



## Comparison of Microwave-assisted, ultrasound-assisted and conventional solvent extraction techniques for the extraction of molybdenum with tributyl phosphate

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### Keywords

- ✓ Molybdenum,
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### Abstract

The main objective of the current work was to evaluate the feasibility of Microwave-assisted Extraction (MAE) and Ultrasound-assisted Extraction (UAE) techniques as compared to conventional extraction for the extraction of molybdenum from HCl and H<sub>2</sub>SO<sub>4</sub> solutions with TBP dissolved in n-hexane. The results show that the equilibrium time was drastically shortened under MAE and UAE from 10 min to 20 s and 03 min to 20 s for extractions conducted with HCl and H<sub>2</sub>SO<sub>4</sub> solutions, respectively. Increase of HCl concentration increases the extraction yield of molybdenum under MW and UAE irradiations whereas the reverse was observed with the increase of H<sub>2</sub>SO<sub>4</sub> concentration. For 1 M HCl, an increase in microwave power enhances slightly the extraction yield for microwave power greater than 60 W. An increase in ultrasound amplitude has slightly increased the extraction of molybdenum and lowered it for 0.10 M H<sub>2</sub>SO<sub>4</sub>. For a microwave power of 100 W and 1 M HCl, the extraction of molybdenum was 50% higher comparatively to conventional extraction. Also for 1 M HCl and for a pulse amplitude of 80%, the extraction yield was 100% much higher than the one obtained under conventional extraction. The application of MAE and UAE clearly highlights that molybdenum can be extracted by using these technologies and that it has contributed to improve the efficiency of conventional solvent extraction. under suitable process conditions.

## 1. Introduction

The pollution of environment caused by the presence heavy metals became at present a critical and a major problem. This pollution engenders a grave ecological imbalance due to the uncontrolled rejections of the chemical pollutants. Nowadays, the environmental protection is an economic and political stake. Heavy metals resulting from diverse industrial activities often appear at very high concentrations in many of their rejections. The recovery or the elimination of these heavy metals contained in diverse sources is an operation of a great importance for the industry and the environment. Among these heavy metals, the molybdenum is a particularly worrisome case because it accumulates in the body and can cause grave disorders.

In the last years, the commercial value of molybdenum has been significantly increased due to the demand on the part of the emergent economies. Molybdenum is one of the most important metal having compounds encountered in many technological fields. It is well recognized as a strategic metal having many important applications in many industrial sectors [1-3]. Molybdenum is a refractory metal used principally as an alloying agent in steel, cast iron and super alloys to enhance strength and wear and corrosion resistance. Molybdenum finds irreplaceable application in medicinal field i.e. nuclear magnetic diagnosis; analytical field as a target element in XRD; as an alloying element in stainless and construction steel to be used in highly corrosive environment. This metal is generally used in alloys because it contributes to increase the steel resistance at high temperatures and corrosion conditions. Molybdenum is also an essential trace element for plants, animals and humans [4-6]. On the other hand, it can be toxic at high concentrations [4, 5]. This metal is relatively rare in the

Earth's crust (estimated abundance is in the range 0.05-40 mg kg<sup>-1</sup> with a mean value of 1.5 mg kg<sup>-1</sup>). In its natural occurrence, molybdenum is found in molybdenite ore at microgram level [7, 8]. The development of purification and extraction processes of molybdenum are very important. The presence of molybdenum in the acid or alkaline leach solutions in trace amount poses problem and solvent extraction technique is applied for its separation. Also, the use of solvent extraction for molybdenum has mainly been devoted to the removal of this metal from uranium circuits. A vast amount of literature [9-29] has been published about the solvent extraction of molybdenum from aqueous media containing different mineral acids using different solvents. The published data include those using various types of commercial organic solvents, such as TBP, phosphine trioxide, sulphoxides, high-molecular weight alkylamines and alkylphosphoric acid esters. Organophosphorus acids, are among the extractants which have found wide application in solvent extraction [14, 15, 18, 19-23, 25]. It is known that molybdenum forms with organophosphorus extractants complexes which are easily extracted into organic solvents. The effect of operating variables on the extraction of molybdenum from different acids solutions with different organic solvents was studied. There are many reports [4-8, 10, 24-30] about the determination of very low concentrations of dissolved molybdenum in different matrices. Inductively coupled plasma optical emission spectrometry (ICP-OES) [9, 11, 12, 15, 25, 27, 30] is one of the most important analytical techniques more convenient for determination of trace amounts of molybdenum.

Solvent extraction is an attractive option which is widely used for the separation and the recovery of various metal ions. However, this technique exhibits important restrictions and drawbacks related to the use of diluents as it is tedious, time-consuming, analytes loss and requires large amounts of toxic organic solvents [5-30]. When the efficiency became one of the main characteristics of a good technique of extraction, several works were dedicated to the solvent extraction of the metals assisted by modern methods such as the microwaves or the ultrasounds. Indeed, these techniques constitute a very interesting alternative which can allow to reach short durations of extraction while maintaining high yields (efficiencies) and selectivities.

Nowadays, a great interest is shown to the new microwave and ultrasounds irradiation techniques in the field of the solvent extraction of the heavy metals. There are at present diverse techniques of extraction assisted by the microwaves applied to the extraction of the not volatile and thermosensibles compounds by solvents of low dielectric constant, in the extraction of ores, the extraction of organic pollutants, of contaminants of grounds, natural products of vegetable origin, in the obtaining of essential oil or aromatic extracts of vegetable origin [31-43]. Microwave radiations showed their big power in the increase of the extraction yields in organic synthesis. The ultrasounds attracted the interest of many chemists and physicists, the works cited in the literature show that the sonication can initiate a chemical reaction, accelerate it or change its course. The sonication plays the role of the agent of transfer of phase which catalyses the reaction at the liquid-liquid interface. The sonication allows to reduce the size of the liquid bubbles of the biphasic media and accelerates strongly the liquid-liquid transfer [42-44]. The use of the microwaves and the ultrasounds seems then interesting for the solvent extraction of the heavy metals and in particular the molybdenum.

New separation methods based on innovative concepts are currently being developed [45-51] as an interesting alternative to traditional solvent extraction. There are several reasons for the growing interest in the use of this technology in the field of metals extraction from solid matrices. The use of microwave irradiation has several advantages, such as faster thermal activation and material selective heating [33-35]. The application of ultrasound waves in chemistry was viewed as a merely convenient technique [34, 36, 42, 43, 45-50]. Ultrasound is known to have great effects on chemical reactions [42-47]. Ultrasound can enhance the rates of mass transfer and reaction in heterogeneous systems. Many studies have been carried out and it is well documented, that the advantages of ultrasound procedures are good yields, short reaction times and mild conditions [37-47]. Ultrasound energy causes its chemical effects through the phenomenon of cavitation, which consists of the production of microbubbles in a liquid when a large negative pressure is applied to it [51, 52]. A literature search did not yield any reference about earlier reports on the solvent extraction of molybdenum under microwave and ultrasound. This paper extends the work to the extraction of molybdenum using these innovative techniques. The extraction of the metal was carried out from hydrochloric and sulphuric acid solutions with TBP dissolved in n-hexane. The aim of this work is to investigate the effect of these new techniques on the extraction of molybdenum.

The goal of this work will be the possibility of enhancing the solvent extraction of molybdenum by using microwave and ultrasound assisted extraction. The aim of the investigation was also to compare the extraction efficiency of molybdenum under microwave and ultrasound irradiation in order to find the optimum extraction conditions. To the best of our knowledge, this is the first time that the solvent extraction of molybdenum using microwave and ultrasound irradiations has been proposed.

In this work, parameters influencing microwave-assisted extraction (irradiation time, irradiation power and the hydrochloric and sulphuric acid concentration) and ultrasound- assisted extraction (sonication time, irradiation amplitude and the hydrochloric and sulphuric acid concentrations), are fully investigated. The results being compared with those obtained under conventional solvent extraction.

