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STUDY OF THE POSSIBILITY OF IRON(II) EXTRACTION USING PHENOL-TYPE OLIGOMERIC EXTRACTANTS

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Abstract: This paper investigates the liquid–liquid extraction of iron(II) ions using oligomeric phenolic extractants synthesized from phenol-formaldehyde resins. The effects of the main physicochemical parameters of the extraction system—including the pH of the aqueous phase, metal-ion concentration, extractant content, and duration of interfacial contact—on the efficiency of Fe(II) extraction were studied. Particular attention was paid to establishing the relationship between the structural features of oligomeric phenolic compounds and their extraction characteristics. It is shown that the use of oligomeric extractants may potentially improve the selectivity of Fe(II) ion extraction and increase the distribution coefficient compared with monomeric phenolic compounds. The observed patterns may be attributable to the presence of several functional groups involved in interactions with metal ions, as well as to the spatial organization of oligomer molecules. Based on the presumed patterns of interaction between the extractant and iron(II) ions, the possibility of complexation accompanied by the formation of chelate-like structures that promote metal retention in the organic phase is considered. The composition and structure of the resulting complexes require additional physicochemical confirmation using appropriate analytical methods.

Keywords: extraction, iron(II), phenolic extractants, oligomers, complexation, liquid–liquid extraction, selectivity.

Introduction.

Iron(II) is an important component involved in various chemical and technological processes and is widespread in liquid industrial waste generated by metallurgical and mining operations. The presence of Fe(II) ions in wastewater necessitates the development of effective extraction methods aimed at reducing the anthropogenic impact on the environment and ensuring the rational use of secondary material resources [1,2].

Therefore, investigating the physicochemical patterns governing the extraction of iron(II) from aqueous solutions represents a relevant scientific and practical task.

Among modern methods for the separation, concentration, and extraction of metal ions, liquid–liquid extraction occupies a special place. It is based on the distribution of a target component between aqueous and organic phases. The efficiency of this process is determined by the nature of the extractant, the acidity of the aqueous medium, the concentration of the metal being extracted, the phase-volume ratio, and the duration of phase contact. The use of phenolic compounds, whose functional groups may participate in coordination interactions with metal ions, is a promising direction for improving extraction technologies.

Oligomeric phenolic extractants synthesized from phenol-formaldehyde resins are of particular scientific interest. Unlike low-molecular-weight phenolic compounds, these structures may contain several potential coordination sites, creating the prerequisites for changes in their complex-forming

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ability and extraction characteristics. The oligomerization of phenolic compounds is considered one possible way to regulate the selectivity of metal extraction and the stability of the resulting complexes. At the same time, the influence of the molecular structure of oligomers on the distribution coefficient and the degree of iron(II) extraction requires experimental determination.

The aim of this work is to investigate the patterns of liquid–liquid extraction of iron(II) ions from aqueous solutions using oligomeric phenolic extractants based on phenol-formaldehyde resins, and to assess the influence of the main physicochemical parameters of the extraction system on process efficiency and selectivity.

Results and Discussion. Particular attention is paid to identifying the relationship between extraction conditions, the structural features of the extractants, and the distribution of Fe(II) ions between the aqueous and organic phases. Based on the similarity between the properties of Fe(II), cobalt, and nickel, the nitrogen-containing oligomer YRB was selected as the iron extractant, and conditions similar to those used for the extraction of cobalt, nickel, zinc, and cadmium were applied [1,2].

Iron(II) was extracted from an ammoniacal iron solution containing 50 g/L $(NH_4)_2SO_4$ and 2.3 g/L Fe(II), using a 0.25 mol/L solution of YRB in toluene. The required pH was maintained by adding ammonium hydroxide to the solution. Extraction was carried out over the pH range of 4.5–9.0.

Phase separation was slow and took 20 min. Since a precipitate of Fe(III) hydroxide gradually formed in the aqueous phase as a result of the oxidation of Fe(II) by atmospheric oxygen, the amount of iron(II) transferred to the organic phase was determined by back-extraction. Back-extraction was carried out with a 6 mol/L HCl solution for 30 min at $V_a:V_o = 1:2$.

