Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Solvent Extraction of Iron(III) From Chloride Solutions in the Presence of Copper(II) and Zinc(II) Using Hydrophobic Pyridyl Ketoximes

Anna Parus[a]; Karolina Wieszczycka[a]; Andrzej Olszanowski[a]
[a] Institute of Chemical Technology and Engineering, Poznań University of Technology, Poznań, Poland

To cite this Article Parus, Anna , Wieszczycka, Karolina and Olszanowski, Andrzej(2011) 'Solvent Extraction of Iron(III) From Chloride Solutions in the Presence of Copper(II) and Zinc(II) Using Hydrophobic Pyridyl Ketoximes', Separation Science and Technology, 46: 1, 87 — 93

To link to this Article: DOI: 10.1080/01496395.2010.498802

URL: http://dx.doi.org/10.1080/01496395.2010.498802

Separation Science and Technology, 46: 87–93, 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496395.2010.498802

Solvent Extraction of Iron(III) From Chloride Solutions in the Presence of Copper(II) and Zinc(II) Using Hydrophobic Pyridyl Ketoximes

Anna Parus, Karolina Wieszczycka, and Andrzej Olszanowski
Institute of Chemical Technology and Engineering, Poznań University of Technology, Poznań, Poland

In this work, oximes of 1-(2-pyridyl)tridekane-1-one and 1-(4-pyridyl)tridecane-1-one were used as model hydrophobic extractants for iron(III) from a chloride media. Both studied pyridyl ketoximes have the ability to extract iron(III) from chloride solutions. The highest degree of iron(III) extraction was observed for 1-(2-pyridyl)tridecane-1-one oxime. During extraction with 4-pyridyl ketoxime, a precipitated complex was observed, which has a disadvantageous effect for the extraction process. Iron(III) could be effectively stripped by 1% HCl from organic solution after extraction. Selectivity extractions from multielemental aqueous solutions containing iron(III) using 2- and 4-pyridyl ketoximes were also studied. The highest extraction percentage and good selectivity was observed for Cu^{2+} from a solution containing 1.0 M Cl^- with 1-(2-pyridyl)tridecane-1-one oxime. A scheme of separation of particular metal ions from mulielemental aqueous solutions was also proposed. The separation of metal ions is possible in three stages of extraction.

Keywords copper(II); extraction; iron(III); pyridyl ketoxime; separation; zinc(II)

INTRODUCTION

Iron(II)/(III) always accompanies copper(II), zinc(II), nickel(II), cobalt(II), and other metals and therefore the separation of iron from other metals is an important problem in hydrometallurgic processes. The selective separation of iron(III) from undesired impurities is an important issue for the concentration or purification of secondary sources. The effective recovery of metal ions is possible only if the separation process is sufficiently selective. Solvent extraction is one of the most widely used methods for the purification and separation of metal ions from different sources. Recently this technique has been increasingly employed to overcome the iron(III) control problem in hydrometallurgy industries (1,2).

The selective extraction of metal ions from industrial wastewater streams and contaminated areas is a topic of great interest.

In the previous decades, several extractants have been used to remove iron(III), bis(2-ethylhexyl)phosphoric acid (D2EHPA) (3–7), and tributhylphosphate (TBP) (8,9). The mixtures of extractants have also been studied, for example: TBP + D2EHPA, D2EHPA + Kelex® 100 (1,9).

M.C. Costa et al. (10–12) have demonstrated that malonamide derivatives (*N,N*′-dimethyl-*NN*′-diphenylmalonamide, *N,N*′-dimethyl-*NN*′-diphenyltetradecylmalonamide and *N,N*′-dimethyl-*N,N*′-dibutylmalonamide) were efficient and selective extractants for the separation of iron(III) from acid chloride media. The iron(III) extraction depended on HCl concentration, and their efficiency is enhanced as the acid concentration in the aqueous phase increases.

Mowafy (13) reported the ability of the 4-chlorophenyl substituted malonamide to extract Fe(III) from chloride solutions. These extractants could be used for the extraction and separation of iron(III) from other metal ions present in waste chloride liquors.

Teke et al. (14) have studied the extraction of iron(III) with bis(Δ^2-2-imidazolinyl)-5,5′-dioxime from binary and muliticomponent nitrate mixtures, which contain cobalt(II), nickel(II), and copper(II). They observed that the extraction of iron(III) increased with the pH value, reaching a maximum in the zone of pH 2.0 and subsequently decreased. Bis(Δ^2-2-imidazolinyl)-5,5′-dioxime extracted selective iron(III).

PC88A, MIBK and Alamine 336 were tested by Lee and Lee (15). The highest extraction percentage was obtained with Alamine 336 in toluene. The separation of iron(III) from nickel(II) was possible with this extractant.

N-methyl-*N*-cyclohexyloctanamide and *N*-methyl-*N*-phenyloctanamide were synthesized and tested to recover iron(III) from a chloride media by Figueira and Paiva.

Received 5 December 2009; accepted 2 June 2010.

