Phosphate removal from secondary effluent of wastewater treatment: characterization and potential re-use as fertilizer of recovered precipitates

Raptopoulou Christina[1], Kalaitzidou Kyriaki[2], Tolkou Athanasia[1], Mitrakas Manassis[2], Palasantza Panagiota-Aikaterini[3] and Zouboulis Anastasios[1]

[1]Department of Chemistry, Aristotle University of Thessaloniki, Greece

[2]Department of Chemical Engineering, Aristotle University of Thessaloniki, Greece

[3]AKTOR S.A., WWTP of "AINEIAS", N. Michaniona, Thessaloniki, Greece

Corresponding author: Department of Chemistry, Aristotle University of Thessaloniki, GR-54124, Greece, Email: christi.rapt@gmail.com

Abstract

Phosphorus is a non-renewable essential element, while it is considered as the primary nutrient responsible for the eutrophication of lakes and rivers. Therefore, phosphorus recovery from wastewaters is an issue of high priority. This study examines the content and the availability of phosphorus in the phosphate precipitates/solids produced by the treatment of secondary effluent at the wastewater treatment plant "AINEIA", near Thessaloniki–Greece. Initially, batch precipitation tests were conducted for ferric phosphate precipitates collection, followed by "Rapid Small Scale Column Tests" (RSSCTs) applied in lab-scale experiments and by using iron oxy-hydroxides (FeOOH) as adsorbent. When the residual concentration of the column reached the strict disposal limit of approximately 1 mg $P\text{-}PO_4^{3-}$ L^{-1}, a regeneration of the column took place and phosphates were recovered from regeneration solution either as calcium, or magnesium salts. Then, the formed solids/precipitates from the aforementioned treatment

processes were analyzed for their phosphorus content and its availability in acidic or basic soil samples. The phosphorus content in ferric phosphate solids was 97 mg P g^{-1}, while in the calcium and magnesium salts was 170 mg P g^{-1} and 64 mg P g^{-1}, respectively. The results about the phosphorus bioavailability revealed that it was satisfactory from Ca^{2+} or Mg^{2+} precipitates. On the contrary, the phosphorus increment by the application of ferric phosphate solids was insignificant.

Keywords: phosphate, precipitates, phosphorus content, bioavailability, fertilizer, phosphorus recovery

Introduction

Phosphorus is one of the main elements contributing to aquatic populations and favouring eutrophication in lakes and rivers (Morse et al., 1998). While excess phosphorus is problematic, it comes also from a limited source (Wang et al., 2005). Phosphate rock in sedimentary deposits is a non-renewable and non-substitutable resource. Hence, it becomes important to look out for other re/sources of phosphorus (Prabhu and Mutnuri, 2014). It is more than desirable to recover phosphorus as an utilizable material that will re-enter phosphorus cycle. Therefore, for sustainability point of view, new technologies take into account the potential to recycle phosphorus. Chemical precipitation is the leading technology for phosphorus recovery (Morse et al., 1998).

Around 90% of the total phosphorus use in the world today is for food production (Rengel, 2008). Plants require adequate phosphorus from the very early stages of growth for optimum crop production (Grant et. al., 2004). Hence, modern agricultural systems are dependent on continual inputs of phosphate fertilizers, because the plant-available phosphorus fraction and the concentration in the soil solution may be insufficient to satisfy plant requirements (Rengel, 2008).

The aim of this study was to investigate whether the phosphorus content in the produced precipitates is high enough to use the precipitates as phosphorus recovery source and if the phosphorus availability of the produced phosphate precipitates to soils allows their potential re-use as fertilizers.

Materials and methods

Wastewater treatment plant

The wastewater treatment plant of "AINEIA" is a conventional one. It receives about 8×10^3 m^3 of influent per day, of which 7×10^3 m^3 d^{-1} municipal waste water and 1×10^3 m^3 d^{-1} domestic septage waste. The plant consists of a combination of conventional preliminary, primary, secondary treatment and ozone disinfection. The treated effluent is discharged into the sea, Thermaikos Gulf. The primary and the secondary sludge are thickened, anaerobically digested and dewatered by belt filter press.

