

# Release of Phosphorus from Laboratory Made Coated Phosphatic Fertilizers in Soil Under Different Temperature and Moisture Regimes

Abhijit Sarkar<sup>1</sup> · D. R. Biswas<sup>1</sup> · S. C. Datta<sup>1</sup> · K. M. Manjaiah<sup>1</sup> · Trisha Roy<sup>1</sup>

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**Abstract** The aim of the present study was to see the release pattern of phosphorus from laboratory made coated phosphatic fertilizers in soil under different temperature and moisture regimes. Four fertilizer materials were prepared by reacting ammonia with phosphoric acid (Product-A and Product-B) and rock phosphate with sulphuric and phosphoric acid (Product-C and Product-D). These materials were coated with polyvinyl alcohol, liquid paraffin and methyl oleate at two levels (2 and 3 %). The coated phosphatic fertilizers along with diammonium phosphate were applied @ 500 mg P kg<sup>-1</sup> soil and incubated at two temperatures (20 and 30 °C) and two moisture regimes (10 and 20). Results indicated that release of P showed a decline trend from first to fourth hour of incubation, then increased and finally reached to a steady state in all the products, except Product-C. The release pattern followed the order: diammonium phosphate > Product-B > Product-A > Product-D > Product-C, corresponding with the mean values of 337.4, 227.9, 211.6, 147.1 and 69.0 mg P kg<sup>-1</sup> soil, respectively. Results also showed the superiority of polyvinyl alcohol coated products over liquid paraffin and methyl oleate coated products. The rate of release of P was greater with increase in temperature from 20 to 30 °C. Thus, it may be concluded that laboratory made coated fertilizers could be used as a source of P which would release P slowly than the water soluble P like diammonium phosphate and supply P for a longer period that synchronizes the crop demand and enhances P use efficiency.

**Keywords** Phosphorus · Coated fertilizer products · Release pattern · Olsen reagent · Temperature and moisture regime

## Introduction

Phosphorus (P) plays several important physiological and biochemical functions in crop plants, animal and microorganisms in relation to nucleic acid, phospholipids, adenosine tri-phosphate (ATP) and adenosine di-phosphate (ADP) molecules and intermediate compounds of respiration and photosynthesis. Phosphorus nutrition is a global issue and a secured supply of P would be an important management for global food security. It is the 11th most abundant element in the earth's crust. At the same time it is also the least mobile element among the major plant nutrients and is unavailable under most of the soil conditions. The available P is low to medium in soils of most states in India [1]. Thus, application of phosphatic fertilizers is very much essential for sustaining crop production and maintaining the soil fertility.

At present diammonium phosphate (DAP) is the most common P-fertilizer used by farmers in India. However, the cost of DAP has increased tremendously in recent past because of the import of raw materials like rock phosphate (RP) and sulphur, required for commercial manufacturing of DAP, from other countries as there are no deposits of high-grade RP (>30 % P<sub>2</sub>O<sub>5</sub>) in India. According to available data, the recoverable global phosphate reserves of all types and grades are estimated to be 60,000 million tonnes (Mt) which are reported to be exhausted in the next 70–175 years [2]. While, total phosphate resource in India is estimated to be 260 Mt, a greater part of which is of low-grade (<20 % P<sub>2</sub>O<sub>5</sub>), and the recoverable phosphate

✉ D. R. Biswas  
drb\_ssac@yahoo.com

<sup>1</sup> Division of Soil Science and Agricultural Chemistry, Indian Agricultural Research Institute, New Delhi 110 012, India

reserves are of the order of 142 Mt [3]. Although direct use of low-grade RP performs reasonably well in acid soil, their use in neutral to alkaline soil is very poor. At the same time they are unsuitable for manufacturing commercial P-fertilizers because of their low P content [4]. The major part of P present in RP is in water insoluble form, which restricts its direct use as P source for crop production. Attempts have been made to improve the efficiencies of these materials by partial acidulation with minimum amount of either sulphuric ( $\text{H}_2\text{SO}_4$ ) or phosphoric acid ( $\text{H}_3\text{PO}_4$ ) [5, 6], dry compaction with water soluble P (WSP)-fertilizers [7] and composting technology [4, 8]. Acidulation is one of the common methods to convert water insoluble P in RP to WSP and citrate soluble P (CSP) which are considered to be the plant available form of P. But, under-utilization of the applied P sources as indicated by their very low use efficiency is a major concern both in terms of economics of the farmers as well as the limited phosphate reserve of the world. In general, P is found to be deficient in acid and calcareous soils due to the presence of high concentration of iron (Fe) or aluminium (Al) and calcium (Ca), respectively. Even in western countries where food and fiber production relies heavily on the application of non-renewable P-fertilizers, much of this fertilizer is gradually rendered unavailable to plants over time as it reacts with soil constituents [9].

Use of slow release fertilizers (SRF) or controlled release fertilizers (CRF) is a new trend to save fertilizer consumption and minimize environmental pollution [10, 11]. The hypothesis is that SRF or CRF would release their content of nutrients gradually and if possible coincide with the nutrient requirements of the plant. These fertilizers are prepared by coating the active soluble component with a membrane that serves as a diffusion barrier. The use of controlled release P-fertilizers appears to have potential for improvement of P use efficiency and crop production because of their release patterns that coincides the crop demand [12, 13]. There are many reports of the use of slow release nitrogenous (N) fertilizers. However, limited information is available on the preparation and use of slow release coated P-fertilizer which could limit the contact of applied fertilizer P with soil, possibly reducing its precipitation and/or adsorption on clay colloids, and increasing its availability to plants. Keeping the above points in view, the present study was undertaken (1) to develop some novel P-fertilizer product by reacting ammonia with  $\text{H}_3\text{PO}_4$  (Product-A and Product-B) and RP with  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  (Product-C and Product-D) and subsequently coating them with three coating agents namely, polyvinyl alcohol (PVA), liquid paraffin (LP) and methyl oleate (MO); and (2) to see the release pattern of P from these materials through an incubation study at varying temperature and moisture regimes in an inceptisol.

