Sorption of Gold Nanorods on Polyurethane Foam as a Way to Obtain a Nanocomposite Material with a Surface Plasmon Resonance for Chemical Analysis Purposes

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Abstract—A method for preparing a nanocomposite material containing gold nanorods on a polyurethane foam matrix, which is of interest in analytical chemistry, has been developed by the sorption modification of the matrix. It is found that the sorption of gold nanorods on polyurethane foam was achieved after 30 min of phase contact in the presence of 0.4 M NaCl as an electrolyte. The dependence of the sorption on time is described by the pseudo–first order kinetic equation with a rate constant of 0.17 min^{-1}. The sorption isotherm is fitted by the Langmuir equation. Calculated in the framework of this model, values of the sorption constant and the sorption capacity are equal to 77.6×10^3 L/mol of Au and 15 mg/g, respectively. The potential possibility of the resulting nanocomposite material application for determining reducing agents by diffuse reflectance spectrometry is demonstrated.

Gold nanoparticles (NPs) attract the attention of various researchers, since both NPs themselves and the materials based on them are widely used in various fields of science and technology [1–12]. Optical properties of NPs caused by surface plasmon resonance (SPR) and exhibited as an intense absorption band in the visible region of the spectrum are of particular interest. The possibility of a significant change in the optical characteristics of NPs as a result of the changes in the frequencies of surface plasmon oscillations makes it possible to use NPs as peculiar chromophoric reagents in chemical analysis [2, 3, 13, 14].

The changes in the cut and shape of nanoparticles and the presence of the contact of nanoparticles with materials with various permittivities results in a change in surface plasmon resonance frequencies. Therefore, currently nonspherical nanoobjects such as nanorods (NRs) of gold, which are characterized by the pronounced presence of several modes of surface plasmon oscillations and, accordingly, a series of bands in the absorption spectrum corresponding to the frequencies of generation of plasmon resonances of the nanoparticles, are actively studied. The existing correlation between permittivity of the environment, the composition of the surface layer, the geometrical dimensions of the NRs, and the SPR spectrum thereof provides

the possibility for developing fundamentally new ways to spectrophotometrically determine the concentration of various compounds that can directly or indirectly change these parameters [15].

One way to stabilize nanoparticles and give them new properties is immobilization thereof on various solid matrices, making it possible to create new nanocomposite materials, often favorably distinguished by their performance, optical, and analytical characteristics. Direct sorption modification of the solid matrix should be attributed to the number of simple and effective ways to immobilize NPs. Therefore, a detailed study of the sorption of NPs on solid materials of various natures, which, as one may hope, will make it possible to study the influence of the NP−environment mutual contact on the frequencies of plasmon oscillations, develop methods for obtaining nanocomposites based on them having the desired optical and chemical characteristics, make assumptions about the mechanisms of sorbent−NP interaction, and prove the variants of the practical use of the obtained materials, is of interest. Polyurethane foam (PUF), which is characterized by good sorption properties, increased resistance to thermo-oxidative destruction, chemical resistance, and cheapness and availability, is a promis-

ing material for obtaining nanocomposite materials [16−18].

In this study the sorption of gold NRs on polyurethane foam as a way to obtain a nanocomposite material with SPR is investigated and the potential ability to use the material in chemical analysis for determining the concentration of reducing agents (e.g., catecholamines) is shown.

EXPERIMENTAL

Polyurethane foam (PUF) based on polyethers was used as a sorbent. PUF tablets with a diameter of 16 mm and a weight of 20 ± 2 mg were beaten by metal punch from industrial polymer sheet. In order to remove impurities, the PUF tablets were placed in acetone and agitated for 10 min; the procedure was repeated twice, after which the tablets were dried under a stream of air.

Chloroauric acid of reagent grade; silver nitrate of analytical grade; cetyltrimethylammonium bromide (CTAB) of reagent grade; sodium borohydride of analytical grade; ascorbic acid, HCl, NaOH, NaCl, $NaNO_3$, HNO_3, $LiNO_3$, and KNO_3 of reagent grade; epinephrine of analytical grade (Sigma-Aldrich); and dobutamine (in the form of hydrochloride, analytical grade, Sigma-Aldrich) were used during the experiments. The reagents were used without further purification.

