

Improvement of P₂O₅ content in Tahoua rock phosphate using synthetic diammonium phosphate

Abstract

The rock phosphate Tahoua (TNP) is a nodular sedimentary phosphate, the vast majority of which is fluoroapatite, with an average P₂O₅ content of around 30%. But it has a range of impurities that prevent its solubility. However, this rock can be used by certain unconventional techniques to prepare a better-quality fertilizer to meet plant nutrient requirements. The aim of this study is to prepare improved rock phosphate at three different particle sizes (63, 100 μm, 160 μm) in order to assess its solubility in perchloric acid solution and distilled water. Diammonium phosphate (DAP) was synthesized at a NH₃:H₃PO₄ molar ratio of 2:1. DAP was produced by reacting two moles of ammonia and one mole of phosphoric acid at laboratory room temperature for 30 minutes with stirring. The resulting product was characterized by X-ray diffraction and infrared spectrophotometry. These analyses confirmed no change in the structural properties of DAP. Next, the percentage mixtures of TNP particle sizes with the synthesized DAP were carried out. Finally, a dissolution study was carried out. The results obtained from the dissolution of improved rock phosphate in perchloric acid solution and in water are respectively at 5% (50.55%; 43.85%; 45.33%); at 10% (48.90%; 46.88%; 43.70%); 15% (52.70%; 54.9%; 54.83%); 20% (60.67%; 63.95%; 60.44%) and 5% (18.88%; 26.20%; 26.20%); 10% (26.66%; 27.30%; 34.92%); 15% (43.18%; 45.86%; 59.68%); 20% (56.72%; 57.66%; 60.88%) respectively. The improvement in rock phosphate increased the level of P₂O₅ dissolved in the solutions. These dissolved P₂O₅ levels in refined rock phosphate are interesting in water, even at 5%.

Key words: diammonium phosphate, natural phosphate, dissolution, perchloric acid, water

I. Introduction

Rock phosphate in general refers to natural mineral assemblages containing a high concentration of phosphate minerals. The terms refer to both unenriched phosphate mine-fertilizers and concentrated products [1]. In addition, phosphate is a sedimentary deposition in apatite form of fluorine, hydroxyl or chlorine Ca₅(PO₄)₃(F, OH, Cl) [2]. Tahoua's merchant phosphate is a nodular sedimentary phosphate, the vast majority of which is fluoroapatite, with an average P₂O₅ content of around 30%, and high levels of Fe₂O₃, Al₂O₃, SiO₂ and organic matter, which affect the merchantability of the nodules [3]. However, Niger's soils remain poor in phosphorus. To remedy this problem, a number of studies have been carried out on the use of Tahoua rock phosphate in agriculture; attempts to apply Tahoua market phosphate directly to agriculture have not been successful, due to its low solubility in water, which is due to its apatite form [4, 5]. The phosphorus in rock phosphate is only available to plants if it is in an assimilable form [6]. It is as essential to agriculture as nitrogen (N) and potassium (K), and is one of the few non-substitutable raw materials [7]. Natural phosphates contain impurities that have a negative impact on product quality. This justifies the need to improve the P₂O₅ content in the natural phosphate. This treatment is carried out by physical and/or chemical processes (granulometry, improvement, etc.). The aim of our work is to enrich Tahoua rock phosphate through upgrading in order to significantly increase its dissolution.

II. Material and methods

II.1. Materials

II. 1.1. Composition of Tahoua rock phosphate

The rock phosphate of Tahoua is a nodular sedimentary phosphate consisting mainly of fluorapatite [3]. Its chemical composition is low in heavy metals (lead, chromium and cadmium), which confirms the environmental and industrial quality of the product [1]. In this case, the general phosphate chemical formula proposed is: $\text{Ca}_{10-x}(\text{K}, \text{Na}, \text{Mg})_x(\text{PO}_4)_{6-y}(\text{CO}_3\text{F}, \text{SO}_3, \text{SiO}_4)_y\text{F}_{2-z}(\text{OH})_z$. x, y and z successively represent the degree of molar substitution, of Ca by K, Na, Sr, Mg; of PO_4 by CO_3F , SO_3 , SiO_4 and of F by OH. The chemical composition of Tahoua rock phosphate is shown in Table I below.

