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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Adsorption of Negative Eosin Ions, Tannin Molecules, and Latex Spheres on Aluminum Oxohydroxide Nanofibers

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Abstract—Adsorption of eosin and tannic acid by a new filter-sorption material was studied. This material has the form of polymeric microfibers having on their surface immobilized particles of the adsorbent, aluminum oxohydroxide nanofibers. The charge and geometrical conditions of adsorption were calculated. The results of these calculations are in agreement with the ion-exchange mechanism for eosin and tannin, and with the electrostatic mechanism for latex spheres.

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One of the most topical areas of research aimed to create nanomaterials is development of new highly filled fibrous and lamellar sorption-active filter materials [1]. To materials of this kind belongs a sorbent based on aluminum oxohydroxide nanoparticles formed in hydrolysis of electric-explosion aluminum nanopowders [2–4]. The main disadvantage of this sorbent is the high hydrodynamic resistance created by the sorbent bed. The solution to this problem was found when aluminum oxohydroxide nanoparticles could be fixed on the surface of microfibers. As a result, filter-sorption materials for water purification to remove various contaminants, including those of microbiological origin, have been obtained [5–9]. These materials are unwoven cloths with a thickness not exceeding 2 mm, in which microfibers create a porous skeleton with pore sizes providing a high filtration rate. Sorbent nanofibers, which are, as a rule, contained in an amount of 10–60 wt %, provide high sorption properties of the material.

However, the model of the structure and operation of the filter [5–9] is qualitative: the adsorption of negatively charged species, including macromolecular organic anions, is attributed to the positive charge on the adsorbent surface. The model can be qualitatively substantiated by the fact that electropositive filter materials, e.g., membranes with a modified charge, can be successfully tested with a solution of an anionic dye (Methanyl Yellow) or with a suspension of latex microspheres with an appropriate size.

At the same time, it has been noted [6] that there is no correlation between the surface potential and the adsorption capacity of a fibrous filter for MS2 bacteriophage, and the communications cited above did not specify the adsorbate–adsorbent charge balance.

Previously, monodisperse latex spheres (diameter 33 nm) modeling virus properties has been used to study the sorption properties of a filter material containing aluminum oxohydroxide nanofibers [11]. However, analysis of the adsorption by this technique is made nephelometrically in the dynamic mode under nonequilibrium conditions, which gives no way of obtaining data for construction of an adsorption isotherm. For this reason, in particular, attempts have been made to use macromolecular compounds, instead of latex spheres, in modeling of the virus adsorption. For example, these are anionic dyes determinable by photocolorimetry, which enables studies in both the dynamic and static modes.

The goal of this study was to obtain quantitative data on the adsorption of macromolecular organic substances, tannin and eosin, and latex spheres modeling properties of viruses. These data are necessary both for determining the possibility of modeling the adsorption of viruses

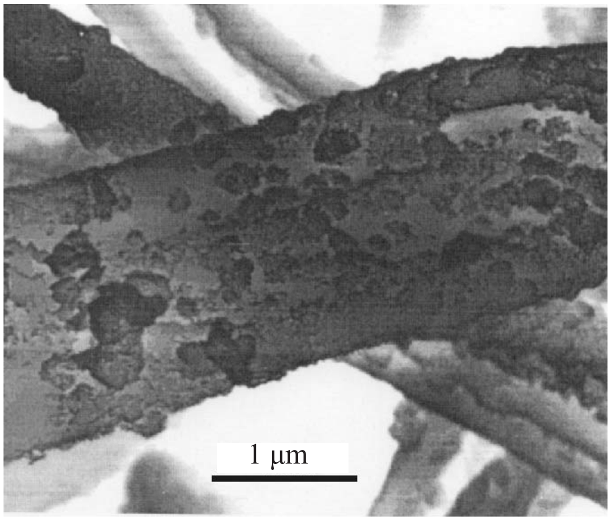

Fig. 1. SEM micrograph of the structure of the filter-sorption material.

by other particles and for elucidating the mechanism of water purification to remove various impurities by the nanofibrous material developed in [9].

The filter-sorption material was produced as described in [9]. The mass fraction of aluminum oxohydroxide Al_2O_3. $1.7H_2O$ in the material was calculated from the mass of Al_2O_3 remaining upon calcination of a weighed portion of the material at 900°C for 2 h. The specific surface area of the material was determined by BET, and the diameter of macropores, by the bubble-point method [12].

