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Thiocarbamoyl chitosan: Synthesis, characterization and sorption of Au(III), Pt(IV), and Pd(II)

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ABSTRACT

Here we suggest a new method of chitosan sulfur derivatives (thiocarbamoylchitosans, TC-chitosans) synthesis via reaction in eutectic two-component system ammonium rodanide–thiourea that allows significant increase of substitution degrees at the reduced time and reagent consumption as compared to conventional synthetic procedures. The sorption properties of TC-chitosans with substitution degrees (DS) from 0.4 to 0.9 toward Au(III), Pt(IV), Pd(II) ions were studied in chloride solutions, including systems with 10 to 1000-fold excess of Fe(III), Cu(II), and Zn(II) over the precious metal ions content. The sorption capacities of TC-chitosans increase with DS and change in the row: Au(III) > Pd(II) > Pt(IV) ≫ Cu(II) > Fe(III) > Zn(II). The maximum sorption capacities of TC-chitosan with DS 0.9 for Pt(IV), Pd(II), and Au(III) were 1.24 mmol/g, 3.43 mmol/g, and 3.81 mmol/g, respectively. Characterization of precious metals oxidation states by the XPS method after the sorption on TC-chitosan revealed that the platinum and gold recovery occurred with reduction of Au(III) to Au(I)/Au(0) and Pt(IV) to Pt(II).

1. Introduction

New efficient selective sorbents are today in high demand, especially, in the filed of recovery, regeneration, and separation of precious and other industrially important metals (Muzzarelli, 1977, 2011). Aminopolysaccharide chitosan is a promising polymeric matrix for the development of functional sorption materials, first of all, due to its hydrophilic nature and the presence of amino group – a stronger donor of electrons compared to hydroxyl groups of other polysaccharides (Babel & Kurniawan, 2003; Guibal, 2004; Varma, Deshpande, & Kennedy, 2004), and secondly, due to vast possibilities of chitosan chemical modification using its two reactive hydroxyl groups and amino group. A number of chitosan functional derivatives with enhanced selectivity and sorption capacities toward precious metal ions are already known (Fujiwara, Ramesh, Maki, Hasegawa, & Ueda, 2007; Guibal, Sweeney, Vincent, & Tobin, 2002; Guibal, Sweeney, Zikan, Vincent, & Tobin, 2001; Zhou, Liu, & Liu, 2009).

The classical approach to the synthesis of sorption materials for selective recovery of precious metals ions is based on the introduction of nitrogen and sulfur-containing functional groups to the polymer backbone. A purposeful chemical modification of chitosan with sulfur-containing groups to enhance its sorption properties toward precious metals ions is known in the literature. Introduction of thiourea and rubeanic acid to chitosan via glutaraldehyde linkers resulted in increase of the sorption capacity up to 1.8 and 3.2 mmol/g for Pt(IV) and Pd(II), respectively (Guibal et al., 2002, 2001). However, insufficient substitution degree did not allow demonstrating to a proper extent all features of chitosan chemical modification. Surprisingly, the residues of N-substituted thiourea covalently grafted directly to the polymer backbone with DS 0.9 did not provide increase of the sorption capacity above the value of 0.3 mmol/g for Pd(II) and Au(III) (Baba, Noma, Nakayama, & Matsushita, 2002). Introduction of unsubstituted thiourea residues to chitosan at very low substitution degree (DS 0.035) was, however, sufficient to bind Ag(I) and render the polymer fungicidal properties (Chen, Wu, & Zeng, 2005). Recently, we have attempted to modify chitosan with thiourea and rubeanic residues without linkers (Pestov, Koryakova, Leonidov, & Yatluk, 2010) that yielded derivatives with sulfur-containing functional groups directly on a polymer backbone at medium substitution degrees (0.31 and 0.43 for thiourea and rubeanic residues, respectively) and maximum sorption capacities for Pt(IV) and Pd(II) 1.1 and 2.5 mmol/g, respectively. This allowed concluding that modification using linkers, which provide higher mobility of functional groups relative to the macromolecular chain, gives at relatively low DS derivatives with significantly enhanced sorption properties. The sorption capacities of some other sulfur derivatives of chitosans was evaluated toward

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ions of 3d-metals only (Chang, Zhang, & Wang, 2009; Metwally, Elkholy, Salem, & Elsabee, 2009; Muzzarelli, Tanfani, Mariotti, & Emanuelli, 1982).

The available data show that (i) there are no revealed correlations between chitosan sulfur derivatives DS and sorption properties toward ions of precious metals; (ii) most studies deal with Pt(IV) and Pd(II) ions, although the same derivatives can be promising for Au(III) recovery as well; (iii) there is a lack of data on the method of synthesis and sorption properties of highly substituted sulfur derivatives of chitosan. The present study was aimed at the development of a simple synthesis of thiocarbamoyl chitosan, providing highly substituted derivatives at reduced reagents consumption and time, and to characterization of the structure and sorption properties of these derivatives for Pt(IV), Pd(II), Au(III) ions with the focus on the recovery mechanism and the effect of DS on selectivity and sorption capacity.

