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N-(2-(2-pyridyl)ethyl)chitosan: Synthesis, characterization and sorption properties

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ABSTRACT

The method of producing N-2-(2-pyridyl)ethylchitosan (PE-chitosan) with substitution degrees (DS) up to 1.2 has been developed using the "synthesis in gel" approach for direct addition reaction between 2-vynilpyridine and chitosan. Investigation of sorption properties has revealed significantly higher affinity of pyridylethyl fragments to Pt(IV)) and Pd(II) ions compared to the unsubstituted amino groups of chitosan. The maximum sorption capacities of PE-chitosan in 0.1 M HCl solution were estimated as 5.56 mmol/g for Au(III), 3.67 mmol/g for Pd(II), and 2.75 mmol/g for Pt(IV). Sorption capacities of PE-chitosan for transition metal ions at pH 4–8 were 1.5–2.6 higher than those of chitosan with the highest values attained for Cu(II) and Ag(I) ions – 1.50 mmol/g and 1.53 mmol/g, respectively. The PE-chitosan application for preconcentration of Au(III) with subsequent elution with HCl/thiourea mixtures was proved to be efficient for atomic absorption spectroscopy analysis of multi-component solutions with low gold content.

1. Introduction

One of the important segments of the new materials market is concerned with reactive functional polymers for versatile applications. In recent years there has been a sustained tendency to utilization of natural polymers and their derivatives as an alternative to synthetic materials, first of all, as efficient flocculants (Bratskaya et al., 2005) sorbents (Muzzarelli, 2011), and catalyst supports (Guibal, 2005). Aminopolysaccharide chitosan produced by deacetylation of chitin, the second most abundant and affordable after cellulose natural polymer, possesses a combination of unique characteristics which stipulates for its extensive application in the forms of as unmodified polymer as derivatives. Due to the presence of primary amino group chitosan can undergo numerous polymer transformations known for polyamines that can yield functional derivatives with specific properties and significantly expand the field of natural polymers application.

Introduction of aromatic and heteroaromatic fragments to the chitosan backbone results in polymers, which can be used as bioactive, sorption, and metal-containing multifunctional materials. Introduction of pyridine (Baba & Hirakawa, 1992; Baba, Masaaki, & Kawano, 1994; Kumar, Dutta, & Dutta, 2009; Rodrigues, Laranjeira, Stadler, & Drago, 2000; Sajomsang, Tantayanon, Tangpasuthadol, & Daly, 2008; Sajomsang, Ruktanonchai, Gonil, & Warin, 2010; Tong, Li, & Xia, 2005) and thiophen (Baba, Kawano, & Hirakawa, 1996) to chitosan backbone is described in literature as a method to modify biological activity and sorption properties of chitosan. Increase of antibacterial activity was reported for N-(4- or 3-pyridylmethyl)chitosan (Kumar et al., 2009; Sajomsang et al., 2008, 2010). Increase of sorption capacity and selectivity toward copper(II) ions was observed for N-(2-pyridylmethyl)chitosan (PM-chitosan) (Baba et al., 1994; Baba, Masaaki, & Kawano, 1998), which is capable to form five-member chelates. Indeed, the sorption capacity of chelate-forming PM-chitosan was three times higher than that of non-chelating N-(4-pyridyl) derivative (Rodrigues, Laranjeira, Favere, & Stadler, 1998). High sorption capacities for noble metal ions were also reported for PM-chitosan derivatives (Baba & Hirakawa, 1992; Baba et al., 1996; Dhakal, Oshima, & Baba, 2008). However, both types of PM-chitosan derivatives containing 4-, and 2-pyridyl groups can be used as supports for metal containing materials (Hu, Cui, Dong, & Fang, 2001; Leonhardt et al., 2010; Rodrigues et al., 2000; Tong et al., 2005) due to the presence of electron donor N-atom of pyridyl ring.

All the heterocyclic derivatives mentioned above were obtained via reactions of reductive alkylation. The main disadvantages of this synthetic method include the necessity of two-stages – aryl- or heteryl-methylidenation of chitosan and subsequent reduction of the product; use of organic solvents (methanol and dimethylsulfoxide), unstable and toxic reductive agents (sodium borohydride or cyanoborohydride). Besides, aromatic aldehydes are not stable substances, which require special storage conditions. More effective method of introduction of pyridyl ring to the chitosan

