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COMPLEXING PROPERTIES OF SILICA GEL-POLYANILINE COMPOSITES WITH GRAFTED HETEROCYCLIC AZO REAGENTS

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Anchorage of 4-(2-pyridylazo)-resorcinol and 1-(2-pyridylazo)-2-naphthol on the surface of silica-polyaniline composite has been carried out using the Mannich reaction. Complexing and ion-exchanging properties of the synthesized adsorbents with respect to cationic and anionic forms of transition metals were studied. Modified with heterocyclic azo reagents composites were shown to adsorb cations of toxic metals via their complexation with the grafted groups and to serve inherent to the pristine silica-polyaniline composite ion-exchanging properties towards anionic forms of multivalent metals.

INTRODUCTION

Modern cleaning technology of industrial wastewater brings in a focus some requirements in development of new adsorbents, foremost their multifunctionality including simultaneous extraction cationic and anionic forms of toxic metals from solutions, non-toxicity, simplicity and relatively low cost in large-scale synthesis. Composite materials based on inorganic oxide matrices and polyaniline principally satisfy these requirements [1–4]. We have carried out *in situ* immobilization of polyaniline on the surface of silica gel by oxidative polymerization of aniline with ammonium peroxodisulfate in the medium of hydrochloric acid analogously to [5, 6]. In accordance with the literature data, polyaniline on the silica surface is deposited as emeraldine base at the chosen conditions of synthesis and ratios of concentrations of reagents [6, 7]. As shown in [5], silica-polyaniline composite (Sil-PANI) synthesized by this method demonstrated adsorption with respect to microquatities of V(V) and Mo(VI) anions in the neutral medium, W(VI) and Cr(VI) anions in the acidic medium. However, complexing properties Sil-PANI composite towards transition metal cations were weak, especially in the acidic and neutral media [8]. A rational explanation for this behavior consists in polyaniline protonation in the acidic medium and following repulsion between transition metal cations and positively charged surface. Adsorption of cations by Sil-PANI composite occurs only in the alkaline medium as a result of deposition of hydroxo-forms rather than complexation.

The goal of this work was to widen fuctionality and improve adsorption properties of the silica-polyaniline composite with respect to transition metal cations by means of grafting of heterocyclic azo reagents 4-(2-pyridylazo)-resorcinol (PAR) and 1-(2-pyridylazo)-2-naphthol (PAN) using one-stage aminomethylation (Mannich) reaction.

EXPERIMENTAL

For the synthesis of the starting Sil-PANI composite the Merk silica gel with a specific surface area of 256 m^2/g and pore size of 12 nm (fraction of particles with a diameter of 0.1–0.2 mm) was applied. As shown in [5], the adsorption activity towards anionic forms of multivalent metals of Sil-PANI composite, synthesized through oxidative polymerization of aniline on the surface of silica gel during one day, was much higher than for composite in which polymerization was carried out only for one hour. Therefore, for further modification Sil-PANI composite synthesized for a day was used.

