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Comparative Evaluation of MgSO₄ and NaHCO₃ for Extracting Available Phosphorus from Calcareous Soils

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The effect of MgSO₄ and MgCl₂ on the release of available soil phosphorus was investigated and compared with the classical method of Olsen using NaHCO₃. The experiments were carried out on soil samples from Al- Hassa oasis, Saudi Arabia. The soil samples were shaken with 0.004, 0.008, 0.5 M MgSO₄, 0.5 M MgCl₂ and 0.5 M NaHCO₃. The results demonstrated that the amount of extractable phosphorus (P) by MgCl₂ was lower than those extracted by NaHCO₃ or MgSO₄. Nevertheless, MgCl₂ extracted P about 33% to 81% of that extracted by NaHCO₃ and MgSO₄ respectively. The application of different levels of P fertilizer did not significantly affect MgSO₄ solution extractability. The correlation coefficients were 0.823, 0.908, and 0.879 for soil treated with 71.4, 142.9, 214.3 kg P₂O₅/h respectively. The original pH of MgSO₄ solutions was 6.7 however, the pH of soil-MgSO₄ suspensions slightly decreased with the increasing MgSO₄ concentrations. On the other hand, the pH of soil suspension in 0.5 M MgSO₄ increased with time, without shaking, reaching 7.6 within 24 h of incubation and then became stable. The same result was achieved when the soil suspension was shaken for 20 minutes. The pH of other MgSO₄ concentrations became stable at 7.6 within 24 h. The amount of extractable P in the presence of MgSO₄ increased with the increasing reaction time. The correlation coefficients between extracted phosphorus with 0.5 M NaHCO₃ and that of extracted with 0.5 M MgSO₄ after shaking for 20 and 30 minutes were 0.938 and 0.892 respectively. Accordingly, a 0.5 M MgSO₄ solution can be efficiently used for extracting available phosphorus from calcareous soils, and without adjusting its pH. Moreover, its use will avoid the limitation of evolution of CO₂ from NaHCO₃ - basic extraction solution upon treatment with acidic molybdate for the determination of phosphorus.

Keywords: MgSO₄, MgCl₂, NaHCO₃, phosphorus, calcareous soil.

INTRODUCTION

Phosphorus (P) is an essential element for the growth of plants and is often applied to crops to increase its yield. The increasing utilization of this element in agriculture has increased the demand to develop efficient methods of extraction followed by analysis in soils, water and residual materials for environmentally relevant forms of P. As a result, many local variations of extractants and laboratory procedures have been designed enabling timely analysis and an improved correlation of soil test results with plant responses within well-defined regions.

Calcium phosphate minerals play an important role in controlling P stability and activity in the P-fertilized soils and P-rich wastewater (Valsami-Jones, 2001 and Hu et al., 2005). The most stable Ca phosphate mineral is hydroxyapatite (Ca₅(PO₄)₃OH; HAP), but other Ca

phosphates reported in the environment include octacalcium phosphate (Ca₄H(PO₄)₃ · 2.5H₂O; OCP), dicalcium phosphate dihydrate (CaHPO₄ · 2H₂O; DCPD), and amorphous Ca phosphate (Ca₃(PO₄)₂ · nH₂O; ACP) (Valsami-Jones, 2001). Formation of more soluble Ca phosphates can be favored kinetically over more stable phases because of faster nucleation (Cao and Harris, 2008). Cao and Harris (2008) studied the effect of CO₃²⁻ and Mg²⁺ on Ca phosphate precipitation under the effect of dairy manure-amended soil leachate having pH 7.1 (system I) and P recovery from flushed dairy manure wastewater having pH 9.2 (system II). They showed that the precipitation of Ca phosphates, an important process in controlling P stability and activity in P-fertilized soils and P-rich wastewater, is often affected by other

Components.

Soil testing for P has been formally conducted in the late 1940s and lately has become a well-established practice. The fundamental goal of soil P testing has always been to determine the "optimum" soil test for P concentration required for the plant growth. The need for additional fertilization for economical return on investment in fertilizer P, could then be predicted. The main objectives of soil P testing are: (i) to "index" the P supplying capacity of soils, thus estimating the time required before fertilization; (ii) most recently, to identify when soils have excess of P, contributing to non point source of surface water pollution. Bary (1948) proposed that an acceptable agronomic soil P test should have the following characteristics: First, soil test should extract all or a proportionate amount of the plant-available P from soils with differing chemical and mineralogical properties. Secondly, it should be accurate and rapid. Thirdly, extracted P by soil test should be well correlated with plant P concentration, plant growth, and the response of plant to added P in fertilizers. Fourthly, it should accurately detect differences in soil P concentrations provided by previous fertilization.