## Material and Methods

### Development of Novel Coated P-Fertilizers

For the development of novel coated P-fertilizers, four novel P-fertilizer products were prepared by reacting ammonia with  $\text{H}_3\text{PO}_4$  at 2:1 and 1:1 ratio (Product-A and Product-B, respectively) and RP with  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  (Product-C and Product-D, respectively). The low-grade RP was obtained from Rajasthan State Mines and Minerals Limited, Udaipur, Rajasthan. Ground RP (100 mesh sieve) contained 17.5 % total  $\text{P}_2\text{O}_5$ , 6.5 % total Ca, 5.6 % total Mg and 1000, 665, 21.7 and 41.7  $\text{mg kg}^{-1}$  of total Fe, Mn, Cu and Zn, respectively. All the products were prepared in a special glass vessel in the laboratory. During the time of reaction, the reactants were constantly stirred to prevent formation of large aggregates and to allow the acid to come in contact with the unreacted particles of RP, thereby make them homogeneous. The materials were then allowed to cool at room temperature for half an hour to complete the reaction, spread over a plastic tray and air-dried for 1 week. On the basis of physical characteristics of coating agents, the materials were then coated with three coating agents namely, PVA, LP and MO at two levels of coating i.e. 2 and 3 % (w/w) in a closed chamber of corning glass bottle with sprayer-atomizer to minimize the disturbance of flowing air during the process in order to get uniform coating. PVA contains hydrophilic ( $-\text{OH}$ ) groups on surface that helps to absorb water to form a water hull, and LP has hydrophobic surface functional groups, which completely repel water molecules and prevent to form primary- and secondary-orthophosphates. Thus, these coatings render the diffusion of P from fertilizer materials, whereas, MO is an inherently volatile compound, which volatilize spontaneously and helps to release P from the coated products in a self oriented manner.

### Characterization of Novel Coated P-Fertilizers

The novel coated P-fertilizer materials were characterized to see their chemical composition. Free acidity ( $\text{pH}_{\text{w}}$ ) of the products was determined by a pH meter using fertilizer material: water ratio of 1:2.5. Total P (TP) content in the fertilizer was determined by digesting the sample (1.0 g) with nitric (25 mL) and perchloric acid (20 mL) followed by estimation of P in the acid digest by spectrophotometrically after developing vanadomolybdo phosphate yellow colour. For determination of WSP, fertilizer material (1.0 g) was placed on a cone of filter paper and leached with distilled water followed by estimation of P content in the leachate spectrophotometrically after developing vanadomolybdo phosphate yellow colour. The residue left after removing the WSP is then transferred into 250 mL

conical flask and digested with neutral normal ammonium citrate solution on a water bath at  $70 \pm 1$  °C for 1 h. The CSP was then removed by filtration through a Buckner funnel. The residue left, representing the citrate insoluble P (CISP), was then digested as in case of TP. The CSP was then calculated by subtracting the sum of WSP and CISP from that of TP as under:

$$\text{CSP} = \text{TP} - (\text{WSP} + \text{CISP})$$

Total N was determined by micro-Kjeldahl method.

Fourier transform infrared spectroscopy (FTIR) was performed for identification and characterization of functional groups present in the novel modified products. For this, powdered sample was used for carrying out the analysis using Bruker: ALPHA, FTIR/ATR system (24 scans, resolution  $4 \text{ cm}^{-1}$ ). Laboratory made products were scanned in the region of  $4000\text{--}400 \text{ cm}^{-1}$  using KBr pellets.

### Analyses of Soil

The bulk soil sample was collected from Songaon village in Haryana (Typic Haplustept). It represents Inceptisol. The soil was air-dried under shade, ground and passed through 2-mm sieve and used for incubation study. The soil sample was analyzed for its initial physicochemical properties as per the standard procedure. Mechanical composition of the experimental soil i.e. proportion of sand, silt and clay size particles were determined by hydrometer method [14]. The pH of soil was determined in 1:2.5 (soil:water) suspension by a digital pH meter as outlined by Jackson [15]. The electrical conductivity (EC) was determined in the supernatant liquid of the same extract with the help of conductivity meter as given by Richards [16]. The cation exchange capacity (CEC) of the soil was determined by ammonium acetate method as described by Jackson [15]. Organic carbon (OC) content in soil was determined by wet oxidation method as outlined by Walkley and Black [17]. Mineral nitrogen ( $\text{NH}_4^+ + \text{NO}_3^-$ -N) in the soil was determined by extracting the sample with 2 M KCl using soil: extractant ratio of 1:10 as per the method described by Keeney and Nelson [18]. For estimation of available P, soil was extracted with 0.5 M  $\text{NaHCO}_3$  [19] and the P content in the extract was determined by ascorbic acid blue colour method [20]. Available K was determined by extracting the soil with 1 N ammonium acetate (pH 7.0) and K content in the extract was measured by a flame photometer [21]. The texture of soil was sandy loam having sand, silt and clay content of 82.4, 15.3 and 12.3 %, respectively. The initial soil had pH 7.11, EC  $0.27 \text{ dS m}^{-1}$ , CEC  $9.46 \text{ cmol (p}^+) \text{ kg}^{-1}$  soil, OC  $2.5 \text{ g kg}^{-1}$ , mineral N  $61.6 \text{ mg kg}^{-1}$ , Olsen P  $4.31 \text{ mg kg}^{-1}$  and  $\text{NH}_4\text{OAc-K}$   $31.9 \text{ mg kg}^{-1}$  soil.

