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**SORPTION  
AND ION EXCHANGE PROCESSES**

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## **Preparation and Properties of Silica Gel with Immobilized Formazan Group**

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**Abstract**—A new sorption material, silica gel with covalently immobilized formazan group, was suggested and characterized. The material was prepared by coupling the immobilized aryldiazonium salt with benzaldehyde phenylhydrazone. The equilibrium and kinetic characteristics of the sorption of Cu(II), Co(II), Ni(II), and Cd(II) from solutions onto the modified silica gel were determined. The material proved to efficiently concentrate Cu(II) from multicomponent solutions. The coordination surrounding of Cu(II) in the complex on the sorbent surface was determined by ESR.

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Interest in chemistry of formazans is due to a set of their valuable properties, which are seldom exhibited in combination by organic compounds of other classes. For example, formazans can exhibit photo- and thermochromic properties, act as effective ligands, serve as redox indicators owing to reversible redox transformation into tetrazolium salts, and exhibit various kinds of biological activity. Therefore, formazans can be used as dyes for various materials, as indicators, as components of optical recording media and photographic formulations, and as catalysts of redox reactions. Data on the synthesis of properties of formazans are summarized and systematized in reviews [1–3] and monographs [4, 5].

Formazans have also important applications in fine organic synthesis as starting compounds for preparing tetrazolium salts [6, 7], verdazyls [8], and various heterocycles [9].

In analytical chemistry, formazans are used for spectrophotometric determination of many elements [10] owing to their capability to form stable colored

complexes [11, 12] exhibiting high molar extinction coefficients.

One of the research lines in chemistry of formazans is preparation of materials with preset properties by immobilization of formazans onto various matrices such as celluloses, organic resins, or silica gels. Such materials can find use in chromatographic and sorption-spectroscopic methods of analysis and in heterogeneous catalysis. A series of sorbents based on ion exchangers [13, 14] and silica gels [15–17], in which formazan molecules are retained on the matrix surface owing to ionic bonds formed, as a rule, between a base site on the matrix surface and a sulfo group of formazan, have been reported. A procedure for covalent immobilization of the most widely used formazan, dithizone, by alkylation with 3-chloropropylated silica gel [18, 19] or by treatment with chlorinated silica gel [20] is also known.

The reported procedures for preparing formazan-containing sorbents involve grafting of a formazan

synthesized in advance. On the other hand, synthesis of formazans on a solid support by the classical Ried's method could expand the range of the prepared materials owing to the variability of substituents in the diazonium salt and hydrazone.

In this study, we developed a procedure for constructing the formazan moiety on the silica gel surface and studied the complexing and sorption properties of the material obtained.

## EXPERIMENTAL

The initial solutions of metal salts were prepared by dissolving accurately weighed portions of  $\text{CuCl}_2$ ,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$  in double-distilled water. Working solutions were prepared by dilution of the initial solutions with double-distilled water immediately before the experiment. 4-(2-Pyridylazo)resorcinol (PAR) (Aldrich) was used as 0.1% solution in double-distilled water. For preparing the sorbent, we used Kieselgel 60 silica gel, 0.04–0.063 mm (Macherey-Nagel), 3-nitrobenzoyl chloride,  $\text{Na}_2\text{S}_2\text{O}_4$  (Aldrich), and benzaldehyde phenylhydrazone.

The pH values of solutions were monitored with an Ekspert-001 device equipped with an ESK-10608 calibrated combined glass electrode. The content of metal ions present separately in the aqueous phase was monitored spectrophotometrically with PAR on an SS2107UV spectrophotometer (Leki). Multielement analysis was performed with an iCAP 6000 inductively coupled plasma atomic emission spectrometer (Thermo Scientific). The solutions were stirred with a KS4000i control shaker–incubator (IKA). The sorption characteristics of the modified silica gel were studied in batch experiments with continuous stirring [21].

