

## LIQUID-LIQUID EXTRACTION OF IRON (III) FROM OUENZA IRON ORE LEACH LIQUOR BY TRIBUTYLPHOSPHATE

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### ABSTRACT

The solvent extraction of iron (III) from the hydrochloric acid leach liquor of iron ore from mine of Ouenza, Algeria with tributylphosphate (TBP) in chloroform was studied. The effect of several parameters, such as contact time, HCl concentration, TBP concentration and chloride inorganic salt (KCl) concentration on the efficiency of extraction of iron was examined at  $19 \pm 2$  °C. It was found that, for 2 min 3M TBP in presence of 5M HCl and 2 M KCl solutions led to a high yield of extraction (98.57 %) of iron (III).

The stoichiometry of the extracted species was determined by using the method of slope analysis. The number of moles of  $H^+$ ,  $Cl^-$  and TBP associated with the extracted species was determined and the extracted species was found to be  $HFeCl_4(TBP)_2$ .

**Keywords:** solvent extraction; iron (III); Tributylphosphate; leach liquor; Mine Ouenza.

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### 1. INTRODUCTION

Mineral leaching is an applied method for recovering precious metals from ores [1]. The use of hydrochloric acid for the dissolution of an iron ore generally results in a solution with a high concentration of ferric iron [2].



The iron of the leach solution is important in hydrometallurgy. Removal or recovery of iron from a chloride-rich solution may be carried out by precipitation or by solvent extraction techniques [3].

Liquid-liquid extraction is one of the most widely used industrial separation processes, allowing the separation, purification and concentration of various metal ions. This method extensively applied by the recovery of appreciable quantities of metallic elements either for the protection of the environment or their recovery for use in the industrial sector [1].

In the extraction of metal ions, the choice of the extractant molecule is a key element of the extraction process [4]. Indeed, it must have a high extracting power and be optionally selective with respect to the targeted metal solute.

Many researchers have carried out solvation extraction to study the recovery of iron (III), where the extractants possess donor atoms (O, N, S, P) without labile hydrogen via these groups, the extractant may partially or totally substitute for the hydration molecules of the cation, and solvate the metal. In the case of an extractant E, a metal cation  $M^{m+}$  and anion  $X^-$ , the extraction is described by the following equilibrium:



The experimental use of this relation makes it possible to determine the stoichiometric coefficients of the equilibrium, by varying a single parameter. Extraction will be all the stronger as the extractant concentration E is high. Similarly, charging the aqueous phase with  $X^-$  ions, in the form of acid or non-extractable salt, favors extraction [5].

It is very difficult to separate iron (III) from aqueous solutions after hydrometallurgical processes of recovering a number of non-ferrous metal ions [6]. In the separation of iron (III) from aqueous chloride, various publications have dealt with the application of organophosphorus acids and derivatives of organophosphorus compounds. Ferric iron has a strong tendency to form complexes with the chloride ion which can be selectively extracted by TBP [7-11].

Tributylphosphate (TBP) is an organophosphate compound ( $C_{12}H_{27}O_4P$ ) characterized by low solubility in water, exceptional chemical resistance, high polarity and very low vapor pressure [12-14].

The presence of the phosphate functional group allowing specific ligand properties and the overall physicochemical properties make TBP an excellent industrial solvent widely used as an extractant and complexing agent [12].

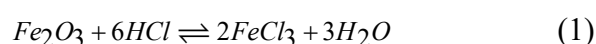
In this work, the influence of the chloride concentration, the aqueous acid concentration and the concentration of extractant on the efficiency of extraction of iron (III) from the hydrochloric acid leach liquor of iron ore from mine of Ouenza, Algeria with TBP in chloroform was studied.