## 2. Material and Methods

### 2.1. Reagents

A commercial organophosphorus extractant named tributyl phosphate (TBP) was used in this study. This solvent extraction reagent with a purity of 97% was supplied by Aldrich (Barcelona, Spain). TBP was used as received and was dissolved in n-hexane (C<sub>6</sub>H<sub>14</sub>, 95%) provided by Panreac (Barcelona, Spain) in order to prepare the organic extracting phases.

As a source of molybdenum (VI), analytical grade ((Mo<sub>7</sub>O<sub>24</sub> (NH<sub>4</sub>)<sub>6</sub>·4H<sub>2</sub>O), purity 99%) was used. All chemicals were of analytical-reagent grade and deionized water was used for the preparation of reagents and standards. Two mineral acids such as hydrochloric acid (HCl, 37% (w/w)) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 96% (w/w)) were used for the preparation of the aqueous phases. These acids were purchased from Panreac (Barcelona, Spain).

A 1000 mg/L molybdenum (VI) stock solution was prepared by dissolving 0.1856 g of the metal salt in doubly distilled deionized water. The molybdenum working aqueous phases were prepared from the stock solution as reported [25]. The initial concentration of molybdenum(VI) in the aqueous phase in all experiments was maintained constant (100 mg/L or nearly 10<sup>-3</sup> mol/L). All aqueous solutions were prepared by dissolving the investigated acid in distilled deionized water. TBP concentration was kept constant throughout, i.e, 40% (v/v). The volumes of aqueous and organic phases were maintained equal to 10 mL.

### 2.2. Instrumentation

Molybdenum determination in the aqueous phase was carried out by means of a model Optima 4300 DV Perkin Elmer inductive coupled plasma atomic emission spectrometry (ICP-AES, Uberlingen, Germany) at a wavelength of 202.031 nm. The experimental conditions of the ICP-AES system are summarized in Table 1. Experiments were carried out in triplicate with the experimental errors of less than 5.0%.

**Table 1:** Instrumentation and operating conditions for ICP-AES.

Wavelength, nm	202.031
RF power, kW	1.45
Integration time, ms	100
Liquid flow rate, mL/min	0.05
Outer gas flow rate, L/min	15
Intermediate gas flow rate, L/min	0.5
Central gas flowrate, L/min	0.7
Viewing height above load coil, mm	5
Injector tube inner diameter, mm	2

### 2.3. Procedures for microwave, ultrasound and conventional extractions

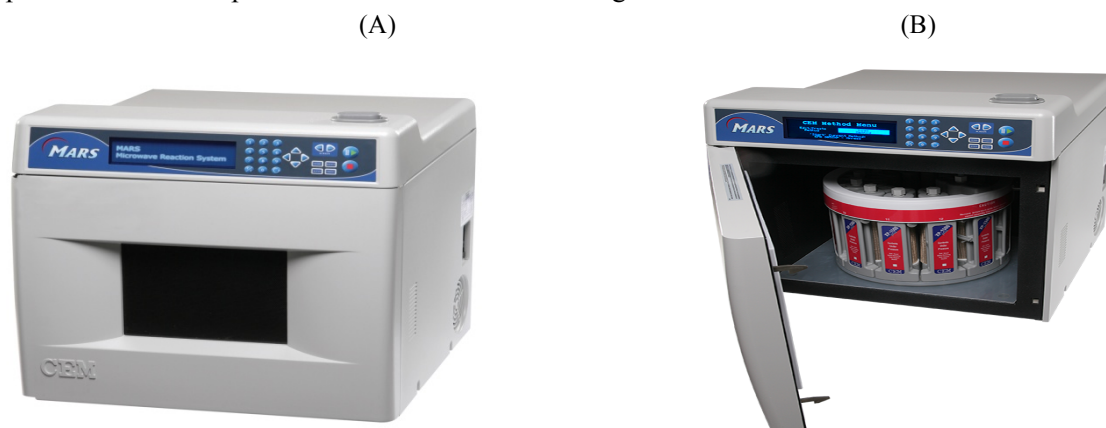
#### 2.3.1. Microwave-assisted extraction

Microwave-assisted solvent extraction (MAE) of molybdenum was performed in a programmable laboratory microwave oven extraction system (RTP-Plus MARS-S model, CEM Corporate Matthews, NC, USA) (Fig. 1). The apparatus is equipped with a digital control system for irradiation time and microwave power. The MARS-S is a multi-mode system which is provided with a magnetron having an operating frequency of 2.45 GHz and delivering a maximum incident nominal power of 1600 W, with a direct control of the temperature via an optical sensor fibre (infrared thermometer) immersed directly in the middle of the oven.

An inboard temperature control system was installed for monitoring and controlling temperature conditions inside the extraction vessels made of poly(tetrafluoroethylene) (PTFE). The temperature data, the power delivered and the time of experiment were all controlled by internal software. The pressure is maintained at 15 PSI. The temperature which was set at 26 °C was measured by an infrared sensor incorporated solely in a control reactor and is programmed at the furnace at the beginning of each experiment.

The microwave extraction procedure was performed by introducing the mixture of the two aqueous and organic phases, previously at defined concentrations in each of the twelve firmly closed vessels. The vessels were then placed symmetrically in the microwave furnace. The sample mixture was then subjected to microwave irradiation for a definite time.

The mixture with the same composition to those conducted under conventional extraction was placed into the closed microwaved assisted extraction and irradiated for a predetermined time. The investigated MAE extraction parameters were microwave power, extraction time and each trial was carried out in triplicate. The temperature of the samples never exceeded 26 °C during extraction tests.



**Fig. 1:** Overall picture of the microwave oven MARS-S (A) external view, (B) interior view

### 2.3.2. Ultrasound-assisted extraction

The device was working throughout the experiment in continuous mode, i.e. cycle = 1, which means how the ultrasound was propagated in 100% of the time throughout the medium. Ultrasound-assisted extraction experiments were carried out with an ultrasound sonicator UP200S manufactured by "Dr. Hielscher", Teltow, Germany. The frequency was constant at 24 kHz for 100 W ultrasonic device, and enabled transient cavitations with bubble implosion effects. The ultrasonic probe was immersed into the mixture directly so that its tip was at the interphase of the two aqueous and organic phases. A schematic illustration of the experimental set-up is shown in Fig. 2. The intensity of the generated ultrasonic waves was determined using a calorimetric method with distilled water as the test solution. Ultrasonic power dissipated was calculated at each amplitude level, with temperature (T) recorded as a function of irradiation time (t) using a T-type thermocouple. From temperature versus time data, the initial temperature rise  $dT/dt$  was determined by polynomial curve fitting. The absolute ultrasonic power P was then given by:

$$P = m C_p \frac{dT}{dt} \quad (1)$$

where  $dT/dt$  is the change in temperature over time ( $^{\circ}\text{C s}^{-1}$ ),  $C_p$  is the specific heat of water ( $4.18 \text{ J kg}^{-1} \text{ }^{\circ}\text{C}^{-1}$ ), and  $m$  is the mass of water (kg).

### 2.3.3. Conventional extraction

Conventional solvent extraction or shaking extraction method was used as reference for comparison with the ultrasound and microwave assisted extraction methods. Under conventional extraction phase mixing was done by shaking the organic solutions composed of TBP dissolved in n-hexane and aqueous solution containing molybdenum in 125-mL separatory funnels at room temperature ( $25 \pm 1$  °C). The metal was dissolved in different mineral acids (HCl, H<sub>2</sub>SO<sub>4</sub>) at a perquisite concentration. Both phases were then brought together for a defined time by mechanical stirring using a mechanical shaker (Promax 1020, Heidolph Instruments, Schwabach, Germany) at 8.5-9 rpm stirring speed. This speed has ensured a perfect agitation of the aqueous and organic phases [25].