Batch precipitation tests – ferric phosphate precipitates

Batch precipitation tests were conducted at a jar test (WiseStir JT-M6C) with a six paddle stirrer at 20 ^{o}C. Proper amount of the reagent ($FeClSO_4$) was added in 1 L sample of secondary effluent under vigorous stirring (250 rpm) for 5 min, followed by gently stirring (50 rpm) for another 25-85 min. Then, the solution was filtered through 0.45 μm membrane filter and the precipitates were collected. The precipitates were dried in the desiccator and portions of them analyzed after being solubilized in 11N H_2SO_4. Their analysis included the determination of phosphate, ferric, magnesium and calcium ions. Phosphate concentration was determined using a UV-Vis spectrophotometer (HITACHIU–5100), following the stannous chloride method at 690 nm and ferric, magnesium and calcium concentrations were measured by flame atomic absorption spectroscopy (Perkin Elmer AAnalyst 800) (APHA, AWWA, WEF, 1992).

"Rapid Small Scale Column Tests" (RSSCTs) – calcium & magnesium salts

"Rapid Small Scale Column Tests" (RSSCTs) were applied in lab-scale experiments, indicating an adsorption capacity of 22 mg PO_4^{3-} g^{-1} by using iron oxy-hydroxides (FeOOH) as adsorbent. When the residual concentration of the column reached the strict disposal limit of 1 mg P-PO_4^{3-} L^{-1} on – site regeneration of the column with 0.016 N NaOH took place and the effluent from the regeneration step was collected and used for P-PO_4^{3-} recovery by precipitation as calcium or magnesium salt, by addition of $CaCl_2$ or $MgCl_2$ solution, respectively. For the preparation of Ca^{2+} and Mg^{2+} solutions a proper amount of $CaCl_2$ or $MgCl_2$ was diluted in distilled water and their concentrations were verified by flame atomic absorption spectroscopy (Perkin Elmer AAnalyst 800). The precipitates were dried in the desiccator and portions of them analyzed after being solubilized in 11N H_2SO_4. Their phosphate concentration was determined spectrophotometrically (HITACHIU–5100) by stannous chloride method and the other ions (ferric, calcium and magnesium) were analyzed by flame atomic absorption spectroscopy (Perkin Elmer AAnalyst 800) (APHA, AWWA, WEF, 1992).

Soil samples preparation

The produced precipitates were examined for their phosphorus bioavailability in acidic and basic soil samples. The samples were air dried, ground and sieved (> 2mm) to remove the large particles. Three replicates of 1 kg acidic soil and three of basic soil were each weighed into plastic bags. For acidic and basic soil, pH and their initial phosphorus content were determined. Proper amounts of each precipitate were added to an acidic and a basic soil portion. The addition of the precipitates was according to their initial phosphorus content, soil's initial phosphorus content and the soil's desired phosphorus content (~43 mg P kg^{-1}_{soil}). The treated soil samples were incubated for 30 d, under aerobic conditions, at room temperature and 10-20 wt.% moisture content. Every 5 d the extractable phosphorus was measured.

Soil extraction

Roots absorb phosphate ions from the soil solution. The inorganic phosphorus in the soil solution is present as orthophosphate ions, usually $H_2PO_4^-$ and HPO_4^{2-}, depending on the soil pH. Soil testing procedures predict phosphorus availability using chemical extractants (Grant et. al., 2004).

Soil test phosphorus was measured by Mehlich 3 (CH_3COOH 0.2 M, HNO_3 0.013 M, NH_4F 0.015 M, NH_4NO_3 0.25 M και EDTA 0.001 M) and Olsen ($NaHCO_3$ 0.5 M) for acidic and basic samples, respectively. For acidic soil samples, phosphorus was extracted by shaking (250 rpm) 2 g soil with 20 mL Mehlich 3 extractant for 10 min. For basic samples, 1 g aliquot was drawn and Olsen extractant was added, instead. Then, the solutions were filtered (Whatman No. 42) and the filtrates were collected for the following phosphate determination spectrophotometrically (Sims, 2000), by stannous chloride method. The soils' phosphorus content calculation was based on the phosphate concentration measured in the filtrates.

Results and discussion

Composition of precipitates

Table 1 presents the percentage composition of the collected precipitates after completion of batch experiments and RSSCTs. The precipitate from the Fe^{3+} addition in the secondary effluent (ferric phosphate precipitate) contained around 9.5 wt.% $P-PO_4^{3-}$. The precipitates from the RSSCTs by the addition of Ca^{2+} and Mg^{2+} (calcium phosphate precipitate and magnesium phosphate precipitate) were 17 wt.% and 6.4 wt.% $P-PO_4^{3-}$, respectively. More specifically, their phosphorus content was 95 mg P g^{-1} for the ferric phosphate precipitate, 170 mg P g^{-1} for the calcium phosphate precipitate and 64 mg P g^{-1} for the magnesium phosphate precipitate.