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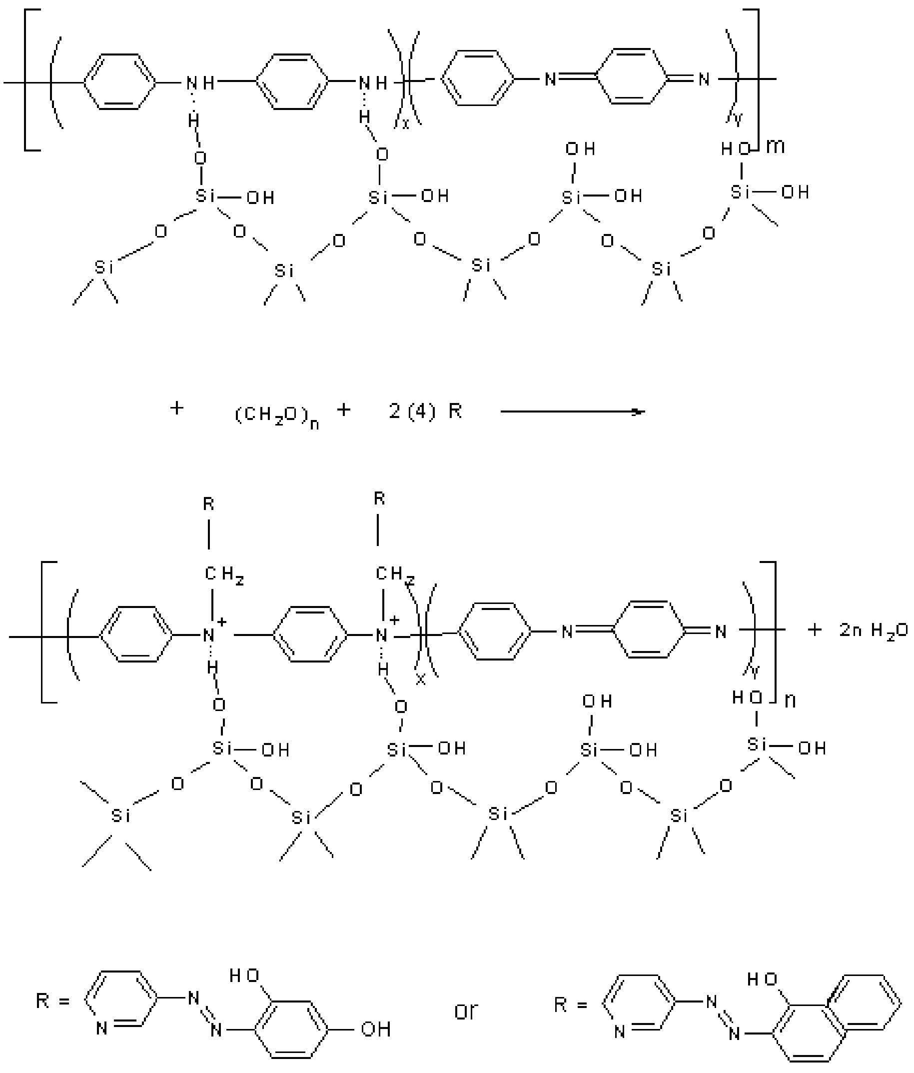
Chemical binding of PAR and PAN on the surface of the Sil-PANI composite was performed using paraform at the optimum for reagents of phenolic type molar ratios of components [9–14], namely PAR: paraform = 1 : 2, PAN: paraform = 1 : 4, as described below.

Synthesis of Sil-PANI-PAR composite. 0.34 g PAR (1.6 mmol) was slowly dissolved in 100 ml of ethyl alcohol at 60 °C for 1 h. Then 0.10 g of paraform and 40 g Sil-PANI composite were added to the solution. The mixture was kept at 60 °C for 5 h then dried at 100 °C for 3–4 h. Product was washed with 20 fold volume of alcohol and dried at 120 ºC to constant weight.

Synthesis of Sil-PANI-PAN composite. 1.994 g PAN (8 mmol) was slowly dissolved in 50 ml of alcohol at 60 °C. 0.96 g of dry paraform (32 mmol) and 40 g of Sil-PANI composite. were added to this solution. Obtained mixture was heated in a water bath at 60 °C for 5 h, then dried at an 100 °C for 3-4 h. Then product was washed with 20 fold volume of alcohol and dried at 120 °C to constant weight.

The general scheme of the synthesis of the Sil-PANI-PAN composite can be represented as follows:



Initial solutions of metal salts with a concentration of 1 mg/ml were prepared by dissolving of precise sample weights of the Analar grade salts $ZnCl_2$, $Pb(NO_3)_2$, $CuCl_2·2H_2O$, $Cd(NO_3)_2·4H_2O$, $NiCl_2·6H_2O$, $FeCl_3·6H_2O$, $Co(NO_3)_2·6H_2O$, $(NH_4)_6Mo_7O_{24}·4H_2O$, $(NH_4)_2Cr_2O_7$, $Na_2WO_4·2H_2O$ and NH_4VO_3 with acidification with appropriate acids in order to prevent hydrolysis in accordance with the methodology [15]. Metal concentrations in the obtained solutions were confirmed by titrimetric analysis. Working solutions were prepared on the day of experiments by dilution with bidistilled water.