The anionic dye eosin ($C_{20}H_6O_5Br_4K_2$) of chemically pure grade and tannic acid ($C_{76}H_5O_{46}$, Alfa Aser) were used as adsorbates without additional purification.

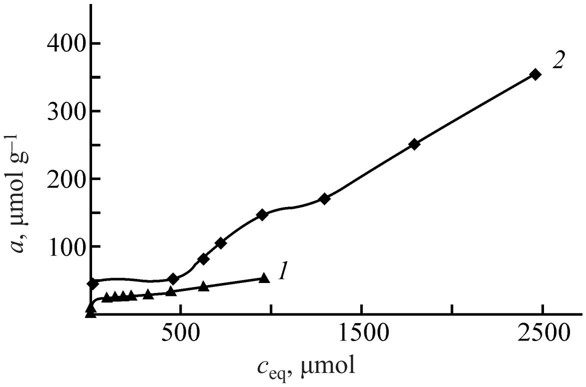

Fig. 2. Amount a of adsorbed substance vs. the equilibrium concentration c_{eq}. (*1*) Eosin and (*2*) tannic acid; the same for Fig. 4.

We performed the adsorption in the static and dynamic modes. The solution concentrations were determined with a KFK-2-UKhL-4.2 electrophotocolorimeter.

To obtain data for construction of adsorption isotherms of eosin and tannic acid, we placed 0.5-g portions of the filter-sorption material in solutions of volume 80 ml and were kept there for four days at a temperature of 18°C, with periodic shaking, for equilibration.

Solutions of tannic acid and eosin were passed through a sample of a filter-sorption material (diameter 35 mm, working part diameter 26 mm). The mass of a sample was 0.56 g. The filtration rate of 3 ml min^{-1} was maintained during the whole run.

The adsorption of model particles was studied in the dynamic mode with polystyrene-based latex spheres 33 nm in diameter, manufactured by Duke Scientific Corp. A 1-ml portion of the starting suspension (11 vol %) was added to 1000 ml of distilled water, the mixture was dispersed in a UZV-4/150 ultrasound bath for 10 min and allowed to stand for 4 h for removing air bubbles, to get the working suspension with a concentration of latex spheres of about 1012 cm^{-3} and turbidity of 1.6 NTU. The suspension was filtered through filter-material samples with an area of 3.8 cm^2 and mass of 0.4 g at a rate of 10 ml min^{-1}. The concentration of latex spheres in the filtrate was determined using a Hanna nephelometer in nephelometric turbidity units (NTU) [11].

The material is a 1.6-mm-thick unwoven cloth composed of acetyl cellulose fibers with an average diameter of 2 μm, which have adhesion-fixed aluminum oxohydroxide nanoparticles on their surface (Fig. 1). Aluminum oxohydroxide particles are attached to the microfiber surface as separate agglomerates, frequently with a spherical shape, 0.2–1.0 μm in size, and as a porous coating with a thickness of 0.2 to 0.7 μm. The structure-forming element of the agglomerates and the coating are chaotically arranged aluminum oxohydroxide nanofibers of 5–8 nm in diameter and 100–200 nm long. The porous structure of the sorbent is mostly represented by mesopores with a size d_p of about 4 nm [13]. The specific surface area of the material (33.3 m^2 g^{-1}) is determined by the specific surface area of the sorbent (100 m^2 g^{-1}) whose fraction in the material is 32.5 wt %.

Figure 2 shows adsorption isotherms of tannic acid and eosin. In accordance with the classification of adsorption isotherm shapes by Giels [14], these adsorption isotherms can be identified as those of the H-type. Isotherms of this kind are observed in those cases when the adsorption is due to formation of chemical compounds or to ion exchange [15]. The second plateau in the isotherm of tannic acid may be due to reorientation of adsorbed molecules in the first layer or to filling of a second layer. The up-tending portions in the isotherms of both adsorbates probably correspond to the formation of a monolayer whose filling occurs when 1 g of the material adsorbs about 47 μmol of tannic acid and 21 μmol of eosin, respectively.

