those of benzene, hexane and cyclohexane at various temperatures [12].

An explanation was put forward concerning the mechanism of sorption vapours of different compounds present in blood products [13].

It can be considered that a very promising option for application of blood products as sorbents is their coating on activated carbon, aimed at combining physical adsorption, characteristic of activated carbons, with the process of swelling of blood products upon sorbing vapours of different compounds.

Such an option is favoured by the high specific surface area, which is typical of activated carbons, as well as the suitable porous texture, due to the possibility of increasing the contact area between vapours

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of substances and the deposited blood products.

The location of the latter phase in the empty space of nano-sized pores of the support restricts (owing to the geometrical dimensions) the size of the separate fragments of the supported blood product down to nanometer size. The following issues arise:

- what is the possible influence of the supported blood phase (formed inside the nanometer-size space of the support) on the porous texture of the support? In what way does the phase deposited in the larger pores of the support prevent the vapour diffusion of the substances towards the phase located in finer pores. In this aspect – is the blocking of some sections of the porous texture of the support by the blood phase in the process of its deposition and the consecutive lyophilization substantial or not?
- How strong is the blood phase bonded to the surface of the support which could be evaluated by the changes in the locations of the supported blood phase after thermal treatment?

For this reason the purpose of the present work was to investigate the influence of the supported blood phase on the porous texture of the support (activated carbon) and the strength of its binding to the support surface during thermal treatment, and on this basis to evaluate the capacity of the proposed new method to prepare sorbents by deposition of lyophilized plasma proteins on active charcoal.

MATERIALS AND METHODS

1. Method for preparing the sorbents

The activated carbon (ACVM), used as a support for the blood plasma, is commercially available product, obtained on the basis of apricot stones with size of the particles about 1.0 – 1.5 mm [14].

The blood plasma was obtained from sheep's blood, delivered by the Institute for contagious and parasitic diseases, Sofia. It was subjected to the following procedure: Alsewer's solution (Bucantz's modification) was poured into a vessel of 250 ml volume. The blood was added to the vessel to attain a blood: solution ratio of 1:1. It was then centrifuged for 20 min at 2 000 rpm (revolutions per minute) to separate the plasma from the mass of erythrocytes.

The sorbent (activated carbon, modified with blood plasma) was prepared by the following procedure: to a continuously stirred blood plasma by means of a magnetic stirrer, was added step by step active carbon until the ratio of 1ml of blood plasma per 1g of active carbon was reached. The stirring was continued until the whole quantity of plasma was absorbed by the carbon. The prepared material was kept for 10-15 min at room temperature, and subsequently transferred in the low-temperature chamber (at 233 K), where it was left for at least 24 hours. The product, obtained in this way, was subjected to vacuum-sublimation drying (lyophilization), at the following temperature regime and duration: from 233 K to 273 K (for 6 hours); from 273 K to 298 K (for 18 hours); at 298 K (for 4 hours). The sample, produced by the above-described method, was denoted as ACB. It was next subjected to thermal treatment in vacuum (1.10^{-2} Torr) for 4 hours at a temperature of 673 K to obtain another sample denoted as ACB-400. The preliminary investigations [7] indicated that under the conditions of maintained vacuum at 673 K, only a partial dehydration was observed and primary destruction of the blood plasma. However the process was accompanied by rupturing of the chemical bonds between the blood plasma and the surface of the support. This enabled us to deduce the strength of bonding with the activated carbon surface on the basis of the occurring migration of the blood phase.

This method for preparation of the sorbent is an original one and it has been published for the first time in the Ph.D. thesis of V. Ivanov [7]. The modifying of the activated carbon with blood plasma has been carried out at the Institute of Cryobiology and Foodstuffs Industry, Sofia.

2. Method for characterization of the new sorbents

The method of low-temperature adsorption of nitrogen (at 77.4 K) was used for determining the location of the supported blood phase inside the porous texture of the activated carbon (prior to and after the thermal treatment of the samples). The adsorption measurements were carried out using a conventional volumetric apparatus.