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backbone is the Michael reaction of direct addition of amino group to α,β-conjugated compounds, e.g. 2-vynilpyridine. In this case the derivatives are obtained within one stage (Pestov, Bratskaya, Azarova, Kodess, & Yatluk, 2011) without reductive agents, which excludes unwanted side reactions. Modification of chitosan using 2-(2-pyridyl)ethyl group results in derivative, similar to PM-chitosan, which is capable to chelate formation but in this case six-member chelates with bivalent metal ions are formed. Comparison of the complexes stability for 2-(aminomethyl)pyridine and 2-(2′-aminoethyl)pyridine with Cu(II) and Ni(II) ions (Anderegg, 1971; Goemmine & Eeckhaut, 1971) shows that overall complex formation constant is by four- and five-orders of magnitude higher for five-member chelates with copper(II) and nickel(II) ions, respectively. Thus, the closest to PM-chitosan derivative in homology series is expected to have lower sorption capacity for transition metals ions, but can have a different trend in selectivity.

Here we report a new synthesis method to obtain N-2-(2-pirydyl)ethylchitosan (PE-chitosan) and the results of investigation of PE-chitosan sorption properties in recovery of noble and transition metal ions, including analytical preconcentration for multi-component solutions.

2. Experimental

2.1. Materials and methods

Chitosan was purchased from JSC “Sonat” (Moscow, Russia). The degree of acetylation (DA) was determined by ^{1}H NMR spectroscopy to be 0.18; average molecular weight of 2.5×10^5 Da was measured using viscometry according to (Gamzazade et al., 1985). 2-Vinylpyridine (Sigma–Aldrich) was distilled before the synthesis and stabilized with hydroquinone (0.05%). All other chemicals were of analytical grade and used without further purification.

The C,H,N-elemental composition was determined by Elemental Analyzer “Perkin Elmer”. ^{1}H and ^{13}C NMR spectra were registered on a spectrometers Bruker DRX-400 and AVANCE-500 at 70 °C to increase the solubility of samples and to achieve better resolution of the signals. Samples were dissolved in D_2O/DCl (concentration 10 mg/ml), sodium 3-(trimethylsilyl)-1-propanesulfonate was used as an internal standard. Suppression of the solvent signal during spectrum registration was achieved by the “presaturation” technique. The substitution degree (DS) was calculated using ^{1}H NMR spectra according to the following formulas:

$$\text{total DS (DS)} = \frac{(m + 2d)}{(m + d + a)}$$

$$\text{monosubstitution DS (DSm)} = \frac{m}{(m + d + a)}$$

$$\text{disubstitution DS (DSd)} = \frac{2d}{(m + d + a)}$$

where m is the mole fraction of monopyridylethylated glucosamine units, d is the mole fraction of dipyridylethylated glucosamine units, and a is the mole fraction of glucosamine units. The calculations of m, d, and a values were performed using integral intensities of the corresponding signals in ^{1}H NMR spectrum.

Thermograms were registered using TGA analyzer (Mettler Toledo).

2.2. Preparation of PE-chitosan

PE-chitosan derivatives with DS 0.4, 0.7, 0.8, and 0.9 were synthesized by the method of chitosan transformation “synthesis in gel” described in (Pestov et al., 2011). Additional modification was performed as follows: the mixture of 0.60 g (0.002 mol) of PE-chitosan·HCl (DS 1.04) and 0.42 ml (0.004 mol) of 2-vynilpyridine, and 2.78 ml water was kept about 10 min until formation of the gel-like mass, afterwards the gel was heated to 70 °C kept for 24 h and cooled. 7.18 ml (0.002 mol) 0.85% HCl was added to the mixture, after homogenization of the solution the product was precipitated with 50 ml of acetone. Then product was extracted by hot isopropanol during 24 h and dried at 50 °C to the constant weight.

To obtain insoluble sorbents, 2.25 g of PE-chitosan was mixed with 250 ml of water containing 21 g NaOH, 7 ml of epichlorohydrine was added to the mixture under constant stirring. After heating the mixture at 50 °C during 2 h, precipitate was filtered, washed with deionized water until negative reaction to Cl^- ions, and dried at 50 °C to constant weight. The value of cross-linking degree was estimated as 20%.

2.3. Sorption and desorption experiment

Sorption and desorption experiments were carried out at temperature 25 °C. To study the sorption properties, PE-chitosan were shaken with the solution of Au(III), Pt(IV), and Pd(II) chlorides in 0.1 M HCl/1 M HCl at solid:liquid ratio 1:1000 during 18 h at 200 rpm. The sorption of transition metal ions (Cu(II), Ag(I), Ni(II), Co(II)) was studied under the same conditions from solutions of 1 M NH_4NO_3, pH 5.3. The sorption capacities were calculated using the difference in initial and equilibrium concentrations of the metal ions determined by the atomic absorption spectroscopy – AAS (Solaar M6, Thermo, USA).