(Table 1 here)

These percentages are high enough for the precipitates to be considered as phosphorus recovery sources. It is important that the precipitates' phosphorus content is within the commercial fertilizers' range. The percentage phosphorus content, in available and commonly used fertilizers, ranges from 4-30% (The Fertilizer Institute, 1976). The Ca^{2+} and Mg^{2+} content in the ferric phosphate precipitate depends on the presence of these ions in the secondary effluent. The Fe^{3+} content in the precipitates from the regeneration solution is due to the slight abruption of the absorbent during the regeneration process.

Also, these solids were analyzed for organic compounds and their carbon content. The organic compounds found consisted of widely used products which are not toxic. The total carbon percentage was determined approximately at around 3% wt.% for Fe^{3+} solids and lower than 1% wt.% for the corresponding of Ca^{2+} and Mg^{2+} precipitates.

Characterization of the precipitates

X-Ray Diffraction (XRD) analysis and Thermogravimetry-Differential Thermal Analysis (TG-DTA) were carried out to characterize the produced solids. Fig. 1 demonstrates the XRD diagrams for the three phosphate precipitates.

(Figure 1 here)

The precipitates are amorphous as the peaks developed in the diagrams are quite board. The presence of phosphates in the precipitates was also confirmed, by the comparison of the diagrams with crystallographic standards from the data base of the Jade software.

Fig. 2 shows the TG-DTA diagrams for the ferric, calcium and magnesium phosphate precipitates.

(Figure 2 here)

The presence of H_2O is obvious in all precipitates and specifically the ferric phosphate precipitate has almost 8 wt.% and the calcium and magnesium phosphate precipitates only 3 wt.% moisture. As for the

ferric phosphate precipitate, the endothermic peak observed at ~260 ^{o}C indicates the transformation of lepidocrocite (γ-FeO(OH)) to maghemite (γ-Fe$_2$O$_3$). In temperatures higher than 350 ^{o}C mass loss is due to the presence of organic materials. At about 150 ºC there is a slight slope change in the TG-DTA curve of the calcium phosphate precipitate, indicating a different type of mass loss, which is because of strongly adsorbed water. A fast change is observed at about 600 ºC and the mass loss is linked to phosphate ions decomposition. In the TG-DTA curve of the magnesium phosphate precipitate, the endothermic modification observed at ~450 ^{o}C was attributed to the transformation of magnesium hydroxide (Mg(OH)$_2$) to magnesium oxide (MgO).

Phosphorus bioavailability

Reactions that reduce P availability in soils occur in all ranges of soil pH but can be very pronounced in alkaline soils (pH > 7.3) and in acidic soils (pH < 5.5). Maintaining soil pH between 6 and 7 will generally result in the most efficient use of phosphate (Busman et. al., 2002). The first soil sample had pH value 4.5 so it was acidic and the other was basic with pH 7.8. At these pH values, phosphorus availability could be moderate. The initial phosphorus content was 40 mg P kg$^{-1}_{soil}$ and 5 mg P kg$^{-1}_{soil}$ for the acidic and the basic soil sample, respectively.

Precipitate by addition of Fe^{3+}

Fig. 3 presents the soil's phosphorus content after the addition of the ferric phosphate precipitate versus incubation time.

(Figure 3 here)

The addition of the precipitate had no effect on the phosphorus content in the acidic soil. That happened due to the complexes that formed between the little amount of the diffused phosphates and the Fe^{3+} and Al^{3+} of the acidic soil. In the basic soil, the phosphorus content slightly increased and reached its

maximum value, approximately 7 mg P kg^{-1}$_{soil}$, at 15 days. The organic matter from the secondary effluent that co-precipitated might affect beneficially the phosphorus release.

Precipitate by addition of Ca^{2+}

Fig. 4 presents the soil's phosphorus content after the addition of the calcium phosphate precipitate versus incubation time.

