

Bionanocompositional chitosan-silica sorbent for liquid chromatography

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Abstract

Preparation of hybrid nanocompositional chitosan/silica sorbent was carried out. It was shown that formation of gel in sol–gel process of hydrolytic polycondensation of tetraethoxysilane (TEOS) with including of chitosan consists of two stages. Suppression of crystallization of chitosan in obtained two-phase system and changes in IR spectra are evidenced of interactions between molecules of chitosan and silanol groups of silica network. The resulting hybrid chitosan/silica sorbent was tested by high-performance liquid chromatography (HPLC).

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1. Introduction

Nanocompositional materials obtained by sol–gel process in situ through the interaction of organic polymers with tetraethoxysilane (TEOS) become widespread due to simplicity of process and effectivity of approach to the development of organic-silica polymeric materials which combine the hardness of silica and polymer functional properties [1–4].

Natural materials are attractive candidates as aerogel precursors due to their potentially low cost and environmentally benign nature. Additionally, these may provide new application opportunities for hybrid materials. Thus, nanocomposite materials, in which the organic phase consists of biopolymers, are of special interest [5,6].

Chitosan is one of such perspective polymers, possessing the regular chain structure and forming true solutions in the dilute water solutions of organic and inorganic acids that allow to include its in sol–gel process in situ in order to prepare the hybrid nanocompositional sorbent for liquid chromatography. Various derivatives of chitosan immobilized on silica gel were proposed to use as chiral selectors for high-performance liquid chromatography (HPLC) [7,8].

However, derivatization can to be accompany with blocking of chitosan functional groups. Chitosan was immobilized on silica gel by adsorption in order to avoid of that [9,10]. Derivatives of chitosan and chitosan must display specific interactions with the silica gel surface: chemical bonding or specific adsorption.

The aim of this paper is to prepared hybrid chitosan/silica sorbent including of chitosan into polysiloxane network during formation of silica gel in hydrolytic polycondensation of TEOS or oligomer of polyethoxysiloxane (PEOS) (so-called sol–gel process in situ).

We were studied the interaction of chitosan with TEOS and oligomer of PEOS. The spherical morphology only was observed for product of interaction of chitosan with oligomer of PEOS. Silica gel encapsulated with chitosan and silica gel modified by adsorption of chitosan was prepared for comparison with hybrid chitosan/silica sorbent. All sorbents were tested by HPLC using hexane/2-propanol mixture as mobile phase.

2. Experimental

2.1. Measurements

The formation of hybrid material at interaction of TEOS with chitosan in acetic acid was studied by using Reotest-2

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rotary viscometer (Veb MLW, Dresden, Germany). IR spectra were registered in Specord 75-IR spectrometer (Bruker, Ettlingen, Germany). The X-ray diffraction patterns were obtained in a Dron-3M (LOMO, Leningrad, USSR). Morphology of hybrid chitosan/silica sorbent was examined on a TEM-100 microscope from Sumi work (Sumi, Ukraine).

The chromatographic experiments were performed on a Shimadzu LC-10Avp Series equipped with a UV-Vis detector (Shimadzu, Kyoto, Japan). The chitosan/silica sorbents were packed into stainless steel columns (150 mm × 4.6 mm i.d. and 100 mm × 4.6 mm i.d.) by the slurry method. The volume of sample injected was 3 μ l.

The hexane/2-propanol mixture was used as mobile phase and *o*-, *m*-, *p*-nitroanilines were used as testing compounds.

2.2. Preparation of chitosan/silica sorbents

High molecular chitosan (M_w 200 000, The Center of Bioengineering RAS, Moscow, Russia) and TEOS from Angarsk work (Angarsk, Russia) (99% purity) were used.

Oligomer of PEOS was obtained by method described previously [11].

Microspherical silica gel (5 μ m) was prepared from oligomer PEOS by method described previously [12].

Silica gel S-300 (5 μ m) was obtained from Lachema 5 (Czechia).

2.2.1. Preparation of chitosan/silica sorbent by sol-gel method

Hundred microliters of 1% chitosan solution in 2% acetic acid and 30 ml of TEOS (or 10 ml of PEOS oligomer) were mixed for 0.5 h at 1800 rpm. Then mixture was poured out into the flask containing 200 ml of 3% ammonium hydroxide solution and was kept for 24 h. The resulting product was filtered off and thoroughly washed in water until neutrality, ethanol, hexane, whereupon dried out at first on the air after that at 80 °C.

