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Sorbents based on mesoporous silicas modified with hydrazide functional groups

The silica-based sorbents characterized by MCM-41 pore structure and modified with hydrazide groups were synthesized. The low-temperature nitrogen sorption method, X-ray phase analysis, FT-IR spectroscopy and scanning electron microscopy were used to determine textural-structural properties of the silica sorbents under investigation. The presence of modifier reduces values of specific surface area. The impregnation method enhances adsorption capacity to a larger extent as compared with the direct synthesis method. The sorption of copper (II), nickel (II), and cobalt (II) from aqueous solutions by the obtained reagents was studied. The study of non-ferrous cations' adsorption evinced that, depending on pH value of the medium, both conjoint extraction and separation of cations were possible. The sorbents can be used to quantitatively separate copper (II) ions from nickel (II) ions. The sorption capacity of the reagents as dependent on the method for modification of the silica base and on the monomer concentration was explored under condition of conjoint metal sorption. The effect of temperature on the sorption of metals by the obtained modified silica at different pH values and the method of their interaction with the surface of the MCM were determined.

Keywords: mesoporous silica; modification; hydrazide; sorption; acids Versatic, non-ferrous metals, impregnation method, direct synthesis.

Introduction

Determination of trace amounts of elements by conventional physical and physico-chemical methods is often impossible due to sensitivity and selectivity limitations and rather complicated composition of the solutions analyzed. So, it is very important to develop novel preparation methods of available and inexpensive sorbents for group extraction of metal ions from aqueous solutions of complicated composition. Combined analytical methods, such as determination of the microcomponents after concentrating procedure, seem to be rather promising. Sorption is the most efficient method of concentrating, as the microcomponents from large volumes of solutions can be concentrated using a relatively small amount of sorbent without organic solvents, required for conventional metal extraction processes.

Recently, attention of the researchers has been attracted to application of mesoporous materials, characterized by both regular pore arrangement and high textural parameters. Thus, mesoporous silicas have been widely used as catalyst support materials owing to their unique structure and physicochemical properties [1–8].

Only few papers are devoted to the use of mesoporous structures in extraction and selective sorption processes [9–15]. From a great variety of sorbents suggested for concentrating of elements, the surface-modified ones are known to have the best sorption characteristics. Chemically modified silicas (CMS) belong to this type of sorbents [16–18]. In the modified silicas the favorable properties of the matrix — high specific surface and high mesopore volume — are combined with the presence of functional groups required for isolation of rare-earth and non-ferrous metal acid complexes. As a rule, functionalized organosilanes (with NH_2-, CN-, and other reactive groups in an organic backbone) as well as the salts of transition metals are used for modification of silica surface [19–24]. In this paper, the MCM-41 silica surface was modified with dimethyl hydrazides based on Versatic tert-carboxylic acids $CH_3R_1R_2CCOOH$ where R_1 and R_2 are alkyl radicals and the total length of hydrocarbon chains is 10–19.

The results obtained allow new methods to be suggested for isolation and separation of complexes of non-ferrous and rare metals from wastewater and technological solutions. These methods are based on concentrating of microcomponents from large volumes of solutions using a relatively small amount of a sorbent without organic solvents. Thus, the study of sorption capacity of mesoporous silica structures is undoubtedly urgent.

Present paper is aimed at the study of nickel (II), cobalt (II), and copper (II) sorption onto the surface of modified mesoporous silica sorbents functionalized with hydrazide and amide groups.

Experimental

The silica base of sorbents with ordered structure of mesopores (MCM-41) was obtained by the template synthesis method under hydrothermal conditions at 100 ºC for 2 days [25]. The following compounds were used: tetraethoxysilane (TEOS) as a source of silicon, cetyltrimethylammonium bromide (CTAB) as a structure-forming agent. The synthesis components were taken at the ratio TEOS 1:CTAB 0.2:NH_3 3.5:H_2O 100.