**Fig. 2:** Scheme of experimental apparatus for ultrasound-assisted extraction.

For each extraction procedure after the extraction time had elapsed, the two phases were transferred in 125-mL separating funnels. Then the two phases were allowed to stay for 10 min and were then disengaged completely. The aqueous phases samples have been analyzed by means of inductively coupled plasma atomic emission spectrometry in order to determine the concentrations of residual molybdenum ions. The concentrations of molybdenum in the organic phase were calculated from a difference in the molybdenum concentrations in the aqueous phase before and after extraction. In all cases, the average of at least three sets of experimental data was reported. Results of extraction experiments will be discussed in term of extraction yield of molybdenum(VI),  $E(\%)$ , defined as follows :

$$E(\%) = \frac{([\text{Mo(VI)}]_i - [\text{Mo(VI)}])}{[\text{Mo(VI)}]_i} \times 100 \quad (2)$$

where:

$[\text{Mo(VI)}]_i$  = the initial concentration of molybdenum ions in the aqueous phase;

$[\text{Mo(VI)}]$  = the concentration of molybdenum ions in the aqueous phase after extraction;

## 3. Results and discussion

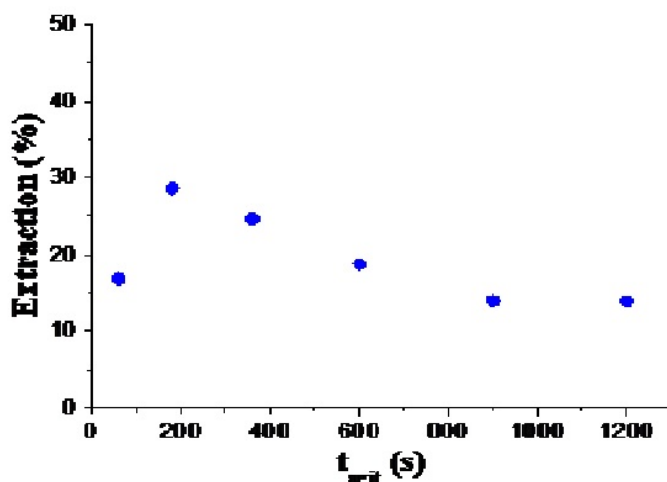
### 3.1. Kinetic study of molybdenum (VI) extraction

The study of the kinetics of the reactions of extractions of metals as a function of diverse physico-chemical parameters represents an important step for the design and the simulation of industrial equipments. Kinetic studies are very important to obtain detailed information on the mechanism of reaction, which is of the greatest help in understanding the solvent extraction chemistry. However, in order to design an extraction process, knowledge of kinetic data is advantageous. However, no data is published on the kinetics of molybdenum extraction with organophosphorus extractants under microwave and ultrasounds irradiations.



### 3.1.1. Effect of phase agitation time under conventional extraction

Experiments on the influence of equilibration time under conventional extraction for molybdenum (VI) extraction have been carried out by shaking at 26 °C for various lengths of time aqueous solutions of 100 ppm molybdenum (VI) and organic solutions of 40% (v/v) TBP dissolved in n-hexane. Results obtained are shown in Fig. 3; it is seen that the system approaches the equilibrium rather slowly (e.g., equilibrium is reached within 20 min of contact), although the difference between 10 min and 60 min is not marked.



**Fig. 3:** Molybdenum extraction yield versus agitation time under conventional extraction.

$[Mo]_{init} = 100 \text{ mg.L}^{-1}$ ,  $[H_2SO_4] = 0.1 \text{ M}$ ,  $[TBP] = 40\% \text{ (v/v)}$   $V_{aqu}/V_{org} = 1$ ,  $T = 26\text{-}28 \text{ }^\circ\text{C}$ .

Under conventional extraction, the extraction yield,  $E(\%)$ , for extracting molybdenum (VI) from 0.1 M  $H_2SO_4$  by TBP at 40% (v/v) dissolved in n-hexane was measured at different phase contact times of both aqueous and organic phases. Fig. 3 shows that the kinetic of molybdenum(VI) extraction is fast early at the beginning of the process. It was found that the extraction yield increases with increasing phase contact time up to 3 min and, after that, the curve levels off. For this latter contact time, the extraction yield reaches a maximum value of 28.7%. The extraction yields rather tend to stabilize to a minimal value of 14% for contact times varying between 900 and 1200 s. It is concluded that the equilibration time for this system is about 3 min. In subsequent experiments, 3 min of contact time were adopted to ensure complete equilibration.

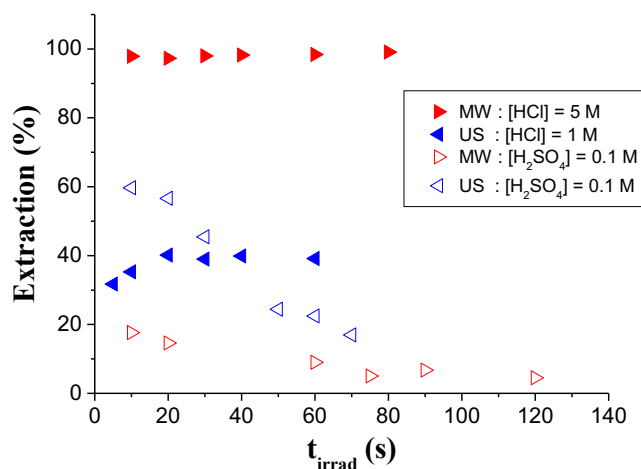
The decreases of the extraction yields are due to the formation of complexes of molybdenum (VI) in the organic phases which are little stable and thus little or not extractible by TBP. In other words, these decreases can be explained by the competition between the extraction of molybdenum (VI) and that of sulfuric acid. Indeed, in these conditions, the TBP has a greater affinity for  $H_2SO_4$  than for the molybdenum (VI) ions.

### 3.1.2. Comparative study of the kinetic of the extraction of molybdenum (VI) (under microwave and ultrasounds irradiations)

Extraction time is one of the most important factors in recent alternative extraction procedures. It is also an important factor to be considered in order to obtain efficient extraction. Generally, maximum extraction efficiency could be achieved when extraction equilibrium is reached. Figure 4 presents the kinetic curves of the extraction of the molybdenum (VI) ions from hydrochloric and sulphuric acid solutions. It also illustrates the comparison of the kinetics of molybdenum (VI) extractions carried out by using the microwave and the ultrasounds irradiations for different operating conditions.

The dependence of the extraction of molybdenum (VI) on irradiation time is presented in Fig. 4. The effect of this variable on the extraction yield of the molybdenum (VI) ion was studied with different aqueous solutions composed of either acids hydrochloric acid at 1 M and 5 M or sulphuric acid at 0.1 M and using organic solutions of TBP at 40% (v/v) dissolved in n-hexane; the irradiation times applied under microwave or

ultrasound were between 05 and 120 s. The volumes of the aqueous and organic phases were both 10 mL in each experiment and the molybdenum concentration of the aqueous phase before the extraction was maintained constant at 100 mg/L.



**Fig. 4:** Molybdenum extraction yield versus microwave and ultrasound irradiation time.  $[\text{Mo}]_{\text{init}} = 100 \text{ mg} \cdot \text{L}^{-1}$ ,  $V_{\text{aqu}}/V_{\text{org}} = 1$ ,  $[\text{TBP}] = 40\%$  (v/v), MW:  $[\text{HCl}] = 5 \text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 0.1 \text{ M}$ ,  $P_{\text{MW}} = 20 \text{ W}$ ,  $f_{\text{MW}} = 2.45 \text{ GHz}$ ,  $T = 26 \pm 0.2 \text{ }^\circ\text{C}$ , US:  $[\text{HCl}] = 1 \text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 0.1 \text{ M}$ ,  $P_{\text{max US}} = 200 \text{ W}$ ,  $f_{\text{US}} = 24 \text{ kHz}$ ,  $A = 20\%$ ,  $T = 26 \pm 0.2 \text{ }^\circ\text{C}$ .

