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Removal of aluminium and iron ions from phosphoric acid by precipitation of organo-metallic complex using organophosphorous reagent

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Abstract

The industrial phosphoric acid (H_3PO_4) is rich of impurities including heavy metals such as aluminum, iron and magnesium which considered the most dangerous metals presents with high quantity (more than 2500 mg/L) in the Tunisian industrial phosphoric acid. This work deals with the iron and aluminum removal from phosphoric acid at low pH by precipitation of organo-metallic complex formed using an organophosphorus reagent (NTMTP). The effect of various parameters such as initial phosphoric acid concentration, initial metal ion concentration, NTMTP amount, contacting time and temperature were investigated for monometallic and bimetallic phosphoric acid solutions. The experimental results obtained, showed that the precipitation-complexation treatment used was effective for the removal of more than 90 % of iron ions and 80 % of aluminum from the phosphoric acid (1M). The highest degrees of acid purification were achieved in the first five minutes of the process.

1. Introduction

The farmers should use more fertilizers to increase the productivity and growth quality of plants, become more effective after the recent blaze of the world level of the alimentary products. According to the study undertaken by the International fertilizer industry association (IFA) published in December 2010, the world use of fertilizers would have increased by 5.2 % into 2009/2010. In 2010, the world exploitation of phosphate raw and the phosphoric acid production increased simultaneously by 10 % compared to 2009 [1]. Another study of Union European concerning the most producer of phosphoric acid all over the word, made by YARA (Finlande, 2014) [2]: show that Tunisia is one of the six first countries of high fertilizer production (Table 1). Taking into account these announced rises, it becomes crucial, for environmental reasons, to avoid to the maximum pollution by metals. Fertilizers containing phosphate which are massively widespread in the grounds must consequently contain fewer impurities. The preliminary elimination of these impurities brought by the phosphoric acid so takes all its sense.

The phosphoric acid is the second mineral acid produced after the sulphuric acid. Its production in Tunisia represents approximately 5000 tons of phosphate in 2014 [2]. It is used mainly as raw material for the production of fertilizers but also in the synthesis of pharmaceutical, alimentary products and formulation of the detergents, etc.

Industrially, it is produced from phosphate raw (Ca_{10} $(PO_4)_6$ F_2) either by thermal way or by wet process according to the reaction:

$$Ca_{10}(PO_4)_6F_2 + 10\,H_2SO_4 + 20\,H_2O \longrightarrow 6\,H_3PO_4 + 10\,CaSO_4.2H_2O + 2\,HF$$

The first way leads to a highly pure acid but it is very expensive in energy. The second, less expensive, provides an acid relatively charged in dissolved impurities or suspension, whose source is clearly the initial phosphate rock.

Table 1: World's Phosphate Production, YARA (Finlande, 2014) [2]

Country	Phosphate production	Country	Phosphate production
China	100.000	Egypt	6.000
Marroco	30.000	Jordan	6.000
United-State	27.100	Tunisia	5.000
Russia	10.000	Saoudi Arabia	3.000
Brasil	6.750	-	-

Indeed, approximately 10% of the impurities contained in the phosphate rock are found in the produced acid [3]. The presence of these impurities affects the quality and the quantity of the phosphoric acid [4, 5]: they influence the physico-chemical properties of the acid, cause problems during its concentration, its storage and its commercialization. For this reason, about 95% of the acid produced by the wet process is directly used as fertilizers and excluded from the use in non fertilizer applications [6].

Among these impurities, iron, aluminum and magnesium are the most dangerous metals presents in the Tunisianindustrial phosphoric acid (44% P_2O_5) (table 2).

Table 2: Principal impurities contained in the Tunisian industrial phosphoric acid (44% P_2O_5).

Al (mg/L)	Fe (mg/L)	Mg (mg/L)	Cd (mg/L)	Cr (mg/L)	Mn (mg/L)	V (mg/L)	Zn (mg/L)
>3700	2500	>5000	30	250	30	60	230

The majority of these heavy metals present such number of common properties, which make them dangerous for the three following principal reasons:

- Heavy metals are non-biodegradable in rapport of time.
- They are toxic with very weak concentrations.
- They tend to accumulate in the alive systems.