Address correspondence to Anna Parus, Institute of Chemical Technology and Engineering, Poznań University of Technology, pl. M. Skłodowskiej – Curie 2, 60-965 Poznań, Poland. Tel.: +480616653688; Fax: +480616653649. E-mail: Anna.Parus@put.poznan.pl

Both compounds efficiently extract iron(III) from hydrochloride solutions. These amides have a good preference to selectively remove iron(III) in the presence of Cu(II), Ni(II), and Zn(II) (16).

Cierpiszewski et al. (17–19) have studied the extraction of zinc(II), iron(II), and iron(III) with solutions of dibutylbutyl phosphate (DBBP) and tributyl phosphate (TBP) from hydrochloric acid solutions. The obtained results showed that iron(II) is slightly extracted by the considered extractant, while DBBP is a very effective extractant of zinc(II). This enables the extraction of zinc(II) selectively from solutions containing iron(II) ions. Iron(III) is extracted very efficiently and should be reduced to iron(II) to minimize its transfer to DBBP.

Many pyridine derivatives form complexes with Cu(II), Cd(II), Zn(II), Co(II), Ni(II), Pd(II) etc. and these compounds could be a potential extractant for metal ions from different solutions. Acorga CLX-50® has been proposed for the extraction of copper(II) from acid chloride solutions (20). The active component of the extractant is di-isodecyl pyridine-3,5-dicarboxylate. Acorga CLX-50® can transfer large amounts of copper(II) from chloride solutions since the loading and stripping operations are governed by the chloride ion concentrations in the aqueous phase. Other pyridine derivatives such as esters and amides are proposed by Bogacki et al. (21), Borowiak–Resterna (22), Cote et al. (23), Szymanowski et al. (24). The extraction abilities of the weak basic organic compounds depend on the structure, position, and number of the functional group (amid and ester) in the pyridine ring.

Pyridine carboxamides are also used to extract of Pd(II) from hydrochloric acid solutions. The alkyl 3- and 4-pyridine carboxamides extracted higher amounts of Pd(II) than 2-pyridine carboxamides (25). Tomaszewska et al. proposed pyridine-carboxamides for the recovery of cadmium(II) from the chloride media. The extraction of cadmium(II) by pyridine-carboxamides depends on the structure and position of substituents in the pyridine ring (26).

Ligands containing an oxime group and pyridine ring are popular in coordination chemistry. The majority of the metal complexes of these ligands have been prepared in the last twenty years. Pyridyl aldo- and ketoximes form complexes with zinc(II), copper(II), silver(I), nickel(II), cadmium(II), and iron(III). The donor atoms of the 2-pyridyl oximes in metal complexes are the nitrogen atoms of the oxime and the pyridyl groups (27–32). The presence of an oxime and pyridine moiety allows the formation of complexes with metals by solvating and/or chelating mechanisms. The formation of complexes of pyridyl ketoxime with metal ions depends on the nature of the solvent, the location of the oxime group in the pyridine ring, and the concentration of the metal ions (27).

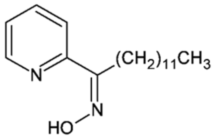
The extraction ability of pyridyl ketoximes to copper(II), zinc(II), and cadmium(II) were studied in our group (33–35). The obtained results showed the influence of the extractant structure (the position of substituents in the pyridine ring), the type of diluents, and the concentration of chloride ions in aqueous feed on the studied metals extraction. 2-Pyridyl ketoximes are strong solvating extractants which extract copper(II) efficiently even at low concentrations of chloride ions. 4-Pyridyl ketoximes are the weaker extractants and the degree of extraction slightly increased with an increase in chloride ion concentration (33). The extraction of cadmium(II) was observed with 2-pyridyl ketoximes and depended on several aspects: solvent type, ligand concentrations, and chloride ion concentrations, while 4-pyridyl ketoximes did not extract cadmium(II) from chloride media (34). Solvent extraction of zinc(II) with pyridyl ketoximes depended on the position of the functional group in the pyridine ring, solvent type and chloride ion level (35).

The purpose of the present work was to conduct fundamental studies on the extractive iron(III) removal from chloride media with 2- and 4-pyridyl ketoximes. We also report studies of selectivity from the chloride media which contain free metal ions: copper(II), zinc(II) and iron(III) with hydrophobic pyridyl ketoximes.

EXPERIMENTAL

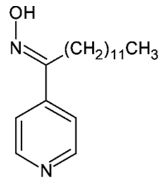
Reagents

Alkyl pyridyl ketoximes (1-(2-pyridyl)tridecane-1-one oxime and 1-(4-pyridyl)tri-decane-1-one oxime) as individual model extractants were used.



1-(2-pyridyl)tridecane-1-one oxime

(2PC12)



1-(4-pyridyl)tridecane-1-one oxime

(4PC12)

Synthesis of pyridyl ketoximes and their characteristics have been described in previous papers (33). Oximes 1-(2-pyridyl)tridecane-1-one and 1-(4-pyridyl)tridecane-1-one were synthesized from the corresponding ketones and hydroxylamine hydrochloride. The ketones were obtained through the addition of the proper Grignard reagent to 2- or 4-pyridinecarbonitrile.