According to figure 4, the different extractions of molybdenum (VI) from 5 M HCl by TBP at 40% (v/v) assisted by microwave irradiations, show that the kinetics are rather fast. The results shown in Fig. 4 indicate that the time needed to reach equilibrium for maximum extraction is 10 s. The minimum equilibration period of 10 s was found to be sufficient for quantitative extraction of Mo (VI). The increasing shaking period up to 80 s had no adverse effect on extraction.

Molybdenum (VI) extraction reached equilibrium after ca. 10 s only from the start of the extraction. This latter irradiation time was found to be sufficient for quantitative extraction of Mo(VI) into the organic phase under the above conditions. It is clear from the figure 4 that the molybdenum (VI) extraction yield is not affected by the time of exposure to the microwave irradiations over the range 10-80 s under the experimental conditions mentioned in the figure caption. The results reported in Fig. 4 show that the extraction is very fast; only 10 s are required to reach equilibrium, corresponding to an extraction yield approximately equal to 100%. All molybdenum was completely extracted within the first 10 s due to the microwave irradiations effects, leading thereafter to good penetration of the TBP into the aqueous phase, and enhancing the transfer of the extractant. Therefore, a longer extraction time was unnecessary once the maximum extraction yield of molybdenum (VI) was achieved. Based on these results, 10 s was selected as optimum irradiation time under microwave for subsequent experiments.

For the system TBP/HCl, where HCl is at 5 M and TBP is at 40% (v/v), the positive effect of the microwaves is expressed in terms of equilibrium time which is shortened by a factor of 18 under microwave irradiations compared to its counterpart obtained under the conventional conditions. This result was to be expected previously probably due to the fact that microwave provides a potential alternative to induce a considerable effect on metal reactions.

The effect of ultrasound on molybdenum (VI) extraction yield by TBP at 40% (v/v) was carried out using 1 M HCl under ultrasounds irradiations. The molybdenum extraction yields versus sonication times were exhibited in Fig. 4. At the extraction time of 5-20 s, molybdenum extraction yield increased when ultrasound irradiation was applied. The results indicated that increasing the sonication time in the domain 20-60 s had no appreciable effect on the molybdenum extraction yield. The extraction equilibrium of molybdenum (VI) characterized by a plateau is reached after a duration of irradiation time of 20 s only. The most appropriate sonication time for ultrasound was found to be 20 s, as it resulted in the maximum of extraction yield of 40%. Thus, a sonication extraction time of 20 s was selected for the latter experiments conducted in this study.

Fig. 4 also plots molybdenum (VI) extraction efficiency against irradiation time for each of the kinetics tests conducted with sulphuric acid solutions under microwave and ultrasounds irradiations. Under microwave irradiations, the evolution of the extraction yields of molybdenum (VI) obtained when the aqueous phase is constituted by 0.1 M H<sub>2</sub>SO<sub>4</sub> shows that the latter decrease from a maximal value of 17.6%, obtained for an exposition time of the microwave irradiations of 10 s, until a much lower value of 04.5%, obtained for a period of microwave irradiations of 120 s. This decrease of the extraction yield is due to a prolonged exposure of the samples to the microwave irradiations.

On the other hand, the dependence of the extraction yields of the molybdenum (VI) ions on ultrasound irradiation times are also presented in Fig. 4. Under ultrasounds irradiations, the extraction yield of the molybdenum (VI) from 0.1 M H<sub>2</sub>SO<sub>4</sub>, decreases strongly from a maximal extraction yield of 59.7 to 16.9%, when the exposure time to the ultrasounds irradiations varies from 10 to 70 s.

These decreases of the extraction yields when the time of exposure to the microwave or ultrasounds irradiations times increase can be explained by the heating effect of over exposure to microwave and ultrasounds irradiations for longer irradiation time, which leads to the degradation of molybdenum complexes. They can also be attributed to the reactions of polymerized species of molybdenum (VI) as well as to the competitive extraction of H<sub>2</sub>SO<sub>4</sub> than of the molybdenum ions. These sections of the plots should give information about the kinetics of the decomposition process.

By using the TBP/H<sub>2</sub>SO<sub>4</sub> system, the extraction yields of molybdenum (VI) obtained under ultrasounds are clearly larger in comparison to their counterparts obtained under microwaves. The yields decrease more rapidly during the first moments under ultrasounds irradiations than under microwave irradiations. The yield obtained under ultrasounds irradiations is 3.4 times much greater than the one obtained under microwave irradiations, and for a period of irradiation of only 10 s.

The gap between the yields obtained under ultrasounds and microwaves irradiations decreases gradually as the irradiation time increases. Within the first irradiation time, the variation is large and then with further increase in irradiation time, the variation is slowed down. The decreases of the yields were also observed by several authors [32, 33, 36, 37, 46] during the extraction of various metals such as copper, chromium and lead, from various acidic media. In their extraction tests, the microwave irradiations times of 10 to 80 s were used and where extraction yields of more than 50% were obtained. On the other hand, for the system TBP/H<sub>2</sub>SO<sub>4</sub>, the positive effect of the ultrasounds is expressed in terms of molybdenum (VI) extraction yields which can be 2 times larger under ultrasounds irradiations than under conventional extraction. The equilibrium time is reduced by a factor of 18 under ultrasounds irradiations that under conventional extraction. On the other hand, the extraction yields obtained under microwave irradiations are clearly lower than their counterparts obtained under conventional extraction. In subsequent experiments, the durations of microwave or ultrasounds irradiations necessary to reach the thermodynamics equilibrium of molybdenum (VI) extraction from each of the investigated acid HCl or H<sub>2</sub>SO<sub>4</sub> by TBP were fixed at 20 s in order to ensure complete equilibration.

### *3.2. Effect of hydrochloric and sulphuric acid concentration under microwave*

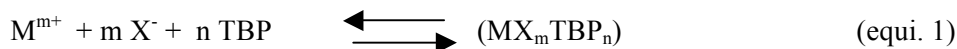
The variations in the extraction of molybdenum (VI) with the concentration of hydrochloric (0.50 - 1.80 M) and sulfuric acids (0.1 - 2 M) under microwave irradiation were studied using an aqueous solution containing 100 ppm of molybdenum (VI) with 40% (v/v) TBP at an O:A ratio of 1:1 and temperature of 25 °C. This study was carried out for 20 s microwave irradiation time and 20 W microwave power.

The efficiency of the extraction of molybdenum (VI) under microwave irradiation depends on the initial concentration of the hydrochloric and sulphuric acids in the aqueous solutions, as can be seen in fig. 5. The molybdenum (VI) extraction from HCl solutions by TBP under microwave irradiation is strongly dependent on the initial HCl concentration in the aqueous phase. Molybdenum extraction increases with increasing HCl acidity.

It can be seen that dilute acid (0.5 M HCl) was less effective for molybdenum (VI) extraction than more concentrated acid (1.8 M HCl). The molybdenum (VI) extraction yield increases considerably by about 8-folds (from 7.9 to 63.4%) with the increase in the HCl concentration from 0.50 to 1.80 M. These results are in accordance with Le Chatelier law governing the thermodynamic equilibria. The enhancement of the extraction



of molybdenum with the increase of hydrochloric acid concentration is explained in terms of the extraction reaction solvation mechanism. The extraction mechanism of TBP consists of forming coordination links between the oxygen P=O and the molybdenum(VI) cations to be extracted according to the following equilibria [19, 20]:



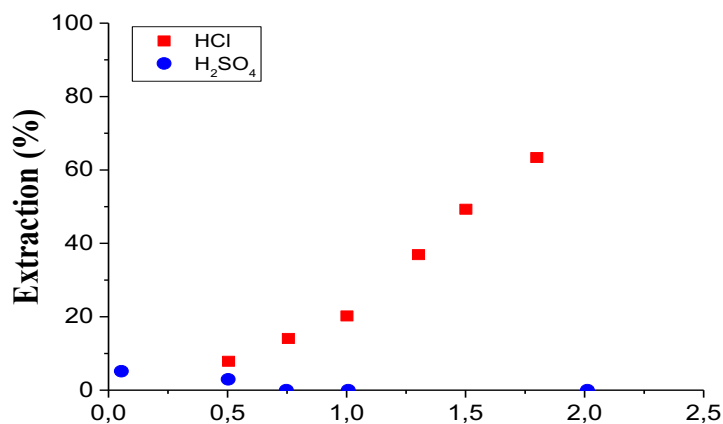
where M is the metallic molybdenum cation,  $X^{-}$  is  $\text{Cl}^{-}$  anion and m and n are stoichiometric coefficients.