Table I: Chemical composition of Tahoua rock phosphate [3].

Major elements	%		Trace elements	Ppm
CaO	49,66		Ti	570,14
P ₂ O ₅	27,98		Nd	486,14
Fe ₂ O ₃	7,15		Sr	430,5
SiO ₂	7,80		Zn	160,11
Al ₂ O ₃	2,42		As	57,22
Na ₂ O	0,53		Cu	22,18
MgO	0,17		Ni	49,6
K ₂ O	0,13		U	32,17
Y ₂ O ₃	0,15		Ba	20,52
MnO	0,11		Cr	19,52
			Pb	7,96
			Cd	3,9

II.1.2. Sample particle sizes

Natural phosphate of Tahoua has been crushed and ground to obtain the targeted quality. It is anodular type sedimentary phosphate and has a total content of around 30% on average. Then, three meshes (63; 100 and 160 μm) of powder of this phosphate were used. The powder of phosphate merchant of Tahoua is shown in Figure 1.

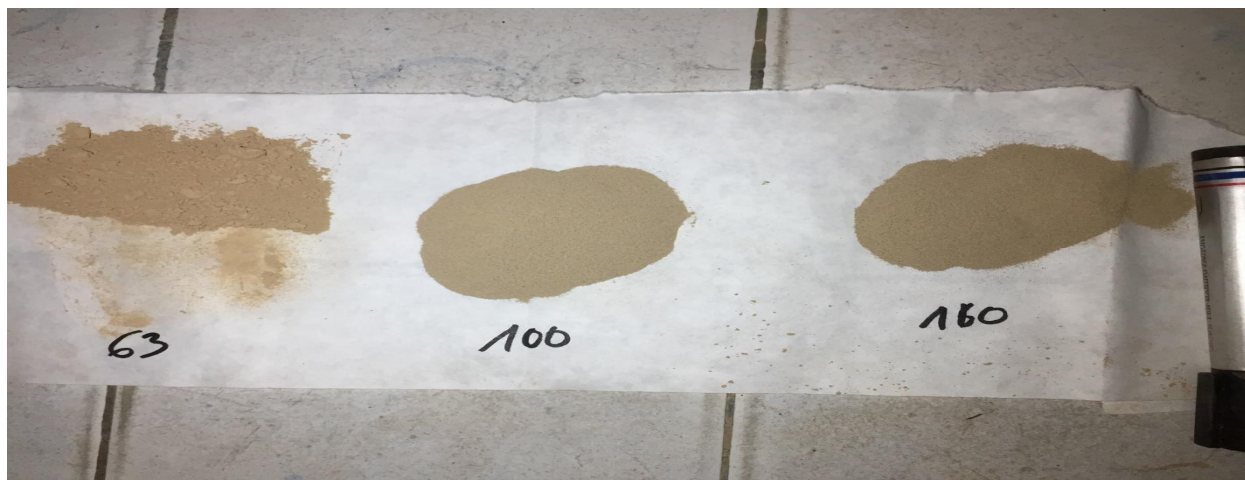


Figure.1: Photograph of merchant phosphate in grain sizes 63; 100; 160 μm

II.1.3. Reagents and solutions

The chemicals used for the preparation of improved diammonium phosphate are prepared from NORMAPUR brand commercial solutions:

- ✓ phosphoric acid (H_3PO_4) is 98% by mass and its density is 1.88;
- ✓ ammonia (NH_3) is 85% by mass and density 0.73;

The solutions used for the dissolution of improved diammonium phosphate are prepared from commercial NORMAPUR brand solutions:

- ✓ perchloric acid (HClO_4) is 65% by mass and its density is 1.61;
- ✓ distilled water

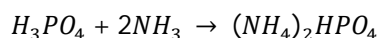
II.1.4. Equipment

- ✓ Infrared spectrometry analyses were carried out using a NICOLET model 5700 FTIR spectrometer on samples of compounds pressed into pellets in KBr.
- ✓ X-ray diffraction analyses were carried out on diammonium phosphate powder using a Thermo Scientific ARL'XTRA X-ray diffractometer.