Adsorption process was studied in the static mode with adsorbent mass of 0.1 g and volume of working solution of 25 cm^3. pH of solutions was supported by adding of appropriate buffers prepared from standard titrimetric substances or ammonium-acetate mixtures and was controlled by ionometer I–130. 2 M.1.

The degree of adsorption (R, %) was calculated using the formula:

$$R = (m_{ads}/m_o)\cdot 100 = (m_o - m)/m_o\cdot 100,$$

where m_o – mass of metal in the initial solution, m_{ads} – mass of adsorbed metal, m – mass of metal in equilibrium solution after adsorption, which is calculated as $m = C\cdot V$, where C – equilibrium concentration of metal and V – volume of the equilibrium solution.

Equilibrium concentrations of the investigated metals in solutions were determined using a spectrophotometer SF-46 (LOMO, Russia) and application of square cuvettes with optical path length of 1 cm by the following methods: Pb(II), Cd(II), Co(II) and Cu(II) – with PAR at $\lambda = 520$, 500, 510 and 490 nm, respectively [16]. For photometric determination of concentrations of zinc(II) in the equilibrium solutions the method of murexide at 455 nm [17] was used, for Fe(III) determination reaction with phenantroline in the presence of a reducing agent, for Ni(II) reaction with dimethylglyoxime [16], and for Mo(VI) – reaction with ascorbic acid in the presence of sulfuric acid and potassium thiocyanate at 470 nm [18]. Diffuse reflectance electronic spectra (DRES) were registered by Specord M40 and IR spectra were obtained using a spectrophotometer Nexus 470 with Fourier-transformation.

RESULTS AND DISCUSSION

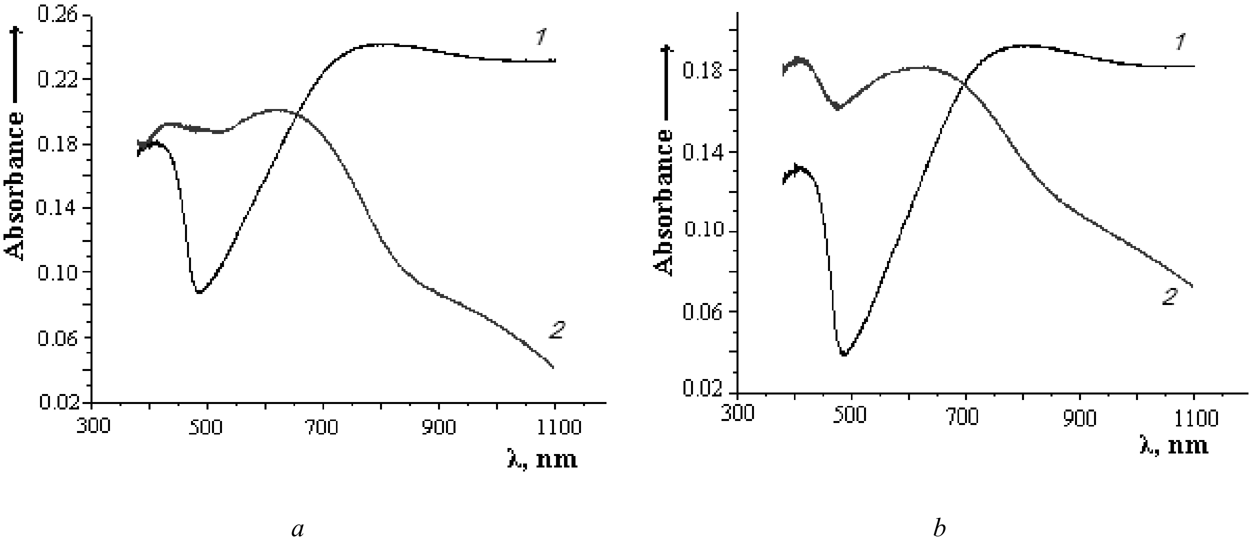
The fact of chemical binding of PAR and PAN to surface of the Sil-PANI composite is confirmed by IR spectroscopy and DRES. Intense absorption bands of silica matrix are observed below 1250 cm^{-1} in IR spectra of both obtained adsorbents. However, the spectral region 1250–3600 cm^{-1} is the most informative on the structure of the synthesized adsorbents (Table 1). IR spectra are characterized by a number of bands of polyaniline on silica [5], as well as the presence of several new bands in 3250–3600 cm^{-1}, corresponding to stretching vibrations υ(O–H) in phenol and bands at 1430–1400 cm^{-1}, attributing to diazo groups [20]. Confirmation of covalent anchorage of PAN and PAR molecules on supported polyaniline in the IR spectra of both adsorbents can serve the presence absorption band at 1460 cm^{-1} which corresponds to the stretching vibrations C–N in the $–CH_2–N=$ groups.