Diffuse reflection and diffuse reflectance spectra in the visible region of the spectrum were recorded on an Eye-One Pro mini spectrophotometer (X-Rite, Switzerland). The measurement of the optical characteristics of aqueous solutions, as well as the control over the distribution of gold nanoparticles in aqueous solution−PUF system were performed on an SF-103 spectrophotometer (Aquilon, Russia). An investigation of the microstructure of the samples of nanocomposite materials was carried out on JSM 7100 F scanning electron microscope with a working resolution of 2 nm (Jeol, Japan). The images were obtained in secondary electrons and recorded in a digital form on a computer. Studies of NRs in the solution were performed by TEM by analyzing the dried slurry using a Libra 200 transmission electron microscope with a cathode with thermal-field emission (Carl Zeiss, Germany) at an accelerating voltage of 200 kV; the information limit of the image registration in bright-field transmission electron microscopy mode is better than 0.1 nm. For the measurements, the samples in the form of slurry in hexane/heptane were applied to a supporting mesh made of copper with a film of Formvar and applied thereto a layer of Formvar®/Carbon Reinforced CopperGrids 3440C-MB carbon (SPI, United States). Deionized water was obtained using the MilliporeSimplicity purification system (Millipore, Germany). A mechanical shaker and a magnetic stirrer were also used.

Gold nanorods were synthesized by the procedure described in [19]. The procedure is based on the direct growth of NRs on seeds of gold NPs at the reduction of chloroauric acid with ascorbic acid in the presence of silver nitrate as a compound that regulates the sizes and ratio of length to the diameter of NRs. A solution of seeds was pre-prepared. To do this, 5 mL of 0.5 mM $HAuCl_4$ solution and 5 mL of 0.20 M CTAB solution were put in a round bottom flask with a volume of 250 mL at stirring, and 600 μL of cooled 0.010 M $NaBH_4$ solution were added dropwise. Within 2 min the solution of seeds became brown. For the synthesis of nanorods, 1.00 mL of 0.0040 M $AgNO_3$, 20 mL of 0.20 M CTAB solution, and 20 mL of 1.0 mM $HAuCl_4$ were put with stirring in the round bottom flask with a volume of 250 mL. A total of 0.25 mL of 0.10 M ascorbic acid was added dropwise to the solution; as a result, the bright yellow solution became colorless. Then, 48 μL of the solution of seeds were added. Within 30 min the solution became reddish brown. The solution temperature during the synthesis was maintained at 30°C. The gold NRs are characterized by two SPR bands in the absorption spectrum at 520 and 650−700 nm, corresponding to the transverse and longitudinal plasmon oscillations, respectively. Figure 1a shows micrograph of NRs and Fig. 1b absorption spectrum of the aqueous solution thereof.

In order to study the sorption of gold NRs on PUF, a colloidal solution of NRs with a certain concentration, an auxiliary reagent (see below), and water were put in the tube. The total volume of all components was 5 mL. The absorbance spectrum of the solution was recorded, after which the PUF tablet was placed in the solution and then pressed with a glass rod to remove air from the pores and shaken on a mechanical shaker for a certain time. Then the tablet was removed, dried between sheets of filter paper, and the diffuse reflection of nanorods sorbed on PUF (as well as the absorbance of the solution after sorption in the range of 400−800 nm) were measured. The adsorption quantity of NRs was found by the difference between the initial and final concentrations of NRs in the solution. In order to determine the concentration of NRs in the solution from the results of the spectrophotometric measurements, a calibration curve relating the absorbance value at 670 nm and concentration of gold NRs in aqueous solution was constructed. The concentration of gold NRs in the phase of PUF was judged by finding the value of Kubelka-Munk function F by the measured values of diffuse reflection coefficient using the formula

$$F(R) = \frac{(1 - R)^2}{2R} = \frac{2.3c\varepsilon}{S},$$

where R is diffuse reflection; ε is sorbate molar absorption coefficient, M^{-1} cm^{-1}; c is its concentration, M; and S is dissipation factor, cm^{-1}.

