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Simple synthesis and chelation capacity of *N*-(2-sulfoethyl)chitosan, a taurine derivative

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ABSTRACT

This study presents a simple and effective synthesis method of *N*-(2-sulfoethyl)chitosan (NSE-chitosan) via a reaction between sodium 2-bromoethanesulfonate and chitosan that allows polymer transformation without using additional reagents and organic solvents. The chemical structure of the obtained NSE-chitosan was characterized by FT-IR and ^{1}H NMR spectroscopies. Thermogravimetric study of NSE-chitosan coupled with FT-IR analysis has shown stability of the polymer up to 200 °C, which almost does not change with the increase of degree of substitution (DS). The sorption of transition and alkaline earth metal ions from multicomponent solutions on NSE-chitosan was investigated. The synthesized sorbents showed the selective recovery of silver(I) and copper(II) ions from ammonium acetate buffer solution. The increase of DS enhanced the selectivity to silver(I) ions sorption in comparison with copper(II) ions. Selectivity coefficients $K_{Ag/Cu}$ increase from 1.3 to 10.9 with DS increasing up to 0.7 (ammonium acetate buffer solution, pH 6.5). Sorption isotherms of transition metal ions on NSE-chitosan with DS = 0.5 have been fitted using Langmuir, Freundlich, and Redlich–Peterson models. The maximum sorption capacities of sorbent in ammonium acetate buffer solution at pH 6.0 were 1.72 mmol/g for Cu(II), 1.23 mmol/g for Ag(I) and below 0.5 mmol/g for Co(II), Zn(II), Cd(II), Pb(II), Mn(II) and Ni(II) ions.

1. Introduction

Chitosan, the linear cationic (1-4)-2-amino-2-deoxy-β-D-glucan with typical degree of acetylation ca. 0.25, is a versatile polysaccharide, which is able selectively chelate transition metal ions owing to the abundance of primary amino groups along the polymer chains (Babel & Kurniawan, 2003; Guibal, 2004; Miretzkya & Cirelli, 2009; Muzzarelli, 2011). Compared to synthetic complexing polymers, chitosan has several advantages, among which there are biocompatible, non-toxicity and availability (Jayakumar et al., 2010; Kurita, 2006), as well as high hydrophilicity and the flexible structure of the polymer chain (Morris, Castile, Smith, Adams, & Harding, 2009; Ogawa, Yui, & Okuyama, 2004), which enables to adopt the necessary configuration for complexation with metal ions (Steinborn & Junicke, 2000; Varma, Deshpande, & Kennedy, 2004; Whitfield, Stojkovski, & Sarkar, 1993).

Presence of amino and hydroxyl groups in the chitosan structure provides opportunities of its modification to increase sorption activity in reactions with metal ions. For this purpose, one can use ion exchange and complexing groups, including the chelating: EDTA and DTPA (Ge & Huang, 2010; Inoue, Yoshizuka, & Ohto, 1999; Repo, Warchol, Kurniawan, & Sillanpaa, 2010), α-amino acid (Becker, Schlaak, & Strasdeit, 2000; Fujiwara, Ramesh, Maki, Hasegawa, & Ueda, 2007; Ramesh, Hasegawa, Sugimoto, Maki, & Ueda, 2008), carboxyalkyl (Sokovnin et al., 2009; Sun & Wang, 2006; Zhao, Mitomo, Yoshii, & Kume, 2004), thiourea (Bratskaya, Ustinov, Azarova, & Pestov, 2011; Guibal, Vincent, & Mendoza, 2000; Pestov, Koryakova, Leonidov, & Yatluk, 2010), pyridylalkyl (Bratskaya et al., 2012; Pestov, Bratskaya, Azarova, Kodess, & Yatluk, 2011; Rodrigues, Laranjeira, Favere, & Stadler, 1998) and sulfogroups (Baumann, Liu, & Faust, 2003; Holme & Perlin, 1997; Jiang et al., 2010; Muzzarelli et al., 1984; Nishimura et al., 1998). The latter type of derivatives with strongly acidic groups allows application of chitosan as anticoagulant (Baumann et al., 2003; Muzzarelli et al., 1984; Nud'ga, Plisko, & Danilov, 1974), antiviral agent (Nishimura et al., 1998), sorbent for metal ions (Pestov et al., 2013; Petrova et al., 2014) and lipoproteins (Gamzazade, Nasibov, & Rogozhin, 1997), polyelectrolyte (Holme and Perlin, 1997). Introduction of sulfogroup to the molecule of chitosan is

