Modern Chemistry
2019; 7(4): 109-113
http://www.sciencepublishinggroup.com/j/mc
doi: 10.11648/j.mc.20190704.14
ISSN: 2329-1818 (Print); ISSN: 2329-180X (Online)

Impact of Phosphorite on pH, Electrical Conductivity and Water Soluble Phosphorous Extracted from Incubated Citrus Waste Compost

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To cite this article:
Mussaddiq Khan Khalil, Dost Muhammad, Shuja Ur Rehman Qureshi, Sultan Nawaz, Farooq Ishaq. Impact of Phosphorite on pH, Electrical Conductivity and Water Soluble Phosphorous Extracted from Incubated Citrus Waste Compost. *Modern Chemistry*. Vol. 7, No. 4, 2019, pp. 109-113. doi: 10.11648/j.mc.20190704.14

Received: August 17, 2019; **Accepted**: October 21, 2019; **Published**: October 30, 2019

Abstract: Citrus waste having acidic reaction may have additional advantage over other organic residues as compost materials in alkaline calcareous soil but the process of its composting is very slow. In this study an attempt was made to access the release of P from RP added citrus waste during 180 of incubation and its effect on pH and EC of the composting media. Citrus waste consisting pulp, fruits skin and juice with total net weight of 500 g (fresh) were added with 0, 15, 30 and 60 g of RP (equivalent to 0, 3, 6 and 12%, respectively) and were incubated in oven at 36°C ± 2 for 180 days. All pots were also added with 20 mL water and 20 g FYM to optimize the moisture level and augment the microbial decay in pots. Results showed that RP mixed citrus waste had higher pH, EC and more water-soluble P as compared to non-treated citrus waste (control) at all incubation intervals of 0, 15, 30, 60, 120 and 180 d suggesting releases of salts and P from RP. These values of pH, EC and water-soluble P increased with increase in RP levels and passage of time which could be associated to neutralization of RP with organic acids of citrus and CO_2 mineralization with time. It is concluded that addition of RP not only enhanced the quality of compost but could also promote the citrus waste decomposition process. Though the higher RP levels was best in our results, but other levels and their consequent effect on soil and crop yields should be assessed along with their environmental risks for wider and long-term recommendations.

Keywords: Phosphorite, Citrus Waste Compost, pH, E.C and Phosphorous Extraction

1. Introduction

An organic matter that is decomposed and recycled as soil amendment and fertilizer is compost. It is nowadays being widely used in organic farming by developed countries. It requires bundles of wetted organic matter known as green waste and require proper care for decomposition of such waste for the formation of humus. In modern composting, compost is prepared in a multistep process with known inputs of water, air and carbon-nitrogen rich materials. Worms helps in decomposition process by shredding of plants matter into light pieces that can be easily breakdown by other small microorganisms. For this bacteria (aerobic) require proper oxygen for proper working and fungi aid in chemical process by converting the matter into heat, CO_2 and NH^+_4. This ammonium formation is used by the plants. When the plants didn't take such form of nitrogen then bacteria aid in conversion to nitrate through the process called nitrification.

During composting a stable product is formed from organic matter that can be stored, handled, transported and applied to the field without any environmental constraint. During composting heat is produced by the metabolic activities of microorganisms that destroys pathogens and weed seeds [1]. These composts are then used not only to enhance soil fertility but also to suppress soil borne pathogens [2, 3].

Composting converts organic matter into a stable substance which can be handled, stored, transported and applied to the field without adversely affecting the environment. Proper composting effectively destroys pathogens and weed seeds through the metabolic heat generated by microorganisms during the process [1]. Such composts are not only suitable for use as a soil conditioner and fertilizer, but can also suppress soil-borne and foliar plant pathogens [2, 3]. This paper describes how citrus waste can be composed, thus converting it into a value-added commodity without specialized equipment or facilities.

Citrus includes oranges, grapefruits, lemons, limes, tangerines and mandarins; are one of the most widely cultivated fruits across the globe. Its production is increasing every year due to increasing consumer demand. Citrus processing industries generate huge amounts of wastes every year and citrus peel waste alone accounts for almost 50% of the wet fruit mass. Citrus wastes are of immense economic value as it contains abundant amounts of various flavonoids, carotenoids, dietary fiber, sugars, polyphenols, essential oils, ascorbic acid and considerable amounts of some trace elements. Citrus wastes also contain high levels of sugars suitable for fermentation for bioethanol production [4], however compounds such as d-limonene must be removed for efficient bioethanol production.