Desorption of Au(III), Pt(IV) and Pd(II) from PE-chitosan phase was studied for derivative with DS 0.8 using solutions of HCl and thiourea at solid:liquid ratio 1:100 (desorption time 18 h). Preconcentration of the metal ions was carried out from solutions in 0.1 M HCl containing 200 mg/L of noble metals. After preconcentration sorbents were rinsed with deionized water, dried and the quantity of noble metal in the sorbent phase was determined by AAS after decomposition of the sorbent in aqua regia. Content of metals in the eluent after desorption was determined by AAS.

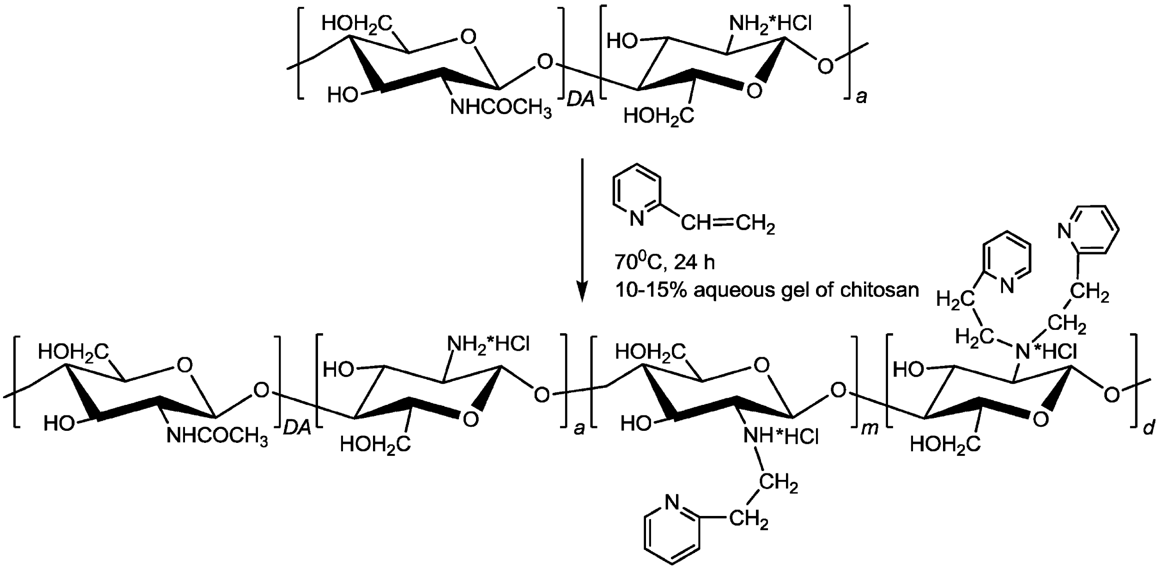
3. Results and discussion

3.1. Preparation of PE-chitosan

Recently, we have introduced a new pyridyl-functionalized chitosan derivative – N-2-(2-pyridyl)ethylchitosan (Scheme 1) and developed method its synthesis using a new synthetic route of chitosan transformation – “synthesis in gel” (Pestov et al., 2011). Variation of modification conditions allows obtaining products with DS below 1. When the synthesis is performed at higher temperature (above 90 °C), a reverse process of 2-vinylpyridine detachment occurs. Increase of chitosan gel concentration is effective up to 20%, further increase results in formation of a heterogeneous reaction mixture that does not assure completeness of the reaction. DS above 1 cannot be reached even at 5-fold mol excess of 2-vinylpyridine due to the predominance of monoselective substitution (Pestov et al., 2011).

To obtain the product with DS > 1, we have suggested to use additional modification of highly substituted PE-chitosan with 2-vinylpyridine. As seen from the data in Table 1, further functionalization of PE-chitosan occurs, but with lower efficiency than that for low molecular weight amines. In the latter case the same approach results in formation of bis-2-(pyridyl)ethyl amine (Oeme, Iovel, Faklyam, & Lukevits, 1995).

Interaction of PE-chitosan with 2-vinylpyridine occurs as a reaction of addition to primary and monosubstituted aminogroups, as the content of both groups is decreased after the reaction. However,



Scheme 1. The "synthesis in gel" condition of preparation and the general chemical structure of PE-chitosan; *DA*, *a*, *m* and *d* are the molar fractions of corresponding glucosamine units.

insignificant increase of DS shows lower reactivity of PE-chitosan compared to chitosan, whereas under the same conditions the amount of bound 2-vinylpyridine is higher for chitosan precursor (Table 1). Most likely, the main reason of the reduced nucleophilicity of PE-chitosan consists in sterical hindrances, which were the cause of retardation of the reaction between chitosan and large excess of 2-vinylpyridine. Thus, obtaining PE-chitosan with DS above 1 is possible when additional treatment with increased mol excess of 2-vinylpyridine is used.

