

Original Research Article

Studies on organic polymer coated DAP fertilizer on **Phosphorus** and Nitrate releasing pattern in calcareous soils

ABSTRACT

An incubation experiment was carried out with DAP coated with chitosan and sodium alginate organic polymers. Treatments comprises of T1: Chitosan coated 75% DAP, T2: Chitosan coated 100% DAP, T3: Sodium alginate coated 75% DAP, T4: Sodium alginate coated 100% DAP, T5: 100 % RDF (SSP) , and T6: 100% RDF(DAP) which were replicated four times in completely randomized block design. Results revealed that 100 % chitosan coated DAP (T2) was found to be superior than all the remaining treatments which was followed by 100% sodium alginate coated DAP (T4). Uncoated DAP and SSP high leachate P in the early stage of incubation study and there after P content was minimal in leachate. It was concluded that coated DAP had less release of P at the start of study and thereafter steady state because of the dissolution of P through the coated membrane. Similar trend was observed in nitrate releasing pattern.

Key words: **Incubation,** **Organic polymers**, Chitosan, Sodium alginate, Leachate P and $\text{NO}_3\text{-N}$

1. Introduction

A crop's nutritional needs can be addressed in a variety of ways. Chemical fertilizer application is one of the most prevalent methods for providing nutrients to crops. Because of reduced soil fertility, intensification of agricultural land use, and the use of high yielding cultivars, the fertilizer consumption has risen over time. However, the current production economics scenario indicates a downward tendency in the benefit cost ratio, implying that farmers cannot earn a profit from production after paying their expenses.

The Control release fertilizer (CRF) is a type of new generation fertilizer that is meant to release plant nutrients in a consistent manner in order to match crop demand [1]. The extensive use of quick release fertilizers (QRF), which have low nutrient absorption efficiency due to their high solubility, has been the key crop production problem. Fertilizer efficiency must be improved by the use of innovative technical implementation. Slow release fertilizer technology is one of the promising technologies that will slow down the pace of nutrient dissolution and hence nutrient release. Slow release **fertilizers** release or convert plant nutrients to a plant-available form at a slower pace than an appropriate reference

soluble product [2]. A coating membrane on the surface of fertilizers can be used to ensure that nutrients are released continuously. Polymers can be utilized to cover fertilizer which supplies nutrients effectively. Organic polymers can be used efficiently in delayed release fertilizer technology because they increase soil quality without causing environmental harm while also allowing for a longer nutrient release pattern. Consistent P availability throughout wheat growth improved growth and yield, and polymer coated DAP could supply P over longer periods of time than uncoated DAP [3]. When a coated fertilizer is applied to soil, nutrients are only available to the soil after the organic layer has degraded. It will take time, and the stage of delayed nutrient release will coincide with the crop's peak demand for nutrients. It was discovered [4] that organically coated MAP granules released P gradually over time, increasing P availability to plants and leading in higher P usage efficiency in maize plants. Coating, encapsulating, and other techniques can be used to develop slow release fertilizers. Coating is a handy way for generating slow release fertilizers since it is simple to prepare and cost-effective to manufacture.

Chitosan is a natural polymer derived from the shells of marine animals such as crabs, lobsters, and shrimp. It's a chitin-derived natural linear polysaccharide. Chitin and chitosan have technical applications in agriculture such as biocide (fungicide, bactericide, pesticide, etc.), nitrogen fertilizer, and bio stimulant or growth regulator [5]. It is abundant in nature and has the potential to produce a water-insoluble film, making it an excellent coating layer. Chitosan is an intriguing biopolymer. Because it is biodegradable, cost-effective, and less hazardous, it has been extensively researched as a major bioactive carrier [6]. Another polymer is sodium alginate which is an anionic polymer derived from brown seaweed that can be used to encapsulate fertilizers as an organic polymer. Alginate is a material for encapsulation applications [7].

