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pH Effect on the Physicochemical Characteristics and Efficiency of Electroflotation Extraction of Low-Soluble Iron Subgroup Metal Compounds from Aqueous Solutions

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Abstract—This paper reports on our study of the pH effect of solutions on the average hydrodynamic diameter (d_{av}) of the particles of the disperse phase and the electrokinetic potential (ζ) of the particles of low-soluble iron subgroup metals compounds using Fe(II, III), Ni(II), and Co(II) compounds as an example. The pH effect of solutions on the efficiency of the electroflotation extraction of metal ions from aqueous solutions containing these ions in individual form or in mixture was studied. The efficiency of the electroflotation extraction of the low-soluble compounds of iron subgroup metals is directly related to the particle size and electrokinetic potential of the particles, which depend on pH. The maximum degree of particle extraction α reached 97–99% at pH values characterized by the maximum hydrodynamic diameter of particles (over 20 μm for Fe(II) and Co(II) compounds and over 50 μm for Fe(III) and Ni(II) compounds) at ζ potentials of up to −10 mV for systems approximated to real wastewater. In the case of the extraction of the disperse phase of the Fe(III)–Ni(II)–Co(II) multicomponent system, the synergic effect was observed: the coextraction of metals was more complete and effective, which may be due to suppressed negative charge. In the range of pH 10–11, the degree of extraction of the Fe(III) disperse phase did not exceed 74%; in the ternary system, it reached 94%.

Keywords: electroflotation, wastewater, iron subgroup metals, disperse phase, ζ potential, pH of medium
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INTRODUCTION

One of the determining stages of the electroflotation extraction of metal ions from wastewater is the formation of a disperse phase. The ions are transferred into disperse form by introducing inorganic reagents in solutions, for example alkalis, phosphates, or carbonates capable of reacting with metal ions to form sparingly soluble compounds. The simplest and at the same time the most effective way of extracting metal ions is their separation in the form of hydroxides or hydrated oxides using only acid-base reagents (i.e., by adjusting the pH of the medium with an alkali).

The choice of iron subgroup metals Fe(II, III), Ni(II), and Co(II) as objects of study was dictated by their wide use in various industries due to the formation of significant amounts of liquid metal-containing waste. The main source of formation of such wastes are electroplating and dimensional electrochemical machining shops, areas, and lines and metallurgical production [1, 2].

An analysis of the Pourbaix diagrams shows that, depending on the pH of the medium, the metal ions exist in the form of sparingly soluble compounds or soluble complexes and free ions. The nature of the resulting compounds depends on the potential and acidity of the medium and the valence state of metals [3, 4]. As is known, when pH changes, the equilibrium of the dissociation reactions of water, acids, bases, and metal hydroxo complexes shifts. Therefore, the main criterion used to determine the medium pH for performing the electroflotation purification is the minimum solubility of the resulting particles of the disperse phase, which obviously favors the maximum extraction of metal ions from the waste water [5]. At the same time, the medium pH can affect the surface characteristics of particles of sparingly soluble compounds, in particular, their size and charge (the electrokinetic potential ζ). As is known, the latter influence the efficiency of electroflotation [6, 7].

For many oxides and hydroxides, at pH 7–11 the potential-forming layer is fully compensated; i.e., all the counterions lie in the adsorption layer. In this case, the ζ potential becomes zero; i.e., an isoelectric region is observed, in which the most complete removal of colloid-disperse particles by electroflotation is possible [6]. On the other hand, it is known that in most cases, the size of particles is critical to the efficiency of their extraction from aqueous solutions (occasionally except particles with a high negative charge).

Therefore, the goal of this study was to analyze the effects of solubility, disperse characteristics, and charge of the particles of insoluble iron subgroup metal compounds on their electroflotation activity in aqueous solutions and to determine the factors that have the greatest effect on the efficiency of electroflotation purification.

EXPERIMENTAL

The object of the present study were solutions containing slightly soluble colloidal-disperse compounds of the iron subgroup metals Fe(II, III), Ni(II), and Co(II) in individual form and in a mixture. The pH effect of the medium on the electrokinetic potential (ζ, mV), average hydrodynamic diameter (d_{av}, μm), and electroflotation activity of the slightly soluble compounds of iron subgroup metals in water (α, %) was studied.