Several reviews address the principles and practices involved in soil testing for P (Sibbesen and Sharpley, 1997; Sims, 1993; Sims, 1997; Sims, 1998 and Sims et al., 2000). Detailed descriptions of the laboratory methods and analytical procedures used to determine P by these methods are provided in other references (Carter, 1993; Frank, et al., 1998; Kuo, 1996; SERA-IEG-6, 1992; Sims and Wolf, 1995 and SPAC, 1992).

Many chemical solutions have been proposed to extract potential forms of P in soils. Bray and Kurtz (1945) suggested a combination of HCl and NH₄F to remove easily acid soluble P forms, largely Al- and Fe-phosphates. McGeorge et al. (1953) stated that the solvent action of CO₂ on phosphorus in calcareous soils was mainly a function of the reaction and that the H⁺ ion activity must be sufficient to overcome ion effect of Ca²⁺ ion in precipitating calcium phosphate. Thus, two reactions with opposite effects on phosphate solubility occur when CO₂ is bubbled through calcareous soil: an increase in solubility caused by a decrease in pH and a decrease in solubility when precipitation of calcium phosphate occurs as a result of the increase in Ca²⁺ activity.

Mehlich (1953) introduced a combination of HCl and H₂SO₄ acids to extract P from the soils of the north-central region of the U.S. Sulfate ions in this acid solution can dissolve Al- and Fe-phosphates in addition to P adsorbed on colloidal surface in the soil. In the early 1980s, Mehlich modified his initial soil test and developed a multi-element extractant which is suitable for removing P and other elements in acid and neutral soils. The modified extractant (Mehlich, 1984) is a combination of acids (acetic (HOAc) and nitric (HNO₃), salts (ammonium fluoride (NH₄F) and ammonium nitrate (NH₄NO₃), and the

chelating agent thylenediaminetetraacetic acid (EDTA).

Olsen et al. (1954) introduced 0.5 M sodium bicarbonate (NaHCO₃) solution at a pH of 8.5 to extract P from calcareous, alkaline, and neutral soils. This extractant decreases calcium in solution (through precipitation of calcium carbonate), and this decrease enhances the dissolution of Ca-phosphates. Moreover, this extracting solution removes dissolved and adsorbed P on calcium carbonate and Fe-oxide surfaces. In addition, they demonstrated that the NaHCO₃ soil test was a good measure of plant-available P. They observed and reported few precautions for extracting soil with NaHCO₃. If the flask containing the aliquot was shaken too vigorously after the addition of the acidified molybdate reagent, some of the solution may be lost because of the rapid evolution of CO₂. Also, failure to follow this precaution with respect to the acidified SnCl₂ or ascorbic acid reducing agents will give erratic results.

An anion exchange resin (Sharpley, 2000) and Fe-oxide impregnated paper (Chardon, 2000) were used in a water matrix as a P-sink to determine available P in a wide range of soils.

Soil-P exists in both organic and inorganic forms. Each form consists of a continuum of many P compounds, existing in equilibrium with each other and ranging from soluble P to very stable or unavailable compounds. A wide variety of methods exists for the extraction of P however, differences in practices may give rise to varying results.

The main objective of this paper is to evaluate the effect of MgSO₄ extractant on the release of available P in comparison with NaHCO₃ and MgCl₂.

MATERIALS AND METHODS

This study was conducted on surface soil samples collected from farms in Al-Hassa Oasis. Soil samples were collected, air dried, crushed using a wooden roller and sieved using minimum agitation through a 2 mm stainless steel sieve and stored in plastic bags. The routine analysis of soil was done according to Cottenie (1980). The total calcium carbonate content of the soil samples were determined according to Nelson(1982). Phosphorus of all soils was spectrophotometrically determined using the phosphomolybdate method (Murphy and Riley, 1962) after extraction with different extractants.

Namely, four extractants, 0.5 M NaHCO₃ (pH 8.5), 0.0042 M MgSO₄, 0.0084 M MgSO₄ and 0.5 M MgSO₄ were used to extract the available P from soil samples (ratio of soil sample to extractant was 1:20). The soil suspension was shaken for 30 min, centrifuged and the supernatant was collected and filtered off and its P-content was determined spectrophotometrically.

