Qualitative and quantitative optimization of phosphoric acid production from phosphate (Youssoufia of Morocco), sulfuric acid, hydrochloric acid, or acetic acid. Validity and irregularity.

Abstract:

The production of fertilizers from phosphate has a significant impact on crop yields. To this end, it is necessary to closely monitor the production of phosphoric acid, an essential component in fertilizer manufacturing. This acid is produced by the reaction of phosphate with sulfuric acid; this is known as the sulfuric acid process.

In Morocco, the sulfuric acid process for phosphoric acid production is, to date, the only process in use. However, it has numerous drawbacks: the generation of large volumes of waste (5 tons of phosphogypsum per ton of P_2O_5 produced), the radioactivity and acidity of the phosphogypsum, the failure to recover by-products of high commercial value, and the existence of strict environmental restrictions, particularly regarding process optimization and the reduction of pollutants.

In this work, we have focused on a new option to reduce the costs and environmental impacts associated with phosphoric acid production, based on the study of two alternative routes to the traditional one: the hydrochloric acid method and the acetic acid method, which may offer greater e<cological and technical advantages for the phosphoric acid industry.

1/ Introduction:

Phosphoric acid, also known as orthophosphoric acid, is a phosphorus-based oxoacid with the formula H_3PO_4. It is a mineral acid obtained by processing phosphate ore or by burning phosphorus. At room temperature, phosphoric acid is a crystalline solid with a density of 1.83, which melts at 42.35 °C. It is typically stored and sold as a ready-to-use solution. It serves as the primary raw material for the production of phosphates (or phosphate salts) and is a key chemical component in the fertilizer industry. It is also a triacid capable of releasing three H+ protons to form bases such as dihydrogen phosphate, hydrogen phosphate, and orthophosphate according to the following dissociation reactions:

$H_3PO_{4\,(s)} + H_2O_{(l)} \rightleftharpoons H_2PO_4^-{}_{(aq)} + H_3O^+_{(aq)}$,	$Ka_1 = 7{,}13\times10^{-3}$	$pKa_1 = 2{,}15$.
$H_2PO_4^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons HPO_4^{2-}\,(aq) + H_3O^+_{(aq)}$,	$Ka_2 = 6{,}38\times10^{-8}$	$pKa_2 = 7{,}20$.
$HPO_4^{2-}\,(aq) + H_2O_{(l)} \rightleftharpoons PO_4^{3-}\,(aq) + H_3O\,(aq)$,	$Ka_3 = 3{,}79\times10^{-13}$	$pKa_3 = 12{,}42$.

Phosphoric acid, currently the primary derivative in phosphorus chemistry, is an essential intermediate in the production of several products, including:

- In inorganic chemistry (fertilizers, detergents, animal feed, metal treatment)
- In organic chemistry: (plasticizers, insecticides, additives for gasoline and lubricating oils) **(R.Boussen: 2007)**

2/ Literature review:

There are two possible processes for the production of phosphoric acid from phosphate rock: the wet process and the thermal process:

Thermal process:

Phosphorus prepared in an electric furnace (a) is oxidized to produce phosphoric anhydride (b), which is then hydrated (c) to form phosphoric acid. The reactions that occur result in the release of CO and phosphorus vapor and the production of calcium silicate slag. The chemical reactions are as follows:

(a) $Ca_3(PO_4)_2+3SiO_2+5C \xrightarrow{heat} 3(CaOSiO_2) + 5CO + 2P$ the temperature ranges from 1450°C to 1500°C.

(b) $P_2 + 5/2\ O_2 \rightarrow P_2O_5$ (c) $P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$

This production method is advantageous because it yields pure phosphoric acid. However, it is costly because it requires a large amount of energy.

Wet process:

The wet process used for the production of phosphoric acid involves three main steps:

*Acidification or attack of natural phosphates with a strong acid, typically sulfuric acid. It should be noted that nitric and hydrochloric acids can also be used.

*Filtration to separate solids, particularly phosphogypsum, from the acid (30% P_2O_5).

*Concentration, by evaporation, of the filtered acid

During the wet production of phosphoric acid, the acid attack on the phosphates partially or completely solubilizes the organic and inorganic impurities they contain, such as phosphogypsum, and causes fluorine contamination: the fluorinated compound CaF_2 in the fluorapatite of the phosphate rock reacts with sulfuric acid during the acidification stage to produce hydrofluoric acid and chlorine. These impurities subsequently affect the color, density, and viscosity of the phosphoric acid.

$Ca_{10}(PO_4)6F_2 + 10H_2SO_4 + 20H_2O\ 6H_3PO_4 + 10CaSO_4.2H_2O + 2HF$

This reaction, typically carried out at 80°C (Rhône Poulenc-Speichim process), also yields phosphoric acid (H_3PO_4) and results in the formation of calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) the main component of phosphogypsum—and hydrofluoric acid (HF). **(F. Habashi:1985)**

2.2: Production of Phosphoric Acid from Fluorapatite and Hydrochloric Acid:

First, we will discuss the synthesis of hydrochloric acid, which is produced by direct combustion: Gaseous dichloride (Cl_2) and dihydrogen (H_2) are burned together at high temperatures (over 2000°C) to form pure hydrogen chloride. This gas is then absorbed into demineralized water. This is known asthe direct synthesis of hydrochloric acid; in this specific case, we are referring more to sulfur. Hydrogen chloride (HCl) is a gas under normal temperature and pressure conditions. Its aqueous solutions are referred to as hydrochloric acid. Hydrochloric acid was discovered in the 15th century by BasiliusValentiniusbut it was not produced industrially until after the ban on the release of hydrochloric acid—a byproduct of the Leblanc process—into the atmosphere. The idea of using hydrochloric acid to decompose phosphate ores was suggested by Liebig in 1865, and later by other chemists such as Horsford and Koefoed.(W.H. Waggaman: 1969) Hydrochloric acid has always been directed toward industries other than the phosphate industry (textiles, plastics, etc.). This is why, according to Habashi, its use in the acidification of phosphate concentrates was never seriously considered.

Another method for preparing hydrochloric acid from sulfuric acid according to:

The reaction for producing hydrochloric acid from sulfuric acid in the presence of sodium hydroxide

$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HC$

The decomposition of phosphate concentrates using hydrochloric acid (HCl) can be represented by the following reactions (a) or (b), depending on the amount of acid used:

(a) $Ca_3(PO_4)_2 + 4HCl \rightarrow CaH_4(PO_4)_2 + 2CaC_{l2}$

(b) $Ca_3(PO_4)_2 + 6HCl \rightarrow H_3PO_4 + 3CaC_{l2}$

After evaporating the solution obtained in reaction (a), a denseand viscous product is obtained, which is unsuitable for use as a fertilizer, primarily due to thehygroscopic properties of the calcium chloride

it contains. Separation of the calcium chloride is still possible by treating the solution with lime (CaO). This yield, according to reaction (c),a precipitate of dicalcium phosphate, which must be washed and then filtered.

