

# Transport through a membrane of Fe(II) and Fe(III) from chloride medium using tri-n-butylphosphate and tri-n-octylamine as carrier

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**Abstract:** The aim of this work is to investigate extraction of divalent iron and trivalent iron from chlorides solutions by Tri-n-butyl phosphate(TBP) and Tri-n-octylamine (TOA) dissolved in kerosene.The physical and chemical parameters have allowed us to obtain the variables giving the optimum extraction efficiency.A chemical modelization has allowed us to suggest the extraction mechanism. The classical behaviour obtained in surroundings has been found, with an anion exchanger mechanism and solvation mechanism.

**Key words:** Iron, transport, solvent extraction, environment, wastewater.

## Introduction

Many industrial wastewater streams contain metal cations, one can quote primarily: iron, chrome, lead, copper, zinc, cadmium...ect contained in the galvanic rejections they have an impact on the environment (plants and the products for current human consumption), even with low contents [Chen L., al. (2016)].

The selective separation of iron (II)/ (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. Usually carried out, the conventional method to treat of wastewater such as solvent extraction which is one of the favored separation techniques because of its simplicity, speed, and wide scope. Solution diffusion is commonly accepted mechanism for this technique of separation [ Flett D.S. (2002)].

Chloride hydrometallurgy has been intensively developed in the last years [Vladimir P. and Kislik S. (2012) ].

## 1. Experimental

### 2.1.Reagents

The reagents used are: iron (II) sulfate-7-hydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and tri-n-octyl amine (93%) obtained from Merk, Germany. Ferric chloride ( $\text{FeCl}_3$ ) (98%) from Fluka, Germany .Tri-n-butyl phosphate (TBP) (> 97%) provided by Carl Erba, USA. Hydrochloric acid (HCl) (35-38%) and sodium hydroxide (NaOH) (98%) from Biochem, USA .Kerosene from Naftal was used as the diluent.

### 2.2. Materials

Iron (II)/ (III) concentration in aqueous phases were analysed by Atomic Absorption spectrometer (AAS) (Analytik Jena, novAA 350), Germany. A pH meter type CRISON from Spain is used to monitor the pH of the aqueous solution during the experiments.

A mechanic stirrer (JANKE KUNKEL, IKA-WERK KS 500) from Germany was used to mix the aqueous and organic phases.

### 2.3.Extraction procedure

Synthetic solutions are prepared to obtain a solution with excess concentrations of iron (II) /(III) than the standards one.

The extraction was carried out in 50 cm<sup>3</sup> glass separatory funnels. The organic to aqueous ratio (O/A) of 1: 1 was used in all tests. The two phases were shaken at stable pH and ambient temperature, the shaking time was set at 10 min for extraction, which was found to be sufficient to reach equilibrium for extraction [Hirato T., al (1992) ].

After a settling time, atomic absorption spectrometer (AAS) was used for determination of the concentration of Fe (II) and Fe (III) in aqueous solutions at 284.2 nm. Besides, the concentration range of each metal ion is [5-100] ppm and the concentration range of HCl is [5.10<sup>-4</sup>-10<sup>-1</sup>] mol/L.

Organic phase consists of the Tri-n-Octyl Amine (TOA) that is chemical formula  $(C_8H_{17})_3N$  ( $R_3N$ ) or Tri-n-butyl phosphate (TBP) diluted in kerosene. The concentration range of each extractant is  $[5 \cdot 10^{-4} - 10^{-1}]$  mol/L. Moreover, the concentration of metal ions in organic phase was calculated from the difference between the concentration in aqueous phase before and after extraction.

## Results and discussion

### 3.1. Effect of concentration of hydrochloric acid HCl on the extraction efficiency.

We have maintained a constant concentration of Fe (II)/ (III) at 100 ppm and different concentrations of HCl varied between  $5 \cdot 10^{-4}$  mol/L and  $10^{-1}$  mol/L for the aqueous phase with Fe (II) /Fe (III) for TOA.

For further extraction's manipulation of Fe (III) and Fe (II), we have set the concentration of hydrochloric acid at  $5 \cdot 10^{-4}$  mol/L,  $10^{-3}$  mol/L respectively

### 3.2. Effect of pH on the extraction efficiency

In order to optimize the pH for maximum removal efficiency, the experiments were conducted with 100 ppm of each metal at the optimal obtained concentration of HCl for pH range [0 – 10] with the organic phase ( $10^{-1}$  mol/L of TBP or of TOA).

, for organic phase consists of  $10^{-1}$  mol/L of TBP or TOA diluted in kerosene. The obtained results are shown in figure 1.