(Figure 4 here)

Phosphorus availability became maximum in 5 days after precipitate addition and reached 75 mg P kg^{-1}$_{soil}$ for the acidic soil. The required time for the maximum availability is important, as the precipitate needs the same time as the widely used fertilizers (4-7 d) to release phosphorus. After this peak, the phosphorus content gradually decreased until reached the equilibrium value and became almost stable (approximately in 10 d). The maximum increment observed in phosphorus content was 35 mg P kg^{-1}$_{soil}$. Phosphorus – calcium complexes high solubility in low pH values was very helpful. Phosphorus diffusion to the basic soil followed the same pattern, but the maximum content value was different. Phosphorus content increased about 11 mg P kg^{-1}$_{soil}$, reaching its maximum value of 16 mg P kg^{-1}$_{soil}$. This lower availability in basic soil was expected as phosphate ions react by combining with Ca^{2+} present in basic soils and form compounds that are solids.

Precipitate by addition of Mg^{2+}

Fig. 5 presents the soil's phosphorus content after the addition of the magnesium phosphate precipitate versus incubation time.

(Figure 5 here)

The phosphorus content in soil after the addition of the magnesium phosphate precipitate varied in the same fashion as in the case of the calcium phosphate precipitate, having the maximum value in 5 d and

reaching equilibrium in 10 d. In acidic soil, the phosphorus content's increase was 13 mg P kg^{-1}_{soil} and in the basic soil 16 mg P kg^{-1}_{soil}. The higher content observed in basic soil compared to the calcium phosphate precipitate was due to the slight higher solubility of the phosphorus – magnesium complexes in alkaline pH range.

Conclusion

Conclusively, the precipitates produced by the treatment of the secondary effluent of "AINEIA", either through batch precipitation tests or RSSCTs, have significant amounts of phosphorus and they are potentially phosphorus recovery source. In addition, as the precipitates' phosphorus content is within the commercial fertilizer range, phosphorus bioavailability tests were conducted. Generally, the results of these tests revealed that phosphorus release from the calcium and magnesium phosphate precipitates to the soil was noteworthy and higher in acidic compared to basic soil, while phosphorus diffusion from the ferric phosphate precipitate occurred only in the basic soil and it was quite low. The next step is the evaluation of phosphorus bioavailability applying biological methods in field trials or greenhouse experiments. In this way, the estimation of the potential re-utilization of the precipitates as fertilizers would be overall and reliable.

References

APHA, AWWA, WEF (1992). Standard Methods for the Examination of Water and Wastewater. American Public Health Association

Busman, L., Lamb, J., Randall, G., Rehm, G. & Schmitt, M. (2002). The nature of phosphorus in soils. University of Minnesota: http://www.extension.umn.edu/agriculture/nutrient-management/phosphorus/the-nature-of-phosphorus/

Grant, C., Bittman, S., Montreal, M., Plenchette, C. & Morel, C. (2004). Soil and fertilizer phosphorus: Effects on plant P supply and mycorrhizal development. Canadian Journal of Plant Science, 85. 3-14

Morse, G., Brett, S. & Lester, G. (1998). Review: "Phosphorus removal and recovery technologies". The Science of the Total Environment, 212, 69-81

Prabhu, M. & Mutnuri, S. (2014). Cow urine as a potential source for struvite production. Int J Recycl Org Waste Agricult, 3(49), 1-12

Rengel, Z. (2008). Bioavailability of phosphorus and mikronutrients in the soil-plant-microbe continuum. In: 5th International Symposium ISMOM 2008, Chile, 24 – 28 November

Sims, G., T. (2000). Soil Test Phosphorus: Overview and Principles. In: G. M. Pierzynski, Ed., Methods for Phosphorus Analysis for Soils, Sediments, Residuals and Water, pp. 5-9. Kansas State University, Manhattan

The Fertilizer Institute (1976). The Fertilizer Handbook (2nd Ed.). Washington, DC.

Wang, J. Burken, J.G., Zhang, X. & Surampalli, S. (2005). Engineered struvite precipitation. Journal of Environmental Engineering, 131(10), 1433-1440

Table 1. Composition of the phosphate precipitates produced by batch tests and RSSCTs.