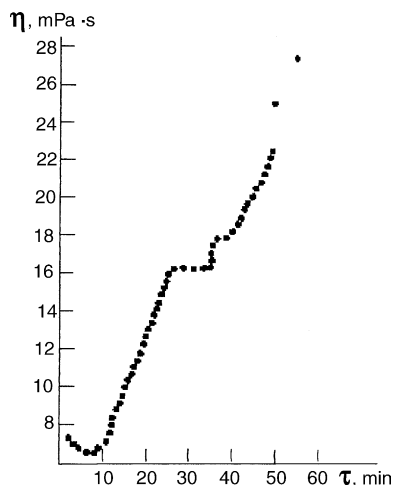


Fig. 1. Dynamic viscosity curves at formation of chitosan/silica hybrid.

The powder, consisting of 1–20 μ m particles of various shapes was obtained by using TEOS. The spherical particles (1–10 μ m) were obtained only using PEOS oligomer. The content of chitosan in this product was 5.1%.

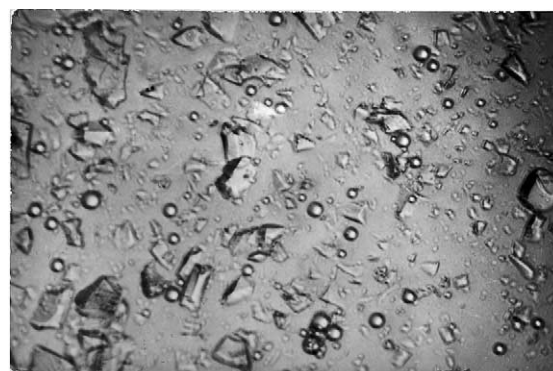
The fraction of 5 μ m particles was separated by method of sedimentation.

2.2.2. Preparation of microspherical silica gel capsulated by chitosan

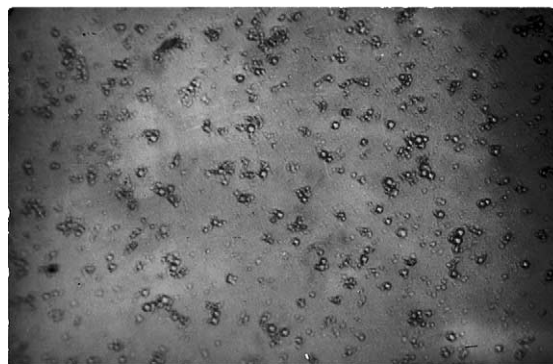
Five grams of microspherical silica gel was dispersed into 100 ml 1% chitosan solution in 2% acetic acid. Then, 3% ammonium hydroxide solution was added drop-wise into suspension as precipitant of chitosan on the particle surface. The capsulated sorbent was filtered off, washed and dried as described above. The content of chitosan was 1.51%.

2.2.3. Preparation of silica gel modified by adsorption of chitosan

Five grams of silica gel S-300 was dispersed into 100 ml chitosan solution in 2% acetic acid for 1 h. After filtering off, washing and drying as described above was obtained the product, containing 1.5% of chitosan.



(a)



(b)

Fig. 2. Micrographs of hybrid chitosan/silica sorbent prepared by using TEOS (a) and PEOS oligomer (b) in sol-gel process in situ.

3. Results and discussion

Structural features of reacting components evidently influences on kinetics and mechanism of gel formation process. As shown viscometric study the gel formation process consists of two stages. In first stage the initial gel forming system represent to be a mixture of 4% chitosan solution in 80% solution of acetic acid and TEOS, which show the properties of true newtonic liquid with $\eta = 8 \text{ mPa}\cdot\text{s}$. The graph in Fig. 1 are plot of the dynamic viscosity, η , as a function of time for TEOS solution during the sol–gel reaction together with chitosan carried out at 60°C .

First induction period is observed from 10 min to 27 min after which probably is started growth of siloxane chains forming as a result of hydrolytically polycondensation of

TEOS grafting to chitosan that is started growth of linear macromolecules. In curve this stage is shown as spasmodic growth of effective viscosity.

Second induction period from 27 to 35 min precedes to formation of spatial network, marked by second step of function $\eta = f(\tau)$ in which viscosity of mixture is $16 \text{ mPa}\cdot\text{s}$. Further it follows a formation of unified network involving all volume.

Taking into account obtained results the synthesis of hybrid chitosan/silica sorbents by using TEOS and PEOS oligomer as a silica precursors were carried out. The use of TEOS leads to formation of powder consisting of particles with different shape (spherical, oval, right-angled and triangular) and size to $10 \mu\text{m}$ (Fig. 2a). The product with particles of spherical shape only was obtained by using