Solvent Extraction Procedure

The extraction was carried out in a test tube using the same volumes (5 mL) of the two phases. The phases were mechanically shaken for 30 min at room temperature. The concentration of the metal ions was always determined in the aqueous phase before and after extraction and after stripping. The concentration of iron(III) present alone in the aqueous solution was controlled by a spectrophotometer for measuring absorbance (using UV-1601PC spectrophotometer Shimadzu). When zinc(II) and copper(II) were present together with iron(III), the content of zinc(II) was determined by ICP–OES and copper(II) and iron(III) were determined by atomic absorption spectroscopy GFAAS.

Unless otherwise stated, the extraction studies were carried out at a constant metal ion concentration equal to 0.001 M; however, the loading test for the concentration of Fe(II) in the aqueous phase was changed from 0.001 to 0.01. The concentration of extractants in the organic phase was changed from 0.002 to 0.01 M. Extraction studies were carried out at constant water activity $a_w = 0.835$ and constant total concentration of ions and molecules dissolved in aqueous solution $\sigma = 8.0$ M, where the chloride concentrations were changed from 0.1 to 4.0 M. NaCl, $NaNO_3$ and $LiNO_3$ were used to adjust the constant water activity ($a_w = 0.835$). Nitrates were selected because they do not form or form very weak complexes with metal ions (23,36,37). At constant a_w and σ, the salting-out effect has the constant influence within the whole range of chloride ion concentration investigated (23,37). In all experiments the pH of the aqueous phases was close to 1.8. Measurements of the pH were made using a 713 pH Meter (Metrohm). Toluene with 10% addition of decan-1-ol was used as diluents. The addition of hydrophobic alcohol improves the solubility of oximes in the organic phase. The concentration of the metal ions in the organic phase was calculated from the difference between the metal ion concentrations in the aqueous phase before and after extraction. The distribution coefficient (D) was taken as the ratio of the metal ion concentrations in the organic phase to the present in the aqueous phase at equilibrium.

RESULTS AND DISCUSSION

Extraction of Iron(III) from Chloride Solutions

The trivalent iron in the aqueous phase forms a variety of complexes in the presence of chloride ions, which can be defined by

$$Fe^{3+} + iCl^- = FeCl_i^{(3-i)+} \tag{1}$$

where $i = 0, 1, 2, 3$, and 4. Thus the total metal ion in the aqueous phase is given by

$$[Fe^{3+}]_{total} = [Fe^{3+}](1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2 + \beta_3[Cl^-]^3 + \beta_4[Cl^-]^4) \tag{2}$$

The values of the stability constant were: $\beta_1 = 4.26$, $\beta_2 = 5.62$, $\beta_3 = 0{,}023$ and $\beta_4 = 0.0025$ (at 1.0 M ionic strength) (38). The percentage composition of different iron–chloride species depend on a concentration of chloride ion and above 1 M Cl the $FeCl_3$ species are essentially (6).

In all experiments the pH of the aqueous phases was close to about 1.8. These experiments were carried out at constant water activity (a_w) and a total concentration (σ) of aqueous species. The results of the influence of chloride ions on iron(III) (Fig. 1) show that iron(III) extraction with 1-(2-pyridyl)tridecane-1-one oxime did not depend on the chloride ion concentrations in the whole studied range (0.1–4.0 M) and was equal to 60%. When 1-(4-pyridyl) tri-decane-1-one oxime was used, the extraction of iron(III) depended on the chloride ion concentration. The iron(III) extraction increased with the chloride ion concentrations up to the maximum at about 1.0 M Cl^-, but thereafter significantly decreased. The extraction maximum was observed at 1.0 M Cl^- and was equal to 25%. In the case of 4-pyridyl ketoxime, the formation of emulsions in the aqueous phase was observed, which could be the result of the formation of the complex precipitated. The formation of emulsion is a disadvantageous effect for the extraction process, because this obstructs the partition of phases and induces on the effectiveness of extraction.

Loading Coefficients

The loading test of iron(III) by 2- and 4-pyridyl ketoximes were examined. The relation between the molar ratio of the iron(III) ions to the extractant in the toluene with 10% addition of decan-1-ol solutions, and the initial iron(III) concentration in the aqueous phase, at constant extractant concentration, shows that the maximum of iron(III) loading approached to 0.0007 and 0.0005 for 2PC12 and 4PC12, respectively (Fig. 2). In the case of 4-pyridyl ketoxime formation of emulsions in the organic phase were observed which could be the reason for a much lower plateau than was predicted.

