Study of the dissolution of Tahoua natural phosphate by mineral acids : hydrochloric acid and sulfuric acid

Abstract

For research purposes on the transformation of natural phosphorus into plant nutrient phosphorus, natural phosphates from Tahoua were dissolved in mineral acids, hydrochloric acid and sulfuric acid.Dissolution was effected at various concentrations (0.01M; 0.1M and 1M) and stirring times (1 hour, 3 hours and 5 hours). The results show that for all two acids (2), the dissolution rate is greater in concentrated acid solutions (1M) and for the 5-hour attack time.These rates are 38.37% and 34.87% respectively for sulfuric and hydrochloric acid solutions.Dissolution of Tahoua natural phosphate depends on the concentration of etching solutions and the etching time.With mineral acids (sulfuric and hydrochloric acid), for example, it increases with concentration.This dissolution offers interesting visions for perfecting phosphate fertilizers.

Keywords :Natural phosphate, dissolution, sulfuric acid, hydrochloric acid.

1. Introduction

Niger's subsoil, like that of many other countries around the world, is rich in various mineral resources (gold, coal, gypsum, phosphate, uranium, limestone, tin, iron, natron, etc.).Unfortunately, very few of these resources are exploited industrially. Moreover, rapid population growth, modest agricultural production due to climatic hazards and degradation of arable land, combined with poverty, have posed a serious threat to food security in our country for several decades.In order to improve agricultural productivity, the soil needs a substantial supply of certain fertilizing elements, notably phosphorus (P), nitrogen (N) and potassium (K), which are the three basic elements of animal and plant life [1].Many studies on the fertilizer phosphorus have shown the essential role of this element in the mineral nutrition of plants [2 ; 3 ; 4 ; 5].Niger has major natural phosphate deposits at Tahoua (reserve estimated at 7,371,812 tonnes) and Parc National du W (reserve estimated at 1.254 billion tonnes) [6].Despite these abundant reserves of rock phosphate, Niger's soils remain extremely low in phosphorus.In order to find solutions to this problem, many studies have been carried out in recent years on the use of Tahoua rock phosphate in agriculture [7 ; 8 ; 9].Trials to apply Tahoua natural phosphate directly to agriculture have failed to produce conclusive results [10 ; 11], due to its very low solubility in water, due to its apatitic form [9].For phosphorus in natural phosphate to be assimilated by plants, it must be available in soluble form ($H_2PO_4^-$ and HPO_4^{2-}). Several studies have been carried out on the dissolution of natural phosphates in mineral acids [12, 13, 14]. In order to make phosphorus from rock phosphate available to plants, we felt it would be useful to undertake this research work, which is part of a vast program conducted in our laboratory since 2003 on the valorization of Tahoua rock phosphate.

2. Materials and methods

2.1. Materials

2.1.1. Phosphate material

The material used in this study is Tahoua rock phosphate powder (merchant phosphate) Figure 1, purchased from the Centrale d'Approvisionnement des Intrants et Matériels Agricoles (CAIMA).The granulometry of this powder is between 100 and 150 µm. Elemental analysis of the mineral has established its chemical composition. Other characteristics of the ore have enabled us to establish its general formula : $Ca_{10-x}(K, Na, Mg)\ x(PO_4)_{6-y}(CO_3F, SO_3, SiO_4)_yF_{2-z}(OH)_z$. Where x represents the degree of molar substitution of Ca by K, Na, Sr, Mg..., y that of PO_4 by CO_3F, SO_3, SiO_4 and z that of F by OH [7 ; 9].

Figure 1 : Tahoua rock phosphate powder studied.

2.1.2. Chemical products

The chemicals used for dissolving in acids (hydrochloric acid and sulfuric acid) and dosing Tahoua natural phosphate are described in Table 1.