Iron for example is present in the majority of commercial phosphates at variable contents going from 0.1-0.4% in Fe_2O_3 Moroccan phosphate [7] up to 3-4% Egyptian phosphate [7, 3]. While iron content, negatively affects the solubility of fertilizer P_2O_5 in water [8]. Many researches show also that aluminum (III) is implicated in a number of toxic process or Alzheimer's disease [9, 10, 11]; therefore high aluminum contents should be avoided.

The elimination of the metal impurities from the phosphoric acid produced worried the scientists especially since the last decade. Among the techniques used, we find the extraction by solvents, the ions flotation, the process of ions exchange, filtration on membrane (ultrafiltration, nanofiltration), opposite osmosis and the electrochemical techniques such as electrodialysis, chemical and electrochemical precipitation or the electrodeposition then adsorption [12, 13, 14, 15].

These methods present some disadvantages at the industrial scale, among them: The use of expensive and sophisticated equipment.

- Difficult operation on industrial site and lack of applicability of certain processes to all the categories of phosphoric acid.
- Difficulty of separation of the phases.

Opposite osmosis is a technique which requires a high consumption of energy due to the high necessary pressure (20 to 100 bar) [16, 17].

- Nano and ultra filtration are expensive and cause problems of clogging of the membrane [18, 19].
- The processes of exchange of ions are not adapted to eliminate metal on an industrial scale from production [20].

- Flotation requires a series of optimization in order to improve the effectiveness of displacement of heavy metal [21, 22].

The most applied objective of this issue relates to the study of the conditions of elimination of these impurities contained in the phosphoric acid. The high cost of the current processes, the deterioration of the medium or the impossibility of getting the wished norms, remain for the moment a barrier to the industrial application of these processes.

The extraction of heavy metals in acidic medium is a delicate problem. The principal difficulty comes to the fact that the majority of the commercial reagents of extraction are weak acids and that the complexes which they form with metals are not very stable in very acidic medium from where a poor capacity of extraction. Moreover among the reagents making it possible to obtain appreciable amount of extraction in very acidic medium (pH lower than 2), few compounds lead to extractions which are at the same time fast and selective.

Generally, a formation of metal complexes is necessary to the transfer of phase and this one can be obtained using a single complexant and by a direct extraction with precipitation and or filtration. This offers interesting possibilities in extraction of heavy metals in acidic media.

Several work concerned the use of the technique of complexation of the heavy metals contained in acidic media [23-27] in coupling with a method of solvent extraction, by flotation or adsorption: we note EHPA, OPAP, SIGNALS 99, Cyanex, HDDNSA, TOA, DNNSA, TPPS, Kelex 100, NaDDT, TOPO, as well as adsorbents like activated carbon, zeolites and the polyamines.

We will so be interested in this work of the use of a complexation method coupled by a direct recovery by precipitation and or filtration of organometallic complexes [23, 25, 27] to reduce to the maximum the content of the iron and aluminum in phosphoric acid.

Several families of precipitating reagents can be considered with an aim of determining their effectiveness of complexing with metals in the phosphoric acid.

2. Experimental

2.1. *Materials*

The phosphoric acid used in this study is a synthetic acid produced by Merck Company of Germany for ProAnalysis. It has a purity of 85 % and a density of 1.71. Concerning the metal salts used to prepare the different contents of iron and aluminum dissociated in the acidic solution: are salts providing by the Sigma Aldrich $AlCl_3.6H_2O$ and $FeCl_3.6H_2O$.

The complexing reagent that we have used is purshased from Aldrich and represents an organophosphorous complexing deriving from the family of nitrilo-tris (methyene) triphosphonic (NTMTP) with a density of 1.3 and 50 % of purity. The choice of this complexant was based from a previous work[23] that had developed a similar reagent (the triphosphonic ester) for high removal of uranium in acidic solutions. His special property is to form stable metal complexes in acid or even very acid medium thanks to phosphonic groupings responsible for the activity of chelating. It is characterized also by the insolubility of the complexes that he formed which makes easy to extract them.