(c) $CaH_4(PO4)_2 + CaO \rightarrow 2CaHPO_4 + H_2O$

Although the P_2O_5 contained in dicalcium phosphate is considered "available," it is not soluble in water and must be acidified before it can be used as a fertilizer.

In the hydrochloric acid process, the industrial production of phosphoric acid can be summarized by the following reactions:

$Ca_{10}(PO_4)_6F_2 + 14HCl \rightarrow 3Ca(H_2PO_4)_2 + 7CaC_{l2} + 2HF$

$Ca_{10}(PO4)_6F_2 + 20HCl \rightarrow 6H_3PO_4 + 7CaC_{l2} + 2HF$

To reduce the volume of waste, it is possible to treat natural phosphate on-site; however, it will not be possible to use the most common and least expensive acid, H_2SO_4, because the gypsum formed during leaching will inhibit its formation. Consequently, it is necessary to use other acids such as hydrochloric acid; although this acid is expensive, it has the advantage of rapidly solubilizing not only the P_2O_5 content of the rock but also the uranium, lanthanides, and radium present, thereby facilitating their recovery or removal **(F. Habashi, F.T. Awadalla: 1988).**

The hydrochloric acid process for the industrial production of phosphoric acid offers severaladvantages, including low impurity levels in the purified phosphoric acid, low volumes of waste (phosphogypsum), and the recovery of rare earth elements contained in phosphate rock **(M. Campos Assunção: 2017)**

2.3 Acetic Acid:

2.3.1: Properties:

Pure acetic acid, with the chemical formula CH3COOH, known as glacial acetic acid, is a colorless, flammable, hygroscopic liquid. Naturally present in vinegar, it gives it its sour taste and pungent odor. The use of acetic acid in chemistry dates back to ancient times. In the 3rd century BC, the Greek philosopher Theophrastus described how vinegar acts on metal to produce pigments useful for art. The ancient Romans boiled sour wine in lead vessels to produce a very sweet syrup called Sapa. The Arab alchemist Jabir Ibn Hayyan (Geber) concentrated acetic acid from vinegar through distillation.

Liquid acetic acid is a hydrophilic protic solvent that can dissolve not only polar compounds such as inorganic salts and sugars, but also nonpolar compounds such as oils, or elements like sulfur, phosphorus, and iodine. These solvent properties and the miscibility of acetic acid make it widely used in the chemical industry. **(A. IdrissiBouraqadi: 2006).**

2.3.2 Production:

Acetic acid is produced synthetically or through bacterial fermentation. Today, the biological method accounts for only 10% of production, due to the high costs associated with recovery and separation from biomass (Boyaval P, Corre C: 1995). Approximately 75% of the acetic acid used in the chemical industry is produced by the carbonylation of methanol (detailed below). The remainder is produced using various alternative methods (oxidation of acetaldehyde or oxidation of ethylene).

Total acetic acid production is estimated at 5 Mt/year (million metric tons per year), about half of which comes from the United States **(Katikaneni, S.P. R., and Cheryan, M.: 2002).** European production is close to 1 Mt/year, and 0.7 Mt/year is produced in Japan. 1.5 Mt/year is recycled, bringing the global market to 6.5 Mt/year.

The majority of non-recycled acetic acid is produced by methanol carbonylation. In this process, methanol and carbon monoxide react to produce acetic acid according to the equation:

$CH_3OH + CO \rightarrow CH_3COO$

2.3.3 Uses:

Acetic acid is the most widely used carboxylic acid. It is a reagent used in the production of many chemicals. Its most common use is in the manufacture of vinyl acetate monomer, followed by acetic anhydride and the production of esters **(Yoneda et al., 2001)**

3/ Phosphates (raw material):

Phosphorus is a relatively scarce element; its concentration in the Earth's crust is 1,180 ppm. It never occurs in its pure form. It is an element essential to life, as it is a component of the cell nuclei of all living organisms. Phosphorus is generally combined with oxygen to form the phosphate radical $PO4^{3-}$.

Phosphates are divided into three categories: basic phosphates or oxyphosphates (O/P > 4), monophosphates (O/P = 4), and condensed phosphates (O/P < 4).

- Basic phosphates or oxyphosphates:

Basic phosphates, or oxyphosphates, are the phosphates with the highest oxygen content; their atomic arrangement is such that some oxygen atoms are not bonded to phosphorus, with the exception of ox apatite: $Ca_{10}(PO_4)_6O$.

- Monophosphates:

Known as orthophosphates, monophosphates are the only phosphates found in nature due to the hydrolysis of condensed phosphates. They are the most stable and the most studied. Their basic structure consists essentially of the isolated (PO4)3- anion. An example is a monophosphate with an organic cation: $(HN_3C_6H_4COOH)_2\,(H_2PO_4)_2,\ 2H_2O$.

- Condensed phosphates:

In condensed phosphates, the anions contain P-O-P bonds. The processes involved are highly varied and lead to four main classes of condensed anions: oligophosphates, polyphosphates with infinite chains, cyclophosphates, and ultraphosphates.

3.1: History:

The need for soil fertilizers to support the continuous development of crops and plant growth has been known since ancient times.

- 1669 – Discovery of phosphorus by the German alchemist Brandt, following the evaporation of large quantities of human urine.
- 1769 – Swedish chemist Gahn demonstrated the presence of phosphorus in bones.
- 1779 – Phosphorus was identified in the mineral pyromorphite, again by Gahn, anda method, developed by Scheele, was established to obtain phosphorus by dissolvingbones in nitric acid.

Orthophosphoric acid (H_3PO_4), which was then reused in the acidification of phosphate rock to produce a superphosphate concentrate, better known today as triple superphosphate.

The late 19th century coincided with the start of industrial production of phosphate fertilizers, which have since become key factors in agricultural development and the fight against hunger. The constant race between explosive global population growth and increased food production makes the use of fertilizers increasingly necessary. (Fernando Pereira: 2003)

3.2: Phosphate Ores:

The typical commercial phosphate ore is a calcium-phosphate concentrate containing approximately 35 to 38% P_2O_5 and 3 to 4% fluorine, with the main impurities being: silica, generally in the form of quartz grains; clays; aluminum phosphates; and iron oxides and hydroxides. The most common trace elements are rare earths (sometimes in significant amounts), U, Sr, Ba, Mg, and Zn.

3.3: Reserves:

In the early 1960s, global production of phosphate ores was clearly dominated by the United States (45%) and Africa (26.3%). Europe, however, remained the leading industrial producer (37.3%), followed by the United States (27.7%) and Africa (1.4%). In 1995, global phosphate rock reserves were estimated at 33 billion tons (data from Mineral Commodity Summaries and DNPM [1996]).