Phosphorite, phosphate rock or rock phosphate is a non-detrital sedimentary rock which holds high amounts of *phosphate* bearing minerals. The phosphate content of phosphorite is at least 15 to 20%; if it is assumed that the phosphate minerals in phosphorite are hydroxyapatite and fluoroapatite, phosphate minerals contain roughly 18.5% phosphorus by weight and if phosphorite contains around 20% of these minerals, phosphorite is roughly 3.7% phosphorus by weight, which is a considerable enrichment over the typical sedimentary rock content of less than 0.2%. The phosphate is present as fluorapatite $Ca_5(PO_4)_3F$ typically in cryptocrystalline masses (grain sizes < 1 μm) referred to as collophane. It is also present as hydroxyapatite $Ca_5(PO_4)_3OH$ or $Ca_{10}(PO_4)_6(OH)_2$, which is often dissolved from vertebrate bones and teeth, whereas fluorapatite can originate from hydrothermal veins. Other sources also include chemically dissolved phosphate minerals from igneous and metamorphic rocks. Phosphorite deposits often occur in extensive layers, which cumulatively cover tens of thousands of square kilometers of the Earth's crust.

2. Objectives

1. To assess the release of P from RP during citrus composting process
2. To evaluate the chances in pH and EC as influenced by the addition of different levels of RP

3. Materials and Methods

Citrus waste was collected from Khyber Bazar Peshawar and bought to the laboratory and was grinded into small pieces. Citrus waste at 500 g was taken in each separate plastic bottle having capacity of 1 kg. Plastic bottle containing 500 g waste was added with 0, 15, 30 and 60 g RP and were labeled as T1, T2, T3 and T4. The RP and waste were thoroughly mixed and added with 20 mL water and 20 g FYM to facilitate the microbial activity. All treatments were replicated two times. After adding FYM all the bottles were placed in incubator at 36° C. The bottles were checked for soluble P, pH and EC at 0, 15, 30, 60, 120 and 180 d of incubation. At time of determination, the required amount of waste was taken from the bottles and the rest were again placed in the incubator. To enhance the aeration, the bottle were opened periodically with 4-5 days interval, the waster were mixed with spatula, kept open for some time and then again placed in the incubator. Water soluble P, pH and EC were determined periodically with the procedure described below:

3.1. pH of the Compost

Thirty grams of citrus waste was taken with the help of balance and was chopped. 60 mL of distilled water was added to make 1:2 dillution. It was shaked with horizantal shaker for 15 to 20 minutes. The filtrate was obtained with suction pump and pH was determined with pH meter. The pH was first calibrated against pH 7.0 and 4.0 before the analysis of sample [5].

3.2. Electrical Conductivity (EC)

Thirty grams of citrus waste was taken with the help of balance and was chopped. 60 ml of distal water is added to make 1:2 dilutions. It was shanked with horizontal shaker for 15 to 20 minutes. The filtrate is obtained with suction pump and EC was determined with EC meter after its proper calibration against 0.01 and 0.1 N KCl solutions [6].

3.3. Phosphorus Concentration

Waste soluble P in the compost was determined in 1:2 compost: water ratio. In this process, 5 mL filtrate used in pH and EC was diluted in 100 mL distilled water. Then 0.5 mL of aliquot was mixed with 5 mL distilled water and 5 mL mixed reagent (ascorbic acid + color regent). The volume was raised to 25 mL and the flasks were kept in dark for 15 minutes. Elemental analysis of phosphorus was done on spectrophotometer at 880 nm wavelength. Each time the machine was calibrated against 0, 2, 4, 6, and 8 mg P L-1 before running the samples [7].