To reach yield goals, it is required to increase the properties of the applied fertilizer by coating it with the appropriate substance. This would boost its use efficiency to the point where they should be able to deliver larger yields even at lower rates of application than with traditional phosphatic fertilizer applications [8]. Phosphorus use efficiency (PUE) can be improved by using polymer coated or controlled release fertilizers (CRF), which release P according to plant demand. However, the coating material should be cost-effective and have good coating characteristics.

Nutrient release patterns can be assessed in the field or in the lab. Environmental parameters that influence nutrient release, including as soil temperature, pH, moisture and microbial activity, change when assessed in the field, therefore nutrient release measures are dependent on current conditions. Despite the usefulness of field approaches for determining the real agronomic efficiency of SRFs and CRFs, a laboratory method capable of promptly

determining the agronomic effectiveness of SRFs and CRFs is also required and determining their nutrient release properties with precision.

With this background, two organic polymers viz., chitosan and sodium alginates were used in the present investigation as coating materials to coat the Diammonium Phosphate in order to study the release pattern of P at different day's intervals in calcareous soils in the incubation experiment. It facilitates to understand the release pattern of nutrient as to synchronize the crop nutrient demand.

2. MATERIALS AND METHODS

Chitosan used for polymer coating was purchased from Marine hydro colloids, Kochi, Kerala. Chitosan specifications are powder form with degree of acetylation >75%, mesh size of 35, solubility 97% in 1% acetic acid, and pH 6.5-8. Sodium alginate was supplied by Sigma Aldrich Fine Chemicals Bioscience, which occurs as white to yellowish brown granular forms and dissolves in water slowly and forms a viscous solution. Commercial grade DAP granular phosphate fertilizer (46% P, &18% N) was used. The experiment was carried out in the Department of Soil Science and Agricultural Chemistry, Tamil Nadu Agricultural University, Coimbatore, India in 2021-2022.

2.1. Preparations of polymer coated DAP

Chitosan was dissolved in 1 percent acetic acid and well mixed to get a homogenous chitosan solution for coating. The chitosan used had a concentration of 2%. The DAP was then sprayed twice with chitosan solution using a hand sprayer. In order to facilitate the drying of acetic acid, the coated fertilizer was placed in a hot air oven at 60°C for 4 hours. Similarly, two sprays of 2 percent sodium alginate dissolved in distilled water were used to coat DAP and it was dried in shade. Thus, sufficient quantity of DAP coated fertilizer with chitosan and sodium alginate were prepared. The dosage of DAP at 100% was 50 kg /ha and for 75 % DAP it was 37.5 kg/ha. The experiment consisted of six treatments viz., T1 - Chitosan coated 75% DAP, T2 - Chitosan coated 100% DAP, T3 - Sodium alginate coated 75% DAP, T4 - Sodium alginate coated 100% DAP, T5 - 100 % RDF (SSP) , and T6 - 100% RDF(DAP) which were replicated four times in completely randomized block design (CRBD).

The bulk soil was taken from the cultivated field of University farm. With an EC of 0.29 dS m⁻¹ and a pH of 8.50, the soil had medium available N (285kg/ha), medium available P (20kg/ha), and high available K (700 kg/ha). The soil was high in calcareousness, with a calcium carbonate level of 18%. The sufficient number of 250 gram capacity funnels was chosen for the study and filter paper was placed over the funnel to hold the soil. For all the treatments, 250 g sieved (2 mesh) soil was used. The recommended

dose of phosphorus (50 kg P₂O₅ /ha) for black gram crop was considered as 100% DAP dosage for leachate study. As the quantity of coated DAP fertilizer worked out for 100% DAP equivalent for 250 gm soil was less than the each granule size of the DAP, the dosage of DAP was increased to five times of 100% DAP equivalent so as to have practical feasibility in conducting the experiment. Accordingly, the quantity of coated DAP weighed and applied to each treatment were as follows. T1 - Chitosan coated 75% DAP (50.85 mg), T2 - Chitosan coated 100% DAP (68 mg), T3 - Sodium alginate coated 75% DAP (50.85 mg), T4 - Sodium alginate coated 100% DAP (68 mg), T5 - 100% RDF (SSP) (195 mg), and T6 - 100% RDF (DAP) (68 mg).