Table 1: Global Phosphate Ore Reserves and Concentrate Production in 1994 and 1995 (Mineral Commodity Summaries and DNPM [1996])

	Basic reserves		Mining production			
Country	(10^9 t)	(%)	1994	(%)	1995	(%)
Morocco	21	63.02	19.8	15.47	20	14.57
United States	4.4	13.22	41.1	32.12	45.5	33.14
South Africa	2.5	7.5	2.5	1.95	3	2.18
Russia	1.1	3.3	10	7.81	11	8à&
Jordan	0.57	1.71	4.22	3.30	5	3.64
Brazil	0.37	1.11	3.94	3.08	3.9	2.84
Tunisia	0.27	0.81	5.7	4.45	6.5	4.74
China	0.21	0.63	26	20.32	27	19.66
Israel	0.18	0.54	4	3.13	4	2.91
Senegall	0.16	0.48	1.6	1.25	1.5	1.10
Togo	0.06	1.18	2.15	1.68	2.4	1.75
Others	2.5	7.5	6.96	5.44	7.5	5.46
Total	33.32	100	127.97	100	137.3	111

After analyzing Table 1, several important points should be highlighted:

- Global phosphate reserves are extremely concentrated. Morocco holds more than 63% of these reserves;
- Global production of phosphate concentrates, estimated at 137.3 billion tons in 1995, was 6.79% higher than in the previous year (127.97 billion tons).

Over the same period, Brazilian production, meanwhile, declined slightly (3,940 Mt in 1994, 3,900 Mt in 1995);

- Global production is clearly dominated by four countries: The United States, China, Morocco, and Russia (together accounting for more than 75% of global production);

3.4: Areas of Application:

Phosphates have a wide range of applications. They are used in biology, ecology, food, and the industrial sector:

Table 2: Major Applications of Industrial Phosphates1

	$P^2O^5(10^3t)$	Percentage
Fertilizer	32000	90
Detergents	1590	4.5
Animal feed	1180	3.3
Food and Beverades	240	0.7
Surface treatement	230	0.6
Water treatement	90	0.25
Dental hygiene	80	0.22
Fireextinguishers	40	0.11
Others	110	0.3
Total	35600	100

- Fertilizers:

Fertilizers are substances—most often mixtures of mineral elements—designed to provide plants with additional nutrients in order to improve their growth and increase crop yields and product quality. They account for by far the largest share of production (90% of global phosphate) **(Kulaif, Y.: 1997)**

Phosphate fertilizers are manufactured from phosphate rocks extracted from the ground. The phosphorus present in these rocks is not available to plants, especially in alkaline soils, as is the case with most soils in Morocco. To make the phosphorus soluble, these rocks are treated with a strong acid.

The main components of fertilizers:

- Primary nutrients (macronutrients): Nitrogen (N), phosphorus (P), and potassium (K).
- Secondary nutrients: Calcium (Ca), magnesium (Mg), and sulphur (S).
- Trace elements: Iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B), molybdenum (Mo), and chlorine (Cl).
- Food:

Phosphates are used to improve food products. They possess several properties that help preserve the best qualities of food and ensure the highest quality; they are effective in several ways:

- Preserve natural taste and color.
- Retain the natural juices of meat and seafood.
- Prevent the growth of certain bacteria.
- *Promote even baking of pastries… etc.
- Industry:

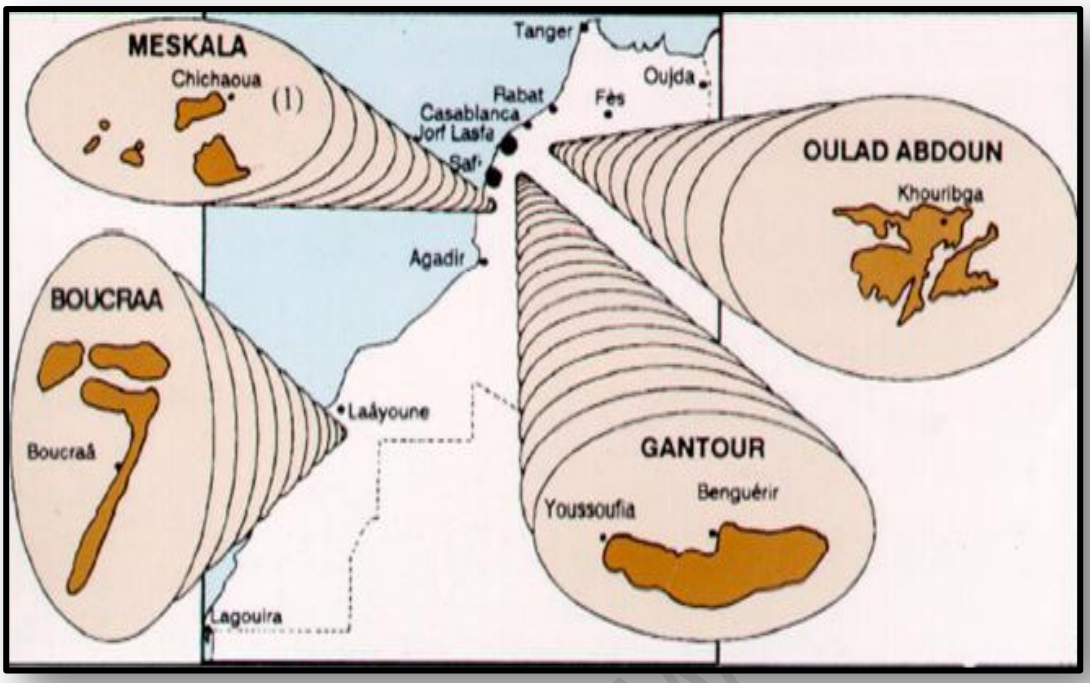
The chemical industry accounts for nearly 6% of global phosphate production, notably:
In the manufacture of phosphate salts, polyphosphates, soaps, detergents,
pharmaceuticals, dental cement, soft drinks, gelatine, food additives,
corrosion inhibitors, wax, fire retardants, and
water treatment chemicals; In sugar refining and the acid disinfection of hard surfaces, As catalysts and laboratory reagents

4 / Phosphates in Morocco:

In Morocco, tens of millions of years ago, before the formation of phosphate deposits, the sea covered the entire region all the way to the Atlantic.Today, we find a large quantity of these fossils in sediments deposited between 70 and 45 million years ago. Entire skeletons, skulls, bones, vertebrae, shark teeth, and other fossils are found in the phosphate deposits.
Moroccan phosphates are characterized by their geographic locations, their commercial qualities, their diversity, and most importantly by their high P2O5 content; Morocco's commercial phosphate, without enrichment, has a content of 30%, calculated as follows: BPL (Bone Phosphate of Lime) = 2.18 * % P2O5. This gives Morocco a special place in the international market; it is the leading exporter of phosphates, with a share of 31.5% in 2011 rising to 33.2% in 2012, and the third-largest producer. Its annual production is 28.4 million tons, with 18 million tons in 2012 at the Khouribga mine and an estimated resource potential of 56 billion tons (OCP 2012). **(H. El Haddi, 2014)**

4.1: Moroccan Phosphate Deposits:

The first traces of phosphate were discovered in Morocco in 1908 at Meskala, then in 1917 at Boujniba in the Khouribga region following three years of exploration that continued until 1921, the year underground mining (extraction and processing) began at Boujniba (Khouribga).