Unlike the original Sil-PANI composite, absorption bands with maximums at 425 and 600 nm are observed in the electronic spectrum of the silica-polyaniline composite chemically modified with PAN (Fig. 1, *a*). According to the literature data [22], availability of these bands indicates that PAN on the surface of modified composite is in the molecular and anionic forms.

There are absorption band with a maximum at 395 nm and a intense broad diffuse absorption band from 500 up to 700 nm in the electronic spectrum of the composite silica-polyaniline chemically modified with PAR (Fig. 1, *b*). In accordance with [23], these bands correspond to molecular (H_2R) and cationic (H_3R^+) forms of PAR on the composite surface.

Table 1. Characteristic absorption bands in the IR spectra of Sil-PANI-PAN and Sil-PANI-PAR composites

Band, cm^{-1}	Type of vibrations	Assignment
	Sil-PANI composite	
~3000	stretching	C–H [5]
~3440	stretching	N–H [5]
1635	stretching	C=N, C=C [5]
	Sil-PANI-PAR and Sil-PANI-PAN composites	
3250–3600	stretching	O–H(phenol) [20]
1500	stretching	C=C (phenol) [20]
1430–1400	bending	O–H (phenol) [20]
	stretching	–N=N– (diazo) [20]
1460	stretching	C–N ($–CH_2–N=$) [21]



a *b*

Fig. 1. Diffuse reflectance electronic spectra of starting Sil-PANI matrices (*a*, *b*, curve *1*), Sil-PANI-PAN (*a*, curve *2*) and Sil-PANI-PAR (*b*, curve *2*) composites

In order to determine the concentration of azo reagents grafted to the surface Sil-PANI nanocomposite, thermogravimetric analysis of samples of the synthesized adsorbents was carried out. The obtained curves were compared with thermograms of the original composite. A comparison of thermograms Sil-PANI-PAN and Sil-PANI showed that in the original composite was about 10 % polyaniline (111.1 mg/g of silica) and 5.05 % (49.6 mg/g or 0.2 mmol/g) of bound 1-(2-pyridylazo)-2-naphthol.

Tables 2 and 3 show the results of study of adsorption properties of the modified composites towards transition metal cations in the static mode at different values of pH and chemical composition of the medium.

The results obtained indicate that, unlike the starting Sil-PANI composite, composites with grafted azo reagents show high adsorption activity with respect to microquantities of Pb(II), Zn(II), Cu(II), Co(III), Ni(II), Fe(III) ions in the near-neutral and weakly alkaline media where these ions exist in the solution in the form of aqua and amino complexes. In particular, adsorption degree of toxic Pb(II) ions by composite modified with PAR, in the neutral medium (background electrolyte consists phosphate buffer) exceeds 95 %, and ions Zn(II) are quantitatively adsorbed by both modified composites in the weakly alkaline medium (pH 8, created with ammonium acetate buffer) in a wide concentration range. These results correlate well with the adsorption properties of chemically modified silica gel with grafted via aminomethylation reaction PAN and PAR [11–14].