The metal ions were transferred into disperse form by adjusting the pH of the medium with a NaOH solution. In the study of single-component systems, the initial concentration of metal ions was 50 mg/L. For multicomponent systems, the total metal concentration was also 50 mg/L at a metal ratio of 1 : 1.

The experiments were carried out in the pH range 3–12. The solutions were filtered to determine the residual metal concentration C_{res} in solutions on “blue tape” filters.

The electroflotation extraction of particles of the disperse phase of poorly soluble compounds of iron subgroup metals was carried out in a non-flow-through apparatus with a volume of 0.5 L and with insoluble electrodes. The anode was a titanium plate with an ruthenium-titanium oxide coating (ORTA); the cathode was a stainless steel grid.

The electroflotation activity of the particles of the disperse phase was evaluated from the degree of extraction α (%) calculated as the ratio of the difference between the initial C_0 and final C_τ metal contents in solution to the initial content (in total in the disperse and ionic forms):

$$\alpha = [(C_0 - C_\tau)/C_0] \times 100\%.$$

The electroflotation activity of particles was studied at bulk current densities of 0.2–0.4 A/L. The time of the electroflotation purification of water is $\tau = 10$ min.

The mass concentration of metals in solutions was measured on an ATANT-AFA atomic absorption spectrometer using the standard method. The particle size was determined by laser diffraction using the physical principle of electromagnetic wave scattering with an AnalyzeTTe NanoTec laser particle analyzer. The ζ potential of particles was determined by measuring the electrophoretic mobility of particles in fluid on a Malvern Zetasizer Nano laser analyzer of the characteristics of submicron and nanosized particles.

RESULTS AND DISCUSSION

Medium pH Effect on the Solubility, Electrokinetic Potential, and Particle Size of the Slightly Soluble Compounds of Iron Subgroup Metals

Previously, we showed that the choice of pH of electroflotation purification of wastewater from metal ions based on the solubility data of the disperse phase is not optimum. It was noted that the efficiency of purification depends on the physicochemical characteristics of the particles of the disperse phase [8].

At the first stage, the pH effect of the medium on the solubility, electrokinetic potential, and particle size of slightly soluble Fe(II, III), Ni(II), and Co(II) compounds in aqueous solutions was studied. A study of the pH effect on the solubility of the particles of the disperse phase of the iron subgroup metals (Fig. 1) revealed that starting at pH 5.0, more than 98% Fe(III) ions form poorly soluble hydroxides, while the Fe(II) ions are completely transferred into the form of slightly soluble compounds starting at pH 7.0. The residual concentration of Fe(II, III) ions in solution is 0.5–0.7 mg/L (curves *3* and *4*, Fig. 1). The maximum complete transition of nickel and cobalt ions into the form of slightly soluble compounds (more than 99%) occurs at pH 9.0 and higher. The minimum residual concentration of Ni^{2+} and Co^{2+} ions in solution does not exceed 0.02 (pH 10) and 0.09 mg/L (pH 11), respectively (curves *1* and *2*, Fig. 1), which is much lower than for iron compounds.

The pH effect on the electrokinetic potential ζ was studied in solutions with low and high contents of sodium sulfate (0.001 and 0.01 M SO_4^{2-} solutions).

The 0.001 M SO_4^{2-} solution characterizes a system with a minimum salt content, which makes it possible to identify the isoelectric region in which the removal of disperse phase particles is most complete [5]. The 0.01 M SO_4^{2-} solution characterizes a system that approximates the real wastewater, which in most cases contains a certain amount of sulfate, which is part of many electrolytes, in addition to the components of the salt of the extracted metal.

