



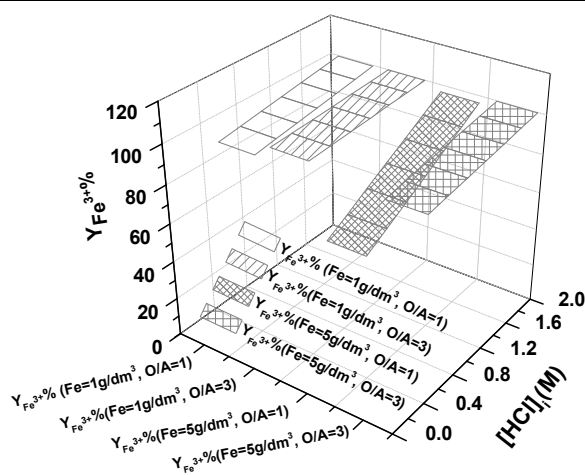
OPTIMIZATION OF Fe(III) EXTRACTION FROM HCl SOLUTIONS BY TDA/KEROSENE USING FACTORIAL DESIGN EXPERIMENTS

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The extraction of Fe³⁺ from aqueous HCl solutions using tri-n-dodecylamine (TDA)/kerosene + 10% 2-octanol has been examined. The influence of HCl concentration, Fe³⁺ concentration, organic to aqueous volume phase ratio (O/A), TDA concentration on the yield of Fe³⁺ extraction have been investigated using 2⁴ factorial design experiments. The effect of temperature on Fe³⁺ extraction was found to be positive and the enthalpy change of the extraction reaction was found to be ($\Delta H^0 = 45.609 \text{ kJ.mol}^{-1}$). The saturation of the extractant with iron can be observed at a number of contact $N \geq 5$. Complete stripping of iron from the loaded TDA/kerosene can be done using 0.05M HCl at 313.15 °K and aqueous to organic volume phase ratio of A/O=4.



INTRODUCTION

Solvent extraction is widely used for the separation and recovery of valuable metals from aqueous solutions and industrial streams.¹ Iron(III) is the remaining element after hydrometallurgical processes of recovering a number of nonferrous metal ions such as Ni²⁺, Co²⁺, Cu²⁺, ... and also the main cation present in the pickling liquor, which has been used to clean steel before any painting or electroplating operation.¹

In fact, iron is ubiquitous in most solvent extraction circuits, because it is dissolved from the mineral feed during the leaching of desired metal by mineral acids (HCl, H₂SO₄, HNO₃, ...) and some time was added to play the role of reductant, so, in all cases iron will affect the selectivity of extracted metal.²

From health point of view, iron is an essential element in human nutrition. Estimates of minimum daily requirement for iron is in the range of 10-50 mg/day. But at high dose is fatal, the average lethal dose of iron is 200-250 g/kg of body weight.³

So iron is not considered as dangerous as heavy metals (Pb, Cd, Hg, ...), but its concentration should not exceed 0.3 mg/L in drinking waters, because it contributes to bad taste, pipe clogging, and clothes, tube, sink, and teeth staining.⁴

Consequently, the recovery of iron(III) from aqueous wastewater is recommended. Since iron(III) is considered an annoying element if its concentration exceeds the permissible limits mentioned above.

A literature survey reveals that many of organo-phosphorous, amine, and amid extractants were

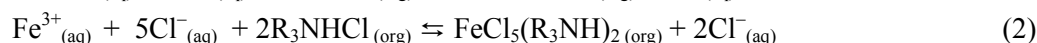
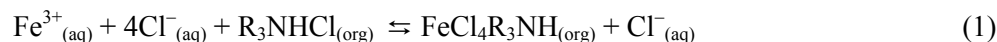
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used to extract iron(III) from different aqueous (nitrate, chloride, sulphate, thiocyanate) media.⁵⁻¹⁸

M. T. Naik *et al.*¹¹ reported that the extraction of Fe(III) from nitrate media using bis(2-ethylhexyl) phosphinic acid, he mentioned that Fe(III) can be quantitatively extracted in the pH range 2-4.5 using 0.009 M bis(2-ethylhexyl) phosphinic acid in hexane.

A. Sandhibigraha *et al.*¹² found that Fe(III) extraction varies with HCl concentration, the loading capacity of 0.1 M di-(2-ethyl hexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono-2-ethyl hexyl ester (PC-88A) and bis-(2,2,4 trimethylpentyl) phosphinic acid (Cyanex 272) was found to be 1.7, 1.3 and 1.8 kg/m³ respectively. He mentioned that Na₂SO₄ and NaCl lowered the extraction efficiency while NaNO₃ enhanced it.

X. H. Mao *et al.*¹³ investigated the extraction of Ca²⁺, Mg²⁺, Al³⁺, Ti⁴⁺ and Fe³⁺ from acidic chloride solutions by trioctylphosphine oxide (TOPO)/kerosene, he showed that Ti(IV) and Fe(III) extractions increase with the increase of HCl concentration in the aqueous phase, leaving behind the other metal ions in the raffinate and that Ti(IV) and Fe(III) can be selectively recovered from the



A. V. L. N. S. H. Hariharan *et al.*¹⁷ reported that Fe(III) can be extracted quantitatively by tetrabutylammonium bromide from HCl, H₂SO₄, HNO₃, HClO₄ media and 2 M HCl can strip completely iron (III) from the loaded organic phase.

M. C. Costa *et al.*¹⁸ studied the extraction of Fe(III) from acidic chloride solutions by N, N'-dimethyl, N, N'-dibutylmalonamide (DMDBMA), N, N'-dimethyl-N,N'-diphenylmalonamide (DMDPHMA), N, N'-dimethyl-N,N'-diphenyl tetradecylmalonamide (DMDPHTDMA). He showed and clarified the important role played by the chemical structure on the metal ion transfer reactions to the organic phase and the selectivity towards Fe(III) and complete stripping of this metal by simple contact of the loaded organic phase (DMDBMA) with water.

This paper aims to investigate the recovery of Fe(III) from aquatic hydrochloric acid solutions by tri-n-dodecylamine/kerosene containing 2-octanol as modifier and using 2⁴ factorial design experiments to select and optimize the best

loaded organic phase by controlling the acidity of the stripping agent.

Bis-(2,2,4 trimethylpentyl) phosphinic acid in kerosene was tested to extract Fe(III) from aqueous sulphate media by I. M. Ahmad.¹⁴ and found that the stoichiometry of extracted metal species was in the form Fe(HSO₄)A₂.2(H₂A₂) and the extraction equilibrium was calculated and found to be (1.41±0.01)×10⁻².