The moisture content was maintained at field capacity all through the experiment in all the treatments. The leachate samples were collected at 10 days interval up to 60th day, from all the treatments for analysis of pH, EC, P content and [9] ammoniacal and nitrate nitrogen [10] by following the standard procedures

2.2. Characterization of coated and uncoated DAP by SEM.

The microscopic morphology of the surface of uncoated DAP and coated DAP with chitosan and sodium alginate was examined using the Scanning electron microscopy (SEM) to better understand the profile of the coating between the fertilizer and the organic polymer with an accelerating voltage of 8 kV. Figure 1, 2, and 3 shows a visual comparison of uncoated and two organic polymers coated DAP fertilizer granules with magnifications of 80 x demonstrating that the film coating completely covered the DAP granules. The surface of uncoated DAP had a rough texture, as shown in Fig. Water molecules may easily enter the fissures and crevices of rough surface, resulting in the rapid release of nutrients from uncoated DAP fertilizer [11]. The coatings of chitosan and sodium alginate on DAP granules (figure 2 and 3 respectively) had a smoother surface than the uncoated DAP granules. Chitosan coated DAP (figure 2), had depicted a smooth surface texture than the sodium alginate coated DAP (figure 3), which implies chitosan coated DAP might have well properties of a coated fertilizer and best performance than sodium alginate coated DAP.

3. RESULTS AND DISCUSSION

3.1. Phosphorus content in Leachate

Phosphorus was analyzed from leachate samples collected at different sampling intervals. The data on P released during the experiment is furnished in table 1. The release of P was found to increase up to 20th day and there after declining trend was noticed in all the treatments. Among the treatments, the uncoated DAP (T6) performed better in releasing P up to 10th day and there after chitosan and sodium alginate coated 100% DAP performed better in registering higher leachate P from 20th day to till incubation experiment was over.

On 1st day T6- DAP uncoated recorded the highest P (6.1 ppm) followed by T5 with 6.0 ppm which were comparable with each other. The rest of the treatments recorded leachate P from 3.6 to 4.2 ppm. On 10th day, among the treatments, T6 -uncoated 100% DAP had high P content (10.6 ppm) in leachate which was significantly higher than all other treatments followed by SSP (8.8 ppm). This may be due to quick dissolution of uncoated SSP and DAP in the initial stages of incubation in particular up to 10th day. Water molecules may quickly infiltrate holes and cracks in the surface of uncoated DAP, resulting in the rapid release of nutrients from the uncoated DAP fertilizer [12]. While coated DAP treatments recorded P between 6.1 and 8.5 ppm. As coated DAP contained organic polymer layer as coating layer, it would have acted as a barrier and dissolution would have been slow and that eventually resulted in slow release of P from coated fertilizer in the initial stages. Reduction in the number of pinholes, which are the principal pathway for consistent P release from coated DAP [13].

In the 3rd stage (20th day), the highest released P was noticed for the chitosan coated 100% DAP (22.8 ppm) which was significantly superior than all other treatments. Next to this, sodium alginate coated 100% DAP had high P (21.8 ppm) followed by T6, T1, T3 and T5 which were significantly different from each other. Comparable highest released P was also observed for the treatments T2 (19.7 & 18.6 ppm) and T4 (19.1 and 17.7 ppm) on 30th and 40th day of incubation respectively (figure 2). In coated DAP, polymer coating would have got disintegrated slowly which might have facilitated to release P at a higher rate in the latter stages of incubation experiment. Better efficiency, as a result of coated fertilizers delayed and gradual release, can help reduce application frequency while also reducing the harmful effects of overdosing [14,15]. With the passage of time, coated fertilizers release nutrients and maintain the correct level of phosphorus for plant requirements [16]. **Controlled release fertilizers reported high value of soil available P than water soluble fertilizers [17].** In comparison to uncoated phosphatic fertilizer sources, polymer coated fertilizers had a reduced possibility of P fixing because of minimal soil contact [18,19]. This was well evidenced in chitosan and sodium alginate coated 100% DAP treatments. This was also supported by [20] and [21]. It is also in agreement with the findings [22] who found that lignin-coated TSP and rosin-coated DAP boosted P availability while decreasing P fixation in calcareous soils. Similar results were reported by [23] who observed that rosin-coated DAPs controlled P fixation in calcareous soils and availability of P was found for extended periods of time. The uncoated DAP and SSP recorded lower leachate P values during the incubation period which may be due to the fact that water soluble fertilizer would have released P in a short period of time and the released P would have precipitated or adsorbed on calcium carbonate and other soil constituents [24, 25]. **The soil under study is with high level of**