The results obtained are presented in Table 1 and Figure 1 as the dependence of the Fe(II) distribution coefficient on the pH of the equilibrium aqueous phase.

Table 1

Extraction of Fe(II) using a 0.25 mol/L solution of the YRB oligomer in toluene ($C_{(Fe,\ initial)}$ = 2.43 g/L; $C_{((NH_4)_2SO_4)}$ = 50 g/L)

No.	Equilibrium pH	XFe, g/L	YFe, g/L	DFe
1	4,50	2,40	0,03	0,01
2	5,10	2,26	0,17	0,08
3	5,83	1,68	0,75	0,45
4	6,35	1,31	1,12	0,85
5	7,05	1,19	1,24	1,04
6	7,75	0,94	1,49	1,58
7	8,25	0,97	1,46	1,50
8	9,0	1,55	0,88	0,57

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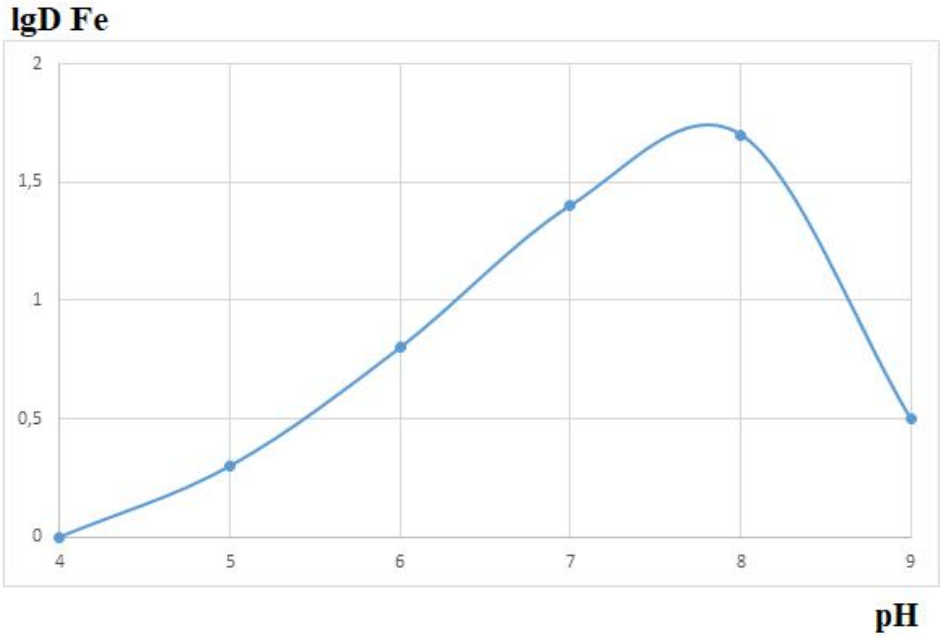


Fig. 1. Dependence of DFe on pH during the extraction of Fe(II) using 0.25 mol/L YRB oligomer in toluene

As can be seen from the data presented, the maximum iron extraction corresponds to pH 7.75. However, under these conditions, a precipitate of Fe(III) hydroxide forms in the aqueous phase because Fe(II) is readily oxidized by air, complicating phase separation. Therefore, ammoniacal solutions with higher pH values were used for further study of Fe(II) extraction with YRB. To stabilize the ammoniacal Fe(II) complexes, which have a low stability constant, the concentration of $(NH_4)_2SO_4$ was increased to 200 g/L. A trial extraction under these conditions, using 0.3 mol/L YRB in toluene from an $FeSO_4$ solution at pH 10 with an iron(II) concentration of 16.64 g/L, at $V_a:V_o = 1:2$ for 30 min, showed that 8.94 g/L of Fe was extracted into the organic phase; at the same time, a precipitate of Fe(III) hydroxide formed in the aqueous phase.

