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Full Articles

Thiocarbamoyl chitosan as a novel sorbent with high sorption capacity and selectivity for the ions of gold(III), platinum(IV), and palladium(II)

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Thiocarbamoyl chitosan (TCC) was synthesized by grafting thiourea on chitosan backbone in eutectic composition of ammonium thiocyanate—thiourea. Insoluble products with the amino group functionalization degree of 0.3—1.1 can be prepared by varying the conditions of polymer-analogous (synthesis in a gel) transformation. Structure of the synthesized chitosan derivatives was characterized by elemental analysis, diffuse reflectance infrared spectroscopy, and the solid state ^{13}C NMR. Study of sorption properties of TCC shows high sorption capacity and selectivity for the ions of gold(III), platinum(IV), and palladium(II) as evidenced by results obtained at pH 2 in the presence of 100—1000-fold excess of iron(III), copper(II), zinc(II), and nickel(II). Sorption capacity of TCC for all ions increases with the increase in the degree of substitution and changes in the series: $\mathrm{Au^{III} > Pd^{II} > Pt^{IV}}$.

Key words: chitosan, thiocarbamoyl chitosan, selective sorbents, ions of gold(III), platinum(IV), and palladium(II).

Due to the hydrophilic nature, polysaccharides possess high sorption capacity for different substrates, including the metal ions. As the adsorbent aminopolysaccharide chitosan is superior to the known cellulose-based materials owing to the presence of the amino groups, which compared with the hydroxyl group are the stronger electron donors for metal ions.[1,2] The cross-linked chitosan can adsorb the ions of nearly all elements of the Periodic Table.[3] Development of mining technology, the separation and recovery of noble metals are topical issues. They involve not only improvement of the separation procedures but also development of novel sorbents with advanced uptake performance. There are known several sorbents designed specifically for the gold(III) ions and the

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platinum group metals. They are based on copolymer of ethyleneglycol vinyglycidyl ether and vinylpyrrolidone modified with thiourea[4] and also on the basis of polymeric thioether, polythiopropane.[5] General disadvantages of the above-mentioned materials, which limited their applications, are low sorption capacity and low accessibility of the sorbents with a complex polymeric structure.

Chemical modification of chitosan by grafting the sulfur-containing groups on the chitosan backbone allows one to increase its sorption capacity and selectivity for the platinum group metals and the precious metals.[6—8] However, the density of the sulfur-containing fragments sufficient to ensure the higher sorption capacity cannot be achieved employing the above-mentioned modification methods. The aim of the present work was to develop the synthetic method for thiocarbamoyl chitosan characterized by a high functionalization degree and investigate its sorption properties for ions of platinum(IV), palladium(II), and gold(III).

Results and Discussion

Previously[9] for the preparation of thiocarbamoyl chitosan (TCC) the use of "the synthesis in a physical gel" procedure was suggested, which included the treatment of chitosan with lithium thiocyanate. This procedure is based on the property of chitosan to disperse, swell, and partially dissolve in the solutions of lithium thiocyanate discovered in our group. It is of note that the water molecules are the competitive nucleophile for the starting reactants and for the reaction product; the side reactions with water molecules lead to the destruction of the thiocarbamoyl group and, consequently, to the decrease in the degree of substitution (*DS*). To overcome this problem, the eutectic two-component composition of ammonium thiocyanate—thiourea rather than water was used to form gel. This eutectic composition serves simultaneously as both the solvent and the reactant, *i.e.*, the reaction proceeds in a nonaqueous gel (Scheme1).

Conditions of thiocarbamoylation of chitosan and the degrees of substitution (the ratio of the amino group functionalized by the thiourea residue to the total number of amino groups in raw chitosan) are given in Table 1. The reaction mixture is a soft gel, which was stored at a certain temperature without stirring. The optimum reaction temperature is 130 °C. At $T < 110$ °C, the reaction mixture is heterogeneous and that decreases the reaction rate; at $T > 150$ °C, the product yield is markedly decreased due to destruction of the polymeric chain. Optimum reaction time is ~4 h. Degree of substitution remains low, when the reaction time was reduced to less than 2 h, while no increase in the substitution degree was observed, when the reaction time was extended beyond 6 h. After the reaction was completed the gel was subjected to the cold extraction with water until no SCN^- ion could be detected in the extract. The polymer prepared is insoluble neither in acidic nor in basic medium.

The composition and structure of the polymer were characterized by elemental analysis (see Table 1) and diffuse reflectance IR spectroscopy. It is impossible to reveal the thiocarbamoyl groups against the background of the intensive absorption bands of the residual acetyl groups (degree of acetylation (*DA*) — 0.16) at 1655 cm^{-1} (Amide I) and at 1592 cm^{-1} (Amide II). However, in differential spectrum obtained by the subtraction of the spectrum of the product from the spectrum of the raw chitosan, a band at 1404 cm^{-1} assigned to the $\mathrm{S{=}\underset{|}{C}{-}N\langle}$ group was observed. The presence of the absorption band at 2057 cm^{-1} characteristic of the S=C=N— fragment indicates small content of the thiocyanate ions, which can be ionically bound onto the polymeric chain. The presence of chitosan thiocyanate is inevitable due to isomerization (Scheme 2) known for ammonium thiocarbamide and ammonium thiocyanate in different protic solvents.[10] Thiocyanic acid (pK_a 0.82) is a fairly strong acid and its total removal by water is impossible.

