STUDY OF SOME PARAMETERS TO OBTAIN THE P$_2$O$_5$ WATER-SOLUBLE FROM PARTIALLY ACIDULATED PHOSPHATE ROCKS (PAPRs) BY SULFURIC ACID

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Abstract: The work presented in this paper deals with the determination of optimum parameters during the partial acidulation of the phosphate ore of Djebel Onk (Algeria) and the determination of P$_2$O$_5$ water-soluble. The first part is devoted to P$_2$O$_5$ conversion rate during partial acidulation of phosphate with different particle sizes (80 μm, 160 μm and 250 μm). These conversion rates are obtained by performing a series of reactions between phosphate and sulfuric acid diluted from 10 to 50 wt% and with reaction times ranging from 10 to 50 minutes. The best conversion rate (38.78%) was obtained at a reaction time of 50 minutes with phosphate particle size of 80 μm and an acid concentration of 50 wt%. The second part, concerns the measurement of P$_2$O$_5$-water-soluble of phosphate partially acidulated (PAPRs) with 40% and 50 wt% sulfuric acid. The percentage of P$_2$O$_5$ soluble in water has reached 14.98% for PAPRs obtained with phosphate particle size of 80 μm and an acid of 50 wt%.

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INTRODUCTION

Phosphorus (P) is an essential nutrient for plants and animals, it’s absorbed mainly during the vegetative growth and, thereafter, most of the absorbed P is transmitted into fruits and seeds during reproductive stages. This nutrient is absorbed by plants in the soil solution as a monovalent anion orthophosphate (H$_3$PO$_4^-$) and divalent (HPO$_4^{2-}$), each representing 50 % of total phosphorus at a pH close to neutral (pH 6-7). At pH 4-6, the H$_3$PO$_4^-$ is about 100 % of the total phosphorus in solution but, at pH 8, its concentration in the plant is about 20 % of the total phosphorus. The amount of phosphorus available to the plant is expressed in P$_2$O$_5$.

It’s well known that phosphates can’t be used directly as fertilizer because of their insolubility. To make them available by plants, phosphates are dissolved by mineral acids in industrial plants. These acids, used in industrial production of fertilizers are mainly sulfuric and nitric acid. The reaction of these acids depends on several factors such as chemical and mineralogical composition of phosphate, specific surface area, acid-rock ratio and agitation speed.

Currently the phosphate rock (PR) is the main source of phosphorus and the phosphate content in PR (or grade) is usually expressed as phosphorus pentoxide (P$_2$O$_5$). Apatites are isomorphous minerals with the general chemical formula Me$_{10}$(XO$_4$)$_6$Y$_2$, where Me represents a cation and XO$_4$ and Y represent anionic groups. A well-known representative member of the apatite group is calcium phosphate hydroxyapatite (HAp) Ca$_{10}$(PO$_4$)$_6$(OH)$_$_2$. One of the main characteristics of the apatite structure is that it enables a large number of substitutions at all three sites (Me, X and Y). The phosphates are composed from a sedimentary apatite showing in their crystal lattice, an extensive isomorphous substitution. Thus, presenting a wide variation in chemical composition and showing a range of properties. In sedimentary deposits, the main phosphate minerals are francolite (carbonate fluorapatite microcrystalline), associated with a variety of other minerals and impurities. The Djebel-Onk (Algeria) phosphate, used in the experiments, is a fluorapatite Ca$_{10}$(PO$_4$)$_3$F. It is characterized by a granular appearance.
(pseudoolithes and pellets), often an organic (diatoms and radiolarians), with particle size belonging to the class of arenites (grains <2 mm). This phosphate is poor in rudite (sedimentary clastic rock with a grain> 2 mm). All-comers ore usually have P₂O₅ between 25 to 28%. Phosphate rock of Djebel Onk has a high substitution of CO₃ (CaO/ P₂O₅ = 1.75 to 1.90) and is generally low in silica and iron.

It is noticed from reported works 4,5,6, that the phosphates from different mines and experimented using various mineral acids give conversion rates different from each other. The study of Mizane et al. and the experiments carried out by Bouykin et al. have showed that the dissolution of phosphate with nitric acid is very high. This process avoids the formation of phosphogypsum, but it does not give the possibility to produce phosphoric acid. Some authors (Rajan et al. and Tan Zhi-Dou et al.) have, from them, studied the partial dissolution of phosphate with a mixture of phosphoric and sulfuric acid.