H. Watanabe *et al.*¹⁵ studied the extraction of Fe(III) from thiocyanate solutions using trioctylamine (TOA) dissolved in cyclohexane, xylene, toluene, carbon tetrachloride, benzene and chloroform. He found that the extractability of Fe(III) is roughly correlated with the dielectric constant of diluents; that is, the smaller the value of dielectric constant, the larger the extractability.

A solvent extraction experiment of FeCl₃ in HCl solution with tri-octyl/decyl amine (Alamine 336) as extractant was conducted by Man-Seung Lee *et al.*,¹⁶ he found that the equilibrium constant of solvent extraction reaction of Fe(III) by Alamine 336 were L_{ex,m}=2.22×10⁴ and K_{ex,d} = 6.41×10⁵, and mechanism of extraction was presented as follows:

operating conditions for Fe(III) recovery. As well as finding the best stripping conditions to strip Fe(III) from the loaded organic phase using HCl as stripping agent.

EXPERIMENTAL

Reagents

The reagents utilized in this work were: Tri-n-dodecylamine used was obtained from Merck with more than 95% purity. The kerosene used was from PEMCO SOLV 110 from PEMCO Chemicals Company and had as main properties: specific gravity 0.8; flash point 343.15 °K; initial boiling point 473.15 °K; final boiling point 523.15 °K; aromatic content < 0.5% (v/v). The hydrochloric acid (37%) was obtained from Merck. The Iron nitrate nonahydrate Fe(NO₃)₃.9H₂O were from AppliChem company with 99% purity. 2-octanol was from BDH company with 97% purity.

Aqueous phase preparation

The aqueous phase of Fe³⁺ was prepared by dissolving the necessary amount of Fe(NO₃)₃.9H₂O and concentrated hydrochloric acid in double distilled water.

Table 1

The aqueous and organic phase solutions used for 2⁴ factorial design extraction experiments

| | [HCl] _i (M) | (Fe ³⁺) _i (g/dm ³) | [TDA] _i / kerosene (M) | 2-Octanol (%) |
|--|---------------------------|--|--|------------------|
| Aqueous Solution1 (Φ _{1aq}) | 0.5 | 1 | Organic phase1 (Φ _{1org}) | 0.2 |
| Aqueous Solution2 (Φ _{2aq}) | 0.5 | 5 | | |
| Aqueous Solution3 (Φ _{3aq}) | 2 | 1 | Organic phase2 (Φ _{2org}) | 0.5 |
| Aqueous Solution4 (Φ _{4aq}) | 2 | 5 | | |

Organic phase preparation

The organic phases of tri-n-dodecylamine were prepared by dissolving the necessary amount of tri-n-dodecylamine in kerosene, 2- octanol was added as modifier to prevent third phase formation. Afterwards, each organic phase was pre-equilibrated with HCl solution which have the same concentration of HCl in the aqueous phase containing Fe³⁺.

Necessary solutions for 2⁴ factorial design experiments

Six solutions, 4 aqueous and 2 organic were prepared as shown in Table 1.

Solvent extraction experiments and analysis

The extraction experiments of Fe³⁺ were carried out at a constant temperature by shaking the aqueous phase and pre-equilibrated organic phases in a shaker bath thermostat (Grant OLS 200), after reaching the equilibrium, the phases were let to stand for 1h, then separated using separating funnel. Iron in the aqueous phases before and after extraction was analyzed using Analytik Jena - Zeenit 700P atomic absorption spectrometer. And the concentration of iron in the organic phase was calculated by mass balance.

The distribution ratio (K_d), the yield of iron(III) extraction (Y_{Fe³⁺} %) and the yield of iron(III) stripping (Y_{Fe³⁺strip} %) were respectively calculated as follows:

$$K_d = \frac{[Fe]_{org}}{[Fe]_{aq}}$$

$$Y_{Fe^{3+}} \% = \left(\frac{[Fe]_{org} \cdot V_{org}}{[Fe]_i \cdot V_{aq}} \right) \times 100,$$

$$Y_{Fe^{3+}strip} \% = \left(\frac{[Fe]_{aq} \cdot V_{aq}}{[Fe]_{org}^{orig} \cdot V_{org}} \right) \times 100$$

Where [Fe]_i, [Fe]_{aq}, [Fe]_{org} refers to concentration of iron in the aqueous phase before extraction, after extraction and organic phase respectively. [Fe]_{org}^{orig} refers to initial concentration of iron in the organic phase before stripping.

RESULTS AND DISCUSSION

Rate of Fe³⁺ extraction in the binary system (Fe³⁺+HCl)/(TDA/kerosene)

To determine the time necessary to reach the equilibrium of Fe³⁺ extraction by tri-n-dodecylamine/kerosene, we studied the effect of time by shaking the organic phase of 0.5M TDA/kerosene containing 10% 2-octanol with an aqueous phase of 2M HCl containing 1g/dm³ Fe³⁺

for different periods of time (0-300 min). The findings were shown in Fig. 1 displaying iron concentration in the aqueous and organic phase and distribution ratio K_d as a function of time. From Fig. 1 we can clearly observe that the extraction of Fe³⁺ reaches the equilibrium at 1h of shaking. Since K_d, Fe³⁺_{org} and Fe³⁺_{aq} are remaining constant after 1h of shaking, all our experiments related to this study were carried out at 3h of shaking to ensure the equilibration.

Factorial design extraction experiments

In order to study the effect of the four main factors (Fe³⁺ concentration in the aqueous phase, HCl concentration, O/A volume phase ratio and TDA content in the organic phase) on the yield of Fe³⁺ extraction by TDA/kerosene, a model of 2⁴ factorial design experiments was constructed as shown in Table 2 to optimize and understand the effect of each parameter on Fe³⁺ extraction and also the interaction between these parameters.

From Table 2 we can see that the best operating conditions ([HCl]_i = 2M, O/A = 3 and [TDA]_i = 0.5M) were observed in Test N^o 14 and N^o 15 for Fe = 1g/dm³ and Fe=5 g/dm³ respectively.

Repeatability of Fe³⁺ extraction experiments

To estimate the error on Fe³⁺ extraction yield by TDA/kerosene, four repeated experiments at the conditions presented in Table 3 were carried out. Taking into consideration the mean of the low and high values of the studied parameters ([HCl]_i=1.25M, (Fe³⁺)_i = 3 g/dm³, O/A=2 and [TDA]_i=0.35M).