calcium carbonate content(18%) where applied P might have fixed as calcium phosphate. The application of coated fertilizer releases P in a controlled manner, P is less available for fixation with calcium, and hence P fixation in calcareous soil can be minimized, thereby period of P availability will be extended

While uncoated SSP recorded the lowest leachate P on 30th (14.8 ppm) and 40th (12.0 ppm) day of incubation. In the latter stages of incubation period, the T2 -100 % chitosan coated DAP had high P on 50th and 60th day (11.0 & 5.1 ppm respectively) followed by T4 –sodium alginate coated 100% DAP which were significantly comparable with each other. The uncoated SSP (T5) and uncoated DAP (T6) registered the lower leachate P as 2.2 and 2.6 ppm respectively on 60th day of incubation. Soil available P decreases at the end of sampling, because of the time dependent sorption - precipitation reactions between soil added and native P [26,27,28].

3.2. Nitrate nitrogen in leachate

Since DAP contains 18 % N, release of nitrogen through the fertilizer was evaluated by analyzing ammoniacal and nitrate nitrogen in the leachate samples. But there was no presence of ammoniacal nitrogen in leachate. Nitrate fractions were only found in leachate. The releasing trend of nitrate nitrogen is given in table 2.

The releasing trend of nitrate nitrogen was similar to phosphorus up to 20th day of observation, which means, nitrate value increased up to 3rd stage there after decreased in all treatments. The uncoated DAP (T6) recorded the highest value of nitrate nitrogen among all other treatments, up to 20th day of observation (Fig.3). During the first stage, uncoated DAP (T6) had high nitrate (21 ppm) was comparable with 100 % chitosan coated DAP (T2) (19.6 ppm). Similar trend was noticed on 10th and 20th day with uncoated DAP (T6) recording highest nitrate value (36.4 and 47.6 ppm respectively) which was followed by coated DAP (T2 and T4) and the lowest value was obtained for SSP treated soil (7.28 and 7.0 ppm respectively). Since uncoated DAP contained no membrane coating, dissolution of nutrients will be easier as compared to coated ones and that would have resulted in high value of nitrate in leachate in those treatments. The P release profiles of the coated DAP granules with biobased oil reached the equilibrium stage approximatively after 144 hours, compared to the untreated DAP granule, which is completely solubilized in less than 2 hours [29]. Results of 30th day sampling revealed that values of nitrate from chitosan coated DAP at both dosages (T1 and T2) and sodium alginate at 100% level (T4) was comparable. While on 40th and 50th day leachate sample recorded high value of nitrate for 100% chitosan coated DAP (30.8 & 23.5 ppm respectively) which was on par with T4 (25.2 ppm) and T6 (24.6 ppm) but on 50th day latter (17.9 ppm) was comparable with T1(17.0 ppm) and T3 (15.1 ppm). In the last stage also, coated DAP treatments (T2 & T4) recorded higher values

