Journal of Engineering Physics and Thermophysics, Vol. 80, No. 3, 2007

ADSORPTION PROPERTIES OF NOVEL MELANIN-CONTAINING GRANULAR PHYTOADSORBENTS

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UDC 541.183.03:53

Some adsorption and physicomechanical characteristics of novel melanin-containing granular phytoadsorbents have been determined. The influence of the binder on the phytoadsorbent adsorptivity for organic substances, benzene, ethyl acetate, and methanol, has been investigated. It has been shown that the adsorptive capacity of the granular phytoadsorbent depends on the nature of the adsorbent and the kind of binder, which is not "inert," and decreases as its content in the granules increases.

In [1], we presented the results of the investigations of the adsorption properties of novel melanin-containing phytoadsorbents that demonstrated certain prospects of using them in a number of technological adsorption processes for extracting vapors of volatile organic substances from the gas phase. At the same time, these investigations revealed that for wide industrial use in the majority of technological processes and technologies of gas and water purification characterized by large volumes and high speeds of filtration of gaseous and liquid media, modification of their physicomechanical properties is needed. If they are used in the original form in these technologies, there will be a considerable carry-over and irretrievable loss of the small fractions of the adsorbent involved in the process, which will decrease the capacity, as well as the economic and technological efficiency of the apparatus. Decreasing the carry-over of particles by lowering the speed of filtration will require much larger sizes and a more complex constructional arrangement of the equipment, and forward or backward flow filtration of the medium in the so-called "squeezed layer" bounded by a fine-mesh net will considerably increase the hydrodynamical resistance of the apparatus and, therefore, the power input. It seems expedient to modify, by means of granulation or tableting, the dispersion characteristics of the phytoadsorbents developed in order to widen their industrial use.

This expediency is also due to the fact that, as is well known [2–4], adsorbents as medicinal preparations find wide application in medicine and veterinary medicine exactly in the form of granules, capsules, or tablets. Consequently, such modification of phytoadsorbents being developed will considerably widen the scope of their application as enteroadsorbents.

It is also known [5] that the choice of particular granulation or tableting parameters permits regulating the intermolecular interaction forces of particles in the final product, the strength, the porous structure, the surface properties, and, accordingly, the adsorption characteristics of the resulting material.

The investigation of the physicomechanical properties and adsorption activity of the phytoadsorbents developed that have changed as a result of modification is not only of great independent scientific interest, but also makes it possible to select those that are most suited for use as techno-, eco-, and enteroadsorbents.

In the present paper, we have investigated the influence of some factors characteristic of the granulation, in particular, the introduction of the binder, on the adsorption properties of the phytoadsorbent.

To modify the physicomechancial properties and adsorption characteristics of the phytoadsorbent in [1], a fraction with particle sizes less than 50 μm was used. Granulation of the original polydisperse phytoadsorbent was performed on a laboratory extrusion plant. The granulation technique was as follows. The binder (starch glue or sugar

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1062-0125/07/8003-0469

TABLE 1. Bulk Density of the Phytoadsorbent versus the Size of Granules, the Type of the Binder, and Its Quantity

Binder	Quantity of binder, mass %						
	5		10		20		40
	Granule diameter, mm						
	3	4	3	4	3	4	4
Starch glue	114	125	134	140	163	—	—
Sugar syrup	—	—	—	—	192	198	229

syrup) at a temperature of 303–313 K was mixed with the phytoadsorbent, cooled to room temperature, charged into the receiving bin of the extruder, and extruded through the spinnerets of a punched grid, the diameter of whose holes was varied from 3 to 5 mm.

The moisture of phytoadsorbent granules after the extruder was 65–70%. The granules obtained with the use of starch glue as a binder were dried in a drying cabinet at a temperature of 373 K for 1 h. The granules obtained with the use of sugar syrup as a binder were dried for the same period at a temperature of 353 K. As a result, granules in the form of cylinders of diameter 3–5 mm and length 5–7 mm with a binder content of 5–40% were obtained.

The bulk density ρ_b and porosity $\varepsilon_{st.l}$ of the stationary layers of the granular phytoadsorbents as well as the strength characteristics of the obtained granules, such as the mean and minimal mechanical compression strength, were determined by the standard methods [6]. The stability of the properties of granules under static and dynamic conditions was estimated by the granule-liquid (water) contact time until they began to break down.

The adsorption isotherms of benzene, ethyl acetate, and methanol vapors were measured by the gravimetric method [6] at 293 K. The specific surface S and the parameter C depending on the adsorption heat were calculated by the Brunauer–Emmett–Teller (BET) equation from the adsorption isotherms in linear form in the region of relative pressures $p/p_s \approx 0.05$–0.2. In so doing, according to [7], the landing strip for the benzene molecule was taken to be equal to 0.4 nm, for the methanol molecule, 0.213 nm, and for the ethyl acetate molecule calculated by its density in the liquid state, 0.442 nm.