To study the effect of shaking time on the release of P from soil under the effect of 0.5 M MgSO₄, 6 soil samples

Table 1. Phosphorus extraction from fertilized calcareous soil with NaHCO₃, MgSO₄ and MgCl₂

Soil Treatment		Amount of extracted P (ppm)		
P ₂ O ₅ /	N/	NaHCO ₃	MgSO ₄	MgCl ₂
Kg acre ⁻¹	Kg acre ⁻¹	0.5M	0.5 M	0.5M
71	71	11.24	11.81	4.76
	142	12.32	15.18	5.30
	214	16.50	16.44	5.65
	284	18.59	17.78	8.00
Average		14.66	15.30	5.93
142	71	12.97	12.89	7.53
	142	14.20	14.67	8.47
	214	14.50	14.94	9.03
	284	17.50	16.00	11.76
Average		14.79	14.63	9.20
214	71	16.43	16.00	5.65
	142	18.40	18.40	6.12
	214	19.50	18.67	6.65
	284	19.89	20.44	7.06
Average		18.56	18.38	6.37

representing different calcareous soils, differing in their calcium carbonate content were collected from different locations in Al Hassa oasis. The soil samples were shaken with 0.5 M MgSO₄ for 5, 10, 20, and 60 minutes (the ratio of soil to extractant solution was 1:20). The P-content in the supernatants was determined following the recommended procedure of Murphy and Riley, 1962.

To compare MgCl₂, MgSO₄ and NaHCO₃ as extracting solutions for P from the soils, 12 soil samples were obtained from field plots that received 71, 142 and 214 kg P₂O₅/acre and 71, 142, 214 and 284 kg N as urea/acre a year before sampling. Super phosphate was thoroughly mixed with the soil. The soil was cultivated with wheat crop. Available P was extracted after half an hour shaking and the supernatant was collected for analysis. The pH of soil suspension in 0.0042 M, 0.0084 M and 0.5 M MgSO₄ with time with and without shaking was determined to study the effect of MgSO₄ on the pH of the calcareous soil.

RESULTS AND DISCUSSION

Phosphorus extraction with NaHCO₃, MgSO₄ and MgCl₂

Data on using 0.5 M NaHCO₃, 0.5 M MgSO₄ and 0.5 M MgCl₂ as extracting solutions for P are shown in Table 1.

The results showed that the average amount of extractable P by NaHCO₃ or MgSO₄ was about three times greater than that by MgCl₂ irrespective of the method of soil treatment. The data demonstrated a high

positive correlation ($r = 0.883$) between the % extraction by NaHCO₃ and MgSO₄.

The application of different levels of P fertilizer on soil did not affect significantly the ability of MgSO₄ to extract phosphorus (Table 1). The correlation coefficients were 0.823, 0.908 and 0.879 for soil treated with 71, 142 and 214 kg P₂O₅ acre⁻¹ respectively. The regression equations between extracted P by NaHCO₃ and MgSO₄ from soils treated with different phosphate fertilizer rates are presented (Table 2). The data reflects that the MgSO₄ solution is an excellent extractant for the available P relative to MgCl₂.

The effect of MgSO₄ concentration on extractable P and soil pH

Different concentrations of MgSO₄ were used to study their effects on the pH of the soil suspension with time and to determine the amount of released P.

The results in Table 3 show that the pH of MgSO₄ extraction solutions of different concentrations is 6.9. The pH of soil-MgSO₄ suspensions decreased with the increase of MgSO₄ concentration. The pH of soil suspension in 0.5 M MgSO₄ increased from 7.5 after 5 minutes to 7.6 after 10 minutes and then got stabilized through the 24 hrs of incubation or after 20 minutes of shaking. At 0.0083 M MgSO₄-soil suspension, the pH was 7.6 after 5 min and increased to 7.8 with time and then it dropped to 7.6 after one hour and remained stable for 24 hours. At 0.043 M MgSO₄ –soil suspension, the pH was 7.8 after 5 minutes and increased to 8.0 within an

Table 2. Regression equations of the extracted P by NaHCO₃ and MgSO₄ from calcareous soil using different rates of phosphate fertilizer.

Treatment Soil	Regression equations	Determination coefficient
Without fertilizer	$^{\$}Y = 4.160 + 0.746 X$	0.883 ^{**}
Treated with 71 kg P ₂ O ₅	$Y = 0.411 + 0.968 X$	0.823 ^{**}
Treated with 142 kg P ₂ O ₅	$Y = 5.599 + 0.610 X$	0.903 ^{**}
Treated with 214 kg P ₂ O ₅	$Y = 6.644 + 0.591 X$	0.879 ^{**}

^{**} : indicated the highly significant effect at 0.01 level. ^{\$}Y = NaHCO₃-P and X = MgSO₄-P

Table 3. The impact of incubation time and shaking at 20 minutes on the pH of soil suspension with of 0.0043 M, 0.0083 and 0.5 M MgSO₄ extraction solution.