Currently, Morocco, with its significant share of global phosphate reserves, is the leading exporter of phosphate and its derivatives. The country's overall market share exceeds 30%. Morocco's currently known reserves are sufficient to meet demand for several centuries. A significant portion of the phosphate reserves consists of sedimentary rock containing substantial amounts of carbonate minerals.
Fig.1: The four phosphate deposits in Morocco

Moroccan phosphates are the most significant in terms of both quantity and quality; these deposits are located in the Gantour (Youssoufia and Benguérir), Messkala (Chichaoua), Oued Eddahab (Boucraâ), and Ouled Abdoun **(Khouribga) (R. Hakkoua et al.: 2016).**

5/ Determination of characteristics based on the conditions selected for the stoichiometry of the reaction between fluorapatite and sulfuric acid.

The reaction to be evaluated is:

$$\mathbf{Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + 20H_2O \rightarrow 10CaSO_4.2H_2O + 2HF + 6H_3PO_4}$$

Based on the selected experimental conditions—specifically, 0.195 N sulfuric acid using a volume of 50 cm^3—we will calculate the exact mass of fluorapatite required, considering the stoichiometry of the reaction.
Sulfuric acid H_2SO_4 is a diacid; the number of equivalents is n = 2.
The molarity is:

We have: $[H_2SO_4] = \frac{0,195}{2}$ $[H_2SO_4] = 0,0975$ mol/l

$n(H_2SO_4) = \frac{0,0975 \times 50}{1000}$ ⟶ $n(H_2SO_4) = 0,00488$ moles

Based on the stoichiometry of the reaction, we have: 1 mole of fluorapatite 10 moles of H_2SO_4
n of fluorapatite 0.00488 moles

n (of fluorapatite) = 0.000488 moles, so the mass of fluorapatite obtained is

m = 0.000488 × 1008 since the molar mass of fluorapatite is 1008 g/mole

m = 0.492 g

Extrapolating to 1 kg of ore, we find:

0.492 → 0.00488 moles of sulfuric acid.

1000 → X

X = 1000 × 0.00488 / 0.492 = 9.92 moles

And in 1000 cm^3 (one liter) of the concentrate, we have 36 N of sulfuric acid and 36/2 = 18 moles

18 → 1000

9.92 → Y

hence Y = 551.1 cm^3

Therefore, according to stoichiometry, 1 kg of fluorapatite requires v = 551.1 cm^3 of 36 N sulfuric acid

4/ Experimental Study:

In this section, we conducted a number of laboratory-scale tests focused on the synthesis of triphosphoric acid from leachates: sulfuric, hydrochloric acid, and acetic acid leachates from phosphate treated at 550°C and raw ore from the Youssoufia deposit, varying the mass to optimize the appropriate quantities of the two reactants (the ore and the acid) in the reaction, which takes place at 85°C, according to the procedure outlined in this study.

4.1: Techniques used in this study:

The procedure was carried out according to the following steps:

- Preparation of the acids.
- Treatment of the ore in a furnace.
- Leaching of the phosphate.
- Stirring and heating to a temperature of 85°C.
- Filtration.
- Titration.

4.2: Ore Processing:

The phosphate had previously undergone heat treatment; we used a muffle furnace to achieve an isothermal temperature of 550°C in order to remove the organic matter characteristic of the Youssoufia deposit phosphates, which appeared black.

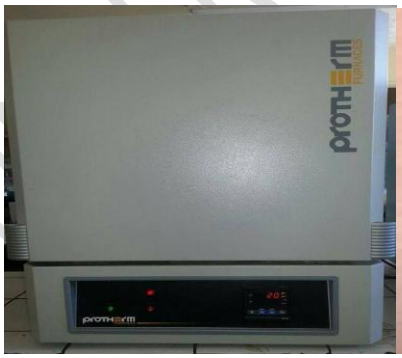


Fig.2: A muffle furnace

Fig.3:Youssoufia phosphate

4.3: Heating to 85°C and filtration of the solution:

Several samples of the ore were treated with 50 mL of the acid in question; the solution was then stirred until the temperature reached 85°C to ensure complete solubilization, and finally filtered to separate the solids.

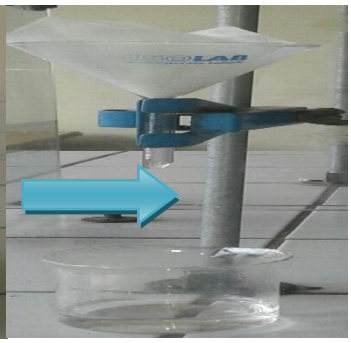


Fig.4: Stirring and heating Fig.5: filtration

4.4: pH Measurement:

Once phosphoric acid has been produced at the required concentrations, the filtrate is analysed using pH measurement to determine its acid-base balance; the base used for this analysis is NaOH (N =0.191 N).

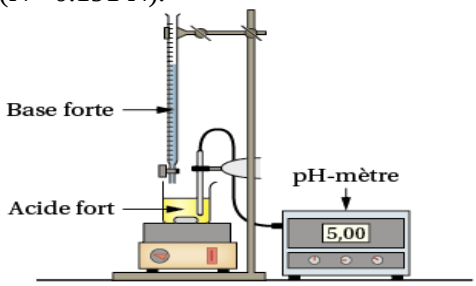


Fig.6:pH meter apparatus

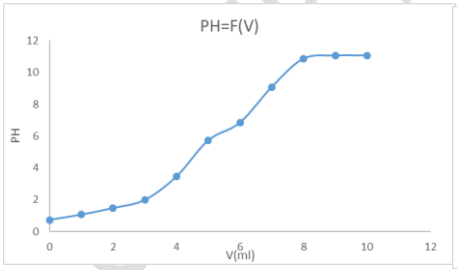
5/ Results and Discussion:

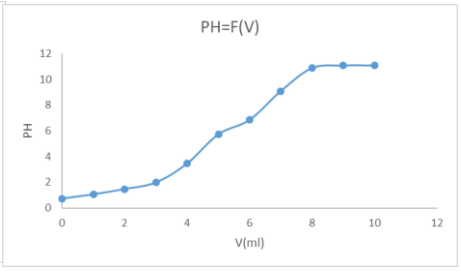
5.1: Use of sulfuric acid:

The production of phosphoric acid from Youssoufia ore and sulfuric acid was carried out in a subsequent study **(M. Aracha, I. Akhajja: 2018) (A. Alaakkad: 2018)**; the ore was used in its raw form and, in another instance, treated at 550°C.