Consequently, the increase of hydrochloric acid concentration in the aqueous phase solution is favorable for the extraction of molybdenum.

The observed trend of increasing molybdenum extraction with increasing hydrochloric acid concentration is consistent with an extraction as a chloro complex. At low acidities ( $[\text{HCl}] < 1 \text{ M}$ ), extraction is low ( $< 10\%$ ) due to molybdenum hydrolysis and polymerization, which gives unextractable species. According to the profile of abundance of each Mo(VI) species [26, 27, 29],  $\text{MoO}_4^{2-}$ ,  $\text{HMoO}_4^{-}$  and  $\text{H}_2\text{MoO}_4$  are one of the most predominant species at the low acidities investigated and where molybdenum (VI) extraction does not occur in great extension.

On the other hand, the effect of increasing the initial  $\text{H}_2\text{SO}_4$  concentration on the extraction of molybdenum (VI) is shown in Fig. 5. The extraction of molybdenum (VI) was found negligible ( $< 6\%$ ) under the present experimental conditions. Although a moderate extraction was observed when it was extracted from 0.1 to 0.5 M  $\text{H}_2\text{SO}_4$  solutions. The extraction yield decreased from 05.1% to 03% and is practically nil when the  $\text{H}_2\text{SO}_4$  concentration varies from 0.5 until 2 M. The decreases are due to the phenomena of competitions between the extraction of molybdenum (VI) with sulfuric acid. This type of behavior indicates the formation of non-extractable and undissociated species in the aqueous phase, or polymerization in the organic phase.

The extraction yields obtained by using  $\text{H}_2\text{SO}_4$  concentrations ranging from 0.1 to 2 M are much less important than those obtained by using HCl at concentrations ranging from 0.5 to 1.8 M. Consequently, the extraction of molybdenum (VI) under microwave irradiations seems more advantageous by using HCl than  $\text{H}_2\text{SO}_4$ .



**Fig. 5:** Molybdenum extraction yield (%) versus concentration of acid (HCl,  $\text{H}_2\text{SO}_4$ ) under microwave irradiation.  $[\text{Mo}]_{\text{init}} = 100 \text{ mg}\cdot\text{L}^{-1}$ ,  $[\text{TBP}] = 40\% \text{ (v/v)}$ ,  $V_{\text{aqu}}/V_{\text{org}} = 1$ ,  $P_{\text{MW}} = 20 \text{ W}$ ,  $f_{\text{MW}} = 2.45 \text{ GHz}$ ,  $t_{\text{irrad MW}} = 20 \text{ s}$ ,  $T = 26 \pm 0.2 \text{ }^\circ\text{C}$ .

### 3.3. Influence of the hydrochloric and sulfuric acids concentrations under ultrasounds irradiations

The effect of the presence of ultrasound irradiation on the extraction of molybdenum (VI) under different concentrations of hydrochloric and sulphuric acids was studied using the same organic and aqueous solutions as described above. Other experimental conditions were as follows: 20 s of sonication time, 200 W ultrasound power and 20% pulse radiation amplitude.

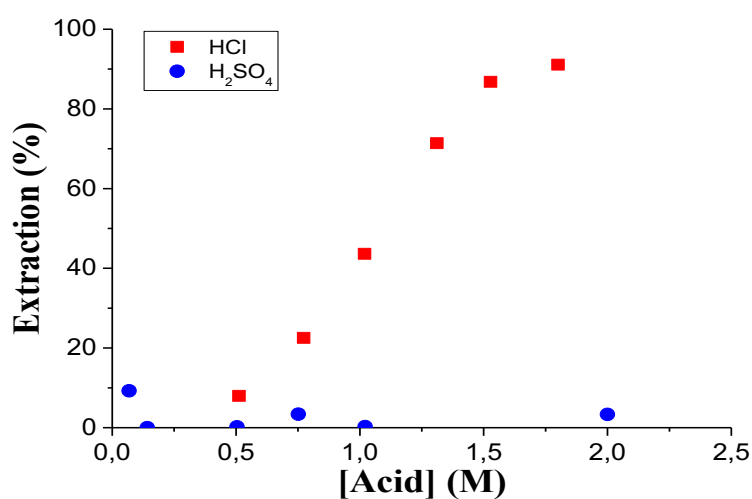
The dependence of the extraction of molybdenum (VI) metal ions with the hydrochloric and sulphuric acid concentration under ultrasound irradiation is shown in Fig. 6. Molybdenum (VI) show an increase in its extraction with increasing the initial HCl concentration. The yield increases markedly from 07.9% at 0.50 M to

91% at 1.80 M. The positive effect of the increase of the HCl concentration resulted in an increase of the yield by a factor of 11.5. Consequently, the increase of HCl concentration in the aqueous phase is favorable for the extraction of molybdenum.

On the other hand, the H<sub>2</sub>SO<sub>4</sub> acidity has little effect upon extraction of molybdenum which only decreases from 09.2 to 0% in the range of acidities examined. It should be noted that molybdenum (VI) ions show negligible extraction (< 10%) over the entire investigated range of sulphuric acid molarity. When the H<sub>2</sub>SO<sub>4</sub> concentration increases from 0.1 to 2 M, the extraction yield slightly decreases from 09.2 to 0%.

Furthermore, molybdenum (VI) is not extracted when the acidity increases from 0.14 to 2 M. These yields are insignificant and their low decreases may indicate some degree of increasing, unfavorable competition between protons and molybdenum (VI) for the ligand binding sites at the highest acid concentrations.

The figure 6 also shows that for the same concentration range of the two acids, i.e 0.5 to 1 M, the maximal extraction yield of molybdenum (VI) reached 43.6% at 1 M HCl. A minimal yield of 8% was obtained at 0.50 M HCl. On the other hand, the yields are nil for H<sub>2</sub>SO<sub>4</sub> concentrations varying between 0.5 and 1 M. The extraction of molybdenum (VI) under ultrasounds irradiations seems more advantageous by using in this order the TBP/HCl than the TBP/H<sub>2</sub>SO<sub>4</sub> systems.



**Fig. 6:** Molybdenum extraction yield versus concentration of acid (HCl, H<sub>2</sub>SO<sub>4</sub>) under ultrasound irradiation. [Mo]<sub>init</sub> = 100 mg.L<sup>-1</sup>, [TBP] = 40% (v/v), V<sub>aq</sub>/V<sub>org</sub> = 1, P<sub>max US</sub> = 200 W, f<sub>US</sub> = 24 kHz, A = 20%, t<sub>irrad US</sub> = 20 s, T = 26 ± 0.2 °C.