However, the data obtained cannot be used to forecast the efficiency of the filter-sorption material under real conditions of its operation: at high rates of a solution flow across a thin layer of the material. Therefore, the adsorption was studied in the dynamic mode. The adsorption elution curves obtained by passing tannic acid and eosin solutions across a bed of the filter-sorption material show time intervals t_0 (min) of a protective effect, which is a function of the starting-solution concentration c_0 (M), i.e., $t_0 = f(c_0)$ (Fig. 3). The dependence of t_0 on the inverse concentration of the starting solution, $1/c_0$, is well approximated by a linear dependence of the type $t_0 = k/c_0$ for both adsorbates (Fig. 4). Such a dependence is in agreement with the mechanism of fast, nearly irreversible adsorption on active surface centers. Because all eosin and tannic acid molecules are retained on the filter-sorption material during the interval of time from the beginning of sorption till t_0, we can easily find the mass m_i (mg) of the retained adsorbate by using the expression

$$m_i = M_i u c_0 t_0, \tag{1}$$

where u is the rate of the solution flow across the filter l min^{-1}, and M is the molar mass of eosin or tannic acid (mg mol^{-1}).

Hence follows the dependence of t_0 on c_0 in the form

$$t_0 = \frac{m_i}{M_i u c_0}. \tag{2}$$

Comparison of the experimentally obtained approximating expression $t_0 = k/c_0$ and Eq. (2) shows that $m_i/M_i u = h$. Hence, with the filter mass m_f (g) known, the sorption capacity a_i of the filter-sorption material can be easily found as m_i/m_f or in the form:

$$a_i = \frac{M_i u c_0 t_0}{m_\text{f}}. \tag{3}$$

The numerical values of the sorption capacity a_i of a sample of the filter-sorption material, calculated by expression (3) from the experimentally determined dependence $t_0 = k/c_0$, were found to be 2.7 mg g^{-1} (3.7 μmol g^{-1}) for eosin and 16 mg g^{-1} (9.4 μmol g^{-1}) for tannic acid, which gave, upon recalculation, the results listed in Table 1.

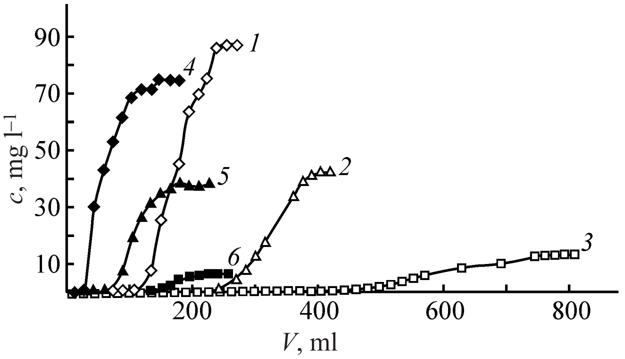

Fig. 3. Concentration c of the substances in the filtrate vs. the passed volume V. (*1–3*) Tannic acid and (*4–6*) eosin. c (mg l^{-1}): (*1, 4*) 100, (*2, 5*) 50, and (*3, 6*) 25.

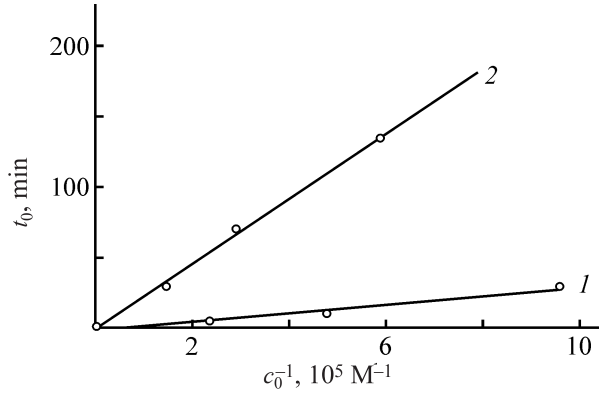

Fig. 4. Protective effect duration t_0 vs. the inverse concentration c_0^{-1} of the starting solution.

Figure 5 shows an adsorption elution curve obtained by passing a suspension of latex spheres through a sample of the filter-sorption material. We used this curve to calculate the capacities in Table 1. The number of microspheres retained by 1 g of the material till an instant of time t_0 was 2.5×10^{13}.

