

Evaluation of phosphorus forms in an organo-phosphate fertilizer

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Abstract

Phosphate rock is the only economic source of phosphorus (P) for production of fertilizers and chemicals. However, the growth of world population will require enhanced food production and consequent increase in fertilizer demand. Nonetheless, global P reserves are limited and it is necessary to explore alternative fertilizer options. The Humifert process is designed to make better use of low-grade phosphate rock by reaction with organic waste. A sequential fractionation procedure was used to evaluate P forms in Humifert fertilizers. Results indicated that the WS – P fraction represented the least (<2% total P), whereas the major fraction was the HCl – P. (> 64% of total P). The fractions WS-Pi, membrane-Pi, NaHCO₃-Pi and NaOH-Pi showed an increase compared with initial sample, and HCl-Pi showed a decrease. The Po fractions (WS – Po; NaHCO₃ – Po and NaOH – Po) also showed an increase in their content when were compared with initial sample.

Key Words

Biosolids, humifert process, sequential P fractionation.

Introduction

Phosphorus (P) is a unique element and it is essential for all life forms. It is generally limiting for plant production, and therefore most agricultural systems need continued inputs of P to increase and maintain productivity (Condrón 2003). Phosphate rock is the only economic source of P for production of fertilizers and chemicals (Oelkers and Valsami-Jones 2008). Approximately 80% of world P production is from sedimentary rocks, while only 17% is from igneous rocks and their weathering products. However, continued world population growth and increased life expectancy induces the enhanced of food production and, consequently, it increase the use of fertilizers. Accordingly, it is necessary to investigate utilisation of low-grade P resources and recycling of waste P. The Humifert process has been developed to improve utilisation of low-grade phosphate rock reserves. The aim of this process is to use phosphate rocks considered by manufactures as low-grade ore. In addition, the Humifert process utilises organic waste such as biosolid to create a composite organo-phosphate fertilizer. The Humifert process involves reacting phosphate rock with organic waste in a bench reactor, with nitric acid that is just formed when nitric oxides come into the mixture (Sternicha 1980; Silverol *et al.* 2007). The apatite grains from the phosphate rock are partially dissolved, releasing PO₄³⁻, which can associate with organic phases present or transformed during the nitric reactions. Then, organo-phosphate compounds are generated, more soluble than natural phosphate rocks, but less soluble than traditional fertilizer. However, little is known about the nature of P generated by the Humifert process. Sequential P fractionation has been an important tool in the study of phosphorus biogeochemistry of soils and sediments for over 50 years (Condrón *et al.* 2005; Pierzynski *et al.* 2005) The fractionation schemes involves sequential extraction with a series of reagents designed to selectively dissolve various forms of P based mainly on the nature and strength of interactions between P moieties and other mineral and organic components. Sequential P fractionation is commonly used in the soils, but currently it has been used to investigate P pools in organic materials (Huang *et al.* 2008). However, sequential P fractionation has not been used to investigate P forms in alternative fertilizers. The objective of this study was to utilize sequential P fractionation to characterize P forms in Humifert fertilizers.

Methods

Humifert

The Humifert compounds were manufactured in a bench reactor. It had been made two kinds of compounds: (1) igneous phosphate rock from Angico dos Dias, Bahia, Brazil and composted biosolids from domestic sewage sludge (PRBC; 4% P); and (2) igneous phosphate rock from Angico dos Dias, Bahia, Brazil and non-composted biosolids from domestic sewage sludge (PRBS, 4%P). The mixture has been submitted a reaction with gaseous nitric acid within the reactor. It had been used different periods of duration, from 2 to 12 hours, to investigate if compound solubility could increase with enhance of time reaction.

Sequential P fractionation

The sequential P fractionation was performed according to Huang *et al.* (2008), but it was realized double fractionation, i.e. each extractor was done twice. This methodology was adopted due the nature of samples, phosphate rock and biosolids, that could have higher P. A 0.5-g (dry weight) Humifert samples was placed in a 50-mL centrifuge tube and sequentially extracted twice with 30 mL each of deionised water; deionized water with a piece of 6 cm² anion-exchange membrane; 0.5 mol/L NaHCO₃ (pH 8.5); 0.1 mol/L NaOH, and 1 mol/L HCl. Each extraction was run for 16 h with end-to-end shaking at 25°C. After each extraction, tubes were centrifuged at 12,000 × g for 10 min and the supernatant passed through a 0.45-µm filter. Membrane-P was extracted by 20 mL of 1 mol/L HCl for 16 h after taking membrane strips out of tubes and removal thoroughly with deionized water. The P fractions were designated as: WS-P (I); WS-P (II); membrane-P (I); membrane-P (II); NaHCO₃-P (I); NaHCO₃-P (II); NaOH-P(I); NaOH-P(II); HCl-P (I) and HCl-P (II). Inorganic P (Pi) was measured using the colorimetric method of Murphy and Riley (1962), and total P (Pt) was measured directly using ICP – ES. Organic P was calculated as the difference between Pt and Pi.

