Int.J.Curr.Res.Aca.Rev.2024; 12(11): 141-149

EXCELLENT PUBLISHERS

International Journal of Current Research and Academic Review

ISSN: 2347-3215 (Online) Volume 12 Number 11 (November-2024)

Journal homepage: http://www.ijcrar.com

doi: https://doi.org/10.20546/ijcrar.2024.1211.012

Comparative Study of the Dissolution of Tahoua Natural Phosphate by Solutions of Mineral Acids (Hydrochloric Acid and Sulfuric Acid) and Organic Acid (Ethylene Diamine Tetraacetic Acid EDTA)

Inoussa Halidou Bassirou[1], Yahouza Zaneidou[2*], Amadou Hamidou Abdoulaye[3] and Zanguina Adamou[1]

[1]Materials, Water and Environment Laboratory, Chemistry Department, Faculty of Science and Technology, Abdou Moumouni University, Niamey (Niger), BP: 10662 Niamey, Niger
[2]Department of Didactics of Disciplines, Faculty of Education Sciences, Djibo Hamani University, Tahoua, BP: 255 Tahoua, Niger
[3]Department of Water and Forestry/Rural Engineering, Faculty of Agronomy, Faculty of Agronomy, Abdou Moumouni University, BP: 10662 Niamey, Niger

**Corresponding author*

Abstract

As part of research into the transformation of mineral phosphorus into plant-available phosphorus, a comparative study of the dissolution of Tahoua natural phosphate (merchant phosphate) in hydrochloric acid, sulfuric acid and ethylene diamine tetra acetic acid (EDTA) solutions was carried out. Dissolution was carried out at various concentrations (0.01mol/L; 0.1mol/L and 1mol/L) and stirring times (1 hour, 3 hours and 5 hours) in the laboratory. The results show that for mineral acids, the dissolution rate is higher in concentrated acid solutions (1mol/L) and for the 5-hour attack time. These rates are 38.37% and 34.87% respectively for sulfuric and hydrochloric acid solutions. For EDTA, on the other hand, the results show that the highest dissolution rate is obtained in the acid solution at low concentration (0.01mol/L). It is of the order of 20.1% over the 5-hour attack time. Dissolution of Tahoua rock phosphate depends on the concentration of etching solutions and the etching time. With mineral acids (sulfuric and hydrochloric acid), dissolution increases with concentration. In EDTA, on the other hand, dissolution is low with increasing concentration.

Article Info

Received: 15 September 2024
Accepted: 29 October 2024
Available Online: 20 November 2024

Keywords

Natural phosphate, Tahoua dissolution, sulfuric acid, hydrochloric acid, EDTA.

Introduction

Phosphate was first used in agriculture as a chemical fertilizer in the late 18th century. Today, around 90% of the world's production of this raw material is used for agricultural development (Zapata *et al.,* 2004; Ferrag Alleg, 2010). Phosphorus is one of the three main nutrients (along with nitrogen (N) and potassium (K)) essential for plant development (Zapata *et al.,* 2004; Isil *et al.,* 2009; Bagayoko *et al.,* 2011), particularly for root growth and fruit and seed ripening. A soil in which all these elements are present in the right proportions is fertile. What's more, in a phosphorus-deficient environment, animal and plant life is virtually impossible. Phosphorus is essential for the production of energy through photosynthesis, and is considered the fuel of plant life to achieve higher yields (Vanden Bossche, 1999; El mokhtar El Ouardi, 2008). Without phosphate, no plant can develop properly. Its deficiency is one of the factors limiting agricultural production. However, the

low water solubility of this minerai means that it cannot be applied directly as a soil fertilizer, due to its apatitic form (Ousmane Mahamane Sani *et al.,* 2023; Zanguina, 2011).