### Incubation Study

An incubation experiment was carried out to see the release pattern of P from the novel coated products of P-fertilizers in soil under laboratory condition at different temperature and moisture regimes. About 10 g soil sample was taken in each plastic bottle having 250 mL capacity with screw cap. All the coated fertilizer materials including one DAP were applied at the rate of  $500 \text{ mg P kg}^{-1}$  soil. The required quantities of P from respective sources were thoroughly mixed with the soil (10 g). In one set, all the samples were maintained at 10 % moisture regime (w/w) by adding distilled water, while in other set, the moisture level was maintained at 20 % (w/w) in order to see P release pattern in soil under field capacity condition. It was assumed that the lower limit of field capacity is 10 % (v/v) and the highest limit of field capacity is 20 % (v/v) which represent the field capacity of normal soil under field condition. These two moisture regimes also justified the availability and solution chemistry of phosphorus in field condition. The samples were then incubated at two temperatures viz., 20 and 30 °C, corresponding to average temperature prevailing during rabi and kharif season, respectively for different incubation periods. Literature suggests that most of the water soluble fertilizers release their nutrient constituent within 5–7 days. Thus, the present incubation experiment was conducted for 120 h to know the initial release properties of manufactured products. The experiment was carried out following factorial completely randomized design (CRD) with three replications. Destructive samples were drawn after 1, 2, 4, 24, 60 and 120 h of incubation and analyzed for available P by extracting samples with 0.5 M  $\text{NaHCO}_3$ , at pH 8.5 as per the procedure outlined by Olsen et al. [19] followed by estimation of P in the extract by ascorbic acid blue colour method [20].

### Statistical Analyses

Statistical analyses of data generated from incubation experiments were carried out using standard analysis of variance [22]. The least significance difference (LSD) between the treatment means was calculated at  $P \leq 0.05$ .

## Results and Discussion

### Characteristics of Novel Coated P-Fertilizers

The characteristics of the coated fertilizers are presented in Table 1. It was observed that Product-A and Product-B had pH values of 8.5 and 7.9, respectively due to the presence of excess amount of  $\text{NH}_3$ . The products evolved from acidulation of RP (i.e. Product-C and Product-D) showed

**Table 1** Characteristics of laboratory made manufactured products of phosphate fertilizers

Characteristics	Product-A (NH <sub>3</sub> :H <sub>3</sub> PO <sub>4</sub> ::2:1)	Product-B (NH <sub>3</sub> :H <sub>3</sub> PO <sub>4</sub> ::1:1)	Product-C (RP + H <sub>2</sub> SO <sub>4</sub> )	Product-D (RP + H <sub>3</sub> PO <sub>4</sub> )
pH	8.5	7.9	2.0	2.4
Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	427.1	402.7	78.4	288.2
Total N (%)	15.4	15.3	Trace	Trace
Total P (%)	25.7	28.8	8.9	21.6
WSP (%)	22.1	24.6	5.2	8.2
CSIP (%)	1.8	0.5	1.0	2.7
CSP (%)	1.8	3.8	2.7	10.7
Shape	Granular or cubical, or hexagonal shaped	Needle shaped	Alveoli shaped	Irregular flakes shaped
Colour	Pale white crystalline	Pure white crystalline	Light grey	Dark grey

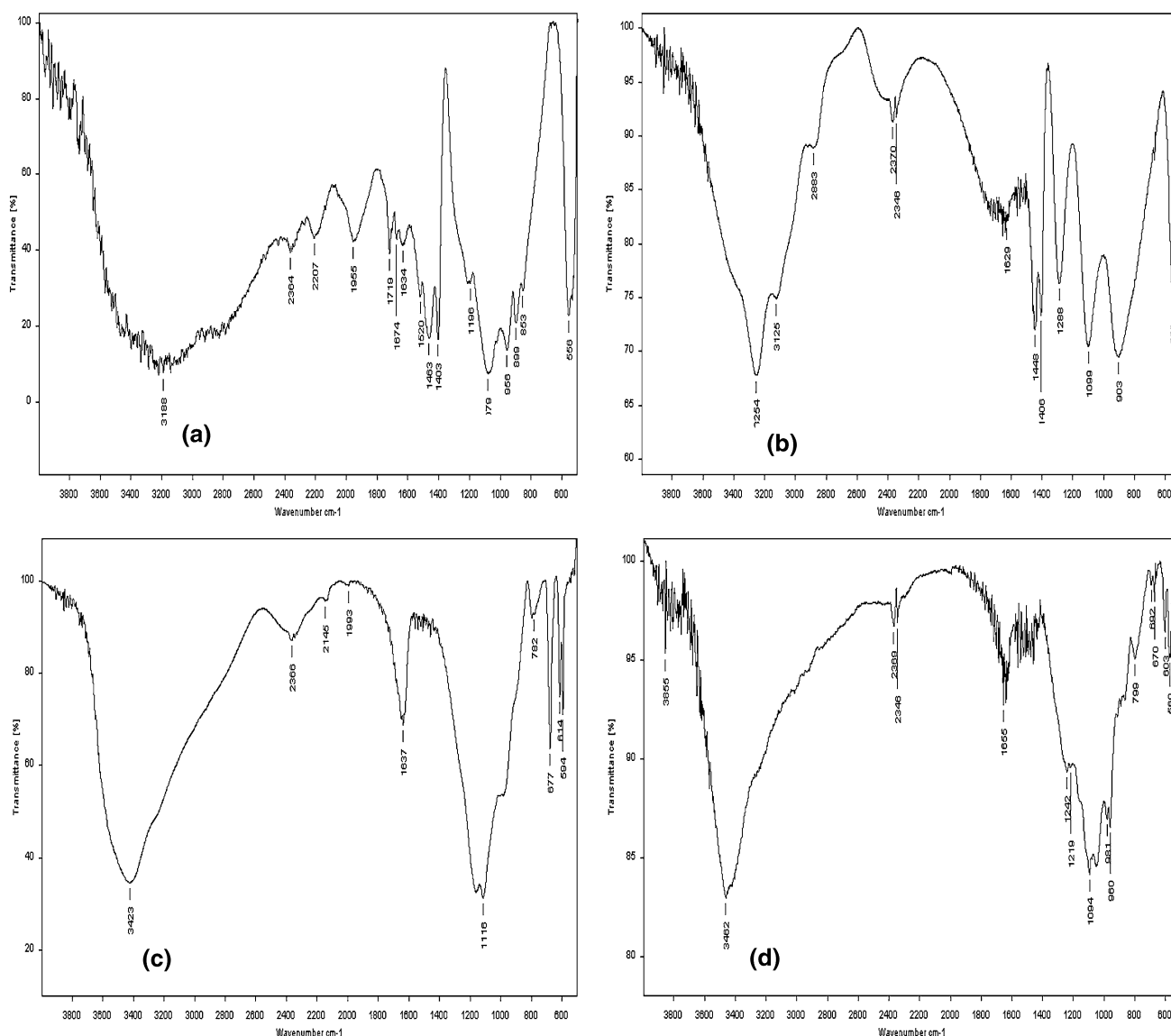
significantly lower pH, which might be because of free acids in the final products. As far as specific surface area is concerned, the products followed the descending order of Product-A > Product-B > Product-D > Product-C.