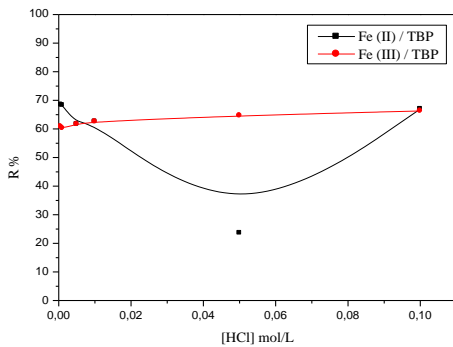
Results (figure1.a) illustrate that TBP extracts more iron (III) compared iron (II). The efficiency extraction of Fe (III) by TBP is indexed by constant values in order to 62%. We note that the extraction of Fe (III) decreased to attend 23% for  $5 \cdot 10^{-2}$  mol/L of HCl beyond it increased.

The reasons for this occurrence can possibly be related with a competition of HCl with Fe (II) /Fe (III) for TBP. For further extraction's manipulation, we have set the concentration of hydrochloric acid at  $5 \cdot 10^{-4}$  mol/L,  $10^{-1}$  mol/L respectively for Fe (II) and Fe (III).

We note that the extraction of iron (II)/ (III) decreases by increasing of the hydrochloric acid concentration with a low values < 50%. This occurrence can due to the competition of HCl

Figure 2 shows that R(%) of Fe(II)/ (III) extracted increases with increasing pH to attend 78% at 5.96 and 94% at 7.22 respectively; beyond this pH the efficiency of its extraction increases. Whereas Fe (III) is more extracted with TBP than Fe(II). It is due to the activation of each extractant in chloride solutions and the species of iron complexes formed.

#### a. TBP



#### b. TOA

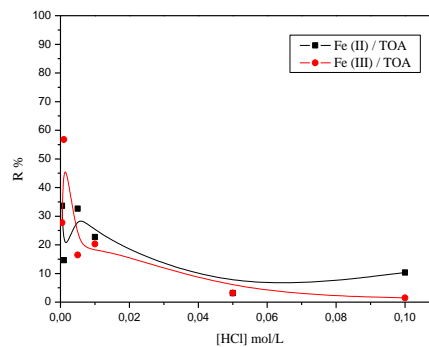
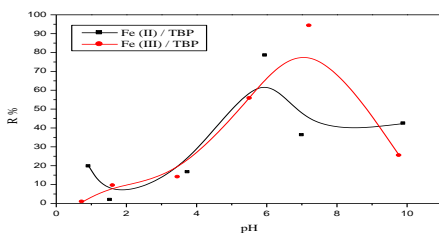


Figure1. Variation of the extraction efficiency of Fe on function of [HCl] by TBP (a) and by TOA(b)

#### a. TBP



#### b. TOA

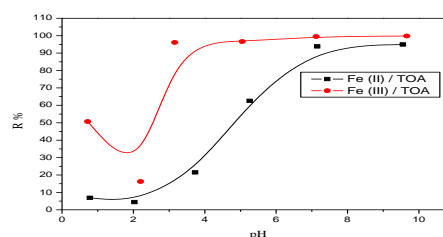


Figure2. Effect of pH on the extraction efficiency with TBP (a) and with TOA (b)

For further extraction's manipulation of Fe (II) and Fe (III), we have set pH at 5.96 and 7.22 respectively.

The results obtained for the study of the influence of pH show that Fe(III) is more extracted than Fe(II). For acidic pH values (<5) the efficiency of the extraction increases to achieved 90%, beyond it is maintained constant

at a high R% > 95%. So iron (II)/ (III) are more extracted on basis pH values of 9.55

### 3.3. Effect of the concentration of extractant on the extraction efficiency.

Results illustrate that the extraction efficiency of Fe(II)/(III) decreases for the range TOA concentration equal to  $[5 \cdot 10^{-4} - 10^{-2}]$  mol/L to attend 70%. For more than  $10^{-2}$  mol / L TOA, it increases to achieve more than 90%.

### 3.4. Effect of metal concentration

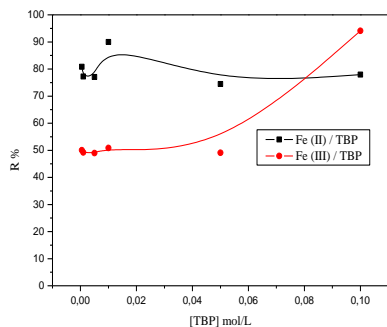
We have maintained a constant concentration of HCl and different concentrations of iron (II)/(III) which varied between [5-100] ppm for the aqueous phase and organic

We put 10mL of the chromium solution (100 ppm) and constant concentration of HCl and values of pH in contact with 10mL of the organic phase consists of the TBP or TOA at concentrations varied between  $5 \cdot 10^{-4}$  mol /L and  $10^{-1}$  mol/L in kerosene. The variation of the extraction efficiency of Fe(II) and Fe(III) on function of the concentration of the TBP or the TOA and was represented in figure 3.

