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New hybrid chelating sorbents with grafted 3-aminopropionate groups based on mixed silicon, aluminum, titanium, or zirconium oxides

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A series of new hybrid organo-inorganic sorbents with the 3-aminopropionate chelating group was synthesized. The synthesis includes the copolycondensation (sol—gel method) of tetraethoxysilane, 3-aminopropyltriethoxysilane, and several modifiers ($MeSi(OEt)_3$, $EtSi(OEt)_3$, $Ti(OEt)_4$, $AlONO_3$, $ZrOCl_2$) followed by carboxyethylation with acrylic acid. The obtained chelating sorbents were characterized by elemental analysis, FT-IR and ^1H NMR spectroscopy, and thermogravimetry. The *N*-carboxylated sorbents have a higher sorption capacity with respect to metal ions (0.5—0.9 mmol g^{-1}, pH 6.3, NH_4OAc, 20 °C) than the starting sorbents with the primary amino group (0.05—0.2 mmol g^{-1}) and manifest high selectivity for copper(II) ion extraction.

Key words: sol—gel method, silica gel, alumina, titanium oxide, zirconium oxide, mixed oxides, chelating sorbents, β-alanine, iminodipropionate.

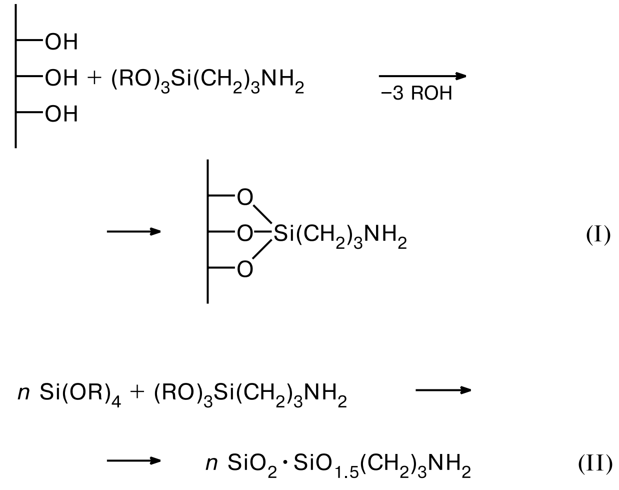
Ion-exchange materials consisting of an inorganic support with covalently linked functional groups are widely used in analytical chemistry.[1—5] Inorganic supports are usually silica gels or metal oxides: alumina,[6] more rarely titania or zirconia,[1,7] and mixed oxide supports.[8]

Two main methods for preparation of hybrid ion-exchange materials are known[9]: chemical modification of the starting supports with organosilicon compounds (Scheme 1, method I) and direct synthesis of a sorbent by the hydrolytic polycondensation of the corresponding alkoxides (Scheme 1, method II).

In the first method, all functional groups are anchored at the support surface, while the second method makes it possible to synthesize sorbents with a higher content of functional groups distributed through the entire volume.

3-Aminopropylsilylated sorbents can be used for the development of amino acid chelating sorbents.[10,11] Silica gels containing iminodiacetate groups are produced in industry (Diasorb-IDK, BioKhimMak, Russia) and successfully used in metal-chelate chromatography,[12] sorption concentrating and separation of complex mixtures of metal ions,[13—15] and in test methods of analysis.[15] These sorbents can be used as complexes with transition metal ions in affinity chromatography of proteins, peptides,[16—18] and carbohydrates.[19]

Scheme 1



R = Me, Et; n = 1/3—3

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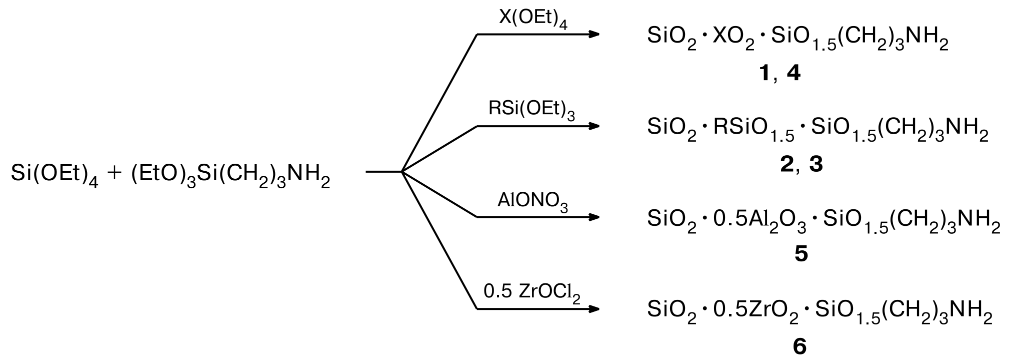
Scheme 2



