

PHYSICAL CHEMISTRY  
OF SOLUTIONS

## Effect of Complex-Former Ion Concentration on the Selectivity of Metal Ion Sorption on Cross-Linked *N*-2-Sulfoethylchitosan

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Received December 5, 2016

**Abstract**—Copper(II), silver(I), cobalt(II), nickel(II), zinc(II), manganese(II), and magnesium(II) sorption isotherms on cross-linked sulfoethylated chitosan with the degree of sulfoethylation DS = 0.7 (SEC 0.7) have been plotted for the individual or collective presence of these ions in solution have been constructed. The capacities of the studied sorbents for the studied metal ions have been calculated by processing the sorption isotherms. SEC 0.7 is found to have the greatest affinity to copper(II) and silver(I); their presence almost completely suppresses the sorption of associated metal ions. The Redlich–Peterson model gives the best fit to the sorption isotherms for collectively present metal ions, indicating the chemical inhomogeneity of the sorbent surface.

DOI: 10.1134/S003602361803018X

### THEORY

Silver is a metal widely used in various industries. In particular, silver is used for the manufacture of catalysts, cables, conductive parts of electrical installations, alloys, jewelry, medicines, etc. [1]. At the same time, silver is classified as a potentially toxic and potentially carcinogenic element [2, 3]. The high biological activity of silver, along with the wide spread of this element, stimulates the development of methods for the analytical determination of silver in a wide variety of objects. In many cases, however, the direct determination of silver(I) by instrumental methods is complicated by the low content of the analyte and by the significant interfering effect of the accompanying metal ions. These factors cause the use of sorption methods for separation and preconcentration in the determination of silver in various objects.

Previously [4–7] we showed that cross-linked *N*-2-sulfoethylechitosans can selectively recover silver(I) ions from complex solutions. Copper(II) ions have the greatest interfering effect on this process. One factor influencing sorption selectivity is the concentration of complex-forming ion. A sorption isotherm plots the equilibrium amount of the sorbed metal ion as a function of its equilibrium concentration in solution. Well-known Langmuir, Freundlich, Redlich–Peterson, Toth, and other models are widely used to fit sorption isotherms [8–10]. Such an analysis of isotherms allows one to draw conclusions about the sorbate's affinity to the sorbent, the nature of its surface, to calculate the capacitance values, etc.

This study is focused on the effect of complex-forming ion concentration on the selectivity of metal ion sorption by an *N*-2-sulfoethylechitosan-based material with DS = 0.7.

### COMPUTATION DETAILS

The sorption isotherms were fitted by Langmuir, Freundlich, and Redlich–Peterson equations [8].

The Freundlich equation is an empirical one; it is used to fit reversible sorption on a heterogeneous surface and has the form

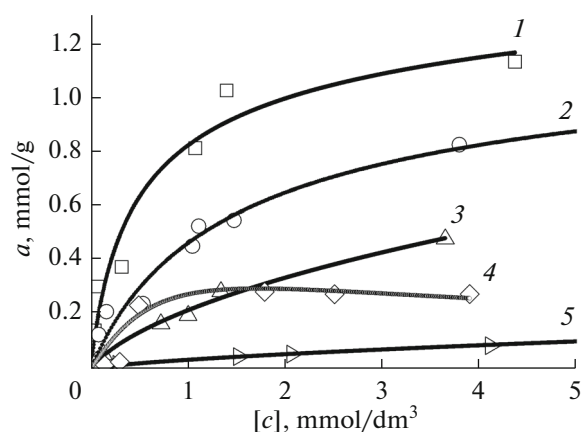
$$a = K_F [c]^{1/n},$$

where  $a$  is the sorbed metal ion amount per unit weight of the sorbent in equilibrium (mmol/g),  $c$  is the equilibrium sorbate concentration in aqueous phase (mmol/L), and  $K_F$  is the Freundlich isotherm constant ((mmol/g) (L/mmol)<sup>1/n</sup>) [8].