Solid-state  $^{13}\text{C}$  NMR spectra of the modified silica gel were recorded at the Resource Center for Magnetic Resonance Methods of Investigation of the St. Petersburg State University with a Bruker Avance III 400 WB spectrometer (operating frequency for  $^{13}\text{C}$  100.64 MHz) at room temperature using CP/MAS Bruker probe with a rotor diameter of 4 mm. The spectra were recorded at a rotor rotation frequency of 10 kHz using the CP TOSS sequence (polarization transfer with suppression of spinning sidebands). Adamantane was used as external reference. The signals are given relative to TMS.

The C, H, N analysis was performed with a Vario Micro Cube analyzer (Elementar). Thermal analysis

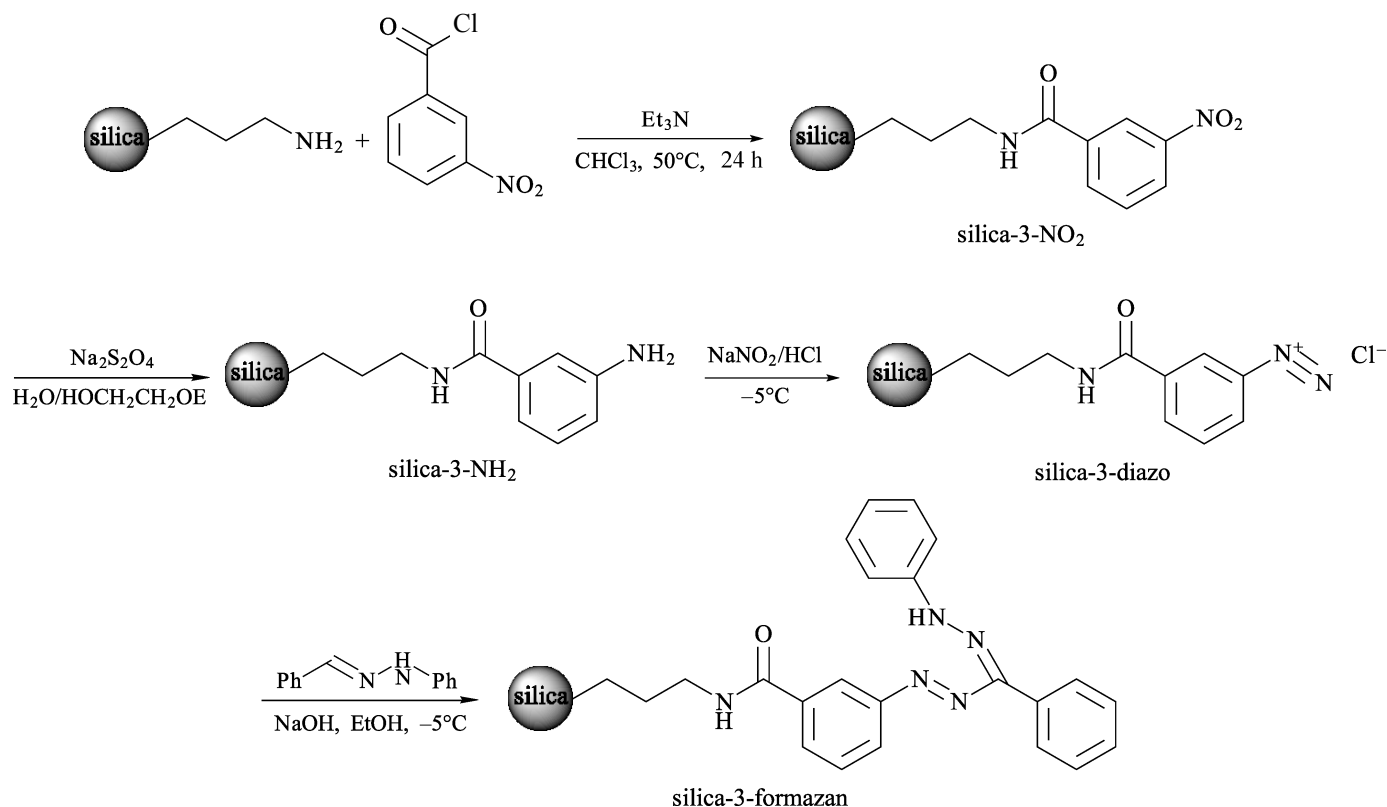
was performed with a Netzsch STA 409 Luxx device for synchronous TG/DTA/DSC analysis in the course of heating at a rate of  $10 \text{ deg min}^{-1}$ . The IR spectra were recorded with an IR Prestige-21 Fourier spectrometer (Shimadzu) using a diffuse reflectance attachment. The ESR spectra were recorded at 295 K with a JES Fa 300 spectrometer (JEOL) in the X range. Measurement conditions: UHF power 1 mW, high-frequency modulation amplitude 0.1 mT.