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performed either by direct sulfonation (Holme and Perlin, 1997; Muzzarelli et al., 1984), including regioselective reaction (Baumann et al., 2003; Nishimura et al., 1998) or sulfoalkylation under alkaline conditions yielding the *N*, *O*-substituted product (Muzzarelli, 1977; Nud'ga, Petrova, Ben'kovich, & Petropavlovskii, 2001) or under acid conditions (Jiang et al., 2010). Polymer transformation in the gel state resulting in a selectively N-substituted polymer (Petrova et al., 2014; Pestov et al., 2013) and introduction of sulfogroup using a linker (Muzzarelli, 1992) have been also described.

Here we report a new synthesis method to obtain *N*-(2-sulfoethyl)chitosan (NSE-chitosan) and the results of investigation of NSE-chitosan chemical properties.

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; an average molecular weight of 2.5×10^5 Da was measured using viscometry according to Gamzazade et al. (1985). Sodium 2-bromoethanesulfonate (98%) was purchased from AlfaAesar. All other chemicals were of analytical grade and used without further purification.

The *C*,*H*,*N*,*S*-elemental composition was determined by a Perkin Elmer Elemental Analyzer. FT-IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer using a diffuse reflectance sampling accessory (DRA). ^{1}H NMR spectra were recorded on a Bruker AVANCE-500 spectrometer at 70 °C to increase the solubility of samples and attain better resolution of the signals. Samples were dissolved in D_2O/DCl (concentration 10 mg/ml); sodium 3-(thrimethylsilyl)-1-propanesulfonate was used as an internal standard. Suppression of the solvent signal during the spectrum recording was realized by the "presaturation" technique. The degree of substitution (DS) was calculated using ^{1}H NMR spectra according to the following formula:

$$\mathrm{DS} = \frac{m + 2 \times d}{m + d + a},$$

where *m*—the mole fraction of monosulfoethylated glucosamine units, *d*—the mole fraction of disulfoethylated glucosamine units, *a*—the mole fraction of glucosamine units. *m*, *d*, and *a* values were calculated using integral intensities of the corresponding signals in ^{1}H NMR spectrum.

Thermograms were registered using a Mettler Toledo TGA analyzer.

2.2. Preparation of chitosan derivatives

N-(2-sulfoethyl)chitosan (NSE-chitosan) with 0.3–0.5 degrees of substitution (DS) was synthesized by the methods of chitosan transformation described in (Pestov et al., 2013; Petrova et al., 2014). NSE-chitosan with DS = 0.7 was synthesized using a similar scheme: the mixture of 3.3 g (0.02 mol NH_2) of chitosan, 10 g (0.02 mol) of sodium 2-bromoethanesulfonate and 26 ml water was thoroughly mixed and heated up to 70 °C for 24 h, then cooled. A volume of 20 ml water was added to the mixture. Upon homogenization of the solution the product was precipitated with acetone. Then the product was extracted by hot ethanol during 24 h and dried at 50 °C to the constant weight. ^{1}H NMR spectra of NSE-chitosan, DS = 0.71 (D_2O/DCl), δ ppm: 2.08 (CH_3), 3.23 (*H*-2 GlcNH$_2$), 3.35 (NHCH$_2$CH$_2$), 3.44-4.10 (*H*-2,3,4,5,6, NHCH$_2$*CH*$_2$), 4.62 (H-1 GlcNHAc), 4.94 (H-1 GlcNH$_2$), 5.06 (H-1 GlcNHCH$_2$CH$_2$), 5.12 (*H*-1 GlcN(CH$_2$CH$_2$SO$_3$H)$_2$).

To obtain insoluble sorbents 3.75 g of NSE-chitosan was mixed with 35 ml of water and pH of solution was adjusted up to 7 by concentrated HCl solution. A volume of 12 ml 25% solution of glutaraldehyde was added to the mixture under continuous stirring and the mixture was kept at 60 °C during 24 h. After cooling the precipitate was filtered, washed with water until negative reaction to Cl^- ions, and dried at 50 °C to the constant weight.

