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Effects of calcination on the solubility of merchant phosphate from Tahoua (Niger) in sulfuric and citric acid solutions

ABDOU GONDAH Ismaila[1], ZANGUINA Adamou[1], OUSMANE Mahamane Sani[2], NATATOU Ibrahim[1,2]

[1]*Department of Chemistry, Faculty of Science and Technology, AbdouMoumouni University of Niamey, Niger*
[2]*Department of Chemistry, Faculty of Science and Technology, University of Agadez, Niger*

Abstract:
In this work, we used merchant phosphate from Tahoua. It is a powder obtained by grinding and physical treatment of rock phosphate nodules and is used as a crop fertilizer. However, it has a low reactivity. This does not favour its direct application to the soil to correct soil phosphorus deficiency in order to increase agricultural productivity. The present work aims to improve the solubility of this product by heat treatment to increase its agronomic efficiency. Tahoua merchant phosphate was calcined at 850°C in an adjustable kiln for two hours. The chemical composition, specific surface area and pore volume of the merchant and calcined products were determined respectively by XRF chemical analysis and BET method. A solubility test of the product was carried out in sulphuric (1M) and citric (0.1M) acid solutions for an attack time of one hour. The results obtained show on the one hand that calcination makes it possible to increase the P_2O_5 content of the ore from 20.6% to 30.8% and to decrease the silica and aluminium oxide contents from 3.47% to 0.059% and from 4.86% to 0.64% respectively. The specific surface area decreased from 390.980m^2/g in merchant phosphate to 407.246m^2/g in calcined phosphate. On the other hand, we have an improvement in the solubility of the product in acid solutions after calcination.

Keywords*: Tahoua merchant phosphate; calcination; solubility; citric acid; sulphuric acid..*

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I. Introduction

For some time, natural phosphates have been considered as an alternative to the use of water-soluble manufactured chemical fertilizers recommended to correct the deficiency of soils in phosphorus in order to increase agricultural productivity. However, not all are suitable for direct application to the ground. The agronomic efficiency of a natural phosphate lies in its reactivity. The latter depends on the content of penta phosphorus oxide (P_2O_5) and the presence of impurities in the ore [1]. Depending on the P_2O_5 content of the ore, natural phosphates are classified as high-grade phosphates (more than 30% P_2O_5); medium grade (20-30% P_2O_5) and low grade (15-20% P_2O_5) [2]. For medium and low grade phosphates, they should be enriched. In Niger, the marketable phosphate from Tahoua has been the subject of several research studies for its direct application recovery in the agricultural field. However, the experiments were not conclusive not only because of the pulverulent nature of the product but especially for its low reactivity [3,4,5,6,7,8,9,10]. This work aims to improve the solubility of Tahoua merchant phosphate by heat treatment in order to increase the bioavailability of phosphorus. Merchant and calcined products were dissolved in sulfuric and citric acid solutions to test solubility. The objective of this work is the improvement of the reactive phosphate of Tahoua merchant in order to relaunch its use in the agricultural field.

II. Material And Methods

2.1. Matériel

2.1.1. Phosphatedmatériel

This is natural phosphate from Tahoua, with a particle size of 100 to 150 µm. It was operated by the National Mining Research Office (ONAREM) and marketed by the central supply of agricultural inputs and materials (CAIMA). We have determined its chemical composition.

2.1.2. Chemical solutions

The chemical solutions used in this work are of commercial origin. Their characteristics are given in table n°1.

Tablen°1 : Characteristics of the chemicals used

Products	Molar mass **[g·mol^{-1}]**	**Density**	Purity [%]	**Origin**
sulfuric Acid	98	1,84	98	Normapur
Citric Acid	192,124	1,66	99,7	Normapur
Antimony and potassium double tartrate	333,93	-	99	Acros Organics
Ammonium molybdate $[(NH_4)_6Mo_7O_{24}\cdot 4H_2O]$	1235,86	-	99	Acros Organics
Acid ascorbic	176,13	-	99,7	Normapur
Monopotassium phosphate	136,1	-	99	Sigma-Aldrich

2.1.3.Apparatus

The apparatuses used during this work are:

- a spectrophotometer of molecular absorption brand Spectronic 20 Milton Roy Company for the determination of dissolved phosphoric anhydride;
- an analytical brand balance mettler model PM3000 for mass measurement; An adjustable Heraeus oven used for the calcination of Tahoua merchant phosphate.