Two methods were used to functionalize the surface of silica specimens: post-synthetic modernization — PM-DMHD and hydrothermal synthesis — HTS-DMHD. Herein, abbreviations DMHD stand for N',N'-dimethylhydrazides. The mentioned compounds are based on the Versatic tert-carboxylic acid fractions with the formula $CH_3R_1R_2CC(O)OH$, where R_1 and R_2 are alkyl radicals with total number of carbon atoms equaling 10.

MCM-41 was modified via the HTS method, the conditions being described above. A functional reagent was introduced into the reaction medium after the formation of a SiO_2 sol during the synthesis of silicon dioxide via CTAB and TEOS interaction. Then hydrothermal treatment of the mixture, followed by separation and drying of the precipitate, was carried out. The template (CTAB) was removed by extraction with ethyl alcohol, acidified with HCl.

The silica framework was functionalized according to the IM method: the MCM-41 sample was placed in a round bottom flask, the calculated amount of DMHD was added and the mixture was refluxed in ethanol medium for 4 hours. Then the reaction mixture was filtered, and the solid residue was dried at 80 ºC to remove the solvent.

Structural pore organization of the silica base was explored by the X-ray phase analysis on the XRD-7000 diffractometer (*Shimadzu*, Japan) using CuK_a-radiation ($\lambda_{av.}$=1.54184 Å) in low-angular 2Θ interval (1.4–10º) with 0.01–0.005º step.

IR Fourier spectrometer, model IFS 66/S (*Bruker*, Germany) was used to explore the structure of modified silica sorbents at 150–4000 cm^{-1}; specimens were 100-fold scanned at room temperature and at 2 cm^{-1} resolution.

Textural parameters of the sorbents (specific surface area, total pore volume, pore diameter, pore size distribution) were determined with use of low-temperature nitrogen sorption at –196 ºC on the ASAP 2020 device (*Micrometrics*, USA) after degassing the material under vacuum at 90 ºC for 3 h.

Structural properties of the copolymers were explored as follows. To adjust the requisite pH value of the 100 ml solution containing only copper (II) ions or conjointly copper (II), nickel (II) and cobalt (II) ions, either hydrochloric acid or ammonium at a respective concentration was added. Next, 0.200 g of modified silica were added to the obtained mix and stirred. 20 Minutes later, residual content of metal ions was determined in the aqueous phase. To this end, the SOLAAR iCE 3500 atomic adsorption spectrometer (*Thermo Fisher Scientific*, USA) was used. The same device was used to determine titers of standard sulfate solutions of copper (II), nickel (II) and cobalt (II).

The values of static metal sorption capacity (E^M), extraction degree (E) and distribution coefficient (D) and separation factor (β) were calculated via the formulas (1–4), with errors not exceeding 5 %.

$$E = (C_0 - C_{eq.})/C_0 \cdot 100\ \%; \tag{1}$$

$$E^M = (C_0 - C_{eq.})V \cdot /\ 1000 \cdot m \cdot M; \tag{2}$$

$$D = (A \cdot 10^3)/C_{Me}; \tag{3}$$

$$\beta = D_{Me1}/D_{Me2}. \tag{4}$$

Herein, C_0 stands for metal concentration in the starting solution, mol/l; C_{eq} — for residual equilibrium concentration of extracted metal in the solution, mol/l; C_{Me} — equilibrium concentration of metal, mg/g; V — volume of the flask, ml; m — weighed portion of sorbent, g; M — molar mass of metal, g/mol; A — equilibrium metal sorption, ml/g.

Thermodynamic characteristics of sorption equilibriums, namely limiting adsorption value (Γ_∞, mol·g^{-1}), and adsorption equilibrium constant (K), were calculated by means of linearization of the Langmuir adsorption isotherm [25]:

$$\Gamma = \Gamma_\infty \cdot K \cdot C/(1+K \cdot C) \tag{5}$$

or rewritten as:

$$C/\Gamma = 1/(K \cdot \Gamma_\infty) + C/\Gamma_\infty \tag{6}$$

Here, Γ stands for adsorption value, mol/g; C — for equilibrium concentration of the substance in the solution, mol/l.

