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Sorption of nickel (II) and manganese (II) ions from aqueous solutions

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Mine water from non-ferrous metal deposits is often contaminated with nickel and manganese ions. The entry of these ions, especially nickel, into surface waters and underground aquifers is undesirable since it has a negative effect on living organisms and worsens the condition of drinking water sources. One of the promising methods for selectively extracting nickel ions and obtaining an eluate suitable for further use is sorption by weakly acid cation exchangers with chelate groups of iminodiacetic acid.

As part of the study, sorption isotherms of nickel and manganese ions by Lewatit MonoPlus TP 207 cation exchanger in mono- and bicomponent systems were obtained. In monocomponent systems, the maximum static exchange capacity (SEC) of the cation exchanger for nickel ions is 952 mmol/dm^3, and in bicomponent systems – 741 mmol/dm^3; for manganese ions– 71 mmol/dm^3 and 49 mmol/dm^3, respectively. It is obvious that the studied cation exchanger has a greater capacity for nickel ions than for manganese ions.

The influence of a temperature increase from 300 to 330 K on the sorption of nickel and manganese ions was established: in monocomponent systems, the maximum degree of extraction of the former increases from 65 to 77 % (SEC from 337 to 399 mmol/dm^3), and the latter from 21 to 35 % (SEC – from 140 to 229 mmol/dm^3); in bicomponent systems, the extraction of nickel ions increases from 59 to 78 % (SEC – from 307 to 429 mmol/dm^3), and manganese ions decreases from 20 to 17 % (SEC – from 164 to 131 mmol/dm^3). The predominant increase in the indicators is due to the filling of the sorption centers of the ion-exchange resins, which are energetically unfavorable for the exchange of counterions at a lower temperature.

The influence of the pH of the solution on sorption was determined: the intensification of the process for nickel ions is observed in the pH range of 8.0-8.5 in a monocomponent solution and 8.0-9.0 in a bicomponent solution, for manganese ions in the range of 8.0-9.5 in both cases. The increase in the degree of extraction of ions and the exchange capacity of the ion exchanger with increasing pH is associated with the appearance of singly charged hydroxocations, dissociation of the functional groups of the sorbent and, to some extent, with the subsequent formation of insoluble forms of nickel and manganese. However, with increasing pH, a decrease in the selectivity of nickel extraction is observed: the ion separation coefficient decreases from 14.0 to 6.0 in the pH range of 6.0-11.0.

Key words: nickel; manganese; chelating cation exchanger; sorption; ion exchange; exchange capacity; mine water, water treatment

Introduction. Nickel and manganese ions are the most typical impurities of mine water at the non-ferrous metal deposits, they are present due to the leaching of copper-nickel ores, manganites, pyrolusite by groundwater. At one of these abandoned fields of the Urals, as a result of underground (artesian) water entering the worked out spaces, mainly located at a depth of 100-300 m, mine water is formed, which is heavily contaminated with these ions (nickel content is up to 1,5 mg/dm^3, manganese – up to 0.7 mg/dm^3 at pH 6.0-7.0) and affecting the state of nearby natural reservoirs and drinking water sources. It is known that there is no reliable mechanism for the self-purification of water from nickel ions (and other non-ferrous metals): nickel is redistributed from one natural reservoir to another, interacting with various living organisms and leading to undesirable consequences.

Among the known methods of purification of mine water from nickel and manganese ions, the most promising one is the sorption by mineral and synthetic materials due to the high degree of metal extraction and the absence of secondary contamination of the treated water compared to traditional methods of treatment [1, 3-5, 9, 10, 12, 23]. The possibility of the selective extraction of valuable impurities from mine water such as non-ferrous and rare metals using special ion-exchange resins is of particular interest. Studies have shown that the best extraction of non-ferrous metals is provided by weakly acidic macroporous cation exchangers with chelate groups of iminodiacetic acid [11, 13-20]. Process flows with multistage selective sorption of non-ferrous metal ions make it

possible to obtain relatively pure concentrated monocomponent solutions that can be used to produce commercial products [7, 22]. When implementing such technology, it is important to know what effect the impurities contained in the purified water can have on each other.

The purpose of the paper is to determine the basic laws of sorption of nickel and manganese ions from aqueous solutions, including the detection of their mutual influence, by typical weakly acid macroporous cation exchange resin with chelate groups of iminodiacetic acid.