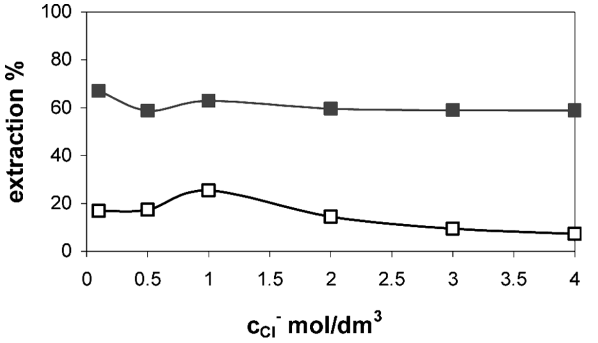


FIG. 1. The extraction of iron(III) from chloride solutions with 1-(2-pyridyl)tridecane-1-one oxime (■) and 1-(4-pyridyl)tridecane-1-one oxime (□) from aqueous solutions at constant water activity $a_w = 0.835$ (extractant concentration. –0.01 M).

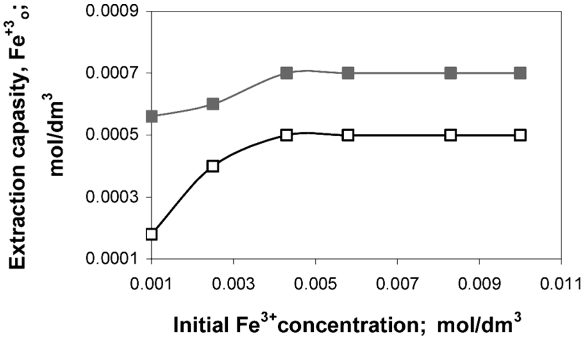


FIG. 2. Loading coefficients of iron(III) from chloride solutions with 1-(2-pyridyl)tridecane-1-one oxime (■) and 1-(4-pyridyl)tridecane-1-one oxime (□) (extractant concentration = 0.01 M, $[Cl^-] = 2.0$ M).

Analysis of Extracted Species and the Stoichiometry of the Iron(III) Reaction by Pyridyl Ketoximes

The influence of oxime concentration on the extraction of iron(III) was also studied. The obtained results indicated that the extraction percentage increased with the increase of extractant concentrations (Fig. 3). In the concentration of oxime 0.005–0.05 M, the extraction increases from 12 to 100% for 1-(2-pyridyl)tridecane-1-one oxime and from 0 to 54% for 1-(4-pyridyl) tridecane-1-one oxime in the concentration of extractant 0.0075–0.01 M.

The compositions of the extracted species were ascertained from the graph of $\log D = \log K + N\log[HL]$, where K is the extraction constant and N was the number of oxime molecules per metal ion involved in the extraction. The slopes of the strength lines are 2.12 and 1.94 for 2PC12 and 4PC12, respectively (Fig. 4). In the case of 4-pyridyl ketoxime the formation of emulsions were observed. Hence, the probable composition of the extractable species is (metal:ligand) 1:2.

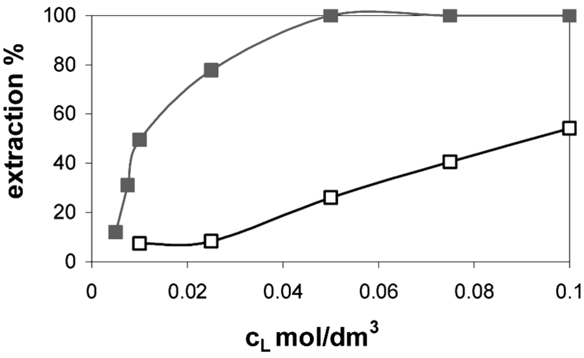


FIG. 3. Effect of the 1-(2-pyridyl)tridecane-1-one oxime (■) and 1-(4-pyridyl)tridecane-1-one oxime (□) concentrations on the iron(III) extraction ($[Fe^{3+}] = 0.001$ M, $[Cl^-] = 2.0$ M).

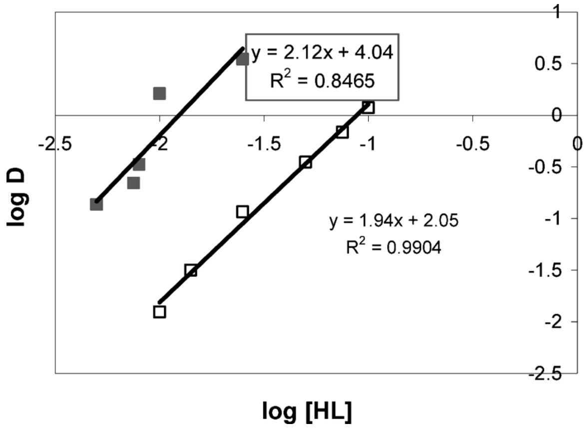


FIG. 4. Influence of equilibrium oxime concentration on iron(III) distribution ratio for 1-(2-pyridyl)tridecane-1-one oxime (■) and 1-(4-pyridyl)tridecane-1-one oxime (□) ($[Cl^-] = 2.0$ M, $[FeCl_3] = 0.001$ M).

The extraction of iron(III) by oxime 2PC12 and 4PC12 from chloride solutions can be described by the following equations:

$$FeCl_{3aq} + 2\ HL_o = FeCl_3(HL)_2o \tag{3}$$

$$HFeCl_{4aq} + 2\ HL_o = HFeCl_4(HL)_2o \tag{4}$$

where HL represents the extractant molecule (2PC12 or 4PC12), and aq and o denote the aqueous and organic phases, respectively.