It can be clearly seen from Table 3 that the repeatability of Fe³⁺ extraction from HCl solution by TDA/kerosene is good. The average of Y_{Fe³⁺} % was found to be 94.87% with very small relative standard deviation (RSD≈0.11 for n=4).

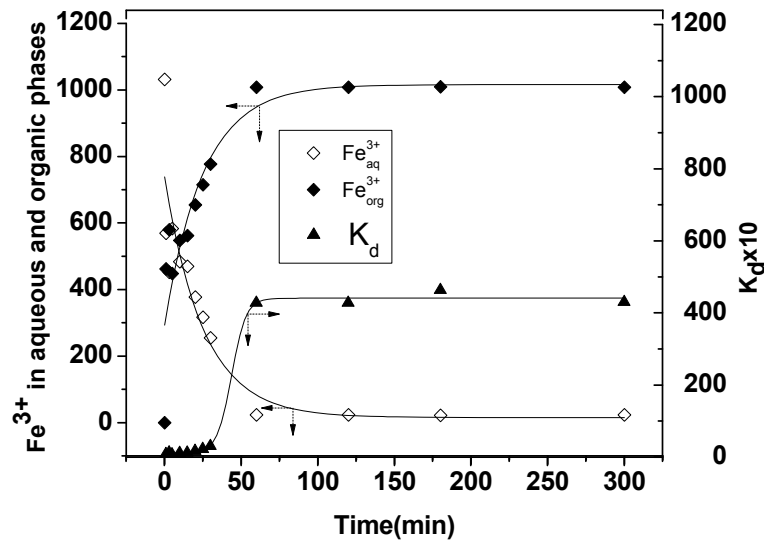


Fig. 1 – Extraction behavior of Fe^{3+} by TDA/kerosene as a function of time. $[\text{TDA}]_i = 0.5 \text{ M} + 10\% \text{ 2-octanol / kerosene}$, $(\text{Fe}^{3+})_{\text{aq}} = 1 \text{ g/dm}^3$, $[\text{HCl}]_i = 2\text{M}$, $\text{O/A}=1$, $T = 313.15 \text{ }^\circ\text{K}$.

Table 2

2^4 factorial design matrix and the response and extraction conditions

| Extraction conditions: $T = 313.15 \text{ }^\circ\text{K}$, shaking time = 3h | | | | | | | | | |
|--|-------------------|-------|-------|-------|-------------------------|---|-----|---------------------------------|-------------------|
| Tests | Reduced variables | | | | Real variables | | | | Response function |
| N^0 | X_1 | X_2 | X_3 | X_4 | $[\text{HCl}]_i$ (M) | $(\text{Fe}^{3+})_i$ (g/dm^3) | O/A | $[\text{R}_3\text{N}]_i$ (M) | $Y_{\text{Fe}\%}$ |
| 1 | -1 | -1 | -1 | -1 | 0.5 | 1 | 1 | 0.2 | 43.160 |
| 2 | +1 | -1 | -1 | -1 | 2 | 1 | 1 | 0.2 | 95.648 |
| 3 | -1 | +1 | -1 | -1 | 0.5 | 5 | 1 | 0.2 | 15.300 |
| 4 | +1 | +1 | -1 | -1 | 2 | 5 | 1 | 0.2 | 61.187 |
| 5 | -1 | -1 | +1 | -1 | 0.5 | 1 | 3 | 0.2 | 68.053 |
| 6 | +1 | -1 | +1 | -1 | 2 | 1 | 3 | 0.2 | 98.953 |
| 7 | -1 | +1 | +1 | -1 | 0.5 | 5 | 3 | 0.2 | 42.167 |
| 8 | +1 | +1 | +1 | -1 | 2 | 5 | 3 | 0.2 | 15.963 |
| 9 | -1 | -1 | -1 | +1 | 0.5 | 1 | 1 | 0.5 | 89.597 |
| 10 | +1 | -1 | -1 | +1 | 2 | 1 | 1 | 0.5 | 99.552 |
| 11 | -1 | +1 | -1 | +1 | 0.5 | 5 | 1 | 0.5 | 59.487 |
| 12 | +1 | +1 | -1 | +1 | 2 | 5 | 1 | 0.5 | 96.355 |
| 13 | -1 | -1 | +1 | +1 | 0.5 | 1 | 3 | 0.5 | 95.980 |
| 14 | +1 | -1 | +1 | +1 | 2 | 1 | 3 | 0.5 | 99.826 |
| 15 | -1 | +1 | +1 | +1 | 0.5 | 5 | 3 | 0.5 | 90.539 |
| 16 | +1 | +1 | +1 | +1 | 2 | 5 | 3 | 0.5 | 99.746 |

Table 3

Repeatability of Fe^{3+} extraction experiments

| Experiment number | $[\text{HCl}]_i$ (M) | $(\text{Fe}^{3+})_i$ (g/dm^3) | O/A | $[\text{TDA}]_i$ (M) | $Y_{\text{Fe}^{3+}}$ (%) | $\overline{Y_{\text{Fe}^{3+}}}$ (%) | SD | RSD |
|-------------------|-------------------------|---|-----|-------------------------|-----------------------------|--|-------|-------|
| 1 | 1.25 | 3 | 2 | 0.35 | 94.91 | 94.87 | 0.103 | 0.109 |
| 2 | 1.25 | 3 | 2 | 0.35 | 94.74 | | | |
| 3 | 1.25 | 3 | 2 | 0.35 | 94.83 | | | |
| 4 | 1.25 | 3 | 2 | 0.35 | 94.98 | | | |

Calculation of coefficients of 2^4 factorial design experiments and their interactions

The full general equation of 2^4 factorial design experiments can be described as follows:¹⁹

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_4 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3 + a_{14}X_1X_4 + a_{24}X_2X_4 + a_{34}X_3X_4 + a_{123}X_1X_2X_3 + a_{124}X_1X_2X_4 + a_{134}X_1X_3X_4 + a_{234}X_2X_3X_4 + a_{1234}X_1X_2X_3X_4 \quad (3)$$

where each variable X_j ($j=1-4$) takes two values -1 (low level) and +1 (high level).

$$Y_{Fe^{3+}} \% = 73.221 + 10.184X_1 - 13.126X_2 + 3.183X_3 + 18.167X_4 - 1.964X_1X_2 - 7.966X_1X_3 - 1.173X_2X_3 - 2.699X_1X_4 + 8.273 X_2X_4 + 1.954X_3X_4 - 4.504X_1X_2X_3 + 5.999X_1X_2X_4 + 3.746 X_1X_3X_4 + 4.646 X_2X_3X_4 + 1.809X_1X_2X_3X_4 \quad (4)$$