It was found that in the 0.001 M SO_4^{2-} solution (Fig. 2), the particle surface of the poorly soluble Fe(II, III); Ni(II); and Co(II) compounds is recharged. The sign of the particle charge changes from positive to negative, the ζ(pH) curves cross the abscissa axis, and the ζ potential becomes zero. The value of the isoelectric point (pI) is 6.2 for the Fe(III) compounds and 7.2 for the Fe(II) compounds (curves *4* and *3*, Fig. 2). When pH of the solutions containing iron compounds increases to 8 and more, the ζ(pH) curves for the Fe(II) and

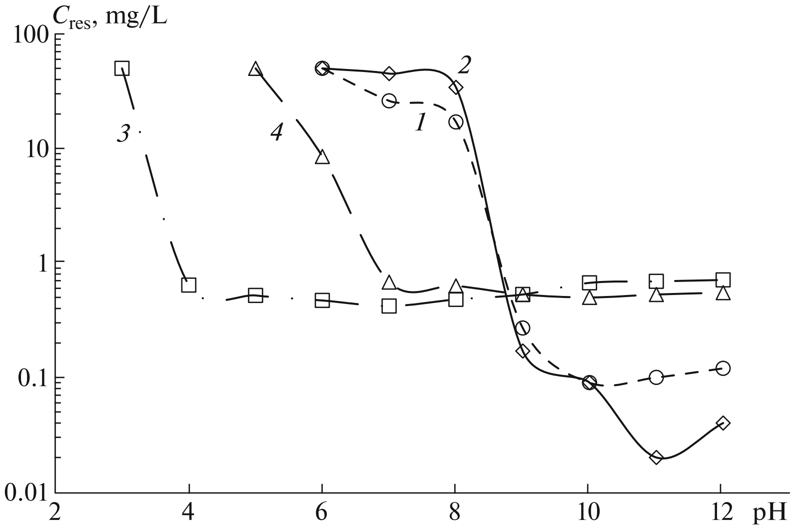

Fig. 1. Dependence of the residual concentration of iron subgroup metals on medium pH in the 0.01 M SO_4^{2-} solution of (*1*) Co(II), (*2*) Ni(II), (*3*) Fe(III), and (*4*) Fe(II).

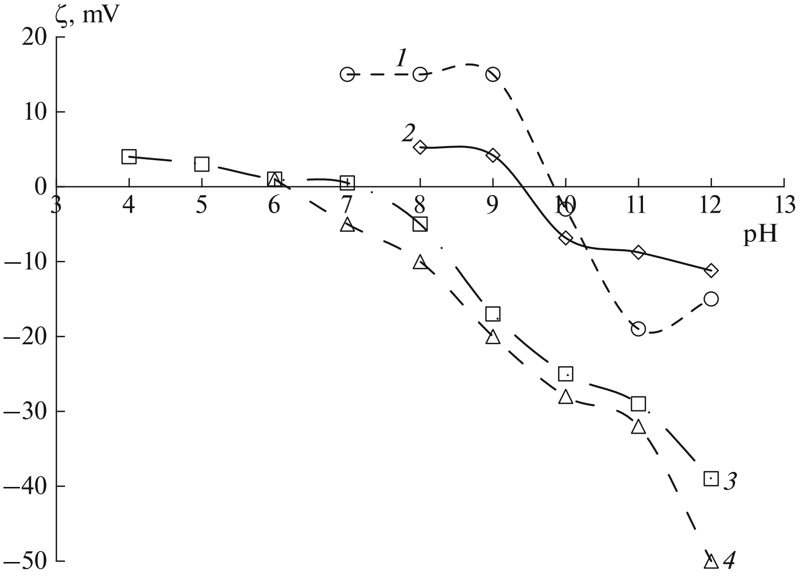

Fig. 2. Dependence of the ζ potential of the particles of the slightly soluble iron subgroup metal compounds on medium pH in the 0.001 M SO_4^{2-} solution of (*1*) Co(II), (*2*) Ni(II), (*3*) Fe(III), and (*4*) Fe(II).

Fe(III) compounds are maximally close to each other, and the electrokinetic potential lies in the range of high negative values (−(40−50) mV).

The isoelectric points of the poorly soluble nickel and cobalt compounds are shifted to the alkaline region and are 9.4 and 9.8, respectively (curves *1* and *2*, Fig. 2). Note that, in contrast to the case of Fe(II) and Fe(III) compounds, an increase in pH of the solutions containing poorly soluble Ni(II) and Co(II) compounds does not lead to a displacement of the ζ potential toward high negative values.