The Langmuir model has the underlying idea that a monomolecular sorbate layer is formed on the sorbent surface and all sorption sites have equal values of the energy and enthalpy of sorption:

$$a = \frac{a_{\max} K_L [c]}{1 + K_L [c]},$$

where  $a$  and  $a_{\max}$  are, respectively, equilibrium sorption and the exchange capacity of the sorbent, mmol/g;  $c$  is equilibrium sorbate concentration in aqueous phase, mmol/L; and  $K_L$  is the Langmuir isotherm constant, L/g [8].



**Fig. 1.** Measured and calculated, by Redlich–Peterson model, metal ion sorption isotherms for (1) silver(I), (2) copper(II), (3) nickel(II), (4) manganese(II), and (5) cobalt(II) on SEC 0.7 in their individual presence in solution (ammonium acetate buffer solution, pH 6.5,  $20 \pm 1^\circ\text{C}$ ).

The Redlich–Peterson equation, which combines the features of Freundlich and Langmuir equations, is used to fit sorption on energetically inhomogeneous surfaces:

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

where  $a$  is equilibrium sorption, mmol/g;  $c$  is equilibrium sorbate concentration in aqueous phase, mmol/L;  $a_R$  and  $K_R$  are Redlich–Peterson isotherm constants,  $\text{L}^\beta/\text{mmol}^\beta$  and  $\text{L/g}$ , respectively; and  $\beta$  is heterogeneity factor [8].

The fitting of metal ion sorption isotherms by the above-considered model equations was carried out using the Origin 8.0 program package.

## EXPERIMENTAL

The preparation and identification of glutaraldehyde-cross-linked *N*-2-sulfoethylechitosan having a degree of amino-group hydrogen atom substitution of 0.7 (SEC 0.7) are described elsewhere [6]. Metal ion (silver(I), copper(II), nickel(II), cobalt(II), zinc(II), manganese(II), and magnesium(II)) sorption isotherms on SEC 0.7 were measured at room temperature by a confined volume method where a sorbent weight (0.0200 g) was added with a 50.0 mL of a solution containing studied metals in a set concentration. The solution pH was adjusted to 6.5 by ammonium acetate buffer solution. Metal ion concentrations in solutions prior to and after sorption were determined by flame atomization atomic absorption spectroscopy on a Solaar M6 spectrophotometer. The solution pH was monitored with an I-160MI ion meter equipped with an ESK-10601/7 combination glass electrode. Deionized water was prepared using a Millipore Milli-Q Academic high water purification system.

## RESULTS AND DISCUSSION

### *Metal Ion Sorption Isotherms on SEC 0.7 in the Individual Presence of Metals in Solution*

Metal ion sorption isotherms on SEC 0.7 were measured at pH of 6.5 (ammonium acetate buffer solution), which pH value provides for the most selective recovery of silver(I) compared to copper(II) [6]. Silver(I) and copper(II) sorption was studied along with nickel(II), cobalt(II), and manganese(II), which are members (as copper(II), too) of the well-known Irving–Williams series [11] (Fig. 1). The increasing equilibrium concentrations of complex-forming ion were found to increase its equilibrium sorption (Fig. 1). The highest sorption capacities were observed for silver(I).

The parameters obtained by fitting metal ion sorption isotherms on SEC 0.7 in terms of the Langmuir, Freundlich, and Redlich–Peterson models are listed in Table 1. The results of fitting the cobalt(II) sorption isotherm using the Redlich–Peterson equation were unsatisfactory because of the low sorption of this ion on SEC 0.7, so they are omitted in Table 1.

