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## SOLUBILIZATION OF PHOSPHATE ROCK BY ORGANIC ACIDS

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### ABSTRACT

Phosphate chemical fertilizers are extensively used to improve agricultural productivity. However, the production of these fertilizers is expensive and can cause environmental damage due to the use of high concentrations of sulfuric acid. Alternatively, microbial solubilization of phosphate rock (PR) is a potential strategy to obtain phosphate fertilizers (biofertilizers). This strategy relies on the ability of some microorganisms to produce organic acids which convert the insoluble PR phosphorus into soluble forms. This study aims to investigate the influence of different organic acids on PR solubilization. For that, the effect of nine organic acids on the solubilization of three phosphate sources was evaluated. The results showed that the effect of the organic acid on PR solubilization is dependent on the source and nature of the phosphate. Citric and oxalic acid were the most efficient organic acids to solubilize PR, being comparable to strong inorganic acids. The strategy proposed could contribute in future developments for the industrial production of phosphate fertilizer using organic acids.

### 1. INTRODUCTION

Organic acids produced by microorganisms have been considered as a potential strategy for PR solubilization (Xu et al., 2004). This strategy is based on the capacity of some microorganisms to produce and release metabolites, such as organic acids which chelate the cations bound to phosphate, the latter being converted into soluble forms, through their hydroxyl and carboxyl groups (Kpombekoua and Tabatabai, 1994). However, there are few studies demonstrating the effect of different organic acids

on PR solubilization (Lazo et al., 2017; Heydarpour et al., 2011; Xu et al., 2004). This study aims to investigate the influence of different organic acids on PR solubilization.

## 2. MATERIALS AND METHODS

The individual effect of each acid was assessed using nine organic and two inorganic acids and water as control. Ascorbic, acetic, formic, gluconic, malic, succinic, oxalic, tartaric and citric acids were the organic acids used. Sulfuric and chloridric acids were the inorganic acids used. All acid solutions were standardized with reference to the molar concentration of 2% wt solution of citric acid ( $0.104 \text{ mol L}^{-1}$ ) (MAPA, 2013). The mass of material (phosphate source) added was calculated to result in a concentration of P at  $0.868 \text{ g L}^{-1}$  (thus the amount of P mass added was always the same, but the amount of total mass of material varied due the differences among the phosphorus concentration in each material). The phosphate materials used were Tricalcium phosphate (TCP) (43.5%,  $\text{P}_2\text{O}_5$ ), Bayovar phosphate rock (BPR) (30.7%,  $\text{P}_2\text{O}_5$ ) and Itafós phosphatic rock (IPR) (20.3%,  $\text{P}_2\text{O}_5$ ). The results were analyzed with the Statistica® 8.0 (Statsoft Inc., Tulsa, OK, USA) software. All experiments were carried out in triplicate at  $30^\circ\text{C}$ , 40 rpm per 6h. The soluble phosphorus was quantified by the Riley and Murphy method (1986).

## 3. RESULTS AND DISCUSSION

### 3.1. Effect of organic acids on phosphate rock solubilization

Figure 1 shows the solubilization efficiency for three phosphate sources on nine organic acids, two inorganic acids and water (control). It was possible to observe the TCP solubility (Figure 1a) above 40% for all acids evaluated, being more soluble in citric and tartaric acid, with an average of 80% and 75% solubilization, respectively. These values were statistically equal as the amount solubilized by sulphuric and chloridric acid. In the sequence, the organic acids: gluconic, oxalic and succinic showed a solubilization efficiency statistically lower than citric, tartaric and chloridric acid, but statically similar to the sulfuric acid. Thus, the potential of these organic acids for TCP solubilization is highly favorable, as they showed a solubilization comparable to strong inorganic acids.

BPR presented an average of 60% solubilization in citric, oxalic and tartaric acids (Figure 1b), without significant differences when compared to the solubilization in sulphuric acid. Chloridric was the best acid for BPR solubilization, showing an average 82% solubilization. For all organic acids tested, it was observed a lower solubilization efficiency for BPR when compared to TCP, except for oxalic acid, which resulted in a similar 60% efficiency for both BPR and TCP.

As for the IPR, oxalic acid was the second best acid in overall and the best organic tested for IPR solubilization with an average of 60% solubilization, which was statistically equal to sulphuric acid (Figure 1c). The highest IPR solubilization was achieved using cloridric acid (82% solubilization), as previously observed for BPR and TCP.

It was observed that oxalic acid presents a great potential to solubilize PR, being comparable to strong inorganic acids such as sulphuric and cloridric acids. This is even more interesting if we take into consideration that these phosphate sources present great complexity and their mineralogical structure makes solubilization more difficult when compared to TCP.