Chemical or biological treatment of the minerai yields mineral and/or organo-mineral phosphate fertilizers containing plant-available phosphorus (McClellan and Van Kauwenbergh, 2004; Ousmane *et al.,* 2017a; Zanguina *et al.,* 2018). Numerous studies have been carried out on the dissolution of natural or synthetic phosphates in conventional acids (Lukas *et al.,* 2008; Koriko *et al.,* 2010; Adel *et al.,* 2012; Ousmane *et al.,* 2017b). As part of the research on the transformation of Niger apatite phosphate to make its phosphorus bio-available to plants, a study of the dissolution of the minerai by mineral acids (hydrochloric acid and sulfuric acid) and by organic acid (ethylene diamine tetraacetic acid EDTA) is being carried out as part of this comparative study. Hydrochloric acid, sulfuric acid and EDTA are the reference acids for the manufacture of phosphate inputs. The aim is to optimize the best acid and concentration for better dissolution of Tahoua Natural Phosphate (TNP), and to suggest possible applications, notably in the manufacture of water-soluble phosphate fertilizers.

Materials and Methods

Presentation of the Study Zone

The Tahoua region is located in the center-west of the country, in longitude between 04° 52' and 6° 41' East and in latitude between 13° 40' North (Nigeria border) and 18° 50' North (Mali border). It is bordered to the north-west by the Republic of Mali, to the east by the regions of Agadez and Maradi, to the south by the Federal Republic of Nigeria and to the west by the regions of Dosso and Tillabéry. It covers an area of 113,317 km², or 8.95% of the national territory.

According to the territorial division, the Tahoua region is subdivided into 12 departments, which are in turn subdivided into urban and rural communes, cantons, villages, hamlets and nomadic camps. The rock phosphate deposit from which the samples were taken for testing is located to the north of the town of Tahoua, on the Tillia track, some 60 km from the town of Tahoua. The first phosphate deposit is located southeast of the village of Innakeur, 63 km from Tahoua, and the second is at Gaoy, 65 km north of Tahoua (Zanguina, 2011; Appleton, 2002) figure 1.

Phosphate material

The material used in this study is Tahoua rock phosphate (merchant phosphate) reduced to powder. The granulometry of this powder ranges from 100 µm to 150 µm (figure 2).

Chemical products

The chemicals used for dissolving (organic and mineral acids) and dosing Tahoua rock phosphate are described in Table 1.

Preparation of acid solutions

We have prepared the following solutions of mineral acids (hydrochloric acid and sulfuric acid) and organic acid (ethylene diamine tetra acetic acid EDTA): Hydrochloric acid, sulfuric acid and ethylene diamine tetra acetic acid (EDTA). For each acid, we prepared three etching solutions with concentrations of 10-2 mol/L, 10-1 mol/L and 1mol/L respectively. The pH of the different solutions is measured using a pH meter of the type pH ION 340i.

Dissolution of rock 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.

Determination 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.

Formulas for processing results

The formulas used to evaluate the results are shown in Table 2.

Results and Discussion

The P_2O_5 rates obtained at the various concentrations and attack times are shown in Table 2 3.

Comparison of mineral acids

The comparative study of Tahoua rock phosphate dissolution as a function of attack time in different mineral acid solutions is shown in figures 3, 4 and 5. Figures 3, 4 and 5 show similar graphs. These graphs show that dissolution in hydrochloric acid and sulfuric acid increases with acid concentration and attack time. Moreover, according to these graphs, the increase in dissolution rate is greater in sulfuric acid than in hydrochloric acid. The highest dissolution rate of 38.37% (Table 3) is obtained with sulfuric acid. Hydrochloric acid gave the lowest dissolution rate, at 19.51% (Table 3). This can be explained by the fact that sulfuric acid is a strong diacid, resulting in the massive release of H^+ ions. Indeed, its first acid function is strong and its second function is weak, according to the following equations:

$$H_2SO_4 \longrightarrow HSO_4^- + H^+ \, (R_1) \; pK_{a1} = -3$$

$$HSO_4^- \longrightarrow SO_4^{2-} + H^+ \, (R_2) \; pK_{a2} = 1{,}9$$

It is clearly shown that the more concentrated the solution, the higher the P2O5 extraction rate. These results are in good agreement with those for the dissolution of Togo phosphate in acid media (Koriko *et al.,* 2010; Koriko, 2010) and PNT (Zanguina, 2011). In the literature, it has been reported that when the pH of the solution decreases or when the concentration is high, an increase in the dissolution rate is observed (Claire, 2005). The dissolution of rock phosphate in the concentrated medium could be justified by the massive presence of H^+ ions. Phosphate dissolution in an acid medium leads to the formation of hydrogen phosphate ions. This is due to the reaction between H^+ and phosphate ions (PO_4^{3-}) in apatite, according to the following reaction equations:

$$PO_4^{3-} + H^+ \longrightarrow HPO_4^{2-} (R_3)$$

$$HPO_4^{2-} + H^+ \longrightarrow H_2PO_4^- (R_4)$$

The high P_2O_5 content can also be justified by the fact that the action of mineral acids (H_2SO_4 and HCl) on rock phosphate is a heterogeneous process that can be conventionally divided into two stages. In the first stage, a rapid exchange reaction takes place on the surface of the phosphate particles until the sulfuric or hydrochloric acid is completely consumed.

In the second stage, dissolution is controlled by the diffusion of phosphoric acid formed during the attack of sulfuric acid in solution, which reacts with the remaining phosphate (Boulahbel, 2010) to finally produce simple superphosphate (Moughli, 2000).

Comparison of mineral and organic acids

For a comparative study of the behavior of rock phosphate in the various acids, we also undertook the dissolution of phosphate in EDTA. The dissolution rates of rock phosphate in the three acids are shown as a function of concentration for the three etching times in Figures 6, 7 and 8.

Figures 6, 7 and 8 show similar graphs for the two (2) mineral acids (hydrochloric acid and sulfuric acid) and inverses for the organic acid (EDTA) for all concentrations and etching times. In fact, with EDTA, the best dissolution rate of 20.1% (Table 3) is obtained at the lowest concentration (0.01 mol/L), while for mineral acids the highest dissolution rates are found at the highest concentration (1mol/L). These are 34.87% and 37.24% (Table 3) for hydrochloric acid and sulfuric acid respectively. These results show that, whatever the concentration, sulfuric acid dissolves phosphate better than hydrochloric acid, and finally EDTA.

From these results, we can conclude that mineral acids are more conducive to the dissolution of Tahoua rock phosphate than organic acids. This may be explained by the fact that, when dissolving rock phosphate, mineral acids (sulfuric acid and hydrochloric acid) are better at releasing H^+ ions that interact with phosphate ions (PO_4^{3-}), thereby increasing ore dissolution (1; 20). EDTA is a weak acid: its first acidity has a pKa_1 equal to 1.99 and the second acidity has a pKa_2 of 2.67. As a result, the amount of H^+ protons produced by the acid is lower. In the literature, organic acids have been reported to dissolve apatites in weakly acidic media (Koriko *et al.,* 2010). The hexadentate ligand structure (with four (4) carboxyl groups and two amine groups):

This suggests that EDTA's dissolution in low-concentration solution is linked to the complexation of metal cations by the acid's conjugate base. This increases phosphate dissolution in this medium. Thus, EDTA has the semi-developed structure.

Table.1 Chemical products

Products	Formule	Molar mass g/mol	Density	Purity	Origin
EDTA	$C_{10}H_{16}N_2O_8$	292,24	-	99%	-
hydrochloric acid	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	-	-	-

Table.2 Formulas for processing results

Parameters	Formuls
Dissolved phosphorus concentration	$[P] = \frac{A - 0,0444}{0,475} \times d$ [P] = Phosphorus concentration in mg/L, d = Dilution factor A = Absorbance.
Mass of dissolved phosphorus	$m_P = \frac{[P] \times V}{S}$ m_P= Mass of dissolved phosphorus (in mg/g); [P] = Dissolved phosphorus concentration determined on calibration curve (in mg/L); V = Dissolution volume in mL (0.1 L) and S = Test sample weight in g (0.1g).
Mass of dissolved phosphoric anhydride (P_2O_5)	$m_{P_2O_5} = 2,29 \times m_P$ $m_{P_2O_5}$ = Mass of dissolved phosphorus pentoxide (P_2O_5) in mg/g mP = Mass of dissolved phosphorus (in mg/g)
percentage of dissolved P_2O_5	$\%P_2O_5 = \frac{m_{P_2O_5}}{1000} \times 100$