Methods of research. For sorption studies, mono- and bicomponent solutions based on nickel and manganese sulfates dissolved in distilled water were prepared. The content of metal ions in them was within the range of 200 ± 20 mg/dm^3. The composition of the model solutions is determined by the presence of the studied components in real conditions (mine water), and their high contents are associated with the need to obtain information about the patterns of the sorption process, determined by the results of chemical analysis of the initial and final solutions, taking into account the minimization of possible errors and the elimination of external diffusion limitations.

According to the results of previous studies on the extraction of non-ferrous metals from various solutions, Lewatit MonoPlus TP 207 cation exchanger (hereinafter TP 207), which is an analog of Purolite S930 and Amberlite IRC-748 ion exchange resins, was chosen as a sorbent [8]. The cation exchange resin was converted to the H$^+$ form using a 10 % solution of sulfuric acid, then it was washed with distilled water to control the sulfate content by a qualitative reaction with barium chloride and, finally, it was kept for two days at room temperature to a constant weight, i.e. transferred to air-dry condition.

As part of the research, changes in the equilibrium concentrations of nickel and manganese ions in mono- and bicomponent solutions upon contact with TP 207 were determined depending on several variables and constant parameters. Firstly, from a change in the ratio of the solution volume to the volume of resin liquid:solid (L:S) (50-5000) at a constant temperature (300 K), pH (6.0), contact time (24 h), and stirring rate (200 rpm). To ensure the selected L:S ratios, 0.01-1 g of ion exchange resin was added to 50 cm^3 of mono- and bicomponent solutions. Secondly, from a change in the contact time of the solution with the resin (2-180 min) at two temperatures (300 and 330 K), the constant ratio L:S (200), pH (6.0), and mixing rate (200 rpm). The studies were in fact carried out at temperatures of 300, 310, 320, and 330 K, but this article presents the dependencies for extreme values, which clearly show an increase in the sorption capacity of the components in a given temperature range. Thirdly, from a change in the pH of the solution (6.0-11.0) with the constancy of L:S (200), temperature (300 K), contact time (180 min), and stirring rate (200 rpm). The pH level adjustment in the alkaline region was carried out with a sodium hydroxide solution.

The content of nickel and manganese ions in solutions was determined on the "Shimadzu AA-7000" atomic absorption spectrophotometer.

Discussion of results. Figure 1 shows the dependences of the degree of extraction (β, %) of nickel and manganese ions on TP 207 based on the L:S ratio from the corresponding mono- and bicomponent solutions.

In monocomponent solutions with the ratio L:S = 50, nickel recovery is 2.3 times higher than manganese, but at L:S = 5000 it reaches a level equitable to both ions. In a bicomponent solution at L:S = 50, the extraction of the first component is 6.2 times higher than the second one, and at L:S = 5000, the extraction of the second tends to zero. Based on this, it can be concluded that the extraction of manganese ions from the solution in the presence of nickel cations is suppressed.

Figure 2 shows the sorption isotherms of nickel and manganese ions from mono- and bicomponent solutions on TP 207 cation exchange resin, where C_E is the equilibrium concentration of the component in the liquid phase (mmol/dm^3), SEC (or Q_E) is the static exchange capacity of the ion exchanger for the extracted ion (mmol/dm^3).