Investigations of the mechanical strength of the obtained granules — ultimate compression strength — have shown that the mean crush strength is 10–12 mPa and the minimum is 5–6 mPa. This points to the fact that it can be used (without destruction of individual granules) in the gas purification technologies as filter beds whose height is sufficient for industrial plants.

As the results of determining the porosity of the stationary layers of samples of the granular phytoadsorbent have shown, it depends on the shape, sizes, packing technique, and other factors, differing widely from the quantity calculated on the assumption that the whole of the layer consists of particles with a certain mean effective diameter determined on the basis of the screen analysis. Its values are in the range of $0.35 \le \varepsilon_{st.l} \le 0.43$, and the smaller value thereby corresponds to the layer of granules of diameter 3 mm and length 7 mm and the larger one — to the layer of granules of diameter 5 mm with the same linear size. Table 1 gives the values of the bulk density for phytoadsorbent granules of length 5 mm depending on their diameter d and the type of binder and its quantity m. As is seen, the bulk density of the granular phytoadsorbent varies over the range of $114 < \rho_b < 229$ kg/m^3. It should be noted that at an equal quantity of the binder it is higher for larger granules, and at equal sizes of granules it is lower in the case of using starch glue as a binder.

The results of the investigation of the resistance of phytoadsorbent granules obtained on the water-soluble binder (starch glue) to destruction in water under static conditions have shown that samples placed in a vessel with water at room temperature do not break down in it for a long time (for more than half a year) and only swell somewhat, increasing their linear sizes.

Continuous filtration of water at a speed of 1 l/min at a temperature of 288–289 K through a layer of a granular phytoadsorbent with a minimum granule diameter of 3 mm and a minimum 5% content of the binder (starch glue) leads to a washing-out of the binder and destruction of individual granules after about 3 h.

At the same time, modeling of the *in vitro* employment of granular phytoadsorbents as enteroadsorbents has shown that when granules with the above characteristics are placed in water at a temperature of 310 K, their disinte-

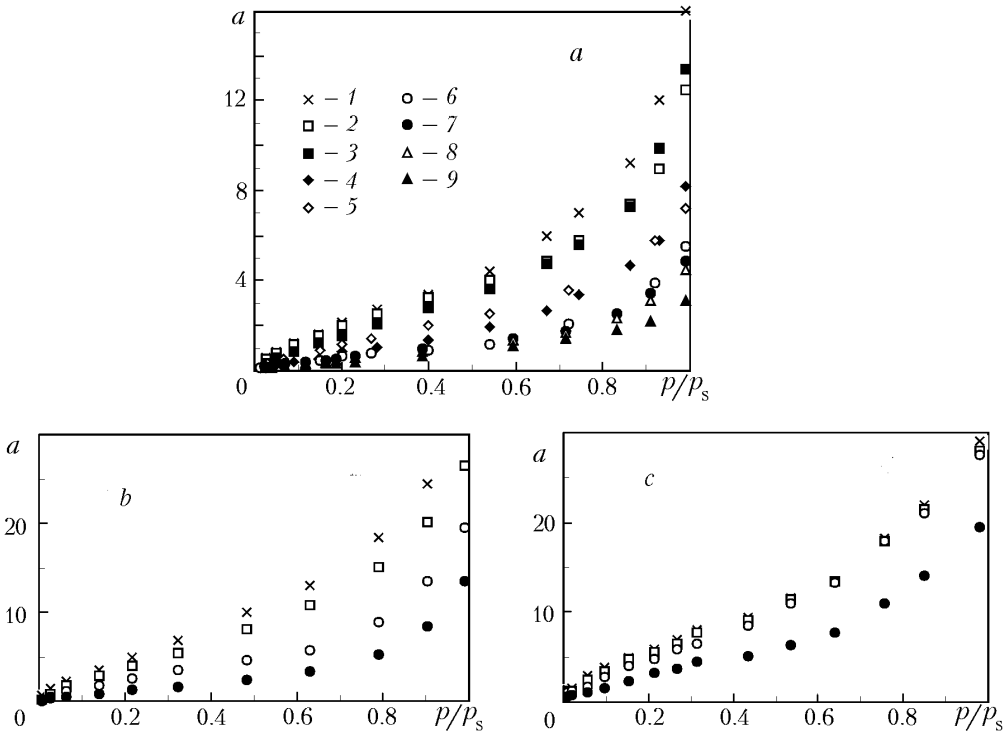

Fig. 1. Adsorption isotherms of benzene (a), ethyl acetate (b), and methanol (c) on the phytoadsorbent at 293 K. Notation 1–9 is given in Table 2.

gration is observed already after 1–2 h. This points indirectly to the fact that as granules move in the gastroenteric tract, their gradual decomposition will occur, thus prolonging the working effect of the phytoadsorbent. Thus, modifying the physicomechanical properties of the original fine-disperse forms of the phytoadsorbent by means of granulation will make it possible to develop enteroadsorbents of prolonged action by regulating the binder content in the granule, its strength, and other characteristics.