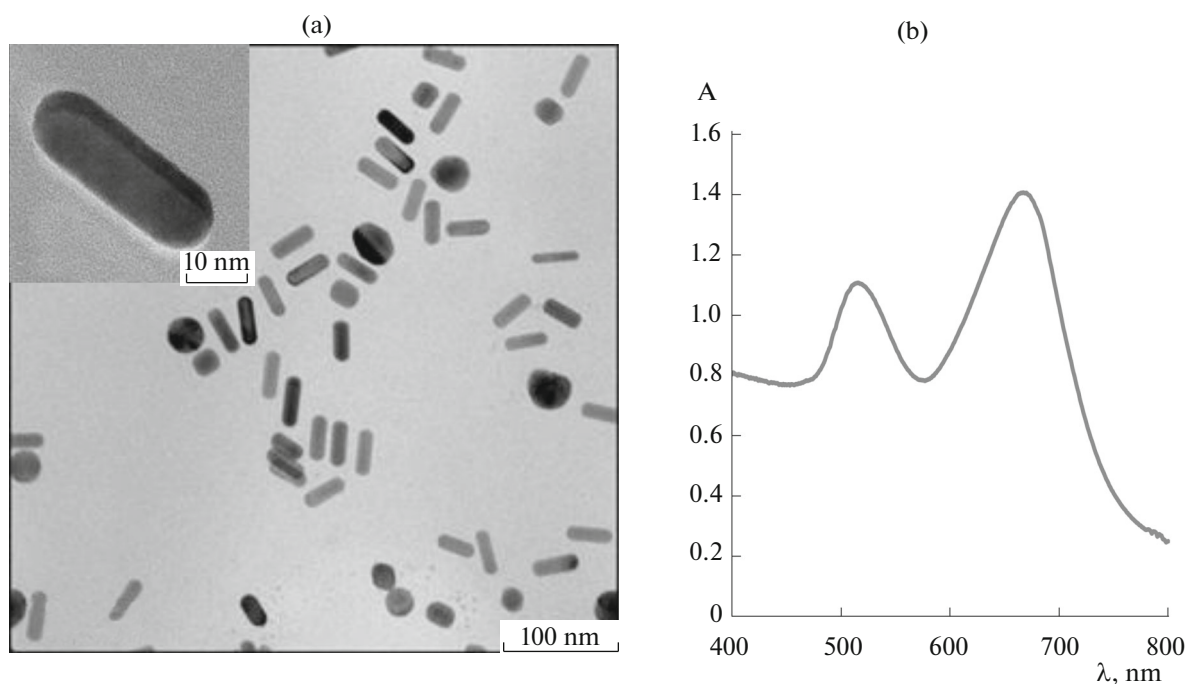**Fig. 1.** (a) Micrograph of gold NRs and (b) absorption spectrum of aqueous solution thereof (c_{NRs} = 100 μg/mL).

RESULTS AND DISCUSSION

Influence of various factors on the sorption of gold nanorods by polyurethane foam. In the preliminary experiments, it was found that gold NRs from aqueous solution are hardly sorbed, apparently, due to the high ζ potential of NRs preventing the overcoming of water–polymer interphase boundary by them. This difficulty may be overcome by the introduction of a strong electrolyte in the solution, which results in the decrease of the thickness of the electrical double layer and ζ potential.

Effect of electrolyte. It was shown that NRs are sorbed almost quantitatively from the solutions containing 0.2 M HCl, NaOH, or NaCl (Fig. 2). In the alkaline medium, the aggregation of NRs is observed and reliable determination of the position of the long-wave maximum becomes impossible.

Effect of cationic surfactant. Since the sorption of cationic surfactant CTAB present in an excess in the mixture after synthesis of NRs may give a positive charge to the polymer surface, which will make the sorption of NRs difficult, the cleaning of NRs from CTAB excess was performed by a twofold centrifugation of the colloidal solution of NRs at 8000 rpm for 30 min, removal of supernatant, and the resolution of NRs in deionized water. Then NRs purified from CTAB excess were sorbed on PUF under the same conditions as the untreated ones. It was found that, for the purified NRs, the improvement of the sorption is actually observed (the degree of the extraction of NRs increases from 87 to 95%). This proves the high affin-ity of NRs to the PUF surface and stresses great prospects of the polymer with respect to sorption removal of NRs. However, since NRs unpurified from CTAB excess are also sorbed on PUF in a degree sufficient from a practical point of view, in further experiments cleaning from CTAB excess was not carried out, considering it an additional step complicating the synthesis of nanocomposite material and leading to the losses of NRs.