The grafting of the thiocarbamoyl group was ambiguously shown by the solid state ^{13}C NMR spectroscopy. In

Scheme 1

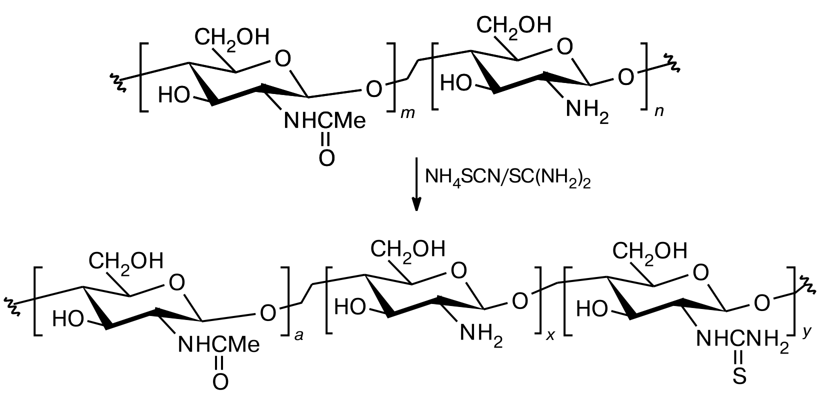
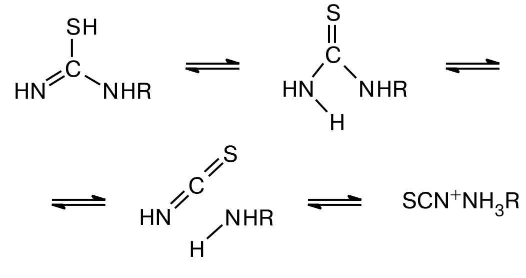


Table 1. Reaction conditions of chitosan thiocarbamoylation and degree of substitution (*DS*) of the products

Reaction conditions			Product characteristics				
T/°C	Reactant : Chitosan	Time/h	Yield (%)	N (%)	S (%)	n_N/n_S	*DS*
			Effect of temperature				
110	14 : 1	2	49	9.26	5.18	4.08	0.22
130	14 : 1	2	42	9.04	6.83	3.02	0.50
150	14 : 1	2	33	11.19	10.35	2.47	0.66
			Effect of the reactant excess				
130	1 : 1	4	72	8.04	1.64	11.2	0.10
130	2 : 1	4	71	9.13	4.28	4.88	0.26
130	4 : 1	4	86	9.65	9.26	2.34	0.75
130	10 : 1	4	85	10.02	12.11	1.89	1.12
			Effect of the reaction time				
150	14 : 1	5	13	19.36	13.76	3.22	0.45
150	14 : 1	8	15	17.81	16.32	2.49	0.67
110	14 : 1	5	91	9.56	7.87	2.78	0.56
110	14 : 1	8	90	9.72	8.04	2.76	0.57

Scheme 2



R = H, chitosan

Fig. 1, the ^{13}C NMR spectra of chitosan species with different degrees of thiocarbamoylation are shown. In contrast to the spectrum of the raw chitosan, the ^{13}C NMR spectra of TCC along with the signal at δ 175 characteristic of the C atom of the carbonyl group exhibit the signal at δ 184, which can be assigned to the carbonyl C atom of the thiocarbamoyl group. The relative intensity of this signal increases with an increase in the degree of substitution. The analytical data suggest the formation of intermolecular covalent cross-links between amino groups of the neighboring macromolecules: RNHCSNHR. However, the polymer possess high swelling ability in water, hence, the level of cross-linking is probably not high and, in the ^{13}C NMR spectra, no signals were assigned to the cross-links.

Modification of chitosan under the conditions described above serves both to graft the functional group on the chitosan backbone and to form the cross-linked supramolecular structure of the polymer, an important advantage for its further application for the uptake of metal ions. Sorption properties of TCC with the degree of substitution of 0.4, 0.7, and 0.9 for the ions of platinum(IV), palladium(II), and gold(III) were studied (Table 2). As it follows from the data obtained, the sorption capacity of the sorbents increased with an increase in the degree of substitution, *i.e.*, the number of the sulfur atoms of the thiocarbamoyl groups. The maximum sorption capacities for the Pt^{IV}, Pd^{II}, and Au^{III} ions of 1.25, 3.43, and 3.82 mmol g^{-1}, respectively, were achieved. The sorption capacity of TCC at pH 2 decreases in the series: $Au^{III} > Pd^{II} > Pt^{IV} \gg Cu^{II} > Fe^{III} > Zn^{II}$. The comparison of the sorption capacity of TCC for 3d and noble metals shows that introduction of the sulfur atom, which is a soft base, noticeably increases the affinity for the precious metal ions, which are the soft acids according to the concept of hard and