X = Si, Ti; R = Me, Et

Data on hybrid sorbents containing 3-aminopropionate groups are few.[11] It is known that *N*-substituted iminodipropionic acids react with copper(II) ions more selectively than their acetate homologues or initial amines.[20,21] This work describes the synthesis of organosilicon ion-exchange resins modified by aluminum, titanium, or zirconium oxides with grafted 3-aminopropionate groups and their sorption properties.

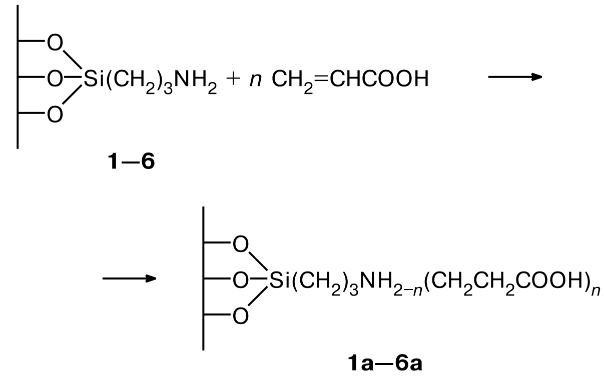
Results and Discussion

The hybrid sorbents containing the primary amino group were synthesized by the copolycondensation of tetraethoxysilane, 3-aminopropyltriethoxysilane, and several modifiers (Scheme 2). Tetraethoxysilane was used instead of a modifier for comparison.

The averaged analytical data of the synthesized samples are presented in Table 1 and show that the C/N ratios for sorbents **1—5** correspond approximately to stoichiometry: sorbent **6** contains a considerable excess carbon content, *i.e.*, hydrolysis of alkoxy groups is incomplete. The hydrogen content found in all samples exceeds the calculated value, which indicates the presence of the bound water.

Carboxyethylation of amines **1—6** with acrylic acid affords *N*-mono- or *N*,*N*-dicarboxyethyl derivatives **1a—6a** (Scheme 3), whose analytical data are given in Table 2. For compounds **1a—3a** and **6a**, the C/N ratio corresponds to the value calculated for the diaddition of acrylic acid. Incomplete addition of acrylic acid is observed for **4a** and **5a**.

Scheme 3



$n = 1.2—2.0$

In addition, in the case of compounds **1a—3a**, a part of the products transformed into a colloid, decreasing their yield. The products isolated by the evaporation of

Table 1. Elemental analysis data for sorbents **1—6**

Sample	Modifier	Found (%)			[C]	[H]	[N]	C/N*	H/N*
		C	H	N	mmol g^{-1}			mol/mol	
1	Si(OEt)$_4$	13.84	4.84	5.18	11.52	48.02	3.70	3.12 (3)	12.99 (8)
2	Si(OEt)$_3$Me	13.53	4.10	4.46	11.26	40.68	3.18	3.54 (4)	12.78 (11)
3	Si(OEt)$_3$Et	16.32	4.93	4.07	13.59	48.91	2.91	4.68 (5)	16.83 (13)
4	Ti(OEt)$_4$	12.71	3.99	4.29	10.58	39.59	3.06	3.46 (3)	12.93 (13)
5	AlONO$_3$	12.06	4.36	5.48	10.04	43.26	3.91	2.57 (3)	11.06 (8)
6	0.5ZrOCl$_2$	9.41	4.38	1.30	7.83	43.46	0.93	8.44 (3)	46.82 (8)

* The calculated C/N or H/N value for the starting support **1—6** is given in parentheses.