Effect of the nature of the cation and the anion of the electrolyte. Figure 3 shows the effect of some of single charged cations and anions on the sorption of gold NRs. For a more precise differentiation of the ions by their effect, the investigation was carried out at reduced ionic strength of 0.1 M, which provided degrees of sorption of NRs no more than 40%. From the histograms, one can see that NRs are most efficiently sorbed on PUF in the presence of Li$^+$ and Cl$^-$; are satisfactorily sorbed in the presence of Na$^+$, K$^+$, and NO$_3^-$; and, in the presence of hydroxide ion, the aggregation of NRs takes place. The decrease in the degree of sorption of NRs in the ranges of Li$^+$ > Na$^+$ > K$^+$ and NO$_3^-$ > Cl$^-$ corresponds to the decrease in the coagulation ability of ions, which confirms the important role of the decrease in the value of the ζ potential of NRs for providing their sorption on PUF. Despite the best characteristics of LiCl in the role of the auxiliary electrolyte for the acquisition of nanocomposite material, in further experiments NRs were sorbed from the solutions containing NaCl as the cheapest reagent providing the satisfactory sorption
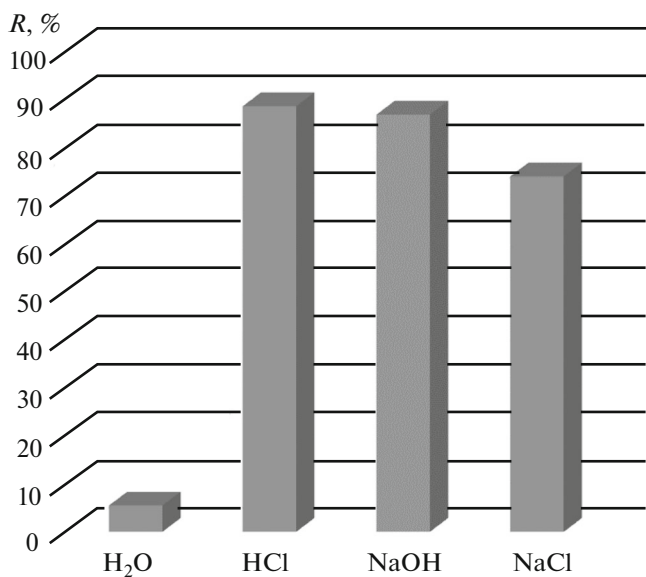
Fig. 2. Percentage of sorbed gold NRs from water and solutions containing 0.2 M HCl/NaOH/NaCl (c_{NRs} = 70 μg/mL, $V = 5$ mL, and $t = 40$ min).

of NRs (according to data of Sigma-Aldrich [https://www.sigmaaldrich.com] on April 12, 2016, the cost of 500 g of LiCl was 16 877.64 rubles, while 500 g of NaCl of the same qualifications were worth 2487.23 rubles).

Effect of electrolyte concentration. As one can see from the comparison of Figs. 2 and 3, the electrolyte concentration has a large influence on the degree of extraction of NRs. From diffuse reflectance spectra and the obtained dependence of the degree of sorption

on NaCl concentration (Fig. 4), it follows that, with its growth, a monotonic increase in the sorption of NRs is observed. Practically maximal sorption is achieved at $c_{NaCl} = 0.4$ M; therefore, in subsequent experiments this NaCl concentration was maintained in the solutions. The preservation of the form of the diffuse reflectance spectra of gold NRs in the PUF phase with the increase in electrolyte concentration indicates the constancy of the state of NRs. Thus, the presence of high electrolyte concentrations does not result in aggregation or other processes, which can greatly affect the optical characteristics of NRs on PUF.

Study of sorption kinetics of gold nanorods on the polyurethane foam. In order to study kinetic characteristics of the sorption of NRs on PUF, absorption spectra of the solutions containing 28 and 14 mg/mL of gold NRs were recorded after the contact with PUF at various times. Integral kinetic curves were constructed by the resulting data (Fig. 5a).