3.2. *Structure of PE-chitosan*

Results of elemental analysis and ^{1}H and ^{13}C NMR spectra allow attributing to PE-chitosan derivatives the following structure (Scheme 1). According to ^{1}H NMR spectra, the reaction of 2-vinylpyridine addition occurs only for amino groups. Typical spectrum of the mono-2-pyridylethylated product is given in Fig. 1S (Supplementary data). The signals assignment was done using the data of (Pestov et al., 2011; Rodrigues et al., 1998) and earlier found correlation between chemical shift of anomer H-atom (H-1 atom of glucosamine units) and character of aminogroups substitution. Chemical shifts of H-1 atom in N-acetylated and in deacetylated glucosamine units are 4.67 and 4.96 ppm, respectively, which is in agreement with the spectroscopy data available in literature for chitosan and its derivatives. Chemical shifts of H-1 in N-mono-2-pyridylethylated and N,N-di-2-pyridylethylated glucosamine units are equal to 5.18 and 5.37 ppm, respectively.

Table 1
Characteristics of the products structure obtained after 2-(2-pyridyl)ethylation of plain chitosan and PE-chitosan (molar ratio NH_2 (or NH):C_7H_7N = 1:2, 70 °C, 24 h, concentration of polymer 14%, degree of acetylation (DA) = 0.18).

Experiment	Polymer	Content of amino groups (mol%)			DS
		NH_2	NHR	NR_2	
1	Precursor	100	0	0	0
	Product	23	69	8	0.85
2	Precursor	17	83	0	0.83
	Product	13	72	15	1.03
3	Precursor	12	73	15	1.04
	Product	0	77	23	1.23

The ^{13}C NMR-spectrum (Fig. 1) showed chemical shifts (δ, ppm) at: 98 (C-1), 58 (C-2), 71 (C-3), 79 (C-4), 76 (C-5) and 63 (C-6), which was in a good agreement with literature data on ^{13}C NMR of plain chitosan (DCl/D_2O) (Rinaudo, Dung, Gey, & Milas, 1992). The appearance of new signals at 129 ppm (C-10, C-12), 144 ppm (C-11), 148 ppm (C-13), and 153 ppm (C-9) – C-atoms of pyridyl ring, 47 ppm (C-7, C-14) and 37–32 ppm (C-8, C-15) was observed.

Thermogravimetric study of PE-chitosan in the form of chlorohydrates with mass-spectroscopic identification of the destruction products shows that the water loss starts from the temperature of 100 °C, while significant dehydration – initial carbonization of the polymer typical for carbohydrates – starts at 175 °C (Fig. 2S, Supplementary data). Further destruction is related to the destruction of the side chain (2-vynilpyridine fragment) – with formation of ketene (*M* = 42), pyridine (*M* = 79), picoline (*M* = 93) and 2-vynilpyridine (*M* = 105). The latter, probably, is formed due to reversibility of addition reaction in the presence of the catalyst. It is worth mentioning that no release of hydrogen chloride was detected, however, identification of ammonium chloride (*M* = 53) assumes its formation during decomposition process. The thermal stability of the PE-chitosan as a free base was found to be limited to 200 °C with the same decomposition products except ammonia formed instead of ammonium chloride. In comparison with chitin and chitosan (DA = 0.16), for which the decomposition temperature

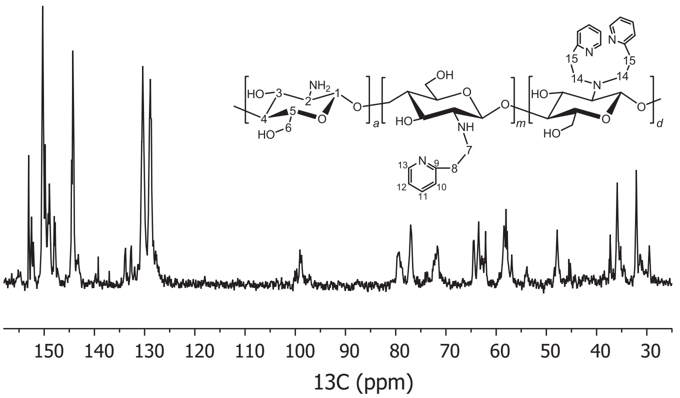


Fig. 1. 126 MHz ^{13}C NMR spectrum of PE-chitosan (D_2O/DCl).