In the presented isotherms, the domain of applicability of the classical models of monomolecular sorption can be distinguished: Henry – initial straight sections; Langmuir and Freundlich are the
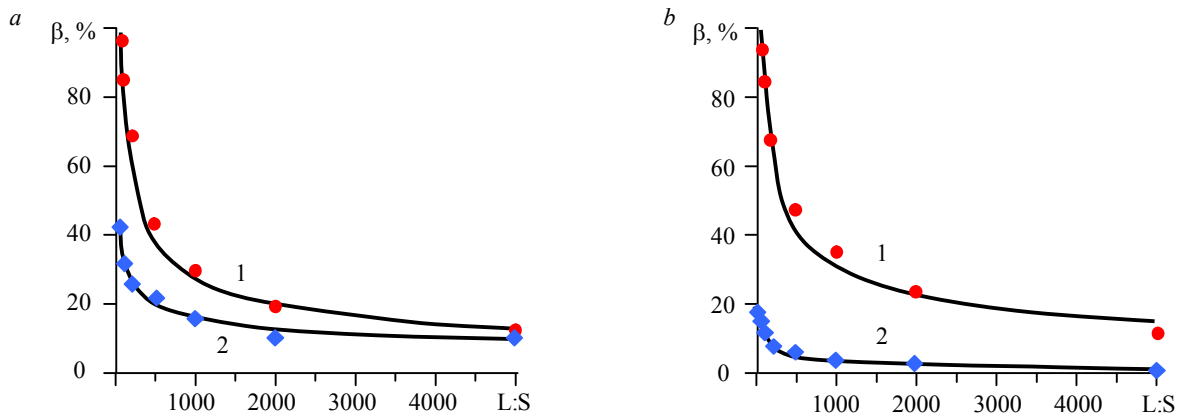
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Fig.1. Dependences of the degree of extraction of Ni^{2+} (1) and Mn^{2+} (2) ions on TP 207 from the L:S ratio
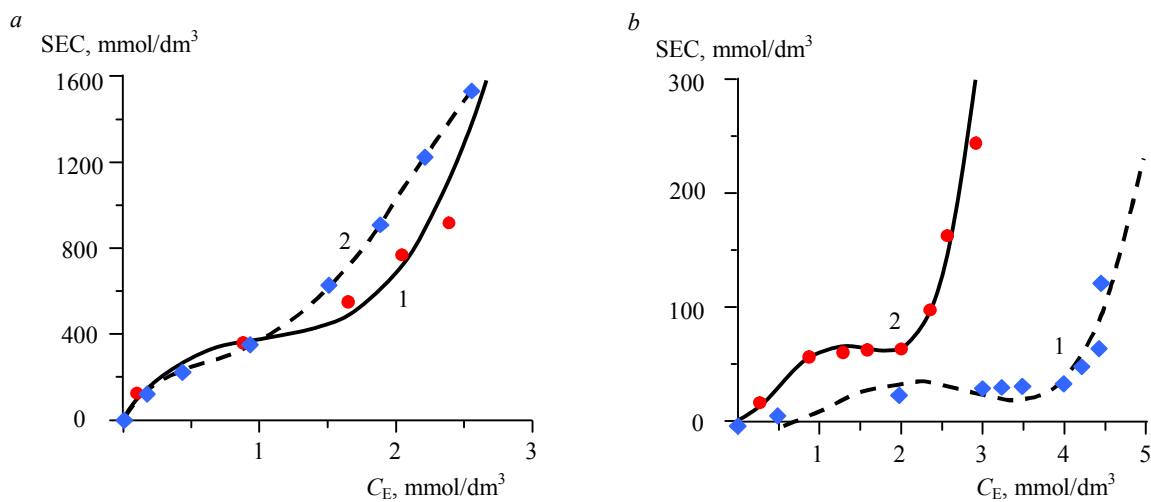in mono- (*a*) and bicomponent solutions (*b*)

Fig.2. Dependences of the static exchange capacity of the TP 207 ion exchanger on the equilibrium concentrations
of Ni^{2+} (*a*) and Mn^{2+} (*b*) in mono- (1) and bicomponent solutions (2)

following sections of a logarithmic nature. The following are sections of an exponential form that cannot be explained by the indicated models. It was suggested that these regions and, in general, S-shaped form of isotherms correspond to the Dubinin-Radushkevich model or the theory of micropore volumetric filling (TMVF), created based on the Polanyi theory of polymolecular adsorption. Within the framework of both theories, it is assumed that the adsorption of the solute by the sorbent does not stop after filling the monomolecular layer, but proceeds further along with the mechanism of formation of polymolecule layers in the field of action of physical adsorption forces. Although TMVF was originally formulated to explain the processes of condensation of a gaseous substance in the micropores of a sorbent, recently its mathematical apparatus is often used to sorb particles of a solute from a liquid phase into a polymer matrix of a sorbent [2].