Table 1: Chemicals

Products	**Formule**	**Molar mass g/mol**	**Density**	**Purity**	**Origin**
Acide chlorhydrique	HCl	36,46	1,19	37%	Prolabo-Normapur

Sulfuric acid	H_2SO_4	98	1,84	95-98%	Prolabo-Normapur
Double potassium antimony tartrate	$C_4H_4O_6$ $K(SbO).0,5H_2O$	333,93	2,6	99%	ACROS ORGANICS
Ammonium molybdate	$(NH_4)_6Mo_7O_{24}.4H_2O$	1235,86	-		ACROS ORGANICS
Ascorbic acid	$C_6H_8O_6$	176,13	-	99,7%	Prolabo-Normapur
Monopotassium phosphate	KH_2PO_4	136,1	-	-	-

2.2 Methods

2.2.1. Preparation of acid solutions

We have prepared solutions of hydrochloric acid and sulfuric acid. For each acid, we have prepared three attack solutions with concentrations of 10^{-2} mol/L, 10^{-1} mol/L and 1mol/L. The pH of the different solutions is measured using a pH meter of the type pH ION 340i.

2.2.2. Dissolution of natural phosphate by acid solutions

100 mg sample and 100 mL acid solution are placed in a 250 mL beaker. Each mixture is kept under magnetic stirring at room temperature. The stirring speed is 500 rpm for attack times of 1, 3 and 5 hours. At the end of each experiment, the reaction mixture is filtered and the filtrate recovered.

2.2.3. Dosage of dissolved phosphorus

In acidic media, phosphate ions react with ammonium molybdate to form a blue phosphomolybdic complex, after reduction by ascorbic acid. The assay was carried out using a CECIL 2011 spectrophotometer at a wavelength of 860 nm.

2.2.4. Formulas for processing results

2.2.4.1. Dissolved phosphorus concentration

Dissolved phosphorus analysis results are expressed as a percentage of P_2O_5. Dissolved phosphorus concentration is determined using the calibration curve (see appendix) based on the formula :

$$[P] = \frac{A - 0{,}0444}{0{,}475} \times d$$

Where:

[P] = Phosphorus concentration in mg/L,

d = Dilution factor

A = Absorbance.

2.2.4.2. Dissolved phosphorus mass

The mass of dissolved phosphorus is determined from the following relationship :

$$m_P = \frac{[P] \times V}{S}$$

Where :

mP = Mass of dissolved phosphorus (in mg/g);

[P] = Dissolved phosphorus concentration determined on the calibration curve (in mg/L);

V = Dissolution volume in mL (0.1 L) and

S = Test sample weight in g (0.1g)

2.2.4.3. Mass of dissolved phosphoric anhydride (P_2O_5)

The mass of dissolved phosphoric anhydride (P_2O_5) in mg/g is determined from the following equation:

$$2P + \frac{5}{2}O_2 \rightarrow P_2O_5$$

$$m_{P_2O_5} = 2{,}29 \times m_P.$$

With :

$m(P_2O_5)$= Mass of dissolved phosphorus anhydride (P_2O_5) in mg/g

m_P = Mass of dissolved phosphorus (in mg/g)

2.2.4.4. Percentage of dissolved P_2O_5

The percentage of dissolved P_2O_5 is deduced using the following relation :

$$\%P_2O_5 = \frac{m_{P_2O_5}}{1000} \times 100$$

3. Results and discussion

3.1. Dissolution of Tahoua natural phosphate in hydrochloric acid

Dissolution of Tahoua natural phosphate in hydrochloric acid solutions was carried out at concentrations of 10^{-2} mol/L, 10^{-1} mol/L and 1 mol/L at times of 1 hour, 3 hours and 5 hours. The results of the dissolved P_2O_5 determination obtained in the filtrate after dissolution in hydrochloric acid solutions at different stirring times are shown in Figures 2, 3 and 4. They show P_2O_5 levels as a function of acid concentration over the attack time. Figure 5 shows the P_2O_5 content of the various hydrochloric acid solutions as a function of attack time.