The experimental device used in this work consists of three micro reactors with double envelope put in series; the capacity of each one is 500 mL (figure 1).

2.2 *Precipitation and complexation Method*

The process initially consists of the following steps;

1. Stirring the acid containing the metal with an appropriate amount of reagent at the ambient temperature for a well-defined time (steps 1-3);
2. Centrifuge the solutions obtained with 6000 rpm during 15 minutes (step 4);
3. filter the remaining solution (centrifugal supernatant) in Buchner system through a membrane in poly sulfone with 0.45 micrometers of porosity (step5);
4. Pass the filtrate for analysis under the ICP (inductively coupled plasma/ atomic emission spectrometry). The different values of concentrations of metal ions are given with 5% of error.

The organo-metallic complex formed by precipitation (step 6) will be passed to DRX and IR analysis for their characterizations.

The optimization of the treatment suggested by precipitation requires the study of the effect of several parameters, such as: initial concentration of the acid, initial content of metal, time of contact, amount of the

complexing reagent, synergy of the two metals in the same solution, temperature, effect of the treatment on the pH of the solution and on the initial content of P_2O_5 of the solution.
Concerning the initial concentration of the phosphoric acid, we have tested three concentrations 1, 3 and 5 M to evaluate the efficiency of the treatment for a diluted and concentrated acid.

Figure 1: Experimental process device.

The choice of the initial metal concentration was with an aim of approaching from the content present in the industrial acid (Al more than 3700 mg/L and Fe nearly to 2500 mg/L). The average value used is about 2500 ppm and like variation, we have studied three concentrations 2000, 3000 and 4000 mg/L. For the time of contact, we have started with 2 hours of agitation to reach equilibrium and to evaluate it up from 5 to 10 minutes.
The ratio between complexing reagent and metal was studied initially in the stoechiometric ratio and then according to several fractions.
The temperature inside the reactor was fixed at 25°C and then it is increased to 80°C to represent the temperature of industrial production.
The precipitation efficiency or the removal percentage R (%) was calculated as:

$$R(\%) = \frac{(Co - Ce) * 100}{Co}$$

Where C_o, C_e are respectively the initial and the equilibrium concentrations of metal in acidic solution (ppm).

5. Results and discussion

A test of precipitation was carried out for the two metals for a molar concentration of phosphoric acid, a content of 2500 mg/L of metal and a stoechiometric ratio NTMTP/metal which refer to 2.13 mL of NTMTP for Al and 1.03 mL for Fe. As a result we have recovered after two hours of agitation a gelatinous white precipitate for aluminum and beige one for the iron. An optimization of the parameters of the process is obligatory to have an effective interpretation.

3.1. Effect of the initial concentration of the phosphoric acid

Three samples were put at fixed temperature 25°C, stirring velocity of 300 rpm, a time of 2 hours of agitation, 2500 mg/L of metal content and a stoechiometric amount of NTMTP/metal. Three concentrations of phosphoric acid were respectively studied 1, 3 and 5 M.
Figure 2 shows well that the concentrated acid medium decrease the aluminum precipitation. It is noticed that with initial acid concentration of 5 M (approximately 25% ± 2% in P_2O_5) the percentage of aluminum removal is approximately 10%.
For the case of iron, the effect of the initial acid concentration does not influence much its elimination, its removal percentage passes from 99 to 80% by increasing the concentration of acid from 1 to 5 M.

3.2 Effect of the time of contact

By fixing the temperature at 25°C, the stirring velocity to 300 rpm, the ratio of NTMTP-metal is stoechiometric, the initial concentration of metal with 2500 mg/L and the initial concentration phosphoric acid is 1M: the analyses with ICP showed that a contact time of one hour is sufficient to recover the maximum of metals.