II.2. Methods

II.2.1. Preparation of DAP synthesis

Samples were taken to synthesize diammonium phosphate. The neutralization of phosphoric acid by gaseous ammonia is an exothermic reaction. The diammonium phosphate product is a source of the two nutrients nitrogen and phosphorus. Diammonium phosphate (DAP) was prepared at a $\text{NH}_3:\text{H}_3\text{PO}_4$ molar ratio of 2:1. DAP was produced by reacting two moles of ammonia and one mole of phosphoric acid at laboratory room temperature for 30 minutes with stirring. The stirring speed was set at 100 rpm. The experiment was carried out at pH 8. The mixture was left to cool for a few minutes to allow crystals to form. The precipitate was filtered and transferred to a clean, dry flask. The resulting precipitate was then left to dry at room temperature and stored in a desiccator. The experimental reaction is shown below.



After synthesizing the diammonium phosphate, we prepared samples by mixing three particle size slices of Tahoua merchant phosphate and synthetic DAP. The samples are shown in Table II.

Table II: Samples prepared

Particle sizes	PNTs (%)	DAP (%)
63 μm	95	5
	90	10
	85	15
	80	20
100 μm	95	5
	90	10
	85	15
	80	20
160 μm	95	5
	90	10
	85	15
	80	20

III. Results and discussion

III.1. Synthesis of diammonium phosphate

We began the synthesis of a phosphate fertilizer diammonium phosphate by neutralizing phosphoric acid with ammonia (final pH 8). The precipitate obtained is shown in figure 2:



Figure 2: Photograph of diammonium phosphate precipitate

The photograph in this figure shows the diammonium phosphate precipitate. The precipitate has been well crystallized. It constitutes two essential nutrients whose structure should consist of less than 30% nitrogen (N) and more than 70% phosphorus (P). It should not be exposed to the open air, as it will gradually lose ammonia. This fertilizer is popular because of its relatively high nutrient content and excellent physical properties. Previous studies have shown a standard quality of 46% phosphate and 18% nitrogen [8, 9]. The nitrogen and phosphorus elements

present are in the form of ammonium (NH_4) and phosphate (P_2O_5), and have a particularly positive effect during the first period of plant development. As a result, DAP is a highly soluble by-product, dissolving rapidly in the soil to release the phosphate and ammonium available to plants.

III.1.1. X-ray diffraction

X-ray diffraction analysis is carried out on the sample powder of synthetic diammonium phosphate. The results are shown in figure 3.