To explore the structure of the surfaces after gravimetrical measurements, the Hitachi S-3400N scanning electron microscope equipped with the energy-dispersive analyzer (*Bruker*, Germany) was used. The surface of the specimens was scanned with x1000 magnification.

Results and Discussion

1. Structure and characteristics of the sorbents

The X-ray phase analysis applied to explore the silica base structure in the low-angle 2Θ = 1.4º–10º interval has shown evidence of reflexes 100, 110, 200, 210 on the X-ray photograph of silica. These reflexes are characteristic of the steric group *P6mm* and confirm hexagonal pore organization (MCM-41) of the material produced. In addition, the X-ray phase analysis has found out modification of MCM-41 silica by means of hydrazide and amide groups to result in disordering the porous structure.

The results of FTIR-spectroscopic (Table 1) investigations permit the assumption that, during modification of the silica base, the silica matrix and the modifying objects most probably interact. This interaction results, at least, in formation of hydrogen bonds and associates. This phenomenon is evinced by reduced intensity of the band at 3900–2900 cm^{-1}. During hydrothermal synthesis (in the presence of an alkali and quaternary ammonium bases under hydrothermal conditions), amides and hydrazides can, in accord with the Hofmann rearrangement, possibly be cleaved with formation of amines.

Table 1

FT-IR spectroscopy of the modified silica sorbents

Sample	Structural fragments							
	OH, H_2O	NH	C=O	C–N	C=N	C–O	H_{as} Si–O–Si	H_{as} O–Si–O	H_s Si–O–Si
SiO_2 (MCM-41)	3000–4000		1636				1236–1091	969	802
DMHD		3252	1658	1523					
HTS-DMHD	3000–3700		1636		1479		1240–1092	964	800
PM-DMHD	3000–3700	3427	1653	1533	1469	1381	1239–1157–1080	968	805

Investigation in textural characteristics of the MCM-41 silica base has evinced the sorption isotherms of the specimens to be shaped typically of organized mesoporous structures, in accord with the IV type of the IUPAC classification (that is, isotherms with clearly expressed capillary condensation of nitrogen) (Table 2).

Table 2

Textural parameters of the sorbents

Sample	E_a, kJ·mole $^{-1}$	Textural characteristics		
		Specific surface area, S_{BET} $m^2·g^{-1}$	Total pore volume, V_{tot} $cm^3·g^{-1}$	Average pore diameter, D nm
SiO_2 (MCM-41)		952	0.59	2.4
HTS-DMHD	54.6	42	0.07	6.3
PM-DMHD	45.6	239	0.20	3.3

The texture and structure of sorbents was studied by low-temperature nitrogen adsorption method (Table 2). According to the data given in Table 2, the sample is a mesoporous material with a high specific surface area (up to 952 $m^2×g^{-1}$). The binding energy values obtained using the TGM method (Table 2) prove the grafted groups to be strongly bound to the support surface [26]. The surface area is significantly reduced upon modification procedure. This effect is the most pronounced in case the grafting and synthesis processes are carried out simultaneously. A decrease in the specific surface area and pore volume can result in deterioration of the MSM adsorption characteristics. However, a rather high content of functional groups (13–22 $mmol×g^{-1}$) and ability of the letter to form six-membered chelate cycles with the complexing ion should be taken into account.

So, these materials can be used as sorbents for concentrating, separation and extraction of nonferrous metals ions from solutions of complicated composition.

The synthesized specimens being planned to be used as sorbents to treat wastewater, adsorption capacity for copper (II), nickel (II) and cobalt (II) ions of the sorbents obtained was explored. Porous structure of a material can appreciably influence the adsorption kinetics. During adsorption, a phenomenon of transferring the substance inside the pores appears. This phenomenon is characteristic of the diffusion mechanism. This stage often determines the time of attaining the adsorption equilibrium. Portions of a metal extracted are dependent on the adsorption conditions — on acidity of the medium and duration of contact between sorbent and solution; therefore, dependence of adsorption on these factors was studied first of all.