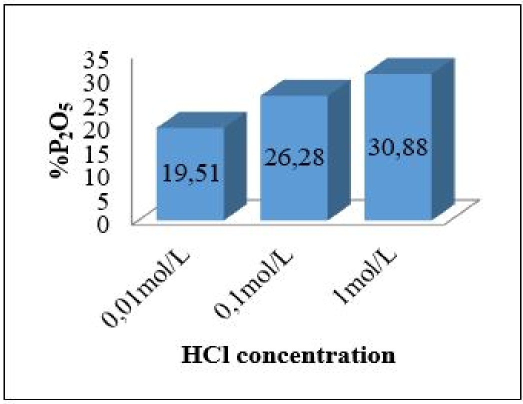

Figure 2 : P_2O_5 **rate dissolved in HCl for 1 hour**

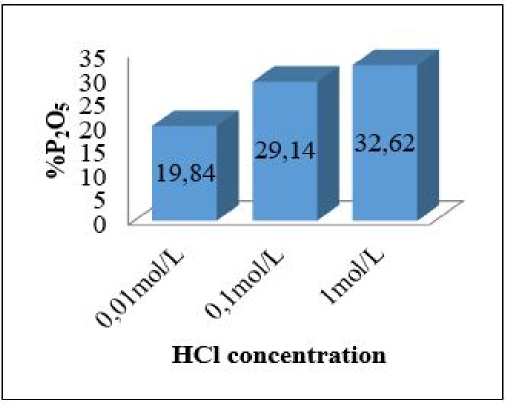

Figure 3 : P_2O_5 **rate dissolved in HCl for 3 hours**

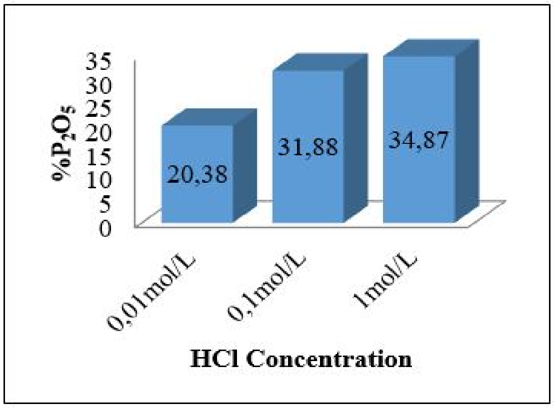

Figure 4 : P_2O_5 **rate dissolved in HCl for 5 hours**

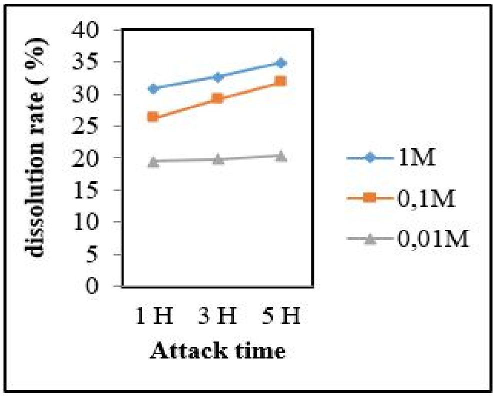

Figure 5 : Variation in dissolved P_2O_5 **as a function of attack time**

Analysis of Figure 2 shows that the percentage of dissolved P_2O_5increases with acid concentration.In fact, for an attack time of 1 hour, the highest dissolution rate is 30.88%, obtained at a concentration of 1 mol/L, compared with 19.51% obtained in the 0.01 mol/L attack solution.Figure 3 shows that dissolved P_2O_5 content varies with acid concentration. The highest dissolution rate is 32.62%, obtained at a concentration of 1mol/L for an attack time of 3 hours.According to the results shown in Figure 4, the higher the acid concentration, the higher the dissolved P_2O_5 content.The best dissolution rate is 34.87%, obtained in the 1 mol/L attack solution over a period of 5 hours.In fact, for the present study, the best rates are obtained in the 1 mol/L attack solution.This explains why this dissolution in a strongly acidic environment is due to the attack of the mineral by H^+ protons.The results of this study are in agreement with those found by H. Adel Sharif, et al. (2012) on the dissolution of Iraqi rock phosphate [15].It can also be seen that this dissolution is at its maximum after a stirring time of 5 hours. These rates are : 34.87%; 31.88% and 20.38% for the respective concentrations of 1M; 0.1M and 0.01M. It can be seen that for the very low concentration of 0.01M, the P_2O_5 level varies very little with stirring time. This is due to the low consumption of H^+ ions.

