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Preparation and Properties of Fibrous Sorbents with Grafted Nanosized Organosiloxane Coatings Containing Complexing Aminomethylenephosphonic Ligands

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Abstract—We have modified fibrous sorbents with the organosiloxane coating containing aminomethylenephosphonic ligands at silicon atoms. The so prepared materials efficiently absorb ions of some transition metals from solutions in aqueous hydrochloric acid.

Keywords: organosiloxane, sorbent, organophosphorous ligand, polymeric coating

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Inorganic and organic derivatives of silicon are recognized as efficient and convenient sorbents to be used in many engineering and analytical applications. Compared with organic sorbents, natural and artificial silica and the related products of modification with organosilicon compounds are more chemically and thermally stable, and possess better mechanical strength. The drawbacks of silica-based sorbents are insufficient efficiency and selectivity.

Fibrous sorbents grafted with organosiloxane containing complex forming, redox-active, or ion exchange ligands do not suffer from these drawbacks [1, 2]. Recently [3–6] attempts have been made to prepare silica containing covalently bound phosphonic acid fragments; however, the so prepared materials were either polyfunctional (contained several types of the grafted units) with low grafting degree [3], or contained the hydrolytically unstable arylphosphonic groups [4].

Herein, we report on preparation of organosiloxane coatings grafted onto different textile materials. Those modified fibers contained aminomethylenephosphonic ligands at silicon atoms and revealed strong complex forming ability. The grafted groups could be classified as phosphorus-containing chelating agents [5]. The amino-containing derivatives of phosphoric acid were more efficient as chelating ligand as compared with the parent acid; thus, its spectrum of possible applications was significantly widened.

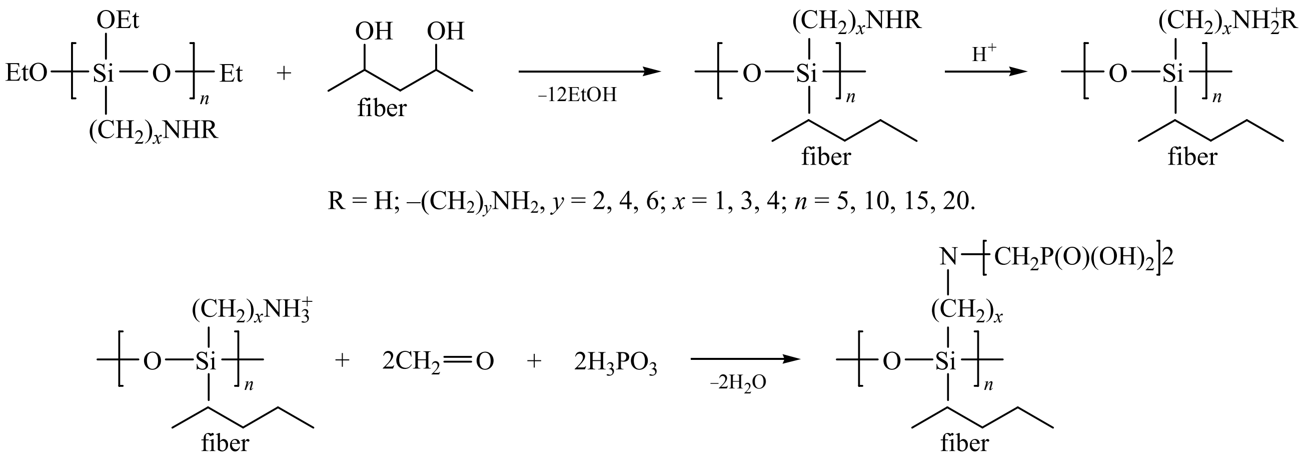
Grafting of the aminomethylenephosphonic ligands at the fibers surface was achieved in two stages. First, the nanosized organosiloxane polymeric coating was covalently bound at the fibers surface; the coating material contained aminoalkyl groups at silicon atoms. The modification was performed by treating of the fiber with aqueous or alcoholic solution of oligo(aminoalkyl)ethoxysiloxane of the desired composition and structure [6]. The siloxane contained functional groups capable of interaction with the reactive groups at the fiber surface to form covalent bonds.

At the second stage, condensation of the grafted amino group with H_3PO_3 and paraformaldehyde occurred via the Kabachnik–Fields reaction [7] (Scheme 1).

The so prepared fibrous sorbents were grafted with nanosized organosiloxane polymeric coatings containing aminomethylenephosphonic ligands at silicon atoms.

Generally, conversion of modification of the covalently bound groups is relatively low [8]. In order to optimize the conditions of preparation of the grafted aminomethylenephosphonic ligands and elucidate the most important factors affecting the reaction conversion, we studied the grafting process using different fibers: molten silica fibers and Belting cotton fabric. The following modification conditions were altered: molar ratio of the components and concentration of the modifier in the grafted layer (see table).

Scheme 1.



R = H; $-(CH_2)_yNH_2$, $y = 2, 4, 6$; $x = 1, 3, 4$; $n = 5, 10, 15, 20$.