The adsorption on the prepared sorbent-support was studied in detail. The optimal contact time of the sorbent-support with a copper-containing solution was shown to be 20 minutes. The adsorption of cobalt and nickel in acidic and neutral media is completed within 60 minutes, and in alkaline medium — within 20 minutes.

The adsorption mechanism in case of the adsorbents with the pore sizes commensurate with the size of the adsorbed molecules is significantly different the one observed on the large-pore adsorbents. No adsorption layers are formed in micro- and mesopores, and adsorption proceeds via a volume-filling mechanism [27].

In wastewater, non-ferrous metal ions are present as mixes; therefore, conjoint adsorption of copper, nickel and cobalt ions was studied. The atomic adsorption spectroscopy applied to control the contents of metal ions in equilibrium solutions during the sorption process had enabled exploring sorption of transition metal ions when conjointly present in solutions and with the regard for mutual influence of ions on the sorption process.

In Table 3 and Figure 1 the data on silica sorbents prepared by the postsynthetic modification (PSM) are shown, the grafting density being different. The molar ratio of the support to the grafted groups varied in the range 1:0 ÷ 1:0.4. The grafting of DMHD groups by the HTS method resulted in a 20-fold reduction of the initial surface area, and these samples were removed from experiment.

Table 3

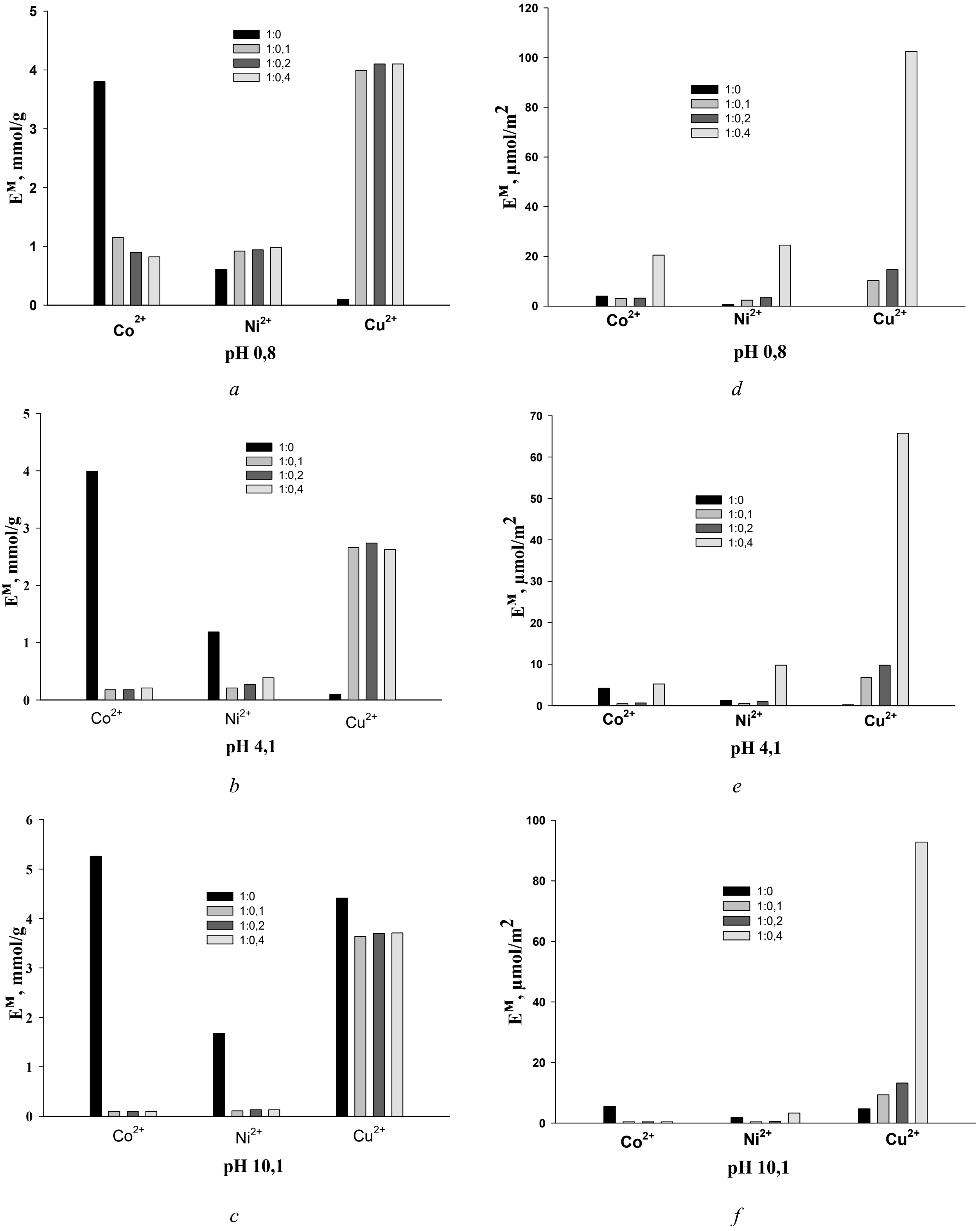
The effect of pH and grafting density on the sorption capacity (E^{M}) of non-ferrous metal ions with silica sorbents obtained by the method of postsynthetic modification