The FTIR spectra of laboratory made Product-A (Fig. 1a) showed sharp peaks with strong intensity in the range of 1463–1403 cm<sup>-1</sup>, representing the presence of NH<sub>2</sub> vibration region and 1196–899 cm<sup>-1</sup>, revealing the P–O–H vibration. It also showed strong intensity peak of 556 cm<sup>-1</sup>, representing the presence of PO<sub>4</sub> functional group. Product-B (Fig. 1b) showed the sharp peaks with strong intensity in the range of 1463–1403 cm<sup>-1</sup>, representing the presence of NH<sub>2</sub> vibration region and 1196–899 cm<sup>-1</sup>, revealing the P–O–H vibration. The vibration and stretching of functional groups namely, O–N=P and –ONO<sub>2</sub> were also observed from the wave number of 905–545 cm<sup>-1</sup> and strong intensity peak of 548 cm<sup>-1</sup>, representing the presence of PO<sub>4</sub> functional group. Product-C (Fig. 1c) represents the peak value at 1116 cm<sup>-1</sup>, corresponding to P–O–H vibration and 614 and 594 cm<sup>-1</sup>, representing the presence of PO<sub>4</sub> functional group. The intensity of FTIR peak of Product-D (Fig. 1d) was similar to that of Product-C, but the difference was that the intensity of percentage transmittance was lower for Product-D.

### Effect of Moisture on Release of P

The data pertinent to 0.5 M NaHCO<sub>3</sub> extractable P status in soil treated with coated manufactured products as influenced by moisture regimes are presented in Table 2. It is evident that after 1 h of incubation, the P release was significantly higher in soil treated with Product-B (238.7 mg P kg<sup>-1</sup>), followed by Product-A, Product-D and Product-C with corresponding values of 166.9, 147.5 and 63.1 mg P kg<sup>-1</sup> soil, respectively. It is also evident that

after 1 h of incubation, the P release was maximum in soil treated with commercial DAP (242.7 mg P kg<sup>-1</sup>), which was used as standard P fertilizer. Similar results were also observed after 2, 4, 60 h for all the coated products (Table 2), except the results obtained after 24 and 120 h. It had been observed that after 24 h (Table 2), Product-A and Product-B were statistically at par in respect to their P release capacity during incubation. Similar trend was followed for Product-D and Product-C as shown in the earlier cases. The commercial DAP released approximately 69 % of its initial active fertilizing nutrient during that time period. However, coated Product-C, Product-D, Product-A and Product-B correspondingly maintained higher amount of P (90, 86.5, 69.4 and 69.1 % respectively, in respect to initial P applied) within it for future release. After 120 h of incubation, among the coated products, it was observed that materials prepared through ammonia and H<sub>3</sub>PO<sub>4</sub> at the ratio of 2:1 (Product-A) resulted in significantly higher amount of release of P than other products. The P release was in the order of Product-A > Product-B > Product-D > Product-C (Table 2). While considering the impact of coating agents under influence of different moisture regimes on P release from manufactured products, after 1 h, PVA coated products released least amount of P (151.4 mg P kg<sup>-1</sup>) as compared to LP (155.0 mg P kg<sup>-1</sup>) and MO (155.8 mg P kg<sup>-1</sup>), the latter two being statistically at par (Table 2). Similar trend was also observed after 2, 4 and 24 h of incubation. However, data obtained after 60 and 120 h indicated that PVA coated products released significantly higher amount of P than MO coated products. However, the performance of LP as a coating agent differs during both cases, and gave an intermediate performance. Data also showed that 3 % of coated materials released P significantly at a slower rate than that of 2 % level of coatings (Table 2). Higher level of coating (i.e. 3 %, w/w) correspondingly reduced the P release by 5.37, 8.51, 6.85,



**Fig. 1** Fourier transform infrared spectroscopy of **a** Product-A ( $\text{NH}_3:\text{H}_3\text{PO}_4::2:1$ ), **b** Product-B ( $\text{NH}_3:\text{H}_3\text{PO}_4::1:1$ ), **c** Product-C ( $\text{RP} + \text{H}_2\text{SO}_4$ ) and **d** Product-D ( $\text{RP} + \text{H}_3\text{PO}_4$ )

2.99, 7.18, and 14.8 % than the products with 2 % level of coating after 1, 2, 4, 24, 60 and 120 h of incubation, respectively. As far as the moisture content (10 and 20 %, v/w) is concerned with increasing moisture level, the release of P also increased significantly, irrespective of products, coating agents as well as coating levels (Table 2). The materials incubated at 20 % moisture regime recorded higher release of P as compared to 10 % moisture level.