When studying extraction, it is important to establish the relationship $Y_m = f(X_m)$, i.e. the extraction isotherm, over the parameter range under investigation. The extraction isotherm makes it possible to determine the capacity of the extractant under the given conditions, as well as the metal-to-reagent ratio in the extract at saturation of the organic phase. In addition, extraction isotherms are required for the technological calculation of the extraction process [3,4].

Iron(II) was extracted from solutions with metal concentrations ranging from 0.1 to 16.6 g/L, while the concentrations of all other components of the aqueous phase were kept constant. The solutions contained 200 g/L $(NH_4)_2SO_4$ and had a pH of 10. The experimental data for iron(II) extraction using a 0.3 mol/L solution of YRB in toluene are presented in Table 2.

The data obtained (Table 2) show that as the concentration of iron(II) in the equilibrium aqueous phase increases, its concentration in the organic phase also increases and reaches saturation at a certain X value. The concentration of iron(II) in the organic phase corresponding to the horizontal saturation

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section of the distribution curves characterizes the extractant capacity under the experimental conditions. In this case, the capacity of the extractant for Fe(II) was 9.0 g/L (0.16 mol/L).

Table 2

Dependence of the equilibrium concentrations of Fe(II) in the organic phase on its equilibrium concentration in the aqueous phase

Extraction conditions: $C_{((NH_4)_2SO_4)}$ = 200 g/L; $C_{(YRB)}$ = 0.30 mol/L

XFe		YFe		D
g/L	mol/L	g/L	mol/L	
0,0	0,002	0,68	0,011	6,9
0,96	0,001	5,02	0,090	5,2
2,03	0,036	7,99	0,143	3,9
3,61	0,065	8,88	0,159	2,5
7,70	0,138	8,94	0,160	1,2
16,56	0,297	9,02	0,162	0,54

The metal-to-reagent ratio in the organic phase was also determined from the extraction-isotherm data. It was found to be 0.53, i.e. close to 0.5. Consequently, two reagent molecules interact with one Fe(II) atom.

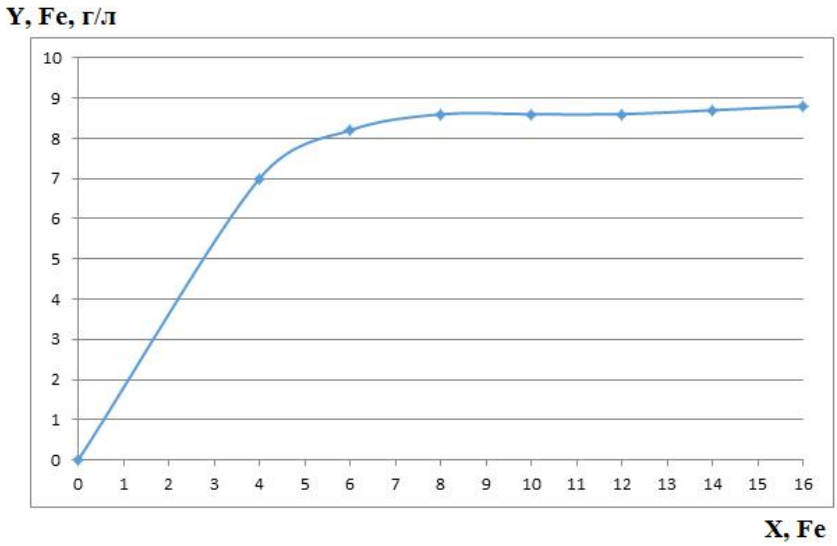


Fig. 2. Fe(II) distribution during extraction with 0.3 mol/L YRB in toluene

To identify the effect of the pH of the equilibrium aqueous phase on the degree of iron(III) extraction, extraction was carried out using a 0.4 mol/L solution of YRB in octane with the addition of 25% octanol, at an aqueous-to-organic phase ratio of V_a:V_o = 1:2 for 30 min. The Fe(III) concentration in the initial solution was 0.49 g/L. Extraction was carried out over the pH range of 4.6–10.6.