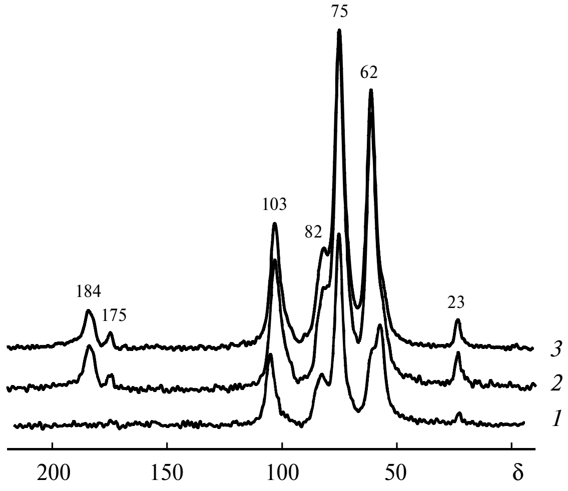


Fig. 1. CP-MAS ^{13}C-{^{1}H} NMR spectra of raw chitosan (*1*) and TCC with *DS* = 0.78 (*2*) and 1.12 (*3*).

Table 2. Data on static exchange capacity of TCC with different degree of substitution (*DS*), pH 2

DS	Exchange capacity/mmol g^{-1}					
	Au^{III}	Pd^{II}	Pt^{IV}	Fe^{III}	Cu^{II}	Zn^{II}
0.4	2.07±0.07	1.78±0.04	0.86±0.03	0.010±0.002	0.052±0.002	0.004±0.003
0.7	3.15±0.08	2.99±0.05	1.16±0.05	0.011±0.002	0.047±0.003	0.002±0.001
0.9	3.82±0.09	3.43±0.08	1.25±0.07	0.010±0.003	0.047±0.006	0.002±0.002

soft bases and acids defined by Pearson (see Table 2). As a result, no effect on the uptake of platinum, palladium, and gold ions were found on evaluating the sorption selectivity at pH 2 using the solutions containing the interfering iron(III) ions in the 50—1000-fold excess relative to the extracted ion (concentration of 0.1—0.4 μg L^{-1}). Thus, this sorbent can be used for extraction of gold from the model and real solutions containing the mixtures of the gold(III) and iron(III) ions, including hydrometallurgical effluents and solutions obtained by oxidation of the gold-containing organic materials, such as brown coal and peat.

In summary, we were able to develop the method for the preparation of the sorbent for selective and efficient precious metal uptake from the solutions containing interfering ions.

Experimental

Chitosan (Sonat, Moscow) with the degree of acetylation *DA* = 16% determined by the ^{1}H NMR spectroscopy was used. The average molecular mass of chitosan of 2.5 • 10^5 Da was determined by viscometry.[11] All reagents were used as purchased. Elemental analysis was performed on a Perkin—Elmer automated analyzer. The degree of substitution was calculated based on the elemental analysis data by the following equation $DS = n_S/(n_N - n_S)$, where n_N is nitrogen content (mol.%), n_S is sulfur content (mol.%). The IR reflection spectra were recorded on a Perkin—Elmer Spectrum One spectrometer equipped with diffuse reflectance accessory (DRA). Solid-state ^{13}C NMR spectra were recorded on a Bruker Avance AV-300 spectrometer (300 MHz).

Thiocarbamoyl chitosan (TCC). A mixture of chitosan (3.3 g, 0.02 mol), ammonium thiocyanate (4.22 g, 0.056 mol), and thiourea (2 g, 0.026 mol) was heated up to 130 °C for 10 min (gel formation step), then heated at 130 °C for 4 h. After cooling, the product was subjected to cold extraction with water (in the Soxhlet extractor) until no SCN$^-$ ion (the salts of Fe^{III}) could be detected and dried at 50 °C to constant weight. Yield 3.7 g. Found (%): C, 37.79; H, 6.32; N, 9.63; S, 8.47. For degree of substitution of 0.68 was calculated (%): C, 37.52; H, 6.28; N, 9.78; S, 8.86.

Study of sorption capacity of TCC. TCC (2.5 mg) was stirred with a solution containing either Pt^{IV} (20—300 mg L^{-1}) or Au^{III} (50—800 mg L^{-1}), or Pd^{II} (50—800 mg L^{-1}) (5 mL) at pH 2 (0.01 *M* HCl) for 18 h. The sorption capacity was calculated by the comparison of the initial and resulting metal concentrations in the solution determined by atomic absorption spectroscopy (Thermo Soolar M6, USA). Sorption of the Fe^{III}, Zn^{II}, and Cu^{II} ions were carried out using the solutions with increasing concentrations of metal in the range of 10—300 mg L^{-1} (0.01 *M* HCl), the sorption capacity was calculated by the amount of metal on the loaded sorbent after its decomposition with aqua regia. The metal concentrations were determined by the atomic absorption spectroscopy.

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