**Preparation of 1-(3-N-propylcarboxamidophenyl)-3,5-diphenylformazan–silica gel.** Step 1. A 500-mL round-bottomed flask equipped with a magnetic stirrer and a reflux condenser was charged with 50 g of 3-aminopropyl silica gel (content of  $\text{NH}_2$  groups  $1.4 \text{ mmol g}^{-1}$ ), a solution of 13 g (0.07 mol) of 3-nitrobenzoyl chloride in 200 mL of chloroform and 11 mL (0.077 mol) of triethylamine were added, and the components were stirred for 24 h at  $50^\circ\text{C}$ . After that, the modified silica gel was filtered off on a glass frit, washed in succession with chloroform, ethanol, water, and again ethanol, and dried in an oven at  $80^\circ\text{C}$ .

Step 2. A 500-mL round-bottomed flask equipped with a magnetic stirrer and a reflux condenser was charged with silica gel prepared in step 1, and 150 mL of ethyl Cellosolve and a solution of 47 g of  $\text{Na}_2\text{S}_2\text{O}_4$  in 150 mL of water were added. The mixture was refluxed for 3 h. After that, the modified silica gel was washed by decantation, filtered off on a glass frit, and washed with water.

Step 3. A three-necked flask equipped with a power-driven stirrer, a dropping funnel, and a thermometer was charged with silica gel prepared in step 2, 100 mL of distilled water, and 18 mL of concentrated HCl. The flask was cooled to  $-5^\circ\text{C}$ , a solution of 12 g of  $\text{NaNO}_2$  in 25 mL of water was added, and the suspension was stirred for 20 min at the same temperature. The resulting suspension was added in portions to a solution of 11.2 g of benzaldehyde phenylhydrazone and 8.4 g of NaOH in 700 mL of ethanol cooled to  $-5^\circ\text{C}$ , and the mixture was stirred for 1 h at  $-5^\circ\text{C}$  and for 20 min at room temperature. The modified silica gel was filtered off and washed in a Soxhlet extractor with ethanol until the wash liquid became colorless. The resulting modified silica gel was dried in an oven at  $75^\circ\text{C}$  to constant weight.

**Preparation of the copper complex on the surface.** A solution of 0.001 g of  $\text{CuCl}_2$  in 0.5 mL of distilled water was added to 20 mL of a borate buffer solution with pH 8, 0.05 g of the sorbent was added, and the mixture was

**Scheme 1.** The synthesis of silica-3-formazan.

allowed to stand for 48 h to reach the equilibrium. After that, the sorbent was filtered off, washed with distilled water, and dried in a desiccator over  $\text{P}_2\text{O}_5$  to constant weight.

## RESULTS AND DISCUSSION

The key intermediate in the synthesis of formazan on the surface, diazonium salt covalently immobilized on silica gel (silica-3-diazo), was prepared by the known procedure [21–23] involving acylation of 3-aminopropyl silica gel with 3-nitrobenzoyl chloride, reduction with sodium dithionite in aqueous ethyl Cellosolve, and diazotization. The subsequent coupling with benzaldehyde phenylhydrazone in ethanol in the presence of alkali yields silica gel with cherry-red coloration (Scheme 1).

The resulting material, 1-(3-*N*-propylcarboxamido-phenyl)-3,5-diphenylformazan–silica gel (silica-3-formazan), was characterized by elemental analysis, thermal analysis, IR spectroscopy, and solid-state  $^{13}\text{C}$  NMR.