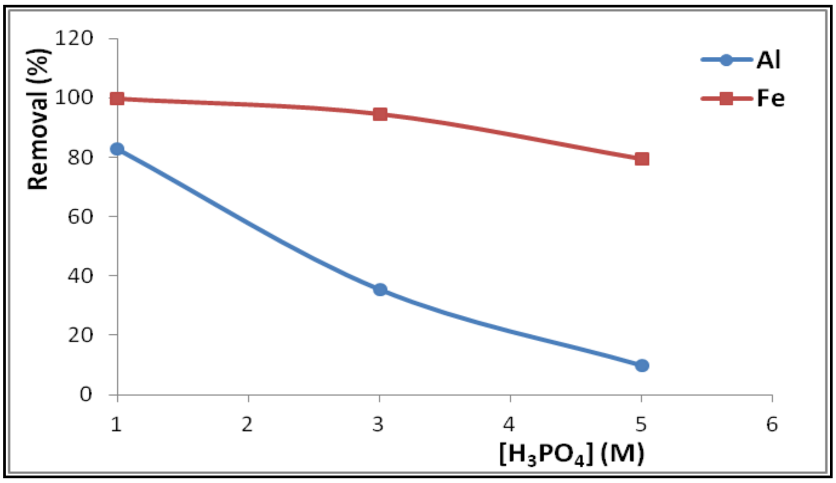

Figure 2: Effect of the initial concentration of the acid for iron and aluminum removal.

Indeed figure 3 shows well that the maximum of elimination did not change during all the hour, the reaction is almost instantaneous. We find that 99% of iron removal and 83 to 85% of aluminum elimination were achieved in the first five minutes. The highest degrees of acid purification were achieved in the first five minutes of the process.

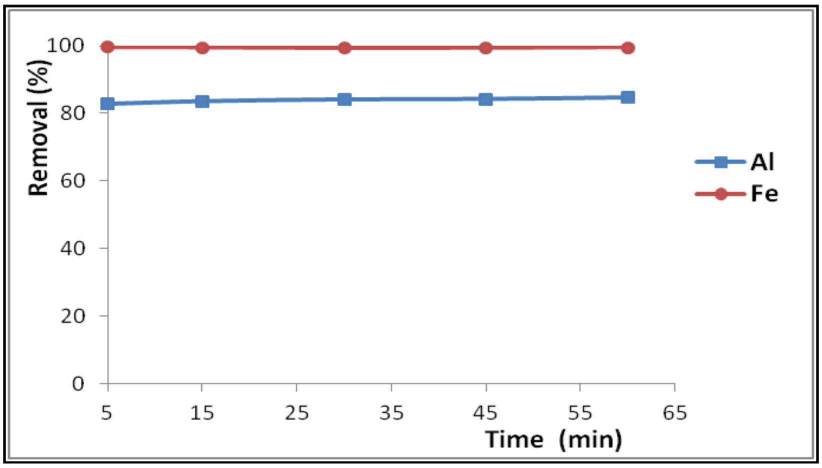

Figure 3: Effect of the time of contact for iron and aluminum removal.

3.3 Effect of the initial concentration of the metal

Six samples were prepared with two metals for a stoechiometric amount of NTMTP-metal, for an initial concentration of acid 1M, one hour of contact time, a temperature of 25°C and for initial concentrations of metal variable from 2000 to 4000 mg/L. According to the obtained results, we noticed that for the case of iron, the increase of the initial concentration of metal slightly modified the capacity of its elimination. The percentage of iron elimination is maximum some is its initial concentration.

Figure 4 shows well that in the case of aluminum, its percentage of removal increases according to its initial concentration. It is noticed that 7% of elimination are obtained while passing from an initial concentration of 2000 to 4000 mg/L.

3.4. Effect of the ratio of metal-NTMTP

By fixing the temperature at 25°C, the stirring velocity to approximately 300 rpm, the initial concentration of metal with 2500 mg/L, the initial concentration of phosphoric acid with 1M: We have varied the metal-reagent ratio in the case of aluminum respectively of (1:$\frac{1}{4}$, 1:$\frac{1}{2}$, 1:$\frac{3}{2}$, 1: 2 to 1: 3) and for the case of the iron of (1:$\frac{1}{4}$ 1:$\frac{1}{2}$ to 1:$\frac{3}{4}$, 1:2 to 1: 3).