The results obtained are presented in Fig. 3 and Table 3.

Table 3.

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Dependence of Fe(III) extraction by a 0.4 mol/L YRB solution in an octane–octanol mixture on the pH of the aqueous phase

No.	Equilibrium pH	XFe, g/L	YFe, g/L	DFe	lg D	E, %
1	4,60	0,480	0,010	0,02	-1,7	2,0
2	4,95	0,480	0,020	0,04	-1,4	4,0
3	5,10	0,122	0,368	3,07	0,49	75,5
4	5,15	0,253	0,237	0,96	0,01	49,0
5	5,20	0,100	0,390	3,90	0,60	80,0
6	5,25	0,186	0,304	1,67	0,22	63,0
7	5,40	0,440	0,050	0,11	-0,96	10,0
8	5,50	0,290	0,200	0,70	-0,15	42,0
9	5,55	0,380	0,110	3,25	0,51	76,5
10	5,90	0,341	0,149	0,46	-0,34	31,0
11	5,95	0,370	0,120	0,14	-0,85	24,0
12	6,35	0,070	0,420	6,0	0,78	86,0
13	6,80	0,110	0,380	3,45	0,54	78,0
14	6,85	0,0150	0,340	2,27	0,37	69,0
15	6,90	0,30	0,460	15,57	1,19	94,0
16	7,10	0,037	0,453	12,43	1,09	92,0
17	7,20	0,050	0,440	8,80	0,98	90,0
18	8,50	0,125	0,365	2,97	0,47	75,0
19	9,30	0,077	0,413	5,45	0,74	84,0
20	10,65	0,051	0,439	8,74	0,94	90,0

As can be seen from the data presented, the experimental points on the dependence DFe(III) = f(pH) show considerable scatter. This may indicate that the extraction process was conducted under non-equilibrium conditions. Therefore, the dependence of the degree of Fe(III) extraction on the phase-contact time at pH 5.2 was additionally studied (Fig. 4, Table 4)

Table 4

Dependence of DFe(III) and EFe(III) on contact time during Fe(III) extraction using a 0.4 mol/L YRB solution in an octane–octanol mixture at pH 5.2 and CFe(III) = 0.49 g/L

No.	Contact time, min	XFe, g/L	YFe, g/L	DFe	lg D	E, %
1	15	0,216	0,281	1,30	0,11	56
2	30	0,229	0,268	1,17	0,07	54
3	60	0,167	0,330	1,98	0,29	66
4	90	0,143	0,354	2,47	0,39	71
5	120	0,087	0,410	4,40	0,67	82
6	180	0,027	0,470	17,41	1,21	99

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The results showed that equilibrium during Fe(III) extraction with YRB is established very slowly; even after three hours of phase contact, equilibrium had not been reached. Therefore, it was necessary to find a system containing an oligomeric extractant that would allow iron extraction with a shorter phase-contact time.