Partially acidulated phosphate rocks (PAPRs) are prepared by reacting PR with H₂SO₄ or H₃PO₄ but with acids concentrations lower than those commonly used to manufacture fertilizers such SSP (single superphosphate) or TSP (triple superphosphate). The term partially acidulated phosphate rocks (PAPRs) describes P fertilizers produced under two distinct technological processes but are similar in chemical composition of their products such as:

- Partial acidulation, i.e. less than the stoichiometric amount of acid required for complete dissolution of PR with H₂SO₄ or H₃PO₄.
- Physical mixture of SSP and reactive phosphate rocks (RPRs).

Processes of PR dissolution can be summarized as follows:\[\text{Ca}_{10} (\text{PO}_4)_{6} \text{F}_2 + y(6-x)\text{H}_2\text{SO}_4 + 3xy\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow y(6-x)\text{CaSO}_4 + (3 + x)y\text{Ca}(\text{H}_2\text{PO}_4)2\text{H}_2\text{O} + (1-y)\text{Ca}_{10} (\text{PO}_4)_{6} \text{F}_2 + y\text{CaF}_2\] (1)

When \( y = 1, x = 0 \rightarrow \text{SSP} \)
\( y = 1, x = 6 \rightarrow \text{TSP} \)
\( 0 < y \leq 0.75 \rightarrow \text{PAPRs} \)

In practice, the degree of PR acidulation ranges from 20% to 50%. As shown by several studies, compared to the SSP and TSP, the PAPRs may be a mean to improve agricultural efficiency at lower cost. Indeed, PAPRs are cheaper than fully acidulated fertilizers because less acid and energy is required per unit of P in the product. Although little information is available in literature on Cd uptake by crops from either PR or PAPRs, PAPR may limit the absorption of this hazardous metal. In addition, PAPRs have the advantage of being often more concentrated than SSP. The solubility of PAPRs depends on the type of composition and concentration of acid used for acidulation, as well as the degree of acidulation, nature, grain size of PR and method of manufacture. For seasonal crops, except for fast growing ones such as squash (Cucurbita maxima), PAPRs are generally as effective as superphosphate fully acidulated. However, it should be noted that the choice of the acid concentration for partial acidulation depends on the chemical composition of each phosphate, as well as the degree of acidulation. For these reasons and because the partial acidulation of PR by H₂SO₄ according to IFDC (International Fertilizer Development Center), is less expensive; the present work is carried out on partial solubilisation of Djebel Onk phosphate.

MATERIALS AND METHODS

The chemical composition of phosphate ore (Table 1) used in this study is determined by different analytical methods: X-ray fluorescence spectrometry and traditional elementary analysis. A quantity of 10g of phosphate is attacked by stoichiometric amounts of a sulfuric acid solution at different concentrations. Experiments were conducted at ambient temperature (about 20°C) and operating parameters such as duration of reaction and speed of agitation are previously fixed. Phosphate is introduced into the reactor equipped with an agitator and stirring is maintained at 200 rev/min (revolutions per minute). In all experiments, the amount of sulfuric acid used is 20% in excess over the stoichiometric amount. After each reaction, the reactor is soaked in a cooling solution to stop the reaction. Then, the product of reaction is filtered and an aliquot part is taken in order to determine the quantity of P₂O₅.

Analysis method of P₂O₅

The assay of P₂O₅ is carried out at 450 nm using the standard apparatus TECHNICON AUTO ANALYZER. This technique is based on the spectrophotometric method using the ammonium phosphomolybdate complex. For all experiments, analytical reagents Normapur are used.
Definition of the P$_2$O$_5$ conversion rate

The conversion rate "α" is the ratio between the amount of P$_2$O$_5$ in phosphate rock and the amount of P$_2$O$_5$ that passes to the liquid phase (soluble phase). The conversion rate expressed in wt % is calculated according to equation (2) presented below:

$$\alpha = \frac{Mt \, P_2O_5}{M \,(P_2O_5)\text{init.}} \times 100\% \quad (2)$$

Where :
- $Mt \, P_2O_5$ : The total mass of P$_2$O$_5$ produced during the reaction
- $M \,(P_2O_5)\text{init.}$ : The initial mass of P$_2$O$_5$ (contained in 10g of phosphate rock).

TABLE 1. Chemical composition of Djebel Onk phosphate ore

<table>
<thead>
<tr>
<th>Chemical compound</th>
<th>wt%</th>
</tr>
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<tbody>
<tr>
<td>P$_2$O$_5$</td>
<td>29.80 – 30.00</td>
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<tr>
<td>CO$_2$</td>
<td>6.40 – 6.80</td>
</tr>
<tr>
<td>CaO</td>
<td>49.50 – 50.00</td>
</tr>
<tr>
<td>MgO</td>
<td>0.85 – 0.95</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>1.10 – 1.20</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.33 – 0.38</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.38 – 0.42</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>2.30 – 3.00</td>
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<tr>
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<td>Cl</td>
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<td>organic matters</td>
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RESULTS AND DISCUSSIONS

Variation of conversion rate as function of time

In this experiment, we found it’s not necessary to carry out the reaction beyond 50 minutes because the slurry resulting from the reaction between phosphate and sulfuric acid begins to be dried. Results show that the conversion rate of P$_2$O$_5$ increases with time during the first 30 minutes but, beyond 40 minutes, the conversion rate tends to be stabilized. This dependency is almost the same as for phosphate of 80 μm, 160 μm or 250 μm (FIGURE 1, FIGURE 2 and FIGURE 3).

