ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 6, pp. 940–946. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © I.L. Shashkova, A.I. Rat'ko, N.V. Mil'vit, E.V. Muravitskaya, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 6, pp. 886–892.

INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

The Use of Chemisorption Technologies in Separation of Multicomponent Mixtures of Metal Ions

I. L. Shashkova[a], A. I. Rat'ko[a], N. V. Mil'vit[a], and E. V. Muravitskaya[b]

[a] *Institute of General and Inorganic Chemistry, National Academy of Sciences of Belarus, Minsk, Belarus*
[b] *Stepanov Institute of Physics, National Academy of Sciences of Belarus, Minsk, Belarus*

Received April 9, 2008

Abstract—The concept of using hemisorption technologies for selective removal of individual ions from multicomponent mixtures was suggested and practically confirmed. Results obtained in experimental separation of the Ni^{2+}–Fe^{3+}–Pb^{2+} mixture with phosphate sorbents are reported.

DOI: 10.1134/S1070427209060020

Ion-exchange materials and chemical substances binding them into difficultly soluble compounds are used for selective extraction of metal ions from solutions.

Previously, nickel phosphate and calcium carbonate have been successively used as chemisorbents for selective extraction of iron(III) ions from two-component Ni^{2+}–Fe^{3+} mixture [1]. The above two-component solutions are formed during processing waste from nickel-iron battery electrodes [2] and electrolytic baths for iron plating.

In the first case, chemisorbent was nickel phosphate, difficultly soluble salt of one of cations being separated. In the given case, selective recovery of iron ions from Ni^{2+}–Fe^{3+} mixture is due to the substitution with formation of less soluble compound, iron phosphate:

$$[Ni_3(PO_4)_2\cdot 8H_2O]_{sol} + 2Fe^{3+} \rightarrow 2(FePO_4\cdot xH_2O)_{sol} + 3Ni^{2+}. \quad (1)$$

In the second case, as chemisorbent for selective absorption of iron(III) ions from a Ni^{2+}–Fe^{3+} mixture $CaCO_3$ was used [1], which contained no cation being recovered. As known [3], the solubility products (SPs) of calcium and nickel carbonates are virtually equal (6.6×10^{-9} and 4.8×10^{-9}, respectively), whereas SP of iron hydroxide formed in contact of iron(III) cations with calcium carbonate is by several orders of magnitude lower (10^{-32}–10^{-33}). Hence, calcium carbonate can selectively recover iron(III) ions from Ni^{2+}–Fe^{3+} mixture.

In this study, the general case of application of chemisorption technologies for selective extraction of ions from two-component and more complex poly-component ion mixtures were considered.

Evidently, chemisorption in polycomponent solutions primarily depends on the ratio between the amount of a sorbent and the concentration of metal cations in solution. If the amount of sorbent is sufficient to provide chemical reaction with formation of less soluble compounds with all cations, then all these cations will be sorbed. In the case when sorbent amount is insufficient, a cation forming less soluble compound should be sorbed first, according to theoretical prediction.

We consider as example the simplest system sorbent-three-component mixture $M^{n+}(1)$–$M^{n+}(2)$–$M^{n+}(3)$. A low soluble salt of one of ions constituting the mixture, $M^{n+}(1)$, (for example, nickel phosphate) is a sorbent, and two other cations, $M^{n+}(2)$ and $M^{n+}(3)$, [for example, iron(III) and lead(II)] form less soluble salts with the sorbent anion.

The contact of nickel phosphate (sorbent) with the solution containing a mixture of three cations (Ni^{2+}, Fe^{3+}, and Pb^{2+}) may lead to two chemical reactions: formation of iron phosphate, less soluble than nickel

phosphate, and formation of the less soluble lead phosphate.