wt.% content	Ferric phosphate precipitate	Calcium phosphate precipitate	Magnesium phosphate precipitate
$P\text{-}PO_4^{3-}$	9.5	17.0	6.4
Fe^{3+}	28.5	4.1	0.7
Ca^{2+}	0.3	12.7	0.05
Mg^{2+}	0.4	0.9	24.0
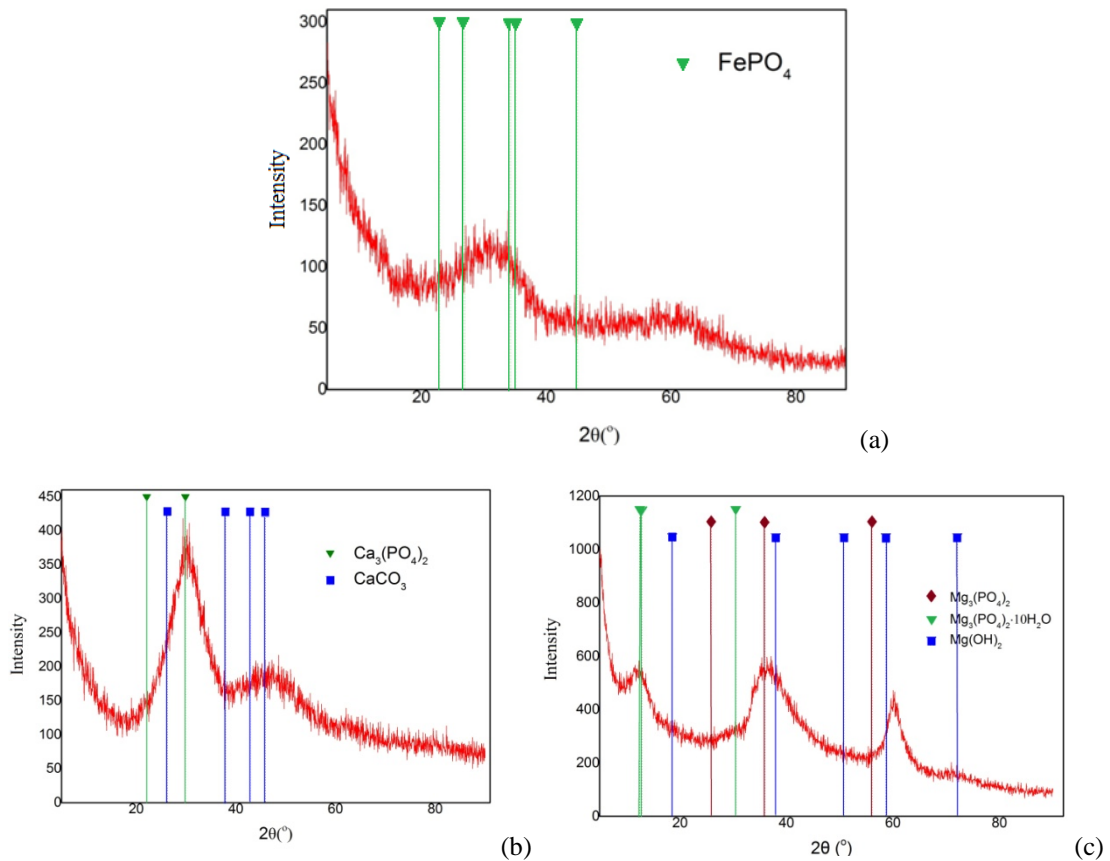
Figure 1. XRD diagrams of a. the ferric phosphate precipitate, b. the calcium phosphate precipitate and c. the magnesium phosphate precipitate.
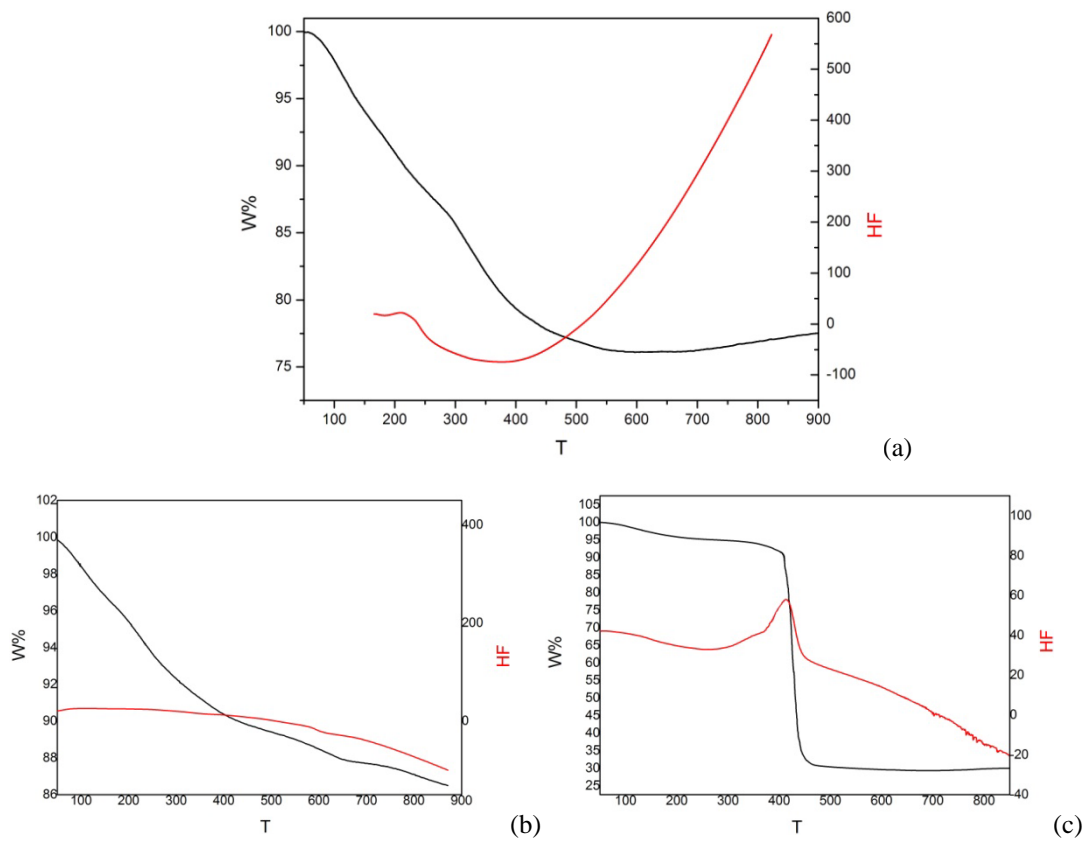
Figure 2. TG-DTA diagrams of a. the ferric phosphate precipitate, b. the calcium phosphate precipitate and c. the magnesium phosphate precipitate.
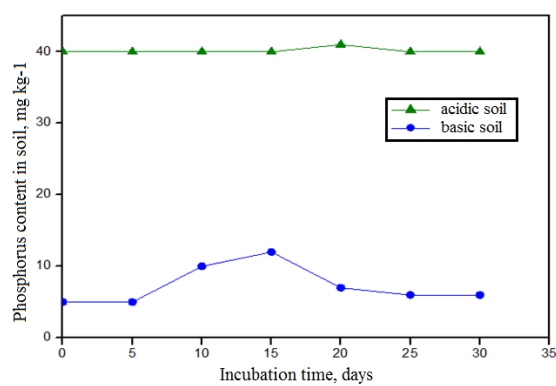