Applying the same methodology of references 20 and 21, the equation (3) can be rewritten by replacing the reduced variables with the real

From the results of Fe^{3+} extraction which was presented in Table 2, the following relationship was constructed:

variables ($[HCl]$, $(Fe^{3+})_{aq}$, O/A, [TDA]) through the following relations:

$$X_1 = \frac{B - b_1}{b_2}, X_2 = \frac{C - c_1}{c_2}, X_3 = \frac{D - d_1}{d_2}, X_4 = \frac{E - e_1}{e_2}$$

$$Y_{Fe^{3+}} \% = -33.241 + 63.549 B - 5.443 C + 22.669 D + 258.142 E + 1.265 CD + 0.993 BC - 4.821 BD - 122.325 BE - 16.619 CE - 44.889 DE - 5.818 BCD + 10.581 BCE + 5.433 CDE + 9.169 BDE + 8.042 BCDE \quad (5)$$

where: B, C, D and E denotes $[HCl]$, $(Fe^{3+})_{aq}$, O/A and [TDA] respectively.

And $b_1, c_1, d_1, e_1, b_2, c_2, d_2$ and e_2 are calculated as follows:

$$b_1 = \frac{B_{\min} + B_{\max}}{2} = 1.25, c_1 = \frac{C_{\min} + C_{\max}}{2} = 3, d_1 = \frac{D_{\min} + D_{\max}}{2} = 2, e_1 = \frac{E_{\min} + E_{\max}}{2} = 0.35$$

$$b_2 = \frac{B_{\max} - B_{\min}}{2} = 0.75, c_2 = \frac{C_{\max} - C_{\min}}{2} = 2, d_2 = \frac{D_{\max} - D_{\min}}{2} = 1, e_2 = \frac{E_{\max} - E_{\min}}{2} = 0.15$$

where: max and min refer to maximum and minimum value of studied variables.

All coefficients of equation (4) were calculated as described by Goupy and Creighton,¹⁹ and presented in Table 4 and also the importance of each coefficient on the general equation (Eq. 4) by using the term of $|a|/E$, where $E = \sigma/\sqrt{N} = 0.0258$. σ is the standard deviation and N is the number of tests which have been carried out.

From Table 4 we can clearly see that the effect of individual parameter on the Fe^{3+} extraction yield follows the order:

$$a_4/E > a_2/E > a_1/E > a_3/E$$

Hence, $[TDA]_i > [Fe^{3+}]_i > [HCl]_i > O/A$ ratio. Consequently, the effect of amine concentration in the organic phase on Fe^{3+} extraction yield will be 5.7, 1.78 and 1.38 times bigger than O/A volume phase ratio, [HCl] and Fe^{3+} concentration in the aqueous phase respectively. The most elevated binary and ternary interaction was observed for $X_2X_4 = 321.29$ and $X_1X_2X_4 = 232.52$ respectively.

Deep observation of the calculated coefficients of equation 4 and their interactions will make us to conclude that all the sixteen coefficients are significant and none of them can be neglected and should be taken into consideration, since all $|a|/E$

values presented in Table 4 are bigger than t-test value ($t_{0.95} = 3.182$ at 95% confidence level and degree of freedom = 3²²).

By using equation 5, we studied graphically the effect of the four important variables [HCl], [TDA], $(Fe)_{aq}$ and O/A volume phase ratio on $Fe(III)$ extraction yield as follows.

Influence of HCl concentration in the aqueous phase on Fe^{3+} extraction

Fig. 2 illustrates the effect of hydrochloric acid concentration on Fe^{3+} extraction by 0.5M TDA/kerosene containing 10% 2-octanol at two different O/A volume phase ratios 1 and 3 and two different Fe^{3+} concentrations (1 and 5 g/dm³) in the aqueous phase. It is seen from Fig. 2 that the yield of Fe^{3+} extraction increases with the rising of HCl concentration in the aqueous phase at constant O/A volume phase ratio, Fe^{3+} concentration in the aqueous phase and TDA concentration in the organic phase. The highly positive effect of HCl concentration in the aqueous phase on $Y_{Fe^{3+}}\%$ can be explained by the fact that the extractable species of $FeCl_4^-$ will be dominated at high HCl concentration, as described in equation 6:

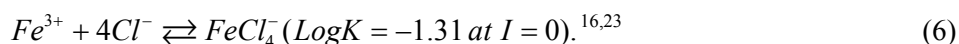


Table 4

Calculated coefficients of 2^4 factorial design experiments related to Fe^{3+} extraction yield and their effects on the general equation (Eq3)

| Reduced variables | Coefficient | Value | $E=\sigma/\sqrt{N}$ | $ a /E$ | Value | Real variables | Coefficient | Value |
|-------------------|-------------|---------|---------------------|----------------|--------|----------------|-------------|----------|
| Constant | a_0 | 73.221 | 0.0258 | - | - | Constant | k_0 | -33.241 |
| X_1 | a_1 | 10.184 | | $ a_1 /E$ | 395.51 | B | k_1 | 63.549 |
| X_2 | a_2 | -13.126 | | $ a_2 /E$ | 509.73 | C | k_2 | -5.443 |
| X_3 | a_3 | 3.183 | | $ a_3 /E$ | 123.62 | D | k_3 | 22.669 |
| X_4 | a_4 | 18.167 | | $ a_4 /E$ | 705.51 | E | k_4 | 258.142 |
| X_1X_2 | a_{12} | -1.964 | | $ a_{12} /E$ | 76.29 | BC | k_{12} | 0.993 |
| X_1X_3 | a_{13} | -7.966 | | $ a_{13} /E$ | 309.34 | BD | k_{13} | -4.821 |
| X_2X_3 | a_{23} | -1.173 | | $ a_{23} /E$ | 45.56 | CD | k_{23} | 1.265 |
| X_1X_4 | a_{14} | -2.699 | | $ a_{14} /E$ | 104.83 | BE | k_{14} | -122.325 |
| X_2X_4 | a_{24} | 8.273 | | $ a_{24} /E$ | 321.29 | CE | k_{24} | -16.619 |
| X_3X_4 | a_{34} | 1.954 | | $ a_{34} /E$ | 75.90 | DE | k_{34} | -44.889 |
| $X_1X_2X_3$ | a_{123} | -4.504 | | $ a_{123} /E$ | 174.93 | BCD | k_{123} | -5.818 |
| $X_1X_2X_4$ | a_{124} | 5.999 | | $ a_{124} /E$ | 232.99 | BCE | k_{124} | 10.581 |
| $X_1X_3X_4$ | a_{134} | 3.746 | | $ a_{134} /E$ | 145.46 | BDE | k_{134} | 9.169 |
| $X_2X_3X_4$ | a_{234} | 4.646 | | $ a_{234} /E$ | 180.41 | CDE | k_{234} | 5.433 |
| $X_1X_2X_3X_4$ | a_{1234} | 1.809 | | $ a_{1234} /E$ | 70.27 | BCDE | k_{1234} | 8.042 |

Moreover, maintaining constant the same experimental conditions with only changing Fe^{3+} concentration from 1 to 5 g/dm³, the yield of Fe^{3+} extraction was decreased, but the quantity of Fe^{3+} extracted was increased which is in accordance with Le Chatelier's principle.