In the solutions containing an excess of the (0.01 M SO_4^{2-}) supporting solution, the particle charge of the poorly soluble Fe(II, III), Ni(II), and Co(II) compounds is negative over the whole pH range. At the moment of the formation of the compounds, the ζ potentials are in the range −(5−10) mV for the Fe(II, III) and Co(II) compounds and −(1−3) mV for the Ni(II) compounds. As for the 0.001 M SO_4^{2-} solutions, at increased pH, the ζ(pH) curves shift toward higher negative values of the ζ potential. Note that there is

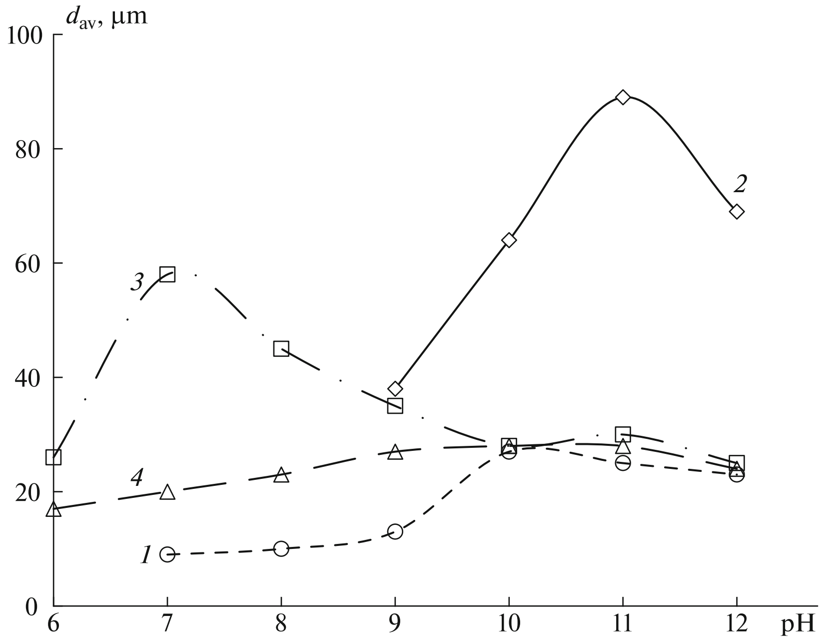

Fig. 3. Dependence of the average hydrodynamic diameter of the particles of the slightly soluble compounds of iron subgroup metals on medium pH in the 0.01 M SO_4^{2-} solution of (*1*) Co(II), (*2*) Ni(II), (*3*) Fe(III), and (*4*) Fe(II).

competition between the SO_4^{2-} and OH^- ions during the sorption on the newly formed particles of the disperse phase since in the region of strongly alkaline pH values, the particle charge of the disperse phase in the 0.01 M SO_4^{2-} solution is 10–15 mV higher positive than in the 0.001 M SO_4^{2-} solution and is –(10–15) mV for Fe(II, III) compounds, –(1–4) mV for Ni(II) compounds, and –(8–10) mV for Co(II) compounds. The presented data are in good agreement with the data obtained earlier and allowed us to propose a mechanism for charge formation of the disperse phase as a function of pH of the solution [6].

Further studies were carried out in solutions containing 0.01 M SO_4^{2-}, which is reasonable from the viewpoint of the use of the results in water purification. The medium pH effect on the average hydrodynamic diameter d_{av} of the particles of the slightly soluble Fe(II, III), Ni(II), and Co(II) compounds was studied (Fig. 3). It was shown that at increasing pH, the d_{av} values of the colloidal disperse compounds of the metals under study pass through an extremum. This can be explained by a slight increase in the solubility of the disperse phase in strongly alkaline regions and the difficulty of coagulation of particles with high negative ζ potentials [9]. The maximum average hydrodynamic diameter is characteristic of the particles of the disperse Ni(II) phase: d_{av} = 89 μm, pH 11 (curve *2*, Fig. 3). The average hydrodynamic diameter of Fe(III) compounds reaches 58 μm at pH 7 (curve *3*, Fig. 3), the values of Fe(II) and Co(II) compounds vary from 25 to 30 μm in the pH range 10–11 (curves *1* and *4*, Fig. 3).