2. Materials and methods

2.1. Materials

Chitosan was purchased from JSC "Sonat" (Moscow, Russia). The degree of acetylation (DA) was determined by ^{1}H NMR spectroscopy to be 0.16; average molecular weight of 2.5×10^5 Da was measured using viscometry according to Gamzazade et al. (1985). Thiourea, ammonium thiocyanate, hydrazine hydrate solution 80% and *N*,*N*-dimethylhydazine were supplied by Sigma–Aldrich (analytical grade).

2.2. Synthesis of thiocarbamoyl chitosan derivatives

Thiocarbamoyl chitosan (TC-chitosan) derivatives were synthesized according to the following procedure: the mixture of 3.96 g (0.024 mol NH_2-groups) chitosan, 5.04 g (0.065 mol) ammonium thiocyanate and 2.4 g (0.031 mol) thiourea was heated up to 130 °C, kept under this temperature for 10 min before formation of a gel-like mass and then extra 4 h under the same temperature, then cooled. The obtained product was extracted by cold water for 48 h until negative reaction of washing waters on SCN^- ions (color reaction with Fe^{3+}) and air-dried. The yield was 4.5 g. The found elemental composition, % was: C, 37.79; H, 6.32; N, 9.63; S, 8.47. For the TC-chitosan with DS 0.7 and the formula: $(C_8H_{13}O_5N)_{0.16}(C_6H_{11}O_4N)_{0.16}(C_7H_{12}O_4N_2S)_{0.55}(C_{6.5}H_{10}O_4NS_{0.5})_{0.13}\cdot 1.05H_2O$ the theoretical elemental composition, % was: C, 37.52; H, 6.28; N, 9.78; S, 8.86. To obtain TC-chitosan with DS 0.4, the synthesis was performed for 2 h at the same ratio of reagents. The found elemental composition, % was: C, 40.43; H, 6.08; N, 9.91; S, 6.25. For the formula: $(C_8H_{13}O_5N)_{0.16}(C_6H_{11}O_4N)_{0.44}(C_7H_{12}O_4N_2S)_{0.35}(C_{6.5}H_{10}O_4NS_{0.5})_{0.05}\cdot 0.4H_2O$ the theoretical elemental composition, % was: C, 40.86; H, 6.36; N, 9.60; S, 6.09. TC-chitosan with DS 0.9 was obtained by mixing 3.96 g (0.024 mol NH_2) chitosan, 12.6 g (0.162 mol) ammonium thiocyanate and 6 g (0.078 mol) thiourea, reaction time was 4 h. The found elemental composition, % was: C, 36.63; H, 5.85; N, 10.53; S, 11.18. For the formula: $(C_8H_{13}O_5N)_{0.16}(C_7H_{12}O_4N_2S)_{0.84}(C_{6.5}H_{10}O_4NS_{0.5})_{0.06}\cdot 1.2H_2O$ the theoretical elemental composition, % was: C, 36.27; H, 6.11; N, 10.64; S, 11.14.

Hydrazinolysis was preformed by hot extraction of 1 g TC-chitosan (DS 0.7) with 25 ml of 80% hydrazine hydrate solution during 7 h and 24 h. When *N*,*N*-dimethylhydazine was used for the extraction, 5 ml of it was dissolved in 20 ml of the appropriate solvent. The hydrazionolysis products were characterized by the elemental analysis.

2.3. Characterization and identification of thiocarbamoyl chitosan derivatives

The elemental compositions of all products were determined on the Elemental Analyzer "Perkin Elmer". The DS were calculated from the elemental analysis data according to the formula: $DS = n_S/(n_N - n_S)$. FTIR spectra were recorded on the "Spectrum One" FTIR spectrometer (Perkin Elmer) using the Diffuse Reflectance Sampling Accessory (DRA). The solid-state ^{13}C NMR spectra were registered on a spectrometer Bruker Avance AV-300 at 300 MHz. Thermograms were recorded using the simultaneous thermal analyzer STA-409PC (Netzsch). The cation-exchange capacity was determined by mixing 0.1–0.25 g TC-chitosan with 10 ml of 0.1 M HCl in 50 ml flask and shaking it for 24 h; then the solution was titrated by 0.05 M NaOH with potentiometric detection of the end-point. The X-ray photoelectron spectroscopy (XPS) studies were carried out by means of the high vacuum photoelectron spectrometer (Specs, Germany) equipped with a monochromatic Mg Kα X-ray source. All the recorded peaks were shifted by the same value to set the C1s peak to 285.0 eV.