pH	Ratio SiO_2/DMHD	S_{BET}, $м^2 \cdot g^{-1}$	E^{M}					
			Co^{2+}		Ni^{2+}		Cu^{2+}	
			$mmol \cdot g^{-1}$	$\mu mol \cdot m^{-2}$	$mmol \cdot g^{-1}$	$\mu mol \times m^{-2}$	$mmol \cdot g^{-1}$	$\mu mol \times m^{-2}$
0.8	1:0.05	950	3.80	4.00	0.61	0.64	0	0.00
	1:0.10	390	1.15	2.95	0.92	2.36	3.99	10.23
	1:0.20	280	0.90	3.21	0.94	3.36	4.10	14.64
	1:0.40	40	0.82	20.50	0.98	24.50	4.10	102.50
4.1	1:0.05	950	3.99	4.20	1.19	1.25	0.00	0.00
	1:0.10	390	0.18	0.46	0.21	0.54	2.66	6.82
	1:0.20	280	0.18	0.64	0.27	0.96	2.74	9.78
	1:0.40	40	0.21	5.25	0.39	9.75	2.63	65.75
10.3	1:0.05	950	5.26	5.53	1.68	1.77	4.41	4.64
	1:0.01	390	0.00	0.00	0.11	0.28	3.64	9.33
	1:0.20	280	0.00	0.00	0.13	0.46	3.70	13.21
	1:0.40	40	0.00	0.00	0.13	3.25	3.71	92.75

A decrease in adsorption parameters observed in some cases (Table 3, Fig. 1 *a–c*) is primarily due to structural changes of the sorbent upon modification. At the same time, the pore size increases significantly. Hence, a pore-size dependent diffusion process is strongly affected by this structural change [27].

Functional groups are reactive enough to bind transition metal ions. So, the adsorption capacity value, or adsorption onto MCM unit surface area, increases proportionally to the grafting density (Fig. 1 *d–f*).