## 2. RESULTS AND DISCUSSION

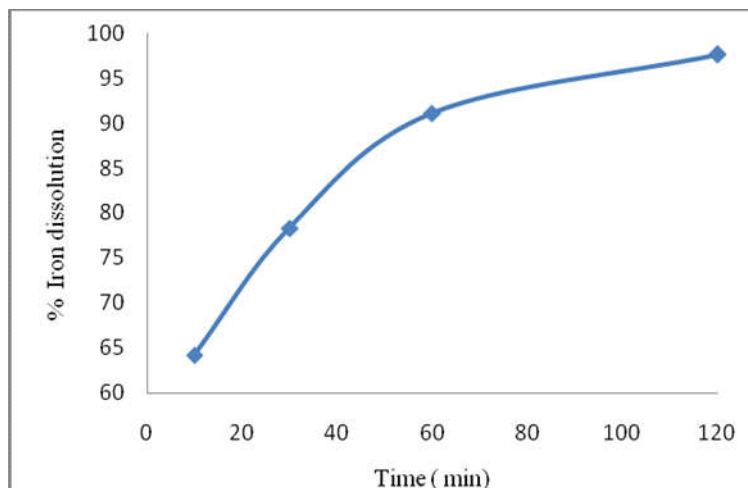
### 2.1. Analysis of the leaching of iron ore with hydrochloric acid

The chemical analysis of the iron ore from Ouenza, Algeria by using X-ray fluorescence spectrometry (XRF) gave the following results: SiO<sub>2</sub>, 1.29; Al<sub>2</sub>O<sub>3</sub>, 0.17; Fe<sub>2</sub>O<sub>3</sub>, 76.19; CaO, 10.18; MgO, 3.86; K<sub>2</sub>O, 0.05; SO<sub>3</sub>, 0.03 (%). The leaching process was applied to the iron ore rock to recover the iron element. Various parameters such as concentration of hydrochloric acid (0.5-12mol/l), leaching temperature (30-80°C), agitation rate (90-450rpm) and (0.063-0.5mm) under different conditions to study their influence on leaching efficiency, and determine the best conditions that give a very high rate of dissolution of iron in hydrochloric acid. Using a particle size of 0.063 mm in 12 mol/l HCl and a solid / liquid ration 1: 100 at 80 °C, in 2 hours with a stirring speed = 360 rpm, about 97.6% of the iron total in the rock was dissolved in the hydrochloric acid solution (Fig .1), this ratio represents an estimated iron (III) concentration of 0.093 M [15].

For an iron ore of hematite type, the reaction of the dissolution of the iron is written as follows [2]:



The solution chosen for extraction by TBP contains about 0.01329 M of iron (III), this concentration was obtained during the leaching of the ore of particle size 0.063 mm in 0.5 mol/l HCl and a solid / liquid ration 1 : 100 at 80 °C, in 1 hour with a stirring speed = 360 rpm.