3.2. Dissolution of Tahoua natural phosphate in sulfuric acid solutions

This natural mineral was also dissolved in sulfuric acid solutions under the same conditions as hydrochloric acid solutions.The results of the determination of dissolved P_2O_5 in the filtrate dissolved in sulfuric acid solutions after 1 hour, 3 hours and 5 hours of agitation are shown in Figures 6, 7 and 8 respectively.Figure 9 shows the phosphate dissolution rate (P_2O_5 rate) as a function of attack time and acid concentration.

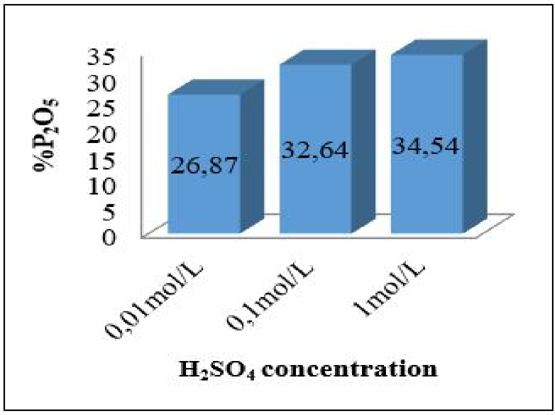

Figure 5 : P_2O_5 rate dissolved in H_2SO_4 for 1 hour

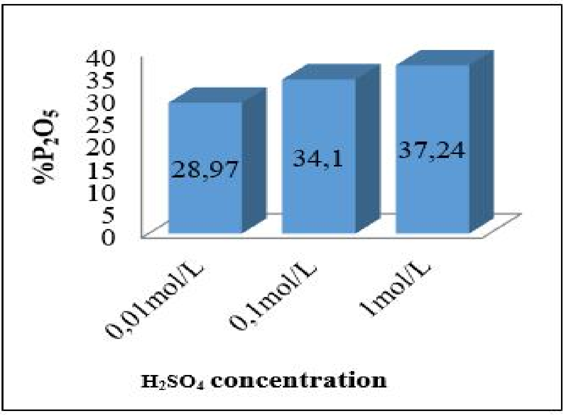

Figure 6 : P_2O_5 rate dissolved in H_2SO_4 for 3 hours

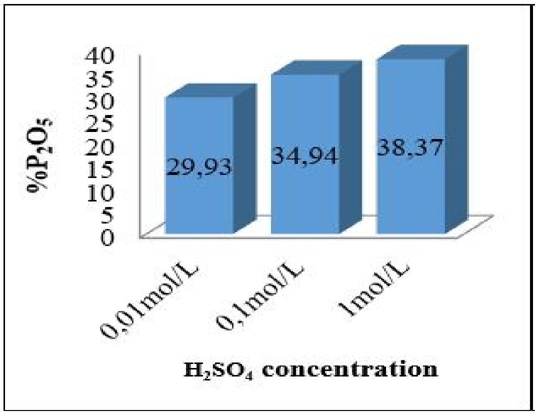

Figure 7 : P_2O_5 rate dissolved in H_2SO_4 for 5 hours

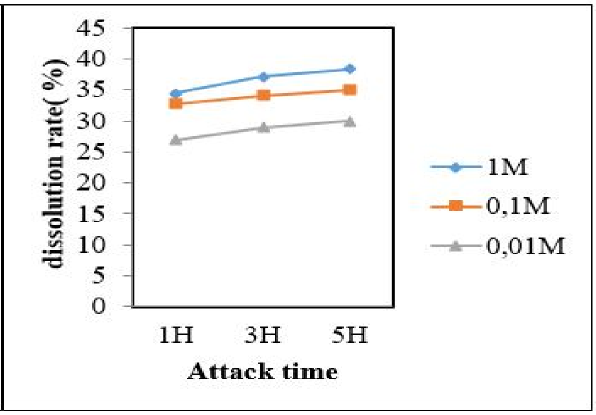

Figure 8 : Variation in dissolved P_2O_5 as a function of attack time

Figure 5 shows that the rate of P_2O_5 dissolution is greater when the solution is concentrated. The best rate of 34.54% is obtained at a concentration of 1 mol/L for an etching time of 1 hour.According to the results shown in figure 6, dissolution increases with acid concentration. The best dissolution rate of 37.24% was obtained at a concentration of 1 mol/L after an attack time of 3 hours.Analysis of the results in Fig. 7 shows that the highest dissolution rate of 38.37% is obtained in the 1 mol/L H_2SO_4 solution over an attack time of 5 hours. It can be concluded from these results that phosphate dissolution in sulfuric acid solutions also gives the best results in the most concentrated solution.It can also be seen that the amount of dissolved phosphate is a function of the attack time: the longer the attack time, the greater the amount of dissolved phosphate. Indeed, the best dissolution rate is 38.37% obtained in the 1 mol/L attack solution and after a stirring time of 5 hours.These results are in good agreement with those obtained for the dissolution of this same ore by several other authors such as M. Koriko, (2010) on Hahotoé-Kpogamé rock phosphate (Togo) [16] and M. Lassis et al (2015) on Djebel Onk rock phosphate (Algeria) [17].These results can be explained by the fact that during the dissolution of natural phosphate in a concentrated medium, there is a significant consumption of H^+ ions and therefore an increase in dissolution [18, 19]. However, Ousmane M. S et al (2023) obtained a dissolution rate of 16%, during their work on the dissolution of Tapoa natural phosphate (Niger) in sulfuric acid for an attack time of 7 hours [20]. This dissolution rate is significantly lower than that obtained during the present research. This low rate may be attributable to the nature of the mineral.

4. Conclusion

This work has enabled us to dissolve Tahoua rock phosphate in hydrochloric acid and sulfuric acid solutions at various concentrations and attack times. The filtrates collected were used to assay dissolved phosphorus. The assay results are expressed as a percentage of dissolved phosphoric anhydride (P_2O_5).The rate of dissolved phosphorus depends on the strength of the acid to dissolve the natural phosphate. The results show that in the case of mineral acids, the dissolved phosphorus content, expressed as % P_2O_5 of Tahoua rock phosphate, increases with increasing acid concentration. Dissolution rates are higher in the 1 mol/L solution.

Therefore, this concentration is appropriate for this dissolution experiment. The results of this study clearly show that the longer the attack time, the greater the dissolution. The best dissolution rates are obtained for an attack time of 5 hours. For our study, this time was chosen for the dissolution of this phosphate. The rate of dissolved phosphorus, in % P_2O_5, under these conditions is 38.37% for sulfuric acid and 34.87% for hydrochloric acid. Under the same conditions, sulfuric acid dissolves TNP (Tahoua Natural Phosphate) better than hydrochloric acid. This suggests that TNP dissolution in both acids increases with the strength of the acid.

REFERENCES

[1] Zapata F and Roy RN. Use of natural phosphates for sustainable agriculture. FAO Fertilizers and Plant Nutrition Bulletin. 2004; 0259-6180.

[2] Bagayoko M, Maman N, Palé S, Sirifi S, Taonda SJB., Traore S, Mason SC. Microdose and N and P fertilizer application rates for pearl millet in West Africa. African Journal of Agricultural Research. 2011; 6(5), 1141-1150.

[3] Rahajaharitompo Rabeharisoa L. Fertility management and phosphate fertilization of ferralitic soils in the highlands of Madagascar. State Doctorate Thesis in Natural Sciences. University of Antananarivo. 2004; 214P.