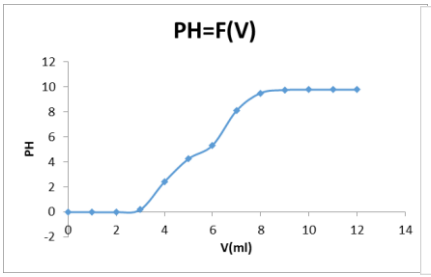
5.1.1: Raw Youssoufia phosphate

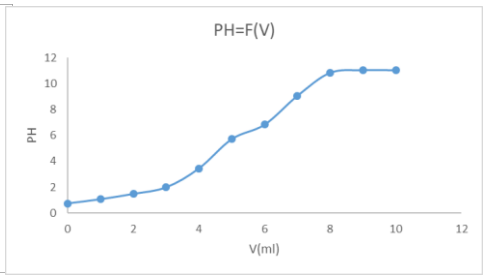
Analysis of the filtrate (10 cm^3) after treatment with sulfuric acid (0.195 N) of raw Youssoufia phosphate ore (m = 0.5 g, m = 1 g, m = 1.5 g, m = 2 g, and m = 2.5 g)



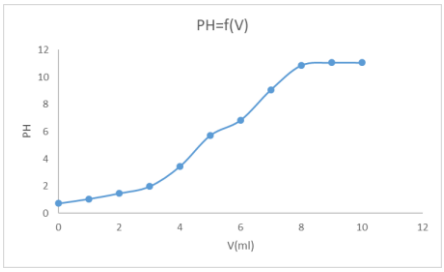


m = 0,5 g m = 1 g





m = 1,5 g m = 2 g



m = 2g

Fig. 7: Analysis of the filtrate (10 cm³) after treatment with sulfuric acid (0.195 N) of raw phosphate ore from Youssoufia (m = 0.5 g, m = 1 g, m = 1.5 g, m = 2 g, and m = 2.5 g)

By analysing these curves plotted on graph paper, we were able to determine the characteristics of the phosphoric acid produced. In the following table, we have compiled the pKa1 and pKa2 values as well as the concentrations of each acid; two acidities were considered: (the primary and the secondary)
The table below presents this study, which details the characteristics of the acid produced as well as its concentration.

Table 3: Characteristics of phosphoric acid derived from raw ore from Youssoufia using sulfuric acid:

m(g)	V_1 (ml)	V_2 (ml)	PKa_1	PKa_2	N_1(N)	N_2(N)
0,5	3,40	8,20	1,00	6,70	0,065	0,092
1	2,22	5,90	0,80	5,60	0 ,042	0,070
1,5	2,00	5,42	0,00	4,75	0,038	0,065
2	2,10	5,50	1,50	6,40	0,040	0 ,065
2,5	1,95	5,30	1,10	6,50	0,037	0,064

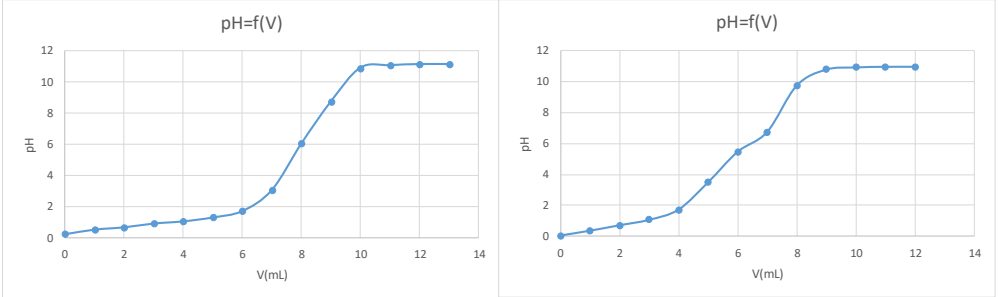
5.1.2: Youssoufia phosphate treated at 550°C in a muffle furnace.

This experimental section is carried out in the following steps:

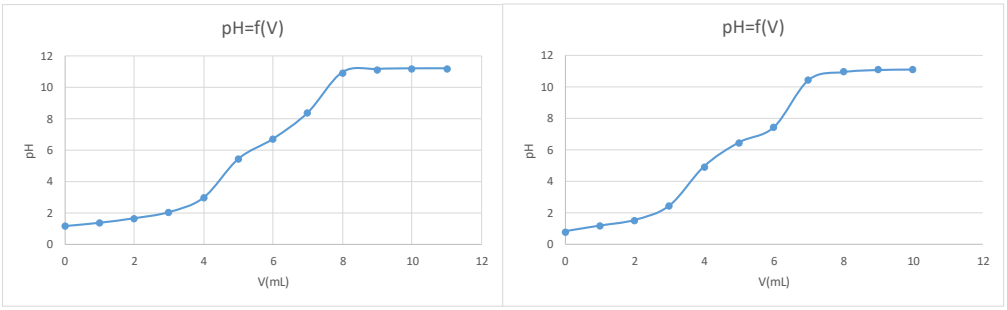
- Treatment of the phosphate ore in a muffle furnace at 550°C under isothermal conditions
- Attack of the phosphate ore with sulfuric acid (H_2SO_4) of 0.195 N strength using a volume of 50cm³.
- Heating and stirring up to 80°C
- Filtration.
- Titration of the phosphoric acid produced using sodium hydroxide (NaOH)

The following curves represent the results of these titrations:

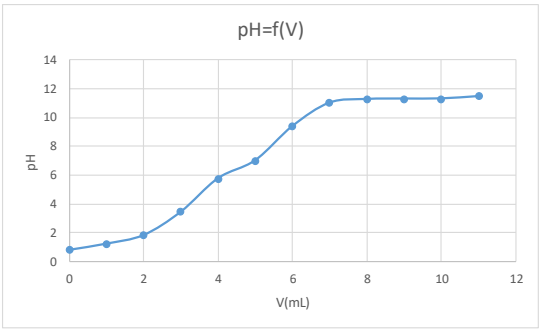
Les courbes suivantes représentent les résultats de ces dosages :



m = 0,5 g m = 1 g



m = 1,5 g m = 2 g



m = 2 ,5 g

Fig:8 Analysis of the filtrate (10 cm³) after treatment with sulfuric acid (0.195 N) of Youssoufia phosphate ore processed in a muffle furnace at 550°C (m = 0.5 g, m = 1 g, m = 1.5 g, m = 2 g, and m = 2.5 g)

Table 4: Characteristics of phosphoric acid derived from ore treated at 550°C with sulfuric acid:

m(g)	V_1 (ml)	V_2 (ml)	PKa_1	PKa_2	N_1(N)	N_2(N)
0,5	3,75	8,20	1,00	6,60	0,072	0,085
1	2,5	6,48	0,90	5,90	0 ,048	0,069
1,5	2,23	5,83	1,65	6,50	0,043	0,069
2	1,90	5,23	1,40	6,70	0,036	0 ,064
2,5	1,7	4,65	1,60	6,50	0,032	0,056

According to the previous tables of characteristics and the figures presented in subsequent studies **(M. Aracha and I. Akhajja: 2018; A. Alaakkad: 2018),** the masses highlighted are 2 g for raw phosphate and 2.5 g for processed phosphate (550°C).