Table.3 P_2O_5 content of acids used

Hours	0,01 mol/L	0, 1 mol/L	1 mol/L	Nature of acid
1	19,51%	26, 28%	30,88%	**HCl**
3	19, 84%	29,14%	29,14%	
5	20, 38%	31,88%	34, 87%	
1	26,84%	32,64%	34,54%	**H_2SO_4**
3	28, 97%	34, 1%	37, 24%	
5	29,93%	34, 94%	38, 37%	
1	14, 56%	4, 63%	0,98%	**EDTA**
3	18, 6%	5, 23%	1, 3%	
5	20, 1%	6, 07%	1, 97%	

Figure.1 Location of the Tahoua rock phosphate deposit

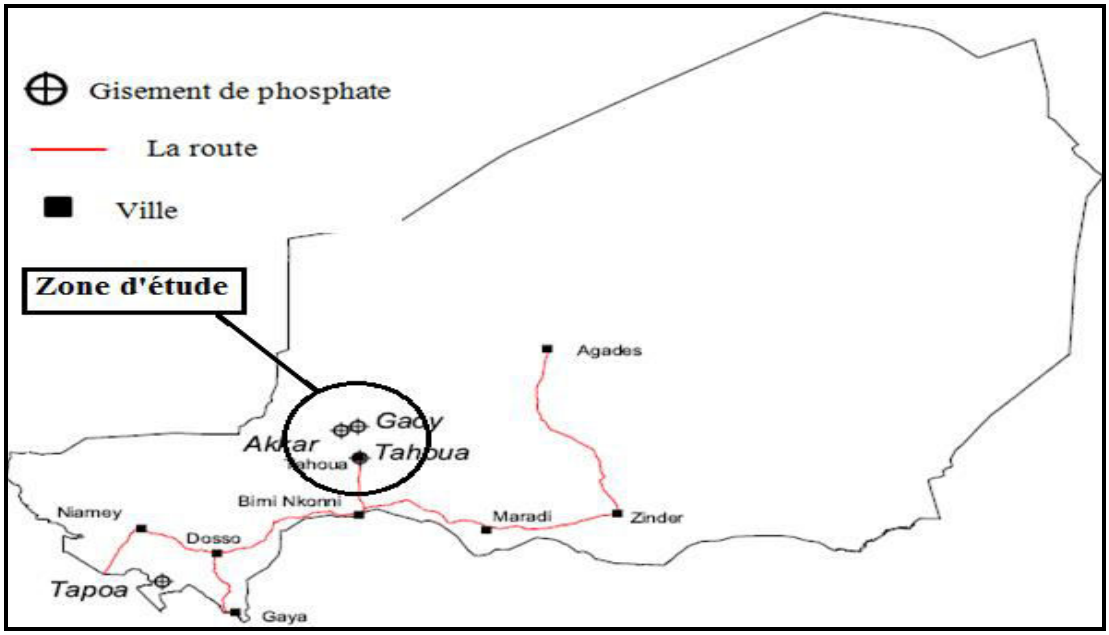


Figure.2 Tahoua rock phosphate powder studied.