Stripping

The water and diluted solution of hydrochloric and sulphuric acid were tested for the stripping of iron(III) from the organic phase (Table 1). Pure water did not strip iron(III) from organic solutions of 1-(2-pyridyl)tridecane-1-one oxime. For 1-(2-pyridy)tridecane-1-one oxime complexes with iron(III) the use of 1% and 5% H_2SO_4 allowed to remove 56.6% and 66.6% of iron(III), respectively. Iron(III) was completely removed when 1% solution of hydrochloric acid was used for stripping. In the case of 1-(4-pyridyl)tridecane-1-one oxime complexes, iron(III) could be effectively stripped from the organic phase by water in the two-stage process (in the first stage 50% of

TABLE 1
Results of stripping of iron(III) from the organic phase

Stripping reagent	Stripping of iron(III) from organic phase with 2PC12 [%]	Stripping of iron(III) from organic phase with 4PC12 [%]
H_2O	0.0	50.0
1% HCl	100.0	100.0
1% H_2SO_4	56.6	—
5% H_2SO_4	66.6	—

iron(III) was stripped) and by 1% HCl in the one-stage (ion(III) was stripped with 100% yield).

Separation of Metal Ions from a Multicomponent Mixture

The selectivity extraction of metal ions from different sources is an important issue in the production of pure metal ions. The effective recovery of metal ions is possible only if the separation process is sufficiently selective.

Our previous studies indicated the ability of pyridyl ketoximes to extract copper(II), zinc(II) and cadmium(II) from chloride solutions. The obtained results showed that the hydrophobic 2-pyridyl ketoximes are better extractants for copper(II) than 4-pyridyl ketoximes. The extraction of copper(II) by 2-pyridyl ketoximes did not depend on chloride ion concentrations. For 4-pyridyl ketoxime, the degree of copper(II) extraction slightly increased from 0.1 M to 2.0 M Cl^-, but above 2.0 M Cl^- it increased rapidly (33). The extraction ability of zinc(II) have 2- and 4-pyridyl ketoximes, but it is dependent on the solvent type, chloride ion concentration, and ionic strength (35). The extraction of zinc(II) was observed for 2-pyridyl ketone oxime in toluene with 10% of 1-decanol and chloroform solutions, but for 4-pyridyl ketone oxime the extraction was observed only in chloroform solution. The extraction of zinc(II) by 2-pyridyl ketoximes in toluene with 10% addition of decanol from the chloride media, with $a_w = 0.835$, increased at the low chloride concentrations (to 1.0 M Cl^-) and then decreased with the increase of chloride concentrations. The extraction percent of zinc(II) from chloride and perchlorate solutions at ionic strength $I = 4$ by 2-pyridyl ketoximes decreases with the increase of ions chloride concentration. However, for 4-pyridyl ketone oxime in chloroform solution the extraction increased up to 80% for 1.0 M Cl^- and then decreased with the increase of chloride concentration.

The selectivitity extraction of metal ions from multielemental aqueous solutions, which contain copper(II), zinc(II), and iron(III) were studied. The extraction experiments for multielemental aqueous solutions were done for the solutions of 1.0 M Cl^- and 2.0 M $Cl^-(a_w = 0.835)$. This level of chloride ion concentration was chosen because at 1.0 M Cl^- a maximum of extraction of zinc(II) with 2-pyridyl ketoximes was observed; the extraction of copper(II) above 2.0 M Cl^- was the highest with 4-pyridyl ketoximes (33,35).

The obtained results indicated that the most selective of copper(II) extraction was observed with 1-(2-pyridyl) tridecane-1-one oxime (Table 2). The greater differences of metal ion extraction were observed for 2-pyridyl ketoxime than for 4-pyridyl ketoxime. It could be observed that Cu^{2+} seem to be extracted by these extractants effectively (extraction percentage was higher than 98%) from the solution which contained copper(II), zinc(II), and iron(III) ions from the solution of 1.0 M Cl^-. From this solution iron(III) was extracted at only 11%, while zinc(II) was not extracted. The different results were observed for the solution containing 2.0 M Cl^-. In this case the selective extraction of metal ions was not observed. Copper(II) was extracted the best (98%), but zinc(II) and iron(III) were extracted at 50% and 18%, respectively.

TABLE 2
Extraction of copper(II), zinc(II) and iron(III) from multielemental aqueous solutions with pyridyl ketoximes

	Extraction percentage [%]					
	2PC12			4PC12		
Concentration Cl^- [mol/dm^3]	Cu^{2+}	Zn^{2+}	Fe^{3+}	Cu^{2+}	Zn^{2+}	Fe^{3+}
1.0	98.35	0.00	11.96	74.03	0.00	20.65
2.0	99.94	50.00	18.00	29.87	16.92	15.00

For 1-(4-pyridyl)tridecane-1-one oxime the similar selectivity was obtained. Copper(II) was extracted better than other metal ions. Extraction percentages of copper(II) was equal to 74% and 20% for iron(III). The extraction of zinc(II) was not detected from this solution (1.0 M Cl^-). Also for the solution 2.0 M Cl^- the selectivity of tested metals was poor, when 1-(4-pyridyl)tridecane-1-one oxime was tested; the extraction percentages were 29%, 16%, and 15% for copper(II), zinc(II), and iron(III), respectively.