Meanwhile, at O/A=3, the yield of Fe^{3+} extraction is >90% whatever HCl concentration in the aqueous phase, while at low O/A volume phase ratio of 1, the extraction behavior is generally similar to that obtained at O/A=3, but with lower $Y_{\text{Fe}}\%$. Since rising O/A volume phase ratio will augment the number of moles of extractant in the organic phase which will consequently be in the favor of Fe^{3+} extraction.

Influence of Fe^{3+} concentration in the aqueous phase on Fe^{3+} extraction

It can be seen from Fig. 3, which represents the variation of $Y_{\text{Fe}}^{3+\%}$, as a function of Fe^{3+} concentration in the aqueous phase at 0.5M TDA/kerosene + 10% (v/v) 2-octanol and at two different HCl concentrations 0.5 and 2M as well as two different volume phase ratios O/A=1 and 3, that high acid concentration 2M will be in the favor of high Fe^{3+} extraction yield and lead to $Y_{\text{Fe}}^{3+\%}$ is > 96% in the whole studied range of Fe^{3+} in the aqueous phase (1-5 g/dm³). Increasing O/A volume phase ratio from 1 to 3 improves $Y_{\text{Fe}}^{3+\%}$. So, the concentration of Fe^{3+} have no big effect on the yield of Fe^{3+} extraction and the extraction is nearly complete when all studied parameters are in the high state level (O/A=3, $[\text{HCl}]_i=2\text{M}$, $[\text{TDA}]_i=0.5\text{M}$).

From Fig. 3 it is clear that $Y_{\text{Fe}}^{3+\%}$ generally decreases with the increase of Fe^{3+} content in the aqueous phase at constant acidity and O/A volume phase ratio, but the quantity of Fe^{3+} extracted will be higher. This can be attributed to the fact that the concentration of extractable species FeCl_4^- will be higher at high initial Fe^{3+} concentration in the aqueous phase.

The most negative effect of Fe^{3+} concentration in the aqueous phase on the $Y_{\text{Fe}}^{3+\%}$ was observed at (O/A=1, $[\text{HCl}]_i = 0.5\text{M}$, $[\text{TDA}]_i = 0.5\text{M}$) during the increase of Fe^{3+} concentration from 1 to 5 g/dm³, since $Y_{\text{Fe}}^{3+\%}$ was dropped from 89.6% to 59.5% but the quantity of Fe^{3+} extracted by TDA was increased from 0.896 g to 2.975 g.

Influence of TDA concentration in the organic phase on Fe^{3+} extraction

Fig. 4 shows the effect of various concentration of TDA in kerosene (0.2–0.5M) containing 10% (v/v) 2-octanol on Fe^{3+} extraction from hydrochloric acid solution of 2M at two different concentration of Fe^{3+} (2 and 5 g/dm³) in the aqueous phase and at organic to aqueous volume phase ratio O/A=3. As shown in Fig 4, the yield of Fe^{3+} extraction strongly increases with the increase of tri-n-dodecylamine concentration in the organic phase. Since the rise of TDA content in the organic phase will lead to high amine salt (TDA.HCl) concentration in the organic phase, then $Y_{\text{Fe}}^{3+\%}$ will consequently increase, due to the availability of more free amine salt in the organic phase to react with FeCl_4^- species present in the aqueous phase.

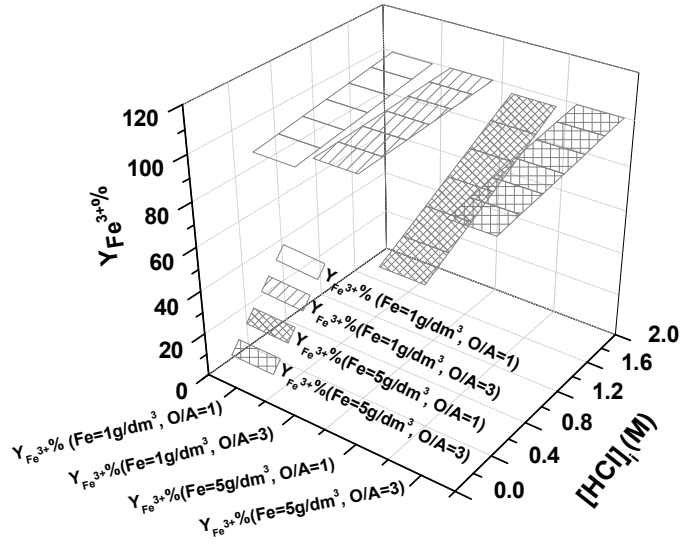


Fig. 2 – Relationship between initial HCl concentration and $Y_{Fe^{3+}\%}$.

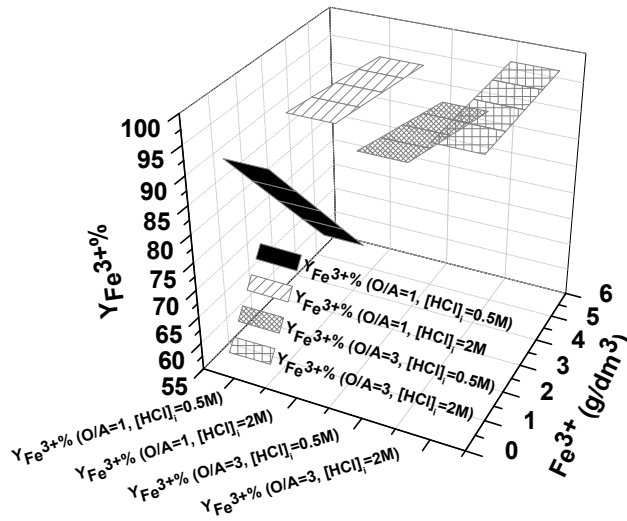


Fig. 3 – Relationship between Fe^{3+} concentration in the aqueous phase and $Y_{Fe^{3+}\%}$.

