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Editors:
Nada Štrbac
Dragana Živković
Svetlana Nestorović

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BACTERIALLY GENERATED H_2SO_4 FROM PYRITE, AS A LEACHING AGENT FOR PHOSPHORUS FROM PHOSPHATE ORE

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Abstract

The object of this study was to investigate the possibility of phosphorus leaching from mixture of phosphate ore and pyrite minerals, in laboratory conditions using sulfuric acid generated by bacterial culture of Acidithiobacillus ferrooxidans (At. ferrooxidans), because the possible application of these mixtures as a natural phosphate fertilizers.
Results obtained show that phosphorus has been leached from the test mixture up to 34,5 % in suspension with At. ferrooxidans, and in the same time, degree of leaching in control suspension (without At. ferrooxidans) was up to 3,8 %

Keywords: *phosphate ore, leaching, Acidithiobacillus ferrooxidans*

1. INTRODUCTION

Phosphate ores are the main source of phosphorus in the nature and are used as row materials for manufacture of commercial phosphate fertilizers and elemental phosphorus which are used in the chemical and the food industry. The ores consist mostly of insoluble calcium phosphate, known as apatite [1]. To become available for the plant, phosphorus needs to be converted into a soluble form, which occurs in nature in the presence of a large number of acidogenic autotrophs and heterotrophs (bacteria, fungi and yeasts), which are capable to dissolve insoluble phosphates due to the production of inorganic or organic acids [2]. Phosphorus is indispensable element for the plants and many industrial applications. It is one of the essential nutrients which plays many roles in metabolism, growth and development of the plants and other living organisms. It has an important role in building macromolecules such as nucleic acids. It also participates in the transfer of energy in the metabolic pathways of biosynthesis and biodegradation [3]. Due to all above mentioned reasons, the soil is fertilized with different types of commercially phosphate fertilizer to improve its fertility.

The object of this study was to investigate the possibility of microbial leaching of phosphorous from phosphate ore from Lisina deposit (Bosilegrad), in the combination with pyrite (from copper mine Bor), by *At. ferrooxidans*, for possible application and direct use of apatite/pyrite mixtureas a natural fertilizer.

2. EXPERIMENTAL

2.1. Prepare of phosphate ore and pyrite for leaching experiments

The phosphate ore sample was originated from Lisina deposit (Serbia). The pyrite sample was originated from copper mine Bor (Serbia). The both samples were pulverized and sieved to pass through 100 μm particle size fractions for chemical, mineralogical and leaching studies. Determination phosphorus was conducted as previously described [4]

2.2. Microbial enumeration

The number of microogranisms was determined using 9K medium [5] by the Most Probable Number Method [6] in 9K medium. All determinations were conducted in triplicate.

2.3. Isolation of microorganisms and preparation of the biomass

At. ferrooxidans strain B2 was isolated from copper sulphide mine wastewater (lake Robule) in Bor, Serbia using serial dilute method in the 9K medium.

2.4. Preparation of bacterial inocula

Pure cultures of *At. ferrooxidans* were prepared for the experiments with three successive reseedings in 500 ml Erlenmeyer flasks containing 100 ml of 9K medium adjusted to pH 2.5 with sulphuric acid. The third reseedings were carried out in 5 dm^3 flasks that contained 1 dm^3 of 9K medium. All flasks were shaken using a horizontal shaker with rotation and temperature set at 200 rpm and 28 ± 1 °C, respectively. After five days, the bacterial cultures was filtered through 0.45 μm membrane filters, washed with 9K iron-free medium (0K) and subsequently resuspended in 20 cm^3 of 0K medium [7].

2.5. Leaching experiments design

The leaching of phosphate was tested using shake-flask testing technique. Experimental conditions were: initial pH of 2.5, 100 rpm, temperature of 28 °C for leaching period of 28 d. Leaching solution (100mL) contained (g/dm3): $(NH_4)_2SO_4$ (3), K_2HPO_4 (0.5), $MgSO_4 \cdot 7H_2O$ (0.5), KCl (0.1), $Ca(NO_3)_2$ (0.01), and H_2SO_4 at a pH of 2.5 in 500mL Erlenmeyer flasks with a pulp density of 10% (m/V) (10 g leaching substrate (7g phosphate ore + 3g pyrite)). Fresh biomass was added and the number of microorganisms in the flask was around 10^6 CFU/mL. As the control, the same mixture but sterilized at 121°C was used.

Number of microorganisms, concentration of P_2O_5 and pH oxidation were analysed each seven days.

3. RESULTS AND DISCUSSION

Leaching experiment of a mixture of phosphate ore and pyrite is performed with bacterial culture *At. ferrooxidans* B2 isolated from the lake Robule of copper mine Bor, Serbia. The *At. ferrooxidans* in the presence of water and oxygen oxidized pyrite to produce sulfuric acid and $FeSO_4$, which is then microbiologically oxidized to $Fe_2(SO_4)_3$. $Fe_2(SO_4)_3$ an extremely strong oxidizing agents under acidic conditions which continues pyrite oxidation. Furthermore, Fe^{3+} ions can oxidize pyrite to sulfur, and then the sulfur can also be oxidized to sulfuric acid, a key ingredient in the process of phosphate dissolution from phosphate ores.

The change of the pH and P_2O_5 leached in the bacterial suspension, as well as in the control suspension, were determined at the beginning and after 7, 14, 21 and 28 days of experiment. The results obtained are presented on Figures 1-2.