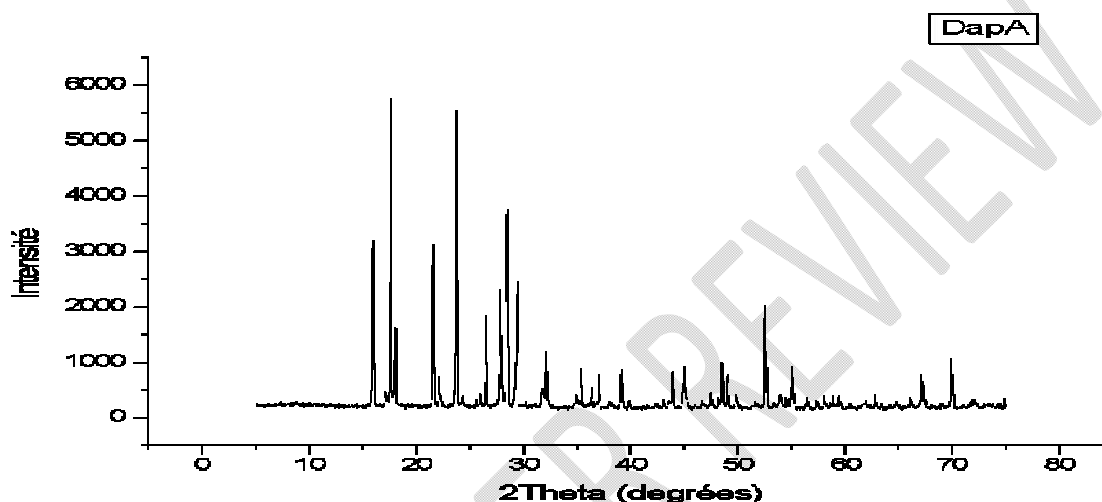


Figure.3: Diffractogram X-ray of diammonium phosphate

The information obtained from synthetic diammonium phosphate powder shows that no crystallized phase is visible. All the lines observed are distributed to diammonium phosphate. However, it cannot be ruled out that the initial powders may be made up of other phases in quantities small enough to be detected by X-rays. Following X-ray diffraction analysis, infrared spectrometry analysis will also confirm that it is synthetic ammonium phosphate in the sample.

III.1.2. Infrared spectrometry

Infrared absorption spectra were recorded in the $4000\text{-}400\text{ cm}^{-1}$ frequency range using a NICOLET FTIR 5700 Fourier Transform spectrometer. Samples dispersed in pure, dry potassium bromide (KBr) were shaped by uniaxial pressing. The infrared spectrum of the synthesized diammonium phosphate powder shows the full range of vibrational modes of the NH_4^+ ammonium and PO_4^{3-} phosphate groups (Figure 4). The wave numbers of the bands observed and their attributions are reported in table III.

Table III: Band IR positions and intensities.

	Position des bandes (cm^{-1})	Intensités
1	894.56108	39.34475
2	939.28913	35.46498
3	1043.65459	42.79041

4	1192.74811	75.19830
5	1446.20708	48.94742
6	1714.57541	76.84278
7	1923.30632	73.74736
8	2124.58257	78.71972
9	2206.58400	75.35291
10	2743.32065	51.25275
11	2966,9609	65,10515
12	3175,6918	78,94623

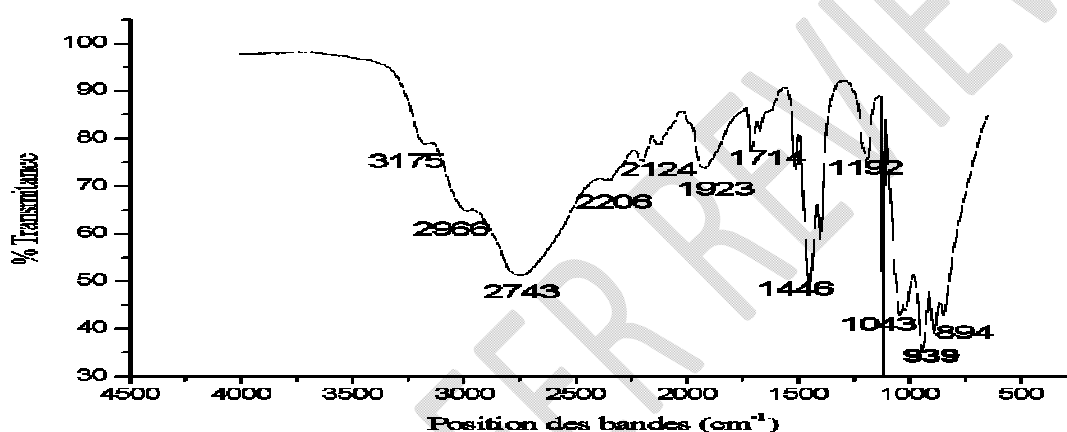
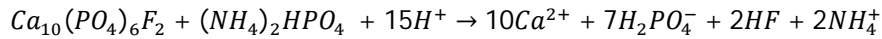