The Freundlich fit of sorption isotherms gave values of  $K_F$ , the parameter that characterizes the metal ion affinity of the sorbent (Table 1). SEC 0.7 was found to have the highest affinity to silver(I) ( $K_F = 0.741$ ). Similar results were obtained previously [6] for SEC 0.5, a sorbent with a lower degree of sulfoethylation. On SEC 0.5,  $K_F$  for silver(I) and copper(II) was 0.587 and 0.515, respectively. Thus, the increasing degree of SEC sulfoethylation increases the silver(I) affinity of the sorbent. This matches the trend we discovered earlier [7] that silver sorption selectivity increases relative to copper as the degree of chitosan sulfoethylation increases.

The increasing order of  $K_F$  values in which metal ions can be arranged is as follows:  $\text{Ag(I)} > \text{Cu(II)} > \text{Ni(II)} > \text{Mn(II)} > \text{Co(II)}$ . This order agrees with the increasing order of sorption capacities determined by the Langmuir equation in which the studied metal ions can be arranged ( $a_{\text{max}}$ , mmol/g, Table 1). The highest values of capacity in the case of SEC 0.7 were obtained for copper(II) and silver(I). For most of the studied metal ions, sorption capacities on SEC 0.5 [6] are lower than on SEC 0.7. Thus, the increasing degree of chitosan sulfoethylation leads to an increase in metal ion uptake for the following reasons. On the one hand, it becomes possible to form a greater amount of chelate complexes involving a metal ion and amino and sulfo functionalities of the sorbent. On the other, part of the metal ions can be recovered via electrostatic interactions with the sulfo groups of SEC 1.0. We showed previously [12] that the contribution of ion exchange into metal ion recovery increases as the degree of chitosan sulfoethylation increases under dynamic conditions.

**Table 1.** Parameters of Langmuir, Freundlich, and Redlich–Peterson models for SEC 0.7 derived from processing of silver(I), nickel(II), cobalt(II), copper(II) and manganese(II) sorption isotherms on SEC 0.7 in the individual presence of the metal ions in ammonium acetate buffer solution (pH 6.5)

Langmuir equation				
Metal ion	$a_{\max}$ , mmol/g	$K_L$ , L/mmol	$R^2$	
Ag(I)	1.293	1.894	0.948	
Ni(II)	0.880	0.334	0.992	
Co(II)	0.274	0.128	0.986	
Cu(II)	1.199	0.622	0.980	
Mn(II)	0.331	2.469	0.882	
Freundlich equation				
Metal ion	$K_F$ , (mmol/g) (L/mmol) <sup>1/n</sup>	$n$	$R^2$	
Ag(I)	0.741	2.868	0.923	
Ni(II)	0.215	1.578	0.992	
Co(II)	0.035	1.450	0.998	
Cu(II)	0.452	3.100	0.954	
Mn(II)	0.205	3.078	0.768	
Redlich–Peterson equation				
Metal ion	$K_R$ , L/g	$a_R$ , L <sup>β</sup> /mmol <sup>β</sup>	$\beta$	$R^2$
Ag(I)	3.391	3.101	0.898	0.937
Ni(II)	0.646	1.952	0.525	0.991
Cu(II)	0.881	0.888	0.936	0.978
Mn(II)	0.551	0.985	1.458	0.906

We compared the copper(II) and silver(I) capacity values obtained for SEC 0.7 against the data reported in the literature for cross-linked chitosan and non-cross-linked chitosan unmodified by additional complex-forming groups. The copper(II) capacity of non-cross-linked chitosan was determined by various research teams to be 2.5 (pH 5.0) [13], 3.2 (pH 3.5) [13], and 1.3 (pH 6.0) [14] mmol/g. For epichlorohydrin- or glutaraldehyde-cross-linked chitosan, the copper(II) ion capacity is also appreciably dependent on the sorbent properties (for example, the degree of desacetylation and the degree of cross-linking of the chitosan) and the parameters of sorption experiment, and falls within the range 0.6–2.6 mmol/g [14–17]. The sorption conditions closest to those used in our study (1 mol/L NH<sub>4</sub>NO<sub>3</sub> solution as the background electrolyte) were implemented in [18]. There were determined the copper(II) and silver(I) capacities of unmodified chitosan, amounting to 0.3 and 0.6 mmol/g, respectively (1 mol/L NH<sub>4</sub>NO<sub>3</sub>, pH 5.3, and individual presence of metal ions in solution). Thus, inserting sulfoethyl groups considerably increases the sorption capacity of chitosan.