Table 2. Dependence of adsorption transition metal cations by Sil-PANI-PAR composite on pH and chemical composition of the medium (weight of adsorbent 0.1 g, volume of solution 25 ml, contact time 24 h)

Cation	**Optimum pH of medium for adsorption**	**Dominating form of existence of ions in solution**	**Maximum degree of adsorption, %**	**Studied range of metal contents, µmol**
Pb^{2+}	6.8	$[Pb(H_2O)_4]^{2+}$	95.89	0.05–2.00
Zn^{2+}	8.0	$[Zn(NH_3)_4]^{2+}$	99.99	0.07–7.70
Cu^{2+}	8.0	$[Cu(NH_3)_4(H_2O)_2]^{2+}$	64.74	0.15–12.50
Ni^{2+}	6.8	$[Ni(H_2O)_4]^{2+}$	97.17	0.42–3.89
Co^{3+}	8.0	$[Co(NH_3)_6]^{3+}$	74.70	0.13–16.95
Fe^{3+}	8.0	$[Fe(NH_3)_n(H_2O)_{6-n}]^{3+}$, $[Fe_3O(CH_3COO)_6]^{+}$	89.80	0.14–8.93
Mn^{2+}	8.0	$[Mn(NH_3)_6]^{2+}$	52.79	0.14–3.64

Table 3. Dependence of adsorption transition metal cations by Sil-PANI-PAN composite on pH and chemical composition of the medium (weight of adsorbent 0.1 g, volume of solution 25 ml, contact time 24 h)

Cation	Optimum pH of medium for adsorption	Dominating form of existence of ions in solution	Maximum degree of adsorption, %	Studied range of metal contents, μmol
Pb^{2+}	6.8	$[Pb(H_2O)_4]^{2+}$	84.00	0.05–2.00
Zn^{2+}	8.0	$[Zn(NH_3)_6]^{2+}$	99.96	0.07–7.70
Cu^{2+}	9.1	$[Cu(H_2O)_4]^{2+}$	51.93	0.15–3.12
Ni^{2+}	6.8	$[Ni(H_2O)_4]^{2+}$	86.43	0.42–4.24
Co^{3+}	8.0	$[Co(NH_3)_6]^{3+}$	73.00	0.13–8.47
Fe^{3+}	8.0	$[Fe(NH_3)_n(H_2O)_{6-n}]^{3+}$, $[Fe_3O(CH_3COO)_6]^+$	98.60	0.14–8.93
Mn^{2+}	8.0	$[Mn(NH_3)_6]^{2+}$	51.80	0.14–5.45

Isotherms of adsorption of cations by the pristine silica gel and modified composites have been studied at the optimum values of the medium acidity. Typical isotherms for ions Co(III) and Ni(II) are shown in Fig. 2 and 3, respectively. Adsorption capacities were calculated from the obtained isotherms both for starting silica and modified composites on its basis (Table 4).

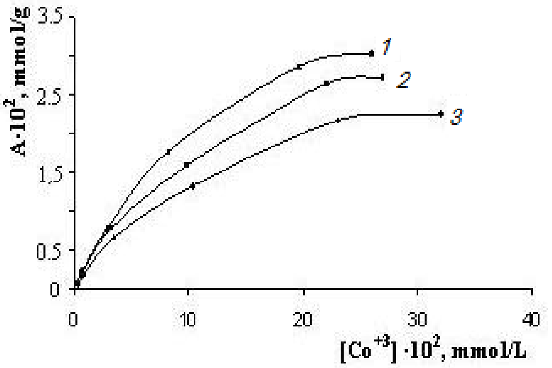


Fig. 2. Adsorption isotherms of ions Co(III) on the surface of Sil-PANI-PAN (*1*), Sil-PANI (*2*) and pristine silica gel (*3*) at pH 8.0

As follows from Table 4, adsorption capacities of Sil-PANI-PAN and Sil-PANI-PAR composites towards all investigated transition metal cations exceed capacity of the starting Sil-PANI composite, probably, owing to complexing properties of the grafted azo reagents.

For confirmation of complexing mechanism of adsorption of cations diffuse reflectance electronic spectra both original composites and samples with adsorbed metals have been registered. Typical DRES of Sil-PANI-PAN composite with adsorbed at pH 6.8 and 9.1 Ni(II) ions are shown in Fig. 4. For composite with nickel adsorbed at pH 6.8 (phosphate buffer), intense absorption band at 510 nm is observed (curve 3) which can be attributed to metal-ligand charge-transfer band. For the sample with Ni(II) adsorbed at pH 9.1 (curve 2), this band is absent, however, absorption band of *d-d* transitions in metal aqua complexes (1000–1100 nm) is available [24]. Therefore, the adsorption activity of the obtained modified composites towards transition metal cations can be caused by complexing capability of the grafted reagents.