Figure.3 Comparison of the dissolution rate of mineral acid solutions with a concentration of 1 mol/L

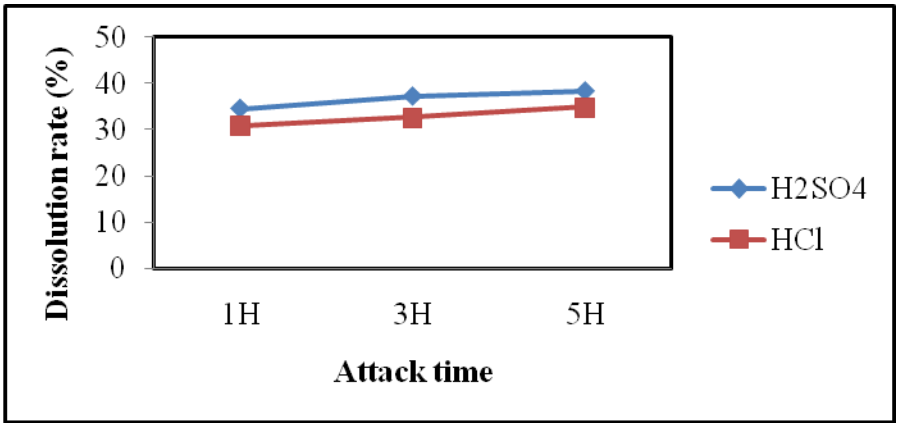


Figure.4 Comparison of dissolution rates of 0.1M mineral acid solutions.

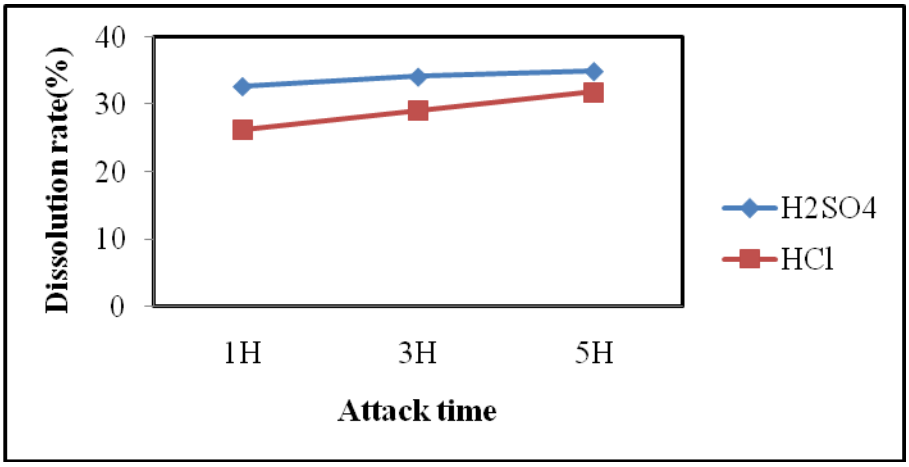


Figure.5 Comparison of the dissolution rate of mineral acid solutions with a concentration of 0.01 mol/L.

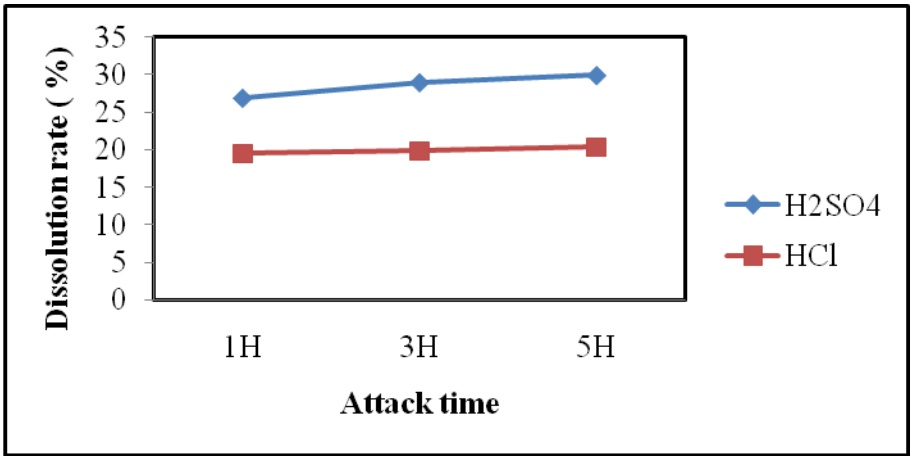


Figure.6 Comparison of dissolution rates of organic and mineral acid solutions as a function of concentrations at 1 hour.