The experimental ratios  $\text{C}/\text{N}_{\text{exp}} = 4.7$ , determined for the modified silica gel by elemental analysis, exceed the calculated ratio  $\text{C}/\text{N}_{\text{theor}} = 3.7$ , whereas for the N/H ratio the pattern is opposite:  $\text{N}/\text{H}_{\text{exp}} = 10.4$ ,  $\text{N}/\text{H}_{\text{theor}} = 7.2$ . As the modification of silica gel occurs in several steps, the C/N and N/H ratios obtained cannot be considered as an exhaustive source of information on the degree of functionalization, because it is impossible to take into account the degree of conversion and contribution of each particular step.

In the thermogram recorded in air (Fig. 1), the first portion of the dependence of the sample weight on temperature in the range  $25\text{--}170^\circ\text{C}$ , corresponding to the weight loss of approximately 3%, is associated with the evaporation of water physically adsorbed on the silica gel surface. The further 21.5% weight loss in the interval  $170\text{--}600^\circ\text{C}$  corresponds to the degradation of the functional organic layer, which is confirmed by the presence of exothermic peaks in the DSC curve at  $T > 380^\circ\text{C}$ . The total weight loss at  $1000^\circ\text{C}$  is about 25.5%, which is consistent with the results of elemental analysis.

The  $^{13}\text{C}$  NMR spectrum of the modified silica gel, silica-3-formazan, is shown in Fig. 2. The signals of the methylene groups of the alkyl bridge (9.7, 22.7, 43.1 ppm), phenyl groups (110–140 ppm), *meso*-C atom of the formazan moiety (147.6 ppm), and amide group (168.0 ppm) are well resolved and consistent with the assumed structure.

In the IR spectrum of silica-3-formazan, we can mention the stretching vibration bands of the  $\text{C}_{sp^3}\text{-H}$  (2891–2974  $\text{cm}^{-1}$ ),  $\text{C}_{sp^2}\text{-H}$  (3068  $\text{cm}^{-1}$ ),  $\text{C=O}$  (1649  $\text{cm}^{-1}$ ), and  $\text{C=N}$  (1602  $\text{cm}^{-1}$ ) bonds.

We evaluated the ability of the material to form complexes with Cu(II), Ni(II), Co(II), and Cd(II). The choice of these elements is governed by data on the coordination activity of 1,3,5-triphenylformazan in solution, which was studied in ethanol [24]. It is known that the complex formation by formazans both in solution and on the solid phase surface is influenced by the kind of the solvent and by its ionic composition and acidity. Variation of these parameters is the most facile tool for controlling the selectivity.

The influence of the solution acidity on the sorption ability of the modified silica gel obtained is characterized by the pH dependence of the distribution coefficients of Cu(II), Co(II), Ni(II), and Cd(II), present separately (Fig. 3). The maximal sorption is observed at pH 8 for Co(II), Ni(II), and Cd(II) and at pH 6–8 for Cu(II). It is known that the extrapolation of the sorption properties of systems containing a single sorbate and a complexing sorbent to more complex multicomponent systems is not always correct, because the restriction of the conformational mobility of the immobilized functional group can give rise to selectivity in the sorbent–sorbate systems. Therefore, we determined the distribution coefficients for single-component solutions and for solutions containing all the four elements at pH 8 and initial concentration of  $1.3 \times 10^{-5}$  M.

Under the conditions of competing sorption from solutions, the distribution coefficients of Ni(II), Cd(II), and Co(II) decrease, whereas that of Cu(II) remains virtually unchanged. Under the optimum conditions, metal ions can be ranked in the following order with respect to the equilibrium retention on the surface of the material (at their initial concentrations) relative to their total amount:  $\text{Cd(II)} < \text{Ni(II)} < \text{Co(II)} < \text{Cu(II)}$ .