Shaking	Time (minutes)	pH of MgSO ₄ and calcareous soil suspension in		
		0.0043M MgSO ₄	0.0083M MgSO ₄	0.5M MgSO ₄
Without shaking	5	7.8	7.6	7.5
	10	7.9	7.7	7.6
	15	8.0	7.8	7.6
	20	8.0	7.8	7.6
	30	8.0	7.8	7.6
	60	8.0	7.8	7.6
	1440	7.6	7.6	7.6
With shaking	20	7.6	7.6	7.6
Extraction solution		6.9	6.9	6.9

hour, then it was dropped to 7.6 and remained stable for 24 hours.

The above results show that the pH of MgSO₄ – soil suspension tends to rise at the onset of the reaction due to the release of Ca²⁺ and CO₃²⁻ from calcareous soils. The formation of HCO₃⁻ ion upon the dissolution of atmospheric CO₂ caused a further rise of pH in dilute MgSO₄ solutions but this was not effective at 0.5 M MgSO₄. After 24 hours, all MgSO₄ – soil suspensions reached to equilibrium at pH of 7.6. This value was also achieved by shaking the suspensions for 20 minutes (Table 3). Kuo and Mikkelsen (1979) reported that the pH of CaCO₃ phosphate suspension was about 7.8 and no change of pH was observed by adding MgSO₄. Accordingly, it is concluded that shaking soil suspension in MgSO₄ would not influence pH changes in the system.

Extractable-P with different MgSO₄ concentrations from calcareous soil treated with P fertilizer

Different MgSO₄ concentrations (0.0043, 0.0083, and 0.5 M MgSO₄) were tested against 0.5 M NaHCO₃ for extracting phosphorus from calcareous soil that was previously treated with different levels of P fertilizer as superphosphate and irrigated with different Mg concentrations as MgSO₄ in irrigation water for 4 wet and

dry cycles. The amount of extracted – P increased by increasing MgSO₄ concentration (Table 4). A highly positive correlation was found between the extracted phosphorus with different concentrations of MgSO₄ and that extracted with 0.5 M NaHCO₃. The correlation coefficients of 0.784, 0.832 and 0.928 were found for the 0.0043 M, 0.0083 M and 0.5 M MgSO₄ solutions, respectively.

The amount of extracted phosphorus with 0.5 M MgSO₄ was almost equal to that extracted with 0.5 M NaHCO₃. There are no significant differences between the two solutions with T-test (0.284). The MgSO₄ solution released Ca²⁺, CO₃²⁻ and PO₄³⁻ ions from the calcareous soil. Then the Mg²⁺ ions would be either adsorbed on soil constituents or formed ion-pairs with CO₃²⁻ or PO₄³⁻ ions. On the other hand the SO₄²⁻ ions would form ion-pairs with Ca²⁺ ions. As a result, the phosphate precipitation as calcium phosphate is reduced. Finally, more available phosphate would be extracted in the form of magnesium phosphate.

Effect of reaction time on the P extraction with 0.5 M MgSO₄

Effect of reaction time on the release of P with 0.5 M MgSO₄ from calcareous soils of varying carbonate

Table 4. Phosphorus extraction with 0.0043 M, 0.0083, 0.5 M MgSO₄ and 0.5 M NaHCO₃ from a calcareous soil.

Soil treatments		Amount of extracted P (ppm)			
P ₂ O ₅ (kg/acre)	MgSO ₄ (Mg/L)	0.0042M MgSO ₄ (Y ₁)	0.0083 M MgSO ₄ (Y ₂)	0.5 M MgSO ₄ (Y ₃)	0.5 M NaHCO ₃ (X)
10	0	0.58	0.60	5.75	5.25
	50	0.58	0.67	6.63	6.50
	100	0.60	0.77	7.38	7.00
	150	0.63	0.77	8.00	8.25
	200	0.63	0.93	13.50	11.75
15	0	0.60	0.88	8.25	7.25
	50	0.70	0.93	9.00	8.00
	100	0.70	0.93	9.88	8.50
	150	0.88	1.07	10.70	9.25
	200	0.88	1.43	12.00	12.00
30	0	0.77	0.98	12.25	13.25
	50	0.93	1.17	13.50	13.50
	100	0.93	1.17	13.50	14.10
	150	1.00	1.17	14.75	14.50
	200	1.03	1.33	20.00	15.00
		Y ₁ = 3.35 + 7.82 X	(r = 0.784 ^{**})		
		Y ₂ = -1.14 + 11.57 X	(r = 0.832 ^{**})		
		Y ₃ = 1.33 + 0.81 X	(r = 0.928 ^{**})		

Table 5. The total carbonate and the available P extracted with 0.5 M NaHCO₃ or with 0.5 M MgSO₄ after different reaction times from different calcareous soils.