#### Effect of Temperature on Release of P

The release pattern of P from different coated manufactured fertilizer products as influenced by temperature

during incubation study are presented in Table 3. After 1 h of incubation it was observed that Product-B registered the largest amount of extractable P ( $178.9 \text{ mg P kg}^{-1}$ ) among the coated products, followed by Product-A ( $172.9 \text{ mg P kg}^{-1}$ ), Product-D ( $155.5 \text{ mg P kg}^{-1}$ ) and Product-C ( $64.6 \text{ mg P kg}^{-1}$ ) which were significantly different among themselves. But commercial DAP (as standard fertilizer), recorded maximum release of P ( $256.2 \text{ mg P kg}^{-1}$ ) as active fertilizing nutrient (Table 3). Similar trend in release of P was also observed after 2, 4, 24, 60, 120 h of incubation, and it maintained in the order of  $\text{DAP} > \text{Product-B} > \text{Product-A} > \text{Product-D} > \text{Product-C}$  (Table 3). But, the extent of P release was much



**Table 2** Effects of applied fertilizer sources, coating agents and coating levels on P release ( $\text{mg kg}^{-1}$ ) as influenced by moisture regimes during incubation

	Periods of incubation					
	1 h	2 h	4 h	24 h	60 h	120 h
<b>Products</b>						
Product-A	166.9 <sup>c</sup>	140.6 <sup>c</sup>	111.8 <sup>c</sup>	153.0 <sup>b</sup>	209.1 <sup>c</sup>	262.4 <sup>b</sup>
Product-B	238.7 <sup>b</sup>	192.1 <sup>b</sup>	147.8 <sup>b</sup>	154.2 <sup>b</sup>	229.9 <sup>b</sup>	225.7 <sup>c</sup>
Product-C	63.1 <sup>e</sup>	59.2 <sup>e</sup>	52.4 <sup>e</sup>	47.2 <sup>d</sup>	62.4 <sup>e</sup>	69.2 <sup>e</sup>
Product-D	147.5 <sup>d</sup>	121.0 <sup>d</sup>	88.5 <sup>d</sup>	67.2 <sup>c</sup>	116.5 <sup>d</sup>	104.3 <sup>d</sup>
DAP	242.7 <sup>a</sup>	274.7 <sup>a</sup>	300.3 <sup>a</sup>	345.0 <sup>a</sup>	386.0 <sup>a</sup>	432.8 <sup>a</sup>
LSD ( $P = 0.05$ )	1.83	2.64	1.62	1.54	1.92	1.78
<b>Coating agents</b>						
Polyvinyl alcohol	151.4 <sup>b</sup>	127.6 <sup>b</sup>	97.6 <sup>c</sup>	93.4 <sup>c</sup>	161.2 <sup>a</sup>	176.6 <sup>a</sup>
Liquid paraffin	155.0 <sup>a</sup>	125.6 <sup>b</sup>	99.6 <sup>b</sup>	103.1 <sup>b</sup>	150.4 <sup>b</sup>	175.4 <sup>a</sup>
Methyl oleate	155.8 <sup>a</sup>	131.4 <sup>a</sup>	103.1 <sup>a</sup>	119.7 <sup>a</sup>	151.7 <sup>b</sup>	144.1 <sup>b</sup>
LSD ( $P = 0.05$ )	1.72	2.29	1.54	1.47	1.80	1.68
<b>Coating levels</b>						
2 % coating	158.3 <sup>a</sup>	133.9 <sup>a</sup>	103.7 <sup>a</sup>	107.0 <sup>a</sup>	160.2 <sup>a</sup>	178.6 <sup>a</sup>
3 % coating	149.8 <sup>b</sup>	122.5 <sup>b</sup>	96.6 <sup>b</sup>	103.8 <sup>b</sup>	148.7 <sup>b</sup>	152.2 <sup>b</sup>
LSD ( $P = 0.05$ )	1.59	1.87	1.44	1.38	1.65	1.55
<b>Moisture regimes</b>						
10 % moisture	148.1 <sup>b</sup>	121.8 <sup>b</sup>	93.5 <sup>b</sup>	97.7 <sup>b</sup>	147.8 <sup>b</sup>	155.0 <sup>b</sup>
20 % moisture	160.0 <sup>a</sup>	134.6 <sup>a</sup>	106.8 <sup>a</sup>	113.1 <sup>a</sup>	161.2 <sup>a</sup>	175.7 <sup>a</sup>
LSD ( $P = 0.05$ )	1.67	1.79	1.56	1.44	1.70	1.82

Different lowercase letters within the same column indicate that treatment means are significantly different at  $P < 0.05$  according to Duncan's Multiple Range Test for separation of means

higher due to changes in temperature regimes than the moisture regimes. After 1 h, materials coated with MO released significantly higher amount of P ( $160.6 \text{ mg P kg}^{-1}$ ) followed by LP ( $142.6 \text{ mg P kg}^{-1}$ ) and least with polyvinyl alcohol ( $135.4 \text{ mg P kg}^{-1}$ ), indicating that polyvinyl alcohol could serve as the best coating agent for slowing down the release of P from coated fertilizers (Table 3). After 2, 4, 24, 60 and 120 h of incubation, it was observed that as a coating material the performance followed in the order of MO > LP > polyvinyl alcohol. Between the two coating levels, it was observed that 2 % coating material released higher amounts of Olsen P as compared to 3 % (Table 3). Higher level of coating (i.e. 3 %, w/w) correspondingly reduced the P release by 5.44, 3.15, 6.60, 12.1, 13.6, and 13.8 % over the products with 2 % level of coating after 1, 2, 4, 24, 60 and 120 h of incubation, respectively. Data revealed that the release of P from coated materials increased significantly with the increase in temperature regime from 20 to 30 °C, and estimated that temperature effect correspondingly increased the P release by 10.8, 10.3, 12.4, 11.3, 7.0 and 7.6 % after 1, 2, 4, 24, 60 and 120 h.