Functionalization of the surface affects the pH range of extraction of metal cations, and separation of metals in the case of joint presence is possible (Table 4).



a, *b*, *c* — *E*^м, mmol·g^{-1}; *d*, *e*, *f* — *E*^м, mcmol·m^{-2}

Figure 1. The effect of pH and density of grafting on the sorption capacity (*E*^м) of non-ferrous metal ions with silica sorbents obtained by the method of postsynthetic modification

Table 4

Effect of pH on the separation of non-ferrous metal cations (joint presence) on the initial MSM-41 and modified IM-DMHD (m_{sorb} = 0.0200 g, V_{flask} = 10 ml, t = 20 min, DMHD/SiO$_2$ = 0.05; 0.1; 0.2

Ions	pH 1.5				pH 5.0				pH 8.7			
	D, μl·m^{-2}		*E*, mmol·m^{-2}		*D*, μl·m^{-2}		*E*, mmol·m^{-2}		*D*, μl·m^{-2}		*E*, mmol·m^{-2}	
	MCM-41	PM-DMHD	MCM-41	PM-DMHD	MCM-41	PM-DMHD	MCM-41	PM-DMHD	MCM-41	PM-DMHD	MCM-41	PM-DMHD
Co	55	130	0.37	0.8	11	109	0.08	0.7	19000	13380	3.9	4.8
Ni	553	610	3.90	5.0	537	369	7.9	5.5	5900	6000	7.4	9.3
β MCM-41	10.1				48818.2				3.2			
β PM-DMHD	4.7				3.4				2.2			
Cu	0	50	0	0.4	28	0	0.23	0	107000	40700	4.5	5.9
Ni	760	930	4.5	5.9	581	750	4.1	5.4	2820	6710	6.5	9.4
β MCM-41	–				20.8				37.9			
β PM-DMHD	20.1				–				6.1			
Cu	0	3420	0	43	0	7940	0	47	134000	5490	4.8	51
Co	107	1040	0.67	7.1	115	190	0.67	2.6	434	2300	1.8	8.9
Ni	577	1400	4.1	3.7	364	780	3.10	5.5	1250	1390	5.7	7.1
β MCM-41	5.4				3.2				Cu^{2+}/Co^{2+} — 308			
									Cu^{2+}/Ni^{2+} — 107			
β MCM-41	Cu^{2+}/Co^{2+} 33				Cu^{2+}/Co^{2+} 42				Cu^{2+}/Co^{2+} 2.4			
	Cu^{2+}/Ni^{2+} 2.4				Cu^{2+}/Ni^{2+} 10				Cu^{2+}/Ni^{2+} 3.9			

As follows from the data obtained, the grafting of hydrazide groups onto silica surface considerably expands the pH range of copper extraction (Tables 3, 4, Fig. 1). The MCM-41 specimen modified with DMHD groups maximally separates copper (II) ions from cobalt (II) and nickel (II) ions in neutral and alkaline media. Ions of the Co(II)–Ni(II) pair can be separated in an alkaline medium. At neutral pH value, ions of the Ni(II)–Cu(II) pair freely separate from one another as the mentioned pair is not adsorbed under these conditions.

The temperature effect on the sorption of metals by the modified silicas was studied at different pH values.

For PM-DGHD samples at low and medium pH values, the sorption capacity was found to be decreased with the temperature rise. This fact indicates physical nature of adsorption.

With high pH values, when non-ferrous metal ions can possibly form complex compounds with DMHD-groups [28, 29], the situation changes. The tangent angle of the ln E vs.1/T (Fig. 2) dependence inverts its sign, i.e. with increasing temperature, adsorption enhances. This becomes possible in case of a chemical reaction on the surface.