We made the calculation in Table 1, taking into account that the adsorption of tannic acid and eosin on the polymeric support can be neglected and the whole external and internal surface area, including mesopores, is accessible to these adsorbates. Only the outer surface of micrometer fibers is accessible to latex spheres, because of its being covered by an impermeable "coat" of aluminum oxohydroxide and globules it forms.

The mass of latex spheres was calculated for a density

Table 1. Adsorbate properties and sorption capacity under static and dynamic conditions

Adsorbate	Mass of molecule or particle, a.m.u.	Conditional particle diameter, nm	Number of particles, cm^{-2}		
			calculated in a monolayer	obtained in statics	obtained in dynamics
Eosin	724	0.66	2.3×10^{14}	3.9×10^{13}	6.6×10^{12}
Tannic acid		0.88	1.3×10^{14}	8.4×10^{13}	16.8×10^{12}
Latex	1700				1.7×10^{9}
microspheres	3.4×10^{7}	33	9.2×10^{10}		

of 1.01 g cm^{-3}. The conditional diameter of molecules was found in the approximation that their shape is spherical, density is 1 g cm^{-3}, and atoms in the molecule are spherical and arranged close to one another.

The number of particles in a monolayer was estimated by dividing the area of 10^{14} nm^2 (1 cm^2) by the area d^2 occupied by a single molecule of eosin (0.44 nm^2) or tannic acid (0.77 nm^2) or by a latex microsphere (1089 nm^2). Taking into account that latex spheres can be only adsorbed on the outer surface of globules and micrometer fibers, we should divide the empirically obtained capacity by the accessible surface area expressed in square centimeters. Taking that the average diameter of microfibers and globules is 2 μm and the density of the composite filter-sorption material is 1.325 g cm^{-3}, we obtain that the specific surface area of the material, accessible to microspheres, is 1.5 m^2 g^{-1}. Then, 1.5×10^9 latex microspheres is adsorbed on 1 cm^2 of the accessible surface area of the adsorbent. Accordingly, we calculated the amount of adsorbed molecules by relating their number to the specific surface area of the material (3.33 5 × 10^5 cm^2 g^{-1}).

Since it was assumed that adsorption of negatively charged particles from the liquid is due to the positive charge on the surface of the filter-sorption material, we made a number of calculations to verify this assumption.

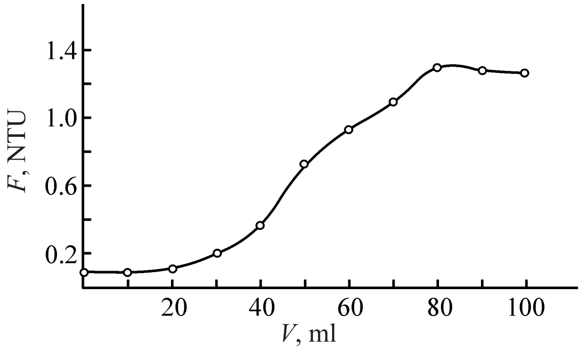

Fig. 5. Filtrate turbidity F vs. the passed volume V of a suspension of latex spheres.

The charge density on the surface of an adsorbent placed in water was calculated in terms of the Gouy–Chapman theory. The surface charge of materials of this kind fluctuates within the range from 86 to 500 mV [6]. With a knowledge of the surface charge, we can estimate the amount of charge per 1 cm^2 of the surface by the formula [16]:

$$\sigma = \sqrt{\frac{\varepsilon RTc_\infty}{2\pi}}\left(\exp^{\frac{Fz\varphi_0}{2RT}} - \exp^{-\frac{Fz\varphi_0}{2RT}}\right), \tag{4}$$

where ε is the dielectric constant of the liquid [replaced in the International System of Units with $\varepsilon\varepsilon_0 = 80 \times 10^{-9}/(36\pi)$]; R, gas constant; T, absolute temperature; c_∞, electrolyte concentration at an infinitely large distance from the solid phase at $\varphi_0 = 0$; φ_0, potential of the phase boundary; z, ion valence; and F, Faraday number.

We made the calculation by taking that $c_\infty = 10^{-5.6} \times 10^3$ mol m^{-3} (pH 5.6), $z = 1$, $\varphi_0 = 0.1$ V, $T = 298$ K.