Based on the above results, we can propose a scheme of process separation of particular metal ions from multielemental aqueous solutions (0.001 M $Cu^{2+}/Zn^{2+}/Fe^{3+}$; 1.0 M Cl^-) (Fig. 5).

The multielemental solutions can be separated in three stages of extraction. In the first extraction stage copper(II) and a small value of iron(III) are transferred to the organic phase using 1-(2-pyridyl)tridecane-1-one oxime. From the loaded organic phase the selectivity stripping of Fe^{3+} is possible using 1% HCl. In the second stage of extraction, ions of Fe^{3+} are transferred to the organic phase and ions of Zn^{2+} remain in the aqueous phase. And in the last extraction stage, Zn^{2+} is transferred to the organic phase, then Zn^{2+} is stripped using pure water from the loaded organic phase.

CONCLUSION

The oximes of 1-(2-pyridyl)tridecane-1-on and 1-(4-pyridyl)tridecane-1-on were used as extractants for iron(III). All studied model hydrophobic pyridyl ketoximes have the ability to the iron(III) extraction from chloride solutions. The highest degree of iron(III) extraction was observed for 1-(2-pyridyl)tridecane-1-one oxime. The extraction of iron(III) with 2-pyridyl ketoxime did not

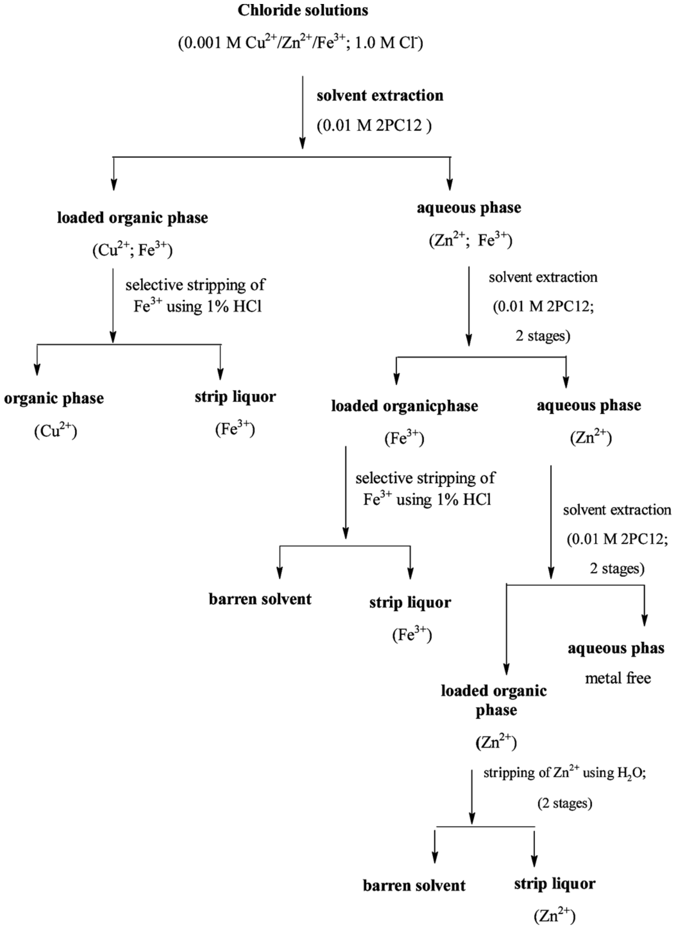


FIG. 5. The separation scheme for the recovery of particular metal ions from mulitelemental aqueous solutions using 1-(2-pyridyl)tridecane-1-one oxime.

depend on chloride ions concentrations, but for 1-(4-pyridyl)tridecane-1-one oxime the extraction percentage increased up to about 1.0 M Cl^-, and thereafter decreased significantly. Additionally, during extraction with 4-pyridyl ketoxime precipitated complex in the organic phase, which is a disadvantageous effect for an extraction process. Iron(III) was effectively stripped from the organic phase with 1% HCl.

The species of iron(III) complexes with pyridyl ketoximes can be proposed as $FeCl_3(4PC12)_2$ and $FeCl_3(2PC12)_2$.

The competitive solvent extraction of copper(II) was observed from multielemental aqueous solutions (0.001 M $Cu^{2+}/Zn^{2+}/Fe^{3+}$) at 1.0 M Cl^- with 1-(2-pyridyl)tridecane-1-one oxime and was equal up to 98%; zinc(II) was not extracted and iron(III) was removed in 11%. The scheme of separating particular metal ions from multielemental aqueous solutions is proposed. The separation of metal ions is possible in three stages of extraction.