Before the measurements, the samples were degassed as follows: Prior to carrying out the adsorption of nitrogen (at 77.4 K), the initial ACVM material and the sample ACB-400 were degassed for 12 h at 523 K and a vacuum < 10^{-4} Torr; as well as the sample ACB, prepared according to the procedure,

described above. They were quickly cooled down to the boiling temperature of liquid nitrogen in the adsorber, which had initially been blown through with argon, then allowed to stay for 0.5 h and degassed for 16 h at 77.4 K and residual pressure < 10^{-4} Torr [15].

The nitrogen adsorption-desorption isotherms were used for determination of the following parameters: the specific surface area A_{BET} (according to the BET equation); the total pore volume V_t (calculated from the nitrogen uptake at a relative pressure of 0.95 according the Gurvich's rule); the micropore volume W_O and the half-width of the slit-shaped micropores for the distribution curve maximum x_O (according to the Simplified equation [16]); the mesopore volume V_{ME} (determined by subtracting W_O from the total pore volume V_t); the mean pore radius R_P (evaluated as the ratio between the doubled total pore volume and A_{BET}, assuming a cylindrical pore model); the mesopores size distribution, estimated from the adsorption branch of the hysteresis loop by the Orr-Dalla Valle's method as described in detail in [17] assuming cylindrical pore shapes.

RESULTS AND DISCUSSION

The parameters, computed on the basis of the nitrogen adsorption-desorption isotherms, are represented on **Table 1**.

Table 1. *Adsorption-textural parameters of the studied samples ACVM, ACB and ACB-400.*

Sample	A_{BET}, m^2/g	V_t, cm^3/g	W_O,cm^3/g	V_{ME},cm^3/g	x_O, *nm*	R_P, *nm*
ACVM	1015	0.92	0.43	0.49	0.9	1.8
ACB	784	0.55	0.34	0.21	0.8	1.4
ACB-400	852	0.68	0.38	0.30	1.1	1.6

From the comparison of these parameters for the sample ACB with the respective values for the ACVM sample it is seen that the supported blood phase in the case of ACB sample does not lead to any drastic change in the values of its textural parameters in regard to those of the initial activated carbon, whereupon the microporous- mesoporous type of texture, characteristic of the ACVM material, is not changed. The observed changes concern, to a greater extent, the porous texture rather than the specific surface area. Thus the decrease in A_{BET} in the case of the ACB sample, compared to that of the ACVM material, is about 23%, while for the same sample (ACB) this decrease in the various types of volumes is as follows: for W_O it is about 21%, for V_t – 40%, and for V_{MES} it reaches 57%.

By comparing the distribution curves of the mesopores (**Figure 1**) and of the micropores (**Figure 2**) with respect to dimensions for the samples ÀÑÂ and ACVM it is seen that the supported blood phase is situated within the entire interval of pores with R_P < 15 nm (**Figure 1**). Moreover, even some of the supermicropores are filled in and, as a result of this and in addition to the decrease in W_O , a shifting of the distribution curve of the ACB sample is observed (**Figure 2**) in the direction of the pores with smaller x_O, 0.8 nm (**Table 1**).

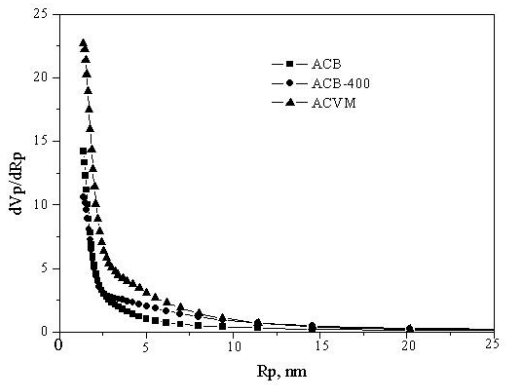

Figure 1. *Curves of the size distribution of the mesopores of the samples ACVM, ACB and ACB-400.*

The thermal treatment of the ACB sample at 673 K in vacuum does not lead to any serious changes in the textural parameters of the ACB-400 sample, compared to those of the ACB sample. As a result of the occurring processes of partial dehydration and destruction of the blood phase in the ACB sample, the increase in A_{BET} in the case of the ACB-400 sample is about 8%, that of W_O - 11%, while that of V_t - 19%. This comparatively insignificant increase of the specified parameters supplies evidence on the low mobility of the phase under the conditions of thermal treatment. The most essential change in the case of the ACB-400 sample is the increase of V_{MES} (30%).

