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Study of the Dissolution of Tahoua Natural Phosphate by Mineral Acids: Hydrochloric Acid and Sulfuric Acid

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

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

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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 (Zapata and Roy 2004). Many studies on the fertilizer phosphorus have shown the essential role of this element in the mineral nutrition of plants (Bagayoko et al. 2011, Rahajaharitompo 2004, Ngaordoum 2007, Boukhenfouf 2011). 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) (Franconi 1981). 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 (Natatou et al. 2005, Natatou et al. 2018, Coraf Action 2011). Trials to apply Tahoua natural phosphate directly to agriculture have failed to produce conclusive results (Coraf Action 2011, National Network of Chambers of Agriculture of Niger 2012), due to its very low solubility in water, due to its apatitic form (Natatou et al. 2005). 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 (Lukas et al. 2008, Koriko et al. 2010, Adel et al. 2012). 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) Fig. 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 (Natatou et al. 2005).

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.

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 1 mol/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.

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	$C_4H_4O_6K(SbO).0,5H_2O$	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	-	-	-

Fig. 1. Tahoua rock phosphate powder studied

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 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 Figs. 2, 3 and 4.

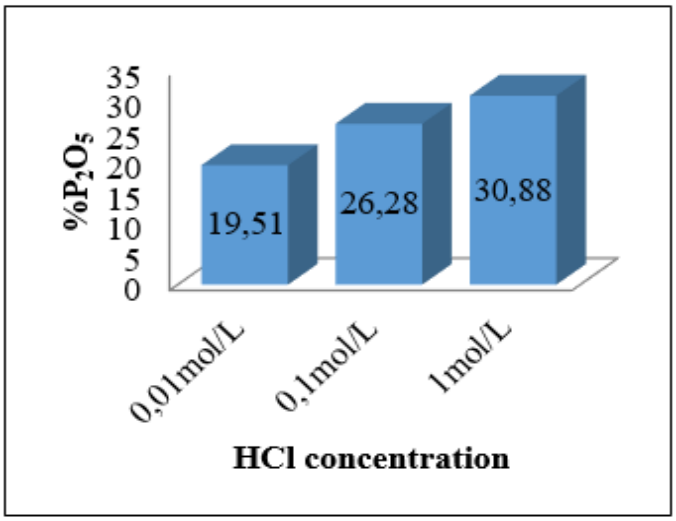

Fig. 2. P_2O_5 rate dissolved in HCl for 1 hour

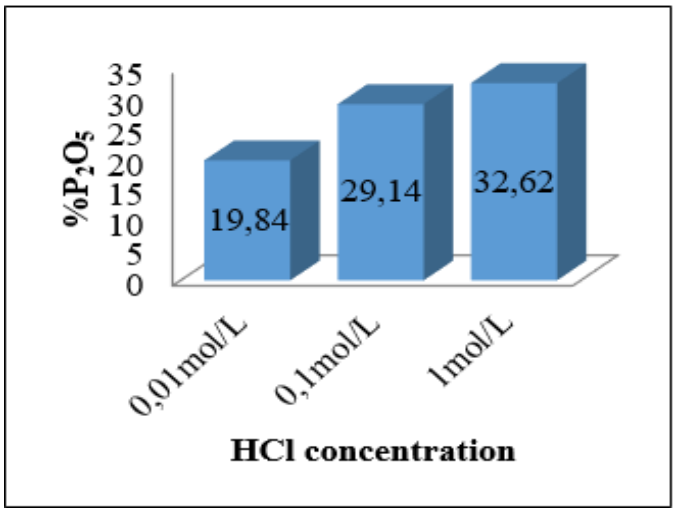

Fig. 3. P_2O_5 rate dissolved in HCl for 3 hour

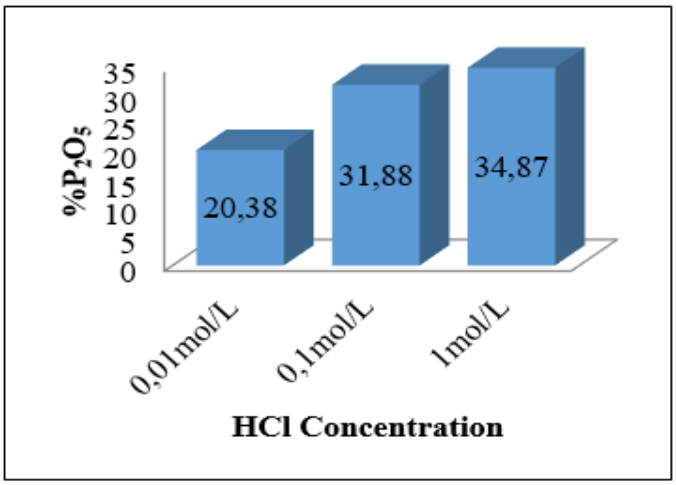

Fig. 4. P_2O_5 rate dissolved in HCl for 5 hour

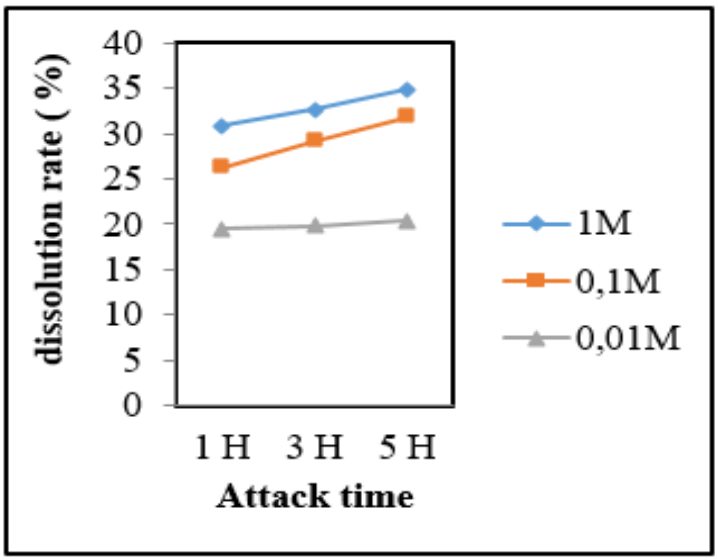

Fig. 5. Variation in dissolved P_2O_5 as a function of attack time

They show P_2O_5 levels as a function of acid concentration over the attack time. Fig. 5 shows the P_2O_5 content of the various hydrochloric acid solutions as a function of attack time.

Analysis of Fig. 2 shows that the percentage of dissolved P_2O_5 increases 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. Fig. 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 Fig. 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 (Adel Sharif et al. 2012). 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 Figs. 6, 7 and 8 respectively. Fig. 9 shows the phosphate dissolution rate (P_2O_5 rate) as a function of attack time and acid concentration.

The analysis of Fig. 5 shows that the rate of P_2O_5 dissolution is more important 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 Fig. 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