2.3. Sorption experiments

To study the sorption properties, NSE-chitosan was shaken with solution containing Cu(II), Ag(I), Ni(II), Co(II), Zn(II), Cd(II), Pb(II), Mn(II), Ca(II), Mg(II), Sr(II), and Ba(II) ions in ammonium acetate buffer (pH 2.0–10.0), ammonia buffer (pH 4.5–10.0), and acetic buffer solutions (pH 2.5–6.5) at solid:liquid ratio 1:2500 during 24–120 h at 200 rpm. The initial concentrations of metals were 1×10^{-4} mol/dm^3. The isotherms of transition metal ions (Ad(I), Ni(II), Co(II), Cu(II), Zn(II), Cd(II), Mn(II) and Pb(II)) sorption on NSE-chitosan with DS = 0.5 were obtained in ammonium acetate buffer solution at pH 6.0. The sorption capacities were calculated using the difference in initial concentration and equilibrium concentration of the metal ions determined by inductively coupled plasma atomic emission spectroscopy using a Thermo Scientific iCAP 6500 spectrometer.

Coefficients of metal ions (M1 and M2) distribution (D) between the solution and the sorbent were calculated according to the formula:

$$D = \frac{C_i - C_s}{C_s},$$

where C_i and C_s are the concentration of the metal ion in the initial solution and the supernatant after equilibrium, respectively.

The coefficient of selectivity $K_{M1/M2}$ was defined as the ratio of distribution coefficients D_{M1} and D_{M2}.

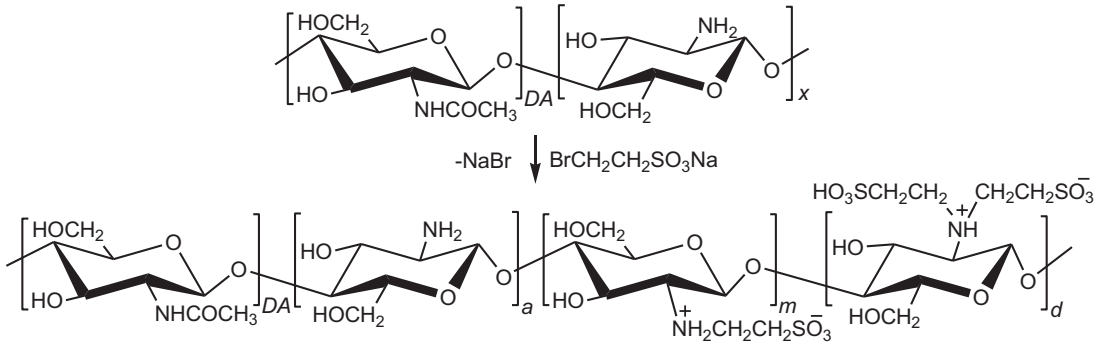
3. Results and discussion

3.1. Preparation of NSE-chitosan

A known method ofsulfoethylchitosan synthesis in a strongly basic heterogeneous conditions using sodium 2-chloroethanesulfonate yields nonselective *N*,*O*-substituted product with a low DS (Nud'ga et al., 1974, 2001). Method of polymer transformations in the gel state in slightly acidic homogeneous conditions (Pestov, Zhuravlev, & Yatluk, 2007; Pestov, Skorik, Kogan, & Yatluk, 2008; Skorik, Pestov, Kodess, & Yatluk, 2012) allows preparation of selectively N-substituted product with an average DS (Pestov et al., 2013; Petrova et al., 2014). In this paper we investigate the interaction of chitosan with sodium 2-bromoethanesulfonate (Scheme 1) without additions of acids and bases. The results obtained indicate that the substitution reaction under such conditions yields selectively N-substituted product (Table 1).

Despite initial heterogeneous reaction conditions, the transformation process yields physical gel of the same quality as chitosan salts gel. Increase of the hydrophilicity and the swellability of NSE-chitosan due to sequential modification of glucosamine units of the polymer promotes the process of gel formation. The same effect was observed in the reactions of chitosan with 3-halopropionic acids (Pestov et al., 2008; Skorik et al., 2012).