Effect of the Physicochemical Characteristics of the Disperse Phase of Slightly Soluble Compounds of the Iron Subgroup Metals on Their Electroflotation Activity

At the second stage of our study, the efficiency of the electroflotation extraction of the insoluble iron subgroup metal compounds from aqueous solutions was studied at different pH values of the medium (Fig. 4). The electroflotation behavior of the Ni(II) compounds was shown to be similar to that of the Co(II) compounds (curves *1* and *2*, Fig. 4). The electroflotation behavior of the Fe(II) compounds is similar to that of the Fe(III) compounds (curves *3* and *4*, Fig. 4). The maximum degree of extraction of the Fe(II, III) compounds is 96–98% in the pH range 7–8 in 10 min after the beginning of purification. An increase in pH results in a significant reduction in the degree of extraction, which does not exceed 80% at pH 10. The maximum degree of extraction of the Ni(II) and Co(II) compounds reaches 98–99% in the pH range 10–11 and does not change when pH of solutions increases to 12.

The effect of the physicochemical characteristics (d_{av}, ζ) of the Fe(II, III), Ni(II), and Co(II) compounds on the degree of their electroflotation extraction from the 0.01 M SO_4^{2-} solutions at pH 6–12 (Table 1) was analyzed. It was shown that the effi-

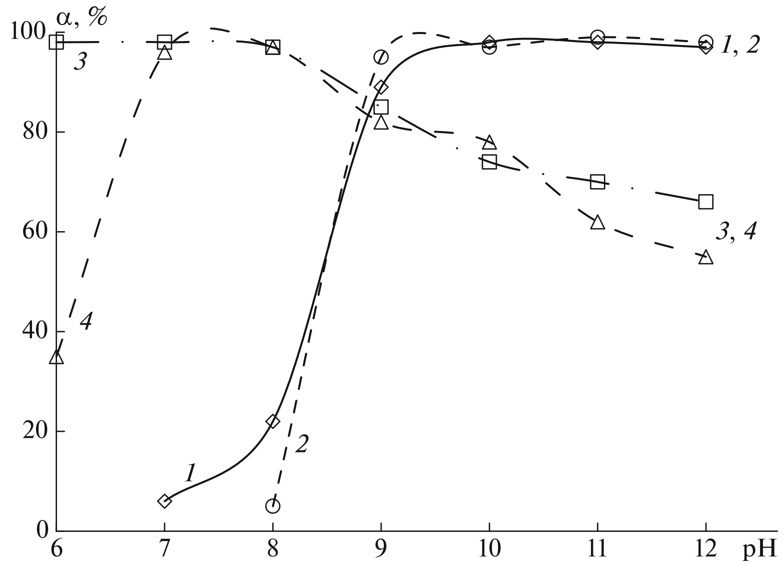

Fig. 4. Dependence of the degree of extraction α of the particles of the slightly soluble compounds of iron subgroup metals on medium pH in the 0.01 M SO_4^{2-} solution of (*1*) Co(II), (*2*) Ni(II), (*3*) Fe(III), and (*4*) Fe(II); τ = 10 min.

ciency of the electroflotation extraction of these compounds in the 0.01 M SO_4^{2-} solution depends on the mean hydrodynamic diameter and the ζ potential of the particles in the disperse phase. The particles with a charge of at least –10 mV are extracted most efficiently. According to the published data, a decrease in the electrokinetic potential leads to hindered coagulation of the particles of the disperse phase on the one hand and to difficulties in the formation of the "disperse phase particle–oxygen/hydrogen bubbles" floatation complexes on the other [9]. This leads to a decrease in the efficiency of the electroflotation extraction of the disperse phase. These effects depend on the nature of the disperse phase and are most pronounced for particles of the poorly soluble Fe(II, III) compounds.

For comparison, data characterizing the electroflotation activity of the slightly soluble Fe(II, III), Ni(II), and Co(II) compounds in the 0.001 M SO_4^{2-} solution were obtained. It was found that the maximum value of α generally corresponds to the degree of extraction in the 0.01 M SO_4^{2-} solutions and is achieved in the isoelectric region of potentials. This is evidently due to facilitated coagulation between particles in the solution, which leads to their rapid coarsening during electroflotation and to facilitated interaction of disperse phase particles with oxygen/hydrogen bubbles.