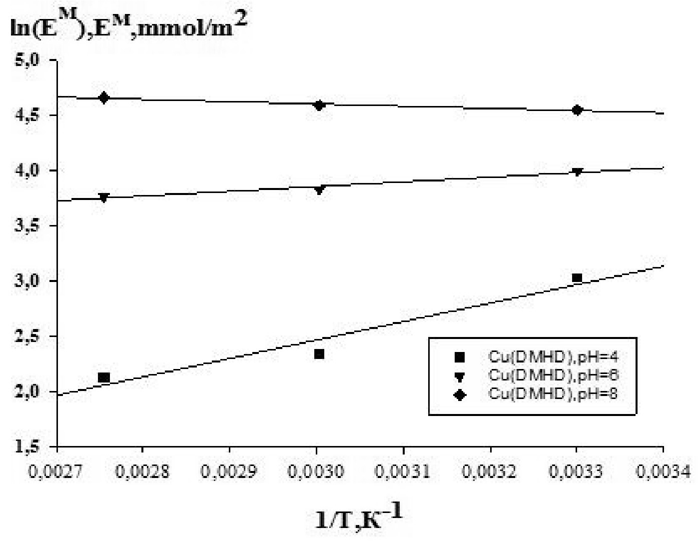
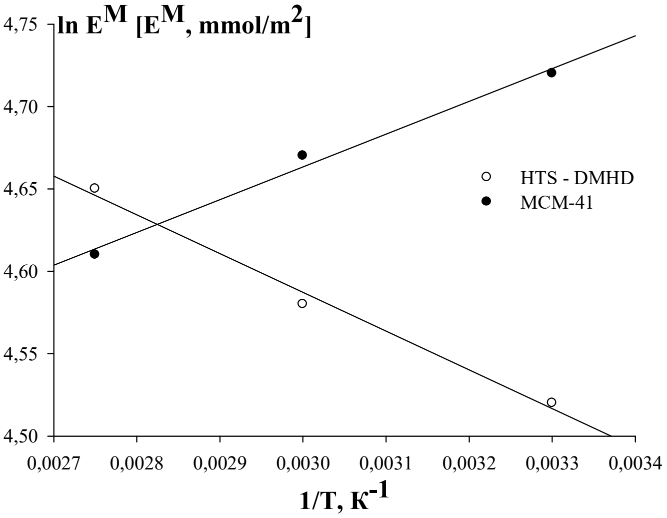


Figure 2. The effect of pH on the temperature dependence of the sorption capacity of the modified silica with respect to Cu^{2+} cations

A similar phenomenon was observed in the case of adsorption of cobalt cations on the surface of the modified silica.

Only physical adsorption onto the initial sorbent surface takes place over the entire pH range studied (Fig. 3).



1 — MCM-41; *2* — HTS-DMHD; m_{sorb} = 0.0200 g; V_{flask} = 10 ml; t = 20 min; pH = 8

Figure 3. Adsorption isotherm of Cu(II) in neutral medium for sorbents:

Chemisorption and covalent bonding with surface functional groups can hinder desorption of metal cations into the solution in further operating cycles of modified sorbents. So, at the next step, the desorption of copper ions from dimethyl hydrazide-functionalized MCM-41 was studied.

Desorption of copper cations from the MSM surface modified by DMHD impregnation was studied at ambient conditions. Copper adsorption was carried out at pH = 8, as at this pH-value copper can be isolated completely. On the contrary, desorption was carried out in an acidic medium, as, according to the data obtained, under these conditions the values of adsorption parameters are significantly lower.

The maximal degree of copper cations' desorption from the surface of sorbents equaled 98 % and was observed at 2M concentration of the acid. In sulfuric acid at 1M concentration, 64 % of copper were desorbed. To reduce concentration of the acid and to increase the degree of copper desorption, the process should be conducted at an elevated temperature. The reason is that physical adsorption largely predominates under these conditions, as is evinced by the adsorption heat values obtained by us.

Conclusions

In this work, structural and adsorptive properties of MCM-41 specimens as influenced upon by (a) modification of their surface with hydrazide groups, and (b) the modification method as well were studied.

Specific surface area of the adsorbent was shown to be significantly reduced after grafting of functional groups. Impregnation method (IM) is more preferable for surface modification than the hydrothermal synthesis (HTS), as in this case surface area reduction is less pronounced and, at the same time, the texture changes are observed. This changes lead to a wider pH-range of extraction and separation of non-ferrous metal cations than the one for the initial MSM.

A comprehensive study to choose the optimal conditions for adsorption and desorption of metal cations (copper (II), nickel (II), cobalt (II)) on the MSM surface modified with chelating functional groups.

The work was performed on the state assignment number AAAA-A18–118032790022–7.