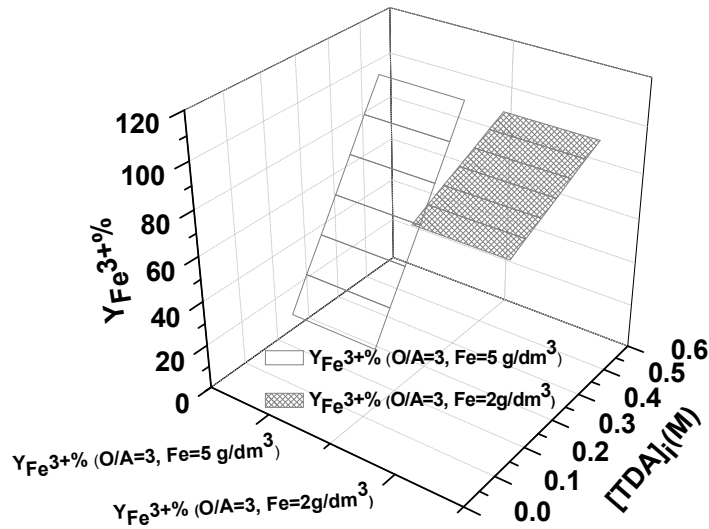


Fig. 4 – Relationship between TDA concentration and $Y_{Fe^{3+}\%}$.

Influence of O/A volume phase ratio on Fe^{3+} extraction

It can be seen from Fig. 5 that the $Y_{\text{Fe}^{3+}}$ increases with the increase of O/A volume phase ratio at constant TDA concentration in the organic phase and iron concentration in the aqueous phase. The effect of O/A volume phase ratio can clearly be observed at low acidity 0.5M HCl than 2M HCl and the $Y_{\text{Fe}^{3+}}\%$ increases from 59% to 90.5% at 0.5M HCl while at 2M HCl the $Y_{\text{Fe}^{3+}}\%$ increases from 96.4% to 99.8% with increasing O/A volume phase ratio from 1 to 3 respectively.

Although, the O/A volume phase ratio is the lower influencing parameter on Fe^{3+} extraction in comparison to TDA, Fe^{3+} concentration and $[\text{HCl}]_i$ parameters, but it should be taken in consideration especially when the extraction process is carried out at low acidity. To insure better transfer of Fe^{3+} from feed solution to the extractant.

Influence of temperature on Fe^{3+} extraction

To investigate the effect of temperature on Fe^{3+} extraction by TDA/kerosene, a 0.35 M TDA/kerosene containing 10% 2-octanol solution was first pre-equilibrated with an aqueous acidic solution of 1.25M of HCl at 313.15 °K and O/A =1 volume phase ratio for 3h, then the amine salt obtained was put into contact with an aqueous solution of 1.25M HCl containing 3 g/dm³ Fe^{3+} , and shaken for 3h at two organic to aqueous phase ratios O/A=1 and O/A=2 and at different temperatures (313.15,

318.15, 323.15, 328.15, and 333.15 °K). The findings of Fe^{3+} extraction were demonstrated in Fig. 6 displaying $\text{Log } K_d$ and $Y_{\text{Fe}^{3+}}\%$ as a function of absolute temperature T and 1/T.

It can be seen from Fig. 6 that $\text{Log } K_d$ and $Y_{\text{Fe}^{3+}}\%$ increase with increasing temperature, That's mean that the extraction reaction of Fe^{3+} by TDA/kerosene is endothermic, the enthalpy change ΔH° was calculated from Vantt Hoff equation and found to be 45.609 kJ/mol. The $\text{Log } K_d$ and $Y_{\text{Fe}^{3+}}\%$ were also increased by increasing O/A volume phase ratio from 1 to 2.

Loading capacity of tri-n-dodecylamine/kerosene

An extractant solution of 0.35 M TDA/kerosene +10% 2-octanol was first of all pre-equilibrated by 2M HCl, then shaken with an aqueous phase of 2M HCl containing 5g/dm³ Fe^{3+} for seven successive times. The results of Fe^{3+} extraction were presented in Fig. 7 in the form of $\text{Fe}^{3+}_{\text{org}}$ and $[\text{TDA}]_i/[\text{Fe}^{3+}]_{\text{org}}$ against the number of contacts (N').

It is obvious from Fig. 7 that Fe^{3+} in the organic phase was increased and $[\text{TDA}]_i/[\text{Fe}^{3+}]_{\text{org}}$ was decreased with increasing N' . Then at $N' \geq 5$, the concentration of Fe^{3+} in the organic phase stayed constant and the saturation of the organic phase was attained at which the ratio $[\text{TDA}]_i/[\text{Fe}^{3+}]_{\text{org}}$ was found to be equal to 2.46.

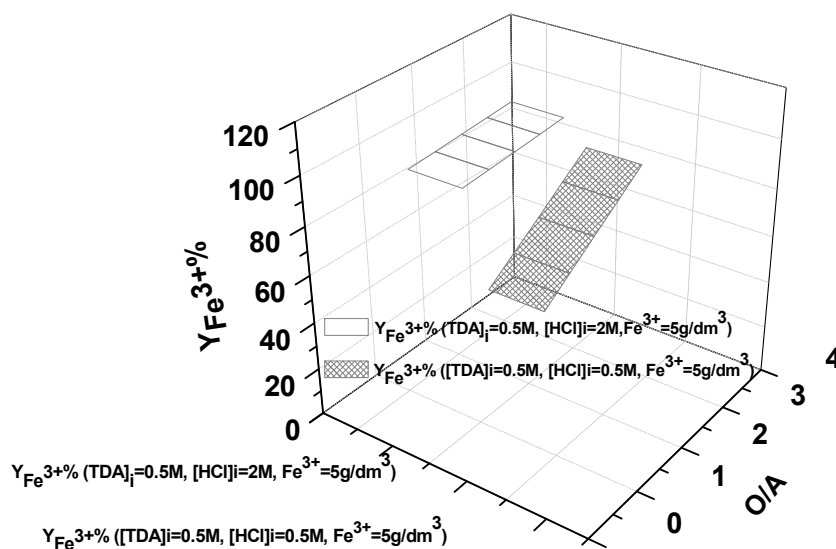


Fig. 5 – Relationship between O/A volume phase ratio and $Y_{\text{Fe}^{3+}}\%$.