2.2. Methods

2.2.1.Calcination of merchant phosphate

Calcination is a process which consists in subjecting a substance to the action of heat without melting it in order to cause a change in its physical and / or chemical constitution. [10]. 100 g samples of the Tahoua merchant phosphate are placed in an oven adjustable to the temperature of 850 ° C for two (2) hours. The calcined product is left to cool in the oven, after stopping the heating for 24 hours

2.2.2. Attack of phosphate by acid solutions

In a 500 ml beaker previously rinsed with demineralized water, 0.2 g of merchant phosphate is introduced (particle size <150 μm) and 200 ml of the acid solution are added. attack. After one hour of stirring at 500 rpm using a magnetic stirrer, the mixture is filtered for a determination of the level of phosphoric anhydride (P_2O_5) dissolved in the filtrate.

2.2.2.1. Complexing solution

The modified Dadin method was used to prepare the complexing solution [11]. Indeed, a mass of 1.056 g of ascorbic acid is dissolved in 200 mL of reagent, prepared by dissolving 12 g of ammonium molybdate, 0.2908 g of antimony and potassium tartrate in a mixture of 1 L d demineralized water and 1N sulfuric acid.

2.2.2.2. Determination of the dissolved phosphorus content

This method is based on the formation of a phospho-molybdate complex whose reduction by ascorbic acid is accompanied by a development of blue coloring. The intensity of the coloring is proportional to the amount of phosphorus present in the solution. 5 ml of the filtrate, 8 ml of the complexing solution are introduced into a 50 ml volumetric flask and the volume is made with demineralized water. After 10 minutes' rest, the dissolved phosphoric anhydride content is assayed using a Spectronic 20 Milton Roy Company brand molecular absorption spectrophotometer at the wavelength of 860 nm according to the Dadin protocol. modified [11]. For a better comparison of the results, the standard solutions as well as the solutions of the samples were studied under the same conditions.

2.2.3. Determination of specific surfaces and microporous volumes

They were determined by the BET method.

III. Result

3.1. Calcination of Tahoua merchant phosphate

The Figure 1 shows the variation in the quantity of Tahoua merchant phosphate during two hours of calcination. The quantity of product introduced into the oven is 100g. At the end of the treatment, the calcined product weighs 91.44 g. These results show that the quantity of the Tahoua merchant has decreased by about 8.55 g.

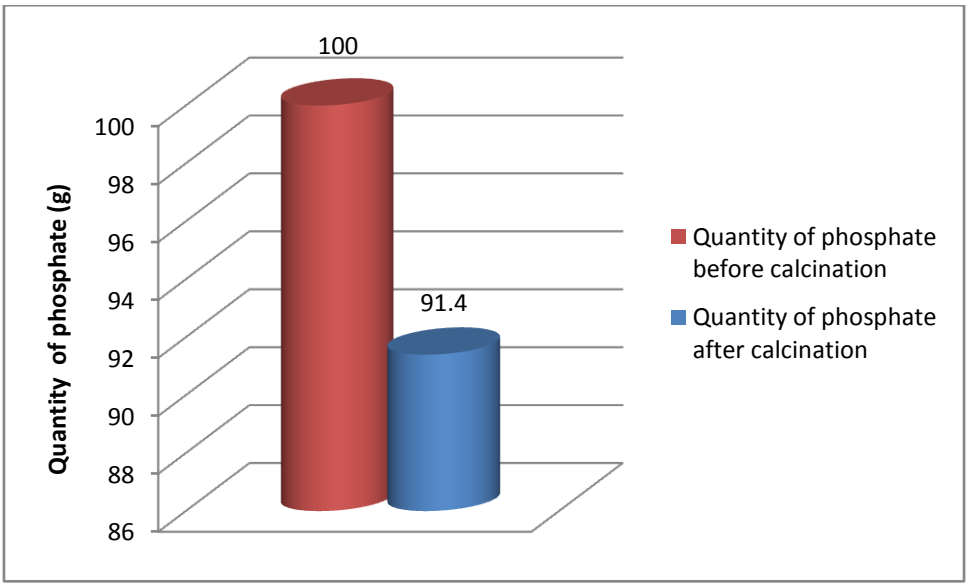

Figure 1: variation of the quantity of Tahoua merchant phosphate during two hours of calcination

3.2. Chemical composition of merchant and calcined phosphates from Tahoua

The chemical composition of Tahoua merchant phosphate before and after calcination was determined by X-ray fluorescence with energy dispersion. The results obtained are presented in Table n°2. The merchant phosphate used in this work is titrating to 20.6% in P_2O_5 before calcination. After calcination, the P_2O_5 content is 30.8%. These results show that calcination has increased the phosphorus pentoxide content of Tahoua's merchant phosphate from 10%.