The reaction (1) yields a neutral salt, i.e., 1 mol-equiv of the phosphate may sorb 1 mol-equiv of either metal or 1 mol-equiv of the sum of both metals. It is clear that if the total content of M^{n+}(2) and M^{n+}(3) in the aliquot solution per 1 mol-equiv of the sorbent does not exceed 1 mol-equiv, the chemisorbent will sorb both these metals completely. When the content in the mixture of cations forming with a sorbent anion less soluble compound, is equal to 1 mol-equiv and higher, i.e., is equal to or higher than the sorbent capacity E, only this cation is sorbed. This is the region of selective absorption $c_M \geq E$, where M^{n+} is a metal cation forming a less soluble compound with the sorbent anion.

The arguments presented show that chemisorption processes can be used for selective removal of ions from mixture and, correspondingly, for separation of complex ion mixtures. This is done by recovering ions alternatively: first, ion forming the least soluble compound with the sorbent is recovered, then the ion next to it in the solubility series is recovered to form the least soluble compound, etc.

In the general case, for any type of the chemisorbents used for selective removal of the metal ion M^{n+} from polycomponent (two and more components) solution of volume V (ml) and concentration c (mol-equiv l^{-1}) of a given metal, a sorbent sample of weight m (g) and capacity E (mmol equiv g^{-1}) should be added to the solution. The weight of the sorbent sample can be calculated by formula:

$$m = \frac{c_M V}{E}. \quad (2)$$

The relation (2) can be used for calculating the weight of the chemisorbent sample used for quantitative removal of the cation, which forms less soluble compound with the sorbent anion, from multicomponent solution. To realize selective recovery in practice, it is necessary to evaluate the concentration of ions being recovered from multicomponent solution and to determine experimentally the chemisorbent capacity for the given cation under similar conditions. This is because the capacity of chemisorbents depends on the composition of difficultly soluble compounds formed during reaction, which is, as a rule, unknown. Depending on the sorption conditions (molar ratio of reagents, concentration and pH of solution), the composition of the reaction product can vary substantially. For example, a study of the sorption properties of calcium hydrophosphate with respect to lead ions [4] showed that, depending on the concentration of lead nitrate solution, the interaction is described by equations:

$$6(CaHPO_4 \cdot 2H_2O) + 10Pb^{2+} = Pb_{10}(PO_4)_6(OH)_2 + 6Ca^{2+} + 10H_2O + 8H^+, \quad (3)$$

$$CaHPO_4 \cdot 2H_2O + Pb^{2+} = PbHPO_4 + Ca^{2+} + 2H_2O, \quad (4)$$

$$2(CaHPO_4 \cdot 2H_2O) + 4Pb^{2+} + H_2O = Pb_4(PO_4)_2(OH)_2 \cdot 3H_2O + 2Ca^{2+} + 4H^+. \quad (5)$$

As seen from the comparison of Eqs. (4), (5), the theoretical capacity of calcium phosphate under the given conditions may vary twice.

To confirm the presented arguments in practice, the absorption of iron(III) and lead(II) ions from multicomponent Fe^{3+}–Ni^{2+}–Pb^{2+} mixtures was studied using nickel and calcium phosphates as sorbents.

The experiment was performed as previously described [1]. Amorphous nickel phosphate sorbent of the composi-tion $Ni_3(PO_4)_2 \cdot 8H_2O$ was synthesized by the known procedure [5]. Calcium hydrophosphate was prepared from chalk and orthophosphoric acid [6].

Ion sorption was studied under static conditions at room temperature. The sorbent sample (0.1 g) was added to 25 ml of the three-component solution under study and stored for 1 day at intermittent stirring. Then, the solid phase was filtered off and the iron(III) content in the liquid phase was determined by atomic-absorption spectroscopy on an AAS-220 spectrometer.

Solutions for study were prepared from chemically pure and analytically pure grade crystal hydrates of iron(III), lead(II), and nickel(II) nitrates.