Analysis of FT-IR spectra of NSE-chitosan demonstrates that aside from absorption bands characteristic for the chitosan molecule at 3376 (O—H, N—H), 2881 (C—H), 1647 (Amide I), and 1061 (C—O, C—C) cm^{-1}, new very intense bands emerge at 1168 and 1040 cm^{-1} that is characteristic for valence vibrations of the S=O bond. According to ^{1}H NMR spectra (Fig. 1) only amino groups are involved into the reaction of chitosan *N*-sulfoethylation. The ^{1}H NMR spectrum of NSE-chitosan demonstrates signals at 4.95,



Scheme 1. Synthesis and chemical structure of NSE-chitosan; *DA*, *a*, *m*, and *d* are the molar fractions of corresponding glucosamine units.

5.06 and 5.12 ppm corresponding to H-1 atom of glucosamine units containing primary, secondary, and tertiary amine, respectively.

Thus, we have here demonstrated a simple and convenient method of *N*-(2-sulfoethyl)chitosan synthesis without the use of additional reagents and organic solvents.

3.2. Thermal properties NSE-chitosan

Thermogravimetric study of NSE-chitosan in the sodium salt form (Fig. 2) with FT-IR identification of the destruction products shows that the first stage in the range 50–110 °C corresponds to the loss of water, including physically adsorbed water. Further destruction in the range 210–300 °C is related to the degradation of the organic matrix and sulfoethyl groups with formation of water, sulfur dioxide and carbon dioxide gases and acetic acid as a product of destruction of residual acetyl groups in the chitosan. Further degradation of NSE-chitosan up to the temperature 500 °C is accompanied by formation of ethylene and ammonia. Characters of thermoanalytical curves (Fig. 2) of NSE-chitosan with different DS are similar, indicating a negligible impact of sulfoethylation degree on the thermal stability of polymer. In general, the NSE-chitosan retains thermal stability up to 200 °C that is significantly lower compared to unmodified chitosan (Kittur, Prashanth, Sankar, & Tharanathan, 2002). The decrease of thermal stability in comparison with unmodified matrix was also found for cellulose sulfoethylated derivatives, but their thermal stability was still 50–60 °C higher compared to the chitosan sulfoethylated derivatives (Hussein, El-Hady, Sayed, & Hefni, 2012; Sazanov et al., 1981).

3.3. Sorption properties of NSE-chitosan

Most papers devoted to physical and chemical properties of chitosan and chitosan-based sorbents deal with sorption of metal ions from individual solutions. Corresponding affinity trends are formulated on the basis of such data (Becker et al., 2000; Cao, Ge, & Lai, 2001; Fujiwara et al., 2007; Inoue et al., 1999; Pestov et al., 2011). The so-called competitive adsorption of metal ions from multicomponent solutions was discussed in the scientific publications only recently. However, reported works on chitosan-based sorbents are limited to relatively simple systems. Most often sorption from binary systems is investigated (Donia, Atia, & Elwakeel, 2007; Elwakeel, El-Sayed, & Darweesh, 2013; Koong, Lam, Barford, & McKay, 2013; Liu, Chen, & Kim, 2012; Vold, Varum, Guibal, & Smidsrød, 2003), much more rare studies concern ternary (Son, Park, Song, & Yoo, 2004; Yan, Dai, Yang, Yang, & Cheng, 2011) or quadruple (Horzum, Boyaci, Eroglu, Shahwan, & Demir, 2010) systems. At the same time little attention has been paid to the sorption of metal ions by chitosan and its derivatives from the complex multi-component systems.

Fig. 3 presents the pH dependences of Ag(I), Cu(II) and Ba(II) ions sorption on NSE-chitosan with DS = 0.7 (under conditions of metal ions co-existence in ammonium acetate buffer solution). For the other studied metal ions, the sorption capacity does not exceed 0.02 mmol/g at pH from 2 to 8 and 0.04 mmol/g at pH from 8 to 10. One can see that the silver(I) and copper(II) ions are selectively removed by sorbent based on NSE-chitosan with DS of 0.7 as well as by polymers with the lower degree of substitution (Pestov et al., 2013; Petrova et al., 2014). Sorption of the other metal ions almost completely suppressed.

The degree of polymer modification with functional groups is one of the most important parameters defining the selectivity of sorption. From this point of view, the studies of sorption properties and their dependences on DS are of particular interest (Bratskaya et al., 2011, 2012; Koong et al., 2013; Sokovnin et al., 2009; Pestov et al., 2011).