According to the official classification of porous systems proposed by M.M.Dubinin and adopted by IUPAC, pores of solid sorbents can be divided into three groups according to size: micropores – up to 2 nm, mesopores – from 2 to 50 nm and macropores – more than 50 nm [21]. The studied cation exchanger TP 207 refers to macroporous resins, the matrix is obtained by copolymerization of styrene and divinylbenzene in the presence of a porogen. The gel phase of such resins is highly dense and penetrated by all types of pores (not only macropores). According to Yu.A.Kokotov [6], during the adsorption of polar substances by the ion exchanger from the liquid phase, they are first absorbed by the gel skeleton with micropores and only after its saturation fill obvious meso- and macropores. It is possible that in the area of high equilibrium concentrations corresponding to large

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values of the L:S ratio (500-2000), and also under conditions of prolonged exposure of the ion exchange resin in model solutions, the contribution of physical adsorption to the sorption process as a whole becomes more significant, which leads to a sharp increase of exchange capacity of ion exchanger, which is observed on isotherms. However, since this phenomenon has a purely physical nature and its effect on the sorption process under dynamic conditions and at relatively low concentrations of the extracted components will be insignificant, in the framework of this study, we will limit it to considering the ion exchange process and using classical models of monomolecular sorption.

When graphically solving the sorption isotherms of nickel and manganese ions, the indices of their extraction were determined in accordance with the Langmuir $C_E/Q_E = C_E/Q_S + 1/(K_{ADS}Q_S)$ and Freundlich models $Q_E = K_S C_E^n$ (Table 1), where Q_S is the ion exchanger capacity corresponding to the complete filling of its surface with a monomolecular sorbate layer (mmol/dm³); K_{ADS} – the constant of adsorption equilibrium (an indicator of the "affinity" of the sorbate for the sorbent); K_S – the Freundlich constant expressing the value of sorption at an equilibrium concentration of sorbate; n – the degree of approximation of the sorption isotherm to a linear form.

Table 1

**Indices of monomolecular sorption of Ni²⁺ and Mn²⁺ on TP 207
from mono- and bicomponent solutions**

Element	Langmuir model			Freundlich model		
	Q_S, mmol/dm³	K_{ADS}	R^2	K_S	n	R^2
Monocomponent solution						
Ni	952.4	0.68	0.964	379.9	0.67	0.979
Mn	70.9	6.05	0.987	60.8	0.11	0.988
Bicomponent solution						
Ni	740.7	1.02	0.991	379.5	0.60	0.985
Mn	48.6	0.51	0.995	18.5	0.42	0.995

The obtained values of the determination coefficients (R^2) for the Langmuir and Freundlich models are comparable. However, it is believed that the first model characterizes the sorption process quantitatively; therefore, we will continue the further study of nickel and manganese extraction from model systems using this model.

The Q_S values in Table 1 indicate a significantly larger capacity of TP 207 cation exchanger for filling the monolayer with nickel ions than with manganese ions: 13.4 times higher in a monocomponent solution and 15.2 times higher in a bicomponent solution. It is known that the K_{ADS} constant characterizes the energy of interaction of the sorbent with the sorbate: the larger the value is, the stronger the interaction. This indicator is most informative for multicomponent systems. Based on the values of K_{ADS} in a bicomponent solution, we can conclude that the interaction of TP 207 cation exchanger with nickel ions is two times stronger than with manganese ions.

It is known that the smaller the radius of the hydratable ion is, the greater its affinity for cation exchange resin, and the higher the selectivity of extraction. According to reference data, the radius of the Mn²⁺ ion is 0.091 nm, and the Ni²⁺ ion is 0.074 nm. Consequently, nickel ions should be better sorbed on TP 207 as compared to manganese ions, which is confirmed by the experimentally obtained results on extraction and exchange capacity.

Table 2 shows the distribution coefficients (K_{DIS}) of nickel and manganese ions in the TP 207 resin phase, determined from the ratio of SEC to C_E when they are extracted from monocomponent and bicomponent solutions. Here, concerning a bicomponent solution, the values of the separation coefficients (D_S) of these ions are given, calculated from the ratio of the established distribution coefficients.

During the formation of a monolayer of nickel and manganese ions on TP 207, the distribution coefficients decrease to 339 and 33, respectively, when they are extracted from monocomponent solutions, and to 386 and 8 when they are extracted from a bicomponent solution. In this case, it can be concluded that the monolayer is more rapidly filled with manganese ions, which is explained by the low exchange capacity of TP 207 cation exchanger for these ions.