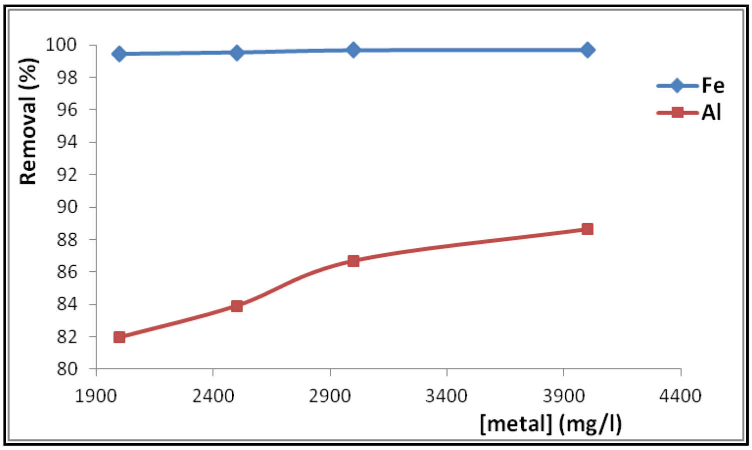

Figure 4: Effect of the initial concentration of metal for iron and aluminum removal.

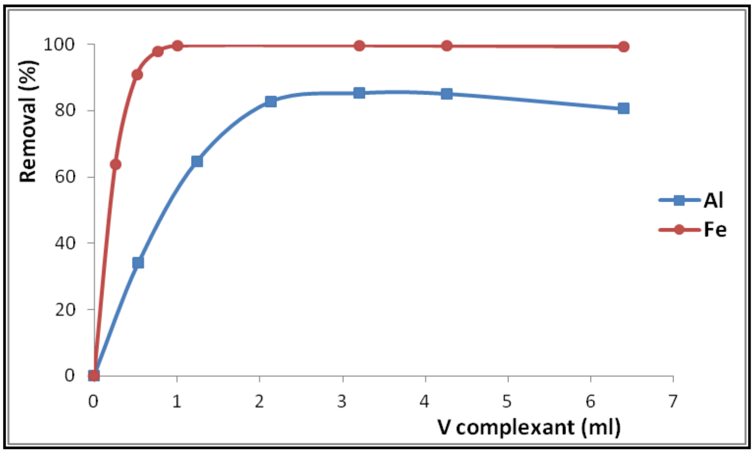

Figure 5: Effect of the metal-NTMTP ratio for iron and aluminum removal.

The analyses by ICP showed that the capacity of elimination of iron reached its maximum 99.6 % for a metal-NTMTP ratio slightly higher than (1:$\frac{3}{4}$). On the other hand, figure 5 shows that in the case of aluminum we notice a maximum of removal near to 85.4 % for a higher ratio of (1:$\frac{3}{2}$).

3.5. Effect of the synergy of the bimetal in same solution

In this part, we wanted to study the effectiveness of the treatment towards the elimination of two metals but this time sets in the same solution. So we are interesting to maximize the removal of aluminum in presence of iron.

Three samples were prepared by varying each time the metal-NTMTP ratioof (1:$\frac{3}{2}$, 1:2 to 1: 3) while reasoning on the aluminum stoechiometry. Figure 6 shows that the capacity of aluminum elimination is improved with the presence of iron; we have noticed that it passed from 85 to 93% for a metal-NTMTP ratio of (1: 2). We can conclude that the presence of other metals sets in the same solution does not affect the effectiveness of the treatment but on the other hand for aluminum for example it maximized its recovery.

3.4. Effect of the Temperature

By fixing the initial concentration of metal at 2500 mg/L and that of the acid with 1M, the time of agitation to approximately 1 hour: we varied the temperature from 25 to 80°C for the two metal solutions for a stoechiometric ratio of iron-NTMTP and a ratio of (1: $\frac{3}{2}$) of aluminum-NTMTP.

The Figure 7 shows well that the temperature does not have an effect on the percentage of removal; we find that iron always reached its maximum capacity of 99% despite the increase of its temperature and similar for aluminum with a light increase from 85 to 87 %.