In multicomponent solutions containing equimolar amounts of Ni(II), Cd(II), Co(II), and Cu(II), and also macrocomponents characteristic of river and seawaters,

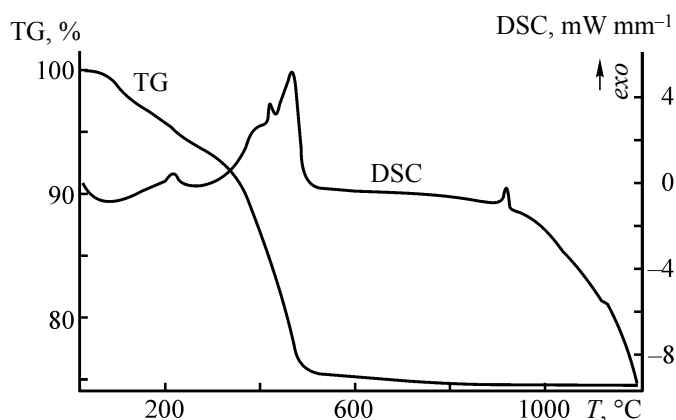


Fig. 1. Thermogram of the silica gel sample with immobilized formazan group. ( $T$ ) Temperature.

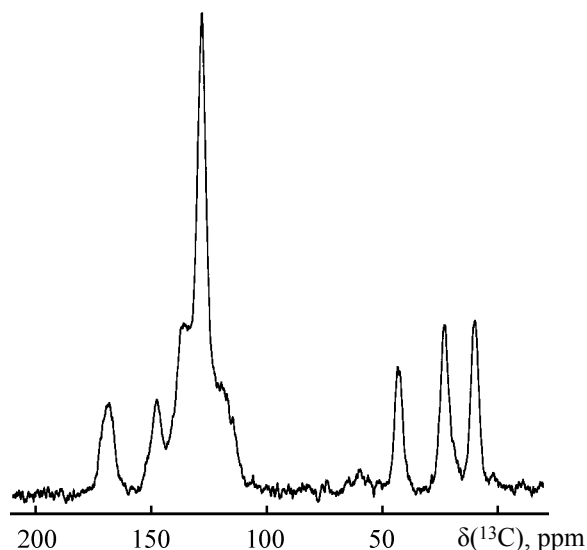
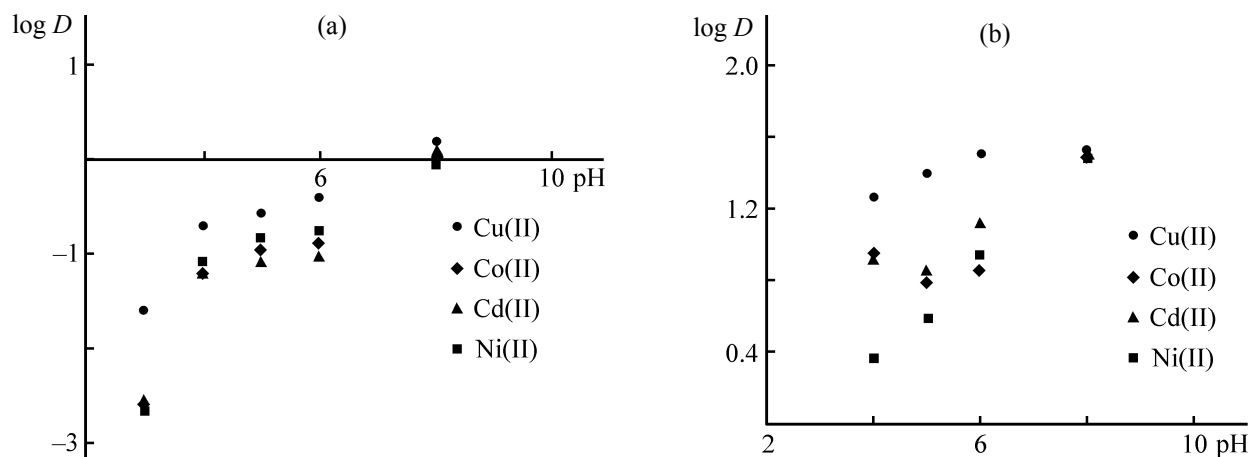


Fig. 2.  $^{13}\text{C}$  NMR spectrum of silica gel with immobilized formazan group. ( $\delta$ ) Chemical shift.

the functionalized silica gel starts to exhibit appreciable selectivity in the uptake of Cu(II) at pH 8 adjusted with the borate buffer solution (see table).