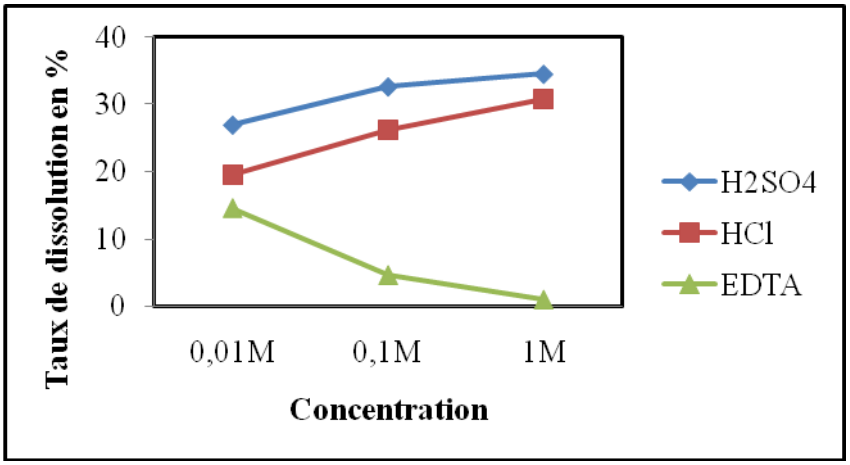


Figure.7 Comparison of dissolution rates of organic and mineral acid solutions as a function of concentration at 3 hours.

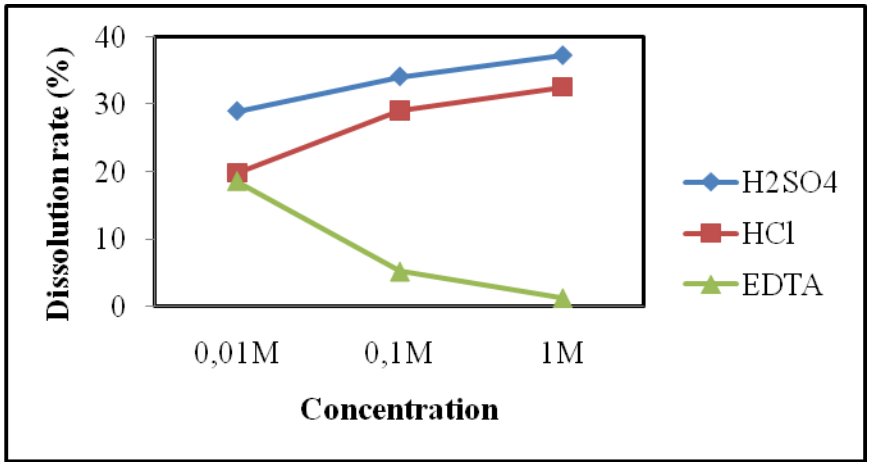


Figure.8 Comparison of the dissolution rate of organic and mineral acid solutions as a function of concentration at 5 hours.