2.4. Sorption and desorption experiments

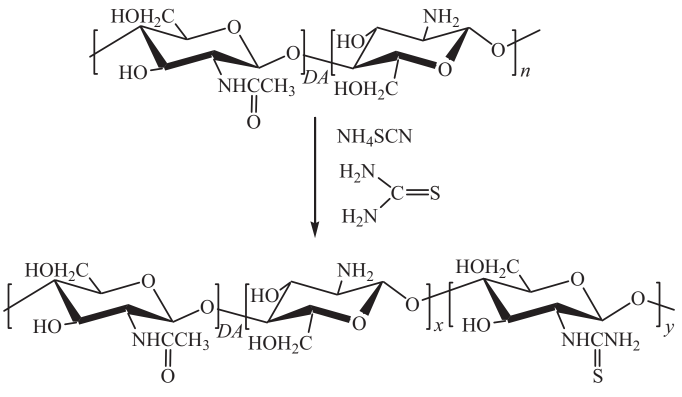
To study the sorption properties, TC-chitosan was shaken with solution of Au(III), Pt(IV), Pd(II) chlorides in 0.01 N HCl at solid:liquid ratio 1:2000 during 18 h at 200 rpm. The initial concentrations of metals were 20–300 mg/l for Pt(IV), 50–800 mg/l for Au(III), and 50–800 mg/l for Pd(II). The sorption capacities were calculated using the difference in initial concentration and equilibrium concentration of the metal ions determined by the atom absorption spectroscopy (Solaar M6, Thermo, USA). To eliminate possible artifacts, the sorption capacity toward Au(III), which was found to be reduced to Au(I)/Au(0) by TC-chitosan, was determined after decomposition of the sorbent in aqua regia by the same method. Sorption of Zn(II), Fe(III), and Cu(II) was studied from solutions with metal contents 10–300 mg/l (0.01 N HCl), sorption capacity was determined as a quantity of the metal found in the sorbent phase after decomposition.

Desorption of precious metals from TC-chitosan was studied for TC-chitosan (DS 0.9) containing 200 mg/g of gold, platinum, and palladium. TC-chitosan (5 mg) was shaken with eluent solution (thiourea/HCl, 2 ml) during 24 h, afterwards the contents of precious metals were determined by atomic absorption spectroscopy.

3. Results and discussion

3.1. Synthesis and characterization of thiocarbamoyl chitosans

The classical method of thiourea N-derivatives synthesis is based on reactions of thioisocyanates. This type of reaction is also known for chitosan (Baba et al., 2002), but it results in *N*,*N*′-disubstituted thiourea with a reduced sorption capacity as compared to mono-substituted thiourea. To obtain chitosan-based sorbents containing functional groups of mono-substituted thiourea, it is necessary to use rodanides in addition reactions or thiourea in reamidation reactions. Chen et al. (2005) used ammonia rodanide in addition reaction with chitosan, but the reaction was carried out in a diluted solution and the functionalization degree was negligible (DS 0.035). Using the gel-effect in polymeranalogous reactions, which we had recently discovered for chitosan (Pestov, Skorik, Kogan, & Yatluk, 2008; Pestov, Zhuravlev, & Yatluk, 2007), we performed synthesis of TC-chitosan via reaction with lithium rodanide (Pestov, Koryakova, et al., 2010). This transformation was feasible due to the ability of chitosan to swell and partially dissolve in aqueous solutions of lithium rodanide and form gel that ensured

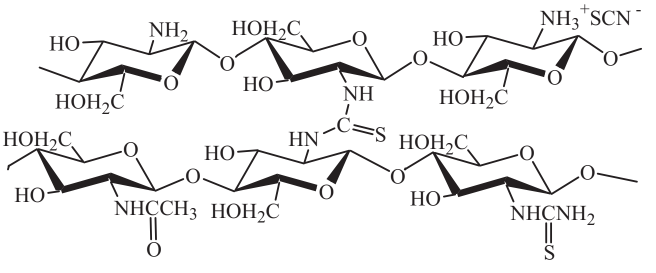


Scheme 1. Synthesis of thiocarbamoyl chitosan.

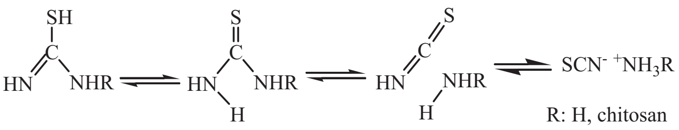
obtaining TC-chitosans with higher DS than it was described in the literature. This approach yields derivatives with medium DS, since water molecules act as competitive nucleophiles to both initial reagent and the reaction product, whose participation in side reactions results in destruction of thiocarbamoyl groups, and, hence, in the reduction of DS. To overcome this disadvantage, we used here for gel formation, instead of aqueous solution, the eutectic two-component system ammonia rodanide–thiourea, which acts as a solvent and reagent simultaneously. It turned out that chitosan in this two-component system forms gels at the temperature range 110–150 °C. Thus, to obtain highly substituted TC-chitosan, the reaction must be carried out in a non-aqueous gel (Scheme 1).

The chitosan modification results are presented in Table 1.The reaction mass comprises a soft gel, which was kept at specific temperature without agitation. 130 °C is the reaction optimal temperature; below 110 °C the medium is heterogeneous; above 150 °C the product yield reduces significantly due to the polymer chain destruction processes. The reaction conduction within shorter time periods (less than 2 h) is inefficient due to the low DS reached, while large time periods (more than 6 h) are not reasonable, since no further increase of DS was observed. After the reaction completion gel underwent extraction by water until negative reaction to SCN^- ions. The obtained polymer is soluble in neither acidic nor basic media that must result from intermolecular cross-linkage. Thus, the gel effect in chitosan polymeranalogous reactions is observed not only in aqueous gels but also in non-aqueous systems with holding all regularities typical for gel technology of chitosan modification. First of all, there is an optimum concentration of polymer for the reaction passing. Secondly, the polymer is obtained directly in a cross-linked form. This ensures advantages of a one-step synthesis of sorbent in comparison with approaches of consecutive chemical modification in solution and cross-linking steps.