Table 2. Data of elemental analysis and ^{1}H NMR spectroscopy for sorbents **1a—6a**

Sample	Found (%)			[C]	[H]	[N]	C/N*	H/N*	n_a**	n_s***
	C	H	N	mmol g^{-1}			mol/mol			
1a	21.63	4.21	2.82	18.01	41.77	2.01	8.94 (9)	20.75 (18)	2.0	1.90
2a	23.40	4.78	2.70	19.48	47.43	1.93	10.11 (10)	24.60 (21)	2.0	1.93
3a	24.33	4.85	2.41	20.26	48.12	1.72	11.77 (11)	27.97 (23)	2.2	1.98
4a	15.48	3.98	2.73	12.89	39.49	1.95	6.61 (9)	20.26 (18)	1.2	1.43
5a	22.53	4.97	3.56	18.76	49.31	2.54	7.39 (9)	19.41 (18)	1.5	1.69
6a	21.19	4.32	2.86	17.64	42.86	2.04	8.64 (9)	20.99 (18)	1.9	2.00

* The calculated value for the dicarboxyethylated product is given in parentheses.

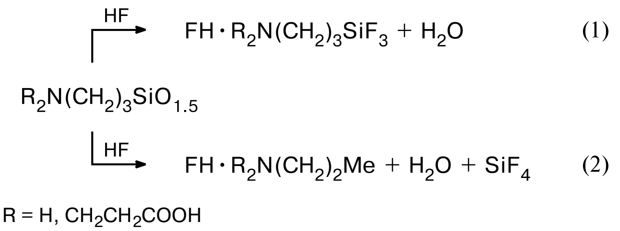
** Degree of carboxyethylation calculated from the elemental analysis n_a = ([C] – k[N])/3[N]; k is the calculated C/N value for the starting support **1—6** (see Table 1).

*** Degree of carboxyethylation calculated from the ^{1}H NMR spectra of the destruction products of treatment of the samples with hydrofluoric acid.

filtrates are highly dispersed and inappropriate for further studies of sorption.

The estimation of the degree of addition n_a from elemental analysis data ignores a possible presence of compounds that can change the C/N ratio in the samples: acrylic and polyacrylic acids, non-hydrolyzed ethoxy groups, *etc*. Therefore, for more reliable determination of the degree of addition, samples **1a—6a** were treated with hydrofluoric acid, the resulting solutions were concentrated in a desiccator, the residue was dissolved in CF_3COOD, and a part of the salts and polyacrylic acid was filtered off. The ^{1}H NMR spectrum of treated product **1a** contains three main groups of signals: 1.1—1.3 ppm ($-CH_2Si\equiv$, $-CH_3$), 1.9—2.2 ppm ($-CH_2-$), and 2.9—3.6 ppm ($=NCH_2-$, $-CH_2CO-$) (Fig. 1). The presence of a signal from methyl protons in the spectrum indicates that the samples are dissolved in HF (Scheme 4, Eq. (1)) and, in addition, the hydrofluoric adduct decomposes (Scheme 4, Eq. (2)).

Scheme 4



No signals of acrylic acid at 6 ppm are observed in the spectra. The degree of carboxyethylation can be calculated from the ratio of non-overlapping signals of methylene protons (see Table 2). The results calculated from the data of elemental analysis (n_a) and ^{1}H NMR spectroscopy (n_s) are consistent, in the most part of cases, within measurement error. The exceptions are samples **4a** and **5a**, which can be explaining by the incomplete addition of acrylic acid.

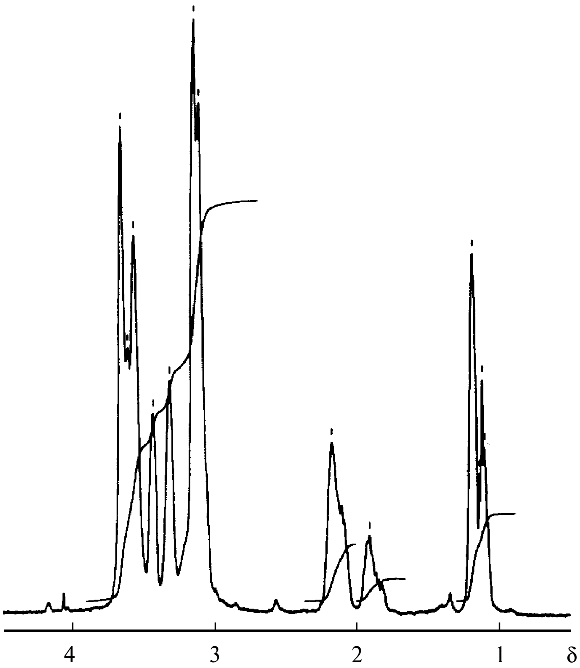


Fig. 1. ^{1}H NMR spectrum (CF_3COOH) of the products of treatment of sorbent **1a** with hydrofluoric acid.