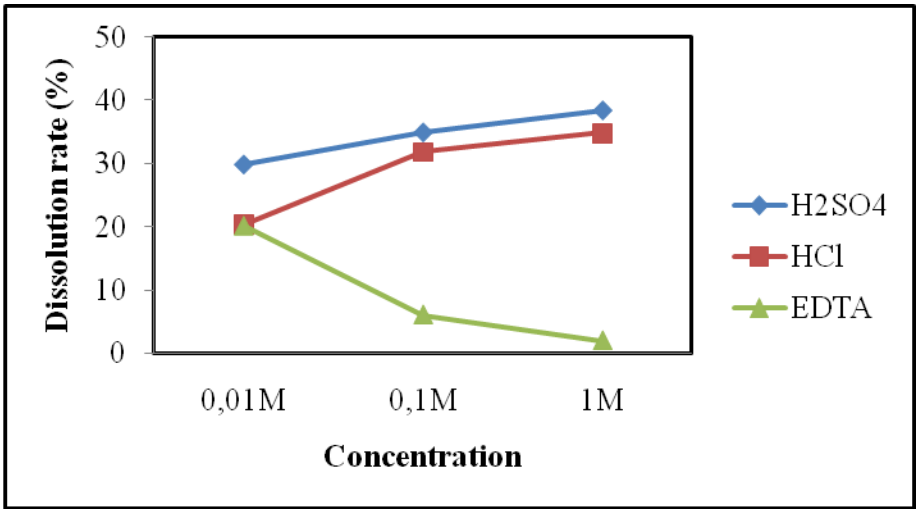
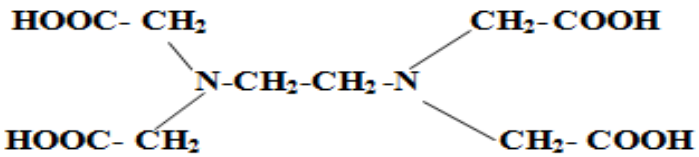


Figure.9



Conclusion

This work enabled us to assess the dissolution of Tahoua rock phosphate in solutions of hydrochloric acid, sulfuric acid (two mineral acids) and EDTA (an organic acid) at various concentrations and with different attack times. The filtrates collected were used to measure dissolved phosphorus. The level of dissolved phosphorus depends on the concentration of the acid used to dissolve the rock 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.

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. The rate of dissolved phosphorus, in % P2O5, under these conditions is 38.37% for sulfuric acid and 34.87% for hydrochloric acid. Under the same conditions, sulfuric acid dissolves Tahoua rock phosphate better than hydrochloric acid. In the case of EDTA, the best dissolution rate, 20.1%, is obtained at the lowest concentration of 10-2 mol/L. These results, in addition to those already obtained in previous work, can be exploited for the agronomic development of Tahoua rock phosphate through the production of phosphate fertilizers in order to reduce the use of imported fertilizers. Likewise, the State can support young local promoters in the valorization of Tahoua rock phosphate into natural fertilizer.

References

Adel, S. H., Shurooq, T. R. and Haider, A. A. (2012). Phosphate Rock Treatment with Hydrochloric Acid for Increasing P2O5 Content. Engineering and Technology Journal, 30: 67-76. http://dx.doi.org/10.30684/etj.30.1.6

Appleton, J D. (2002). Local phosphate ressources for sustainable developement in sub-Saharan Africa. British Geological Survey Report, CR/02/121/N, 153P.

Bagayoko M., Maman N., Palé S., Sirifi S., Taonda S. J. B., Traore S., Mason S. C., (2011) Microdose and N and P fertilizer application rates for pearl millet in West Africa, African Journal of Agricultural Research, 6(5), 1141-1150. https://doi.org/10.5897/AJAR10.711

Boulahbel, H. (2010). Etude de la réaction de formation du superphosphate simple fabriqué à partir des phosphates de Djebel Onk. Mémoire de magister

en catalyse. Université Badji Mokhtar-Annaba, 100P.

Claire, C. (2005). Etude expérimentale de la cinétique et des mécanismes d'altération de minéraux apatitiques. Application au comportement d'une céramique de confinement d'actinides mineurs. Thèse de doctorat de l'université Toulouse III en géochimie expérimentale.

El mokhtar and El Ouardi., (2008) Étude de la calcination du phosphate clair de youssoufia (Maroc), Afrique SCIENCE, 04(2), 199 – 211.

Ferrag Alleg, S. (2010). Recyclage des eaux et récupération des schlamms phosphates issus des procédés de classification gravimétrique. Valorisation et gestion des ressources minérales. Mémoire demagister Université Badji Mokhtar-Annaba. 115P.

Isil A., Sefik I., Firat A., Abdurrahman S., Candan H., (2009) Determination of mineral phosphate species in sedimentary phosphate rock in Mardin, SE Anatolia, Turkey by sequential extraction, Microchemical Journal 91, 63–69. https://doi.org/10.1016/j.microc.2008.08.001.