One can notice that sorption of metal ions on NSE-chitosan decreases with increase of DS. However, the selectivity of the silver ion sorption increases more significantly in comparison with copper(II). This fact is confirmed by the corresponding selectivity coefficients $K_{Ag/Cu}$ (Table 2).

Table 1
Conditions of *N*-sulfoethylation of chitosan with sodium 2-bromoethanesulfonate and characteristics of obtained products (24 h).

Conditions of reactions		Characteristic of products		
Molar ratio chitosan:reagent	Concentration of polymer dispersion (%)	*T* (°C)	Sulfur content (%)	DS[a]
1:1	12	70	8.94	0.71
1:2	12	70	9.22	0.72
1:2	21	50	6.46	0.45
1:2	21	70	7.48	0.55
1:3	12	70	9.66	0.78[b]
1:3	12	90	9.32	0.70
1:4	12	70	8.92	0.68
1:5	8	70	9.01	0.70

[a] Degree of substitution is calculated from the ^{1}H NMR spectroscopy data.
[b] Degree of substitution is the same value when carrying out the reaction for 48 h.

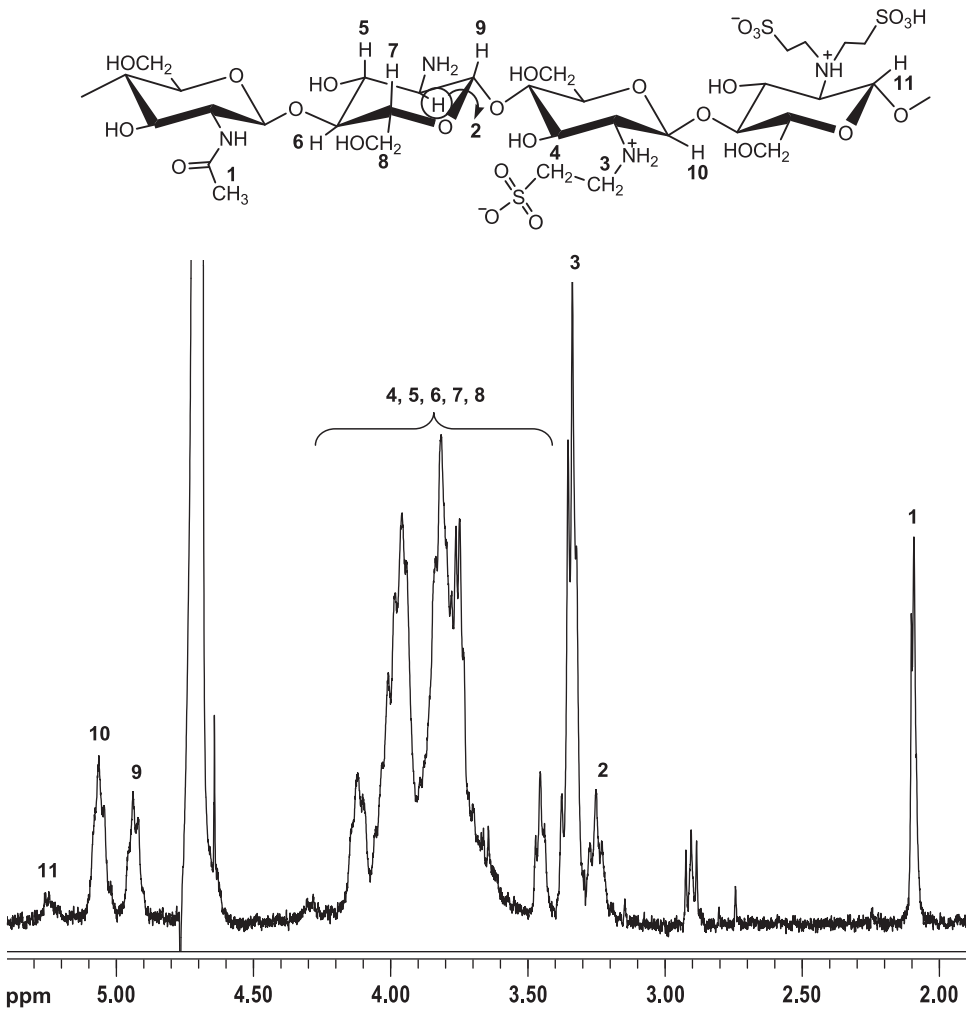


Fig. 1. 400 MHz ^{1}H NMR spectrum of NSE-chitosan with DS = 0.7 (D_2O/DCl).