Experimental data were approximated within the frameworks of several kinetic adsorption models, models of pseudo−first and pseudo−second orders, as well as a Weber-Morris diffusion model. The values of the squares of correlation coefficients (R^2) are 0.9959, 0.9948, and 0.9799 for the solutions containing 28 μg/mL of gold NRs and 0.9973, 0.9964, and 0.9731 for the solutions containing 14 μg/mL of NRs, which indicates the best concordance of the observed behavior of the system to the pseudo−first order kinetic model (Fig. 5b). Based on the values of the parameters of the model, the sorption rate constant was calculated, which was equal to 0.17 min^{-1}.
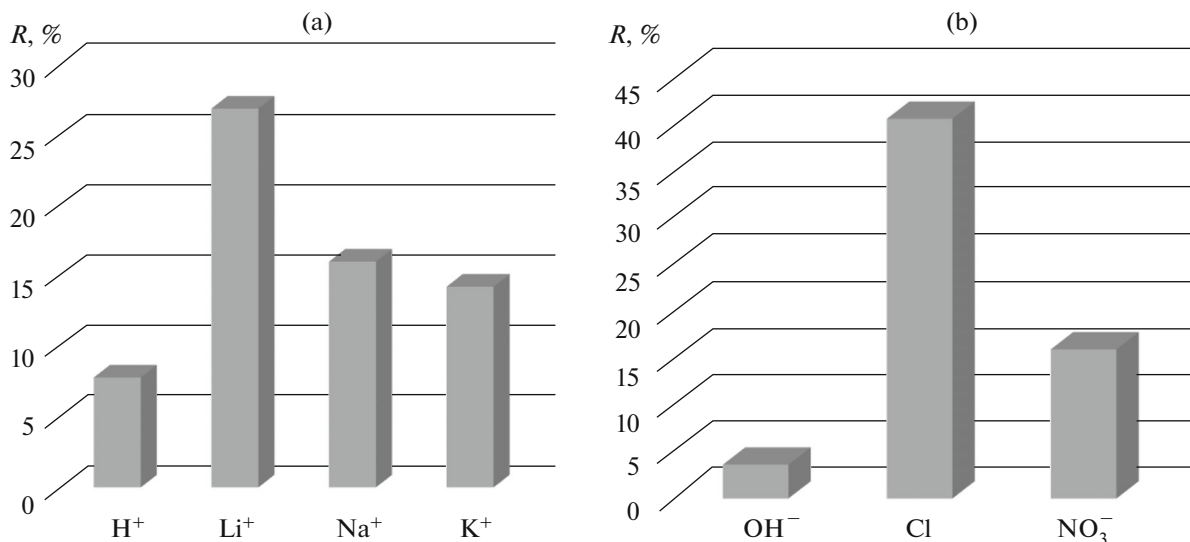

Fig. 3. The influence of the nature of (a) cation and (b) anion of the electrolyte on the sorption of gold NRs ($c_{NRs} = 25$ μg/mL, $c_{ions} = 0.1$ M, $V = 5$ mL, $t = 40$ min, and counterion: (a) NO_3^-, (b) Na^+).
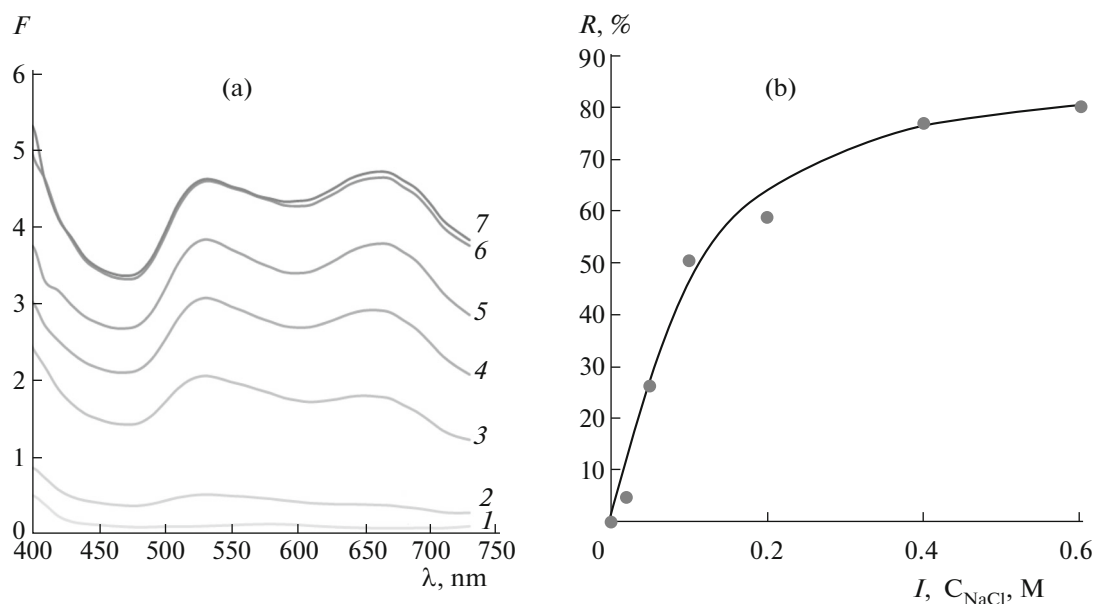
Fig. 4. (a) Diffuse reflectance spectra of PUF modified with gold NRs from the solutions containing 25 μg/mL of NRs and (*1*) 0, (*2*) 0.02, (*3*) 0.05, (*4*) 0.1, (*5*) 0.2, (*6*) 0.4, and (*7*) 0.6 M NaCl and (b) the dependence of the degree of sorption of NRs on NaCl concentration ($V = 5$ mL and $t = 30$ min).
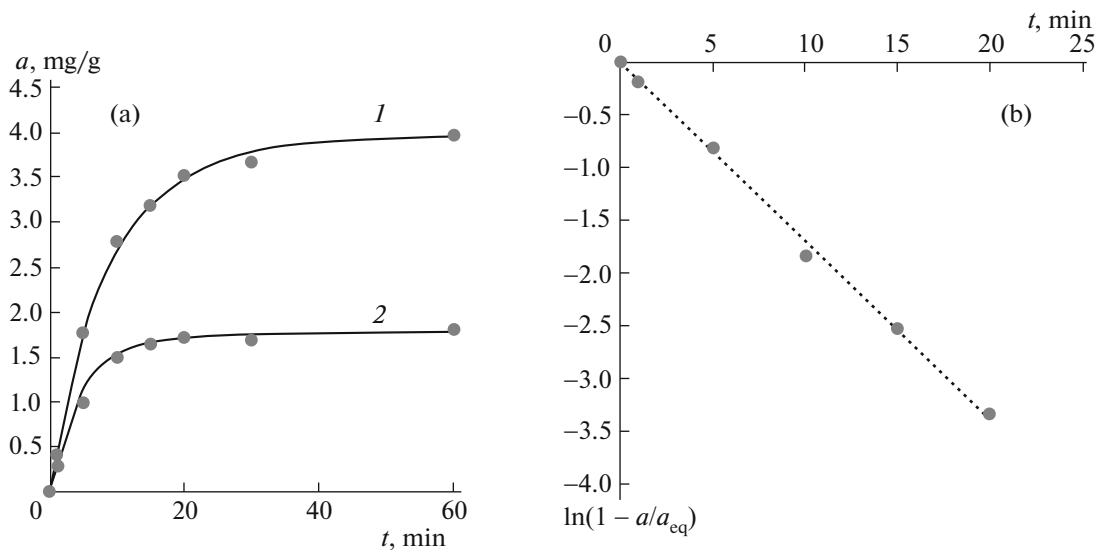