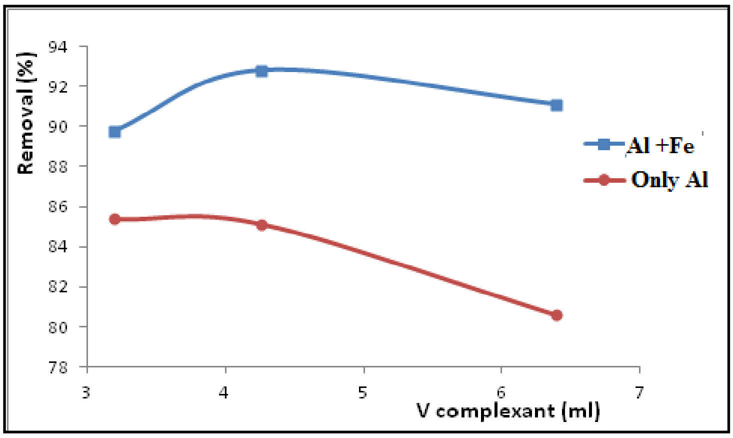

Figure 6: Effect of the synergy of two metals for iron and aluminum removal.

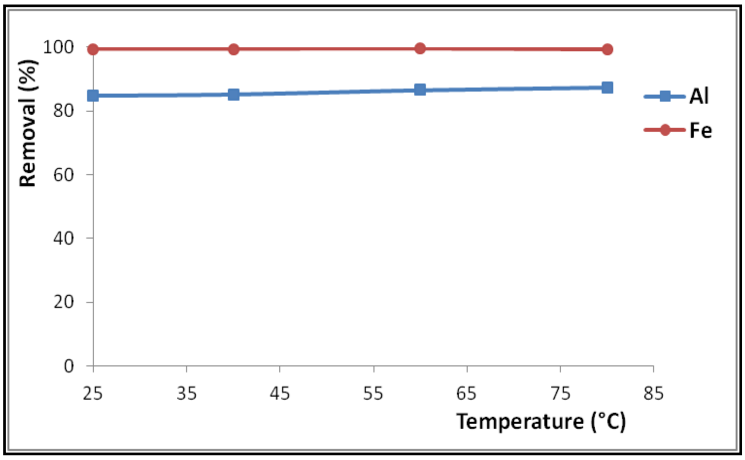

Figure 7: Effect of the temperature for iron and aluminum removal.

3.5. Effect of the treatment on the pH of the solution

We have studied the influence of the treatment on the variation of the pH of the solution containing two metals with a molar initial concentration of phosphoric acid. It is noticed that it has a light reduction in the pH some is the initial concentration of metal (figure 8 and figure 9). This variation of the pH is justified because the reaction of the complexation of metal is accompanied by the release of the H^+ ions[16] and then by the reduction in the pH of the solution. The reaction of the complexation is mentioned below:

$$C_3H_{12}O_9NP_3 + M^{3+} \longrightarrow C_3H_9O_9NP_3M + 3\ H^+$$

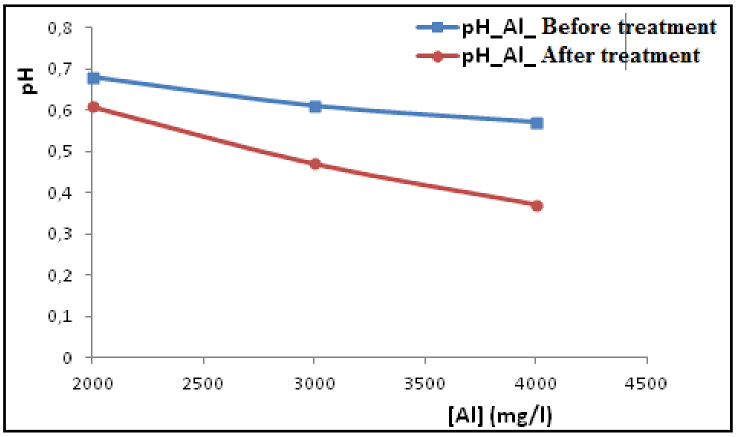

Figure 8: Effect of the treatment on the pH of the solution containing aluminum.