### Effect of Incubation Study

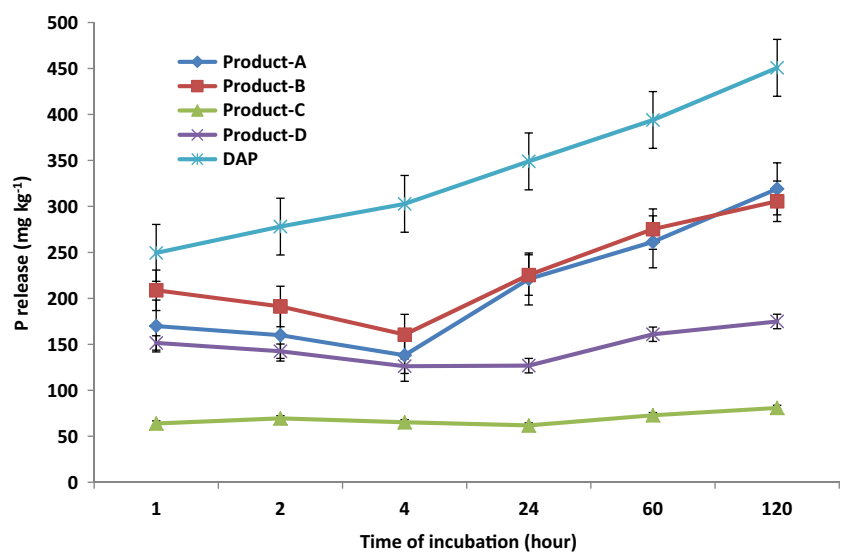
The results obtained in the soil incubation studies with various newly manufactured products revealed that, in general, the amount of Olsen P in soil decreased slightly in treatments receiving Product-A, Product-B and Product-D after 2 and 4 h of incubation (Fig. 2), thereafter, the release of P increased significantly up to 120 days. Irrespective of coating agents and coating levels, Product-C showed significantly lower amount of release of P than other products. It was observed that the trends in decrease in P were sharp for temperature regimes at different periods in all the products with the exception of Product-C, as its release patterns followed a gradual curve with period of incubation. The release of P from different products revealed that commercial DAP released significantly higher mean P followed by Product-B > Product-A > Product-D > Product-C, corresponding with the mean values of release of 337.4, 227.9, 209.0, 147.1 and 69.0  $\text{mg P kg}^{-1}$ , respectively (Fig. 3).

As far as the coating agent is concerned, it was observed that materials coated with polyvinyl alcohol released lesser

**Table 3** Effects of applied fertilizer sources, coating agents and coating levels on P release ( $\text{mg kg}^{-1}$ ) under the influence of temperature regimes

	Periods of incubation					
	1 h	2 h	4 h	24 h	60 h	120 h
<b>Products</b>						
Product-A	172.9 <sup>c</sup>	179.4 <sup>c</sup>	164.4 <sup>a</sup>	289.2 <sup>c</sup>	313.8 <sup>c</sup>	375.9 <sup>c</sup>
Product-B	178.9 <sup>b</sup>	190.3 <sup>b</sup>	173.4 <sup>b</sup>	296.6 <sup>b</sup>	320.6 <sup>b</sup>	385.5 <sup>b</sup>
Product-C	64.6 <sup>e</sup>	79.6 <sup>e</sup>	78.0 <sup>e</sup>	76.2 <sup>e</sup>	83.4 <sup>e</sup>	92.6 <sup>e</sup>
Product-D	155.6 <sup>d</sup>	164.0 <sup>d</sup>	164.0 <sup>d</sup>	186.4 <sup>d</sup>	205.4 <sup>d</sup>	245.4 <sup>d</sup>
DAP	256.2 <sup>a</sup>	281.4 <sup>a</sup>	305.2 <sup>a</sup>	352.9 <sup>a</sup>	402.0 <sup>a</sup>	468.7 <sup>a</sup>
LSD ( $P = 0.05$ )	1.95	1.80	1.64	2.48	2.45	2.10
<b>Coating agents</b>						
Polyvinyl alcohol	135.4 <sup>c</sup>	147.1 <sup>c</sup>	136.6 <sup>c</sup>	206.3 <sup>c</sup>	222.6 <sup>c</sup>	258.4 <sup>c</sup>
Liquid paraffin	142.6 <sup>b</sup>	152.4 <sup>b</sup>	138.9 <sup>b</sup>	211.8 <sup>b</sup>	230.5 <sup>b</sup>	275.1 <sup>b</sup>
Methyl oleate	151.0 <sup>a</sup>	160.6 <sup>a</sup>	159.3 <sup>a</sup>	218.2 <sup>a</sup>	239.4 <sup>a</sup>	291.0 <sup>a</sup>
LSD ( $P = 0.05$ )	1.82	1.55	1.42	2.28	2.26	1.95
<b>Coating levels</b>						
2 % coating	147.0 <sup>a</sup>	155.8 <sup>a</sup>	149.9 <sup>a</sup>	225.7 <sup>a</sup>	247.6 <sup>a</sup>	295.2 <sup>a</sup>
3 % coating	139.0 <sup>b</sup>	150.9 <sup>b</sup>	140.0 <sup>b</sup>	198.5 <sup>b</sup>	214.0 <sup>b</sup>	254.5 <sup>b</sup>
LSD ( $P = 0.05$ )	1.67	2.27	2.16	2.05	2.03	1.78
<b>Temperature regimes</b>						
20 °C temperature	135.7 <sup>b</sup>	145.8 <sup>b</sup>	136.5 <sup>b</sup>	200.8 <sup>b</sup>	223.0 <sup>b</sup>	264.8 <sup>b</sup>
30 °C temperature	150.3 <sup>a</sup>	160.8 <sup>a</sup>	153.4 <sup>a</sup>	223.4 <sup>a</sup>	238.6 <sup>a</sup>	284.9 <sup>a</sup>
LSD ( $P = 0.05$ )	1.79	2.03	1.95	1.98	2.16	2.01