Fig. 5. (a) Integral kinetic sorption curve of gold NRs on PUF and (b) its representation in the pseudo-first order model ((*1*) $c_{NRs} = 28$ μg/mL and (*2*) $c_{NRs} = 14$ μg/mL, $c_{NaCl} = 0.4$ M, and $V = 5$ mL).

Analysis of sorption isotherm of gold nanorods on polyurethane foam. In order to construct the isotherm, gold NRs were sorbed from the solutions with various concentrations thereof. Phase contact time was 30 min, after which the equilibrium was considered attained. The concentration of NRs in the equilibrium solution was determined spectrophotometrically. Using the data, a sorption isotherm was constructed (Fig. 6a) which may be attributed to the Langmuir class, i.e., described by the equation

$$a = a_m \frac{KC}{1 + KC},$$

where C is the equilibrium concentration of NRs in the solution, μg/mL; a is the sorption value, mg/g; a_m is limit sorption value, mg/g; and K is sorption constant, L/mg.
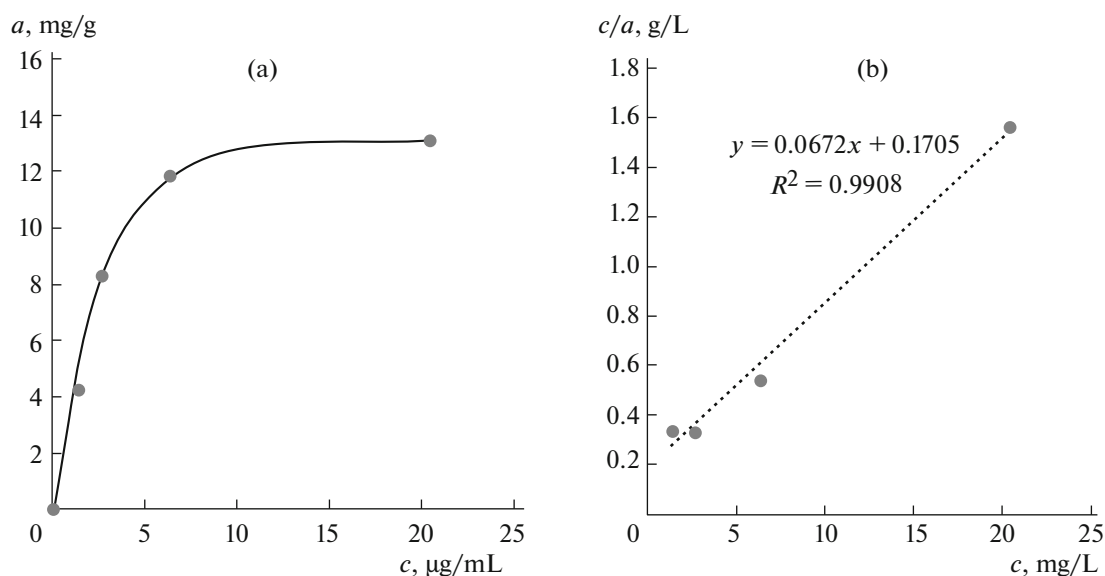
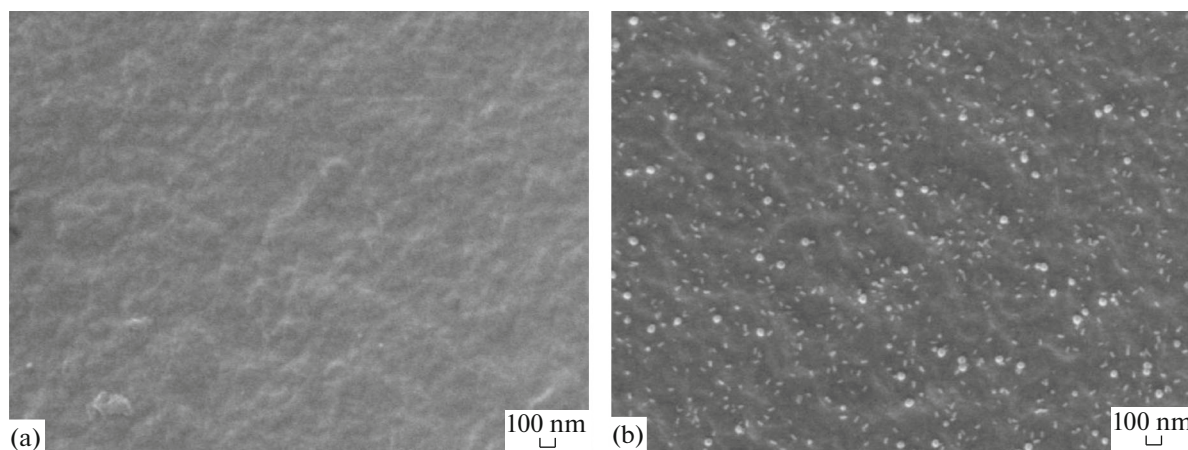**Fig. 6.** (a) Sorption isotherm of NRs on PUF and (b) its representation in the coordinates of $c/a-c$ ($c_{NaCl} = 0.4$ M, $V = 5$ mL, and $t = 30$ min).

Fig. 7. Micrographs of (a) the initial PUF and (b) the PUF modified with gold NRs ($c_{NRs} = 30$ μg/mL, $c_{NaCl} = 0.4$ M, $V = 5$ mL, and $t = 30$ min).

The applicability of the equation was verified by rectification in coordinates C/a of C (Fig. 6b):

$$\frac{C}{a} = \frac{1}{a_m K} + \frac{C}{a_m}.$$

From the data, the values of the limited sorption of NRs on PUF $a_m = 15$ mg/g, sorption constant $K = 0.394$ L/mg $= 77.6 \times 10^3$ L/mol of Au, and the Gibbs free energy $\Delta G^\circ_{298} = -RT\ln K = -28$ kJ/mol of Au were calculated.