Figure 4: Infrared spectrum of diammonium phosphate

The results of infrared absorption spectrometry analysis of the synthesized precipitate are: 3175,2966, 2743,2206 2124, 1923,1714, 1446, 1400, 1192, 1043, 939 and 894 cm^{-1} . Their spectra have all visible vibrational modes (Figure III.4). The bands observed around 3175,2966, 2743,2206 2124, 1923,1714, 1446 and 1400 cm^{-1} , characterize the NH_4^+ group and the bands around 894, 939, 1043 and 1192 are attributed to the vibrations of the PO_4^{3-} phosphate ions. These bands are close to those published in the literature [10]. Chemical bonds can provide direct information on the presence of chemically bound species on the surface of the treated solid. Infrared spectroscopy confirms the structure of diammonium phosphate.

III.2. Dissolution of improved Tahoua rock phosphate

A mixture of Tahoua market phosphate and diammonium phosphate was used to increase the phosphorus content. The rock phosphate used is a sedimentary phosphate made up mainly of fluorapatite, with an average content of around 30% P_2O_5 , but it does contain impurities [11]. The decomposition reaction of fluoroapatite takes place on the surface of solid materials without a catalyst. So, dissolution of solid materials takes place by breaking the lowest-energy bonds. On the other hand, P-O bonds are not broken so that the structure is not completely destroyed [12]. In an acidic environment, phosphate in the form of PO_4^{3-} ions captures H^+ ions to form HPO_4^{2-} or H_2PO_4^- ions, depending on the strength of the acid. This is the decomposition reaction between fluoroapatite [13] and diammonium phosphate fertilizer decomposed in solution. The balance equation for the dissolution reaction is shown below:



As shown in the equation, the dissolution of the improved DAP fertilizer results in the consumption of proton H^+ , the release of ammonium ions NH_4^+ and the formation of hydrofluoric acid. We then studied the dissolution of ores in perchloric acid and distilled water. This was carried out with the aim of assessing the level of dissolved P_2O_5 by measuring P_2O_5 in the various filtrates collected after etching. The results of this study will be presented and discussed in the following paragraphs.

III.2.1. Solubility of improved PNT in distilled water

We dissolved diammonium phosphate fertilizer in water. The results obtained are shown in figure 5. She represents the dissolution rate of improved DAP in water.