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**The values of the distribution and separation coefficients of Ni^{2+} and Mn^{2+} ions
during their sorption from mono- and bicomponent solutions on TP 207 at different L:S**

Coefficient	L:S ratio						
	50	100	200	500	1000	2000	5000
Monocomponent solution							
K_{DIS} (Ni)	521.8	521.8	408.4	338.9	375.2	385.7	600.6
K_{DIS} (Mn)	41.5	32.7	64.3	84.4	136.4	211.8	378.1
Bicomponent solution							
K_{DIS} (Ni)	521.8	521.8	386.1	409.6	490.8	554.5	600.6
K_{DIS} (Mn)	11.7	8.2	15.0	27.6	36.0	35.3	30.6
D_S (Ni/Mn)	63.6	44.6	25.7	14.8	13.6	15.7	19.6

Coefficients D_S characterize the ability of the sorbent to separate mixtures of various ions in solution. Since the obtained values of the coefficient are significantly greater than unity, the separation of the mixture of nickel and manganese ions can be effectively performed using TP 207 ion exchanger.

Figure 3 shows the kinetic curves of sorption of nickel and manganese ions from mono- and bicomponent systems on TP 207 cation exchange resin at 300 and 330 K and L:S = 200, where τ is the duration of contact (exposure) of the sorbent with the liquid phase (s).

Obviously, the increase in the temperature of the solution from 300 to 330 K leads to an increase in the static exchange capacity of TP 207 ion exchange resin concerning nickel ions. So, during sorption from a monocomponent system, in the first two minutes, SEC increases from 61 to 184 mmol/dm^3 (extraction – from 12 to 35 %), and after 45 minutes – from 276 to 399 mmol/dm^3 (extraction – from 65 to 77 %), reaching its maximum at a given ratio L:S. In the case of a bicomponent system, in the first two minutes, the SEC increases from 61 to 153 mmol/dm^3 (extraction – from 12 to 28 %), and after 90 minutes (the area goes out of the given range) – from 276 to 429 mmol/dm^3 (extraction – from 59 to 78 %), also reaching its maximum value. It should be noted that at a temperature of 300 K the value of SEC equal to 276 mmol/dm^3 was obtained in 45 minutes in a monocomponent solution and 90 minutes in a bicomponent solution. At the same time, both at 300 K and 330 K the SEC value of 399 mmol/dm^3 was reached after 45 min in both cases. Thus, it can be assumed that with a decrease in temperature in the system, the sorption of nickel ions somewhat slows down in the presence of manganese ions, and vice versa with its increase.
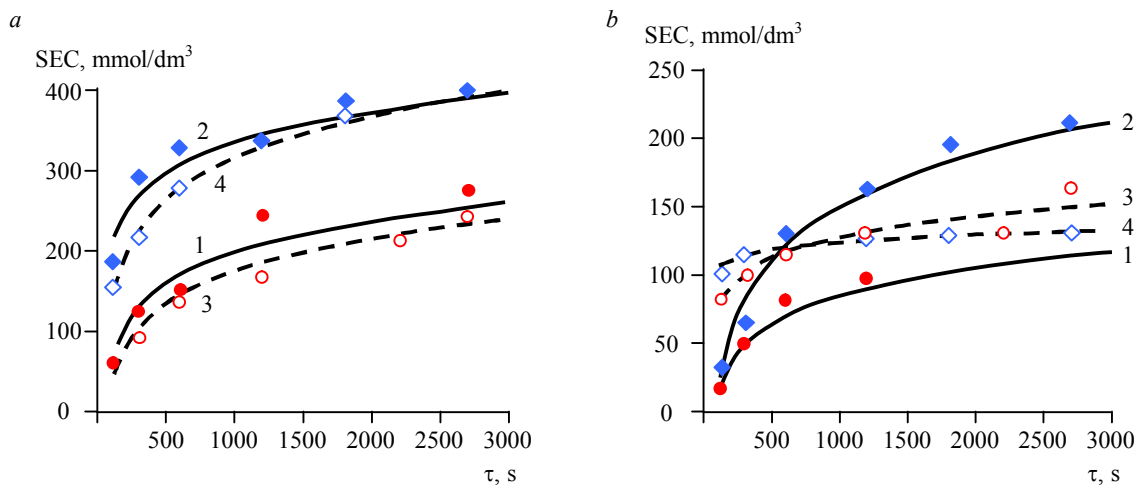

Fig.3. Dependences of the static exchange capacity of the ion exchanger TP 207 upon sorption of Ni^{2+} (*a*) and Mn^{2+} (*b*) ions on the duration of contact with monocomponent (1, 2) and bicomponent (3, 4) solutions at temperatures of 300 K (1, 3) and 330 K (2, 4)