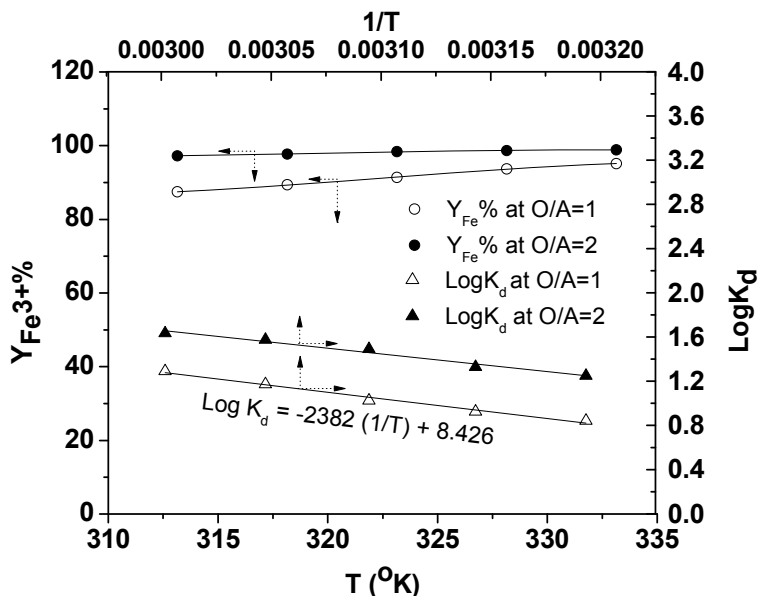


Fig. 6 – Relationship between temperature and $Y_{Fe^{3+}}\%$ and $LogK_d$.
 $[TDA]_i = 0.35\text{ M} + 10\%$ 2- octanol /kerosene, $(Fe^{3+})_{aq} = 3\text{ g/dm}^3$, $[HCl]_i = 1.25\text{ M}$

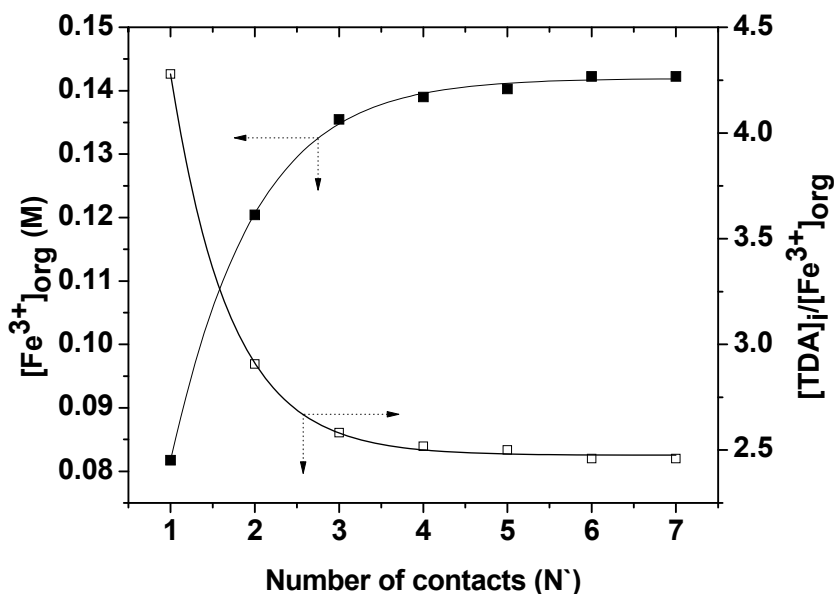


Fig. 7 – Relationship of $[Fe^{3+}]_{org}$ and $[TDA]/[Fe^{3+}]_{org}$ against the number of contacts.
 $[TDA]_i = 0.35\text{ M} / \text{kerosene} + 10\%$ 2-octanol, $(Fe^{3+})_{aq} = 5\text{ g/dm}^3$
 $O/A = 1$, $T = 313.15\text{ }^\circ\text{K}$, $N = 1, 2, 3, 4, 5, 6, 7$.

Back extraction of Fe^{3+} from TDA/kerosene

Stripping experiments were carried out by shaking the organic phase 0.35 M TDA/kerosene containing 10% 2-octanol as modifier and loaded with 4.509 g/dm^3 of Fe^{3+} with different concentration of HCl ranging from 0-5 M, at two different temperatures 313.15 and 333.15 $^\circ\text{K}$, and maintaining O/A volume phase ratio constant and equal to 1 for 3h of shaking. The results were presented in Fig. 8 in the form

of $Y_{stripp}^{Fe}\%$ as a function of HCl concentration in the aqueous phase.

From Fig. 8 it can be clearly seen that the yield of Fe^{3+} stripping decreases with the increase of HCl concentration in the aqueous phase and also the temperature has a negative effect on $Y_{stripp}^{Fe}\%$ from TDA/kerosene. The best $Y_{stripp}^{Fe}\% \approx 70\%$ was observed at $[HCl] = 0.05\text{ M}$, and $\text{Temp} = 313.15\text{ }^\circ\text{K}$.

To optimize the stripping process and determine the best A/O volume phase ratio to

strip most of iron from the organic phase we studied the effect of A/O volume phase ratio on Fe^{3+} stripping by conducting the stripping experiments at $[\text{HCl}] = 0.05\text{M}$ and $T = 313.15\text{ }^\circ\text{K}$ and varying A/O ratios from 1/16 to 4/1 the results were presented in Fig. 8 in the form of $Y_{\text{stripp}}^{\text{Fe}}$ % as a function of A/O ratio. From Fig. 8 we can see that A/O = 4/1 leads to a complete stripping of Fe^{3+} from TDA/kerosene. Consequently, the optimum conditions of iron stripping from TDA/kerosene are: $[\text{HCl}] = 0.05\text{M}$, $T = 313.15\text{ }^\circ\text{K}$, A/O = 4/1).

Flowsheet for Fe^{3+} removal from aqueous HCl solutions

Based on the data obtained from this study, we suggest the following flowsheet which is described in Fig. 9, to recover Fe^{3+} from aqueous HCl solutions by tri-n-dodecylamine. The feed solution of HCl (~2M) containing $1\text{--}5\text{ g/dm}^3\text{ Fe}^{3+}$ was put into contact with 0.5 M TDA/kerosene +10% 2-octanol in two extraction stages at O/A=3 and $313.15\text{ }^\circ\text{K}$, then the loaded organic phase rich in Fe^{3+} was completely stripped in one cycle with diluted HCl solutions (0.05M) at A/O=4 ratio and $T = 313.15\text{ }^\circ\text{K}$. The stripped organic phase is recycled, while the strip solution rich in iron(III) is subjected to

evaporation process for Fe^{3+} concentration, after that the Fe^{3+} can be either precipitated with concentrated sodium hydroxide to obtain pure $\text{Fe}(\text{OH})_3$ after filtration, or crystallized to have pure FeCl_3 .