As was noted above, the contact of nickel phosphate with the solution containing a mixture of three cations [(nickel(II), iron(III), and lead(II)] should lead to two chemical reactions: one with formation of iron phosphate, less soluble than nickel phosphate, and another with formation of less soluble lead phosphate. It was established experimentally that the iron(III) cation is sorbed first from the above solution, i.e., the iron(III) ion and the phosphate ion form the least soluble compound, basic iron phosphate [7]. To determine the capacity of nickel phosphate for iron(III) ions, we studied the absorption of Fe^{3+} from iron nitrate solution of varied concentration containing no other cations. The obtained absorption isotherm is

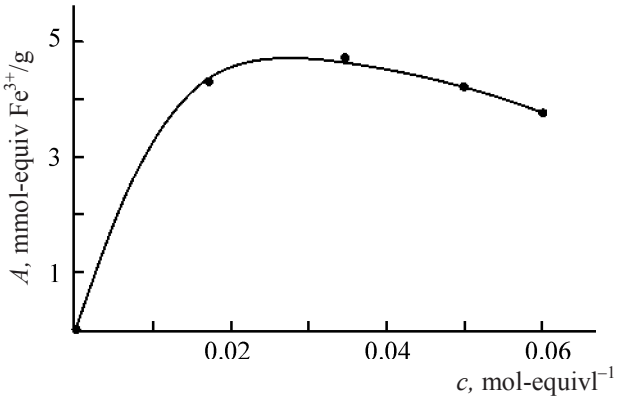

Fig. 1. Isotherm of iron(III) sorption with nickel phosphate. (*A*) Sorption and (*c*) concentration of initial $Fe(NO_3)_3$ solutions; the same for Fig. 3.

demonstrated in Fig. 1. As seen, the maximal capacity of nickel phosphate for iron in nitrate solutions is 4.5 mmol-equiv g^{-1} of the sorbent.

According to the arguments presented, a region of selective absorption of Fe^{3+} cation from multicomponent mixtures corresponds to solutions, whose aliquots contain more than 4.5 mmol-equiv Fe^{3+} per 1 g of the sorbent.

The isotherms of iron(III) and lead(II) sorption from three-component Fe^{3+}–Ni^{2+}–Pb^{2+} solution are presented in Fig. 2a. As seen, the absorption of both cations increases in proportion to concentration as the total content of iron(II) and lead(II) in the solution increases from 0 to 0.08 mol-equiv l^{-1}. In this range of concentrations the degree of removal from solution is 100% for iron and 80–100% for lead (Fig. 2b). When the total concentration of iron(III) and lead(II), c_Σ (mol-eqiv l^{-1}), increases further, the absorption isotherm separates onto two branches. The iron(III) absorption continues to grow to maximum value and then passes a plateau, whereas the lead(II) absorption decreases to zero value. The amount of sorbed iron(III) at the plateau corresponds to the previously determined capacity of nickel phosphate for iron.

A general run of the experimentally obtained curves is well consistent with the above theoretical consideration, whereas the quantitative parameters of the process somewhat deviage from the prediction. For example, at $c_\Sigma \geq 0.09$ mol-equiv l^{-1}, i.e., in the region of selective Fe^{3+} absorption the theory predicts no Pb^{2+} absorption. At the same time, Pb^{2+} absorption is present amounting the 3 mmol-equiv g^{-1} at the selectivity point at $c_\Sigma = 0.09$ mol-equiv l^{-1} and virtually disappears only at $c_\Sigma = 0.22$ mol-equiv l^{-1}. Thus, the experimentally observed region of selective iron(III) sorption is shifted along the abscissa axis toward higher concentrations with respect to theoretical value, from $c_\Sigma = 0.09$ mol-equiv l^{-1} to $c_\Sigma = 0.22$ mol-equiv l^{-1}. However, at $c_\Sigma > 0.22$ mol-equiv l^{-1} the degree of iron(II) recovery from solution is only 50%. The optimal conditions for selective iron(III) recovery in the system under consideration are observed at $c_\Sigma = 0.1$ mol-equiv l^{-1}. In this case, the degree of iron(III) recovery from