The snap analysis of degree of aminoalkyl groups conversion into aminomethylenephosphonic ones was performed by treating the fiber with ninhydrin [9]. The absence of solid phase coloration revealed the absence of residual aminoalkyl groups at the fiber surface, whereas the pristine fibers and the polyfunctional phases turned blue. That approach was very efficient, as it allowed rapid estimation of the modification degree without any chemical analysis.

The organophosphorous ligand immobilization was confirmed by elemental analysis and IR spectroscopy.

As the coating composition at the modified fiber could be non-uniform, determination of the amount of grafted groups required special processing of elemental analysis data [8]. First, comparison of elemental analysis data for the aminoalkyl-containing fiber and the phosphorylated product gave the overall increase of organic species content at the fiber surface. Assuming that the increase of an element content in the modi-fied fiber was due to grafting of the $-CH_2P(O)(OH)_2$ fragments at the aminoalkyl group, amount of the aminomethylenephosphonic groups φ_4 (mol/g) could be calculated as follows:

$$\varphi_4 = P/(A{\cdot}n \times 100),$$

with P, increase of the element content; A atomic mass of the element; and n number of the determined element in the grafted fragment.

Selected parameters of the fibers used for grafting with aminomethylenephosphonic ligands, and the modification conditions

Fiber	Sample	φ_1[a], wt %	φ_2[b], mmol/g	Molar ratio of the reactants $NH_2 : H_3PO_3 : CH_2O$	φ_3[c], mmol/g	Yield, %
Molten silica	S-1	1	2.36	1 : 2 : 2	3.77	80
	S-2	1	1.30	1 : 3.4 : 3.6	2.47	95
	S-3	1	1.03	1 : 4.4 : 6.3	1.99	97
	S-4	1	0.82	1 : 4.4 : 6.3	1.59	97
	S-5	1	0.57	1 : 4.4 : 6.3	1.10	97
	S-6	1	0.45	1 : 4.4 : 6.3	0.86	96
Belting fabric	B-1	3	3.9	1 : 4.4 : 6.3	7.41	95
	B-2	5	6.5	1 : 4.4 : 6.3	12.48	96
	B-3	10	13.0	1 : 4.4 : 6.3	25.48	98
	B-4	15	19.5	1 : 4.4 : 6.3	38.61	99

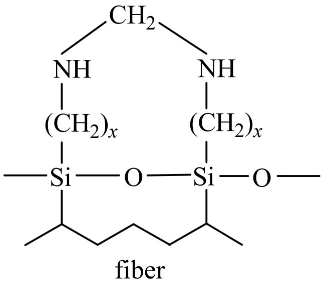
[a] φ_1 is a content of organosiloxane coating at the fiber; [b] φ_2 is content of the grafted amino groups; [c] φ_3 is a content of the grafted aminomethylenephosphonic ligands.

Elemental analysis data confirmed the suggested modification mechanism.

Effect of the modification conditions on yield of the grafted aminomethylenephosphonic ligands was investigated using the molten silica fiber KN-11m (samples S-1, S-2, S-3, S-4, S-5, and S-6) and the Belting cotton fabric (Art. 2030) (samples B-1, B-2, B-3, and B-4) (see table). Conversion of the amino groups into aminomethylenephosphonic ligands was above 80% at stoichiometric ratio of the reactants. With 1.7-fold excess of paraformaldehyde and H_3PO_3, the conversion degree was up to 95–99%.

Further increase of the modifiers excess (up to the 3-fold) decreased the yield of the grafted aminomethylenediphosphonic acid.

We suppose that the observed decrease of the modification efficiency could be due to the side reaction of condensation between the grafted amino groups with formaldehyde molecule.



Excess of paraformaldehyde in the solution, clustering of the grafted groups, and shrunk conformation of the grafted molecules could stabilize the so formed condensation product.

Likely, the primary grafted amino groups were more reactive than the secondary ones. For example, the grafted ethylenediamines gave the corresponding diphosphorylated amines with yield of 90%.

IR spectra of the prepared sorbents contained absorption bands at 2920–2850 and 1660–1580 cm^{-1}, assigned to vibrations of C–H and C–C bonds in the grafted hydrocarbon fragments, respectively. The absorption band assigned to vibration of P=O group (1240–1140 cm^{-1}) overlapped with the bands due to siloxane fragments vibrations, and could not be analyzed. Assignment of the spectral bands of the grafted acid was performed by comparison with spectra of the aminoalkyl-modified fibers and of their protonated forms. Modification of the fiber led to disappearance of the strong band at about 1516 cm^{-1} (protonated amino group vibrations), and the band at about 1698 cm^{-1} appeared. The bands at 3689 cm^{-1} were due to stretching of OH group of the phosphonic acid, and the absorption at around 3350 cm^{-1} was assigned to the zwitter-ion form of the grafted ligand.

Sorption of V(V), Mo(VI), and W(VI) ions with the prepared fibrous sorbents was studied.