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Concerning manganese ions extracted from a monocomponent system, under the conditions of a temperature increase from 300 to 330 K, the following is observed: after 2 minutes, the SEC increases from 16 to 33 mmol/dm^3 (recovery from 3 to 5 %), and after 90 minutes – from 131 to 229 mmol/dm^3 (extraction – from 20 to 35 %), reaching its maximum at this ratio L:S. The increase in the exchange capacity of the ion exchanger is obvious and logical. In the case of a biocomponent solution, in the first two minutes, the SEC increases from 82 to 98 mmol/dm^3 (extraction – from 10 to 13 %), and after 10 minutes – from 115 to 131 mmol/dm^3 (extraction – from 12 to 17 %), reaching its maximum value. Despite a significant increase in the exchange capacity of TP 207 resin for manganese ions when nickel ions appear in the system, the final values of SEC are two times lower than in the absence of nickel ions and, therefore, are achieved much faster.

In general, the growth of SEC of cation exchange resin associated with an increase in the temperature of the liquid phase is due to the filling of ions with sorption centers, for which the exchange of counterions is energetically disadvantageous at a lower temperature.

Table 3 shows the distribution coefficients (K_{DIS}) and separation (D_S) of nickel and manganese ions in the TP 207 cation phase when they are extracted from monocomponent and bicomponent solutions at an exposure time of 2 to 180 min (120-1800 s) and temperatures of 300 and 330 K.

Table 3

The distribution and separation coefficients of Ni^{2+} and Mn^{2+} ions during their sorption by TP 207 ion exchanger at different contact times with mono- and bicomponent solutions and temperatures of 300 and 330 K

Coefficient	Exposure time τ, s								
	120	300	600	1200	1800	2700	3600	5400	10800
Monocomponent solution (300/330 K)									
K_{DIS} (Ni)	24.0/98.2	55.5/228.2	75.0/305.8	160.0/330.1	175.9/516.0	202.5/585.5	219.6/585.5	257.3/585.5	289.0/585.5
K_{DIS} (Mn)	4.6/9.5	14.6/20.0	25.7/45.0	31.8/60.0	34.5/71.5	37.7/81.6	41.8/88.7	45.0/96.9	53.3/96.9
Bicomponent solution (300/330 K)									
K_{DIS} (Ni)	24.0/69.3	38.6/114.5	64.9/180.0	86.1/283.0	117.9/360.0	160.0/467.8	180.0/540.5	202.5/630.4	257.3/630.4
K_{DIS} (Mn)	20.0/27.0	24.6/32.3	29.3/37.9	32.2/37.9	34.3/37.9	36.3/37.9	39.5/37.9	45.0/37.9	45.0/37.9
D_S (Ni/Mn)	1.2/2.6	1.57/3.5	2.2/4.8	2.7/7.5	3.4/9.5	4.4/12.3	4.6/14.3	4.5/16.6	5.7/16.6

The distribution coefficients of nickel and manganese ions change similarly to the degree of their extraction from solutions and the static exchange capacity of TP 207 ion exchange resin. Of interest is the dynamics of changes in the separation coefficients of ions in a bicomponent system. In the first 5 min at the temperature of 300 K, the coefficients are quite close to unity, which indicates the difficulty of ion separation at a short contact time. With an increase in the exposure time of the ion exchanger in the solution to 45-90 min during the approach of the concentration of manganese ions in the solution to the equilibrium, the separation coefficient reaches 4.4-4.6, and after reaching it increases by 180 min to 5.7. An increase in the temperature of the liquid phase to 330 K leads to a sharp increase in the values of the separation coefficients: 2.1-3.7 times more than the values obtained at a temperature of 300 K in the entire studied range of contact duration and reaches its maximum value in this range – 16.6. The intensive growth of the separation coefficient at a temperature of 330 K is due to a more rapid achievement of the equilibrium concentration of manganese ions in solution: after 10 minutes of contact with cation exchange resin.

Figure 4 shows the dependences of the static exchange capacity of TP 207 ion exchange resin concerning nickel and manganese ions, as well as the degree of their extraction from the hydrogen index (pH) in monocomponent and bicomponent solutions in the range of the latter 6.0-11.0 at L:S = 200.