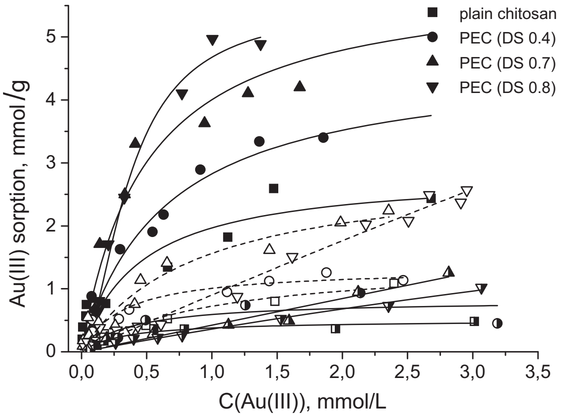


Fig. 2. Sorption isotherms of Au(III) on PE-chitosan derivatives varying on DS: closed symbols – 0.1 M HCl; open symbols – 0.4 M HCl; half-open symbols – 1 M HCl, solid lines correspond to the fits of isotherms in 0.1 M and 1.0 M HCl, dash lines – to the fits of isotherms in 0.4 M HCl.

is equal to 350 and 284 °C, respectively (Kittur, Prashanth, Sankar, & Tharanathan, 2002), PE-chitosan is a derivative with lower thermal stability.

Thus, introduction of 2-(2-pyridyl)ethyl functional groups to the chitosan backbone was confirmed using several methods of analysis. The introduced functional fragments are predominantly represented by mono-2-(2-pyridyl)ethylated amino groups, which determine sorption activity of the new derivatives.

3.3. Sorption properties of PE-chitosan

3.3.1. Sorption of platinum(IV), gold(III), and palladium(II)

Earlier we have investigated sorption properties of PE-chitosan (DS 0.8) cross-linked with glutaraldehyde for Pt(IV) and Pd(II) ions (Sopena et al., 2011). Although the significant increase of sorption capacities after functionalization was confirmed, the data obtained for a single derivative had not allowed concluding on changes in sorption selectivity trends after modification. Besides, the data on Au(III) and Ag(I) ions sorption on PE-chitosan were not reported.

Fig. 2 shows the sorption isotherms of Au(III) on PE-chitosans with different DS from HCl solutions of various concentrations. One can see that the sorption of Au(III) on PE-chitosan increases with increase of DS, but substantially decreases with increase of HCl concentration. One can also see that increase of HCl concentration results not only in reduction of sorption capacity, but also in transition from high affinity to low affinity isotherms. Similar trend was observed for the sorption of Pd(II) and Pt(IV), although for the latter ions the effect of chloride concentration was much less pronounced (Figs. 3S and 4S, Supplementary data). The difference in sorption of Pt(IV) and Pd(II) ions from HCl solutions was suggested to result from more complex speciation of Pt(IV) in solutions. Significant effect of HCl concentration on sorption of noble metal ions suggests that the predominant mechanism of sorption is anion-exchange on protonated amino and pyridyl groups, which is hindered by the presence of competitor chloride ions. When chelation mechanism is realized, as we previously reported for thiocarbamoyl chitosan derivatives, the HCl content does not effect the sorption of noble metal ions in the studied range of Cl^- concentration (Bratskaya, Ustinov, Azarova, & Pestov, 2011).

To follow the selectivity and affinity trends in sorption of noble metal ions on PE-chitosan derivatives varying in DS the sorption, the isotherms were fitted with Langmuir equation. Analysis of the data presented in Table 2 enables one to make several important conclusions. First of all, one can see that introduction of ethylpyridyl group change the affinity of the plain chitosan. The sorption constant (K_L) significantly increases with increase of DS for Pt(IV) and Pd(II), but only slightly changes for Au(III) ions in 0.1 N HCl solutions. Secondly, K_L for Pt(IV) and Pd(II) sorption on PE-chitosan from solutions of 0.4–1.0 N HCl is higher for PE-chitosan in comparison with the plain chitosan, while for Au(III) an opposite trend is observed. At the same time, the sorption capacities of PE-chitosan are highest for Au(III) regardless on DS and HCl concentration. Increase of sorption capacities for all noble metal ions can be related to the increase of the number of anion-exchange centers with increase of DS. The general trend of sorption capacity of PE-chitosan for noble metal ions (Au(III) > Pd(II) > Pt(IV)) is typical for most of the N-containing sorbents (Myasoedova & Komozin, 1994), and, most likely, reflect the difference in chlorocomplexes structure and speciation rather than higher affinity of ethylpyridyl groups to Au(III) ions. It should be mentioned that increase of PE-chitosan DS up to 1.0 does not result in proportional increase of sorption capacity toward Pt(IV) and Pd(II) ions (Table 2). Thus, the investigations were limited to the derivatives with DS 0.8–1.0 and sorption properties of highly substituted PE-chitosan with DS 1.2 were not studied in details.