Results of elemental analysis and IR spectroscopy allow attributing to TC-chitosan derivatives as in the following structure (Scheme 2).



Scheme 2. The general chemical structure of thiocarbamoyl chitosan (the ratio of functional groups is not presented).



Scheme 3. Isomerization and tautomerisation of thiocarbamoyl chitosan.

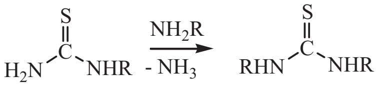
Analysis of the cation-exchange capacities of TC-chitosan (Table 1) shows the presence of non-substituted amino groups. IR-spectroscopy of diffuse reflection appears to be incapable to detect the presence of the thiocarbamoyl group on the background of intensive absorption bands “amide I” (1655 cm^{-1}) and “amide II” (1592 cm^{-1}) of residual acetyl groups (DA 0.16). However, after subtracting the initial chitosan spectrum from that of the product, one can detect the absorption band corresponding to the bond S=C–N< at 1404 cm^{-1}. The presence of the absorption band at 2057 cm^{-1} corresponding to the bond S=C=N– indicates residual insignificant amounts of rodanide ions that can be retained only by ionic bonds. Nevertheless, hot extraction should have washed the polymer from rodanide ions. That is why a part of the latter is formed as a result of isomerization (Scheme 3) known for thiocarbamide and ammonium thiocyanate in different protonic solvents (Belevskii, Sarukhanov, Kharitonov, & Ismail, 1997).

To state more unambiguously the introduction of thiocarbamoyl group, we used the solid-state ^{13}C NMR spectroscopy. Unlike the case of initial chitosan, the TC-chitosan ^{13}C NMR spectrum, aside from the signal at 175 ppm corresponding to the carbons of acetamido groups, has the signal at 184 ppm, which intensity increases with DS increase (Pestov, Bratskaya, Slobodyuk, Avramenko, & Yatluk, 2010). The sample insolubility indicates the formation of intermolecular covalent cross-linkages and binding a thiocarbamoyl group with amino groups of adjacent macromolecules.

Thermogravimetric study of TC-chitosan coupled with analysis of gaseous destruction products has shown the presence of adsorbed water that can be attributed to the first endothermic process at 128 °C (Fig. 1S, Supplementary data). Beginning of TC-chitosan destruction, which occurs with intensive water release, was registered at 235 °C. This type of thermal destruction – carbonization by the dehydration process – is typical for all carbohydrates. Compared to chitin and chitosan with deacetylation degree 0.84, whose destruction starts at 350 °C and 284 °C, respectively (Kittur, Prashanth, Sankar, & Tharanathan, 2002), TC-chitosan is a less thermally stable derivative. During TC-chitosan decomposition another endothermic process occurring with ammonia release was detected at 242 °C (Fig. 1S, Supplementary data). Most likely, it is related to the formation of thiocarabamoyl linkages according to Scheme 4.

Quantitative analysis of the released ammonia has revealed that its content decreases with increase of TC-chitosan DS that is in good agreement with the content of primary amino groups in derivatives available for the reaction (Scheme 4).

The possible processes of thiourea isomerization, destruction with hydrogen sulfide release, and addition reaction are summarized in Scheme 5. However, release of hydrogen sulfide was not detected at any stage of polymer destruction. Moreover, if the reaction presented in the right-hand part of the scheme does occur, the presence of salts of disubstituted guanidine must be detectable



Scheme 4. Cross-linking reaction of thiocarbamoyl chitosan occurring with ammonia release.

Table 1
Conditions of chitosan thiocarbamoylation reaction and DS of the obtained products, ratio $NH_4SCN:(NH_2)_2CS = 2.1:1$.

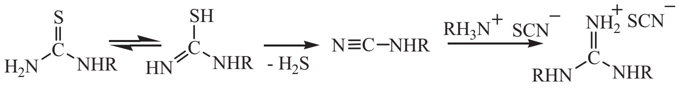
No. of test	Conditions of reactions				Characteristic of products			
	t (°C)	Reagent molar excess	Time (h)	Yield (%)	Found (%)		DS	Static exchange capacity (HCl) (mg-equiv/g[a])
					N	S		
Temperature increase								
1	110	14	2	49	9.26	5.18	0.22	–
2	130	14	2	42	9.04	6.83	0.50	1.78 (1.93)
3	150	14	2	33	11.19	10.35	0.66	–
Reagent excess increase								
4	130	1	4	72	8.04	1.64	0.10	–
5	130	2	4	71	9.13	4.28	0.26	–
6	130	4	4	86	9.65	9.26	0.75	0.39 (0.42)
7	130	10	4	85	10.02	12.11	1.12	–
Reaction time increase								
8	150	14	5	13	19.36	13.76	0.45	–
9	150	14	8	15	17.81	16.32	0.67	0.79 (0.82)
10	110	14	5	91	9.56	7.87	0.56	–
11	110	14	8	90	9.72	8.04	0.57	1.24 (1.34)

[a] Values calculated from the DS of TC-chitosan are given in parentheses.

in IR spectrum as bands at 1680 and 1595 cm^{-1}. However, these bands were not observed even for the difference spectrum due to the presence of the intensive bands at 1621 and 1510 cm^{-1}.