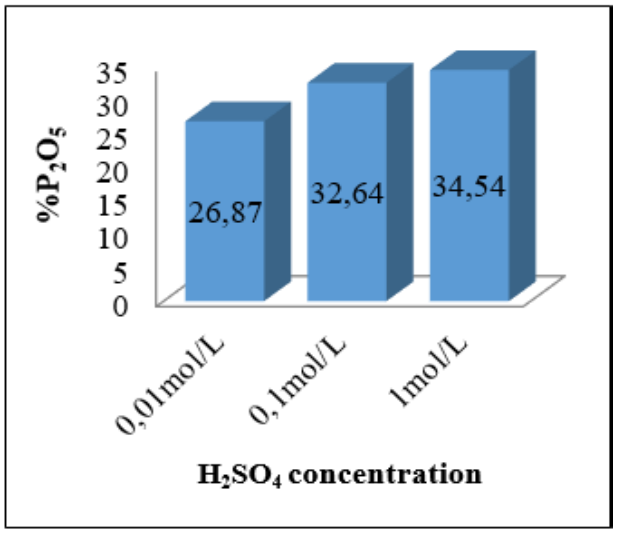

Fig. 6. P_2O_5 rate dissolved in H_2SO_4 for 1 hour

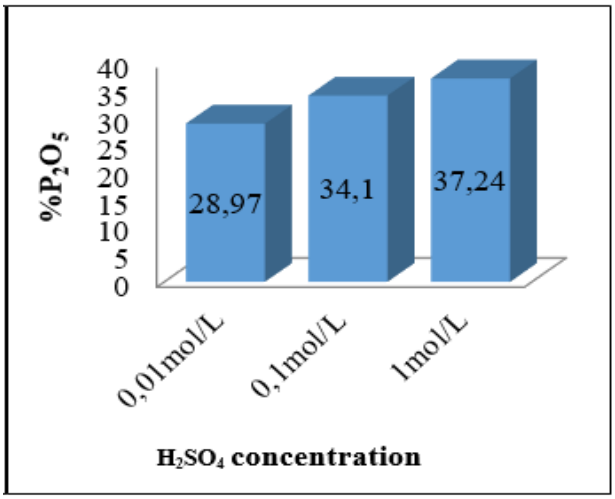

Fig. 7. P_2O_5 rate dissolved in H_2SO_4 for 3 hour

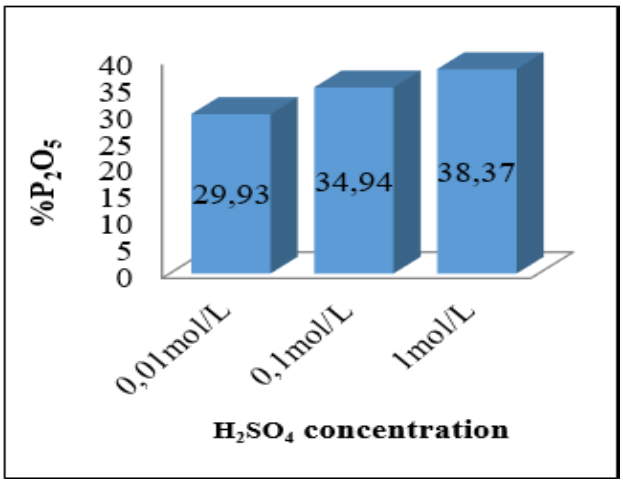

Fig. 8. P_2O_5 rate dissolved in H_2SO_4 for 5 hour

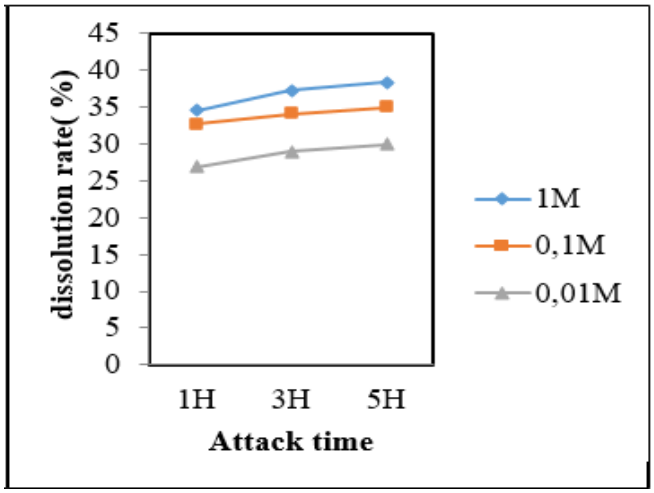

Fig. 9. Variation in dissolved P_2O_5 as a function of attack time

of this same ore by several other authors such as M. Koriko, (2010) on Hahotoé-Kpogamé rock phosphate (Togo) (Koriko 2010) and M. Lassis et al (2015) on Djebel Onk rock phosphate (Algeria) (Lassis et al. 2015). 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 (Koriko et al. 2010, Ousmane et al. 2017). 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 (Ousmane et al. 2023). 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.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

We hereby declare that no generative artificial intelligence technologies such as large language models (ChatGPT, COPILOT, etc.) and text-image generators were used during the writing of this manuscript.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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