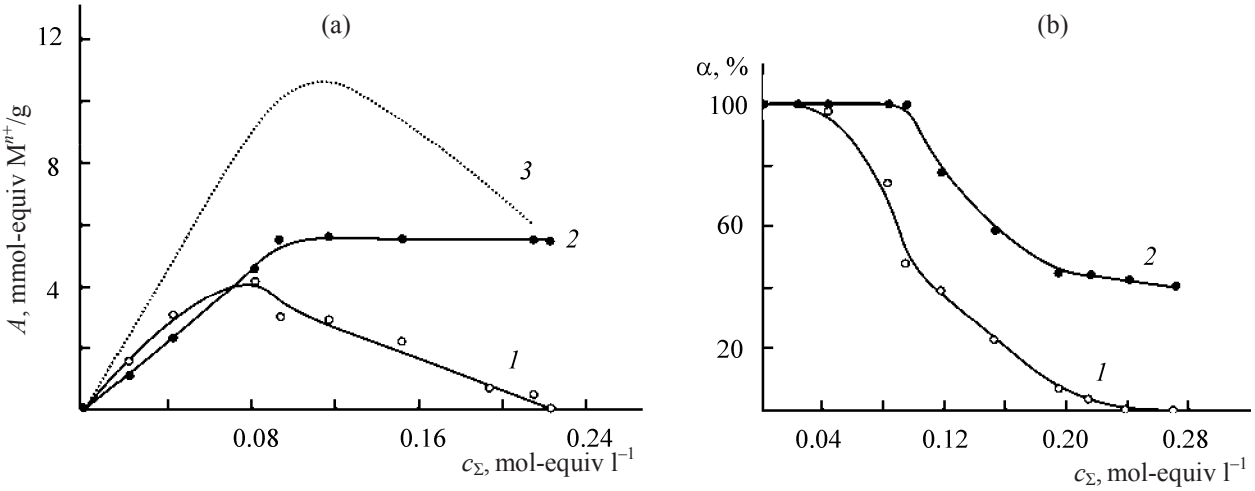

Fig. 2. (a) Isotherms of iron(III) and lead(II) sorption with nickel phosphate and (b) degree of removal from three-component Fe^{3+}–Ni^{2+}–Pb^{2} system. (*A*) Absorption of corresponding metal cation, (α) degree of recovery of corresponding metal cation from solution, and (c_Σ) total concentration of iron(III) and lead(II) in initial solutions; the same for Fig. 4. Cation: (*1*) Pb^{2+}, (*2*) Fe^{3+}, and (*3*) Ni^{2+}.

Table 1. Change in concentration of nickel(II) ions in the course of recovery of metal ions with nickel(II) phosphate

Ni^{2+} concentration in initial solution, mol-equiv l^{-1}	Volume of purified solution, l	Sorbent weight, g	Ni^{2+} concentration in equilibrium solution, mol-equiv l^{-1}	Ni^{2+} released, mmol-equiv g^{-1}
0.016	0.025	0.200	0.035	2.4
0.031	0.025	0.200	0.060	3.6
0.049	0.025	0.200	0.123	9.3
0.064	0.025	0.200	0.143	9.9
0.083	0.025	0.200	0.175	11.5
0.126	0.025	0.200	0.187	7.6
0.147	0.025	0.200	0.205	7.3
0.149	0.025	0.200	0.197	6.0
0.156	0.025	0.200	0.172	2.0

solution is 100%, whereas about 40% of the lead(II) ions is coprecipitated.

Change in nickel(II) concentration in the course of the chemisorption in the system studied is demonstrated in Table 1. As seen, the nickel concentration in equilibrium solutions is higher than in initial solutions. This shows that the chemisorption is the substitution reaction described by Eq. (1). The maximum position on the sorption isotherm of nickel (Fig. 2a, dotted) coincides with the maxima positions on the corresponding curves for iron(III) and lead(II) and the amount of nickel passed into the solution is close to the total sorpbed amount of lead and iron.