ACKNOWLEDGEMENTS

This work was supported by the Polish State Committee for Scientific Research grant BW 32/003/09 and GR 32/3357/09.

REFERENCES

1. Saji, J.; Reddy, M.L.P. (2001) Liquid-liquid extraction separation of iron(III) from titania wastes using TBP-MIBK mixed solvent system. *Hydrometallurgy*, 61: 81.
2. Hirato, T.; Zhi-Chu, W.; Hamada, Y.; Majima, H. (1992) Improvement of the stripping characteristics of Fe(III) utilizing a mixture of di(2-ethylhexyl)phosphoric acid and tri-n-butyl phosphste. *Hydrometallurgy*, 28: 81.
3. Sato, T.; Nakamura, T.; Ikeno, M. (1985) The extraction of iron(III) from aqueous acid solutions by di-2-ethyl hexyl phosphoric acid. *Hydrometallurgy*, 15: 209.
4. Cote, G. (2000) Hydrometallurgy of strategic metals. *Solv. Extr. Ion Exch.*, 18: 703.
5. Irato, T.; Zhi-Chu, W.; Hamada, Y.; Majima, H. (1992) Improvement of the stripping characteristics of Fe(III) utilizing a mixture of di-(2-ethylhexyl) phosphoric acid and tri-n-buthylphosphate. *Hydometallurgy*, 28: 81.
6. Biswas, R.K.; Begum, D.A. (1998) Solvent extraction of iron(III) from chloride solution by D2EHPA. *Hydrometallurgy*, 50: 153.
7. Biswas, R.K.; Begum, D.A. (1999) Study of kinetics of forward extraction of iron(III) from chloride medium by di-(2-ethylhexyl) phosphoric acid in kerosene using the single drop technique. *Hydrometallurgy*, 54: 1.
8. Miralles, N.; Sastre, A.M.; Figuerola, E.; Martinez, M. (1992) Solvent extraction of iron(III) by bis(2,4,4-trimethylpentyl)phosphinic acid: Experimental equilibrium study. *Hydrometallurgy*, 31: 1.
9. Sahu, K.K.; Das, R.P. (2000) Mixed solvent systems for the extraction and stripping of iron(III) from concentrated acid chloride solutions. *Metall. and Mat. Trans.*, 31B: 1169.
10. Costa, M.C.; Martins, M.; Paiva, A.P. (2004) Solvent extraction of iron(III) from acidic chloride media using *N,N*′-dimethyl-*N,N*′-dibutylmalonamide. *Sep. Sci. Technol.*, 39: 3573.
11. Paiva, A.P.; Costa, M.C. (2005) Application of *N,N*′-tetrasubstituented malonamides to the recovery of iron(III) from chloride solutions. *Hydrometallurgy*, 77: 103.
12. Costa, M.C.; Carvalho, A.; Uryga, A.; Paiva, A.P. (2003) Solvent extraction of iron(III) from hydrochloric acid solutions using *N,N*′-dimethyl-*N,N*′-diphenylmalonianamide and *N,N*′-dimethyl-*N,N*′-diphenyltetradecylmalonamide. *Solv. Extr. Ion Exch.*, 21: 653.
13. Mowafy, E.A. (2007) Application of *N,N*′-dimethyl-*N,N*′-di(4-chlorophenyl)tetradecyl malonamide for the selective recovery of iron(III) from concentration chloride solutions. *Solv. Extr. Ion Exch.*, 25: 791.
14. Teke, M.; Mercimek, B.; Ali Özler, M.; Ayar, A. (2004) Selective of iron(III) from aqueous nitrate solution in the presence of cobalt(II), copper(II) and nickel(II) ions using bis(Δ^2-2-imidazolinyl)-5,5-′-dioxime. *Analytical Science*, 20: 853.
15. Lee, M.S.; Lee, K.J. (2005) Separation of iron and nickel a spent $FeCl_3$ etching solution by solvent extraction. *Hydrometallurgy*, 80: 163.
16. Figueira, J.L.; Paiva, A.P. (2009) Solvent extraction of iron(III) from chloride media by *N*-methyl-*N*-alkyloctanamide derivatives. *Sep. Sci. Technol.*, 44: 2928.
17. Cierpiszewski, R.; Miesiąc, I.; Regel-Rosocka, M.; Sastre, A.M.; Szymanowski, J. (2002) Removal of zinc(II) from spent hydrochloric acid solutions from zinc hot galvanizing plants. *Ind. Eng. Chem. Res.*, 41: 598.