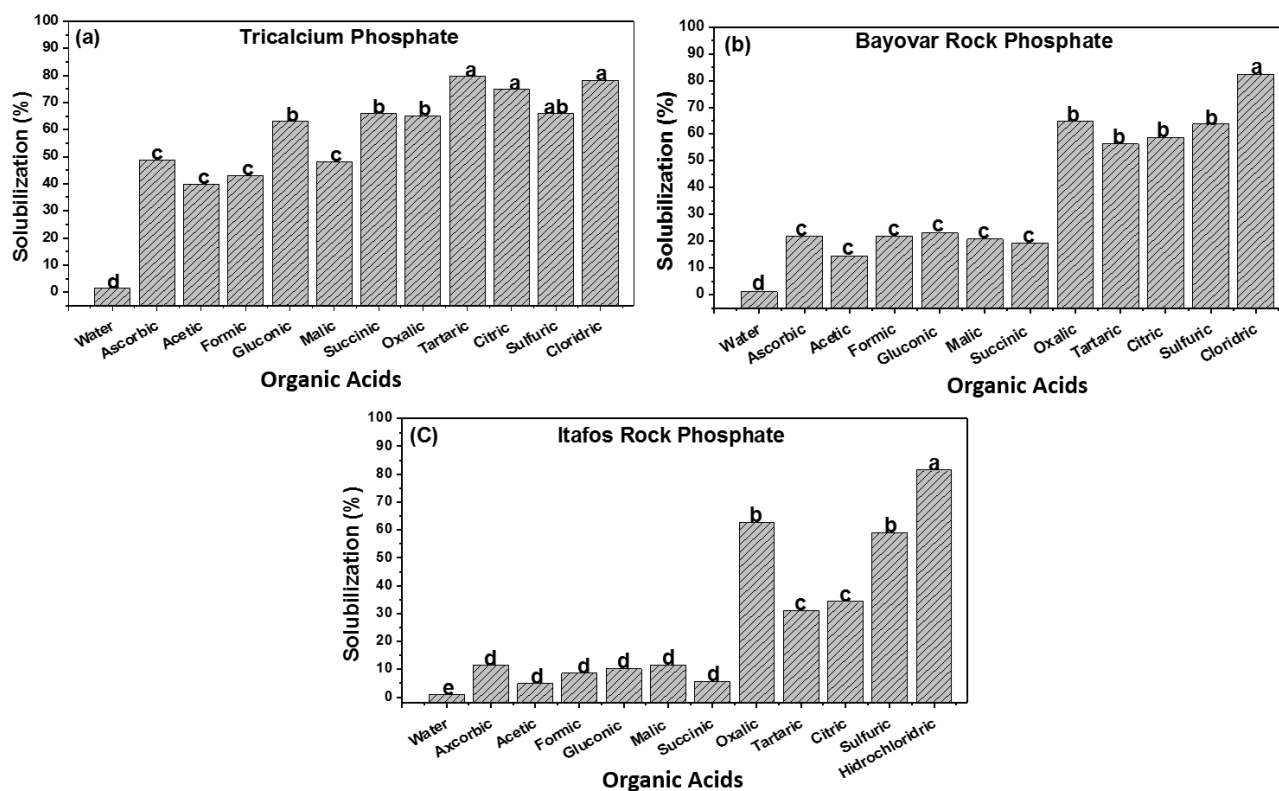


Figure 1. Solubilization efficiency for different phosphate sources on organic and inorganic acids at 40 rpm, 30°C and 6 h. **a)** Tricalcium phosphate. **b)** Bayóvar phosphate rock. **c)** Itafós phosphate rock. \*Different letters mean that there is significant difference among treatments, ANOVA, test Tukey 95% confidence.

It was observed that the position and the amount of carboxylic groups of the organic acids influenced the solubilization. Altogether, PRs showed a lower solubilization in the monocarboxylic acids (acetic, formic, and gluconic) than dicarboxylics (malic, succinic, tartaric) and tricarboxylics (citric acid) for all

phosphate sources tested. However, the oxalic acid was an exception. This can be explained by the different dissociation constant (pKa) of each acid. Organic acids with lower pKa (for example oxalic and citric acid) demonstrated higher potential to solubilize the phosphates sources.

#### 4. CONCLUSIONS

The results showed that the type of organic acid influenced phosphorus solubilization in the three phosphate sources studied. The organic acids with higher number of carboxylic groups and lower pKa showed better potential to phosphorus solubilization. Citric acid and especially oxalic acid were the most efficient to solubilize phosphate rocks. BPR and IPR showed a solubilization around 60% in oxalic acid, which is comparable to phosphorus solubilization in sulfuric acid (used in the industrial fertilizer production process). The strategy proposed can contribute to advances in large-scale development for phosphate fertilizers production using organic acids.

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