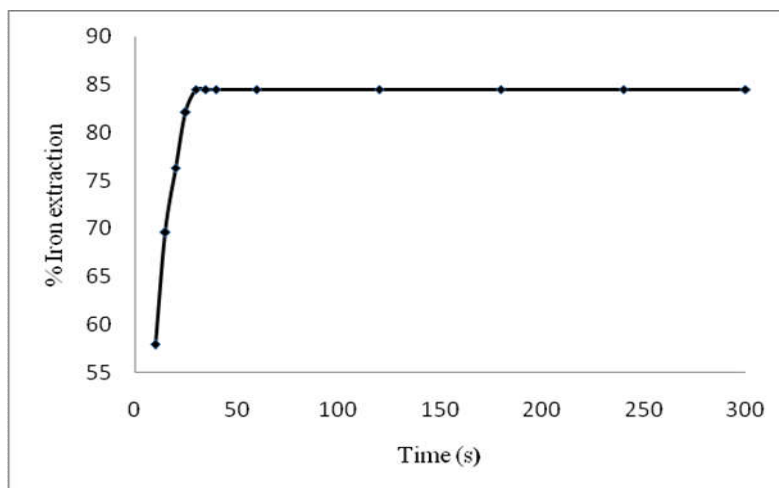


**Fig.1.**Effect of HCl concentration on iron ore dissolution [15]

## 2.2. Analysis of the extraction of iron (III) with TBP dissolved in chloroform

### 2.2.1. Effect of contact time on the extraction of iron (III)

The iron (III) extraction was studied with different contact times to determine the equilibrium reaction time for subsequent experiments under the following conditions :  $[\text{Fe}] = 0.01329\text{M}$ ,  $[\text{TBP}] = 1\text{M}$ ,  $[\text{HCl}] = 5\text{M}$ ,  $[\text{KCl}] = 2\text{M}$ , ratio (O / A) 1:1, stirring rate 300 rpm and reaction temperature of  $19 \pm 2^\circ\text{C}$ . The results are presented in Fig.2.



**Fig.2.** Effect of contact time on iron extraction

Fig.2. shows that as the contact time increased from 10s to 30s the percentage of iron extraction increases rapidly from 57.9 to 84.45 %. After 30s min the extraction remains

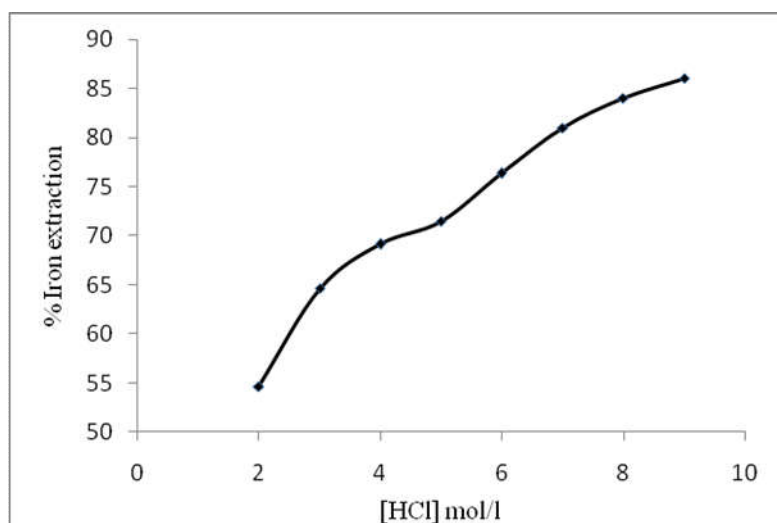
constant until 5 min. So the extraction in these conditions was reached within only 2 min and it was chosen as the reaction time for all the following experiments.

### 2.2.2. Effect of HCl concentration

The hydrochloric acid concentration in feed liquor has an important influence on iron extraction [16]. It has been reported that  $\text{FeCl}_3$  in the presence of HCl contributes to form  $\text{HFeCl}_4$  which could then combine with TBP in the extracted complex and facilitates extraction reaction [9].

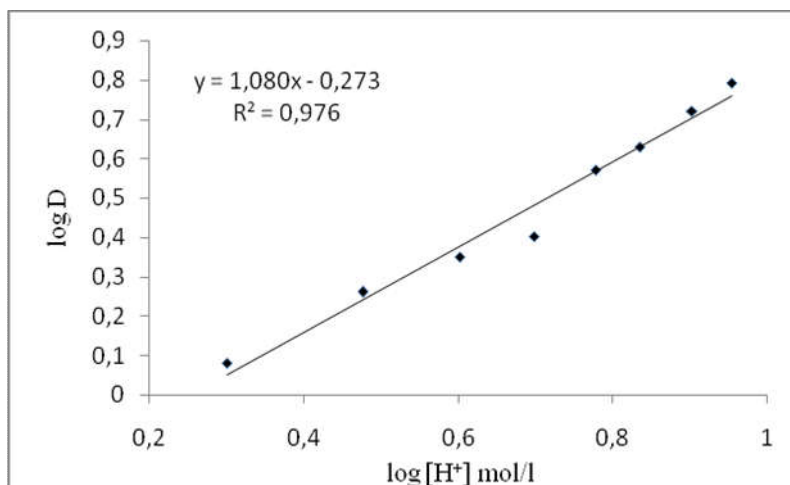
The effect of HCl concentration in the range of 1 to 9 M has been investigated using a constant KCl concentration of 2 M on iron (III) extraction. The extractions were carried out with a TBP of fixed concentration equal to 0.5 mol/l in chloroform at a temperature of  $19 \pm 2$  °C and the results are given in Fig.3.