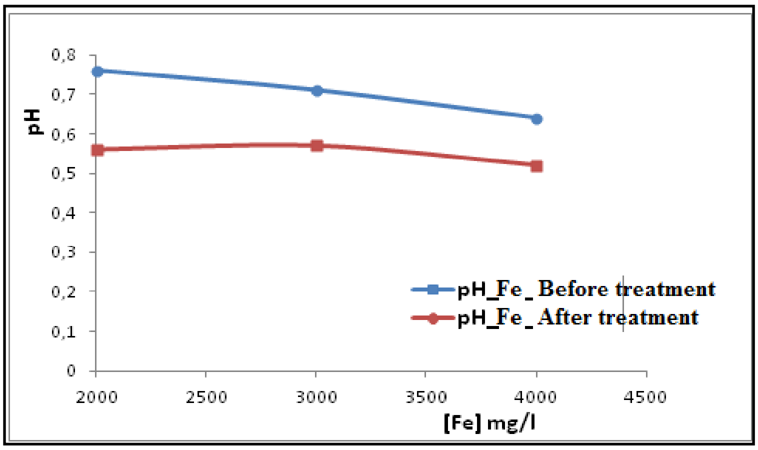

Figure 9: Effect of the treatment on the pH of the solution containing iron.

3.6. Effect of the treatment on the P_2O_5 content of the solution

While varying the initial concentration of the metal and with a stoechiometric ratio of the NTMTP/metal, we have studying the effect of the treatment of metal on the initial concentration of phosphoric acid.

Figure 10 show that it has an excess of P_2O_5 after the treatment for the two metals, which is explained by the contribution of the phosphate ions through the complexing reagent since it is also an organophosphorouscompound. It is noticed that excess for iron increases by 12 to 18% whereas for aluminum is 1 to 6% if we have varying the initial metal concentration from 2000 to 4000 mg/L.

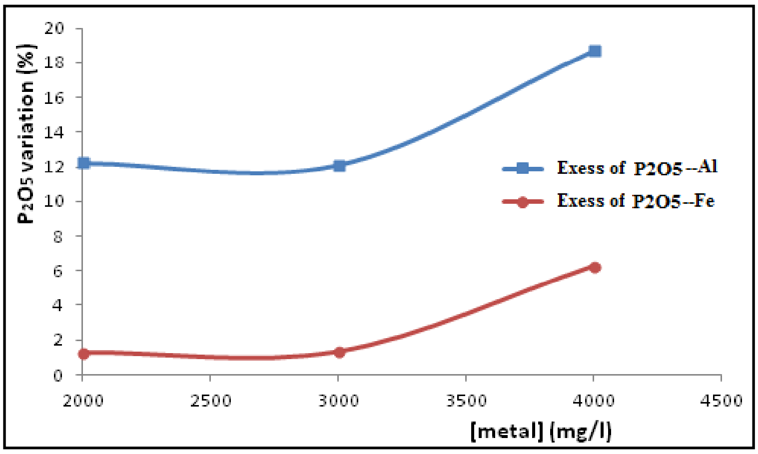

Figure 10: Effect of the treatment on the P_2O_5 initial content of the solution.

Conclusion

This work concerned the purification of phosphoric acid containing high percentages of aluminum and iron (more than 2500 mg/L). The method of precipitation used in this study to remove these metalswith an organophosphorous reagent then recovered by Buchner filtration, has exploiting high degree of purification.

We obtained more than 99 % for iron removal and more than 85% for aluminum one in molar phosphoric acid solutions, an ambient temperature, a 2500 mg/l of initial metal content and for a stoechiometric ratio of iron-NTMTP and a ratio of (1: $\frac{3}{2}$) of aluminum-NTMTP.

The synergy of the two metals in the same solution, was improved the recovery of aluminum. Its removal passes from 85 to 93 % for an aluminum-NTMTP ratio of (1: 2).

These very promising results encourage us to extend the protocol to other ions present in the acid, such as cadmium, magnesium and or with other types of complexing reagents and why not apply this treatment to an industrial acid.

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