Co-Extraction of the Slightly Soluble Compounds of Iron Subgroup Metals from Aqueous Solutions

In the practice of sewage treatment in galvanochemical industries, systems with single metal ions are extremely rare. Wastewater is often treated in the general stream and therefore contains ions of at least two

Table 1. Effect of the solubility, particle size, and ζ potential of the slightly soluble Fe(II,III), Ni(II), and Co(II) compounds on their electroflotation activity at pH 6–12

pH	Disperse phase											
	Fe(II)			Fe(III)			Co(II)			Ni(II)		
	d_{av}, μm	ζ, mV	α, %	d_{av}, μm	ζ, mV	α, %	d_{av}, μm	ζ, mV	α, %	d_{av}, μm	ζ, mV	α, %
6	17	–6	35	26	–8	98	–	–	–	–	–	–
7	20	–4	96	58	–7	98	9	–5	6	–	–	–
8	23	–5	97	45	–8	97	10	–3	22	29	–3	5
9	27	–7	82	35	–9	85	13	–4	89	38	–1	95
10	28	–12	78	30	–10	74	27	–8	98	64	–1	97
11	28	–17	45	28	– 15	70	25	–10	98	89	–4	99
12	25	–28	52	25	–25	66	23	–12	97	69	–5	98

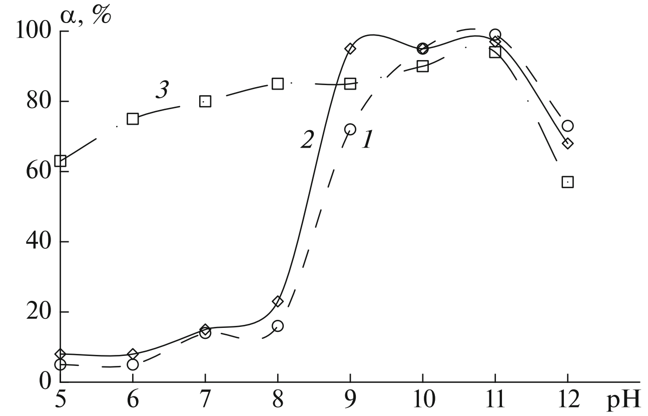

Fig. 5. Dependence of the degree of extraction α of the particles of slightly soluble compounds of iron subgroup metals in the Fe–Ni–Co ternary system on medium pH in the 0.01 M SO_4^{2-} solution: (*1*) Co(II), (*2*) Ni(II), and (*3*) Fe(III); τ = 10 min.

or three metals that form poorly soluble compounds at different pH values. The values of the minimum solubility of the individual compounds can differ from each other by two or three units.

Therefore, the co-removal of the iron subgroup (Fe(III), Ni(II), and Co(II)) ions in the Fe–Ni–Co ternary system was studied in a wide range of pH values of the medium. The data obtained are presented in Fig. 5. The electroflotation activities of the iron subgroup metals were compared in the pH ranges 7–8 (the maximum extraction efficiency of the Fe(III) compounds) and 10–11 (the maximum extraction efficiency of the Ni(II) and Co(II) compounds).

It was found that the efficiency of the electroflotation extraction of the slightly soluble Fe(III) compounds from the Fe–Ni–Co ternary system in the pH range 7–8 is lower than that of the solution with individual Fe(III). Thus, at pH 8, the degree of iron extraction is 10% after the start of the process, reaching 85% for the ternary system and 98% for the solution containing individual Fe(III). At the same time, in the pH range 10–11, the opposite effect is observed: the degree of extraction of Fe(III) from the ternary system is higher than from the solution containing individual Fe(III). In the given pH range, α is 94% for the slightly soluble iron compounds in the multicomponent system and 74% for the individual compounds.

Note that in the pH range 7–8, the degree of extraction of poorly soluble Ni(II) compounds in the ternary system is much higher than for the individual form and reaches 23%. This can be explained by the sorption of nickel ions on the newly formed iron and cobalt hydroxides. At the same time, the extraction of individual nickel in the given pH range with allowance for the obtained solubility data (curve *2*, Fig. 1) can be explained by ion flotation [10].