Some characteristics of nanocomposite material and the prospects of its analytical use. The presence of gold NRs on a PUF surface was confirmed by electron microscopic studies. Figure 7 shows micrographs of the initial PUF and PUF modified with gold NRs. In the micrograph (Fig. 7b), one can see that gold NRs are distributed on the PUF surface. Despite the presence of some small aggregates, the vast majority of NRs are in a free state, which determines the possibility of their relatively easy interaction with the compounds sorbed on PUF at concentrations thereof in the solution that are not high. Through the example of catecholamines (epinephrine and dobutamine), the potential possibility of the use of the obtained material for determining the concentration of the reducing agents in the presence of silver nitrate was shown. It was found that, after the treatment of PUF modified with gold NRs with silver nitrate, a bathochromic shift in the maximum of SPR of NRs in the diffuse reflec-
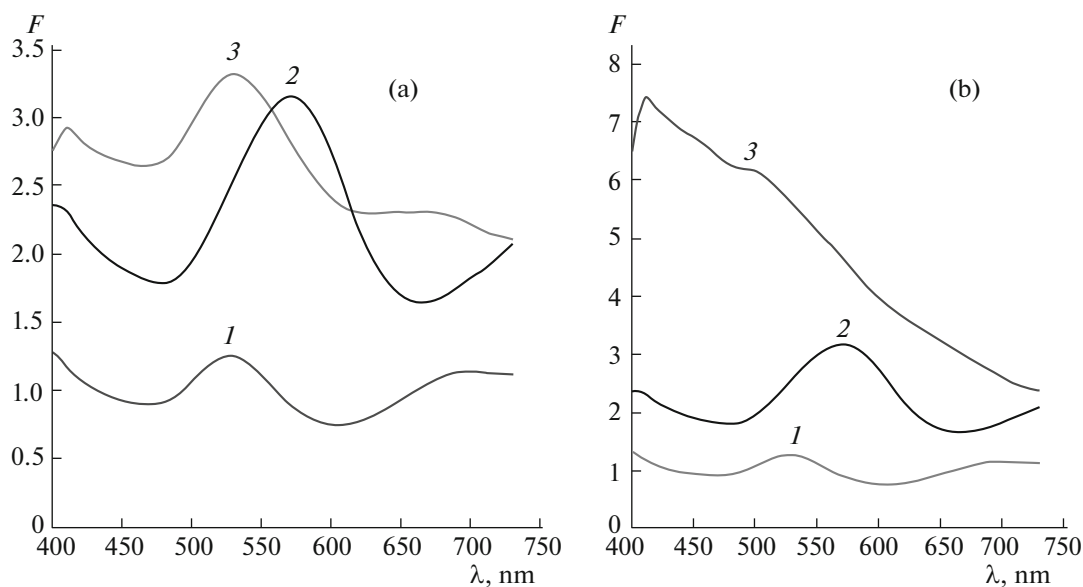
Fig. 8. Diffuse reflectance spectra of nanocomposite material (*1*) before and (*2*) after the interaction with silver nitrate and (*3*) further interaction with catecholamine ((a) epinephrine, (b) dobutamine; (*1*) c_{NRs} = 30 μg/mL, c_{NaCl} = 0.4 M, V = 5 mL, and t = 30 min; (*2*) 5 mL of 0.001 M $AgNO_3$, treatment for 20 min; and (*3*) interaction in a mixture of 2 mL of glycine buffer (pH 9.5) and 12.5 μM of catecholamine, V = 5 mL, and t = 10 min).

tance spectra of the samples is observed. The shift decreases with the further interaction of the material with catecholamines, which, apparently, is due to the reduction of silver ions under the action of these compounds (Fig. 8). Similar observations were noted for NRs in solution [15, 20]. The strongest changes, accompanied by the appearance of the intensive absorption band at 410 nm, is observed in the case of dobutamine, which is probably due to the formation of silver nanoparticles on the PUF surface in the presence of this compound. In our opinion, these optical effects may be the basis for an approach to the use of PUF modified with NRs in the role of solid phase nanoreagent for determining the concentration of reducing agents.

CONCLUSIONS

The sorption of gold nanorods from an aqueous solution on the polyurethane foam was studied. The influence of the nature and concentration of the electrolyte on the degree of sorption of NRs was revealed; it was found that the degree of sorption is strongly dependent on the ionic strength. The degree of sorption is influenced by the nature of the electrolyte; the maximal effect of the studied ions was observed in the presence of Li^+ cation and Cl^- anion. Time dependence of the sorption is described by pseudo−first order kinetic equation with a rate constant of 0.17 min^{-1}. The sorption isotherm is fitted by the Langmuir equation. Values of the sorption constant and the sorption capacity calculated in the framework

of this model are equal to 77.6 × 10^3 L/mol of Au and 15 mg/g, respectively. A nanocomposite material based on polyurethane foam and gold nanorods was obtained from aqueous solutions by the sorption modification of polyurethane foam. The potential possibility of the use thereof for determining the reducing agents by diffuse reflectance spectrometry was demonstrated.

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