The instrumental data of phosphorous is converted into percent (%) by following

$$Phosphorus\ (mg\ kg-1) = \frac{Reading\ x\ Volume\ made}{Weight\ of\ Sample} x\ Dilution\ Factor$$

4. Results and Discussion

The release of P from RP during citrus waste compositing was evaluated in the department of Soil and Environmental

Sciences, The University of Agriculture, Peshawar during 2016. Citrus waste collected from Peshawar city was added with different levels of RP at 0, 3, 6 and 12% w/w basis (fresh) and were incubated at 36 oC for 180 d. Changes in pH, EC, and water soluble P were determined at 0, 15, 30, 60, 120 and 180 d of incubation which are given and described below:

4.1. Changes in pH in RP Mixed Citrus Waste

The results showed that with increase in RP levels from 0 to 60 g RP per 500 g citrus waste, the pH significantly increased with each increment. However, the differences at d0 were not significant though they were much higher than control. With passage of time the differences among treatments and as well as from control widened revealing significant differences with time. At d15 for example the differences between the T_2 (15 g RP per 500 g citrus waste) and T_3 (30 g RP per 500 g citrus waste) and at d30 between the T_1 and T_2 were not significant but significantly lower than T_4 (RP 60 g per 500 g citrus waste). After 120 d of incubation and similarly at d 180 the difference among all treatments and control were significant and were higher for higher RP application. These results suggested that pH increased with RP levels and with passage time this effect was strengthened. For the given treatment as well as the control the pH of the citrus was increase. For example, in control the pH increased from 4.39 at d 0 to 5.19 at d180. Similarly, for T_4 this pH increased from 4.75 to 8.03 revealing increases but with different ration. The increase in higher RP treated citrus waste was more than the lower or control pots. This phenomenon is also reflected in Figure 1. The increase in pH with RP is associated that organic acids in the citrus waste would have been consumed during the reaction which would have resulted in higher pH. These results are close to findings [8] who observed increase in soil pH when RP was added to acidic soil. The rock phosphate consists lime and upon mineralization it release Ca-salts which may increase the pH compost. Similarly, with increase in pH with time would have been associated to decomposition of acidic compounds in the citrus wastes. The ideal pH of composting material is about 6-8 meaning that addition of RP not only enhance the P content in the compost (improve quality) but also fasten the decomposition process by mediating its pH.

Table 1. *Changes in pH of the citrus waste compost during 180 d of incubation as influenced by different levels of RP.*

Rock Phosphate (g per 500 g citrus waste)		Time of incubation (Days) 0	15	30	60	120	180
T_1	0	4.39 a	4.54 c	4.70 c	4.85 c	5.01 d	5.19 d
T_2	15	4.70 a	4.91 b	5.35 b	5.90 b	6.43 c	6.70 c
T_3	30	4.71 a	4.97 b	5.61 ab	6.05 b	6.99 b	7.40 b
T_4	60	4.75 a	5.18 a	6.00 a	6.63 a	7.74 a	8.03 a

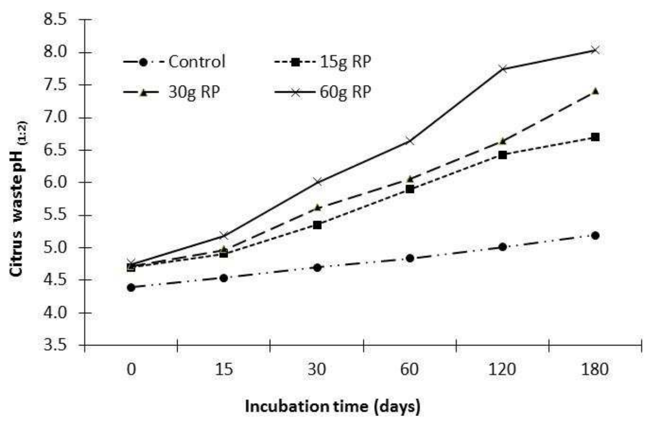

Figure 1. *The graph shows the relation between pH and days of Incubation of citrus waste treated with different levels of rock phosphate (RP).*