It is clear from the figure that the iron (III) extraction percentage increases with increasing HCl concentration. Therefore,  $[\text{HCl}] = 9$  mol/l was noted as the optimum concentration for iron (III) extraction, where approximately 86.08% extraction efficiency was achieved.



**Fig.3.** Effect of HCl concentration on extraction of iron (III)

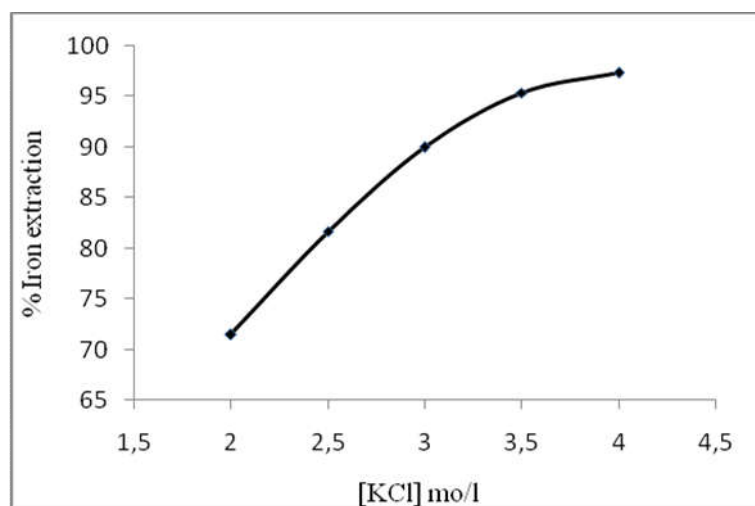
The plot of  $\log D$  versus  $\log [\text{H}^+]$  Fig.4 has a slope of 1.08 supports the presence of one hydrogen ion in the extracted iron complex.



**Fig.4.** Plot of log D versus log [H<sup>+</sup>] mol/l for the extraction of iron (III)

### 2.2.3. Effect of KCl concentration

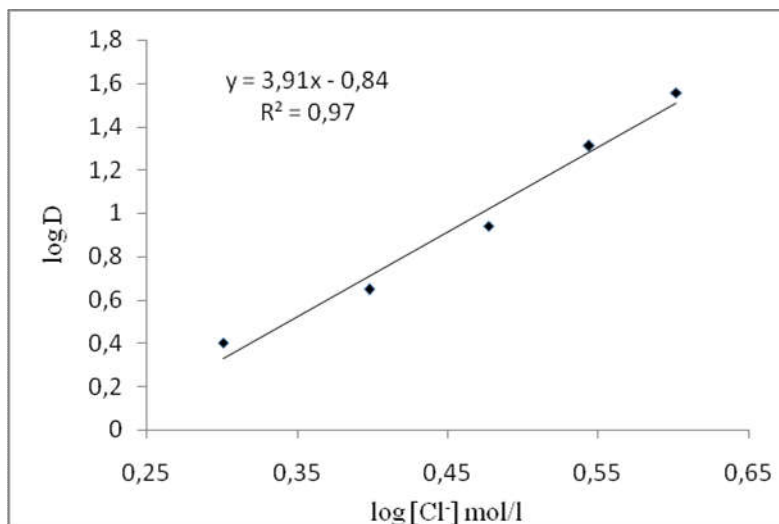
The effect of chloride ions on the extraction of iron (III) by 0.5 mol/l of TBP in chloroform from leach liquor containing 5 mol/l of hydrochloric acid was investigated. The chloride concentration was varied by adding different amounts of [KCl]. The results are presented in Fig.5.