of nitrate nitrogen as compared to other treatments. The DAP fertilizer coated with organic polymer like chitosan and sodium alginate would have slowly disintegrated in the initial stages and further they would have dissolved with progress in period of incubation when contact with soil that might have resulted in higher values of nitrate nitrogen in T2 and T4 treatments. The increased concentration of $\text{NO}_3\text{-N}$ in the leachate from the controlled-release fertilizers towards the end of the leaching analysis revealed that the release of nitrate nitrogen from the coating and subsequent hydrolysis and nitrification takes a little longer [30]. It was also reported [31] that urea coating with ethyl cellulose had very slow releases in the beginning, then a consistent release, followed by a period of declining release of N and he also observed same trend with lignin based controlled urea fertilizer. It is in agreement with the work of [32] who studied double coated urea with polyacrylic acid - celite and sodium alginate and reported that steady increase in N release of 39 to 94 percentage with progress in incubation period from two to twenty-five days. It is also confirmed with leaching column study [33] who found that commercially available controlled-release formulations had significantly lower leaching losses of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ than dry soluble fertilizers. In all the stages 100% recommended dose of SSP registered lowest value of nitrate nitrogen, since the fertilizer contained no nitrogen and the nitrate nitrogen was contributed from the soil available pool of nitrogen only.

Average value of the nutrient release for seven sampling days revealed that the 100% chitosan coated DAP had released high amount of phosphorus (12.8 ppm) per leachate sampling compared to all other treatments during the period of experimentation which implies steady release of the coated fertilizer. The single super phosphate (SSP) applied treatments had shown less amount of leachate P because of the quick dissolution of fertilizer and conversion to insoluble P. The same trend was observed in case of leachate $\text{NO}_3\text{-N}$ (Figure 4).

3.3. Changes in leachate pH and EC

Leachate samples collected during the initial and final stages were analyzed for pH and EC, and the relevant data is shown in table 3. There was not much variation in pH and EC between initial and final sampling leachate due to treatments. However, numerical increase in pH and EC were noticed in the last stage (60th day) leachate sampling as compared to initial stage. The values recorded for pH were from 7.55 to 8.01 on 1st day and from 7.86 to 8.39 on 60th day sampling for various treatments. Similarly EC values recorded for various treatments ranged from 0.32 to 0.68 dSm^{-1} on 1st day and from 0.48 to 0.77 dSm^{-1} on 60th day sampling (Table 3)

Table 1. Effect of coated Diammonium Phosphate fertilizer on leachate phosphorus at different interval days of incubation experiment (mean of four replications)

Treatments	Phosphorus in leachate samples (ppm) at different interval days of incubation						
	1	10	20	30	40	50	60
T1 - Chitosan coated 75% DAP	4.0	7.1	17.8	17.5	16.8	7.2	4.3
T2-Chitosan coated 100% DAP	4.2	8.5	22.8	19.7	18.6	11.0	5.1
T3-Sodium alginate coated 75% DAP	3.6	6.1	16.7	17.0	16.1	5.2	3.8
T4-Sodium alginate coated100% DAP	4.2	8.3	21.8	19.1	17.7	11.6	5.0
T5 - 100 % RDF (SSP)	6.0	8.8	15.8	14.8	12.0	4.0	2.2
T6-100 % RDF (DAP)	6.1	15.1	19.5	16.7	14.8	8.2	2.6
Mean	4.8	9.40	19.1	17.5	16.05	7.9	3.88
SED	0.37	0.36	0.45	0.41	0.62	0.52	0.57
CD @ 0.05	0.78	0.77	0.96	0.88	1.31	1.11	1.21

RDF –Recommended dose of fertilizer

Table 2. Effect of coated Diammonium Phosphate fertilizer on leachate nitrate nitrogen at different interval days of incubation experiment (mean of four replications)