4.2. Changes in EC in RP Mixed Citrus Waste

The table 2 showed the effect of different treatments of RP applied from 0 to 60 g per 500g of citrus waste on EC within 180 days of incubation. The EC significantly increased with each increment of RP suggesting its solubilization from dissolved organic acids in citrus wastes as well as due to CO_2 mineralization released during microbial oxidation of organic compounds. The increases in EC with passage of time in control as well as in treated citrus wastes affirm this assumption of RP mineralization with CO_2. In control significant increase in EC were observed with mean values of 4.09 dS m^{-1} at d_0 to 6.20 dS m^{-1} at d_{180}. However, with passage of time the differences among treatments increased revealing differential microbial activity in the treated and control plots that could be associated to pH changes brought about by different treatments (Table 1, Figure 1). At all days of incubation, the differences between treatments were significant and values of EC increased with each increment of P with higher respective values at higher RP level i.e. 60 g RP per 500 g citrus waste. At d0 the EC in this treatment was 5.65 dS m^{-1} which as 38.14% higher than control and it increased up to 9.16 higher 49.16% over control at d_{180}. This phenomenon is also reflected in Figure 2 showing increases in EC with RP levels and time of incubation with increasing effect of RP with time.

The increase in EC is associated to release of different salts such as Ca soluble salts that are released from RP during citrus waste composting and have resulted in higher EC whereas the increases time are associated with CO_2 mineralization and release of inorganic soluble radicals and compounds. In acidic soil, when RP is applied to soil it releases the P and C [8] reducing the need for liming and Ca fertilizer application. This suggests that RP in acidic condition can increase the EC by releasing different Ca salts. Similarly, decomposition of citrus waste through microbial activity which releases different organic acids as well as carbonic acid (H_2CO_3) through CO_2 production would have mineralized RP that would have resulted in increases in EC with time as well as among the treatments.

Table 2. *Change in citrus waste EC (dS m^{-1}) compost during 180 d of incubation as influenced by different levels of RP.*

Rock Phosphate (g per 500 g citrus waste)		**Time of incubation (Days)**					
		0	**15**	**30**	**60**	**120**	**10**
T_1	0	4.09 d	4.86 d	5.03 d	5.34 d	5.86 d	6.20 d
T_2	15	5.17 c	5.60 c	5.94 c	6.51 c	7.11 c	7.86 c
T_3	30	5.36 b	5.86 b	6.21 b	6.94 b	7.90 b	8.71 b
T_4	60	5.65 a	6.15 a	6.49 a	7.21 a	8.48 a	9.16 a

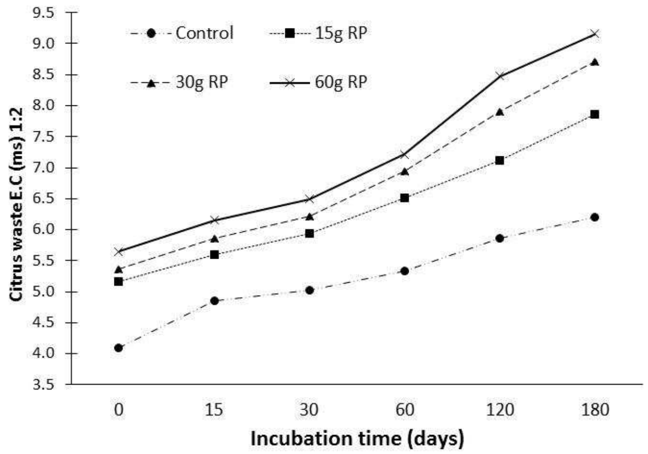

Figure 2. *The figure shows the relation between EC and days of Incubation of citrus waste with different treatments of rock phosphate.*

4.3. Phosphorous Concentration (mg kg^{-1}) of Citrus Waste

Table 3 shows the effect of different treatments of rock phosphates from 0 to 60 g RP per 500 g citrus waste on phosphorous concentration (mg kg^{-1}) within 180 days of time of incubation. The P concentrations significantly increased with each increment of RP levels and with incubation intervals from 0 to 180 of incubation. Right from the beginning of addition of RP to citrus waste resulted in higher water soluble P which increased with increasing in RP levels and the higher P as 55.29 mg kg-1 at 60 g RP mixed with 500 g citrus waste at d_0 followed by mixing of 30 and 15 RP with 500 g citrus waste, respectively. Addition of 15 g RP with 500 g citrus waste resulted in water soluble P of 45.78 mg kg^{-1} which 7.6 times higher than control i.e. without RP. With passage of time the differences between treatments as well as with control widened but all increased with increase in time as compared to at d_0. In control treatment, the P concentration increased from 6.01 mg kg^{-1} at d_0 to 9.54 mg kg^{-1} at d_{180} showing increases of only 3.53 mg kg^{-1} (58.74%) whereas in treatment receiving 60 g RP per 500 g citrus waste the RP increased from 55.29 to 113.45 with 58.16 mg kg-1 equals to 105.2% during 180 of incubation. These results suggested that P concentration increased with RP levels and with passage time this effect their effects became more vivid and as such the increase in higher RP treated citrus waste was more than the lower or control pots. This phenomenon is also reflected in Figure 3.