Soil Number	CaCO ₃ %	Available P (ppm)				
		0.5 M NaHCO ₃ (Y)	10 min. (X ₁)	20 min. (X ₂)	30 min. (X ₃)	60 min. (X ₄)
1	8.26	1.63	1.20	2.10	3.20	3.20
2	13.30	4.02	2.40	4.30	4.80	5.80
3	14.0	5.40	3.30	5.25	5.50	6.00
4	17.81	3.89	1.40	3.40	4.00	4.20
5	16.60	4.40	3.00	4.00	4.60	6.00
6	22.50	5.53	2.80	4.50	6.80	7.10

Regression equations for X₁ to X₄ with Y and correlation coefficient (r) were:

$$Y = -0.732 + 1.002X_1 \quad (r = 0.835^{***})$$

$$Y = 0.947 + 1.036X_2 \quad (r = 0.938^{***})$$

$$Y = -0.665 + 1.225X_3 \quad (r = 0.892^{***})$$

$$Y = -0.703 + 0.960X_4 \quad (r = 0.904^{**})$$

contents is reported in Table 5. Six soil samples were analyzed in this study. The results (Figure 1) show that extractable P in MgSO₄ was increased with increasing reaction time. These increments suggest that the equilibrium was not reached in any of the samples for over one-hour extraction period. The curves however tended to level off after 30 minutes for the soil of low

initial phosphorus. The initial content of P did not affect the extractable P (Table 5).

The results indicated that the CaCO₃ content did not affect the extraction time of available P in spite that the magnitudes of extractable P were highly different. The correlation coefficients between extracted phosphorus with 0.5 M NaHCO₃ and 0.5 M MgSO₄ after shaking for