Earlier we applied hydrazine hydrate solution for deacetylation of chitin–glucan complexes that in some cases resulted in complete deacetylation of chitinous part of the polysaccharide complex (Skorik, Pestov, & Yatluk, 2010). The same approach was used here for dethiocarbamoylation of TC-chitosan (DS 0.7): residual DS of TC-chitosan was 0.2 and 0.1 after 7 h and 24 h of treatment, respectively. Further increase of treatment time did not affect elemental composition of the product. It is worth mentioning that both TC-chitosan and hydrazinolysis product were insoluble in acids that confirms preservation of intermolecular cross-linkages by thiocarbamoyl groups having low reactivity due to the steric hindrances. Comparison of content of thiocarbamoyl groups participating in cross-linking (calculated according to the TC-chitosan (DS 0.7) formula) with residual TC-chitosan DS after hydrazinolysis give an experimental evidence that about 10% of thiocarbamoyl groups is involved into cross-linkages. To confirm that new cross-linkages were not formed between residual aldehyde groups of chitosan and hydrazine molecules, plain (unmodified) chitosan was treated under the same conditions as TC-chitosan and was found to retaining solubility in dilute acids. Application for hydrazinolysis potentially stronger nucleophile, *N*,*N*-dimethylhydazine, resulted, however, in lower efficiency of TC-chitosan dethiocarbamoylation. Residual DS reached under the same experimental conditions as were used in hydrazine treatment remained notably higher – 0.3. Most likely, in this case the role of increased steric hindrances was more profound compared to the increased nucleophilicity of the reagent.

Thus, the presence of each type of functional groups shown in general structure of TC-chitosan (Scheme 2) was confirmed by several analytical methods. Due to the high content of sulfur-containing (thiocarbamoyl) and nitrogen-containing (amino) functional groups the TC-chitosan derivatives obtained have high potential as sorbents for precious metals ions.



Scheme 5. Possible transformations of thiourea.

3.2. *Sorption properties of thiocarbamoylchitosans*

Despite good sorption properties toward many metal ions plain chitosan lacks for selectivity that significantly limits its application. It is well known that introduction of N- and S-containing functional groups does not only increase the sorption capacity of the polymeric sorbents but also remarkably enhances their selectivity in accordance with the Pearson's HSAB principle. Previous studies of precious metals uptake by sulfur-containing chitosan derivatives revealed that the optimum pH of the process is about 2 (Baba et al., 2002; Guibal et al., 2002, 2001), so here we have fixed this parameter in the study of TC-chitosans sorption properties.

Figs. 1–3 demonstrate that thiocarbamoylation of chitosan, indeed, notably improves the sorption properties of the plain polymer toward ions of Au(III), Pt(IV), and Pd(II). Independently of the TC-chitosan functionalization degree, the quantitative recovery of a precious metal ions is feasible at initial metal concentration up to 100 mg/l for Au(III) and $\sim$50 mg/l for Pt(IV) and Pd(II). The maximum sorption capacity of TC-chitosan derivatives increases with DS, i.e. thiocarbamoyl groups content, and reaches at DS 0.9 values for Pt(IV) – 1.24 mmol/g, for Pd(II) – 3.43 mmol/g, and for Au(III) – 3.81 mmol/g.

Comparison of the data obtained for the highly substituted TC-chitosans with the available in the literature data for S-containing chitosan derivatives and selected synthetic polymers show that

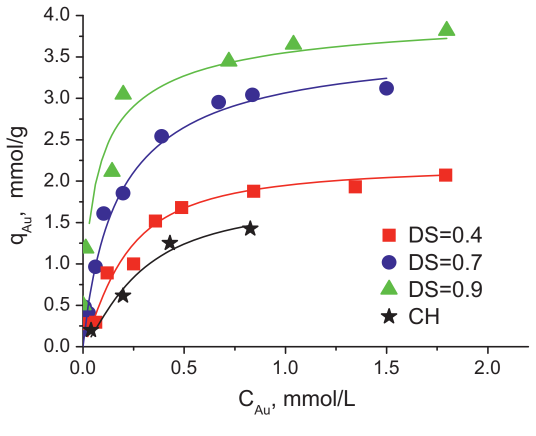


Fig. 1. Sorption isotherms of Au(III) on thiocarbamoyl chitosans varying in DS, pH 2 (CH – plain (unmodified) chitosan cross-linked with glutaraldehyde).

Table 2
Sorption properties of S-containing polymers toward noble metal ions.