Table n°2 :Chemical composition of Tahoua merchant phosphate before and after calcination

MajorElements in %				**TracesElements in ppm**		
	MerchantPhosphate	**Calcined Phosphate**			**merchantPhosphate**	**CalcinedPhosphate**
CaO	53,18	51,13		**Sr**	4579,02	3191,69
P_2O_5	20,6	30,8		**Sc**	41,667	212,18
Fe_2O_3	9,89	14,88		**Nb**	39,967	150,73
Al_2O_3	4,64	0,485		**Ba**	Trace	501,52
SiO_2	3,35	0,051		**Cu**	219,68	60,23
MnO	0,931	0,751		**Zr**	301,96	200
MgO	0,763	0,015		**Zn**	8,246	5,03
TiO_2	0,346	0,2		**Bi**	Trace	28,5
Na_2O	0,081	<0,001		**Hg**	Trace	3,869
K_2O	0,048	<0,001		**La**	Trace	0,48
LOI	5,2	1,1		**Hf**	24,06	41,465

LOI : Loss of Ignition

3.3. Specific surfaces and volumes of micropores

The specific surfaces of merchant and calcined phosphates from Tahoua were determined by the method of Brunauer, Emmett and Teller (BET). For merchant phosphate, the specific surface obtained is 390.980m^2/g, while it is 407.246m^2/g for calcined phosphate. These results show that calcination increases the specific surface of the merchant phosphate from Tahoua. As for the micropore volumes, it went from 0.354 cc/g before calcination to 0.363 cc/g after the heat treatment.

3.4. Study of the dissolution of merchant and calcined phosphates in the 1N sulfuric acid solution

The Figure 2 reports the P_2O_5 level of the merchant phosphates from Tahoua and calcined in the 1M sulfuric acid solution. It is 24.71% for merchant phosphates from Tahoua while it is 51.75% for the same merchant phosphate calcined at 850 ° C for two hours.

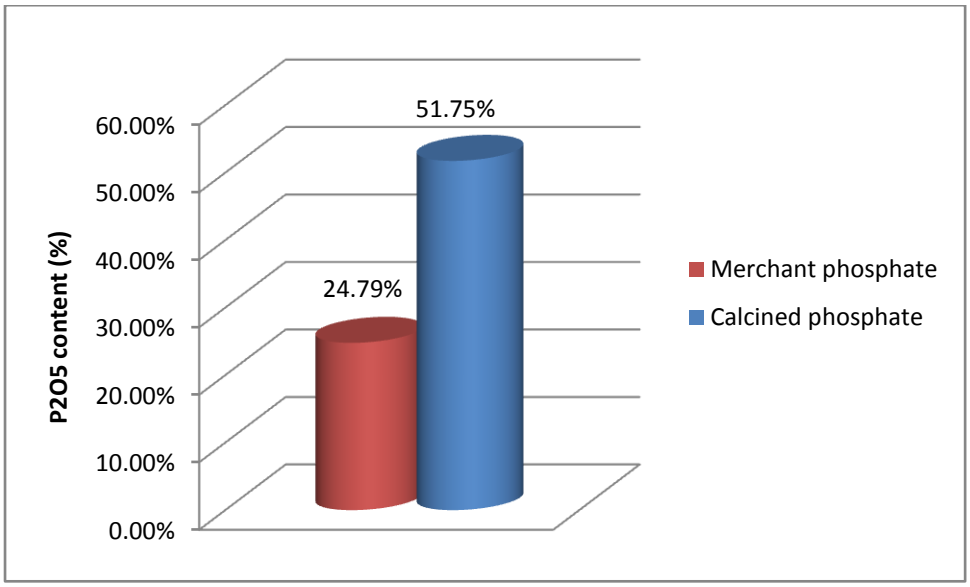

Figure 2:P_2O_5 content of merchant phosphates from Tahoua and calcined in 1M sulfuric acid solution

3.5.Study of dissolution of merchant phosphates and calcined in 0.1M citric acid solution The results of the study of the dissolution of merchant phosphates from Tahoua and calcined in citric acid solution are shown in Figure 3 below. The P_2O_5 contents obtained are 3.19% and 21.7% respectively.