**Fig.5.**Effect of KCl concentration on extraction of iron (III)

As seen, the figure illustrates an increase in iron extraction from 71.48 to 97.29 % with an increase in chloride concentration. This shows the association of chloride ions in the extracted iron complex.

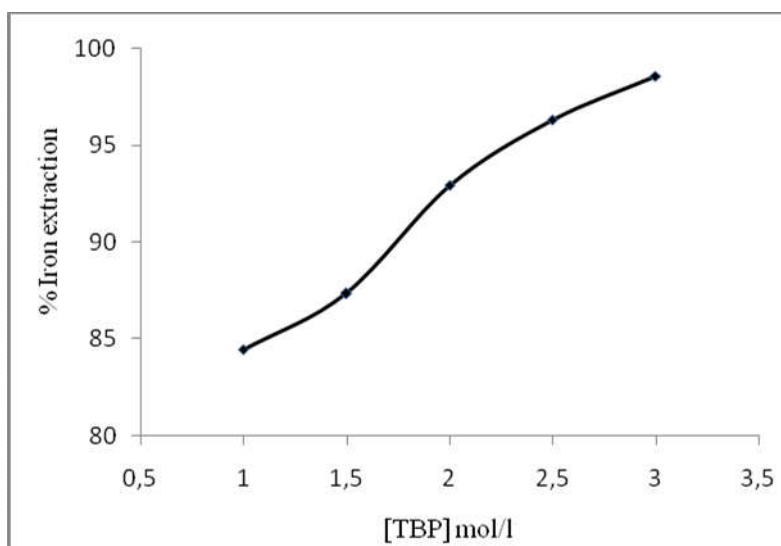
The linear plot of  $\log D$  vs  $\log [Cl^-]$  in Fig.6 with slope value of 3.9 indicating the involvement of four chloride ions in the extracted complex of iron (III).



**Fig.6.**Plot of  $\log D$  versus  $\log [Cl^-]$  mol/l for the extraction of iron (III)

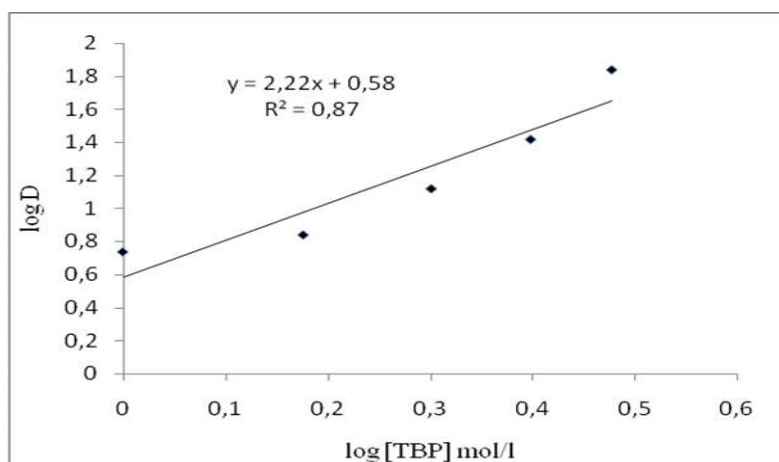
#### 2.2.4. Effect of TBP concentration

The effect of TBP concentration within (1 - 3 M) on the extraction of iron (III) from the aqueous solution bearing 2 M KCl and 5 M HCl was studied. The experimental results plotted in Fig.7, shown that the percentage of iron (III) extracted increase rapidly from 84.45 to 98.57 % with increasing TBP concentration.



**Fig.7.**Effect of TBP concentration on extraction of iron (III)

The plot of log D vs log [TBP] for extraction of iron (III) as presented in Fig.8, illustrates the slope of 2.2 which indicates that two molecules of TBP participate in the extraction of iron (III).