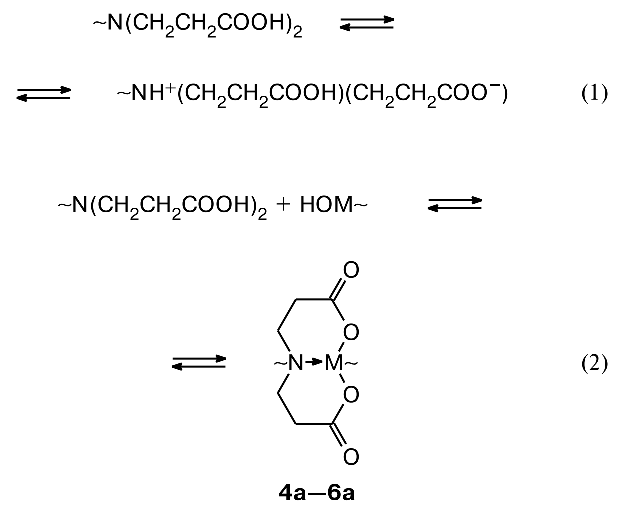
A comparison of the absorption band intensities in the diffuse reflectance IR spectra of samples **1a—6a** at 1700—1300 cm^{-1} (Table 3) showed that in samples **4a**, **5a**, and **6a** the carboxyl groups exist predominantly in the salt form. This means that complex compounds can form (Scheme 5, reaction (2)) along with inner salts (Scheme 5, reaction (1)).

The spectrum of sample **5a** exhibits a noticeable shift of the absorption band of the carboxylate group to 1591 cm^{-1}, which is probably caused by a different structure of the complex.

Table 3. Assignments in the IR spectra (ν/cm^{-1}) of sorbents **1a—6a**

Sorbent	COOH	COO$^-$	CH
1a	1722	1576	1463, 1400
2a	1721	1581	1457, 1400
3a	1716	1581	1460, 1404
4a	1715	1578	1404
5a	1716	1591	1460, 1402
6a	1718	1582	1400

Scheme 5



M = Ti (**4a**), Al (**5a**), Zr (**6a**)

To characterize the ion-exchange properties of the sorbents, we used ^{1}H NMR spectroscopy of broad lines. The ^{1}H NMR spectra of samples **1a—6a** (−150 °C, 90 MHz) are presented in Fig. 2. The spectrum deconvolution into the components corresponding to lines from one-, two, and three-spin systems is shown in Fig. 3. The assignment of these components to the corresponding proton groups in the composition of the samples showed that all products contain hydroxyl groups, three-spin systems of the H_3O^+ type, and strongly bound water in different ratios (Table 4). A change in the amount of the H_3O^+ type is of the greatest interest, because the proton exchange capacity with respect to hydrogen ions is one of the main characteristics of ion-exchange sorbents. The amount of acidic protons H_3O^+ decreases in the series **1a—3a** and is approximately the same for compounds **4a—6a**. Taking into account the concentration of acidic protons, the sorbents can be arranged by proton exchange capacity in the order **1a** > **2a** ≈ **4a** ≈ **5a** ≈ **6a** > **3a**.

Table 4. Data of ^{1}H NMR spectroscopy of broad lines (mol.%)

Assignment*	1a	2a	3a	4a	5a	6a
≡SiOH···O< (*1*)	0.1	0.5	0.1	1.6	0	0.1
H_2O (*3*)	27.6	33.7	54.4	40.7	37.0	41.7
H_3O^+ (*4*)	68.4	58.5	37.5	57.7	58.6	58.2
≡SiOH (*2*)	3.8	7.2	8.0	0	4.4	0

* Designations are given in Fig. 3.