Sorbent	Sorption capacity (mmol/g)			Reference
	Au(III)	Pt(IV)	Pd(II)	
Thiourea chitosan derivatives			2.54	Guibal et al. (2002)
Rubeanic acid chitosan derivatives			3.24	Guibal et al. (2002)
Thiourea chitosan derivatives		1.8		Guibal et al. (2001)
Thiourea modified chitosan microspheres (DS ~0.5)		0.66	1.04	Zhou et al. (2009)
2,5-Dimercapto-1,3,4-thiodiazole chitosans	1.00	0.07	0.15	Li et al. (2009)
Glycine modified cross-linked chitosan	0.86	0.63	1.11	Ramesh et al. (2008)
L-Lysine modified chitosan	0.36	0.66	1.01	Fujiwara et al. (2007)
Rubeanic acid modified chitosan	3.07			Arrascue, Garcia, Horna, and Guibal (2003)
Thiocarbamoylchitosan (DS 0.68)		1.11	2.40	Butewicz et al. (2010)
Thiocarbamoylchitosan (DS 0.31)		0.49	1.24	Pestov, Koryakova, et al. (2010)
Melamine–formaldehyde–thiourea chelating resin	0.25			Aydin, Imamoglu, and Gulfen (2008)
Bisthiourea–formaldehyde chelating resin	3.63			Atia (2005)
S-containing polymers POLYORGS series	0.92–7.1	0.1–1.79	0.16–3.56	Myasoedova and Komozin (1994)

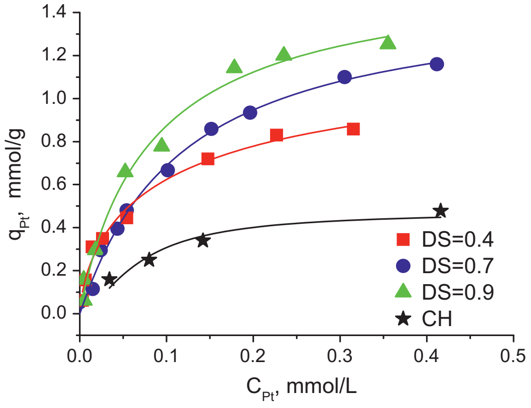


Fig. 2. Sorption isotherms of Pt(IV) on thiocarbamoyl chitosans varying in DS, pH 2 (CH – plain (unmodified) chitosan cross-linked with glutaraldehyde).

maximum sorption capacities of TC-chitosan for Au(III), Pt(IV) and Pd(II) are higher than values previously reported for chitosan derivatives and comparable with those for the best S-containing chelating resins (Table 2). Another trend confirmed by investigations of TC-chitosan sorption properties is lower sorption capacities of thiourea chitosan derivatives for Pt(IV) over Pd(II) independently of the synthesis route and functional group linkage used (Table 2).

Two mechanisms of metal ions sorption on chitosans containing thiourea functional groups were suggested – ion-exchange and complexation (Guibal, 2004; Guibal et al., 2002, 2001). Although ion-exchange can in general contribute to the mechanism of precious metals uptake by S-containing polymers, we have previously shown that sulfate, nitrate, and chloride anions only slightly decreased Pt(IV) and Pd(II) sorption on TC-chitosan with DS 0.7–0.83 (Butewicz et al., 2010). Besides, it was found that maximum sorption capacities of TC-chitosans for Au(III) remain the same in 0.1–1 M HCl solutions (Fig. 2S, Supplementary data). These facts illustrate predominant role of S-containing functional groups in uptake of precious metal by TC-chitosans.

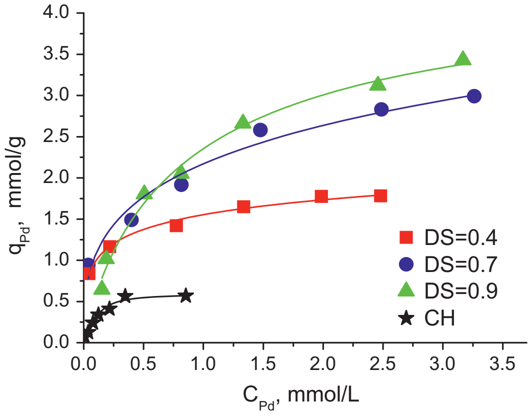


Fig. 3. Sorption isotherms of Pd(II) on thiocarbamoyl chitosans varying in DS, pH 2 (CH – plain (unmodified) chitosan cross-linked with glutaraldehyde).

Total N- and S-content in sorbents is often used in the literature to calculate theoretical sorption capacities for precious metals ions (Guibal et al., 2002). However, considering incapability of acetamide nitrogen and secondary amino group of thiourea (Scheme 2) to metal ions sorption, and taking into account ability of thiourea for coordination of metals via sulfur atom only, as a monodentate ligand (Bowmaker et al., 2009; Berta, Spofford, Boldrini, & Amma, 1970; Gale, Light, & Quesada, 2006; Piro, Castellano, Piatti, Bolzán, & Arvia, 2002), we have concluded that the ratio suggested in the literature for calculation of sorption capacity (N + S)/M = 2 (Guibal et al., 2002) is not typical for the studied type of sorbent. Matching the content of N- and S-containing functional groups in polymers with maximum sorption capacities of TC-chitosan with different substitution degrees (Table 3) revealed that the mechanism of precious metals sorption depends on both – DS and nature of the metal ions.