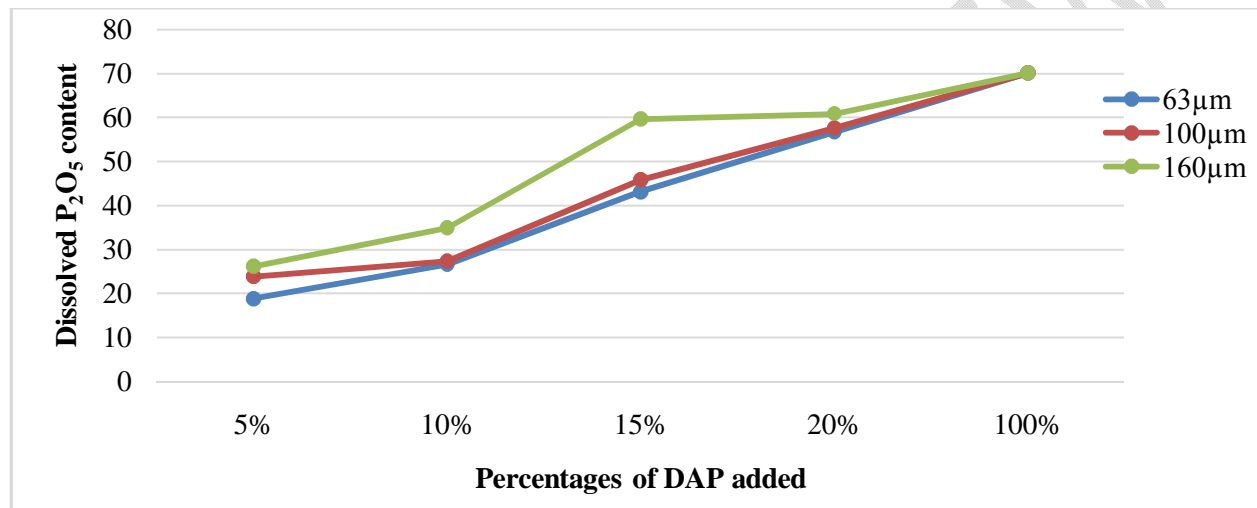


Figure 5: Dissolved P_2O_5 content of enhanced NTP in water

The analyses of the dissolution of improved rock phosphate in distilled water clearly show that P_2O_5 levels increase when the amount of DAP is increased. The dissolution results obtained for improved diammonium phosphate are: for 63µm (18.88%, 26.66%, 43.18%, 56.72%, 70.12%); for 100µm (23.86%, 27.3%, 45.86%, 57.66%, 70.12%) and 160µm (26.2%, 34.92%, 59.68%, 60.88%, 70.12%). These results show that the rate is higher at 160 µm. This could be due to the effect of granulometry. Authors have shown that P_2O_5 content is higher at grain sizes between 100 and 160µm. Then, the best rates of dissolution of improved diammonium phosphate fertilizer are obtained with the addition of 20% of synthetic DAP in 160µm grain size rock phosphate and the lowest rate of dissolution of improved TNP in distilled water obtained with the addition of 5% of DAP. This shows that the combination of Tahoua rock phosphate with diammonium phosphate fertilizer resulted in an increase in water-soluble P_2O_5 . We can see that the more DAP is added, the higher the dissolution rate. Adding even a small amount of DAP to rock-phosphate significantly improves the rate of phosphate dissolution in solution. This sharp rise in the rate of NTP dissolution could be attributed to the addition of DAP to NTP, which is overloaded with metallic elements, influencing its solubility, and is perfectly soluble in water. Similar results have been observed for the dissolution of diammonium phosphate fertilizers with the addition of DAP [4, 14]. Although we haven't yet applied it in agriculture, the results obtained could increase the agronomic efficiency of the crop. In fact, it provides a rapid response to the plant's needs during start-up, as it acts directly on the roots to enhance plant development. In this case, the phosphate ion is presented in the form of the bivalent HPO_4^{2-} ion, and to become monovalent $H_2PO_4^-$, it must find an H^+ proton in the medium. The increase in solubility can be explained by the release of phosphate particles from the decomposition of DAP in this medium. This results in a significant consumption of H^+ ions in the medium, increasing the dissolution of ores [1, 15]. The

products obtained must therefore be of high solubility, less expensive and give good yields in agricultural production, especially if used at the time of sowing with grain as a starter fertilizer. Because of its nitrogen content, it is imperative for crops that need these nutrients in their initial phase. Nitrogen doesn't change its structure, so it can be used by plants. However, there are several ways of improving rock phosphate to enhance its solubility. So, it is noted that this improved rock phosphate fertilizer is a beneficial product for farmers. It can be accessible and less expensive than the product obtained on the market.