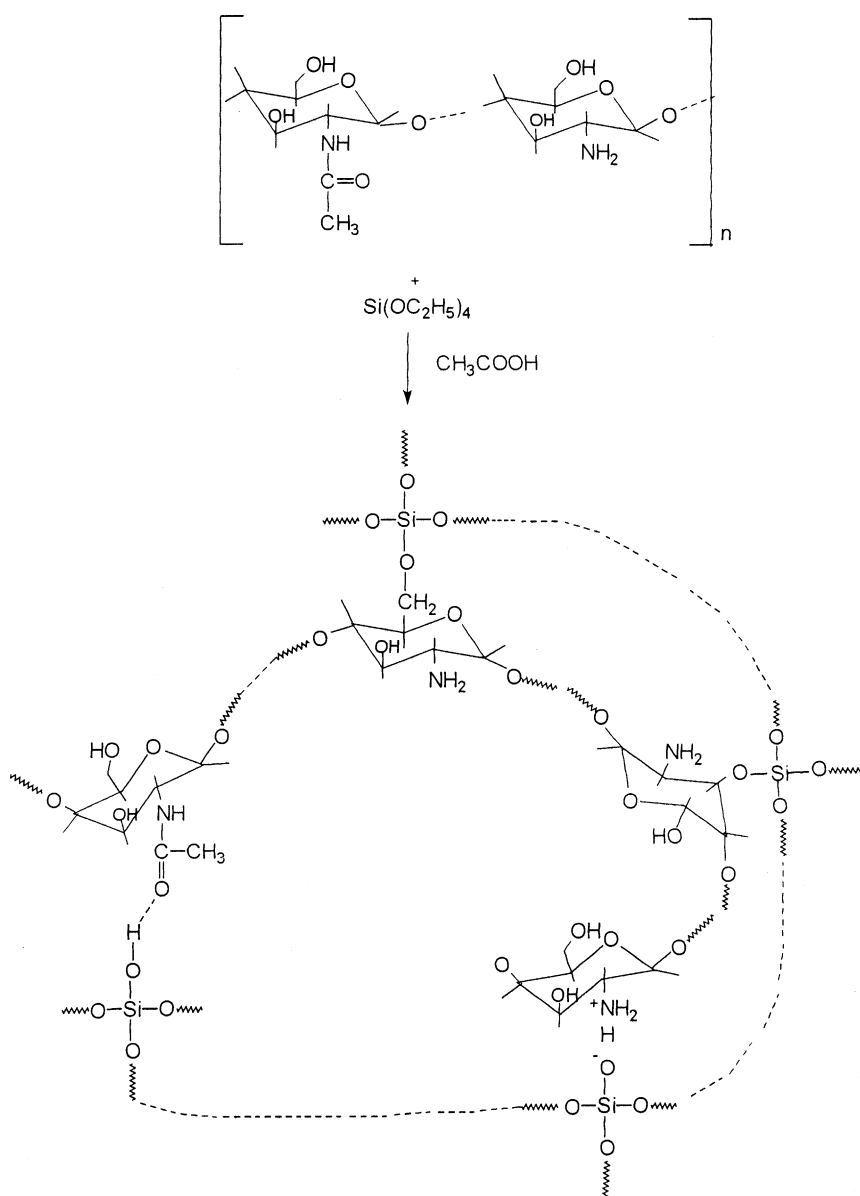


Fig. 3. Hypothetic scheme of interaction between silica and chitosan.

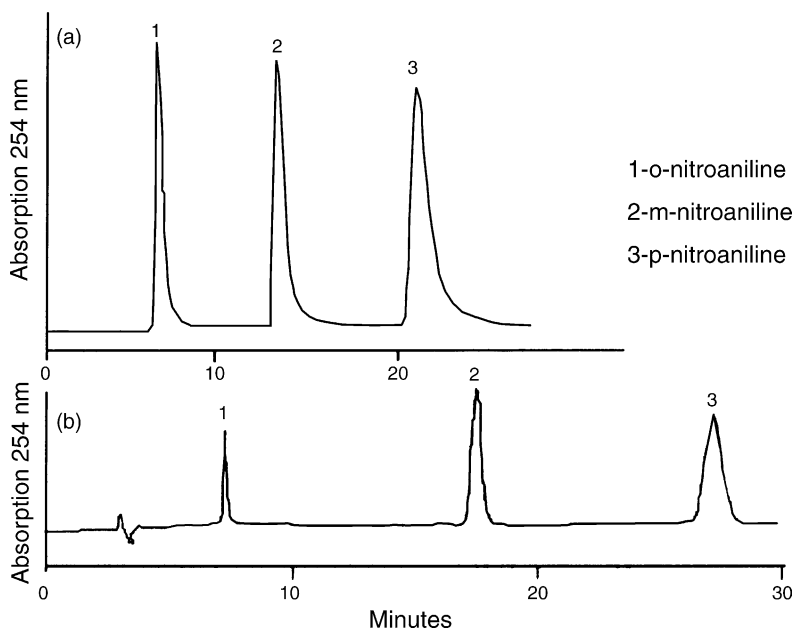


Fig. 4. Resolution of tested compounds on silica gel modified by adsorption of chitosan, column (150 mm \times 4.6 mm i.d.) (a) and silica gel encapsulated by chitosan, column (100 mm \times 4.6 mm i.d.) (b) (flow rate: 1 ml/min; UV detection: 254 nm).

in sol-gel process of oligomer PEOS by viscosity 96 cSt (Fig. 2b).