Extrapolating for 1 kg of raw ore, we find:

2 → 0.00488 moles of sulfuric acid.

1000 → X

X = 1000 × 0.00488 / 2 = 2.44 moles

And we have 36 N sulfuric acid concentrate in 1000 cm³ (one liter), which is 36/2 = 18 moles

18 → 1000

2.44 → Y

hence Y = 135.6 cm³

Therefore, for 1 kg of raw Youssoufia phosphate ore, we need 135.6 cm³ of 36 N sulfuric acid

Extrapolating for 1 kg of ore treated in a muffle furnace at 550°C, we find:

2.5 → 0.00488 moles of sulfuric acid.

1000 → X

X = 1000 × 0.00488 / 2.5 = 1.95 moles

And we have in 1000 cm³ (one liter) of the concentrate 36 N of sulfuric acid and 36/2 = 18 moles

18 → 1000

1.95 → Y

hence Y = 108.3 cm³

Therefore, for 1 kg of Youssoufia phosphate ore treated at 550°C in a muffle furnace, we need 108.3 cm³ of 36 N sulfuric acid.

5.2 Use of Hydrochloric Acid:

Under the same operating conditions, several samples of Youssoufia phosphate were treated with 50 mL of 0.196 N hydrochloric acid, with temperature near ebullition, the resulting filtrates were analysed using a pH meter (10 cm³), and then graphs were plotted of these titrations (pH = f(V)) as a function of the different masses of raw ore and those of ore treated at 550°C.

5.2.1: Results of the titration of raw Youssoufia ore treated with hydrochloric acid:

The figures below show the variation in the pH of the acid produced as a function of the titration volume:

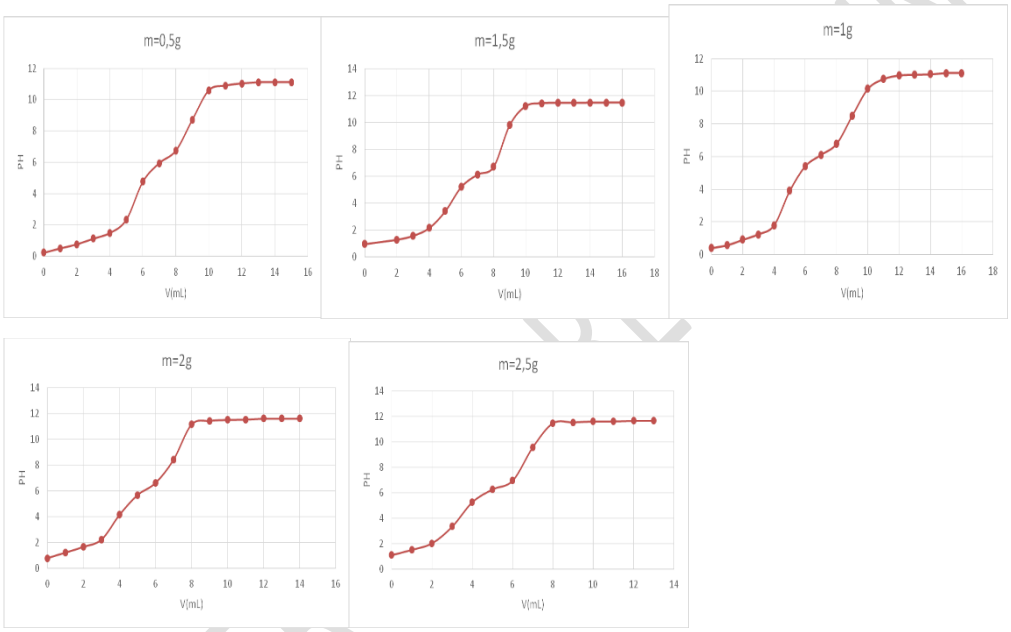


Fig. 9: Analysis of the filtrate (10 cm³) after treatment with hydrochloric acid (0.196 N) of raw Youssoufia phosphate ore (m = 0.5 g, m = 1 g, m = 1.5 g, m = 2 g, and m = 2.5 g)

After analysing these curves for the various raw phosphate ore samples from the Youssoufia deposit, the characteristics of the resulting acid were identified, as shown in the following table:

Table 5: Characteristics of phosphoric acid produced from raw ore from Youssoufia using hydrochloric acid:

m(g)	V_1 (ml)	V_2 (ml)	PKa_1	PKa_2	N_1(N)	N_2(N)
0,5	2,70	7,30	0,99	6,20	0,052	0,088
1	2,35	6,70	1,00	6,10	0 ,045	0,083
1,5	2,1	5,95	1,7	5,70	0,040	0,074
2	1,90	5,60	1,60	6,20	0,036	0 ,071
2,5	1,55	5,00	1,85	6,27	0,030	0,066

5.2.2: Results of the analysis of Youssoufia ore treated at 550°C and leached with hydrochloric acid:

In this study, the phosphate samples underwent thermal pre-treatment at 550°C in a muffle furnace; the following figures show the variation in the pH of the phosphoric acid produced as a function of the volume of each treated phosphate sample:

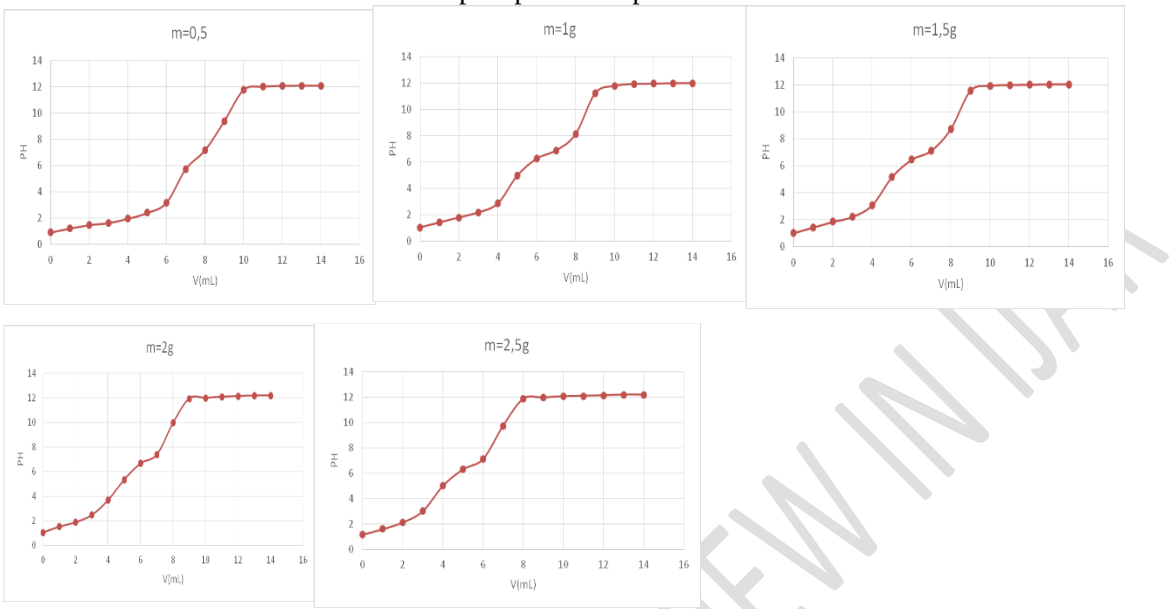


Fig. 10: Analysis of the filtrate (10 cm³) after treatment with hydrochloric acid (0.196 N) of Youssoufia phosphate ore processed in a muffle furnace at 550°C (m = 0.5 g, m = 1 g, m = 1.5 g, m = 2 g, and m = 2.5 g)

Analysis of these curves yields the results shown in the following table, which presents the various characteristics of the phosphoric acid obtained after the analysis of each sample

Table 6: Characteristics of phosphoric acid derived from Youssoufia ore treated at 550°C with hydrochloric acid:

m(g)	V_1 (ml)	V_2 (ml)	PKa_1	PKa_2	N_1(N)	N_2(N)
0,5	3,20	7,70	1,70	6,70	0,061	0,086
1	2,30	6,45	1,90	6,60	0 ,044	0,079
1,5	2,35	6,45	2,00	6,80	0,045	0,078
2	2,20	6,10	2,00	6,70	0,042	0 ,074
2,5	1,85	5,30	2,05	6,65	0,035	0,066

5.2.3: Interpretation for the case of hydrochloric acid as a working reagent:

When using hydrochloric acid, we adopt three recommendations to optimize the amount deemed appropriate

1. distinguishing between the first two acidities
2. varying the pH range of the two acidities (so-called pH sweep)
3. varying the pKa values

Based on these conditions and by carefully observing the preceding curves, we note an optimization in the conditions of the selected experiments

*2 g for the raw ore

*2.5 g for the ore treated at 550°C

According to the preceding characteristic tables and the figures produced, the masses we have highlighted are 2 g for the raw phosphate and 2.5 g for the treated phosphate, which results in an acid

volume of 668.5 cm³ (N = 7.33 N) for the raw ore and a volume of 534.8 cm³ (N = 7.33 N) for the ore treated at 550°C per 1 kg of ore.

5.3: Use of Acetic Acid:

In this case, we explored the use of acetic acid (0.195 N) as an innovative new approach to reducing the costs and environmental impacts associated with phosphoric acid production.

5.3.1: Results of the titration of raw ore from Youssoufia treated with acetic acid (heated to 85°C):

The following figures show the variation in the pH of the produced acid as a function of the volume of acid added:

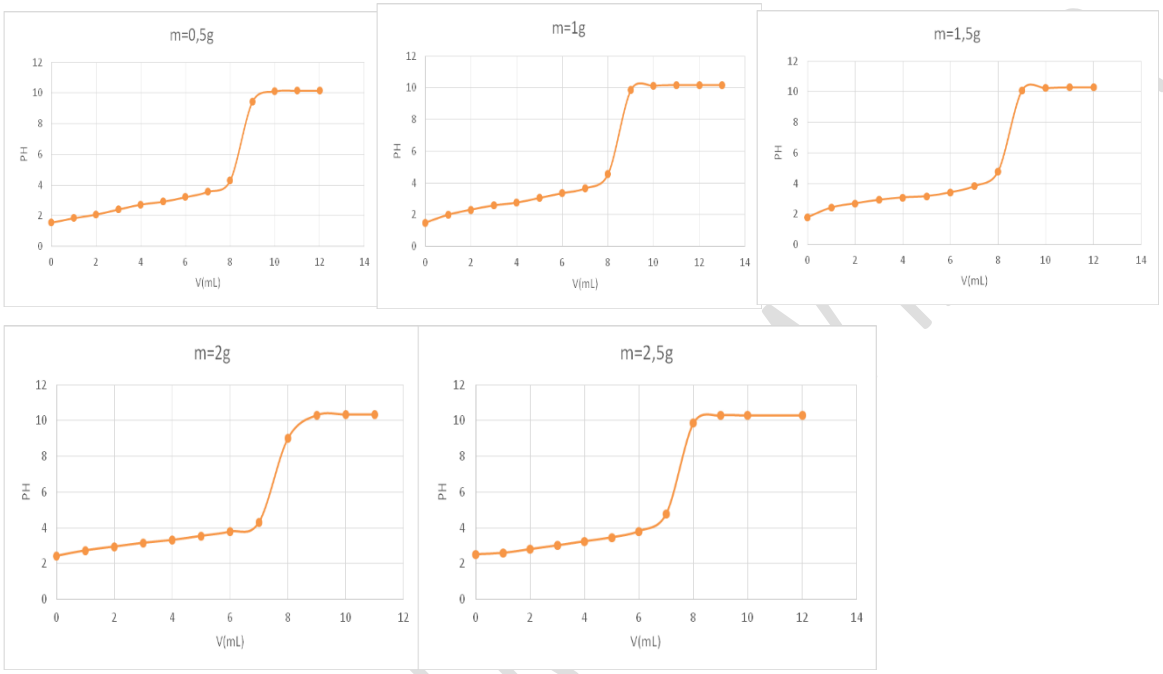


Fig.11: Analysis of the filtrate (10 cm³) after treatment with acetic acid (0.196 N) of Youssoufia phosphate ore processed in a muffle furnace at 85°C (m = 0.5 g, m = 1 g, m = 1.5 g, m = 2 g, and m = 2.5 g)

The following table presents the characteristics of the phosphoric acid produced based on the analysis of previous curves:

Table 7: Characteristics of acid derived from raw Youssoufia ore using acetic acid:

m(g)	V (ml)	PKa	N(N)
0,5	4,20	2,80	0,080
1	4,35	2,90	0 ,083
1,5	4,30	3,05	0,082
2	3,88	3,30	0,074
2,5	3,85	3,20	0,073

5.3.2: Results of the titration of raw ore from Youssoufia treated with acetic acid (0.195 N) (heating temperature was 96°C):

In this case, we increased the heating temperature of the solution to enhance the solubilization reaction of the raw ore by acetic acid; after pH measurement, we obtained the following curves:

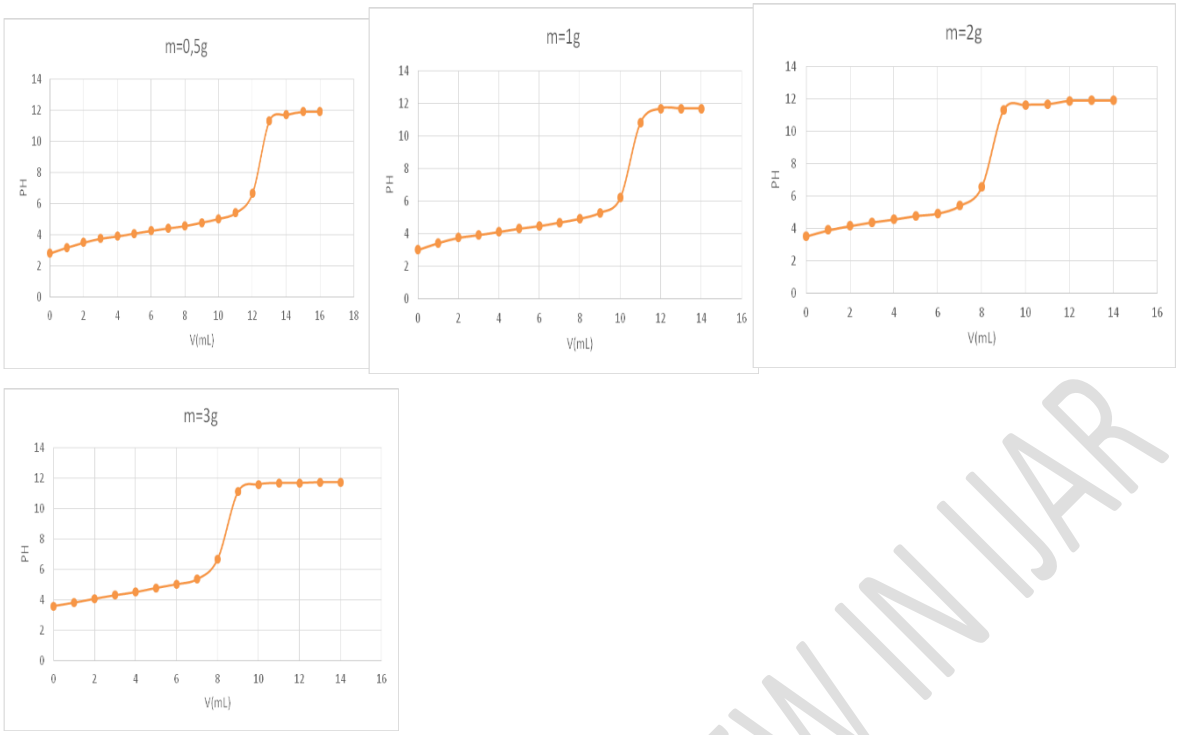


Fig.12: Analysis of the filtrate (10 cm³) after treatment with acetic acid (0.196 N) of Youssoufia phosphate ore processed in a muffle furnace at 92°C (m = 0.5 g, m = 1 g, m = 1.5 g, m = 2 g, and m = 3 g)

Based on these curves, we have highlighted the main characteristics of the phosphoric acid produced; these are clearly outlined in the following table:

Table.8: Characteristics of acid derived from raw Youssoufia ore using acetic aid

m(g)	V (ml)	PKa	N(N)
0,5	6,25	4,30	0,120
1	5,45	4,40	0 ,104
2	4,13	4,60	0,079
3	4,23	4,60	0,081

Based on these two results, we observed the following for the experimental temperatures (85°C and 96°C):

- the titration volumes increase with the mass of the ore
- the acids could not be distinguished from one another
- the pKa values observed in each case are similar to that of acetic acid (pKa = 4.75)

Consequently, we concluded that to obtain phosphoric acid, it is strictly necessary to have a strong acid, whether mono- or dibasic. A qualitative discrepancy was observed

Conclusion:

The production of phosphoric acid from phosphate using the sulfuric acid process has numerous drawbacks: the generation of large volumes of hazardous waste and environmental impacts associated with the storage of phosphogypsum. It is the only process currently used in Morocco; however, since the country imports raw sulphur to produce sulfuric acid, the adoption of an alternative process is necessary both to reduce sulphur imports and to minimize chemical impacts on the environment by incorporating the principles of green chemistry.

To achieve these goals, we conducted this study on the synthesis of phosphoric acid using hydrochloric acid (0.196N) and acetic acid (0.195N) as leaching agents (alternatives to sulfuric acid) for phosphate ore from Youssoufia, both in its raw state and after treatment at 550°C.

By varying the ore mass with the aim of optimizing the appropriate quantities of the two reagents under stoichiometric reaction conditions, we operated under conditions that were identical for all three processes, following the same steps: acid leaching of the ore, heating, filtration, and finally pH titration of the resulting phosphoric acid.

For the sulfuric acid route, based on the results of a subsequent study **(M. Aracha. I. Akhajja: 2018) (A. Alaakkad: 2018)**, the masses we noted were 2 g for raw phosphate and 2.5 g for treated phosphate under the specific operating conditions chosen; extrapolating the experiment to 1 kg yields an acid volume of 135.4 cm^3 (N=36N) for the raw ore and a volume of 108.3 cm^3 (N=36N) for the ore pre-treated thermally at 550°C.

For the use of hydrochloric acid, the optimized amounts are also 2 g for raw phosphate and 2.5 g for treated phosphate, which results in an acid volume of 668.5 cm^3 (N = 7.33 N) for the raw ore and a volume of 534.8 cm^3 (N = 7.33 N) for the ore pre-treated thermally at 550°C, relative to 1 kg of ore.

Volume of HCl (N=7.33N) per 1 kg of raw ore	Volume of HCl (N = 7.33 N) per 1 kg of ore pre-treated at 550°C	Volume of H_2SO_4 (N=36N) per 1 kg of raw ore	Volume of H_2SO_4 (N=36N) per 1 kg of ore pre-treated at 550°C
668,5 cm^3	534,8 cm^3	135,4 cm^3	108,3 cm^3

The volumes of concentrated acids listed correspond to the number of moles required for the titration; in industrial applications, a sufficient amount of water must be added as a solvent. Similarly, the contents must be heated to a temperature between 80 and 85°C.

Regarding the use of acetic acid, it is observed that the titration volumes increase with the mass of the ore; the acids could not be distinguished, and the pKa values noted in each case resemble that of acetic acid (pKa = 4.75).So, we note an irregularity in this case. Consequently, we concluded that to obtain phosphoric acid, it is strictly necessary to use a strong acid, whether mono- or di-acidic.

Ultimately, it appears that hydrochloric acid is the best route, even though it is costly, and it offers the advantage of not only solubilizing the P_2O_5 contained in the rock but also any rare earth elements that may be present, and it provides a good solution to environmental issues. Similarly, with this method, we avoid using sulphur, which is a polluting by product; to neutralize it, several reagents must be used, which are costly and harmful to the environment.

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