Such increase in the selectivity of the Cu(II) uptake by the functionalized silica gel at higher initial concentrations of the sorbates and the total solution mineralization increased to 35  $\text{g L}^{-1}$  suggests the formation of stable Cu(II) complexes on the surface [25].

It seemed interesting to study in more detail the specificity of the interaction of the material with Cu(II). To determine the sorbent capacity for Cu(II), we obtained the integral dependences of the sorption

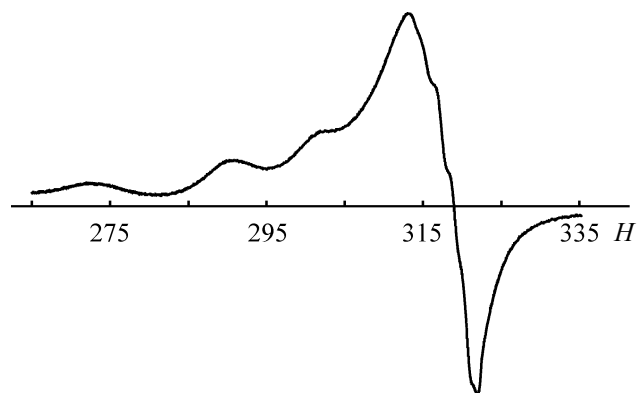


**Fig. 3.** Distribution coefficient  $D$  of Co(II), Ni(II), Cu(II), and Cd(II) in the sorbent phase as a function of pH of the solution. (a) Initial silica gel and (b) silica-3-formazan.

capacity on the Cu(II) equilibrium concentration at pH 8. The Cu(II) sorption isotherm under the chosen conditions at the Cu(II) concentration in the range from 0.078 to 0.075 mM has only the Henry portion and is linearized in the coordinates  $A$  ( $\text{mmol g}^{-1}$ )– $c_e$  (mM) with a slope of  $146 \text{ L g}^{-1}$ . Experiments showed that, under the conditions of the competing sorption, the contribution of the sorption capacity of the unmodified silica gel surface for all the elements is 10–15% of the maximal capacity of silica-3-formazan.

The maximal sorption capacity, which was found to be equal to  $0.08 \text{ mmol g}^{-1}$ , was determined at pH 6 adjusted with acetate buffer solution. In more alkaline solutions, poorly soluble  $\text{Cu}(\text{OH})_2$  is formed.

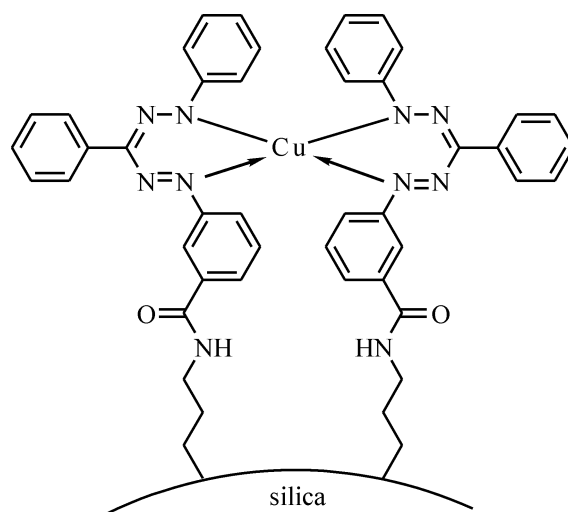
There are data that the ability of many materials to take up metal ions at  $\text{pH} > 5$  is determined to a greater