Figure 1a presents a series of adsorption isotherms of benzene on the original fine-disperse 1 and granular 2–9 phytoadsorbent samples. According to the IUPAC classification [8], the obtained adsorption isotherms of benzene vapors can be identified as physical adsorption isotherms of types II and III. On the original sample 1, as well as on the granular samples 2–5 they have a clearly defined initial convex (with respect to the pressure axis) section characteristic of the type II isotherm. As the binder fraction in the samples increases, the form of the benzene adsorption isotherm changes, approaching type III, which points to a weakening of the adsorbent–adsorbate interaction.

Since the presence of the binder decreases the phytoadsorbent concentration in the bulk of the granule, then, as is seen from Fig. 1a, the adsorptivity of granular samples naturally decreases with increase of its fraction. The above-mentioned change in the form of the adsorption isotherm as well as the sharp decrease in the benzene adsorption on granules at a 20% content of the binder are also characteristic of the adsorption of ethyl acetate (see Fig. 1b).

A somewhat different dependence was observed for the adsorption of methyl alcohol (see Fig. 1c). Unlike benzene and ethyl acetate, all adsorption isotherms of methanol had a clearly defined initial convex section. The adsorptivity of granules containing 5% of starch glue (sample 2) remained practically unchanged, and that of granules containing 20% (sample 6) is comparable to the positive capacity of the original fine-disperse phytoadsorbent (sample 1). The decrease in the value of the methanol adsorption on sample 7 (20% of sugar syrup) is not as sharp as for benzene and ethyl acetate. It should also be noted that the adsorption on granules, in which the binder fraction is 20%, for all adsorptives is lower in the case of using sugar syrup.

The analysis of the adsorption data by the BET method performed for comparison purposes (Table 2) points to an apparent change in the specific surface of samples calculated from the volume of the monolayer of benzene, ethyl acetate, and methanol depending on the diameter of granules and the binder content in them.

TABLE 2. Adsorption-Structural Characteristics of the Original 1 and Granular 2–9 Phytoadsorbent

Sample number	*d*	*m*	*S*	*C*	Sample number	*d*	*m*	*S*	*C*
Benzene					Ethyl-Acetate				
1	—	—	59	13	*1*	—	—	126	15
2	3	5	54	10	*2*	3	5	120	11
3	4	5	45	11	*6*	3	20	69	10
4	3	10	30	9	*7**	3	20	44	6
5	4	10	31	8	Methanol				
6	3	20	20	12	*1*	—	—	202	15
*7**	3	20	24	6	*2*	3	5	197	12
*8**	4	20	22	6	*6*	3	20	191	11
*9**	4	40	16	7	*7**	3	20	129	7

*Binder — sugar syrup.

Since the phytoadsorbent contains different surface functional groups [1], one of the factors determining the wide spread of *S* values is obviously the fact that in determining the specific surface by the BET method the effect of localized adsorption that corrupts the BET data is neglected. Even in the case of benzene adsorption the presence in its nonpolar molecule of π-electrons imparts a specific character to its adsorption.

The change in the form of the benzene and ethyl acetate isotherms with increasing binder fraction from the clear type II to type III is obviously due to the fact that the binder molecules block the active adsorption centers. And the phytoadsorbent–adsorbate interaction energy decreases therewith (the parameter *C* value decreases). No change in the isotherm form is observed in the methanol–granular phytoadsorbent system. This points to the fact that both starch glue and sugar syrup are not "inert" towards vapors of this adsorbate.

The investigations performed have shown that the adsorptivity of the granular phytoadsorbent depends on the nature of the adsorptive, the kind of the binder, and the concentration composition and size of granules. Changing the kind of the binder and its quantity, one can attain a minimal decrease in the adsorption capacity of granular phytoadsorbents compared to their original monodisperse form. For instance, for a phytoadsorbent with granules of diameter 3 mm and a 20% content of starch glue the adsorption capacity for methanol throughout the range of the investigated pressures decreases by no more than 2%, i.e., this phytoadsorbent has the highest efficiency in adsorbing methanol vapors.

Thus, modifying the physicochemical properties of the original fine-disperse forms of the phytoadsorbent by granulating them opens up the possibility of using them in industrial technologies for extracting or separating organic components in the gas phase, as well as in medicine as enteroadsorbents of prolonged action.

NOTATION

a, quantity of adsorption, mass %; *C*, parameter of the BET equation; *d*, granule diameter, mm; *m*, binder content in granules, mass %; p/p_s, relative pressure; *p*, pressure of adsorptive vapors, Pa; p_s, pressure of saturated vapors of the adsorptive at a temperature of 293 K, Pa; *S*, specific surface, m^2/g; $\varepsilon_{st.l}$, porosity of stationary layers; ρ_b, bulk density, kg/m^3. Subscripts: s, saturated; b, bulk; st.l, stationary layer.

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