### 3.4. Comparison with conventional extraction

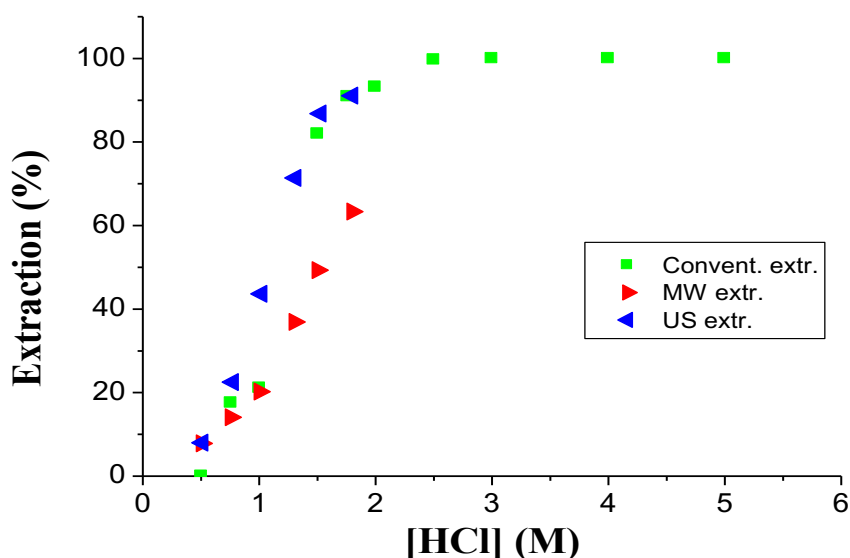
In this section the aqueous phases acidities having allowed to obtain low yields under conventional extraction are used to perform the tests of extractions of the molybdenum (VI) under microwave and ultrasounds irradiations.

#### 3.4.1. Influence of the concentration in HCl

In Fig. 7, a comparison is made of the molybdenum (VI) extraction, at various HCl concentrations conducted under the two extraction methods (microwave and ultrasound) to the conventional extraction method. Extractions yields values of molybdenum (VI) increased in a similar trend with the increase of HCl concentration. When the HCl concentration increases from 0.50 to 1.80 M, we attend a sensitive rise of the yield for three modes of extractions. The yields obtained under ultrasounds irradiations are, on the other hand, practically the same order of magnitude as those obtained under conventional extraction. It should be noted that under microwaves or ultrasounds irradiations, when HCl concentration is 0.50 M, a yield of 07.9% is obtained while under conventional extraction the yield is practically nil.

For HCl concentrations varying between 0.76 and 1.80 M, the maximal difference between the yields obtained under conventional extraction and those obtained under microwave irradiations reached 66.2% at 1.50 M HCl

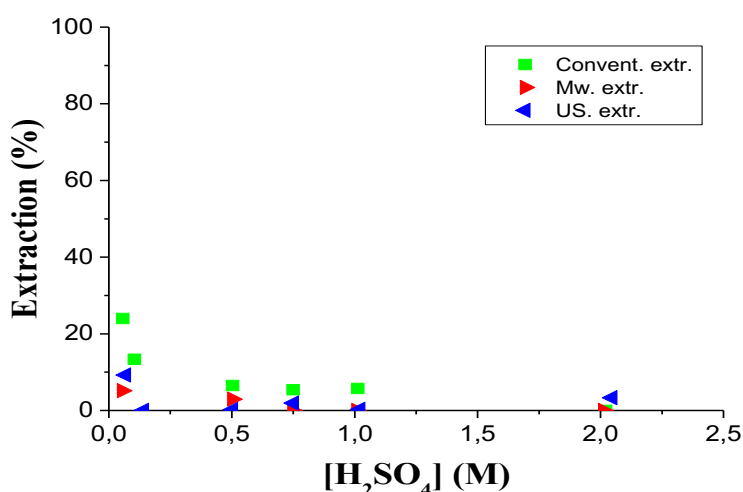
(Fig. 7). The effect of the activation by the ultrasounds irradiations the most marking for HCl concentrations ranging from 0.76 to 1.80 M, is obtained at 1 M HCl and where 43.6% of molybdenum were extracted. Moreover, noting that the latter yield is the double of that obtained under conventional extraction. The extraction of molybdenum (VI) under microwave or ultrasounds irradiations is therefore more advantageous compared with its conventional extraction only at 0.50 M HCl. For 1 M HCl, the use of the ultrasounds seems to be the most advantageous. On the other hand, for HCl concentrations varying between 0.76 and 1.80 M (with the exception of HCl at 1 M), the extraction of molybdenum (VI) under microwave irradiations is not advantageous because the obtained yields are lower than those obtained under conventional extraction.



**Fig. 7:** Molybdenum extraction yield versus concentration of HCl under conventional extraction:  $[\text{Mo}]_{\text{init}} = 100 \text{ mg.L}^{-1}$ ,  $[\text{TBP}] = 40\% \text{ (v/v)}$ ,  $V_{\text{aqu}}/V_{\text{org}} = 1$ ,  $T = 26\text{-}28 \text{ }^\circ\text{C}$ ,  $t_c = 10 \text{ min.}$ , under microwave irradiation:  $P_{\text{MW}} = 20 \text{ W}$ ,  $f_{\text{MW}} = 2.45 \text{ GHz}$ ,  $t_{\text{irrad MW}} = 20 \text{ s}$ ,  $T = 26 \pm 0.2 \text{ }^\circ\text{C}$  and under ultrasound irradiation:  $P_{\text{max US}} = 200 \text{ W}$ ,  $f_{\text{US}} = 24 \text{ kHz}$ ,  $A = 20\%$ ,  $t_{\text{irrad US}} = 20 \text{ s}$ ,  $T = 26 \pm 0.2 \text{ }^\circ\text{C}$ .

### 3.4.2. Influence of the concentration in sulfuric acid

In Fig. 8, a comparison is made of the molybdenum extraction, at various  $\text{H}_2\text{SO}_4$  concentrations conducted under the two extraction methods (microwave and ultrasound) to the conventional extraction method.

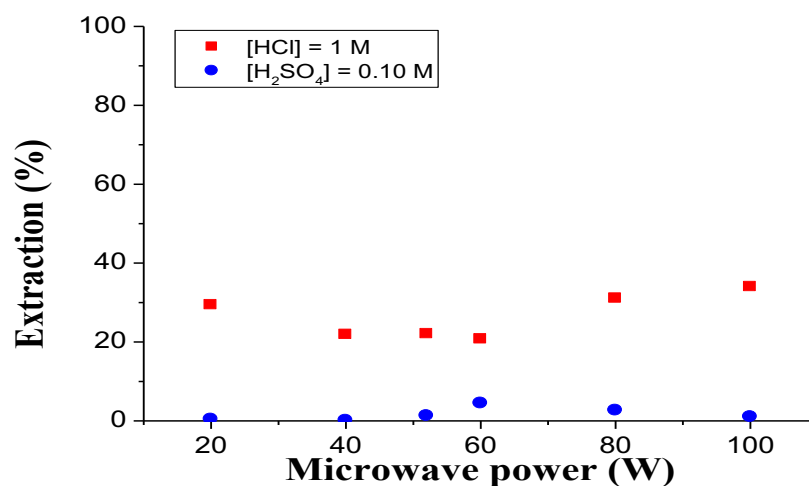


**Fig. 8:** Molybdenum extraction yield versus concentration of  $\text{H}_2\text{SO}_4$  under conventional extraction:  $[\text{Mo}]_{\text{init}} = 100 \text{ mg.L}^{-1}$ ,  $[\text{TBP}] = 40\% \text{ (v/v)}$ ,  $V_{\text{aqu}}/V_{\text{org}} = 1$ ,  $T = 26\text{-}28 \text{ }^\circ\text{C}$ ,  $t_c = 3 \text{ min.}$ , under microwave irradiation:  $P_{\text{MW}} = 20 \text{ W}$ ,  $f_{\text{MW}} = 2.45 \text{ GHz}$ ,  $t_{\text{irrad MW}} = 20 \text{ s}$ ,  $T = 26 \pm 0.2 \text{ }^\circ\text{C}$  and under ultrasound irradiation:  $P_{\text{max US}} = 200 \text{ W}$ ,  $f_{\text{US}} = 24 \text{ kHz}$ ,  $A = 20\%$ ,  $t_{\text{irrad US}} = 20 \text{ s}$ ,  $T = 26 \pm 0.2 \text{ }^\circ\text{C}$ .