**Fig. 4.** ESR spectrum of the Cu(II) complex with modified silica gel. ( $H$ ) Magnetic induction.

extent by the formation of insoluble hydroxo complexes. To gain information on the coordination surrounding of Cu(II) in the complex formed on the surface of modified silica gel, we recorded the ESR spectrum (Fig. 4) of the material after the copper sorption from the solution under the optimum conditions found. The spin Hamiltonian parameters ( $g_{\perp} = 2.0487$ ;  $g_{\parallel} = 2.215$ ;  $A_{\parallel} = 11.9 \text{ mT}$ ;  $A_{\perp} = 1.86 \text{ mT}$ ) suggest the formation of the  $\text{CuN}_4$  coordination core, possible at the Cu : formazan ratio of 1 : 2. The suggested structure of the complex formed on the surface is shown in Fig. 5.

The participation of two functional groups simultaneously in the formation of a complex on the surface



**Fig. 5.** Suggested structure of the Cu(II) complex formed on the surface of modified silica gel.

Selectivity coefficients of silica gel with covalently immobilized formazan groups in the system with metal ions simultaneously present in the solution; pH 8,  $m(\text{sorbent}) = 0.05 \text{ g}$

Total mineralization, $\text{g L}^{-1}$	$c_0$ , $\mu\text{g mL}^{-1}$	$\beta_{\text{Cu/Co}}$	$\beta_{\text{Cu/Ni}}$	$\beta_{\text{Cu/Cd}}$	$\beta_{\text{Co/Ni}}$	$\beta_{\text{Co/Cd}}$	$\beta_{\text{Ni/Cd}}$
0.084 <sup>a</sup>	0.25	210	169	57	0.8	0.3	0.3
	0.5	47	36	24	0.8	0.5	0.7
35 <sup>b</sup>	0.25	479	247	1536	0.5	3.2	6.2
	0.5	1440	609	5994	0.4	4.2	9.8

<sup>a</sup>  $c_{\text{Na}^+} = 5.8 \text{ mg L}^{-1}$ ,  $c_{\text{K}^+} = 3.4 \text{ mg L}^{-1}$ ,  $c_{\text{Mg}^{2+}} = 20.0 \text{ mg L}^{-1}$ ,  $c_{\text{Ca}^{2+}} = 2.1 \text{ mg L}^{-1}$ ,  $c_{\text{Cl}^-} = 5.7 \text{ mg L}^{-1}$ ,  $c_{\text{SO}_4^{2-}} = 12.0 \text{ mg L}^{-1}$ ,  $c_{\text{HCO}_3^-} = 35.0 \text{ mg L}^{-1}$ .

<sup>b</sup>  $c_{\text{Na}^+} = 10.6 \text{ g L}^{-1}$ ,  $c_{\text{Mg}^{2+}} = 2.5 \text{ g L}^{-1}$ ,  $c_{\text{Ca}^{2+}} = 0.4 \text{ g L}^{-1}$ ,  $c_{\text{K}^+} = 0.4 \text{ g L}^{-1}$ ,  $c_{\text{Cl}^-} = 18 \text{ g L}^{-1}$ ,  $c_{\text{SO}_4^{2-}} = 2.7 \text{ g L}^{-1}$ ,  $c_{\text{HCO}_3^-} = 0.15 \text{ g L}^{-1}$ .

is indirectly confirmed by the fact that the copper sorption kinetics can be described by a pseudo-second-order equation suggesting that the sorption rate is controlled by the chemical reaction between the functional groups and the sorbate in a 2 : 1 ratio.

Complexing sorption materials are complex addends whose chelating ability largely depends on the preparation procedure, structural and adsorption characteristics, and uniformity of the grafted functional groups. These factors largely complicate the interaction stoichiometry in the sorbent–sorbate system and hinder finding the time dependence of the sorption ability of the material. The analysis of kinetic relationships can be simplified by decreasing the reaction order when performing the kinetic experiments with one of the components (functional groups in our case) taken in excess. Such ratio is kept in the course of further preconcentration of the analytes.