We observed that the extraction efficiency of Fe(II) is averaged 77-80%. Furthermore, Fe(III)'s efficiency took constant values at 50% for the less concentration of TBP, than it increases to 94.12 % for  $10^{-1}$  mol/L TBP.

phase consists of the TBP  $10^{-1}$  mol/L in kerosene. The obtained results are shown in figure 4.

#### a. TBP



#### b. TOA

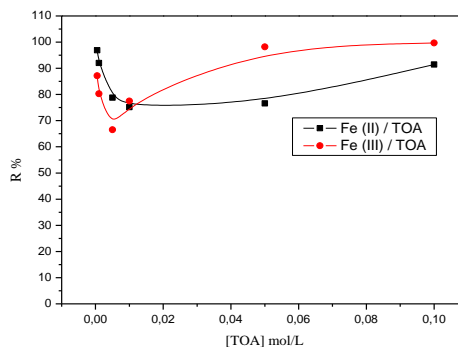
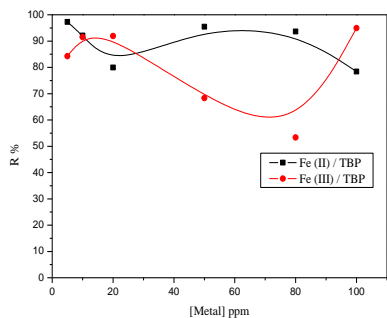


Figure 3. Variation of the extraction efficiency of iron on function of concentration of extractant

#### a. TBP



#### b. TOA

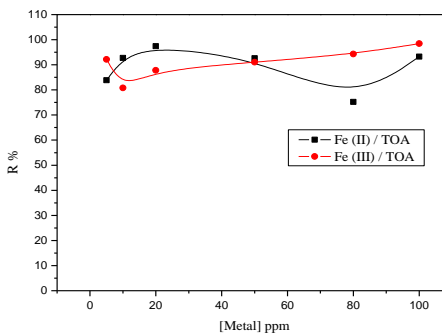
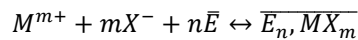


Figure 4. Variation of the extraction efficiency of iron on function of [Metal] by TBP(a) , by TOA(b)

We can contest that efficiency's extraction is more than 53% for all the range of iron concentration studied by TBP and also by TOA.

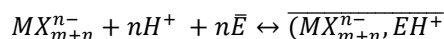
### 3.5. Mechanism extraction

The equation of solvation mechanism is :



### Conclusion

Several studies [Frankfeld J.W. and Li N.N. ( 1977)] showed that extraction of metals using tertiary amines with long carbon chains (such as TOA) occurs by the following mechanism:



M: Metal, E: Extractant, X: Anion, H: Hydrogene, (n,m) :stoichiometric coefficient.

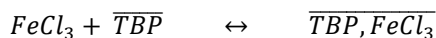
By using species distribution diagrams, we proposed the following mechanism:

### Solvation mechanism by TBP:

For Fe<sup>2+</sup>:

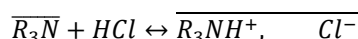


For Fe<sup>3+</sup>:



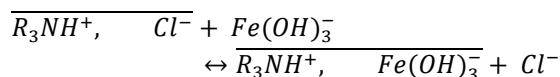
### Anionic exchanger mechanism by TOA:

a- Protonation of tertio Amine:

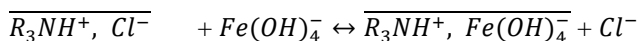


b- Extraction anions

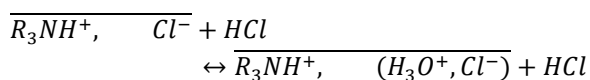
Fe (II) :



Fe(III) :



c- Competition of extraction of sulfuric acid



In this work we was studied the recovery and valorization of divalent and trivalent iron chloride medium using TBP and TOA as carrier.

The extraction efficiencies of iron (II) /(III) obtained are for the Fe(II) extracted in the order of at 97% for low

concentration of HCl 0.1mol/L TBP and 0.1mol/L TOA at pH equal to 5.96, 9.55 respectively.

The Fe(III) extracted by TOA at pH = 9.66, HCl 10<sup>-3</sup> mol/L achieves 99%; when it attends 94% by TBP at pH =7.22 and HCl 10<sup>-1</sup>mol/L.

It seems that TOA is more efficient carrier than TBP witch used for separation of iron ions from chloride solutions. Furthermore, Fe (III) is extracted better than Fe (II).

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