CONCLUSION

Factorial design experiments is a useful and effective method to optimize iron(III) extraction from HCl solutions, using limited number of experiments and reduce the quantity of chemicals used and cost.

The affinity between Fe^{3+} and TDA is clearly observed at high acid concentration where the extractable species of FeCl_4^- is predominant.

Using high TDA concentration and A/O volume phase ratio have positive effect on $Y_{\text{Fe}}\%$.

Temperature has positive effect on Fe^{3+} extraction which indicate that the extraction of iron(III) with TDA/kerosene is endothermic.

The saturation of TDA/kerosene is observed at number of contact ($N \geq 5$).

Stripping of iron from the loaded organic phase is simple and complete using either very diluted hydrochloric acid (0.05M) or water, and preferably diluted acid to accelerate phase separation during the settlement.

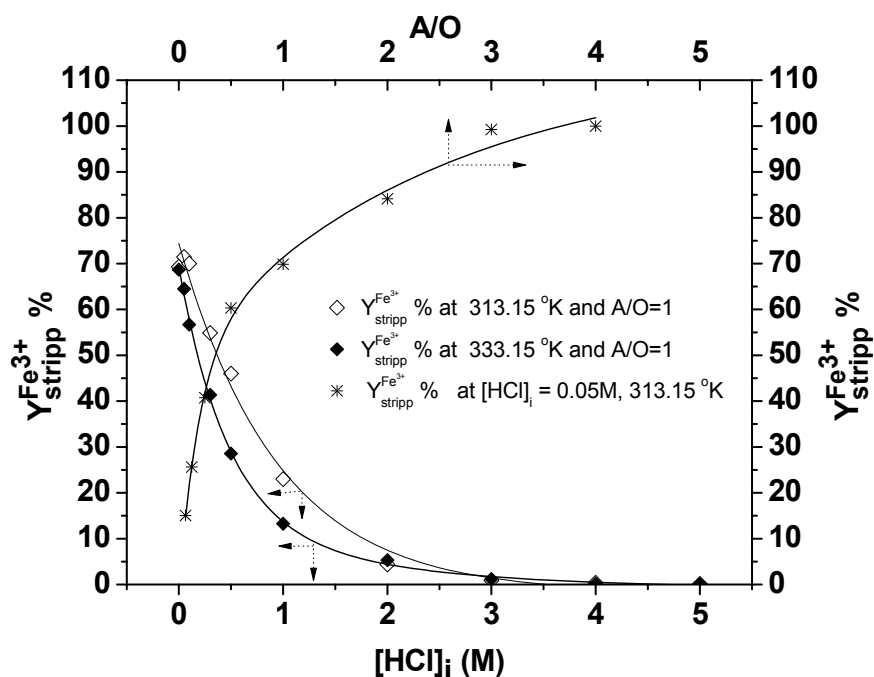


Fig. 8 – Back extraction of Fe^{3+} from the organic phase 0.35M TDA/kerosene.

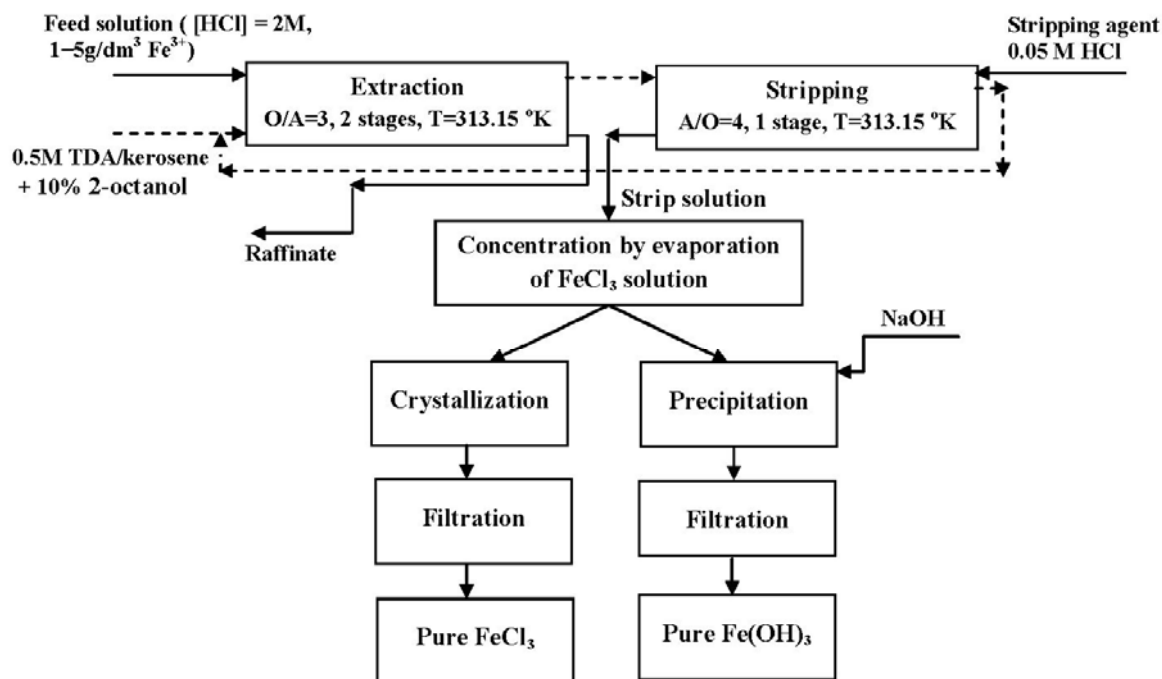


Fig. 9 – Suggested flow-sheet for iron(III) removal from aqueous hydrochloric acid solutions using tri-n-dodecylamine/kerosene + 2-octanol system.

Finally, we can say that the results obtained from this study could be very useful to: 1- recover iron from waste water, at first time by transforming all iron species to Fe(III) by simple oxidation step using hydrogen peroxide, then performing the extraction by TDA/kerosene + 10% 2- octanol. 2- improve iron determination in very diluted aqueous solutions, by simple pre-concentration of iron using TDA/kerosene + 10% 2-octanol, then employing Atomic Absorption, Inductively coupled plasma techniques or UV-visible spectrophotometer for its determination 3- purification of iron(III) salts.

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