Figure 3. Phosphorus content variation in soil versus incubation time, after the addition of the ferric phosphate precipitate.
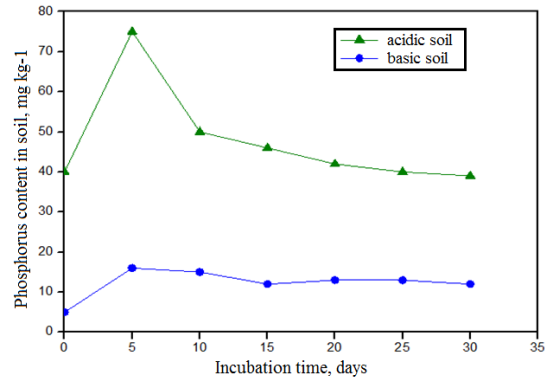
Figure 4. Phosphorus content variation in soil versus incubation time, after the addition of the calcium phosphate precipitate.
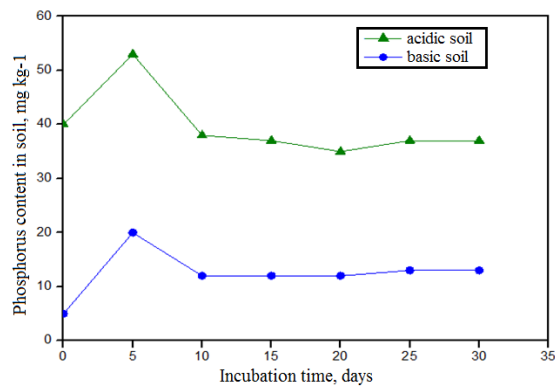

Figure 5. Phosphorus content variation in soil versus incubation time, after the addition of the magnesium phosphate precipitate.