[4] Ngaordoum D. Study of the effects of different doses of natural phosphate from Burkina on the characteristics and agronomic efficiency of corn straw accounts. Thesis of engineer in agronomy. Polytechnic University of Bobo-Dioulasso (U.P.B). 2007; 53P.

[5] Boukhenfouf W. Concentration of uranium-application to agricultural fertilizers. Doctoral thesis in nuclear engineering. Ferhat Abbas-Sétif University. 2011; 100p.

[6] A. Franconi, J. Julien and I. Zibo. Specific study of the main mineral substances and their geological context. Mineral plan of the Republic of Niger, volume IV 2nd volume. 1981; 725P.

[7] Natatou I, Zanguina A, Khalid I, Boos A, Guille J, Rastegar F and Burgard M. Physicochemical characterization of Tahoua natural phosphate. Ann. Chim. Sc. Mat. 2005; 30 (1), 67-76P.

[8] I. Natatou, A. Maman, A. Zanguina, I. Khalid, A. Boos and M. Burgard, (2004). Physicochemical studies of Tahoua merchant phosphate (Niger). J. Soc. Ouest-Afr. Chim; 018; 137-148P.

[9] Natatou I, Zanguina A, Ikhiri K, Boos A, Guille J, Rastegar F, Burgard M. Physicochemical characterization of Tahoua natural phosphate (Niger). Annals of Chemistry-Materials Sciences. 2005; 30: 67-76.

[10] Coraf Action. Phosphates, a wealth for West African agriculture. Information note. 2011; n°59, 16P.

[11] National Network of Chambers of Agriculture of Niger. Phosphate / research has been insisting for 40 years on this limiting factor of rainfed crops investing in. 2012

[12] Lukas B, Dana R, Ales H. Kinetics of dissolution of calcium phosphate (Ca-P) bioceramics. Processing and Application of Ceramics. 2008; 2: 57-62.

[13] Koriko M, Zanguina A, Tchangbedji G, Mohamed E M, Natatou I, Mohamed H, Mohamed S. Study of the dissolution of phosphates from Hahotoé-Kpogamé (Togo) by natural humic acids. J. Soc. Ouest-Afr. Chim. 2010; 030, 41-47.

[14] Adel S H, Shurooq TR, Haider A A. Phosphate Rock Treatment with Hydrochloric Acid for Increasing P2O5 Content. Engineering and Technology Journal. 2012; 30 : 67-76.

[15] Adel Sharif H, Shurooq Talib R, Haider Abd A. Phosphate Rock Treatment with Hydrochloric Acid for Increasing P2O5 Content. Eng. &Tech. Journal. 2012; Vol.30, No.1, 10.

[16] Koriko M. Extraction, characterization, chemical reactivity of natural humic substances with Hahotoé-Kpogamé phosphates and their photodegrading properties. Physicochemistry of materials. Doctoral thesis of the universities of Lomé (Togo) and blaise pascal of Clermont Ferrand (France). 2010; 158p.

[17] Lassis M, Mizane A, Dadda N, Rehamnia R. Dissolution of Djebel Onk phosphate ore using sulfuric acid. ENMM-20. 2015; No, 5.

[18] Moursalou K, Adamou Z, Gado T, Mohamed E M, Ibrahim N, Mohamed H, Mohamed S. Study of the dissolution of phosphates of Hahotoé-Kpogamé (Togo) by natural humic acids. J. Soc. Ouest-Afr. Chim. (2010) 030; 41 - 47

[19] Ousmane M S, Zanguina A, Natatou I. Treatment of Natural Phosphates of Tahoua (Niger) by Some Conventional Acids. European Scientific Journal August. 2017; 13(24): 1857 – 7881

[20] Ousmane M S, Mamane S A A, Abdou G I, Zanguina A and Natatou I. Treatment of natural phosphate from tapoa (niger) by mineral and organic acids. Int. J. Adv. Res. 2023; 11(11), 314-321.