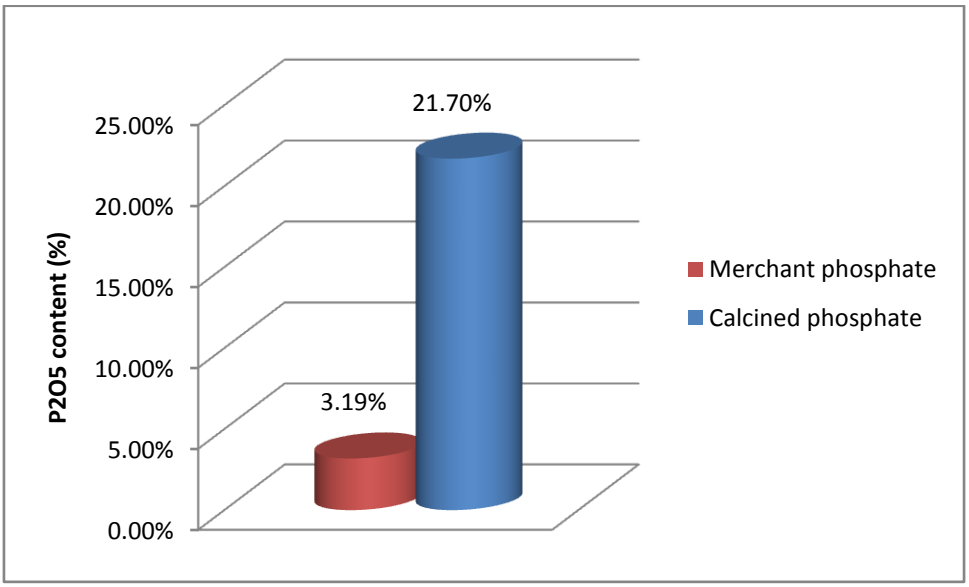

Figure 3: P_2O_5 content of merchant phosphates from Tahoua and calcined in 0.1M citric acid solution

3.6. Comparative study of the dissolution of the two types of ores

The results obtained during the dissolution of merchant and calcined phosphates in 1Msulfuric acidand 0.1Mcitric acidsolutions are reported in table 2. The P_2O_5 content obtained for merchant phosphate in 1M sulfuric acid and 0.1Mcitric acidsolutions is 24.7 and 3.19% respectively while it is 51.75 and 21.79% for calcined phosphate. . In general, the dissolution content of calcined phosphate is much higher than that of merchant phosphate in both the 1M sulfuric acid solution and the 0.1M citric acid solution.

IV. Discussion

The results obtained on the variation in the quantity of Tahoua merchant phosphate during two hours of calcination show that the mass of the sample goes from 100 g before calcination to 91.44 g after calcination. This reduction in mass of 8.55 g (8.55%) would firstly be linked to the departure of free water, organic matter in the form of carbon dioxide and water linked to the network. On the other hand, it is linked to the reduction of aluminum oxide (4.86% to 0.64%), of magnesium oxide (0.763% to 0.015%; of silica (3.47 to 0.059). %) (Table 2 above). In fact, it is reported in the literature that during the heat treatment of natural phosphate, the water

starts to follow when the temperature is around 600 ° C, followed by the material organic in the form of carbon dioxide (CO_2), and carbonates from 800 ° C [13].

It is reported in the literature that analyzes carried out on a hundred samples of natural phosphate from Tahoua show that the content of phosphorus penta-oxide in the ore varies from 18 to 35% [7]. We have taken up the chemical composition of the Tahoua merchant phosphate that we used in this work. The merchant phosphate used in this work is titrating to 20.6% in P_2O_5 before calcination. After calcination the P_2O_5 content at 30.8%. This increase may be linked to the reduction in the apatite of the amount of water, organic matter and the aluminum oxide content (from 4.86% to 0.64%) and silica (from 3.47% to 0.059%). Similar results were observed during the calcination of clear phosphate from Youssoufia (Morocco) whose Bone Phosphate of Lime (BPL) content experienced a 10% increase [13]. We can also note a reduction in the content of aluminum oxide (from 4.86% to 0.64 and of silica (from 3.47% to 0.059%).

For merchant phosphate, the specific surface obtained is 390.980m^2 / g, while it is 407.246m^2 / g for calcined phosphate. This increase can be explained by the increase in the volume of micropores at the time of calcination. Indeed, the volume of micropores increased from 0.354 cc / g before calcination to 0.363 cc / g after the heat treatment.

In general, the dissolution content of calcined phosphate is significantly higher than that of merchant phosphate in both the 1M sulfuric acid solution and the 0.1M citric acid solution. This remarkable increase could be due to the reduction of oxides (alumina, silica, MgO…) and organic matter as well as the increase in the P_2O_5 content observed after calcination. It could also be linked to the increase in the specific surface which increased from 390.980m^2 / g in merchant phosphate to 407.246m^2 / g in calcined phosphate. Ces results show that calcination can be a means to improve the agronomic quality of Tahoua phosphate.

V. Conclusion

We calcined the Tahoua merchant phosphate at 850 ° C for two hours, which enriched the ore with phosphoric anhydride (P_2O_5) from 10%. We then performed dissolution tests on merchant phosphate and calcined phosphate from Tahoua. The results obtained show that calcined phosphate dissolves better than phosphate, which works in both the 1M sulfuric acid solution and the 0.1M citric acid solution. These results can be used to revive thinking for a possible resumption of the use of merchant phosphate from Tahoua both in the agricultural field and in the production of phosphoric acid.

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