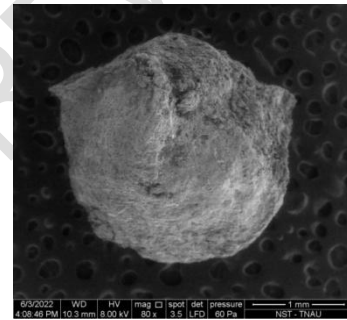
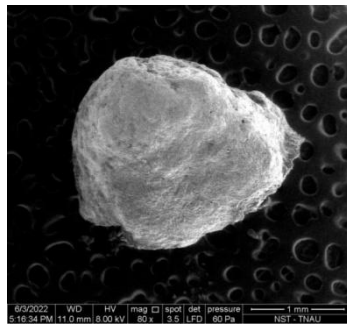
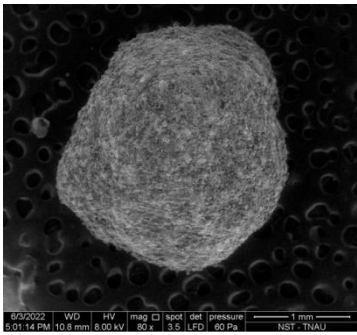
Treatments	Nitrate nitrogen in leachate samples (ppm) at different interval days of incubation						
	1	10	20	30	40	50	60
T1-Chitosan coated 75% DAP	12.6	28	37.9	28	18.2	17.0	8.4
T2- Chitosan coated 100% DAP	19.6	30.8	42	32.2	30.8	23.5	14
T3- Sodium alginate 75%coated DAP	12.6	25.2	39.2	26.6	15.4	15.1	9.8
T4- Sodium alginate coated100% DAP	14	29.4	42	30.8	25.2	23.2	12.6
T5- 100 % RDF (SSP)	6.4	7.28	7.0	9.5	7.8	6.7	5.6
T6- 100 % RDF (DAP)	21	36.4	47.6	26.8	24.6	17.9	10.5
Mean	14.36	26.18	35.95	25.66	20.34	17.26	10.16
Sed	2.13	1.85	2.28	2.09	3.33	1.65	1.79
CD @ 0.05	4.49	3.89	4.79	4.39	7.01	3.47	3.76

RDF –Recommended dose of fertilizer

Table 3: Influence of coated DAP fertilizer on pH and EC (dSm⁻¹) changes in incubation experiment (mean of four replications)

Treatments	pH at initial and final days of incubation		EC(dSm ⁻¹) at initial and final days of incubation	
	1	60	1	60
T1-Chitosan coated 75% DAP	8.05	8.29	0.32	0.51
T2-Chitosan coated	8.01	8.39	0.39	0.48

100%DAP						
T3-Sodium alginate		7.99	8.40	0.68	0.77	
75%coated DAP						
T4-Sodium alginate		7.65	7.86	0.42	0.55	
coated100% DAP						
T5-100 % RDF (SSP)		7.73	8.39	0.55	0.66	
T6- 100 % RDF (DAP)		7.55	8.27	0.54	0.65	
Mean		7.83	8.26	0.48	0.60	
CD @5%		NS	NS	NS	NS	



(a) (b) (c)
 Fig .1 Scanning electron microscopy (SEM) images at 80 x magnification for (a) uncoated DAP, (b) Chitosan coated DAP, (c) Sodium alginate coated DAP

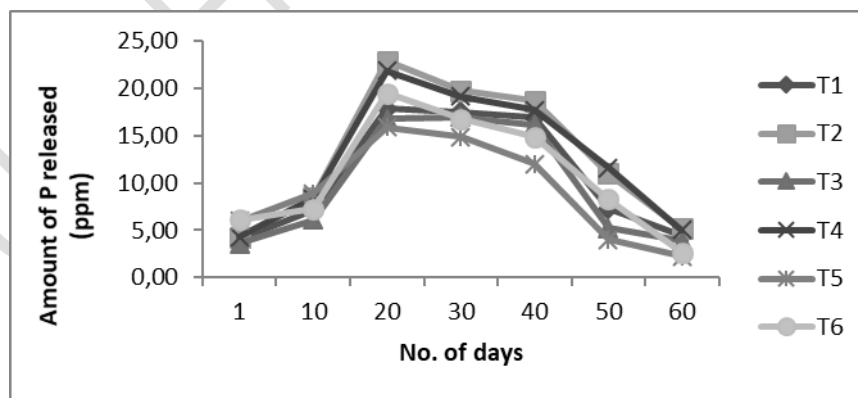


Fig. 2. Effect of coated Diammonium Phosphate fertilizer on leachate phosphorus (ppm) in incubation experiment