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Гидразидті функционалды топтармен модификацияланған мезокеуекті кремнеземдер негізіндегі сорбенттер

Кремнезем негізіндегі кеуегі МСМ-41 болатын, Versatic трет-карбон қышқылдары фракциясының негізіндегі гидразидті топтармен модификацияланған сорбенттер синтезделіп алынды. Азоттың төменгі температуралы сорбциясы, рентгенфазалық анализ (РФА), ИҚ-спектроскопиясы және сканерлейтін электрондық микроскопия әдістері арқылы зерттелінетін кремнеземді сорбенттердің текстуралық-құрылымдық қасиеттері анықталды. Адсорбциялық және десорбциялық беттерінің сәйкес келуі сорбент құрылымының реттілігін көрсетеді. Модификатордың болуы меншікті беттік ауданының кемуіне әкеледі. Сулы ерітіндідегі мыс (ІІ), никель (ІІ) және кобальттың (ІІ) сорбциясы зерттелді. Сіңдіру әдісі, тура синтез әдісіне қарағанда, модификацияланған кремнеземнің адсорбциялық қабілеттілігін арттырады, бұл бастапқы МСМ салыстырғанда түсті металдарды бөліп алудың pH диапазонын кеңейтуге мүмкіндік береді. Түсті металдар катиондарының сорбциясын зерттеу ортаның pH көрсеткішіне байланысты катиондарды бірге немесе жекелей бөліп алуға болатынын көрсетті. Сорбенттер мыс (ІІ), никель (ІІ) иондарын мөлшерлік бөліп алуда қолдануға болады. Кремнеземді негіздің модификация әдісі және металдардың бірлескен сорбциясы кезіндегі мономер концентрациясына реагенттердің сорбциялық қабілеттілігінің тәуелділігі зерттелді. pH әртүрлі шамаларындағы және олардың МСМ беттік қабатымен әсерлесуі нәтижесінде модификацияланған кремнезем негізінде алынған металдар сорбциясына температураның әсері анықталды. Сорбенттің беттік қабатындағы мыс катиондарының десорбциясы анықталды.

Кілт сөздер: мезокеуекті кремнезем, модифицикация, гидразид, сорбция, Versatic қышқылдары, түсті металдар, сіңдіру әдісі, тура синтез.

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Сорбенты на основе мезопористых кремнеземов, модифицированных гидразидными функциональными группами

Синтезированы сорбенты на основе кремнезёмов со структурой пор МСМ-41, модифицированные гидразидными группами на основе фракций — трет-карбоновых кислот Versatic. Методами низкотемпературной сорбции азота, рентгенофазового анализа (РФА), ИК-спектроскопией и сканирующей электронной микроскопии определены текстурно-структурные свойства исследуемых кремнеземных сорбентов. Совпадение адсорбционной и десорбционной ветвей свидетельствует о высокой степени упорядоченности структуры сорбента. Наличие модификатора приводит к уменьшению значений удельной площади поверхности. Исследована сорбция меди (II), никеля (II) и кобальта (II) из водных растворов полученными реагентами. Метод пропитки увеличивает адсорбционную способность модифицированного кремнезема в большей степени по сравнению с методом прямого синтеза, что позволяет существенно расширить диапазон pH извлечения и разделения цветных металлов по сравнению с исходным МСМ. Изучение сорбции катионов цветных металлов показало, что, в зависимости от значения pH среды, возможны как совместное извлечение, так и отделение катионов. Сорбенты могут быть использованы для количественного отделения ионов меди (II) от ионов никеля (II). Определена зависимость сорбционной способности реагентов от способа модификации кремнезёмной основы и концентрации мономера при совместной сорбции металлов. Определены влияние температуры на сорбцию металлов полученными модифицированными кремнеземами при разных значениях pH и способ их взаимодействия с поверхностью МСМ. Изучена десорбция катионов меди с поверхности сорбента.

Ключевые слова: мезопористый кремнезем, модифицикация, гидразид, сорбция, кислоты Versatic, цветные металлы, метод пропитки, прямой синтез.

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