Noteworthy, for chitosans that are not modified by additional complex-forming groups, silver(I) capacities are relatively low compared to copper(II) capacities. So, the capacity of silver(I)-imprinted and epichlorohydrin-cross-linked chitosan was 1.1 mmol/g [19]. The glutaraldehyde-cross-linked imprinted chitosan had a silver(I) sorption capacity of 0.8 mmol/g [20]. Thus, the silver(I) sorption capacities for SEC 1.0 exceed the values reported for non-cross-linked, cross-linked and imprinted chitosans.

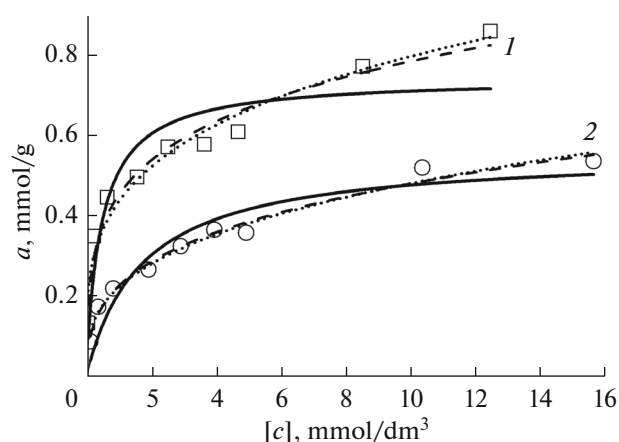
For all of the studied metal ions, except for silver(I), the Redlich–Peterson equation provides the best fit of experimental data, evidencing a chemical inhomogeneity of the sorbent surface (Table 2). On the studied material, metal ion sorption can be due to the involvement of primary and secondary amino, sulfo, and hydroxy groups in complexing. For some metal ions (copper(II), cobalt(II), and nickel(II)), relatively high correlation coefficients were also obtained when sorption isotherms were fitted by Langmuir and Freundlich equations. This good fit was due to the fact that, under certain conditions, the Redlich–Peterson equation can convert to the equations of these models. For silver(I) sorption isotherm,

**Table 2.** Parameters of Langmuir, Freundlich, and Redlich–Peterson models derived from processing of silver(I) and copper(II) sorption isotherms on SEC 0.7 in the collective presence of the metal ions in solution

Langmuir equation				
Metal ion	$a_{\max}$ , mmol/g	$K_L$ , L/mmol	$R^2$	
Ag (I)	0.747	2.062	0.849	
Cu (II)	0.576	0.575	0.926	
Freundlich equation				
Metal ion	$K_F$ , (mmol/g) (L/mmol) $^{1/n}$	$n$	$R^2$	
Ag(I)	0.436	3.821	0.958	
Cu(II)	0.231	3.053	0.978	
Redlich–Peterson equation				
Metal ion	$K_R$ , L/g	$a_R$ , L $^\beta$ /mmol $^\beta$	$\beta$	$R^2$
Ag(I)	9.987	20.939	0.782	0.968
Cu(II)	2.492	9.581	0.716	0.982

unlike for the other metal ions studied here, the highest correlation coefficients were obtained with the Langmuir model. This indicates that a monomolecular sorbate layer can be formed upon silver sorption on the SEC 0.7 surface.