Results

All the P fractions obtained showed that WS – P was the least (<2% total P), whereas the major fraction was the HCl – P. (> 64% of total P). The different P fractions varied with type of biosolid and the duration of attack in Humifert reactor (Table 1). The fractions WS-Pi, membrane-Pi, NaHCO₃-Pi and NaOH-Pi showed an increase compared with initial sample (0h) in accordance with duration of attack in Humifert reactor (Table 1). The increase in these fractions could indicate that Humifert process had effectively converted phosphate rock P to more soluble forms, which is confirmed by decreases in HCl-Pi.

Table 1. Amounts of inorganic P (Pi) in WS, Mem, NaHCO₃, NaOH and HCl fractions.

Humifert compounds	WS (I) (µg P/g)	Mem (I) (µg P/g)	NaHCO ₃ (I) (µg P/g)	NaOH (I) (µg P/g)	HCl (I) (µg P/g)
PRBC 0h	31,43	554,38	375,85	1494,50	11579,21
PRBC 2h	47,04	727,64	506,70	1648,68	11774,74
PRBC 4h	139,25	1166,56	617,41	1662,70	10601,54
PRBC 6h	161,95	1251,27	657,67	2020,10	12133,22
PRBC 8h	157,69	1205,07	647,60	2020,10	10829,66
PRBC 10h	349,56	1559,28	775,09	2139,24	10503,77
PRBC 12h	316,58	1501,53	765,02	2258,38	10308,23
PRBS 0h	53,07	538,98	318,82	1017,96	10080,11
PRBS 2h	46,33	512,03	328,89	1690,73	12296,16
PRBS 4h	53,77	650,64	359,08	1929,00	10308,23
PRBS 6h	55,19	623,69	365,79	1697,74	10731,89
PRBS 8h	115,49	789,24	526,83	1816,87	10894,84
PRBS 10h	311,97	1701,74	754,96	2307,43	10699,30
PRBS 12h	283,95	1805,70	785,15	2608,78	10243,06

The Po fractions (WS – Po; NaHCO₃ – Po and NaOH – Po) also showed an increase in their content when were compared with initial sample (Table 2). Increases in Po fractions were probably mainly due to transformations of organic matter during the production process based on associations between P species and organic matter components. The behavior of fractions (increase and decrease) in PRBC and PRBS samples were the same way, but PRBC contained more Pi and Po than PRBS.

Conclusions

The results of this study demonstrated that sequential P fractionation could be an interesting tool to evaluated alternative fertilizers. The amounts of P extracted by sequential fractionation showed that Humifert process was capable to modify the initial compound, which could indicate more solubility and consequently, more P available to plants. Therefore, for the experimental validation of sequential P fractionation of alternative fertilizers is necessary modifications in the procedure to assess more P. Additionally, the use of other techniques such as ³¹P NMR (³¹P nuclear magnetic resonance spectroscopy) could provide more detailed information on the types of p compounds present in the Humifert materials is useful to analyze more precisely the P species found in the Humifert compounds. Further studies are also required to characterize the relationship between P species and organic matter in the Humifert compounds and their dynamics and bioavailability in the soil.

Table 2. Amounts of organic P (Po) in WS, NaHCO₃ and NaOH fractions.

Humifert compounds	WS (I) ($\mu\text{g P/g}$)	NaHCO ₃ (I) ($\mu\text{g P/g}$)	NaOH (I) ($\mu\text{g P/g}$)
PRBC 0h	1854,41	173,44	332,02
PRBC 2h	2775,11	238,10	147,02
PRBC 4h	8215,60	240,67	392,30
PRBC 6h	9554,79	341,19	402,74
PRBC 8h	9303,69	250,98	274,05
PRBC 10h	20624,09	358,98	455,81
PRBC 12h	18678,07	299,55	428,45
PRBS 0h	3130,84	138,91	410,95
PRBS 2h	2733,26	162,79	545,98
PRBS 4h	3172,69	239,17	478,87
PRBS 6h	3256,39	135,47	273,17
PRBS 8h	6813,63	236,67	455,50
PRBS 10h	18406,04	283,23	454,19
PRBS 12h	16752,97	283,80	452,95

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