III.2.2. Solubility of enhanced NTP in perchloric acid solution

The determination of phosphoric anhydride in the filtrates resulting from the attack of improved natural phosphate with NTP:DAP ratios of 95:5; 90:10; 85:15 and 80:20 by the perchloric acid solution yielded the results shown in figure 6. The results obtained after dissolution of the improved NTP are respectively at 5% (50.55%; 43.85%; 45.33%); 10% (48.90%; 46.88%; 43.70%); 15% (52.70%; 54.9%; 54.83%); 20% (60.67%; 63.95%; 60.44%). We note an increase in dissolved P_2O_5 content regardless of the small portion of DAP fertilizer added to the NTP. The P_2O_5 content is higher in the 63 micrometer NWP particle size range with the addition of 5-10% DAP, whereas with the addition of 15-20% DAP, it is higher for particle sizes greater than or equal to 100 micrometers. This increase in dissolution rate could be linked to the specific surface area of the phosphate particles and the addition of DAP. In this case, the DAP is completely dissolved in the acid solution. In this case, several studies have been carried out on the evolution of phosphoric anhydride content as a function of percentage and granulometry [4, 8]. The results found are identical to those observed in the case of phosphate attack by conventional acid solutions, but the dissolution of solutions of this acid is much greater [8]. The results of this study show that the extent of dissolution depends on the addition of DAP, particle sizes and the attack of hydronium ions H_3O^+ . Overall, we found significant consumption of H_3O^+ ions in the medium. This phenomenon could be explained by the strength of the acidity of this acid [14]. These results are comparable to those found by several studies such as: Von Semel and colleagues produced the fertilizer to obtain good quality crystalline ammonium phosphate using ammonia and technical grade phosphoric acid, which was freed of most impurities after precipitation in an organic solvent [16]. The solubilization rates of improved TNP we obtained are higher than those obtained by [15, 16] for the dissolution of Tahoua merchant phosphate; Tahoua calcined rock phosphate [1]. Improved NTPs could be at an advantage, given that Tahoua rock phosphate is low in heavy metal content (lead, chromium and cadmium). This is a guarantee of the product's environmental and industrial quality [17]. This is all the more important as farmers use these mixtures to add phosphate fertilizers to agricultural soils. But over-application of fertilizers over time can potentially damage soil structure and water-holding capacity. These factors not only disrupt microbial populations, but also reduce soil fertility [18].

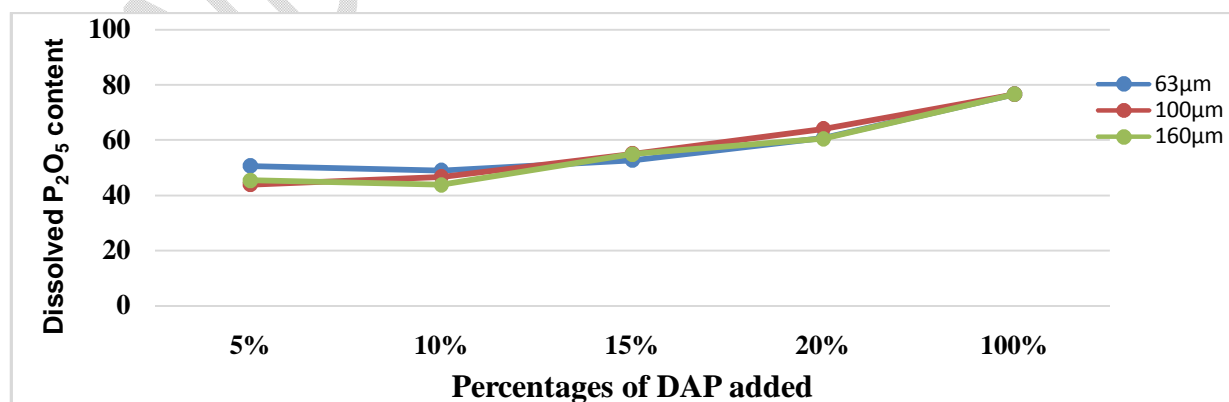


Figure 6: Dissolved P_2O_5 content of perchloric acid-enhanced TNP

Conclusion

In the course of this work, we synthesized diammonium phosphate. At the end of the process, it was characterized by X-ray diffraction and infrared spectrophotometry. These analyses confirmed no change in the structural properties of DAP. We then studied the dissolution of improved rock phosphate in perchloric acid and distilled water. The results obtained from the dissolved phosphorus assay, expressed as a percentage of phosphoric anhydride (P_2O_5), showed that the addition of diammonium phosphate up to a content of 20% in rock phosphate significantly increases the nutritional properties of fertilizers in terms of phosphorus content. The results show a significant increase in the P_2O_5 content of fertilizers and in the phosphorus content with the addition of DAP up to 20% of Tahoua rock phosphate.