Thus, studying the effect of complex-forming ion concentration on metal ion sorption on SEC 0.7, we have shown that, when present individually in solution, other transition metals, apart from silver(I), are



**Fig. 2.** Measured and calculated, by Langmuir (solid lines), Freundlich (dotted), and Redlich–Peterson (dashed lines) models, metal ion sorption isotherms for (1) silver(I) and (2) copper(II) on SEC 0.7 in their collective presence in solution (ammonium acetate buffer solution, pH 6.5, 20 ± 1°C).

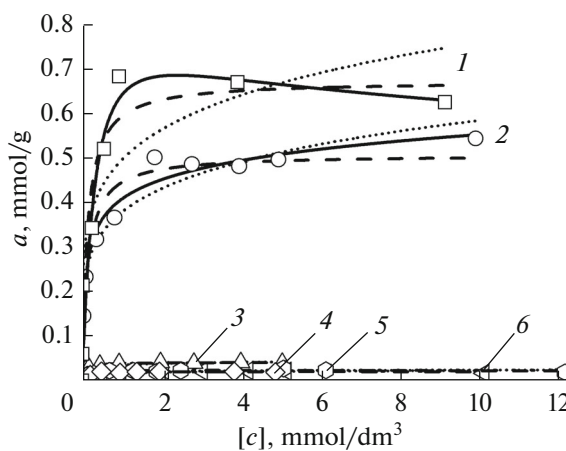
recovered to a considerable degree on the *N*-2-sulfoethylchitosan-based material. However, it is difficult to infer how the concentration affects sorption selectivity from an inspection of isotherms obtained in the individual presence of metal ions in solution. Therefore, the next stage of our work was to study metal ion sorption on SEC 0.7 in their collective presence in solution.

#### *Metal Ion Sorption Isotherms on SEC 0.7 for in Collective Presence of Metals in Solution*

Metal ion sorption isotherms on SEC 0.7 were obtained for a two-component system (copper(II) and silver(I) ions) (Fig. 2) and a six-component system (copper(II), silver(I), cobalt(II), nickel(II), magnesium(II), and zinc(II) ions) (Fig. 3).

As the number of components in the studied systems increases, the capacity of SEC 0.7 decreases appreciably for all of the studied metal ions (Figs. 2, 3) compared to the results obtained in the individual presence of metals in solution (Fig. 1). Since the number of sorption sites on the SEC 0.7 surface is limited, the greatest recovery under competitive sorption conditions is observed for those metal ions that form the most stable complexes with the functionalities of the sulfoethylated chitosan [21], namely, for copper(II) and silver(I). The uptake of interfering ions (nickel(II), cobalt(II), magnesium(II), and zinc(II)) is suppressed almost completely (Fig. 3).

The results of processing the isotherms measured for the two- and six-component systems are shown in Table 2 and Table 3, respectively.



**Fig. 3.** Measured and calculated, by Langmuir (dashed lines), Freundlich (dotted lines), and Redlich–Peterson (solid lines) models, metal ion sorption isotherms for (1) silver(I), (2) copper(II), (3) nickel(II), (4) zinc(II), (5) magnesium(II), and (6) cobalt(II) on SEC 0.7 in their collective presence in solution (ammonium acetate buffer solution, pH 6.5, 20 ± 1°C).

**Table 3.** Parameters of Langmuir, Freundlich, and Redlich–Peterson models derived from processing of silver(I), nickel(II), cobalt(II), copper(II), zinc(II), and magnesium(II) sorption isotherms on SEC 0.7 in the collective presence of the metal ions in solution