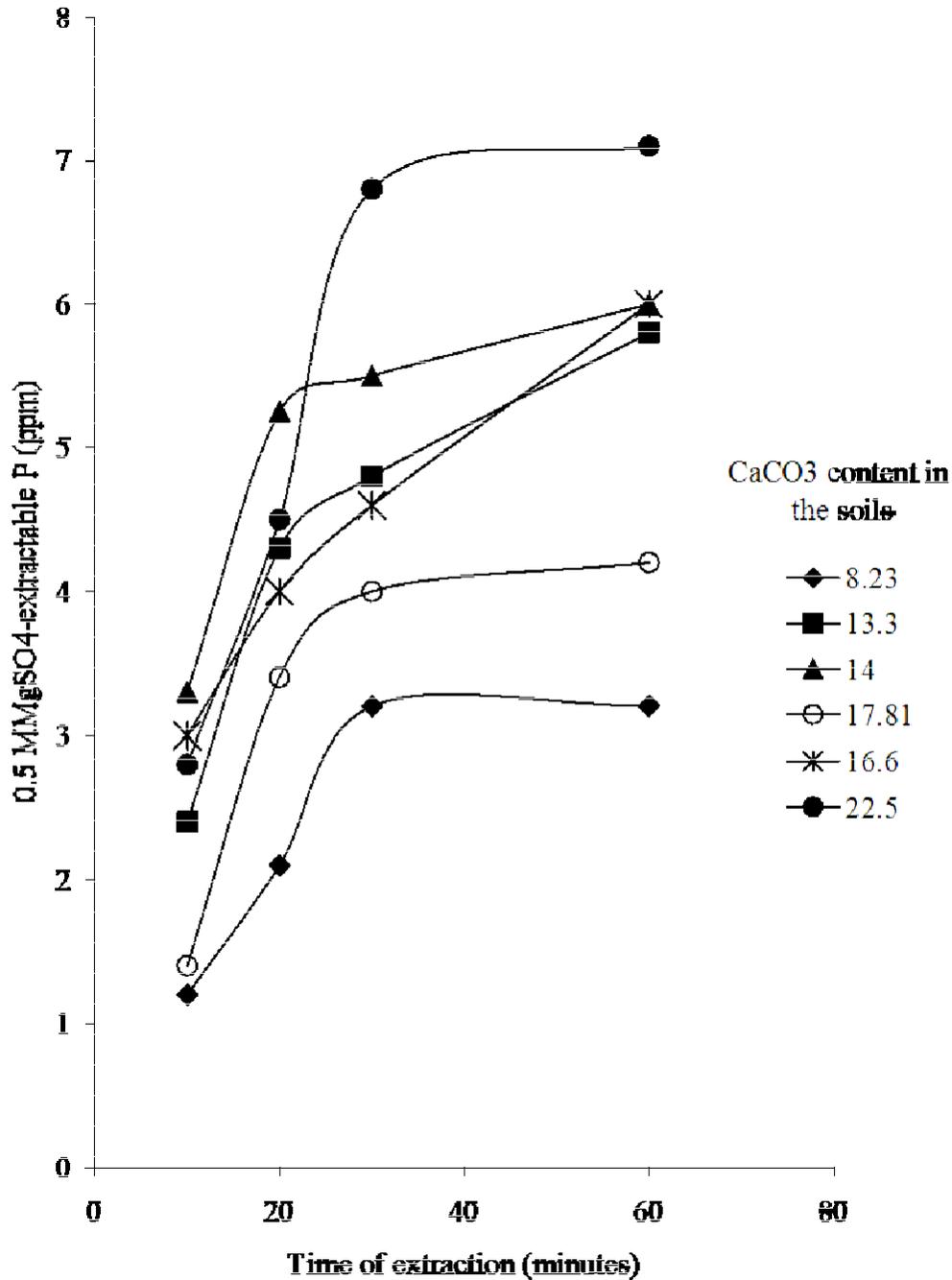


Figure 1. Effect of extraction time with 0.5 M MgSO₄ on the extracted phosphorus from several calcareous soil

20 and 30 minutes with 0.5 M MgSO₄ were 0.938 and 0.892 respectively. This means that the amount of extracted phosphorus after shaking for 20 and 30 minutes were almost equal to that extracted with the 0.5 M NaHCO₃ method. Therefore, shaking samples for 20 minutes in 0.5 M MgSO₄ solution can be used to extract available phosphorus from calcareous soils.

It appears from the above results that MgSO₄ solution can be used to extract available P from calcareous soils.

The MgSO₄ reacts with CO₂ to form MgCO₃ so that the CO₂ effect on the solubility of calcium carbonate can be reduced. Calcium ion might be released, but Ca²⁺ - SO₄²⁻ ion pairs and gypsum could be formed, leaving less or no Ca²⁺ to precipitate in phosphate forms. The bonding energy of phosphate with Mg²⁺ is less than with Ca²⁺ on carbonates and amorphous materials; therefore, PO₄³⁻ is more subjected to extraction. Boulton et al. (1962) in their study on the effect of Mg on the formation of calcium

phosphate precipitates noted the formation of dicalcium phosphate. The increase in Mg tended to cause a slight increase in induction time and decrease in the amount of P precipitate. These effects could be accounted for by the fact that the chelation of Mg^{2+} tended to increase the Ca^{2+} and decrease the pH of the supernatant solution without significantly affecting its phosphate content. The studies done by Zaki (1989) and Kamh (1989) showed that soluble P increases with the increase of the incubation time in the presence of Mg^{2+} due to an inhibition of phosphate adsorption on the surface of pure carbonate and calcareous soil constituents.

CONCLUSION

As a result of this study, it can be concluded that, $MgSO_4$ can be used to extract available P from highly calcareous soil without the need to adjust the pH. Also, the evolution of CO_2 with the addition of the molybdate solution is avoided by the use of $MgSO_4$ instead of the $NaHCO_3$. This means that the expected loss of part of the aliquot before the P-complex colour is developed can be avoided and also prevents the errors due to the instability of the pH of $NaHCO_3$ solution (Olsen et al., 1954).

The correlation of $MgSO_4$ -P with both P-uptake and P-application has to be further investigated. Such study would confirm the reaction time that required for different calcareous soils and after different phosphate fertilization levels.

Also, shaking samples for 20 minutes in 0.5 M $MgSO_4$ solution is sufficient for maximum extraction of available phosphorus from calcareous soils. Furthermore, $MgSO_4$ solution can be used without adjusting its pH. In addition, its use will avoid the evolution of CO_2 from $NaHCO_3$ extractant solution when molybdate solution was added.

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