Following the presented dependences, a significant increase in the extraction of nickel ions and the exchange capacity of cation exchange resin in the case of a monocomponent solution occurs in the pH range of 8.0-9.0 (β from 63 to 97 %; SEC from 329 to 504 mmol/dm^3), and in the case of bicomponent – in the pH range of 8.0-8.5 (β – from 59 to 81 %; SEC – from 325 to 445 mmol/dm^3). However, while the growth of indicators characterizing the sorption of nickel ions is more abrupt,
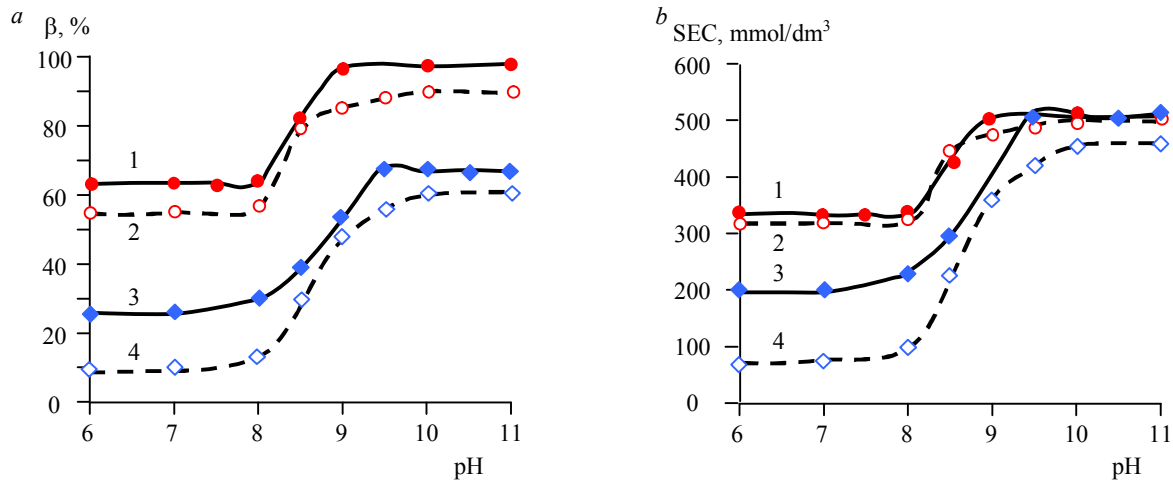
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Fig.4. Dependences of the degree of extraction (a) and the static exchange capacity of TP 207 (b) upon sorption of Ni^{2+} (1, 2) and Mn^{2+} (3, 4) ions on the pH of monocomponent (1, 3) and bicomponent solutions (2, 4)
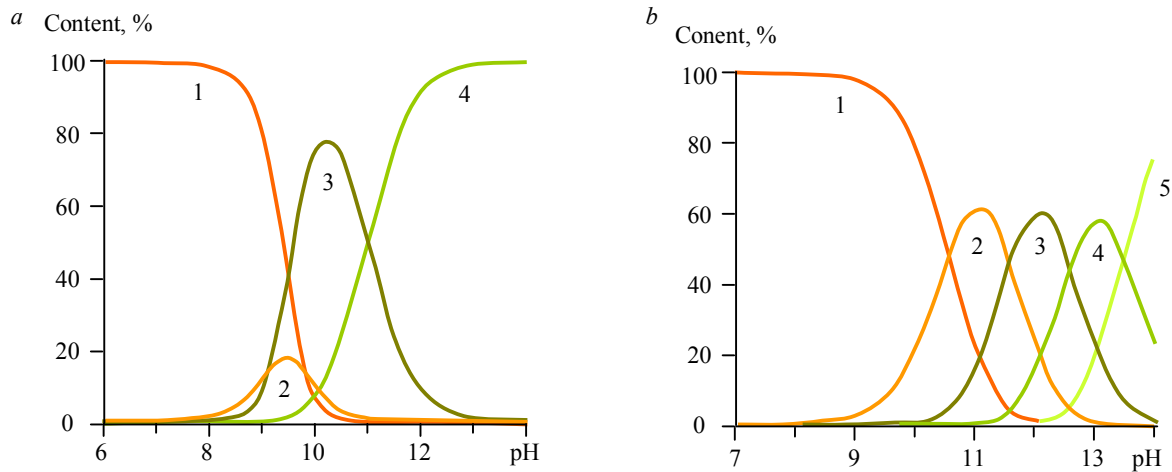

Fig.5. Dependence of the content of ionic forms of nickel (a) and manganese (b) on the pH of the liquid phase
$1 - Me^{2+}$; $2 - Me(OH)^{+}$; $3 - Me(OH)_2$; $4 - Me(OH)_3^{-}$; $5 - Me(OH)_4^{2-}$

spasmodic, for manganese ions it is smoother and stretched over a wider range of values of the hydrogen index: 8.0-9.5 and in the monocomponent (β – from 30 to 67 %; SEC – from 230 to 505 mmol/dm^3), and in bi-component (β – from 13 to 56 %; SEC – from 98 to 421 mmol/dm^3) solutions.