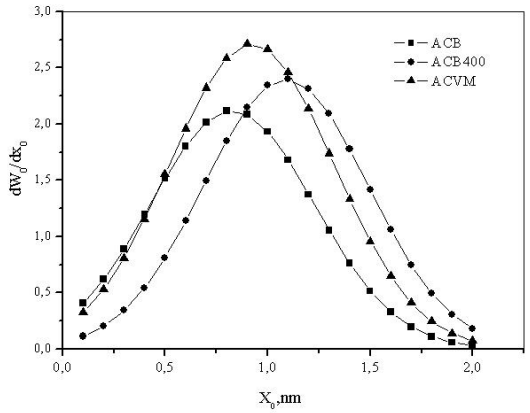

Figure 2. *Curves of the size distribution of the micropores of the samples ACVM, ACB and ACB-400.*

The comparison of the size distribution curves of the mesopores of the ACB and ACB-400 samples (**Figure 1**) helps to localize the interval of R_P of the mesopores, where as a result of the thermal treatment a part of the porous space is liberated - R_P: 2.5 – 11.5 nm. The analysis of the size distribution curve of the micropores of the ACB-400 sample (**Figure 2**), indicates that the growth of V_{MES}, juxtaposed to the same parameter in the case of the ACB sample is associated with a reverse process, namely – partial filling of the fine mesopores and, respectively, a secondary blocking of a share of the micropores space (x_O is shifted from 0.8 in case of ACB to 1.1 nm in the case of the ACB-400 sample).

Therefore, the blood phase is strongly bound to the carbon surface and it is not inclined to facile migration under normal conditions. This is confirmed by the fact that the thermal treatment in vacuum at 673 K does not lead, even partially, to restoring the primary (initial) texture of the ACVM material.

In addition to the size distribution curves of micro- and meso-pores, the calculated textural parameters of the samples also reveal that the blood phase is located mainly in the mesoporous space of the samples, in view of the following:

- The strongest decrease is in the value of V_{MES} of ACB (compared to ACVM);
- The least affected parameters are the volume of the micropores (W_O), respectively the values of x_O (**Table 1**).

The latter facts are also connected with the fact that the molecular mass of the blood plasma is very high and practically (with the exception of some specific fragments) it is not able to penetrate into the micropores, while the blood phase inside the mesopores (the so called "transport" pores) blocks the access to a part of the micropores. For this reason, as well as because of the strong bonding of the functional groups of the blood phase with the carbon surface, the thermal treatment in vacuum does not lead even to partial restoring of the primary (the initial) texture of the ACVM material.

CONCLUSIONS

On the basis of the above-described investigation, as well as in view of the values of the ratio W_O/V_{MES} for the studied samples (**Table 1**): ACVM – 0.88, ACB – 1.62 and for ACB-400 – 1.27, it can be concluded that as a consequence of the deposition of the blood plasma upon ACVM material and the lyophilization following afterwards, there occurred changes in the initial mesoporous texture (the sample ACB), accompanied by filling (pore blocking) of parts of the porous space. **In spite of this fact, however, the preservation of a high specific surface area in the case of the ACB sample (784 m^2/g) showed that the blood phase was distributed comparatively uniformly on the surface of the initial active carbon. This could ensure an effective contact and interaction on the inter-phase boundary surface between the blood phase and the vapours of the toxic compounds during sorption. The available volume of the micro-pores and the sufficiently preserved 'transport' meso-porosity, implied in this specific case the participation of physical adsorption characteristic of the activated carbon.**

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