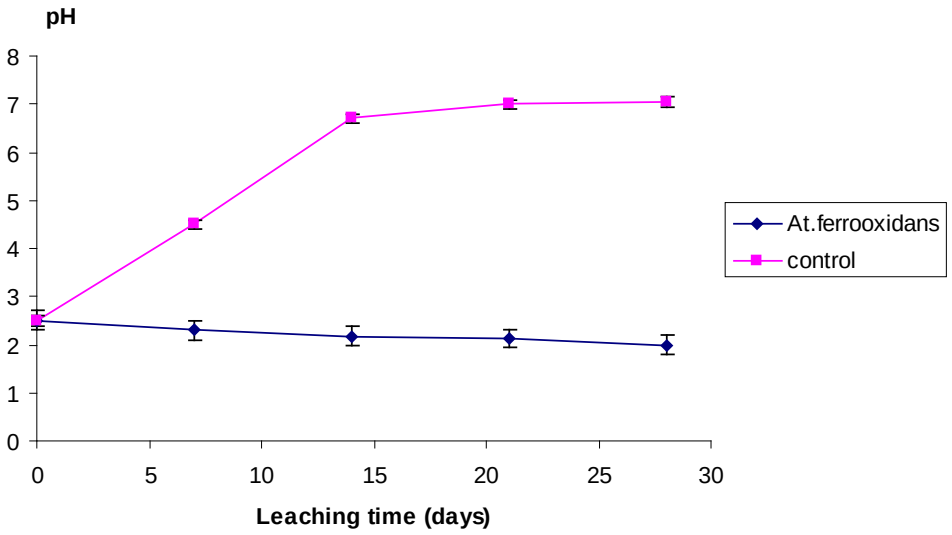

Figure 1 *- pH profiles of leach suspensions during experiments*

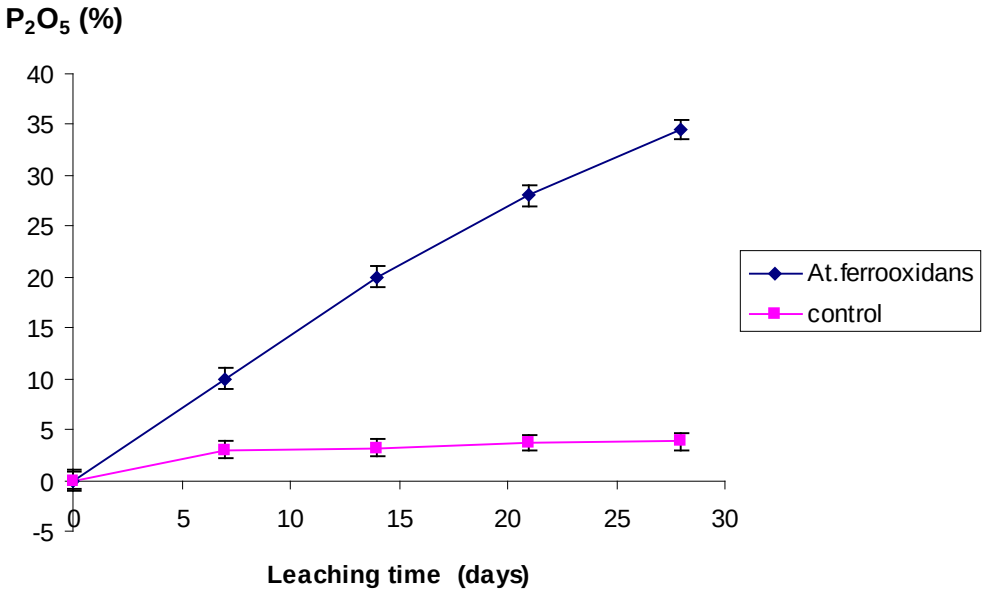

Figure 2 *- Percentage phosphorus recovery (% P_2O_5) from phosphate ore during leaching experiments*

Obtained results show that phosphorus solubilization from phosphate ore was associated with the decrease of pH, which is directly correlated with concentration of bacterially produced sulfuric acid and $Fe_2(SO_4)_3$ in leaching medium.

The percentage of P_2O_5 leached, resulting from the activity of *At. ferrooxidans* B2, (i.e. the effective P_2O_5 leaching), was calculated by subtraction of percentage P_2O_5 leaching in the control suspension from that in the *At. ferrooxidans* B2 suspension, and it equals 30.7 %.

The data of study confirm the role of microorganism in pyrite oxidation, as well as in process of phosphorus leaching from phosphate ore.

The leaching rate of P obtained in this study was comparable to the previously described leaching data of phosphorus solubilization from phosphate ore with acidophilic sulphur- and iron-oxidizing bacteria [8].

4. CONCLUSIONS

The results of study show that *At. ferrooxidans* have a very important role in the dissolution of phosphorus from phosphate ore. This bacteria can oxidize ferrous ion, elemental sulfur or sulfide to produce sulfuric acid, thus creating an acidic environment which helps the solubilization of phosphorus from insoluble phosphate ores.

Treatment of soil with phosphate minerals in combination with pyrite and acidophilic iron- and sulfur- oxidizing bacteria could become an attractive and alternative way to improve the quality of alkaline soils, due to low cost and environmental acceptance.

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