Table 2
Parameters of Langmuir model for noble metals ions sorption on PE-chitosan varying in substitution degrees (DS), K_L – Langmuir constant, Q_{max} – maximum sorption capacity.

DS	0.1 N HCl			0.4 N HCl			1 N HCl		
	K_L (L/mmol)	Q_{max} (mmol/g)	R	K_L (L/mmol)	Q_{max} (mmol/g)	R	K_L (L/mmol)	Q_{max} (mmol/g)	R
Sorption of Au(III)									
0	3.11	2.00	0.92	3.22	1.0	0.97	3.00	0.50	0.94
0.4	3.10	3.27	0.94	2.74	1.1	0.97	1.73	0.97	0.93
0.7	3.51	4.58	0.96	2.71	2.1	0.98		NS	
0.8	3.33	4.98	0.94		NS			NS	
1.0	3.25	5.56	0.91		NS			NS	
Sorption of Pd(II)									
0	3.52	0.89	0.98	0.50	2.5	0.98	0.41	1.03	0.98
0.4	3.71	2.79	0.98	1.21	2.68	0.97	0.42	1.65	0.95
0.7	7.44	3.30	0.94	7.50	3.0	0.97	0.40	2.21	0.99
0.8	5.42	3.65	0.98	6.34	2.98	0.90	0.41	2.39	0.98
1.0	5.50	3.67	0.95		ND			ND	
Sorption of Pt(VI)									
0	2.31	0.55	0.93	5.89	0.59	0.97	2.10	0.69	0.88
0.4	2.33	2.00	0.94	6.20	1.3	0.93	3.14	1.49	0.99
0.7	6.00	2.50	0.96	8.57	1.58	0.98	1.90	2.00 (NS)	0.98
0.8	3.44	2.70	0.86	4.89	2.13	0.82	1.92	2.34 (NS)	0.97
1.0	3.52	2.75	0.91		ND			ND	

NS – plateau of sorption isotherm was not reached; ND – not determined.

Table 3
Desorption of Au(III), Pt(IV) and Pd(II) from PE-chitosan (DS 0.8) and plain chitosan (CH).[a]

HCl, N	0.5	1	2	5	0.1	0.1	0.1	0.1	0.1	1
Thiourea, M	0	0	0	0	0.1	0.2	0.5	1	2	2
Pt, % (PE-chitosan)	12 ± 7	14 ± 2	17 ± 2	35 ± 11	43 ± 5	40 ± 1	34 ± 1	37 ± 4	33 ± 2	38 ± 4
Pt, % (CH)	37 ± 1	74 ± 5	100	88 ± 10	77 ± 4	77 ± 2	75 ± 4	75 ± 6	72 ± 6	66 ± 8
Pd, % (PE-chitosan)	33 ± 8	34 ± 6	44 ± 1	70 ± 2	73 ± 5	80 ± 4	77 ± 4	74 ± 10	100	100
Pd, % (CH)	62 ± 8	65 ± 9	65 ± 8	82 ± 10	83 ± 1	100	98 ± 2	97 ± 3	100	100
Au, % (PE-chitosan)	39 ± 4	42 ± 9	52 ± 2	50 ± 4	79 ± 7	92 ± 8	91 ± 7	95 ± 3	96 ± 3	95 ± 5
Au, % (CH)	2.4 ± 0.3	2.8 ± 0.5	3.9 ± 0.3	6 ± 2	22 ± 1	32 ± 5	36 ± 3	42 ± 3	49 ± 3	47 ± 5

[a] Sorption of noble metals ions was carried out from solutions in 0.1 N HCl.

The data obtained in sorption experiments also suggest that ethylpyridyl groups bind ions of Pt(IV) and Pd(II) stronger than the plain chitosan. This fact is in good agreement with data on desorption of Au(III), Pt(IV) and Pd(II) ions from the sorbent phase (PE-chitosan, DS 0.8) using solutions of HCl and HCl/thiourea (Table 3).