References

- [1]. Abdoul. B, i, a., (2019). Effect of treatment on the solubility of Tahoua rock phosphate in sulfuric acid and citric acid. Master's thesis in inorganic chemistry at the Abdou moumouni University of Niamey, 52p.
- [2]. Boujier v, (2007). Influence of monohydrogenophosphate and fluorophos-phosphate ions on phosphogypsis properties and phosphoplater reactivity. PhD thesis in process engineering. Ecole nationale supérieure des mines de saint-etienne
- [3]. Ousmane m. S, (2018). Physicochemical characterizations, improvement of agronomic efficiency by phosphocomposting of ni-ger natural phosphates. PhD thesis in applied sciences, universitéabdoumoumouni de nia-mey.116p.
- [4]. Bassirou. I, halidou, (2015). Comparative study of the dissolution of tahoua natural phosphate in various mineral and organic acids. Mémoire de master en chimie inorganique, Université Abdou moumouni de Niamey, 60p.
- [5]. Ousmane mahamanesani, zanguinaadamou, natatouibrahim. (2017). Treatment of natural phosphates from tahoua (niger) by some conventional acids.
- [6]. 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 docto-rat en physico-chimie des matériaux, université abdoumoumouni de niamey, 149p.
- [7]. Akila. D, zahia f, (2016). The influence of heat treatment on the granulometry of beige phosphate ore from kef es sannoun djebel onk deposit. Master's thesis in mineral resources valorization. Universitéabderrahmane mi-ra bejaia.
- [8]. Angela magda, rodicapode, corneliamuntean, mihaimedeleanu and alexandrupopa, (2010). Synthesis and characterization of ammonium phosphate fertilizers with boron. Doi: 10.2298/jsc090228064m
- [9]. Greigeri. J, (1970-1971). Recherche de phosphate dans la région de tahoua, rapport agence canadienne pour le développement international au niger, 1970 -1971.
- [10]. Elliott. J.C, (1994). Structure and Chemistry of the apatite and other Calcium Orthophosphates, Elsevier Science B.V., Amsterdam
- [11]. Claire. C., (2005). Etude expérimentale de la cinétique et des mécanismes d'altération de minéraux apatitiques. Application to the behavior of a minor actinide confinement ceramic. PhD thesis in experimental geochemistry, universitétou-louse iii.
- [12]. Valyasko v. M., kogardo l. N., khodakovskiy. L., (1968). Stability of fluorapatite, chlorapatite and hydroxylapatite in aqueous solutions at different temperatures. Goech. Inter. 5, pp. 21-30.
- [13]. A. B. Kouyate et al. (2020) / int. J. Biol. Chem. Sci. 14(9): 3285-3296, 2020 doi: <https://dx.doi.org/10.4314/ijbcs.v14i9.25>
- [14]. D.s. Rana, a. Dass,*g.a.Rajanna, and a.k. Choudhary.(2018). Fertilizer phosphorus solubility effects on indian mustard-maize and wheat-soybean cropping systems productivity. Doi:10.2134/agronj2018.04.0256
- [15]. Moursaloukoriko, (2010). Extraction, characterization, chemical reactivity of natural humic substances with hahotie-kpogame phosphates and their photodegrading

properties. Thesis in organic chemistry from université ne blaise pascal - clermont-ferrand ii; université de lomé, 159 pages.

- [16]. Von semel, g.d.; schibilla, e., (1975). Process for the manufacture of crystal-lized ammonia phosphates. Us patent number 3894143
- [17]. Natatou, I, A. Maman, A. Zanguina, I. Khalid, A. Boos and M. Burgard, (2004). Physico-chemical studies of merchant phosphate from Tahoua (Niger). J. Soc. Ouest-Afr. Chim; 018; p.137-148.
- [18]. [17]. Naomi williams, (2024). The ultimate guide to inorganic fertilizers. Maison Blog. <https://www.hans-chem.com/fr/le-guide-ultime-de-lengrais-phosphate/>

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