**Fig.8.**Plot of log D versus log [TBP] mol/l for the extraction of iron (III)

Therefore, based on the slope analysis of the obtained experimental data, the most probable composition of the extractable species can be represented by:

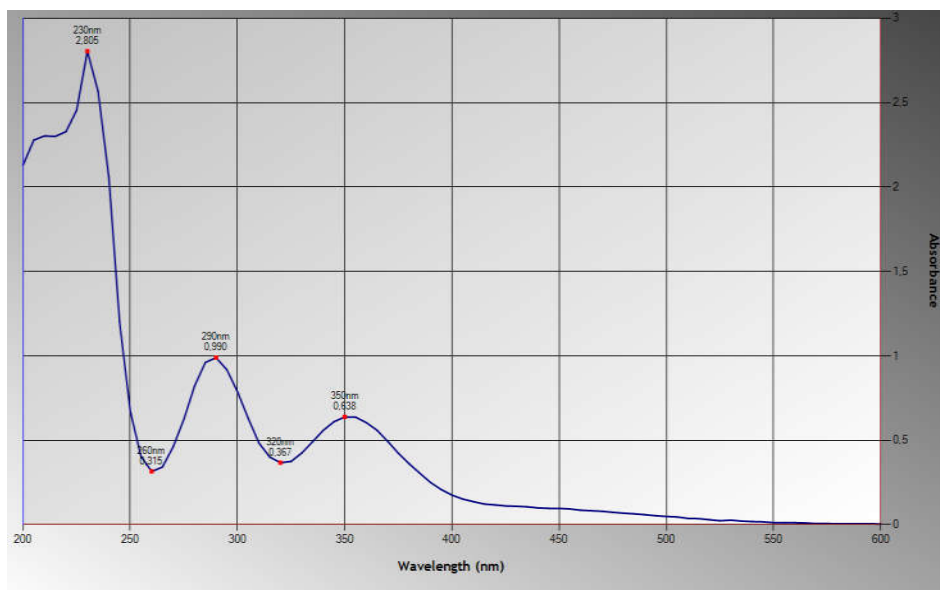


This is in agreement with the previously reported data for the extraction of iron (III) from hydrochloric acid solutions with TBP [17-18].

### 2.3 UV and IR spectral studies

The yellowish brown color of the aqueous solution indicates the presence of tetrahedral species  $FeCl_4^-$  and octahedral species  $[FeCl_4(H_2O)_2]^-$  because of charge transfer band in the ultraviolet spectra in which tails coming into the visible [19]. The aqueous and organic phases were examined by the UV-Visible spectra. From the spectra of leach liquor of iron ore in hydrochloric acid in the presence of KCl Fig.9, the characteristic bands at around 230, 290, 350 nm are due to the formation of  $FeCl_4^-$  [20]. When compared the spectrum of the organic phase with that of the aqueous phase, it can be seen that the absorptions are in the same frequencies of spectrum of the aqueous solution, containing the stoichiometric composition of  $HFeCl_4(TBP)_2$  according to the equilibrium equation (2).