One can see that elution of Pt(IV) and Pd(II) is much more efficient from the phase of plain chitosan, while Au(III) is more efficiently eluted from the PE-chitosan phase. This confirms the trend of sorption constant (K_L) changes for chitosan and PE-chitosan (Table 2) and allows making a complex stability row for PE-chitosan as Pt(IV) > Pd(II) > Au(III). The data of Table 3 have an important application output. Obviously, N- and S-chitosan derivatives can be used not only for recovery of metal ions from technological solutions, as it is usually stated (Arrascue, Garcia, Horna, & Guibal, 2003), but also for selective concentration of noble metal ions from solutions with low content of noble metals and high content of transition metal ions. After preconcentration whether the sorbent can be decomposed in aqua regia for analysis of solutes or, alternatively, noble metal ions can be eluted by small volume of HCl/thiourea mixture and analyzed, for example, by atomic absorption spectroscopy (AAS) (Mokhodoeva, Myasoedova, & Kubrakova, 2007). The latter option is more reliable in analysis of samples with low concentration of gold, which is known to form volatile compounds during heating that can result in significant underestimation of gold content (Mitkin, Galizky, & Korda, 2000). The data presented in Table 3 suggest that PE-chitosan can be efficiently used for preconcentration and subsequent elution of Au(III), whereas its application for Pt(IV) preconcentration requires further decomposition of the sorbent for AAS analysis. The data on Au(III) preconcentration from solution containing 0.1 ppm of gold and 0.5 g/L of Fe(III) and subsequent determination of gold after elution with 0.1 M HCl/0.2 M thiourea (Fig. 5S, Supplementary data) by "introduced-found" method show that over 95% of gold can be concentrated on PE-chitosan and eluted for determination by AAC. This allows recommendation of PE-chitosan for gold analysis by AAS without oxidative destruction of the sorbent matrix.

Comparison of sorption properties of PE-chitosan obtained by a new method with those of PE-chitosan and its homologous derivative PM-chitosan reported in literature revealed significant deviations between data obtained by different authors. The sorption capacity of PM-chitosan does not exceed 0.3 mmol/g for Au(III) (Baba et al., 1996), and 0.2 mmol/g for Pt(IV) and Pd(II) (Baba & Hirakawa, 1992; Baba et al., 1996). The template modification of PM-chitosan results in increase of sorption capacity up to 0.5 mmol/g for Au(III) and 0.3 mmol/g for Pd(II) (Dhakal et al., 2008). Remarkably low sorption capacity of the derivative with DS 0.9 (Baba et al., 1996) can be related to very high cross-linking degree obtained with epichlorohydrine. Due to the rigid structure, not all the sorption centers are accessible; moreover, quaternization of pyridine ring with loss of nucleophilicity of N-atom is also possible in this case. We have recently reported the strong effect of cross-linking agents on the sorption capacity and selectivity for imidazol derivatives of chitosan (Bratskaya, Pestov, Azarova, Avramenko, & Yatluk, 2011). Thus, taking into account possible differences in matrix structure of cross-linked PE-chitosan and PM-chitosan derivatives reported in literature and obtained here, the conclusion on differences in sorption properties of two homologues cannot be formulated.

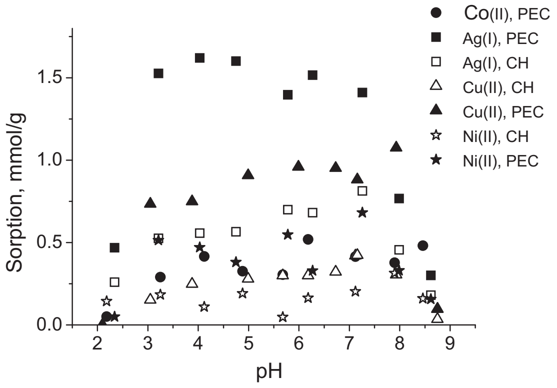


Fig. 3. pH-dependence of transition metals ions sorption on unmodified chitosan (CH) and PE-chitosan DS 0.8 (PEC).

3.3.2. *Sorption of silver(I), copper(II), nickel(II) and cobalt(II) ions*

The possibility of using functionalized derivatives to increase the sorption capacity for Ag(I) ions and to separate Ag(I) from the mixtures with Au(III)/Pt(IV), Pd(II) has not been yet considered for pyridyl derivatives of chitosan. Preliminary investigations showed that Ag(I) sorbs on PE-chitosan in cationic form in the same pH range as other transition metal ions (Pestov et al., 2011).