The observed sorption phenomena originate from the appearance of sulfoethyl groups in the chitosan structure that allows considering NSE-chitosan as a derivative of 2-aminoethanesulfonic acid (taurine). Taurine forms the most stable complexes with silver(I) and copper(II) (Petrova & Neudachina, 2013), therefore adsorption of these ions on NSE-chitosan is significantly enhanced. Complexes of metal ions with taurine are less stable than similar complexes with ammonia (Lur'e, 1989; Petrova and Neudachina, 2013). Thus, it is possible to assume that the decrease of stability of copper(II) and silver(I) complexes with functional groups of NSE-chitosan differentiates polymer affinity to silver(I) and copper(II) ions, and, therefore, increases selectivity of sorption.

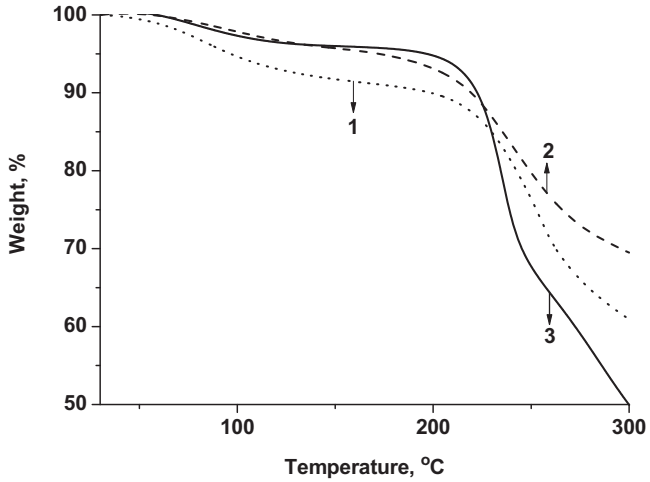


Fig. 2. TGA investigation of NSE-chitosan with DS = 0.3 (1), 0.5 (2) and 0.7 (3).

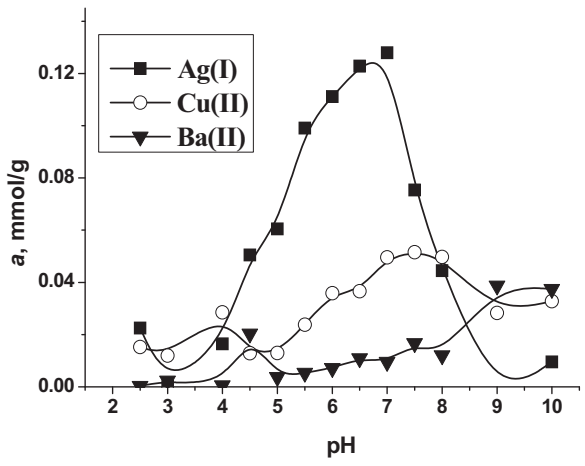


Fig. 3. The pH dependence of sorption *a*, mmol/g, of the metal ions by NSE-chitosan with DS = 0.7. Co-existence of metal ions in ammonium acetate buffer solution.

Table 2
Selectivity of sorption on NSE-chitosan depending on DS in ammonium acetate buffer solution.

DS	$K_{Ag/Cu}$		
	pH 6.0	pH 6.5	pH 7.0
0.3	1.8	1.3	3.0
0.5	5.4	4.5	2.6
0.7	7.1	10.9	6.0

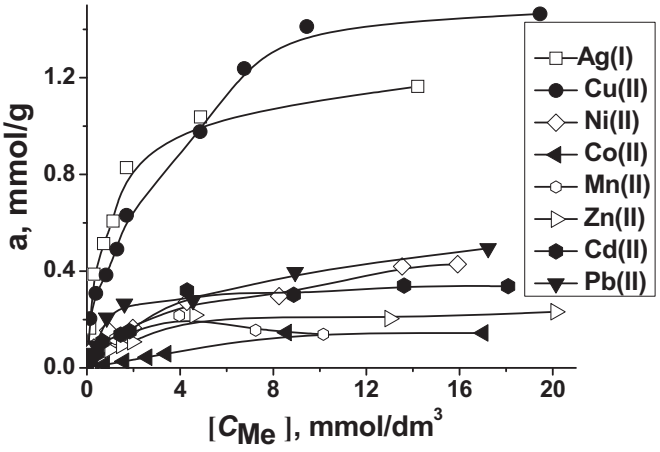


Fig. 4. Sorption isotherms of transition metal ions on NSE-chitosan with DS = 0.5; ammonium acetate buffer solution with pH 6.0. $T = 293 \pm 2$ K.