The degree of extraction of slightly soluble Co(II) compounds in the pH range 7–8 in the ternary system is 16 and 22% for individual cobalt. Thus, the efficiency of cobalt extraction appears to be largely due to its solubility in this pH range (curve *1*, Fig. 1).

In the pH range 10–11, the degree of extraction of poorly soluble Ni(II) and Co(II) compounds in the ternary system does not differ from that of individual metals and is 95–99%. Note that an increase in pH from 11 to 12 leads to a sharp decrease in the efficiency of metal extraction from the Fe–Ni–Co ternary system from 94–99% to 57–68% for all components (Fig. 5). On the other hand, in solutions containing individual metal ions, in the pH range 11–12, the efficiency of the extraction of the slightly soluble Ni(II) and Co(II) compounds does not change and is 98–99%, and the efficiency of iron extraction is 70–74% (Fig. 4).

The physicochemical characteristics of the disperse phase of slightly soluble Fe(III), Ni(II), and Co(II) compounds were compared for individual compounds and for compounds in the ternary mixture at pH 7–8 and 10–11. The effect of the charge and size of the disperse phase on the efficiency of electroflotation was analyzed. The data obtained are presented in Table 2.

Table 2. Effect of the particle size and ζ potential of the slightly soluble Fe(III), Ni(II), and Co(II) compounds on their electroflotation activity for individual compounds and in a ternary system

Disperse phase	pH 7–8			pH 10–11		
	d_{av}, μm	ζ, mV	α, %	d_{av}, μm	ζ, mV	α, %
Single-component Fe, Ni, and Co systems						
Fe(III)	45–58	–(7–8)	97–98	28–30	–(10–15)	70–74
Ni(II)	10–29	–(1–3)	0–5	64–89	–(1–4)	97–98
Co(II)	9–10	–(3–5)	6–22	25–27	–(8–10)	97–98
Fe–Ni–Co ternary system						
Fe(III)	20–30	–(1–5)	80–85	30–40	–(6–10)	90–94
Ni(II)			14–23			95–99
Co(II)			14–16			95–99

It was found that in the Fe–Ni–Co ternary system, the average hydrodynamic diameter and the electrokinetic potential of the particles of the disperse phase are averaged. Thus, in the pH range 6–7, the average hydrodynamic diameter of the particles of the disperse phase of the Fe–Ni–Co system is 20–30 μm, and an increase in pH of solutions leads to coarsening of particles to 30–40 μm (pH 7–8). At increased pH of solutions, the electrokinetic potential of the particles shifts toward higher negative values: from –(1–5) mV at pH 6–7 to –(6–10) mV at pH 10–11.

CONCLUSIONS

Thus, our study showed that the choice of pH of electroflotation purification of aqueous solutions from insoluble compounds of iron subgroup metals based on the solubility data is not optimum. It was found that the efficiency of purification depends on the particle size and charge of the disperse phase. As pH of the medium increases, the mean hydrodynamic diameter of the particles of the Fe(II, III), Ni(II), and Co(II) disperse phase passes through an extremum (more than 20 μm for Fe(II) and Co(II) compounds and more than 50 μm for Fe(III) and Ni(II) compounds), and the electrokinetic potential of the particles does not drop below –10 mV. Under these conditions, the efficiency of electroflotation is maximum, the degree of extraction of the disperse phase α reaching 97–99%.

A study of the physicochemical characteristics and electroflotation activity of the Fe(III)–Ni(II)–Co(II) multicomponent system showed that the particles of the disperse phase have a strong influence on one other: the average hydrodynamic diameter and the electrokinetic potential of the particles are averaged. A synergistic effect is observed, which consists in a more complete extraction of metal ions in the highly alkaline range (pH 10–11). In the weakly alkaline range (pH 7–8), the presence of Ni(II) and Co(II) ions leads to difficulties in extracting the poorly soluble Fe(III) compounds.

The obtained data are important for understanding the mechanism of electroflotation purification of aqueous solutions from metal ions and are of practical interest for purification of industrial wastewaters containing iron subgroup metals.

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