The intensification of the process of extraction of the studied ions with increasing pH of the medium is due to several factors. First, following the dependencies shown in Fig.5, at pH ≥ 8.0, singly charged hydroxocations $Ni(OH)^{+}$ and $Mn(OH)^{+}$ appear. It is known that due to lower energy costs, ion exchange proceeds more easily with singly charged cations than with doubly charged ones. Secondly, with increasing pH, the dissociation of the functional groups of the resin increases. Thirdly, the formation of insoluble hydroxides of nickel and manganese, including those deposited on the surface and in the pores of the ion exchanger matrix, can have some effect on the growth of indicators. According to Fig.5, the formation of $Ni(OH)_2$ occurs at pH ≥ 8.5, and $Mn(OH)_2$ at pH ≥ 10.0. It is not possible to quantify the contribution of the latter factor to the sorption process.

Table 4 shows the values of the distribution coefficients (K_{DIS}) and separation (D_S) of nickel and manganese ions in the TP 207 cationite phase when they are extracted from monocomponent and bi-component solutions in the pH range of 6.0-11.0.

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Table 4

**The distribution and separation coefficients of Ni^{2+} and Mn^{2+} ions
during their sorption from mono- and bicomponent solutions on TP 207 at different pH**

Coefficient	pH value							
	6.0	7.0	8.0	8.5	9.0	9.5	10.0	11.0
Monocomponent solution								
K_{DIS} (Ni)	321.4	313.6	306.2	840.1	5195.9	7615.1	8100	8100
K_{DIS} (Mn)	63.8	63.8	79	96.3	151.5	365.3	499.5	379.9
Bicomponent solution								
K_{DIS} (Ni)	240.6	246.5	258.0	746	1115.5	1438.4	1723	1723.0
K_{DIS} (Mn)	17.1	19.9	27	75.4	165	227.3	275	280
D_S (Ni/Mn)	14.07	12.38	9.56	9.89	6.76	6.33	6.27	6.15

Significantly large values of the distribution coefficients of nickel ions during their sorption from a monocomponent solution in the pH range of 9.0-11.0 compared with similar indicators for a bicomponent solution are due to small final equilibrium ion concentrations: 0.1 mmol/dm^3 versus 0.3 mmol/dm^3, respectively. In the rest, the dynamics of changes in the distribution coefficients of both nickel ions and manganese ions correlates with other indicators of sorption (β and SEC).

From the values of the separation coefficients presented in Table 4, it follows that an increase in the pH of the liquid phase leads to a decrease in the separation efficiency of nickel and manganese ions by the TP 207 ion-exchange resin. Therefore, for the selective separation of nickel ions and, accordingly, for limiting the sorption of manganese ions, the solution acidity should be in the neutral region: pH 6.0-7.0.

Conclusion. In the joint presence of nickel and manganese ions in aqueous solutions, for the selective extraction of the former, it is advisable to use weakly acidic macroporous cation exchangers with chelate groups of iminodiacetic acid. The effect of manganese ions on the sorption of nickel ions is insignificant since nickel ions have a high affinity for this class of ion-exchange resins and significantly suppress the extraction of the former. This is also confirmed by experimental data: the sorption properties (exchange capacity, extraction depth, adsorption equilibrium constant) of one of the most accessible cation exchangers of this class (Lewatit Monoplus TP 207), according to the results of laboratory studies, turned out to be significantly higher concerning nickel ions than with manganese ions, increasing with temperature. An increase in the pH of the solution also leads to an improvement in the absorption of nickel ions, which is explained by the appearance of singly charged hydroxocations, dissociation of the functional groups of the sorbent, and, possibly, the appearance of insoluble hydroxides. However, the selectivity of the extraction of nickel ions decreases due to the intensification of the absorption of manganese ions, which is confirmed by the dynamics of the separation coefficient.

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