Sorption of the ions with the B-4 sample was studied using the model solutions containing 1 to 4 mg/L of the extracted element.

pH of the model solutions was varied between 1 and 5; study of the neutral or alkaline solutions (pH > 5) was pointless, as under those conditions the extracted elements could precipitate in the form of hydrolyzed compounds.

Extraction of the studied ions was the most complete at pH 4; further experiments were performed at such acidity of the model solutions.

Equilibrium sorption capacity of the B-4 sorbent with respect to the studied ions was determined at pH 4.

It was found that the B-4 sorbent was efficient towards extraction of V(V) ions (350 mg per 1 g of the coating), whereas the capacity towards Mo(VI) (212 mg/g) and W(VI) (220 mg/g) ions was somewhat lower.

To conclude, the prepared fibrous sorbents coated with nanosized organosiloxane polymer material containing aminomethylenephosphonic ligands are promising materials for extraction of V(V), Mo(VI), and W(VI) ions from natural and industrial solutions.

EXPERIMENTAL

For preparation of aminoalkyl-containing fibers, oligo(aminoalkyl)ethoxysiloxanes of the desired composition and structure were used [6].

Solvents (toluene, benzene, diglyme, and dioxane) were dried over metal sodium and distilled. Chloroform was distilled over P_2O_5 after shaking with concentrated H_2SO_4. In some experiments, the ^{13}C-enriched paraformaldehyde (Fluka) was used. H_3PO_3 (99%, Aldrich) was used as received.

IR spectra were recorded using the Specord M80 spectrometer.

Concentration of the grafted groups was determined from elemental analysis and potentiometric titration data. Content of phosphorus was determined as described elsewhere [10]. To do so, 0.1 g of the sorbent was put into the 50 mL volumetric flask, and then 0.6 mL of glacial acetic acid and 0.2 mL of Br_2 were added. The mixture was heated at the sand bath till bromine discoloration, and then 5 mL of 25 wt % solution of sulfuric acid, 10 mL of 0.25 wt % solution of sodium vanadate, and 10 mL of 5 wt % solution of ammonium molybdate were added. The solutions were diluted with distilled water to a total volume of 50 mL and incubated during 30 min till the coloration development. Absorbance of the mixtures was measured at 430 nm (the KFK-2 photocolorimeter, optical path 1 cm). Calibration was performed using the unmodified fiber with potassium dihydrophosphonate additive. The calibration equation was as follows: $\varphi_3 = 1.13D_{430} + 0.052$ ($r = 0.998$) with D_{430}, the solution absorbance and φ_3, concentration of the grafted aminomethylenephosphonic acid.

Protolytic properties of the sorbents were studied by pH-metric heterogeneous titration. To do so, 0.2 g of the sorbent was put into the beaker containing 25 mL of KCl solution (0.1 mol/L), and was titrated with 0.1 mol/L NaOH upon stirring.

Preparation of aminoalkyl-containing fibers *(general procedure).* Oligo(aminoalkyl)ethoxysiloxane was grafted onto the fiber surface via successive impregnation of the fiber with alcoholic or aqueous solution of the oligomer (1 wt %), drying in air, and thermal treatment (140°C, 20 min). The procedure was repeated several times, till the desired mass increase (1, 3, 5, or 10%) was achieved.

The aminoalkyl-containing samples were protonated with aqueous solution of acetic acid (3 wt %), followed by washing with methanol and air-drying. The samples were protonated immediately before their modification via the Kabachnik–Fields reaction.

Preparation of *N*-alkylamino-*N,N*-dimethylphosphonate-containing sorbents *(general procedure*, S-1 as an example). 10 g of protonated aminoalkyl-containing fiber S-1 (grafted NH_2 groups concentration of 1.3 mmol/g), suspended in mixture of 30 mL of benzene and 90 mL of diglyme, was introduced into the three-necked flask equipped with mechanical stirrer, dropping funnel, and reflux condenser with calcium-chloride tube. Then, 0.8 g (26 mmol) of paraformaldehyde was added, and 21.32 mL (26 mmol) of H_3PO_3 (10 wt % solution in diglyme) was introduced. After the acid addition, the mixture was heated up, collecting the azeotropic distillate (Dean–Stark apparatus). After water elimination had ceased, the modified fiber was separated off, washed with diglyme and ethanol, and dried in air at 100°C and then in vacuum at the same temperature.

Other fibers were modified similarly.

Determination of the modified fiber sorption capacity. 50 mg of the sorbent was vigorously stirred with 50 mL of the metal salt solution in aqueous hydrochloric acid (pH 1 to 5, the metal ion concentration of 1 to 4 mg/L). After equilibration, the sorbent was filtered off and washed with distilled water at the filter. The aqueous fractions were combined, and residual metal ions were determined by photometry (KFK-2) [11]. Sorption capacity was expressed as metal ion content in 1 g of the polymeric coating upon saturation. The model solutions were prepared from solid NH_4VO_3, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and $Na_2WO_4\cdot 2H_2O$ (*chemical pure* grade).

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