Organic acids and humic substances produced during decomposition are mainly involved in P solubilization process [9, 10]. The nature of organic acids produced has a considerable effect on the solubilization of insoluble phosphates. Citric acid has maximum P solubilizing efficiency followed by oxalic, maleic and formic acids. The position and type of functional group within each acid seems to be a dominant factor that influences the amount of released P [11]. The increase with time could be associated to CO_2 mineralization and since microbial activity changes with pH and slats concentration so different treatments results in different RP levels. The higher the RP level had more suitable pH especially in the lower incubation intervals and hence resulted in higher P concentrations.

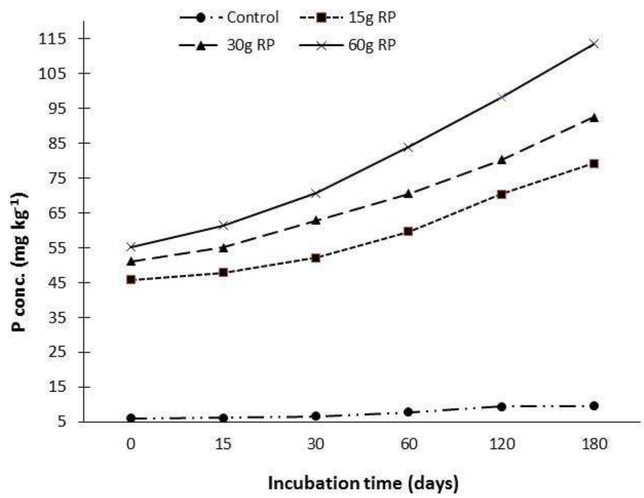

Figure 3. *Figure shows the relation between Phosphorous Concentration (mg kg^{-1}) of citrus waste compost and days of incubation at different treatments of RP.*

Table 3. *Change in P concentrations (mg kg^{-1}) of citrus waste compost during 180 d of incubation as influenced by different levels of RP.*

Rock Phosphate (g per 500 g citrus waste)		**Time of incubation (Days)**					
		0	**15**	**30**	**60**	**120**	**180**
T_1	0	6.01 c	6.18 c	6.72 d	7.85 d	9.46 d	9.54 d
T_2	15	45.78 b	47.82 b	52.13 c	59.65 c	70.43 c	79.18 c
T_3	30	51.0 ab	55.09 a	62.86 b	70.54 b	80.22 b	92.51 b
T_4	60	55.29 a	61.45 a	70.62 a	83.91 a	98.26 a	113.45 a

5. Conclusions and Recommendation

1. The RP mixed citrus waste had higher pH, EC and more water-soluble P as compared to non-treated citrus waste (control) during 180 days of incubation suggesting releases of salts and P from RP.
2. These values of pH, EC and water-soluble P increased with increase in RP levels from 15 to 60 g per 500 g citrus waste and with each intervals of the incubation time from 0 to 180 days. The higher EC and P release with incubation time could be associated to CO_2 mineralization.
3. The increase in soil pH with RP also improved as the apparent microbial activity especially of bacteria is higher at alkaline pH which resulted in more vivid differences among the RP levels and as well as with control with passage of time.
4. This could be concluded that RP addition to citrus waste not only enhance the quality of compost but could also promote the citrus waste decomposition process which otherwise is regarded very slow due to its acidic nature.
5. Addition of RP is recommended to citrus waste to enhance the process and quality and final compost. Though the higher RP levels was best in our results, but other levels and their consequent effect on soil and crop yields should be assessed along with their environmental risks for wider and long-term recommendation.

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