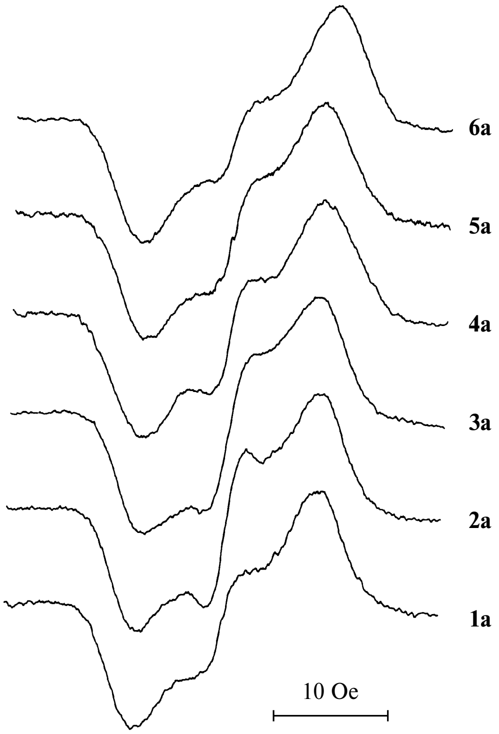


Fig. 2. ^{1}H NMR spectra of broad lines of sorbents **1a—6a**, $T = -150$ °C.

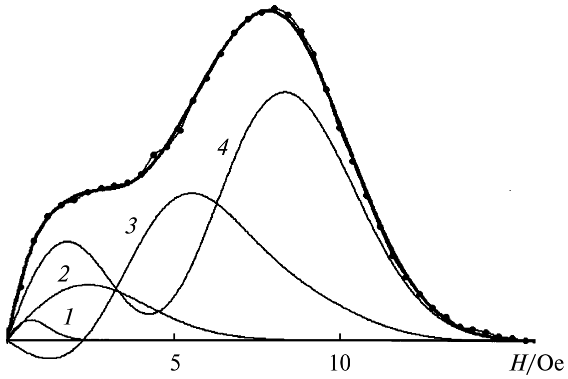


Fig. 3. Results of deconvolution of the ^{1}H NMR spectrum of sorbent **1a**: *1*, ≡SiOH...O<; *2*, ≡SiOH; *3*, H_2O; and *4*, H_3O^+.

As indicated by the broad components in the ^{1}H NMR spectra at room temperature, water exists in the sample structure in the bound state (Fig. 4). According to the obtained data (see Table 4), the water content increases in samples **1a—3a**. The thermogravimetric analysis of samples **1a—3a** (Table 5) shows a similar tendency. However, this trend is not observed for other samples (**5a**

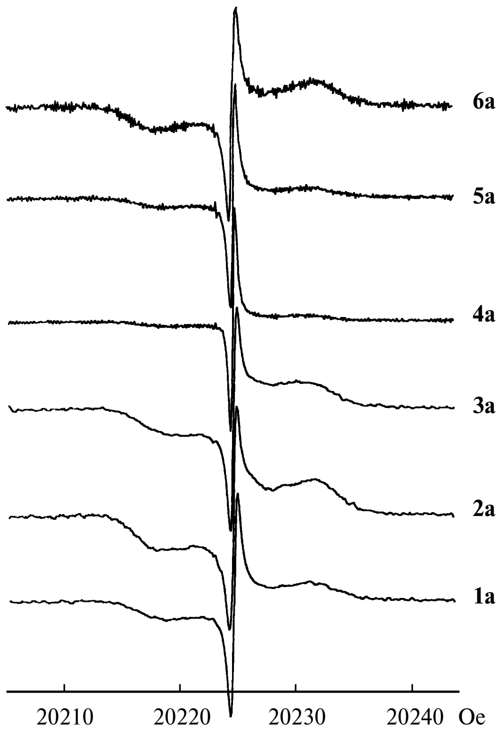


Fig. 4. ^{1}H NMR spectra of broad lines for sorbents **1a—6a**, $T = 20$ °C.

Table 5. Thermogravimetric data for **1a—6a**

Sorbent	Losses below 100 °C (%)	Temperature of exothemic peaks/°C
1a	8	250, 360
2a	5	260, 360
3a	12	250, 420
4a	16	270, 320
5a	2	280, 380, 420
6a	1	280, 420, 460