Koriko M., Zanguina A., Tchangbedji G., Mohamed E. M., Natatou I., Mohamed H., Mohamed S., (2010) Etude de la dissolution des phosphates de Hahotoé-Kpogamé (Togo) par les acides humiques naturels, J. Soc. Ouest-Afr. Chim., 030, 41-47.

Koriko, M. (2010). Extraction, caractérisation, réactivité chimique des substances humiques naturelles avec les phosphates de Hahotoé-Kpogamé et leurs propriétés photo dégradantes. Physico-chimie des matériaux. Thèse de doctorat des universités de Lomé (Togo) et de blaise pascal de Clermont Ferrand (France). 158p.

Lukas, B., Dana, R., Ales, H., (2008) Kinetics of dissolution of calcium phosphate (Ca-P) bioceramics. Processing and Application of Ceramics, 2: 57-62. https://doi.org/10.2298/PAC0801057B

McClellan G. H., Van Kauwenbergh S. J., (2004) Caractérisation des phosphates naturels. In Utilisation des phosphates naturels pour une agriculture durable. Bulletin FAO, Edition de F. Zapata et R. N. Roy., 13, 17 - 22.

Moughli, L. (2000). Les engrais minéraux, caractéristiques et utilisations.

Ousmane M. S., Zanguina A., Tchegueni S., Laouali S., Dan Lamso N., Natatou I., (2017a) Étude de la solubilisation des phosphates naturels de Tahoua (Niger) au cours de la biodégradation des résidus agroalimentaires, Afrique SCIENCE, 13(2), 179-189. https://doi.org/10.1016/j.cej.2006.06.005.

Ousmane M. S., Zanguina A.,Natatou I., (2017b)Traitement des phosphates naturels de tahoua (Niger) par quelques acides conventionnels, Eurpean Scientific Journal, 13(24)176-185. http://dx.doi.org/10.19044/esj.2017.v13n24p176

Ousmane Mahamane Sani1, Mamane Souley Abdoul Aziz2, Abdou Gondah Ismaila2, Zanguina Adamou1 and Natatou Ibrahim1 (2023). Traitement du phosphate naturel de la tapoa (niger) par des acidesminéraux et organiques. Int. J. Adv. Res. 11(11), 314-321. https://doi.org/10.21474/IJAR01/17830

Vanden Bossche, H. (1999). Devenir du phosphore apporté sur les sols et risques de contamination des eaux de surface. Cas des boues de stations d'épuration. Thèse de doctorat en sciences de la terre de l'université de Rennes I, 295P.

Zanguina A., Mella M. T., Addam K. S., Ousmane G., (2018) Development of Compost from Agro-foodResidues: Analysis of the CropNutrients and Trace Elements, American Scientific Research Journal for Engineering, Technology, and Sciences (ASRJETS), 43(1), 1-12

Zanguina, A. (2011). Contribution à la caractérisation physico-chimique et à la mise en valeur Agronomique de phosphate naturel de Tahoua (Niger): Essais de fabrication de certains engrains minéraux et de phospho-compost. Thèse de doctorat en Physico-chimie des Matériaux, université Abdou Moumouni de Niamey.

Zapata, F. and R. N. Roy, (2004). Utilisation des phosphates naturels pour une agriculture durable. Bulletin FAO Engrais et nutrition végétal N°13 ISSN 0259-6180, 176P.

How to cite this article:

Inoussa Halidou Bassirou, Yahouza Zaneidou, Amadou Hamidou Abdoulaye and Zanguina Adamou. 2024. Comparative Study of the Dissolution of Tahoua Natural Phosphate by Solutions of Mineral Acids (Hydrochloric Acid and Sulfuric Acid) and Organic Acid (Ethylene Diamine Tetraacetic Acid EDTA). *Int.J.Curr.Res.Aca.Rev.* 12(11), 141-149. doi: https://doi.org/10.20546/ijcrar.2024.1211.012