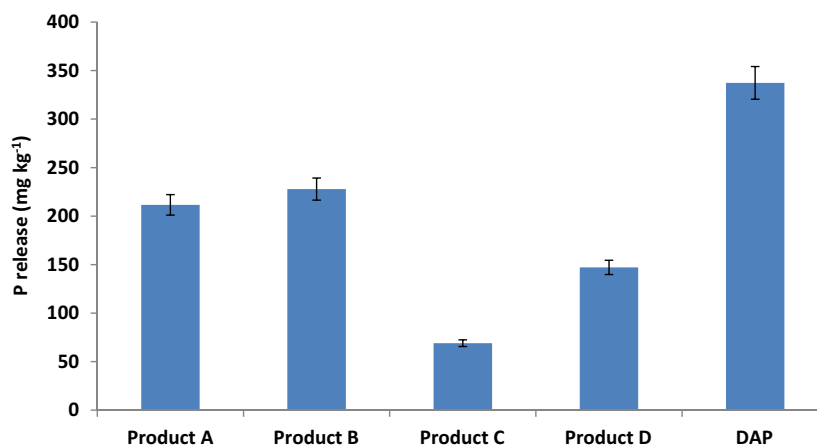
Different lowercase letters within the same column indicate that treatment means are significantly different at  $P < 0.05$  according to Duncan's Multiple Range Test for separation of means

**Fig. 2** Release pattern of P ( $\text{mg kg}^{-1}$ ) from different laboratory made coated phosphatic fertilizers in an Inceptisol

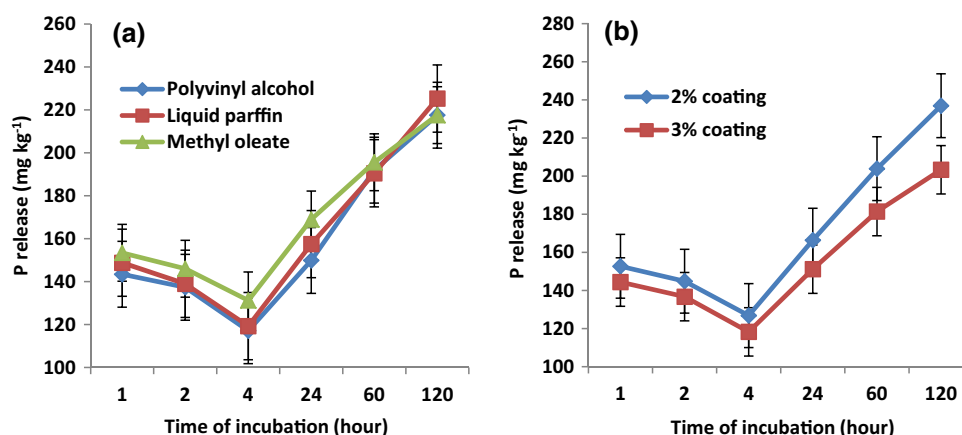
amount of P throughout the incubation period, indicating its superiority as coating agent over LP and MO coated products (Fig. 4a). As far as the levels of coating were concerned, 2 % level of coating always released higher amount of P (Fig. 4b) than the higher level of coating

(3 %) indicating that 2 % level of coating may not be sufficient to make the product having better slow release properties. Among the two moisture levels, the release pattern of P was greater at 20 % moisture level than that of 10 % moisture level (Fig. 5a). It was observed that the

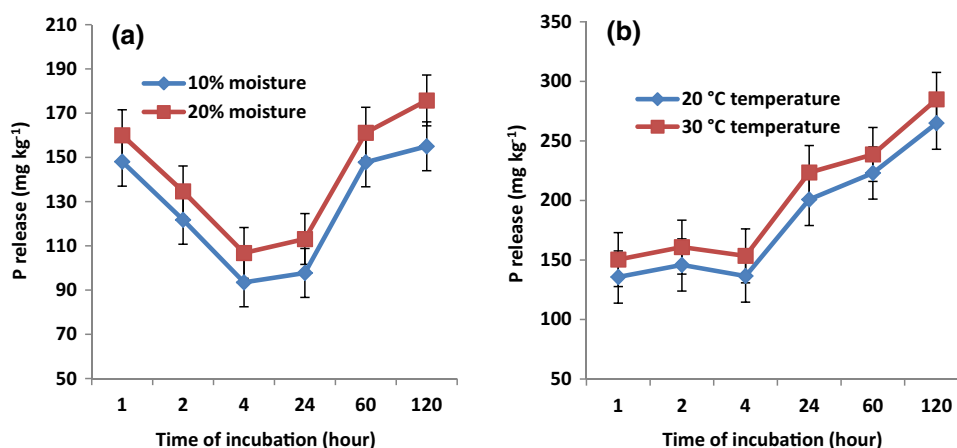
**Fig. 3** Overall mean release of P ( $\text{mg kg}^{-1}$ ) from different laboratory made coated phosphatic fertilizer products in an Inceptisol



**Fig. 4** Influence of **a** coating agents and **b** coating level on release pattern of P ( $\text{mg kg}^{-1}$ ) from different laboratory made coated phosphatic fertilizers in an Inceptisol



**Fig. 5** Influence of **a** moisture regimes and **b** temperature on release pattern of P ( $\text{mg kg}^{-1}$ ) from different laboratory made coated phosphatic fertilizers in an Inceptisol



release of P from all the products increased significantly with the increase in temperature from 20 to 30 °C (Fig. 5b).