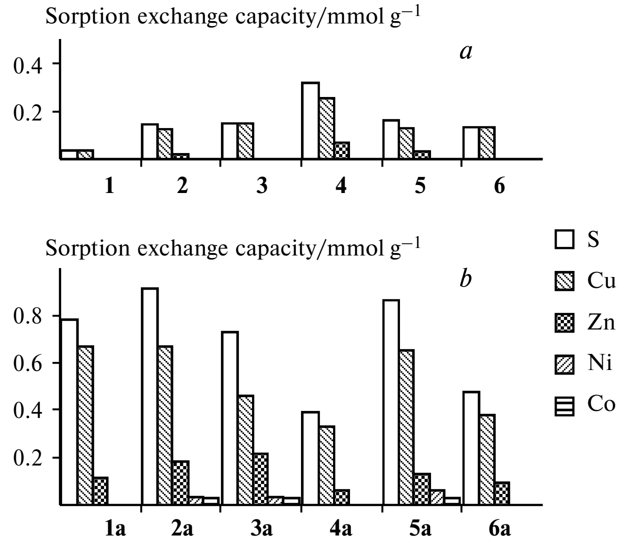


Fig. 5. Results of transition metal ion sorption by samples **1—6** (*a*) and **1a—6a** (*b*). Sorption conditions: $C_{\mathrm{M}^{2+}} = 0.025$ mol L^{-1}, $V = 25$ mL, m(sorbent) = 0.3 g, pH 6.3, 20 °C.

and **6a**). In a higher temperature region, the sorbents decompose, and the decomposition pattern depends on the nature of an inorganic support.

The sorption capacity of the synthesized samples was studied in a solution containing Ni^{2+}, Co^{2+}, Cu^{2+}, and Zn^{2+} cations. The presented diagrams show that the capacity of the biscarboxyethylated sorbents (Fig. 5, *b*) is higher than the capacity of the corresponding sorbents with the primary amino group (Fig. 5, *a*). Compared to the starting sample **4**, the capacity of monocarboxyethylated sample **4a** has increased insignificantly. The order of decreasing sorption capacity of carboxyethylated sorbents determined from the overall amount of sorbed metals, **2a** > **1a** > **5a** > **3a** > **6a** > **4a**, does not coincide with the order of changing sorbent capacity derived from the content of amino groups (see Table 2, [N]): **1a** ≈ **4a** ≈ **6a** ≈ **2a** > **3a** > **5a**. Evidently, the accessibility of functional groups for complexation with metal cations is decisive for the sorption capacity.

All the samples are strongly selective for extraction of copper ions. Under the studied conditions, Ni^{2+} and Co^{2+} ions are not virtually sorbed, and only Zn^{2+} ions are competitive with Cu^{2+} ions. The order of decreasing selectivity for copper extraction with respect to the sum of metals is as follows: **1a** ≈ **4a** > **6a** > **5a** > **2a** > **3a**. The sorbents containing a lower content of the ≡SiOH groups extract copper more selectively (see Table 4). Probably, the contribution of nonselective formation of silicates and/or polyacrylates increases in this series (Scheme 6).

Scheme 6

$$2\ {\equiv}\mathrm{SiOH} + \mathrm{M}^{2+} \longrightarrow {\equiv}\mathrm{SiO{-}M{-}OSi}{\equiv} + 2\ \mathrm{H}^+$$

$$(\mathrm{CH_2CHCOOH})_n + 0.5n\ \mathrm{M}^{2+} \longrightarrow (\mathrm{CH_2CHCOOM_{0.5}})_n$$

M = Co, Ni, Cu, Zn

Among the synthesized sorbents, the most promising is compound **1a**, which exhibits the highest selectivity for copper ion extraction and a considerable sorption capacity. It is most likely that one of the methods for enhancing the selectivity of copper extraction is a decrease in the contribution of nonselective sorption of the support.

Experimental

^{1}H NMR spectra of broad lines were recorded on a Tesla BS-477 modified spectrometer. ^{1}H NMR spectra of solutions were obtained on a Bruker DRX 400 spectrometer. Diffuse reflectance IR spectra were recorded on a Perkin—Elmer Spectrum-One spectrometer. The C,H,N analyses were carried out on a Perkin—Elmer automated analyzer. Thermograms were obtained on a MOM OD-102 derivatograph.

To study sorption, a sorbent (0.3 g) was added to a solution (25 mL) of metal acetates (M = Ni, Co, Cu, and Zn, $C_{\mathrm{M}^{2+}}$ = 0.025 mol L^{-1}) and ammonium acetate (0.1 mol L^{-1}) with pH 6.3. The mixture was stirred and stored for 24 h. The sorbent was filtered off, and the metal cation content was determined in the filtrate by atomic emission spectroscopy on an Optima 4300 DV spectrometer with a relative determination error of at most 5%. The amount of sorbed ions was calculated from the difference in concentrations between the initial and final solutions.