**FIGURE 1.** Conversion rate of P$_2$O$_5$ as a function of time and H$_2$SO$_4$ concentration for phosphate particle size: 80 μm.

**FIGURE 2.** Conversion rate of P$_2$O$_5$ as a function of time and H$_2$SO$_4$ concentration for phosphate particle size: 160 μm.

**TABLE 1.** Chemical composition of Djebel Onk phosphate ore

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**Determination of P$_2$O$_5$ water-soluble**

The partially acidulated phosphate obtained previously at different concentrations of H$_2$SO$_4$ is brought into contact with distilled water for periods of 2 to 30 days to measure the P$_2$O$_5$ water-soluble. This experiment is described as follows:

The sample of 1 g of partially acidulated phosphate is brought into contact with 400 ml of distilled water in a closed bottle. Then, after a defined period, the bottle is agitated for 15 minutes and to resulting solution it is added distilled water to fill the volume of 1000 ml. This solution is stirred again then filtered on the paper-filter. Allowed to stand the filtered solution, then, 5 ml of the filtrate was taken to determine the amount of P$_2$O$_5$ by the spectrophotometric method.
Influence of $\text{H}_2\text{SO}_4$ concentration

FIGURE 1, FIGURE 2 and FIGURE 3 show that the conversion rate of $\text{P}_2\text{O}_5$ increases with increasing $\text{H}_2\text{SO}_4$ concentration. This increase is about 10% of $\text{P}_2\text{O}_5$ when the acid concentration is raised from 10 at 50% wt%. Beyond 30% $\text{H}_2\text{SO}_4$ concentration, the conversion rate is significantly higher but when working with acid below 30%, the conversion rates become close to each other. When using the acid above 30%, the conversion rate suddenly increases by about 5.5% regardless of the size of the phosphate.

Influence of particle size of phosphate

The experiments conducted with different dimensions of phosphate (80 μm, 160 μm and 250 μm) showed that particle size has a significant influence on the partial phosphate acidulation. As shown in FIGURE 1, FIGURE 2, and FIGURE 3, the 80 μm phosphate particle size gives better results. If an acid of 50%, is used, the gain in conversion rate is about 2% when working with a 80 mm phosphate instead of 250 μm.

$\text{P}_2\text{O}_5$ Water-soluble

The curves in FIGURE 4, FIGURE 5 and FIGURE 6 were obtained by acidulation of phosphates of varying sizes with sulfuric acid concentration of 40 wt% and 50 wt% because these acids gives better conversion rates (see FIGURE 1, FIGURE 2 and FIGURE 3). FIGURE 4, FIGURE 5 and FIGURE 6 shows that PAPRs obtained with the acid 50 % give $\text{P}_2\text{O}_5$ water-soluble more than the PAPRs obtained with acid 40%. This difference is approximately 0.5% for all particle size of phosphate. Comparing FIGURE 4, FIGURE 5 and FIGURE 6 it can be observed that the phosphate with 80 μm particle size used for the preparation of PAPRs gives the best percentage of $\text{P}_2\text{O}_5$ water-soluble (14.98%). This experiment on the solubility of PAPRs shows that when PAPRs is brought into contact with distilled water for periods ranging from 2 to 30 days, it is observed that $\text{P}_2\text{O}_5$ water-soluble increased progressively during the first 10 days. After the 16th day, the dependence of the residence time and $\text{P}_2\text{O}_5$ water- soluble is almost constant.
FIGURE 6. P₂O₅ water-soluble as a function of residence time for phosphate particle size: 250 μm

CONCLUSION

This work showed that the studied phosphate gives PAPRs with good water solubility. The PAPRs obtained by these phosphates can substitute the SSP because they are economically profitable and probably less harmful to the environment (to be confirmed by other studies). This is especially true because it is accepted that some heavy metals contained in phosphates rock will dissolve at high acid concentrations. The PAPRs of Djebel Onk also contains residual phosphates that may become bioavailable to plants. From this point of view, it will be interesting if agricultural researchers in the rhizosphere field complete this work by investigating in-depth the bioavailability of phosphorus issued from these phosphates.

REFERENCES