Evidenly, the observed experimental features of chemisorption in the system studied are due to the following reasons: according to the literature data, phosphate ions and iron(III) cations under certain conditions can form stable sols coagulating to gels. The process strongly depends on the ionic composition of the solution, its pH, and total content of salts in it. Excess amount of iron(III) cations with respect to phosphate ions and the presence of nitrate ions in solution [8] are additional gelation-facilitating factors. Apart from this, Fe^{3+} and Pb^{2+} cations in the studied system can form stable homo- and heteropolynuclear hydroxo complexes in the form of stable sols. Evidently, in the course of the chemisorption under these conditions, different ions may be sorbed by iron phosphate. At the same time, the simultaneous absorption of lead may be due to the formation of double iron-lead phosphates. For the pattern observed in the experiment, both processes may be responsible. The obtained experimental data show that the true chemical processes proceeding in chemisorption are reasonably complex chemical reactions, which cannot be always described adequately by one chemical equation, like Eq. (2). In each given case, the optimal conditions for chemisoprtion should be chosen experimentally.

The results more adequate to theoretical consideration were obtained with calcium hydrophosphate sorbent. The SP of $CaHPO_4 \cdot 2H_2O$ virtually equals to SP of nickel phosphate. Therefore, calcium hydrophosphate, like nickel phosphate, can sorb iron(III) and lead(II) cations from the three-component system studied.

Figure 3 demonstrates the isotherm of iron(III) absorption from one-component $Fe(NO_3)_3$ solution with calcium hydrophosphate. As seen, the maximum sorption capacity for iron(III) in nitrate solutions at $c_{Fe^{3+}} = 0.06$ mol-equiv l^{-1} is 10.2 mmol-equiv g^{-1}.

Figure 4a shows the isotherms of Fe^{3+} and Pb^{2+} sorption from three-component nitrate Ni^{2+}–Fe^{3+}–Pb^{2+}

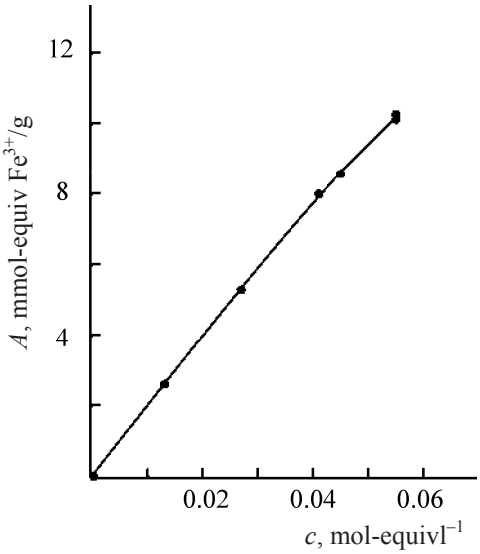

Fig. 3. Isotherm of iron(III) sorption with calcium phosphate.