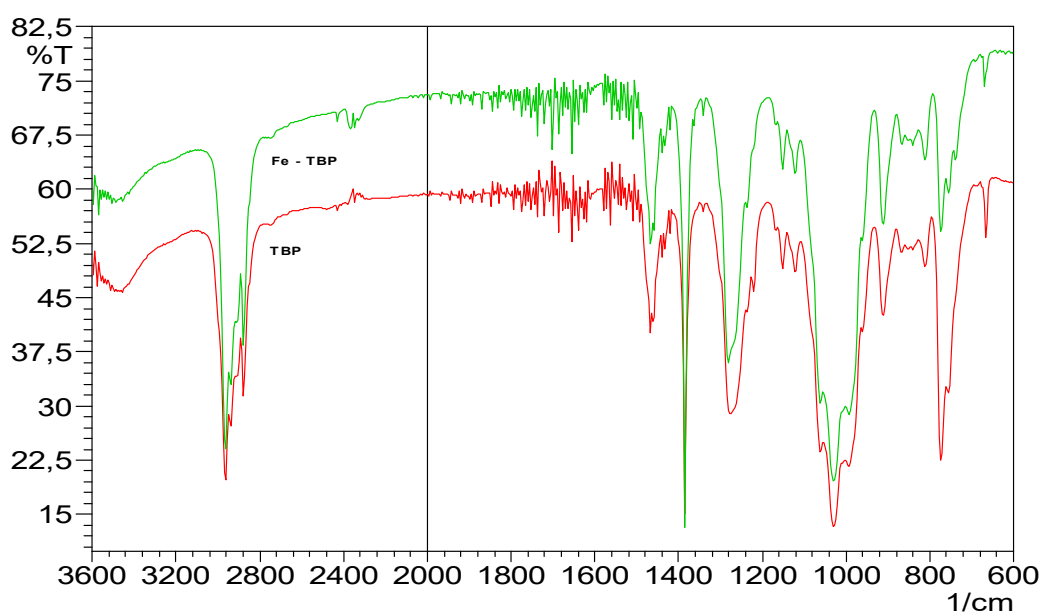




**Fig.9.**UV- Vis spectrum of iron complex with tributylphosphate

The functional group P=O is the only part of TBP which is able to exert the solvent electron donor [20]. To confirm this, the organic extract with TBP in chloroform from the hydrochloric acid leach liquor of iron ore aqueous solution was examined by IR spectroscopy. The spectra of TBP alone and TBP-Iron (III) are shown in Figure.10.

From Figure.10, it can be seen that the band associated with the vibration of the P=O bond (around  $1273.9\text{ cm}^{-1}$ ) [21], in the presence of iron, shifts towards the high frequencies of ( $1280.65\text{ cm}^{-1}$ ), these changing indicate the possibility of bonding between iron and TBP.



**Fig.10.**IR spectra of extractant and iron loaded organic phase

### 3. EXPERIMENTAL

#### 3.1. Reagents and solutions

- The commercial extractant TBP (tributylphosphate) ( $C_{12}H_{27}O_4P$ ) 97% without further purification.
- Organic diluents chloroform was pre-equilibrated with aqueous solution of NaCl and distilled water.
- The leachate liquor contained 0.01329 M of iron III.
- Potassium chloride.
- Hydrochloric acid.
- Potassium thiocyanate solution (KSCN).

#### 3.2. Extraction Procedures

The experiments were carried out by shaking equal volumes (10 ml) of aqueous phase; mixture of leach liquor, hydrochloric acid and potassium chloride and organic phase containing (0.5 to 3 M TBP) diluted in chloroform, the mixture was mechanically stirred (300 rpm) for 2 min at a temperature of  $19 \pm 2$  °C. Once the mixing phases were separated, the iron (III) concentration in the aqueous phase was determined by spectrophotometric and thiocyanate method and measured the absorbance at 465 nm using a UV-Visible spectrophotometer JENWAY-7315. The concentration of Fe (III) in the organic phase was calculated from the mass balance. The percentage extraction (% E) was calculated by the following equation [22]:

$$\%E = \frac{D}{D+1} 100$$

The equilibrium slope method ( $\log D$  vs  $\log [H^+]$ ,  $\log [Cl^-]$  and  $\log [TBP]$ ) has been used to analyze the experimental data for each extraction system. The distribution ratio (D) was determined as follows [22]:

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

### 4. CONCLUSION

Using 0.063mm particle size in 12M HCl with solid/ liquid ration 1:100 within 2 hours and at 80°C, about 97.6% of iron (III) was passed from Ouenza iron ore into solution.

The results of fundamental studies on the solvent extraction of iron (III) from hydrochloric acid leach liquor contains about 0.01329 M of iron (III) by TBP in chloroform showed that the extraction of metal ions increased with increasing HCl, KCl, TBP concentrations. The composition of the extractable species is found to be  $\text{HFeCl}_4(\text{TBP})_2$  With 5M HCl, 2M KCl and 3M TBP at  $19 \pm 2^\circ\text{C}$  about 98.57% of iron (III) was extracted.

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