Decrease of (N + S)/M ratio with increasing DS corresponds to the reduction of ion-exchange contribution to the mechanism of precious metal ions uptake. This process is also related to the decrease of primary amino groups, capable to protonation and ion-exchange. On the contrary, increase of thiourea groups contents with DS results in increasing contribution of coordination via S-atom to precious metal ions uptake. At DS 0.9, when there is no primary amino groups in TC-chitosan, the ratio (N + S)/M becomes close to 1 that confirm possibility of coordination only via S-atom.

As one can see from Table 3, the ratio (N + S)/M for Au(III) sorption on TC-chitosan with DS 0.7–0.9 is below 1. Such superequivalent sorption of gold was previously reported for the fibers containing thiourea and (Tang, Lu, & Zeng, 2001) and thioamide groups (Liu, Li, & Tang, 2002) when reduction of Au(III) specious to Au(0) was detected upon adsorption. One of the most powerful techniques of evaluating the oxidation state of the metals upon sorption is X-ray photoelectron spectroscopy (XPS). A good example of XPS potential in chitosan-complexes characterization was given in Dambies, Guimon, Yiacoumi, and Guibal (2001), where the changes in molybdenum oxidation state after adsorption on plain chitosan was proven. The XPS-data presented in Fig. 4 indicate changes in the oxidation states of Au(III) and Pt(IV) after the sorption on TC-chitosan. Analysis of high resolution XPS spectra shows that binding energy of Pt $4f_{7/2}$ electrons is 73 eV, that corresponds to the Pt(II) (Moulder, Stickle, Sobol, & Bomben, 1992). Although the typical for Au-$4f_{7/2}$ band lies at 83.9 eV (Fuggle & Martensson,

Table 3
The values of (N + S)/M ratio for TCC of different substitution degrees.

DS	Content of element (%) (mmol/g)		Max sorption (mmol/g) (ratio (N + S)/M)			
	N		S	Pt(IV)	Pd(II)	Au(III)
	Total	Capable to metal ions sorption[a]				
0.4	9.91 (7.08)	(2.04)	6.25 (1.95)	0.86 (4.6)	1.87 (2.1)	2.87 (1.4)
0.7	9.63 (6.88)	(0.48)	8.47 (2.65)	1.16 (2.7)	2.60 (1.2)	3.45 (0.9)
0.9	10.53 (7.52)	(0)	11.18 (3.49)	1.24 (2.8)	3.43 (1.0)	3.81 (0.9)

[a] Contents of N-containing functional groups capable to metal sorption were calculated as (N_{total} * 0.84 – S*2) mmol/g, where 0.84 corresponds to the deacetylation degree of chitosan-precursor.

1980), increase of binding energy to about 0.5 eV was previously reported for nanosized gold particles (Huang, Chiu, Wang, Meen, & Yang, 2007). However, the binding energy found for Au $4f_{7/2}$ (85.0 eV) in TC-chitosan can be more reasonably assigned to Au(I) with possible presence of about 10% of elemental gold (with accordance to the peak deconvolution).

Desorption experiments revealed that gold and palladium can be recovered with efficacy over 90% from TC-chitosan by thiourea/HCl solutions with thiourea concentration 0.5–1 M (Table 4). Very low efficacy of desorption of all precious metals with HCl solutions without chelating agent (thiourea) also confirms that ion-exchange mechanism does not play a governing role in the precious metals uptake by TC-chitosan. When sorbents form with precious metals ions outer-sphere complexes, desorption of Au(III), Pd(II), and Pt(IV) with HCl solutions is rather significant (Ramesh, Hasegawa, Sugimoto, Maki, & Ueda, 2008).

Evaluation of TC-chitosan sorption properties toward the ions of 3d-metals, which are major components interfering to precious metals uptake from technological solutions and natural objects, shows that the sorption capacities of all TC-chitosan with DS 0.4–0.9 are negligible for Cu(II), Zn(II), Fe(III) ions and do not exceed values of 0.052 mmol/g, 0.004 mmol/g, and 0.01 mmol/g, respectively (Table 1S, Supplementary data). Under the same conditions (pH 2) sorption capacities of the plain chitosan (deacetylation degree 0.87) cross-linked with glutaraldehyde are 0.3 mmol/g and 0.2 mmol/g for Cu(II) and Zn(II) ions, respectively (Juang & Shao, 2002). Thus, thiocarbamoylation of chitosan provides almost 10-fold decrease in unspecific sorption of 3d-metal ions. Such a reduction of sorption capacities of TC-chitosan results from different binding mechanisms for 3d-metal ions and ions of precious metals. As follows from the experimental data obtained, with increasing DS the leveling effect of thiocarbamoylation on electron-donor capability of amino group, which results not only in decrease of basicity but also of nucleophilicity of amino-group. Thus, despite decrease of the protonation degree with increase of TC-chitosan DS, capability of derivatives to act as N-ligands decreases. Besides, the primary amino group of the formed thiourea residue does not show electron-donor properties as well. As a result, functionalization of primary amino-groups of chitosan, which determine its sorption capacity toward 3d-metal ions, is drastically reduced. In accordance with the Pearson's principle, introduction of sulfur atom, which is softer base compared to nitrogen atom, significantly increases the affinity of the chitosan to soft acids – precious metal ions.