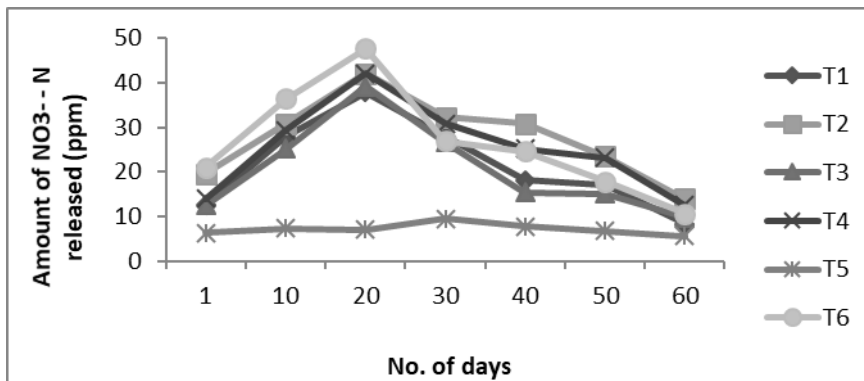


Fig. 3 Effect of coated Diammonium Phosphate fertilizer on leachate nitrate nitrogen (ppm)in incubation experiment

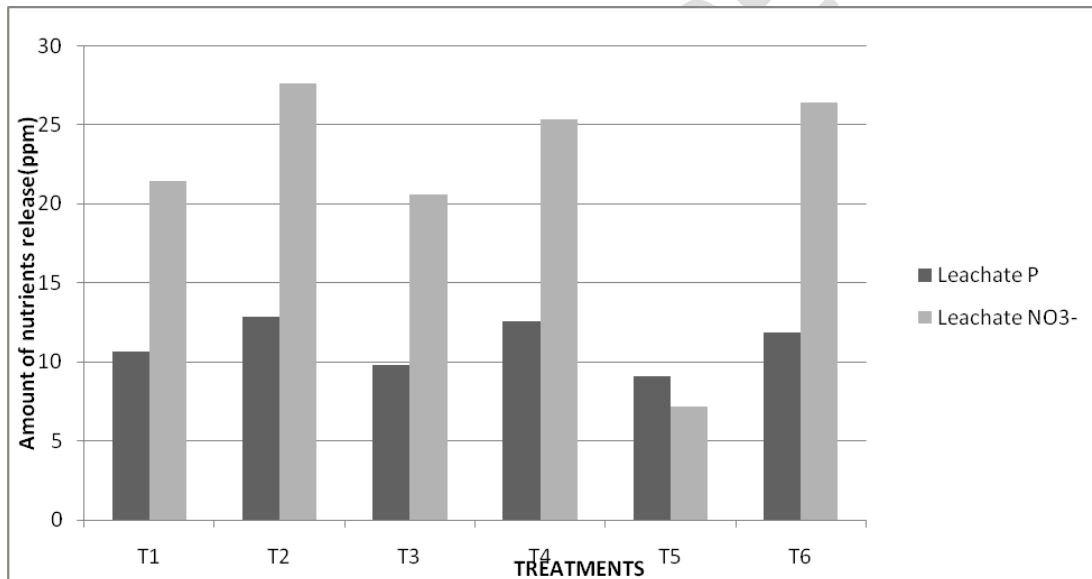


Fig. 4. Effect of coated Diammonium Phosphate fertilizer on leachate phosphorus and nitrate nitrogen (ppm)in incubation experiment(mean of seven sampling intervals)

4. CONCLUSION

The coating acts as a barrier, preventing soil-fertilizer contact and limiting interactions between the soil and nutrients (such as phosphorus fixation). The nutrient release can influence nutrient availability. Under calcareous soil conditions, coated DAP was found to be effective in releasing phosphorus slowly over an incubation period as compared to uncoated DAP and SSP fertilizers. Among the treatments, DAP 100 % coated with

chitosan and sodium alginate had slow rate of P release in the initial stages and there after it had steady release of P till last stage of leachate sampling. While uncoated DAP and SSP had faster release of P in the initial stages of sampling and there after P content in leachate was found lower. Similar trend was observed with nitrate nitrogen release for coated and uncoated DAP fertilizers.

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