The choice of the initial concentrations of the analytes for performing kinetic experiments is an important step of the study, because the parameters calculated from the equations are conventional and depend on the initial sorbate concentration [25]. The integral dependences of the sorption capacity on time for the single-component system with Cu(II) and for the four-component system containing Cu(II), Ni(II), Co(II), and Cd(II) (initial concentrations 0.031 and 0.018, 0.11 and 0.062 mM; these values ensure the required excess of functional groups) were processed in linear coordinates of the pseudo-first and pseudo-second order equations [26] suggesting that the sorption process is controlled by the chemical reaction. Calculation of the inadequacy variance and comparison of its ratio to the reproducibility

variance with the tabulated value allowed determination of the adequacy of the pseudo-second-order equation for describing the kinetics of the sorption of Cu(II), Ni(II), Co(II), and Cd(II) onto modified surfaces at the chosen concentration levels. The maximal sorption capacities of the materials for metal ions  $A$  ( $\text{mmol g}^{-1}$ ), calculated from the pseudo-second-order equations, coincide with the experimental values ( $A_{\text{theor}} = 0.016$ ,  $A_{\text{exp}} = 0.014 \text{ mmol g}^{-1}$ ), which also confirms the adequacy of the chosen kinetic model. When describing the kinetics using the pseudo-second-order equation, it is possible to calculate not only the initial sorption rate, the sorption rate constants, and the half-sorption time, but also the maximal sorption capacity for the chosen initial sorbate concentration. The ratios of the sorption capacity for the given metal ion in the single- and four-component systems for Cu(II), Ni(II), Co(II), and Cd(II) are equal to 1, 0.27, 0.71, and 0.71, respectively, i.e., in all the cases except Cu(II) the sorption capacity decreases under the conditions of competing sorption.

The formation of stable complexes on the surface complicated finding a desorbent that would ensure quantitative or partial but highly reproducible elution of Cu(II). We have not reached the positive result with 3 M HNO<sub>3</sub>, 6 M HCl, 1 and 2 M EDTA, and 1 and 2 M solutions of thiourea in 1 M HCl. Therefore, we examined the possibility of the Cu(II) detection in the sorbent phase by the X-ray fluorescence method. To this end, we prepared reference samples by pelletizing the modified silica gel after joint sorption [both in the batch mode,  $m(\text{sorbent}) = 0.05 \text{ g}$ , and under column conditions,  $V_{\text{max}}$  of solution passed 300 mL,  $m(\text{sorbent}) = 0.05 \text{ g}$ ] with the binder (H<sub>3</sub>BO<sub>3</sub>). To take into account the possible nonquantitative Cu(II) sorption under the conditions of

competing sorption, the residual Cu(II) concentration in the eluate was monitored by inductively coupled plasma atomic emission spectroscopy. The dependences of the analytical signal on the metal content were processed in accordance with IUPAC recommendations. The linearity range in X-ray fluorescence determination of Cu(II) on the modified silica gel appeared to be 2–25 µg/50 mg sorbent, and the detection limit ( $3\sigma$  criterion), 2.8 and 4.7 µg/50 mg sorbent for the batch and column preconcentration modes, respectively.

The possibility of determining Cu(II) under the chosen conditions by X-ray fluorescence analysis on silica gels containing covalently immobilized formazan groups was checked with a model mixture, artificial seawater prepared in accordance with the recommendations. According to the results obtained, the root-mean-square deviation in determination of 5 µg of Cu(II) in 100 mL of a water sample is 0.09.

### CONCLUSIONS

The formazan moiety was covalently immobilized on the silica gel surface. Significant competing effect is observed in sorption from solutions containing Cu(II), Co(II), Ni(II), and Cd(II) in equimolar amounts. High selectivity to Cu(II) under the conditions of competing sorption is preserved at different levels of initial concentrations and total mineralization of the solutions. An ESR study revealed the formation of the CuN<sub>4</sub> coordination core on the surface of functionalized silica gel in the reaction with Cu(II) at pH 8. The possibility of determining Cu(II) in multicomponent aqueous solutions by sorption in the batch and column modes, followed by X-ray fluorescence analysis, was demonstrated.

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