As seen from Fig. 3, with pH increase and increase of fraction of deprotonated amino and ethylpyridyl groups the efficiency of coordination of transition metal cations by PE-chitosan and chitosan increases. The sorption capacity of PE-chitosan in pH range 4–8 is in average 1.5-2 times higher than for plain chitosan. The most

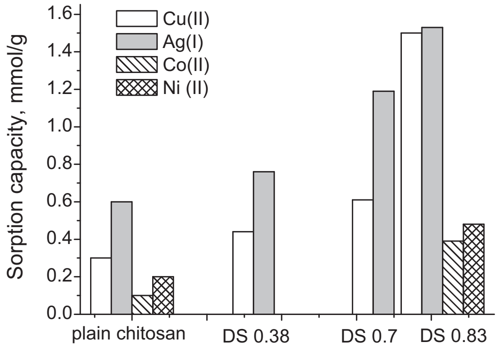


Fig. 4. Maximum sorption capacities of plain chitosan and PE-chitosan for transition metal ions (pH 5.3, NH_4NO_3 1 M).

remarkable increase of sorption capacity after ethylpyridylation is observed for Cu(II) and Ag(I) ions (Fig. 4).

Comparison of the PE-chitosan sorption capacities obtained here and reported in (Baba et al., 1996, 1998; Dhakal et al., 2008) shows that in the latter case capacities do not exceed 0.2 mmol/g, possibly, due to the difference in the matrix structure. However, the results reported in (Rodrigues et al., 1998) for non-cross-linked PM-chitosan give the value of the sorption capacity for Cu(II) at pH = 7.6–1.6 mmol/g, which is very close to the value found here for PE-chitosan (DS 0.8).

Despite the increase of sorption capacity, the selectivity row for PE-chitosan does not differ from that of chitosan Cu(II) > Ni(II) > Co(II) and corresponds to the classical Irving–William series (Irving & Williams, 1953). The negligible sorption capacity of PE-chitosan for transition metal ions at pH < 2 assure possibility to selectively separate noble metal ions from the multi-component solutions.

The difference in optimal conditions for Ag(I) and Au(III), Pt(IV), Pd(II) sorption virtually allows group separation of these metals that can not be achieved with N-,S-containing sorbents showing comparable selectivity for Ag(I) and Au(III) (Talanova, Zhong, Kravchenko, Yatsimirskii, & Bartsch, 2001).

Fig. 4 show that highly substituted PE-chitosan derivatives have remarkably high sorption capacity for Ag(I) ions, which is 2.6 times higher than that of the plain chitosan. Taking into account that sorption occurred under the conditions corresponding to efficient complex formation (deprotonated N-containing groups and eliminated Ag^+–H^+ competition for sorption center) one can estimate the maximum sorption capacity for PE-chitosan with DS 0.8 as 3.5 mmol/g and 1.75 mmol/g approximately, if PE-chitosan acts as bidentate or monodentate ligand, respectively. Comparison of theoretical and experimental values for sorption capacity suggests that chelating function of 2-(2-aminoethyl)pyridyl fragment is not realized in interaction between PE-chitosan and Ag(I), although 1:1 complexes of Ag(I) and 2-(2-aminoethyl)pyridyl are known (Uhlig & Maaser, 1963). However, the structure of this complex is indentified to be of polymeric character that allows considering it as a non-chelate compound (Senel, Yilmaz, & Harrison, 2005). Coordination of Ag(I) with more than one pyridyl fragment was also reported in (Talanova et al., 2001) for synthetic polymers containing pyridyl and bipyridyl functional groups.

4. Conclusions

Here we have suggested a new route to obtain heterocyclic chitosan derivative – N-2-(2-pyridyl)ethylchitosans with DS up to 1.2 using “synthesis in gel” approach. We have shown that introduction of pyridylethyl functional group significantly increased chitosan sorption capacities, which were found to be higher than those reported in literature for chitosan derivatives and most synthetic polymers having heterocyclic functionalities. Analysis of trends in changes of Langmuir constant for noble metals sorption on PE-chitosan of different DS from HCl solutions has shown that Pt(IV) and Pd(II) chlorocomplexes were more strongly bound by pyridylethyl fragments, whereas the chlorocomplex of Au(III) formed stronger complexes with plain chitosan. This tendency was confirmed by desorption of noble metal ions from PE-chitosan and chitosan phase using HCl/thiourea eluents. High recovery degrees for noble metal ions and a negligible sorption of transition metal ions on PE-chitosan at pH < 2 allows its application for selective preconcentration of gold, platinum and palladium ions from multi-component solution for quantitative analytical determination, as well as for recovery of noble 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.2011.08.081.

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