Competitive sorption of silver(I) and copper(II) ions on chitosan cross-linked by epichlorohydrin was studied elsewhere (Song, Li, Xu, & Wang, 2012). It was shown that at pH 5.6 this sorbent mainly removes the copper ions(II); selectivity coefficient $K_{Ag/Cu}$ is equal to 0.54. Chitosan fiber selectivity was investigated toward the ions of silver(I), copper(II), iron(III) and cadmium(II) (Horzum et al., 2010). It was shown that under conditions of competitive sorption this material preferably removes copper over silver. Thus, it is possible to compare results obtained in the present work with described in literature for unmodified chitosan, and to conclude that the modification of chitosan with sulfoethyl groups enable one to increase considerably the selectivity of extraction of silver(I) ions over copper(II) ions from ammonium acetate buffer solution.

Fig. 4 shows the equilibrium adsorption isotherms obtained for (Ag(I), Ni(II), Co(II), Cu(II), Zn(II), Cd(II), Mn(II) and Pb(II)) ions on NSE-chitosan with DS = 0.5. A relationship was observed between the amount of metal ion adsorbed on the adsorbent surface and the remaining metal ion concentration in the aqueous phase at equilibrium. It was shown that the adsorption capacity increased with the equilibrium concentration of the metal ion in solution, progressively saturating the sorbent. Thus, the highest sorption values are observed for copper(II) and silver(I) ions.

The isotherms obtained were described using Langmuir

$$a = a_m \frac{K_L \times [C]}{1 + K_L \times [C]},$$

Freundlich

$$a = K_F \times [C]^{1/n},$$

and Redlich–Peterson models (Foo & Hameed, 2010; Limousin et al., 2007; McKay, Ho, & Ng, 1999)

$$a = \frac{K_R \times [C]}{1 + a_R \times [C]^{\beta}},$$

where K_L, K_F, K_R, a_R—Langmuir, Freundlich and Redlich–Peterson constants, dm^3/g, $dm^3/(mmol^{1-1/n}\,g)$, dm^3/g, $dm^3/mmol^{1-1/\beta}$, respectively; $1/n$ and β—heterogeneity coefficients; a и a_m—equilibrium and maximum metal sorption, mmol/g; $[C]$—equilibrium concentration, $mmol/dm^3$.

Table 3
The Langmuir, Freundlich and Redlich–Peterson parameters for transition metal ions sorption on NSE-chitosan with DS = 0.5 at $T = 293 \pm 2$ K.

Freundlich model

Metal ion	K_F ($dm^{3/n}(mmol)^{1-1/n}$)	$1/n$	R^2
Cu(II)	0.515	0.391	0.953
Ag(I)	0.587	0.289	0.932
Co(II)	0.028	0.625	0.892
Zn(II)	0.086	0.355	0.878
Cd(II)	0.130	0.402	0.882
Ni(II)	0.136	0.417	0.983
Pb(II)	0.181	0.354	0.958
Mn(II)	0.099	0.263	0.688

Langmuir model

Metal ion	K_L (dm^3/g)	a_m (mmol/g)	R^2
Cu(II)	0.350	1.717	0.977
Ag(I)	1.092	1.230	0.987
Co(II)	0.105	0.245	0.939
Zn(II)	0.453	0.259	0.952
Cd(II)	0.372	0.444	0.931
Pb(II)	0.665	0.479	0.935
Mn(II)	1.318	0.187	0.831
Ni(II)	0.362	0.471	0.948