The results obtained during these series of experiments are presented in Fig. 8. The results show that the  $\text{H}_2\text{SO}_4$  concentration do not greatly influences the extraction of molybdenum. For the three extraction methods, the increase of the  $\text{H}_2\text{SO}_4$  concentration resulted only in a slight decrease of the yield of extraction of the molybdenum (VI). Under conventional extraction, the extraction yields were found to decrease from 24 to 0% when the  $\text{H}_2\text{SO}_4$  concentration was varied from 0.1 and 2 M, respectively. From a practical point of view and contrary to our expectations, no positive effect of the ultrasounds or the microwaves irradiations on the molybdenum extraction was observed. Molybdenum is not extracted at 0.14-2 M  $\text{H}_2\text{SO}_4$  under microwaves and ultrasounds irradiations. The extraction of molybdenum (VI) by the conventional method is more advantageous than that conducted under microwave or ultrasounds irradiations in the range of 0.1-2 M  $\text{H}_2\text{SO}_4$  (Figure 8). The extractions yields values are very close for both microwave and ultrasounds irradiations in the acidity range (0.5-2 M). The yields obtained under ultrasounds irradiations are 1.8 times more greater than those obtained under microwave irradiations, for 0.1 M  $\text{H}_2\text{SO}_4$ . While the yields obtained under conventional extraction are 4.7 and 2.6 times greater than those obtained under microwave and ultrasounds irradiations, respectively, for 0.1 M  $\text{H}_2\text{SO}_4$ . For these diverse tests of extractions of molybdenum (VI) conducted under microwave and ultrasounds irradiations from HCl and  $\text{H}_2\text{SO}_4$  solutions, the yields are obtained at a much lower time compared with time used under conventional extraction, that is a ratio ( $t_{\text{agit}}/t_{\text{irrad MO}} = 30$ ) in the case of HCl and a ratio ( $t_{\text{agit}}/t_{\text{irrad MO}} = 9$ ) in the case of  $\text{H}_2\text{SO}_4$ . These ratios of time are calculated for microwave and ultrasounds irradiations times of 20 s and agitations times under conventional extraction of 10 and 3 min for HCl and  $\text{H}_2\text{SO}_4$ , respectively.

### 3.5. Effect of microwave power on molybdenum extraction

To investigate the effects of microwave power on molybdenum (VI) extraction, the tests were performed under the following typical conditions: The extraction of Mo(VI) ions ( $100 \text{ mg.L}^{-1}$ ) was conducted from 1 M HCl and 0.1 M  $\text{H}_2\text{SO}_4$  solutions with 40% (v/v) TBP, the range of microwave power was 20-100 W and the microwave irradiation time was 20 s. The microwave power is an important factor to be considered during metal extraction studies. Fig. 9 shows the plots of percent extraction of molybdenum (VI) versus microwave irradiation power for extraction of molybdenum (VI) with TBP from 1 M HCl solutions.



**Fig. 9:** Influence of microwave power on the extraction yield of molybdenum from 1 M HCl and 0.10 M  $\text{H}_2\text{SO}_4$  solutions.  $[\text{Mo}]_{\text{init}} = 100 \text{ mg.L}^{-1}$ ,  $[\text{TBP}] = 40\%$  (v/v),  $V_{\text{aqu}}/V_{\text{org}} = 1$ ,  $f_{\text{MW}} = 2.45 \text{ GHz}$ ,  $t_{\text{irrad MW}} = 20 \text{ s}$ ,  $T = 26 \pm 0.2 \text{ }^\circ\text{C}$ .

The results show that for extractions conducted from 1 M HCl with the increase of microwave power, initially a sharp decrease in extraction yield was obtained with the increase in microwave power from 20 W to 60 W. The extraction yield show a minimum of 21% corresponding to a 60 W power supply. Increasing the power beyond this value tends to increase extraction yield slightly which can be explained by a better activation of the extraction reaction. The molybdenum efficiency reaches 40.1% when the microwave power is set at 100 W. When the microwave power was increased from 60 W to 100 W more electromagnetic energy was transferred to the extraction system quickly and improved the extraction efficiency. Obviously, the increasing of microwave

power beyond 60 W leads to a higher extraction rate of molybdenum. Therefore, 100 W of microwave power was used in the further experiments.

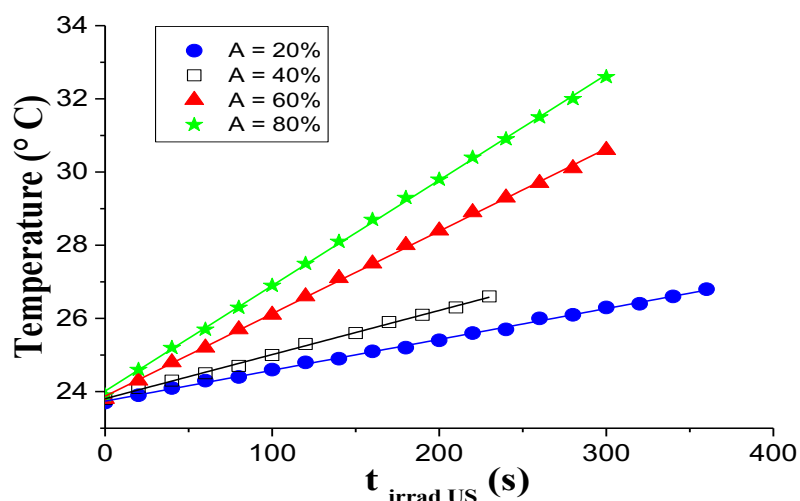
In microwave field, the migration of ionic species or rotation of dipolar species promote the liquid-liquid reaction process due to the increased contact area of reactants. This last yield is obtained for 20 s microwave irradiation. Comparatively, the yields obtained for microwave power greater than 60 W are certainly more important than the yield obtained under conventional extraction which is only 21.1%. This last yield is obtained for an agitation time relatively slightly longer of 10 min. The extraction yield of molybdenum (VI) under microwave was about 2-folds of that extracted under conventional extraction. Also, the results show that the time of extraction for conventional extraction was about 30-folds of time of extraction with microwave irradiation, respectively. According to these results, microwave irradiations can greatly reduce the extraction time for the same conditions of extraction compared with conventional extraction method.

The effect of microwave power on the extraction yield of molybdenum (VI) is shown in Fig. 9 when the extractions are made from 0.10 M  $\text{H}_2\text{SO}_4$  aqueous phases. The extraction yield remained almost unchanged over the microwave power range 20-60 W. The increase of the microwave irradiation power of the microwave irradiations has no notable impact on the extraction of the molybdenum (VI). The extraction yield of molybdenum (VI) is poor as very low yield of 01.6% are obtained under the present experimental conditions. The activation by the microwave irradiations is not apparently visible. These values of yields are much less important than the one obtained under conventional extraction which is equal to 13.4%. This latter yield was obtained for 3 min agitation time of aqueous and organic phases.

### 3.6. Influence of the ultrasound radiation amplitude on the calorimetric power

The electric power is one of the parameters generally used to characterize the ultrasounds systems. It is an important factor to be considered during metal extraction under ultrasounds irradiations. The acoustic power corresponds to the transmitted energy by sound waves to the reaction medium.

In the equation 1, for the calculation of the calorimetric power (acoustics) dissipated under ultrasounds irradiations, the term  $(dT/dt)$  is approximated by the numerical value of the slope of the lines obtained (Fig. 10). The results of the calorimetric study are recorded in table 2.



**Fig. 10:** Examples of recording of temperature during calorimetric experiments for diverse ultrasound irradiation amplitudes,  $m = 200$  g and  $f = 24$  kHz.