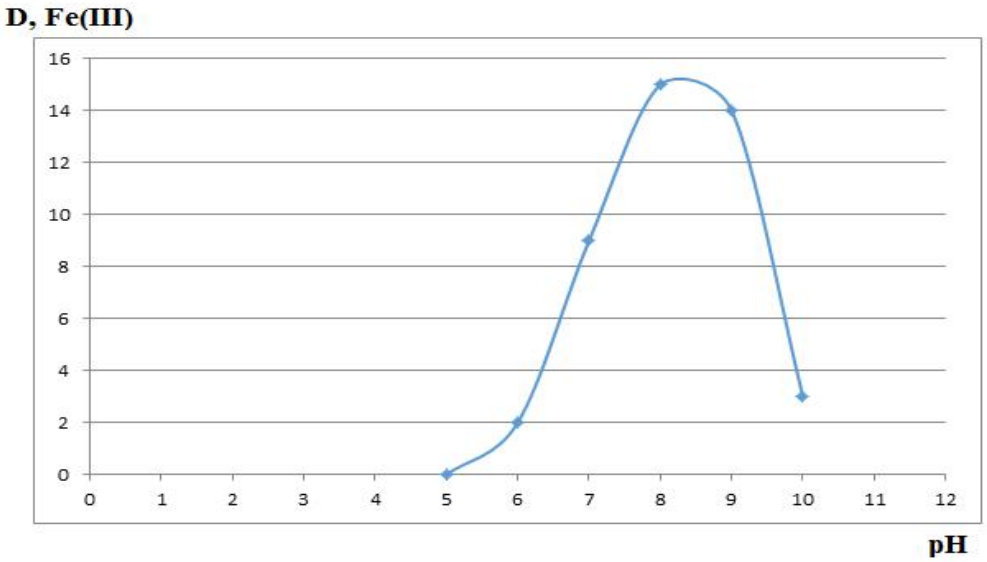


Fig. 3. Dependence of DFe(III) on pH

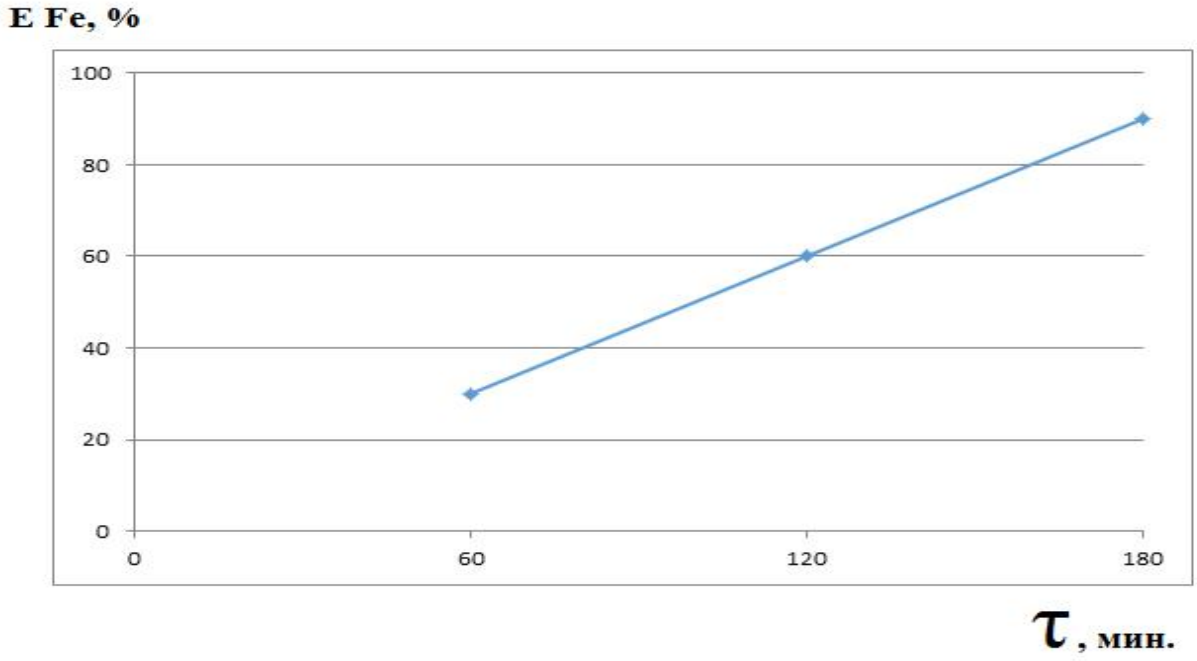


Fig. 4. Dependence of the degree of Fe(III) extraction on contact time

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Conclusion. In accordance with the proposed metal-to-reagent ratio, the extractable complex forms in the organic phase through interaction of the metal with two extractant molecules, as a result of replacement of the proton of one of the hydroxyl groups of the YRB molecule by the extracted metal. Thus, the spectrum of iron complexes extracted with YRB should contain an absorption band corresponding to the vibrations of the remaining hydroxyl groups of the extractant; however, its intensity should be lower than the intensity of the OH-group band in the original extractant.

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