The charge of a latex microsphere was calculated in terms of the same theory by the formula [16]

$$Q = \frac{r\varepsilon(1 + r\chi)\varphi_0}{e}, \tag{5}$$

where r is the particle radius; $1/\chi$, thickness of the "ionic atmosphere"; and e, elementary charge.

In doing so, we found the thickness of the ionic atmosphere, using the theory of strong electrolytes, by the equation [16]

$$\frac{1}{\chi} = \sqrt{\frac{\varepsilon RT}{8\pi F^2 \Sigma c_i z_i^2}}, \tag{6}$$

where c_i and z_i are the concentration and charge of ions of ith type in solution.

Table 2. Calculated adsorption parameters

Adsorbate	Conditional charge Q of a particle, elementary charge units	Conditions of the adsorption process			
		static		dynamic	
		fraction of occupied accessible surface	degree of charge neutralization	fraction of occupied accessible surface	degree of charge neutralization
Eosin	2	0.51	193	0.010	34
Tannic acid	1	0.65	850	0.043	170
Latex microspheres	7			0.014	0.10

In the calculation, the concentration of H^+ ions in water we taken to be $c_i = 10–5.6 \times 10^3$ mol m^{-3} (pH 5.6), and the charge of ions, $z_i = 1$ (H^+).

The degree of neutralization of the adsorbent charges by the adsorbate was calculated as the ratio between the charge of molecules (particles) adsorbed on 1 cm^2 and the charge density on the adsorbent surface (Table 2).

It can be seen from the data in Table 2 that adsorbed molecules of tannic acid and eosin bear a considerably larger charge than that necessary for neutralizing the surface charge, so that the adsorption mechanism is not electrostatic. By contrast, latex microspheres neutralize only 10% of the surface charge in adsorption in the dynamic mode. The sorption capacity for eosin and tannic acid under static adsorption conditions is 5–6 times higher that in the dynamic conditions. If we assume that this ratio is preserved for latex spheres and the degree of charge neutralization under static conditions is 0.5–0.6, then it is apparent that the electrostatic mechanism can well account for the results of sorption of latex spheres.

In the case of molecular anionic adsorbates, the most probable adsorption mechanism is that on active surface centers in mesopores of aluminum oxohydroxide. The adsorption capacities for tannic acid and eosin, measured in number of molecules per 1 cm^2 of the adsorbent surface, differ by approximately a factor of 2, which is equal to the charge ratio of the respective anions. This is evidence in favor of the ion-exchange mechanism. The calculated data in Table 2 are also consistent with the Van der Waals adsorption mechanism of molecules and latex spheres: in all cases, the experimentally determined capacity is always lower than the geometrical capacity of a monolayer.

The high rate of water purification to remove impurities is due to the accessibility of the adsorption surface in all cases. For latex spheres, this is electrostatic adhesion to the outer surface of microfibers and globules. In the case of tannic acid and eosin, the accessibility is due to the fact that, first, the width of pores substantially exceeds the linear dimensions of the molecules and, second, the length of these pores is less than 1 μm, a value considerably smaller than that in granulated materials, in which the grain size and, consequently, also the pore size are commonly on the order of millimeters.

CONCLUSIONS

(1) The morphology of a new filter-sorption material was determined: acetyl cellulose fibers (2 μm) bear a layer (0.2–0.7 μm) of nanofibers (5–8 × 100–200 nm) and globules (0.2–1.0 μm) composed of the same aluminum oxohydroxide nanofibers; these layers and globules have a dense structure with mesoporosity (4 nm). Pores between microfibers and globules are about 2 μm in size.

(2) The static and dynamic capacities for the adsorbates studied were determined (μmol g^{-1}): 47 and 9.4 for tannic acid, 21 and 3.7 for eosin, respectively; the dynamic capacity for latex spheres is 2.5×10^{13} g^{-1}.

(3) It was demonstrated by calculation that molecules of tannic acid and eosin are adsorbed on the entire internal surface area of the material (33.3 m^2 g^{-1}) by the ion-exchange mechanism. At the same time, the amounts of charge on the adsorbent surface and latex spheres were calculated and it was shown that these spheres can only be adsorbed on the outer surfaces of microfibers and microglobules (surface area 1.5 m^2 g^{-1}) by the electrostatic or Van der Waals mechanism.

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