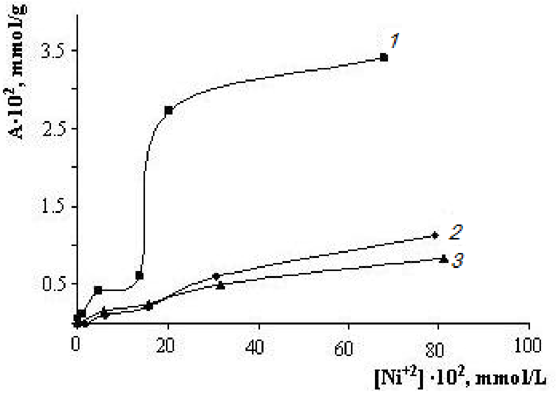


Fig. 3. Adsorption isotherms of ions Ni(II) on the surface of Sil-PANI-PAR (*1*), Sil-PANI (*2*) and pristine silica gel (*3*) at pH 6.8

After addition the buffers of different chemical nature into working solutions with metal ions aqua, amino, acetate, chloride, citrate or other ligands dominate in the primary coordination sphere depending on the composition of the buffer solution (Tables 2 and 3). In the course of adsorption grafted PAN or PAR molecules enter the primary coordination sphere with formation mixed-ligand complexes on the surface of the composite.

Table 4. The values of adsorption capacity of the Sil-PANI, Sil-PANI-PAN and Sil-PANI-PAR composites with respect to transition metal ions in the static mode under optimum pH for each metal

Cation	**Sil-PANI-PAR**		**Sil-PANI-PAN**		**Sil-PANI**
	Adsorption capacity, mmol/g	**Optimum pH**	**Adsorption capacity, mmol/g**	**Optimum pH**	**Adsorption capacity, mmol/g**
Zn(II)	0.077	8.0	0.031	8.0	0.024
Pb(II)	0.019	6.8	0.019	6.8	0.003
Cu(II)	0.056	8.0	0.033	7.0 (aqueous solution)	0.030
Fe(III)	0.036	8.0	0.030	7.0	0.020 (pH 7.0) 0.015 (pH 8.0)
Co(III)	0.030	8.0	0.030	8.0	0.026
Ni(II)	0.032	6.8	0.013	6.8	0.011
Mn(II)	0.030	8.0	0.012	8.0	0.010

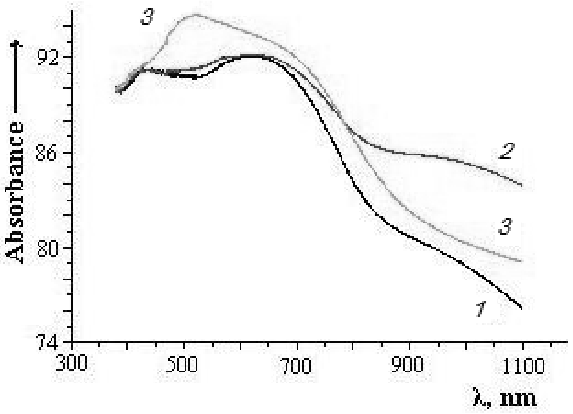


Fig. 4. Diffuse reflectance electronic spectra of Sil-PANI-PAN composite (*1*), after adsorption 200 μg nickel from solution with pH 6.8 (*2*) and after adsorption 150 μg Ni from solution with pH 9.1 (*3*)

We have studied an effect of the Sil-PANI surface modification with PAR or PAN on alteration of ion-exchanging properties of the composite towards the anionic forms of multivalent metals, namely Cr(VI), Mo(VI), W(VI) and V(V) anions. The results are summarized in Tables 5 and 6. As follows from the obtained data, both synthesized adsorbents removed very well Cr(VI), Mo(VI), W(VI) from the acidic solutions and V(V) in the neutral medium. Only for Mo(VI) a dependence of optimum adsorption on acidity of the medium is changed in comparison with the original composite [5]. It can be caused by a partial change in the mechanism of adsorption from ion-exchanging to complexing. This assumption is confirmed by the fact that the sorption capacity of both modified composites towards polymolybdates ions is slightly increased in comparison with the original composite.