Langmuir equation				
Metal ion	$a_{\max}$ , mmol/g	$K_L$ , dm <sup>3</sup> /mmol	$R^2$	
Ag(I)	0.672	7.502	0.924	
Ni(II)	0.041	14.941	0.996	
Co(II)	0.022	10.504	0.924	
Cu(II)	0.507	7.118	0.951	
Mg(II)	0.024	10.103	0.893	
Zn(II)	0.021	9.436	0.960	
Freundlich equation				
Metal ion	$K_F$ , (mmol/g) (L/mmol) <sup>1/n</sup>	$n$	$R^2$	
Ag(I)	0.496	5.399	0.813	
Ni(II)	0.036	9.055	0.960	
Co(II)	0.018	9.577	0.810	
Cu(II)	0.378	5.300	0.956	
Mg(II)	0.020	12.454	0.825	
Zn(II)	0.018	7.602	0.878	
Redlich–Peterson equation				
Metal ion	$K_R$ , L/g	$a_R$ , L <sup><math>\beta</math></sup> /mmol <sup><math>\beta</math></sup>	$\beta$	$R^2$
Ag(I)	2.369	2.696	1.138	0.928
Ni(II)	0.607	14.6332	1.002	0.996
Co(II)	0.146	5.799	1.096	0.939
Cu(II)	8.068	18.787	0.888	0.978
Mg(II)	0.168	6.415	1.059	0.890
Zn(II)	0.143	6.120	1.089	0.968

Analyzing the correlation coefficient values ( $R^2$ ), we may infer that the Redlich–Peterson equation provides the best fit to metal ion sorption from multicomponent systems. This evidences a chemical inhomogeneity of SEC 0.7, in particular, the involvement of different groups in sorption.

Compared to the results obtained for the individual presence of metal ions in solution, a systematic decrease is observed in parameter  $K_F$  of the Freundlich equation for the two-component system and six-component system, this parameter characterizing the metal ion affinity of the sorbent. The greatest values of this parameter were obtained for silver(I) and copper(II). For the other metal ions,  $K_F$  did not exceed 0.04 because of the competing effect of copper(II) and

silver(I). The sorption capacities of SEC 0.7 to these metal ions, determined by fitting the sorption isotherm by the Langmuir equation, were also insignificant (Table 3). For copper(II) and silver(I), there is observed some decrease in capacity compared to the results obtained in the individual presence of metal ions in solution (Table 1). Noteworthy, the greatest values of the affinity parameters and sorption capacity in the collective presence of metal ions in solution were obtained for silver(I).

The above results may be compared to copper(II) and silver(I) recovery on chitosan in their collective presence in solution. Epichlorohydrin-cross-linked chitosan recovers copper(II) to a greater extent compared to silver(I) recovery [19]. Horzum et al. reported the selectivity series for a chitosan-based fiber under competitive sorption conditions: Cu(II) > Fe(III) > Ag(I) > Cd(II) [22]. Thus, functionally unmodified chitosan recovers copper(II) to a greater extent than it recovers silver(I). Mao et al. reported opposite results [23]. They determined silver(I) and copper(II) capacities for tripolyphosphate-cross-linked chitosan, equal to 0.77 and 0.24 mmol/g, respectively. However, Mao et al. themselves suggested that a considerable contribution to copper(II) and silver(I) recovery comes from interaction with the cross-linking agent.

Thus, it has been established that chitosan modification by sulfoethyl groups makes it possible to appreciably change the selectivity properties of this polymer. In the collective presence of metal ions, copper(II) and silver(I) suppress the sorption of associate metal ions over a wide range of equilibrium concentrations.

## CONCLUSIONS

We have studied the effect of the complex-forming ion concentration on the recovery of metal ions on the material based on cross-linked *N*-2-sulfoethylechitosan. Metal ion sorption isotherms have been obtained in the individual and collective presence of metal ions in solution. The sorption isotherms have been mathematically processed to determine the metal ion sorption capacities of SEC 0.7 and the affinities of sorbates to the sorbent surface, and to suggest the sorption scheme. A considerable mutual influence of metal ions has been elucidated in their sorption on sulfoethylated cross-linked chitosan, this influence consisting in suppression of the recovery of associate metal ions by copper(II) and silver(I) ions.

## ACKNOWLEDGMENTS

The reported study was founded by RFBR according to the research project no. 16-33-00110 mol\_a.

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*Translated by O. Fedorova*