18. Grzeszczak, A.; Regel-Rosocka, M. (2007) Extraction of zinc(II), iron(II) and iron(III) from chloride media with dibutylbutylphosphate. *Hydrometallurgy*, 86: 72.
19. Regel-Rosocka, M.; Szymanowski, J. (2005) Iron(II) transfer to the organic phase during zinc(II) extraction from spent pickling solutions with tributyl phosphate. *Solv. Extr. Ion Exch.*, 23: 411.
20. Dalton, R.F.; Price, R.; Quan, P.M.; Stewart, D. (1982) Process for the extraction of metal values and novel metal extractants. *Eur. Pat.*, 57: 797.
21. Bogacki, M.B.; Jakubiak, A.; Cote, G.; Szymanowski, J. (1997) Dialkyl pyridine-carboxlates extraction ability towards copper(II) from chloride solutions and its modifications with alcohols. *Ind. Eng. Chem. Res.*, 36: 838.
22. Borowiak-Resterna, A. (1999) Extraction of copper(II) from acid chloride solutions by *N*-dodecyl- and *N,N*-dihexylpyridinecarboxamides. *Solv. Extr. Ion Exch.*, 17: 133.
23. Cote, G.; Jakubiak, A.; Bauer, D.; Bajer, J.; Szymanowski, J.; Mokili, B.; Poitrenaud, C. (1994) Modeling of extraction equilibrium for copper(II) extraction by pyridine-carboxylic acid ester from concentrated chloride solutions at constant water activity and constant total concentration of ionic or molecular species dissolved in the aqueous solutions. *Solv. Extr. Ion Exch.*, 12: 99.
24. Szymanowski, J.; Jakubiak, A.; Cote, G.; Bauer, D.; Beger, J. (1993) In: *Solvents in the Process Industries*, Logsdail, D.H.; Slater, M.J., eds.; *Proc. ISEC'93*. SCI-Elsevier Applied Science, London, 1311.
25. Szymańska, I.; Borowiak-Resterna, A.; Wiśniewski, M. (2003) New pyridine-carboxamides for rapie extraction of palladium from acidic chloride media. *Hydrometallurgy*, 68: 159.
26. Tomaszewska, M.; Borowiak-Resterna, A.; Olszanowski, A. (2007) Cadmium extraction from chloride solutions with model N-alkyl and N,N-dialkyl-pyridine-carboxamides. *Hydrometallurgy*, 85: 116.
27. Milios, J.C.; Stamatatos, T.C.; Perleps, S.P. (2006) The coordination chemistry of pyridyl oximes. *Polyhedron*, 25: 134.
28. Murugesu, M.; Abboud, K.A.; Chrisou, G. (2004) New hexanuclear and dodecanuclear Fe(III) cluster with carboxylate and alkoxide-based ligands from cluster aggregation reactions. *Polyhedron*, 23: 2779.
29. Stemmler, A.J.; Kampf, J.W.; Pecoraro, V.L. (1995) Synthesis and crystal structure of the first inverse 12-metallacrown-4. *Inorg. Chem.*, 34: 2271.
30. Reiner, D.; Poe, D.P. (1977) Removal of iron, copper, cadmium, cobalt and nickel from sodium hydroxide by precipitation and extraction with phenyl-2-pyridyl ketoxime. *Analytical Chemistry*, 49: 889.
31. Martinez, J.; Aiello, I.; Bellusci, A.; Crispini, A.; Ghedini, M. (2008) Tetranuclear zinc complexes of ligands containing the 2-pyridyl oxime chelating site. *Inorg. Chim. Acta*, 361: 2677.
32. Papatriantafyllopoulou, C.; Kostakis, G.E.; Raptopoulou, C.P.; Terzis, A.; Perlepes, S.P.; Plakatouras, J.C. (2009) Investigation of the $MSO_4 \cdot \chi H_2O$ ($M = Zn$, $\chi = 7$; $M = Cd$, $\chi = 8/3$)/methyl 2-pyridyl ketone oxime reaction system: A novel Cd(II) coordination polymer versus mononuclear and dinuclear Zn(II) complexes. *Inorg. Chim. Acta*, 362: 2361.
33. Klonowska-Wieszczycka, K.; Olszanowski, A.; Parus, A.; Zydorczak, B. (2009) Recovery of copper(II) from chloride solutions using hydrophobic pyridyl ketone oximes. *Solv. Extr. Ion Exch.*, 27: 50.
34. Parus, A.; Konowska-Wieszczycka, K.; Olszanowski, A. Solvent extraction of cadmium(II) from chloride solutions by pyridylketoximes. *Hydrometallurgy* (in print).
35. Klonowska-Wieszczycka, K.; Olszanowski, A.; Parus, A. Solvent extraction of zinc(II) from chloride solutions by hydrophobic alkyl-pyridyl ketone oximes. (In press.)
36. Davis, A.R.; Chong, C. (1972) A laser Raman study of aqueous copper nitrate solution. *Inorg. Chem.*, 11: 1891.
37. Cote, G.; Jakubiak, A. (1996) Modelling of extraction equilibrium for zinc(II) extraction by a bibenzimidazole type reagent (ACORGA ZNX50) from chloride solutions. *Hydrometallurgy*, 43: 277.
38. Saji, J.; Prasada Rao, T.; Ramamohan, T.R.; Reddy, M.; Redy, P. (1999) Studies on the liquid-liquid extraction of iron(III) and titanium(IV) with 3-phenyl-4-benoyl-5-isoxazolone. *Tantal*, 50: 1065.