The evolution of the temperature of 200 g of distilled water according to the exposure time under the ultrasounds irradiations is represented in figure 11. This figure shows clearly that the temperature of the water increases linearly with the exposure time under the ultrasounds irradiations, for all the tested ultrasound radiation amplitudes. The calibration plots (Fig. 10) show that the ultrasound radiation amplitude influences strongly the temperature of the water for the diverse sonication time durations of the ultrasounds irradiations tested. When the ultrasound radiation amplitude increases the temperature increases, for the diverse time of the



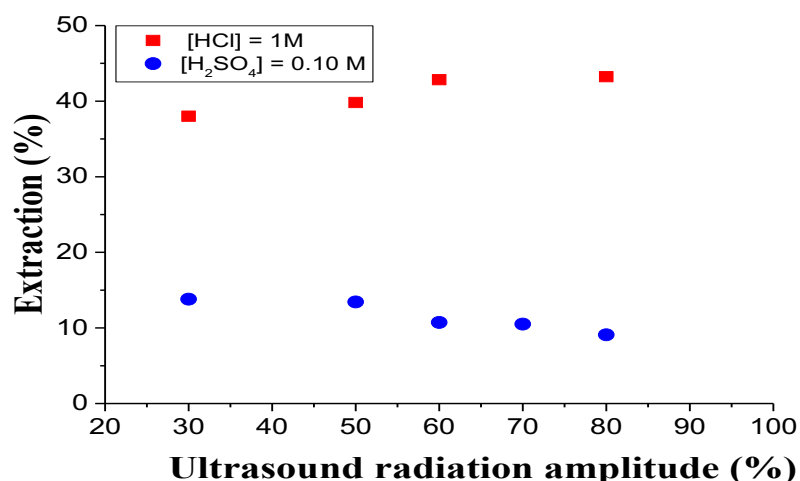
used ultrasounds irradiations. From table 2, the obtained results unequivocally show that the ultrasound radiation amplitude influences strongly the calorimetric power. The increase of the ultrasound radiation amplitude from 30% to 80% resulted in an significant improvement in the calorimetric power dissipated under ultrasounds irradiations which increases from 7 W to 24.1 W, respectively.

**Table 2:** Calorimetric power (acoustics) dissipated according to the ultrasound irradiation amplitude.

Ultrasound radiation amplitude, %	Slope (dT/dt), K.s <sup>-1</sup>	Calorimetric power, W
20	0.0084	7.0
40	0.0121	10.1
60	0.0226	18.9
80	0.0288	24.1

### 3.7. Influence of sonication ultrasound radiation amplitude

In order to obtain the maximum extraction yield of molybdenum (VI), effects of the pulse radiation amplitude varying from 20 to 80% on the extracted yield were studied. Aqueous solutions contained 100 ppm Mo(VI) dissolved in either 1 M HCl or 0.1 M H<sub>2</sub>SO<sub>4</sub>, whereas organic solutions were of 40% (v/v) TBP in n-hexane. The extraction of molybdenum (VI) was carried out under the following conditions: 20 s of ultrasound irradiation time with 200 W ultrasound power and 24 kHz ultrasound frequency. Fig. 11 shows that the ultrasound radiation amplitude influences in a significant way the yield of molybdenum (VI) extraction.



**Fig. 11:** Influence of ultrasound radiation amplitude on the extraction yield of molybdenum from 1 M HCl and 0.10 M H<sub>2</sub>SO<sub>4</sub> solutions. [Mo]<sub>init</sub> = 100 mg.L<sup>-1</sup>, [TBP] = 40% (v/v), V<sub>aq</sub>/V<sub>org</sub> = 1, P<sub>max US</sub> = 200 W, f<sub>US</sub> = 24 kHz, t<sub>irrad US</sub> = 20 s, T = 26 ± 0.2 °C.

It was found that for the extractions conducted from 1 M HCl, when the radiation amplitude was increased from 30% to 80%, the yield of molybdenum (VI) increases slightly from 38% to 43.2%, there is 13.8% increase in extraction of molybdenum (VI). For an ultrasound radiation amplitude of 80%, the yield obtained is practically the double of that obtained under conventional extraction and which is equal to 21.1%.

The increase of the extraction yield of molybdenum (VI) with the ultrasound radiation amplitude is due to the large number of cavitation bubbles generated by the ultrasounds irradiations [40, 41, 51]. There is therefore a better activation of the extraction reaction by the ultrasounds. The yields are obtained for an ultrasound irradiation time of 20 s. This latter time is much lower than the agitation time of both phases of 10 min used under conventional extraction.

Fig. 11 also shows that ultrasound radiation amplitude has a significant effect on the extraction of molybdenum (VI). On the other hand, when the extraction of molybdenum (VI) takes place from 0.10 M H<sub>2</sub>SO<sub>4</sub>, the plot of percentage extraction vs. ultrasound radiation amplitude showed that the extraction yield was proportional to pulse ultrasound radiation amplitude and that the extraction yield slightly decreases from a maximal extraction

yield of 13.8% to 09.1% as the ultrasound radiation amplitude increases. The unfavorable effect of the increase of the ultrasound radiation amplitude from 30 to 80% has engendered a relative decrease of 51.7% of the extraction yield. This may be due to competition between molybdenum and H<sub>2</sub>SO<sub>4</sub> to associate with the extractant [19]. This type of behavior indicates the formation of non-extractable species in the aqueous phase at higher concentration, or polymerization in the organic phase. The ultrasounds have therefore an unfavorable effect on the extraction reaction of the molybdenum (VI). The amplitude of ultrasound energy was found to have a negative effect on molybdenum extraction efficiency (i.e., the higher the amplitude of the ultrasound source, the lower the extraction yields). This fact could be related to the so-called decoupling effect [52].

The maximal difference between the yields obtained from 0.10 M H<sub>2</sub>SO<sub>4</sub> under ultrasounds irradiations, for an ultrasound radiation amplitude of 80%, and that obtained under conventional extraction which is 13.4%, can reach the value of 46.8%.

By comparison, it should be noted that for the series of extractions of the molybdenum (VI) conducted under ultrasounds irradiations, the yields are obtained at a much lower time compared with that used under conventional extraction in a ratio ( $t_{\text{agit}}/t_{\text{irrad US}} = 30$ ) in the case of 1 M HCl and a ratio ( $t_{\text{agit}}/t_{\text{irrad US}} = 9$ ) in the case of 0.10 M H<sub>2</sub>SO<sub>4</sub>. These ratios are calculated for ultrasounds irradiations times of 20 s and agitations times under conventional extraction of 10 and 3 min in the case of 1 M HCl and 0.10 M H<sub>2</sub>SO<sub>4</sub>, respectively. The intensity of the ultrasounds irradiations transmitted to the media is directly related to the ultrasound radiation amplitude of the sonotrode. Generally, the increase of the intensity of the ultrasounds irradiations causes an increase of the sonochemical effect. However, a high vibration ultrasound radiation amplitude generates a large number of cavitation bubbles that will block the passage of these ultrasounds irradiations [38, 40, 41].

Consequently, the MAE and UAE methods reported in this study proved to be efficient methods for extracting molybdenum from aqueous acidic solutions with TBP in considerably shorter extraction times. The extraction yields were better compared to conventional solvent extraction method [15, 19, 23, 25].

## Conclusion

The present investigations clearly highlight that molybdenum can be extracted by Microwave-assisted Extraction (MAE) and Ultrasound-assisted Extraction (UAE) techniques from hydrochloric and sulphuric aqueous acid solutions using an organophosphorus extractant (TBP) dissolved in n-hexane. In addition, the conventional extraction was also used and compared to MAE and UAE methods. The effects of irradiation time, microwave power, ultrasound irradiation amplitude and acid concentration were investigated under MAE and UAE. In general, both extraction method and operating condition significantly affected the extraction yield of molybdenum. The main advantages of these non-conventional techniques are the large reduction in extraction time and the higher extraction yields obtained at low HCl concentrations (HCl < 1 M). For 1 M HCl high extraction yields were also obtained for 100 W irradiation power under MAE and 80% pulse amplitude under UAE. These high extraction yields obtained by applying MAE and UAE techniques can be attributed to an increase of surface area under the action of mechanical activation. The current employed techniques MAE and UAE proved to be efficient and confirmed their reliability for the extraction of molybdenum. These MAE and UAE technologies will certainly be more attractive extraction methods in the future.

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