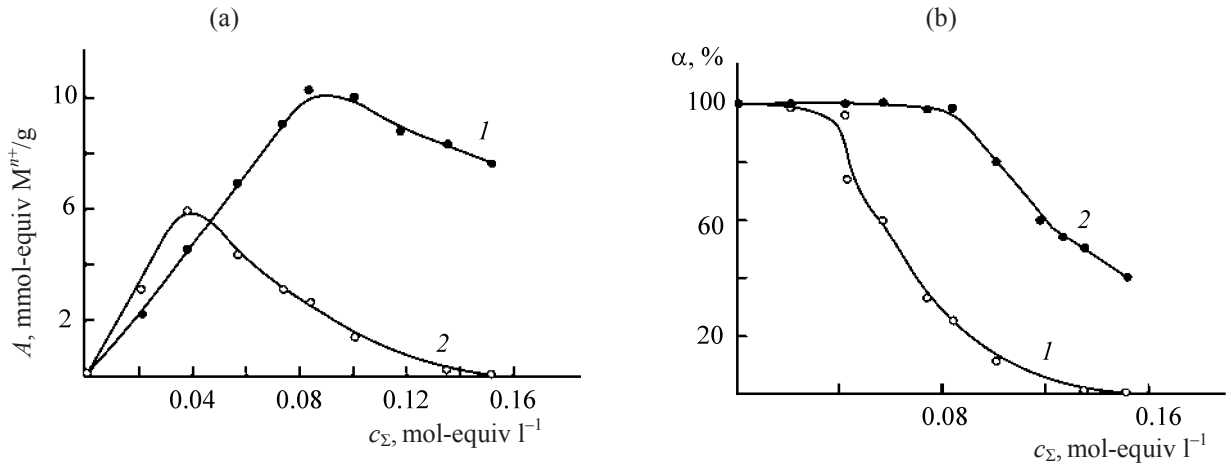

Fig. 4. (a) Isotherms of iron(III) and lead(II) sorption with calcium phosphate and (b) degree of removal from three-component Fe^{3+}–Ni^{2+}–Pb^2 system. Cation: (*1*) Fe^{3+} and (*2*) Pb^{2+}.

solution with calcium phosphate sorbent. As seen, the absorption of both cations increases proportionally to the solution concentration as c_Σ increases from 0 to 0.040 mol-equiv l^{-1} and then intersect. After that, the sorption of iron(III) continues till the sorption capacity for is attained, whereas the lead(II) sorption gradually decreases.

The total concentration c_Σ, at which the calcium phosphate capacity for iron(III) is attained, is 0.085 mol-equiv l^{-1}. Thus, a theoretically predicted region of selective absorption of iron should be at $c_\Sigma \geq$ 0.085 mol-equiv l^{-1}. However, the absorption of lead is absent only at $c_\Sigma > 0.14$ mol-equiv l^{-1}. This means that, as in the previous case, the true region of iron selective

Table 2. Change in nickel(II) ion concentration during sorption of metal ions with calcium phosphate

Ni^{2+} concentration in initial solution, mol-equiv l^{-1}	Volume of purified solution, l	Sorbent weight, g	Ni^{2+} concentration in equilibrium solution, mol-equiv l^{-1}	Sorbed, mmol-equiv g^{-1}	Degree of removal from solution, %
0.010	0.050	0.20	0.010	0	0
0.021	0.050	0.20	0.021	0	0
0.024	0.050	0.20	0.023	0.3	4
0.031	0.050	0.20	0.030	0.3	3
0.040	0.050	0.20	0.040	0.0	0
0.045	0.050	0.20	0.044	0.3	2
0.053	0.050	0.20	0.052	0.3	2
0.055	0.050	0.20	0.053	0.5	4
0.061	0.050	0.20	0.060	0.3	2
0.064	0.050	0.20	0.061	0.5	3
0.073	0.050	0.20	0.070	0.5	3
0.082	0.050	0.20	0.082	0.0	0

Table 3. Change in soluton concentration during separation of metal ions with calcium phosphate

Solution	Ion concentration, mol-equiv l^{-1}			Removal degree, %		
	Fe^{3+}	Ni^{2+}	Pb^{2+}	Fe^{3+}	Ni^{2+}	Pb^{2+}
Initial	0.019	0.021	0.019	–	–	–
After first stage of separation	0	0.021	0.013	100	0	33
After second stage of separation	–	0.021	0	–	0	100

absorption is shifted toward higher concentrations with respect to theoretical prediction. At the same time, compared to the previous system, this shift is less considerable and the lead absorption in the region from c_Σ = 0.085 mol-equiv l^{-1} (theoretical selectivity point) to c_Σ =0.14 mol-equiv l^{-1} (experimental selectivity point) is much less, from 0 to 2 mmol-equiv g^{-1}.

The concentrations of nickel(II) ions in solution before and after sorption are given in Table 2. As seen, the nickel(II) concentration in equilibrium solution is virtually the same as in initial solutions, i.e., a variation is slight, contrary to the case of the previous system.

As in the previous system (Figs. 2a, 4a), selective sorption of iron(III) ions without simultaneous sorption of concurrent lead ions occurs solely at very high concentrations, with the degree of iron removal from solution not exceeding 40–50% (Fig. 4b).

The ion separation in the region c_Σ = 0.08–0.09 mol-equiv l^{-1} is optimal. Under these conditions, the degree of iron(II) removal from solution is 100% and the amount of lead passed into the precipitate, about 20%.