In the present study, the main WSP that is produced in the process involving reaction of ammonia with  $\text{H}_3\text{PO}_4$  is mono- or di-ammonium phosphate. While, the main WSP that is produced in the process involving reaction of low-grade RP with mineral acids namely,  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  is

mono-calcium phosphate. The kinetics of phosphate release and sorption in pure systems and soils has drawn considerable attention in recent years. The kinetic interpretations, however, are often conflicting. The concentration of soil solution P is controlled by the equilibrium between the soil sorption system, soil solution and precipitated P compounds. When soil solution comes in contact with sufficient P, the soil's sorption capacity becomes



increasingly saturated until a point is reached when precipitation of sparingly soluble compounds will occur [23]. Conversely, if the solution P concentration is small, the sorption complex will desorb P to a degree that corresponds to the solubility of the least stable compound present. Any further desorption will see that P compound dissolves and replenishes the sorption system. It is commonly the dissolution of species that is the rate limiting step [24]. In the present study, it was observed that irrespective of coating levels and moisture regimes the average release of P from Product-B was maximum throughout the incubation period of 120 h followed by Product-A, Product-D and Product-C. On the basis of P release, the least performer was found with Product-C that might be due to the presence of inherent gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) that produces during preparation. The performance of PVA coated materials was better than the other two coating agents. It is observed that PVA is unique among polymers used as coating agent for this study, as it consists of surface hydrophilic ( $-\text{OH}$ ) groups that may form a water hull surrounding the products, that enhances slow release properties and releases less P in soil. The chemical compound of PVA is made up of large, multiple-unit molecules. It is not build-up in polymerization reactions from single-unit precursor molecules known as monomers. Instead, PVA is made by dissolving another polymer such as methanol and treating it with an alkaline catalyst such as sodium hydroxide. The resulting hydrolysis, or “alcoholises,” reaction removes the acetate group from the PVA molecules without disrupting their long-chain structure. It is also employed as a component of adhesives and emulsifiers, as a water-soluble protective film that forms crosslinks over the surface of the water soluble fertilizer material and slow down the release pattern of P from the manufactured coated products. Han et al. [25] showed that the application of formaldehyde led inter-molecular and intra-molecular linkage of  $-\text{OH}$  between starch and PVA molecules and therefore the hydrophilic groups were reduced. So it could be confirmed that the water absorbency of the blend films decreased with the application of formaldehyde. Therefore, water and  $\text{NH}_4^+$  permeability also decreased with formaldehyde content (when it is above 10 %, w/w) because of the decreasing affinity between film and water molecules resulting from the crosslinking reaction between starch and PVA by formaldehyde. However, when the formaldehyde content is lower (below 10 %, w/w), the gap between molecules introduced by crosslinking reaction, which increased the water and  $\text{NH}_4^+$  permeability rate. While studying the release rates of P from seven coated CRFs having different coatings or substrates ( $\text{NH}_4^+-\text{N}$ ,  $\text{NO}_3^--\text{N}$ , P, K, Mg, Fe and Mn) under controlled environmental conditions, Broschat et al. [26] reported that the release rates were slower than

those for  $\text{NH}_4^+-\text{N}$ ,  $\text{NO}_3^--\text{N}$ , and K. They also reported that polymer coated CRFs are resilient to high temperature with an increase in nutrient release rate of around 20 % for a temperature increase of 30–40 °C. They observed uneven release of nutrients with more rapid release during the early period and a decline in release rate over the latter part of the period. This pattern is most accentuated at 40 °C [27].

Liang and Liu [28] reported that incorporation of kaoline nanopowder into superabsorbent polymer can decrease the diffusion coefficient of urea release from urea loaded composite hydrogel. Recent study of Sarkar et al. [29] demonstrated that incorporation of nanosized clay into superabsorbent polymer matrix decreases the rate of nutrient release from fertilizer loaded clay/polymer composites in distilled water which could be used effectively as a slow release fertilizer. In another study, Sarkar et al. [30] reported that fertilizer loaded NCPC would be a promising formulation to reduce the loss of N and P and hence maintain better availability of P and N in the soil. They also found that smectite/polymer composite was found to be the best in terms of slow nutrient release property than that of kaolinite/polymer or illite/polymer composite. Better slow release property of the former might have contributed to lower fixation of P and hence better recovery in the leachate as compared to the other products. Erro et al. [31] developed a new type of superphosphate called organic complexed superphosphate by the introduction of organic chelating agents, preferably a humic acid (HA), into the chemical reaction of single superphosphate (SSP) production. This modification yielded a product containing monocalcium phosphate complexed by the chelating organic agent through Ca bridges. Theoretically, the presence of these monocalcium phosphate–humic complexes inhibits phosphate fixation in soil, thus increasing P fertilizer efficiency.

## Conclusion

From the above mentioned results, it may be concluded that the release of P from different coated products increases sharply from the first hour followed by a gradual decrease and thereafter with passage of time increases the release of P gradually, except Product-C. In all cases, Product-C which was prepared by reacting RP with  $\text{H}_2\text{SO}_4$  releases lower amount of P throughout the incubation study. Release of P from all the coated products was greater at higher moisture regimes (20 %, w/w), while the release of P was greater when temperature was maintained at 30 °C than that at 20 °C. Throughout the incubation study of 120 h, the release of P from coated products was less than the commercial DAP fertilizer. Thus, new modified coated fertilizer could be developed by treating ammonia with phosphoric

acid (ammoniated product) or reacting RP with mineral acids (acidulated product) followed by coating with a suitable coating agent which could release P at a slower rate that would coincide the crop demand. It could be concluded that laboratory made coated fertilizers could be used as a source of P which would release P slowly than the costly water soluble P like DAP and supply P for a longer period that synchronizes the crop demand and enhances P use efficiency. Further, detailed study is needed to see the effectiveness of these novel coated fertilizers as source of P to crops under field conditions at various locations for commercial application.

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#### Compliance with Ethical Standards

**Conflict of interest** Authors have not declared any conflict of interest.

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