Table 5. Adsorption activity Sil-PANI and Sil-PANI-PAN composites towards Cr(VI), Mo(VI), W(VI) and V(V) anions in the static mode

Anions	**Optimum pH for adsorption**	**Maximum degree of adsorption, %**	**Sorption capacity, mmol/g**	
			Sil-PANI-PAN	**Sil-PANI**
WO_4^{2-}	1.7	93.19	0.94	4.10
MoO_4^{2-} $[Mo_6O_{21}]_6^-$ $[Mo_7O_{24}]_6^-$	1.7	80.11	0.01	0.09
$HCrO_4^-$	1.7	99.84	0.04	0.41
VO_3^-	distilled water	41.80	0.01	0.12

Table 6. Adsorption activity Sil-PANI and Sil-PANI-PAR composites towards Cr(VI), Mo(VI), W(VI) and V(V) anions in the static mode

Anions	Optimum pH for adsorption	Maximum degree of adsorption, %	Sorption capacity, mmol/g	
			Sil-PANI-PAR	Sil-PANI
WO_4^{2-}	1.0	93.20	0.57	4.10
MoO_4^{2-} $[Mo_6O_{21}]_6^-$ $[Mo_7O_{24}]_6^-$	1.7	79.56	0.14	0.09
$HCrO_4^-$	1.7	99.99	0.43	0.41
VO_3^-	distilled water	32.20	0.013	0.12

At the same time adsorption capacity of the Sil-PANI-PAN composite towards tungstate ions is decreased about 4.4 times, chromate ions 11.7 times, and vanadate ions 15 times. These data can be explained by a decrease in the number of available ion-exchanging sites of polyaniline after modification. For the Sil-PANI-PAR composite a decrease in adsorption capacity compared with the original composite was detected only for tungstate ions. For chromate and vanadate ions a slight increase in sorption capacity was observed, which also may be explained by additional complexing mechanism. Really, complexes V(V) with PAR in aqueous solutions are well known and they have practical application in liquid chromatography [25]. Quantitative adsorption of microquantities of Cr(VI) ions by both synthesized adsorbents (Tables 5, 6) and integrity of their high adsorption activity towards microamounts of W(VI) ions were detected.

CONCLUSION

Chemical modification of the surface of the silica-polyaniline composite with 4-(2-pyridylazo)-resorcinol and 1-(2-pyridylazo)-2-naphthol has been carried out. Realization of the Mannich reaction was confirmed by IR spectroscopy, DRES and results of thermogravimetric analysis. The obtained adsorbents are characterized by polyfunctional properties and demonstrate high adsorption activity towards cationic and anionic forms of transition metals.

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Комплексотвірні властивості композитів силікагель-поліанілін з прищепленими гетероциклічними азореагентами

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З використанням реакції Манніха здійснено хімічне закріплення 4-(2-піридилазо)-резорцину та 1-(2-піридилазо)-2-нафтолу на поверхні композиту силікагель-поліанілін. Досліджено комплексотвірні та йонообмінні властивості синтезованих адсорбентів. Встановлено, що модифіковані композити адсорбують катіони токсичних металів за рахунок комплексоутворення з прищепленими азореагентами і зберігають йонообмінну здатність щодо аніонних форм багатовалентних металів, яка притаманна вихідному композиту.

Комплексообразующие свойства композитов силикагель-полианилин с привитыми гетероциклическими азореагентами

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С использованием реакции Манниха осуществлено химическое закрепление 4-(2-пиридилазо)-резорцина и 1-(2-пиридилазо)-2-нафтола на поверхности композита силикагель-полианилин. Исследованы комплексообразующие и ионообменные свойства синтезированных адсорбентов. Установлено, что модифицированные композиты адсорбируют катионы токсичных металлов за счет комплексообразования с привитыми азореагентами и сохраняют в отношении анионных форм многовалентных металлов ионообменную способность, присущую исходному композиту.