The second stage of the separation of Ni^{2+}–Fe^{3+}–Pb^{2+} mixture, in particular, removal of lead(II) ions from two-component Ni^{2+}–Pb^{2+} solutions obtained after removal of Fe^{3+} ions from three-component Ni^{2+}–Fe^{3+}–Pb^{2+} mixture, offers no difficulties. The process proceeds in accordance with the theoretical prediction, and no nickel(II) ions is sorbed simultaneously with lead. Table 3 demonstrates, as example, how the lead(II), iron(III), and nickel(II) concentrations in solution change during successive removal of iron(III) and, then, of lead(II) ions from one of solutions with their total concentration c_Σ = 0.038 mol-equiv M^{n+}/l.

Despite the above-noted specific features of the chemisorption, observed in particular in the first stage of iron removal, the use of the phosphate sorbents considered allows quantitative removal of one cation (Pb^{2+}) after another (Fe^{3+}). Consequently, the separation of ions from solution is well suited to the purpose in hand: the remaining solution containing only Ni^{2+} can be used in further cycles. The study showed that the solid phase is not always a pure product.

It should be noted that a very large capacity of chemisorbents for multiple-charged metal ions impedes their use for selective removal of ions from dilute solutions. This is because the liquid:solid ratios (i.e., the ratios between the sorbent mass and the solution volume) required to proceed properly heterogeneous chemical reactions cannot be attained. For example, removal of lead(II) compounds from a 100-ml solution with a concentration of 20 mg l^{-1} with 0.9 g of calcium phosphate is complete. This l:s ratio is however too small to be realized in practice. At the same time, the chemisorption procedures considered may be realized in sufficiently concentrated solutions and be promising for selective removal of cations from concentrated solutions of electrolytes, in particular, from those obtained during processing of spent plating solutions. The experimental study showed that in this case, virtually all difficultly soluble phosphates of double- and triple-charged metal ion are suitable for recovery of iron(III) cations through formation of the least soluble compound with phosphate anion.

The chemisorption procedures for separation of nonferrous and heavy metals can be realized using the solubility series of sulfides, carbonates, hydroxides, and phosphates. All these substances form difficultly soluble compounds with the above metals. However, phosphates are more advantageous, because they,

contrary to hydroxides and carbonates, are stable in acid solutions, up to pH 1, and, contrary to for example sulfides, have no foul odor.

CONCLUSIONS

(1) Chemisorption procedures can be used for selective removal of individual ions from multicomponent mixtures under the specified conditions.

(2) The heterogeneous chemical processes can be accompanied by the side reactions of various origin, which accounts for inconsistency between the experimentally obtained values and theoretical prediction. This can be for example said about the shift of the experimentally observed selectivity region toward higher solution concentrations.

REFERENCES

1. Shashkova, I.L., Mil'vit, N.V., and Rat'ko, A.I., *Zh. Prikl. Khim*., 2005, vol. 78, no. 11, p. 1859.
2. Demidov, A.I., and Krasovitskaya, O.A., *Zh. Prikl. Khim*., 2000, vol. 73, no.10, p.1656.
3. Lur'e, Yu.Yu., *Spravochnik po analiticheskoi khimii* (Handbook on Analytical Chemistry), Moscow: Khimiya, 1967.
4. Shul'ga, N.V., Shashkova, I.L., and Samuskevich, V.G., *Zh. Prikl. Khim*., 1999, vol. 72, no. 11, p. 1852.
5. Klement, R. and Haselbeck, H., *Z. Anorg. Allgem. Chem*., 1964, vol. 334, nos. 1–2, p. 27.
6. Shchegrov, L.N., *Fosfaty dvukhvalentnykh metallov* (Phosphates of Divalent Metals), Kiev: Naukova Dumka, 1987.
7. Shashkova, I.L., Rat'ko, A.I., and Kitikova, N.V., *Zh. Prikl. Khim*., 1997, vol. 70, no. 11, p. 1787.
8. Prodan, I.E., Eshchenko, L.S., and Pechkovskii, V.V., *Zh. Neorg. Khim*., 1989, vol. 34, no. 8, p. 2012.