Redlich–Peterson model

Metal ion	K_R (dm^3/g)	a_R ($dm^{3\beta}/mmol^{\beta}$)	β	R^2
Cu(II)	0.658	0.443	0.951	0.974
Ag(I)	1.608	1.512	0.942	0.987
Co(II)	0.017	1.34×10^{-10}	8.051	0.999
Zn(II)	0.082	0.121	1.331	0.962
Cd(II)	0.128	0.152	1.222	0.927
Pb(II)	0.826	3.376	0.751	0.961
Mn(II)	0.105	0.058	2.071	0.971
Ni(II)	1.569	10.456	0.614	0.981

Langmuir model assumes monolayer adsorption (the adsorbed layer is one molecule in thickness), when adsorption can occur only at a finite (fixed) number of definite localized sites, which are identical and equivalent, with no lateral interaction and steric hindrances between the adsorbed molecules, even on adjacent sites. The Freundlich model is an empirical equation for the sorption onto a heterogeneous surface. Redlich–Peterson isotherm is a hybrid isotherm featuring both Langmuir and Freundlich isotherms, which incorporate three parameters into an empirical equation. According to this model, the mechanism of sorption is a hybrid and does not follow ideal monolayer adsorption. In the limit, it approaches Freundlich isotherm model at high concentration and is in accordance with the low concentration limit of the ideal Langmuir condition.

The calculation of the parameters in the Langmuir, Freundlich, and Redlich–Peterson equations was carried out using mathematical package Origin 8.0. Table 3 presents the relevant constants together with correlation coefficients (R^2).

The maximum adsorption capacity (a_m) obtained from Langmuir model for Ag(I) and Cu(II) are higher than the values found for Ni(II), Co(II), Zn(II), Cd(II), Mn(II) and Pb(II)) showing the following capacity order:

$$Cu(II) > Ag(I) \gg Pb(II) \approx Ni(II) \approx Cd(II) > Zn(II) \approx Co(II) > Mn(II).$$

The sorption capacity of NSE-chitosan with DS = 0.5 for copper(II) and silver(I) ions is in average two times higher than for plain chitosan (pH 5.3, NH4NO3 1 M) (Bratskaya et al., 2012).

The parameter K_F in Freundlich equation is a measure of the sorbate affinity to the sorbent surface. Data in Table 3 show that NSE-chitosan with DS = 0.5 has highest affinity to silver(I) and high enough to copper(II) ions. Much lower values of the

K_F parameter were obtained for cobalt(II), nickel(II), cadmium(II), zinc(II), lead(II), and manganese(II). Thus the affinity trend in sorption of transition metal ions on NSE-chitosan with DS = 0.5 is: Ag(I) > Cu(II) ≫ Pb(II) > Ni(II) ≈ Cd(II) > Mn(II) ≈ Zn(II) > Co(II). These results are consistent with the selective properties of this material (Petrova et al., 2014).

The best fit of the experimental data was obtained using Redlich–Peterson isotherm for all metal ions. High R^2 values were obtained using Langmuir model to fit sorption isotherms of copper(II), silver(I) and cadmium(II) ions, and Freundlich model for sorption of nickel(II) and lead(II) ions. So, one can conclude that the sorbent surface is chemically non-uniform, i.e. functional groups are of various chemical natures (sulfo-, hydroxy- and aminogroups).

4. Conclusion

Here we have suggested a new route to obtain sulfoalkyl chitosan derivative—*N*-(2-sulfoethyl)chitosan with DS up to 0.7 using "synthesis in gel" approach. We have shown the possibility of sulfoalkylation of polymer by reaction of nucleophilic substitution without use of a strong base and organic solvents. These conditions of chitosan transformation allow referring the developed approach to methods of "green chemistry". As the reaction proceeds under neutral conditions, polymer-analogous transformations yields selectively N-substituted products. The thermal stability of NSE-chitosan is lower than that of unmodified chitosan and sulfoderivatives of cellulose. Possibility to use the synthesized materials for the separation of silver(I) and copper(II) ions from a mixture of interfering metal ions is demonstrated. It is established that selectivity of sorption of silver(I) ions over copper(II) ions increases with increase of percentage of *N*-2-sulfoethyl groups in sorbent. NSE-chitosan with DS = 0.5 demonstrates high capacity for Cu(II) and Ag(I) ions: 1.72 and 1.23 mmol/g, respectively. These features of chitosan interaction with metal ions results from formation of taurine derivative.

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