Diffractograms of samples of hybrid sorbent is evidence of amorphous character of structure while initial chitosan is characterized by clear peaks at 2θ equal 20, 22 and 25° . Apparently, suppression of crystallization of chitosan occurs in hybrid material.

In IR spectra are revealed bands at $1090\text{--}1020\text{ cm}^{-1}$, relating to Si–O–Si and Si–O–C valent vibrations. Wide band

of absorption in the field of 3400 cm^{-1} related to symmetrical valent vibration of free NH_2 and OH groups and H-bonding interactions. On this data difficult to detect the interaction between components but changes in absorption bands of amide-groups of chitosan in the field of 1650 cm^{-1} and silanol group in the field of 960 cm^{-1} allow to assume a formation of H-bonds between silanol groups silica network and amide- and oxy-groups of chitosan, the ionic bonds between chitosan amino groups and silanol groups,

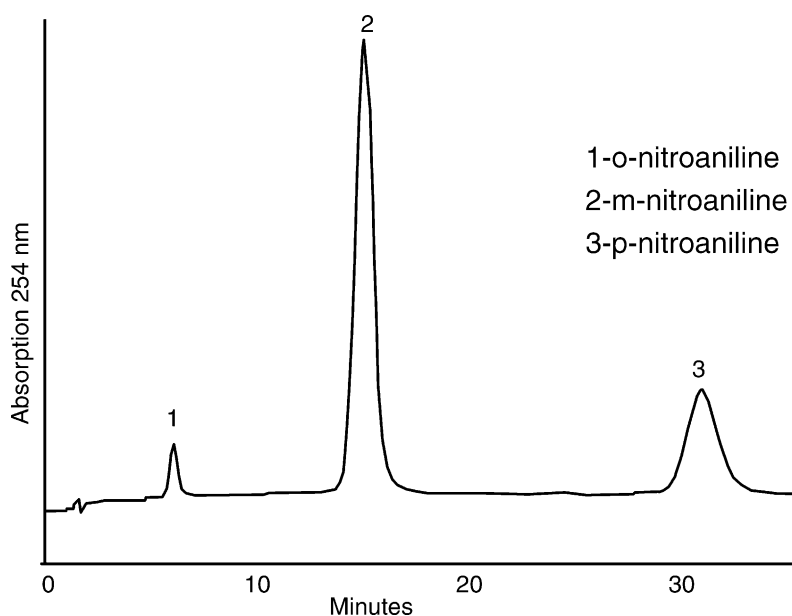


Fig. 5. Resolution of tested compounds on hybrid chitosan/silica sorbent prepared by sol-gel method, column (100 mm \times 4.6 mm i.d.) (flow rate: 1 ml/min; UV detection: 254 nm).

Table 1
Chromatographic results

Nitroaniline compounds	Encapsulated sorbent		Hybrid sorbent	
	α	R_s	α	R_s
<i>o</i> -/ <i>m</i> -	3.8	3.4	3.0	1.6
<i>m</i> -/ <i>p</i> -	1.6	1.7	2.2	1.6
<i>o</i> -/ <i>p</i> -	6.3	4.4	6.5	3.5

as well a covalent bonds in result of esterification of chitosan hydroxy-groups on silanol groups of silica network (Fig. 3).

Such bonding of chitosan in silica network is important, since non-bonded amino group will permit to realize different chemical transformation for preparation of products with special properties (biocatalysts, supports for chromatography, etc.).

The chromatographic results show that hybrid chitosan/silica sorbent prepared by sol–gel method (hybrid sorbent) and encapsulated silica gel by chitosan (encapsulated sorbent) on the separation efficiency of tested compounds expressed by resolution (R_s) and separation factor (α) are similar (Table 1). However they are differed from adsorptional modified silica gel by absence of tails in chromatographic peaks (Figs. 4 and 5).

Thus, chitosan/silica sorbent prepared by sol–gel method on the separation efficiency does not yield to sorbents of silica gel encapsulated of chitosan and modified of chitosan by adsorption method.

However, the way of its preparation is remarkable for procedure in one stage due to use of sol–gel process in situ.

4. Conclusion

New hybrid chitosan/silica sorbent was prepared by sol–gel method in situ. It was shown that gel formation consist from two stage. Suppression of crystallization and changes in absorption bands of IR spectra of hybrid chitosan/silica sorbent are evidenced about creation of structure determined their properties, which is reflected on chromatographic behavior of this sorbent.

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