Synthesis of sorbents 1 and 1a. Distilled water (2.5 g, 0.075 mol) was added dropwise for 5 min at 0—5 °C to tetraethoxysilane (10.4 g, 0.05 mol). Then, 3-aminopropyltriethoxysilane (5.5 g, 0.025 mol) was added to the mixture. The mixture was stirred until the onset of gel formation and was left for 16 h at ~20 °C. The gel formed was powdered and dried at 100 °C to constant weight. Sorbent **1** was obtained in a yield of 5.9 g.

A solution of acrylic acid (4.3 g, 0.06 mol) in water (55 mL) was added to the obtained product (5.4 g, 0.02 mol of N). The mixture was stirred for 10 h at ~100 °C. A precipitate was filtered off, washed with water to neutral pH, and dried to constant weight at 100 °C. Sorbent **1a** was obtained in a yield of 4.16 g.

Synthesis of sorbents 2 and 2a. Distilled water (2.5 g, 0.075 mol) was added dropwise for 5 min at 0 °C to a mixture of methyltriethoxysilane (4.45 g, 0.025 mol) and tetraethoxysilane (5.2 g, 0.025 mol). Then, 3-aminopropyltriethoxysilane (5.5 g, 0.025 mol) was added to the mixture. The mixture was stirred until the onset of gel formation and left for 16 h at room temperature. The gel formed was powdered and dried at 100 °C to constant weight. Sorbent **2** was obtained in a yield of 5.45 g.

Acrylic acid (4.3 g, 0.045 mol) in water (35 mL) was added to product **2** (4.05 g, 0.015 mol N). The mixture was heated in a water bath with stirring for 10 h. A precipitate was filtered off, washed with water to neutral pH, and dried to constant weight at 100 °C. Sorbent **2a** was obtained in a yield of 1.76 g.

Synthesis of sorbents 3 and 3a, 4 and 4a. The sorbents were synthesized similarly to sorbents **2** and **2a**. In the case of sorbent **3**, ethyltriethoxysilane was used instead of methyltriethoxysilane, and sorbent **3** was obtained in a yield of 6.11 g. The carboxylation of **3** gave 2.09 g of sorbent **3a**. In the case of sorbent **4**, tetraethoxysilane was used, and the yield was 6.2 g. Its carboxylation afforded sorbent **4a** in a yield of 5.49 g.

Synthesis of sorbents 5 and 5a. Alumosol (13% alumina, NO_3^- equimolar to Al) (10 g, 8.8 mL, 0.025 $AlONO_3$) and methanol (30 mL) were added to tetraethoxysilane (5.2 g, 5.6 mL, 0.025 mol). Then, 3-aminopropyltriethoxysilane (5.5 g, 5.8 mL, 0.025 mol) was added to the mixture with vigorous stirring at 0 °C. First, a gel-like precipitate formed, which was further dissolved almost completely. The mixture was stirred until a compact gel formed and left for 16 h. The gel was powdered and dried at 100 °C. The yield of sorbent **5** was 5.5 g.

The resulting product (3.8 g, 0.015 mol) was triturated in a mortar, and a solution of NaOH (0.6 g, 0.015 mol) and acrylic acid (4.3 g, 0.075 mol) in water (35 mL) was added. The mixture was refluxed for 10 h, and a precipitate was filtered off, washed with water to pH 7 (3×100 mL), and dried. The yield of sorbent **5a** was 4.15 g.

Synthesis of sorbents 6 and 6a. Tetraethoxysilane (5.2 g, 5.6 mL, 0.025 mol) was added to a solution of $ZrOCl_2 \cdot 8H_2O$ (4 g, 0.0125 mol) in methanol (15 mL). The mixture was stirred to homogenization. 3-Aminopropyltriethoxysilane (5.5 g, 5.8 mL, 0.025 mol) in methanol (15 mL) was added with vigorous stirring and cooling in an ice-cold bath. First, a gel-like precipitate formed, which was further dissolved almost completely. The mixture was stirred until a compact gel formed and stored for 16 h. The gel was powdered and dried at 100 °C. The yield of sorbent **6** was 5.4 g.

The resulting product (4.4 g, 0.004 mol N) was triturated in a mortar, and NaOH (0.16 g, 0.004 mol) acrylic acid (0.86 g, 0.012 mol), and water (20 mL) were added. The mixture was refluxed for 10 h, and a precipitate was filtered off, washed with water to pH 7, and dried. The yield of sorbent **6a** was 4.89 g.

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