Thus, selectivity of TC-chitosan results from interplay of two opposite tendencies – inhibition of hard base (amino group) and introduction of soft base (thiocarbamoyl group). This effect is

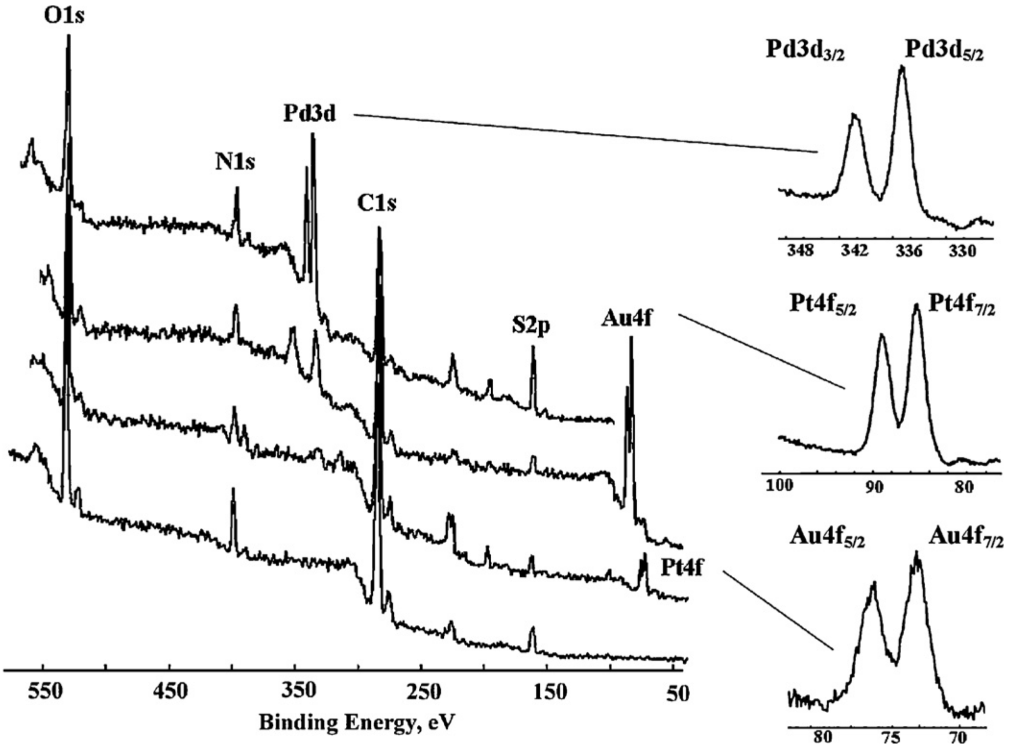


Fig. 4. XPS spectra of thiocarbamoyl chitosan, DS 0.9 before – (1) and after the sorption of Pt(IV) – (2), Au(III) – (3), and Pd(II) – (4).

Table 4
Desorption of Au(III), Pt(IV) and Pd(II) from TC-chitosan (DS 0.9).

HCl (M)	0.05	0.05	0.05	0.05	0.05	1	1	2	5
Thiourea (M)	0.05	0.1	0.25	0.5	1	0.5	0	0	0
Pt (%)	37 ± 5	42 ± 5	46 ± 2	38 ± 6	38 ± 3	46 ± 3	<1	<1	<1
Pd (%)	67 ± 5	69 ± 1	83 ± 3	93 ± 4	97 ± 1	77 ± 3	<2	<2	<2
Au (%)	69 ± 1	71 ± 6	89 ± 1	88 ± 1	92 ± 2	89 ± 1	<1	<1	<1

observed even for the derivatives with medium DS that allows effective selective recovery of precious metal ions from solution containing 1000-fold excess of the main interfering ion – Fe(III).

4. Conclusion

Here we have suggested a principally new method to form polymeric matrix for precious metals sorption. An important advantage of the proposed route to the synthesis of thiocarbamoyl derivatives of chitosan in gel consists in the possibility to attain high functionalization degree with simultaneous formation of cross-linked supramolecular structure of the polymeric sorbent. The high substitution degrees of TC-chitosan provide remarkable increase of its sorption capacity for Au(III), Pt(IV), Pd(II) ions in acidic media. The maximum sorption capacities found for highly substituted TC-chitosan (DS 0.9) are higher than the values reported in the literature for other chitosan sulfur derivatives and for most of the N- and S-containing synthetic polymers. We showed that TC-chitosans were applicable for recovery of precious metals from solutions containing up to 1000-fold excess of interfering ions – Cu(II), Fe(III), Zn(II).

Analysis of precious metals sorption mechanism by XPS showed that uptake of Au(III) and Pt(IV) by TC-chitosan occurs with reduction of these metals species to Au(I)/Au(0) and Pt(II), while the oxidation state of Pd(II) was unaffected. The dominating mechanism of the precious metal ions uptake by TC-chitosan is coordination via S- and N-containing functional groups with minor contribution of ion-exchange mechanism. We showed that gold and palladium could be eluted from the TC-chitosan with efficacy over 90% by thiourea/HCl solutions that makes possible the TC-chitosan application for recovery of precious metals from technological solutions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbpol.2011.04.008.

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