

Effect of Phosphorus Loaded Organically Modified Nanoclay-polymer Composite on Release and Fixation of Phosphorus and its Uptake by Wheat (*Triticum aestivum L.*)

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A greenhouse pot culture experiment was conducted with wheat (variety: HD 3059) as a test crop to assess the effect of nanoclay-polymer composite made by in-situ polymerization of acrylic acid-acrylamide in presence of cetyltrimethylammonium bromide treated nanoclay on availability of phosphorus, its uptake by wheat, percent phosphorus fixation and phosphorus use efficiency at different growth stages viz. crown root initiation, tillering and flowering. Phosphorus uptake by plant increased from 3.32 mg kg⁻¹ in conventional diammonium phosphate fertilizer treatment to 8.71 mg kg⁻¹ in nanoclay-polymer composite treatment in Alfisol, the corresponding values for Inceptisol being 4.45 to 9.78 mg kg⁻¹. Soil phosphorus fixation percentage reduced from 60 to 19 in Alfisol and varied from 50 to 0 in case of Inceptisol at flowering stage while fertilizer phosphorus use efficiency increased from 16 to 47% in Alfisol and 21 to 51% in Inceptisol by changing diammonium phosphate application to phosphorus loaded nanoclay-polymer composite application. Therefore, the use of cetyltrimethylammonium bromide treated modified nanoclay-polymer composite as a fertilizer carrier would be a promising option to reduce production cost and increase nutrient use efficiency especially in case of phosphorus whose availability in soil is abysmally low.

Keywords: Modified nanoclay, cetyltrimethylammonium bromide, nanoclay-polymer composite, phosphorus, controlled release.

Phosphorus (P) is the second most important essential nutrient which acts as a catalyst in regulating various biochemical reactions that involve energy transfer inside plant. However, its unique chemistry in soil like high reactivity and slow rate of diffusion result in lower use efficiency, as only 15-30% of applied fertilizer P is taken up by the crops in the year of its application (Syers *et al.*, 2008). Soil application of phosphatic fertilizers due to their high solubility leads to fixation by soil constituents and consequently severe wastage and heavy economic loss of P occurs. Therefore, a supply system which can minimize P loss as well as supply P to crops synchronizing their P demand,

maintaining higher crop yield would be a promising option in reducing P losses.

In this context, nanoclay-polymer composites (NCPCs) are one of the recent alternatives to current fertilizer deployment and may act as a new viable option in regulating efficient nutrient supply. Nanoclay-polymer composites, a reaction product of clay-polymer interactions, represent a new class of materials in which nano-sized clay (at least one dimension) are dispersed in polymer matrix and have unique physical, mechanical and rheological properties (Brechet *et al.*, 2001). Reports indicated that increased cross linking density due to introduction of clay in polymeric network leads to controlled release property of NCPCs which can be synchronized with crop growth stage. This will

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minimize loss of nutrients, increase biomass yield and nutrient uptake (Wu *et al.*, 2008; Wang *et al.*, 2009). This slow release property of NCPCs can be utilized to increase nutrient use efficiency.

On the other hand, incompatibility between hydrophilic clay and hydrophobic polymer often causes agglomeration of clay mineral in the polymer matrix. Therefore, surface modification of clay minerals has become new avenue of research in field of NCPCs (Alexandre and Dubois, 2000). Organically modified NCPCs are prepared by treating clays with surfactants (quaternary ammonium salt: Cetyltrimethylammonium bromide, CTAB) resulting improved barrier properties of clay. Such modified clays are commonly referred to as organoclays. Hydrophobic nature of these clays offers tremendous improvement in mechanical and rheological properties but little information is available regarding nutrient retention and release from these modified NCPCs. With this aforementioned background, effect of organically modified NCPCs on release and fixation of P and its uptake by wheat grown in Alfisol and Inceptisol were studied.

MATERIALS AND METHODS

Preparation of modified NCPC

Organically modified nano-bentonite was prepared by replacing exchangeable ions of sodium (Na^+) with the quaternary ammonium salt: Cetyltrimethylammonium bromide (CTAB) as shown in figure 1. Nanoclay-polymer composites were synthesized from this modified nano-bentonite by the procedure as described by Liang and Liu (2007). Acrylic acid (11 ml) and acrylamide (2.3 g) were neutralized with ammonia at 60% (6.98 ml). 1.1 g of modified nano-bentonite and 15 ml of water were added to it. Under nitrogen atmosphere, the cross linker N, N-methylene bis-acrylamide was added @ 0.5% (0.06 g) to the acrylic acid/acrylamide/clay mixture solution and temperature was increased slowly to 70°C with vigorous stirring after the radical initiator ammonium persulphate (0.16 g) was introduced to the mixed solution.

Loading with diammonium phosphate (DAP) fertilizer

The prepared products were loaded with DAP fertilizer (14 gm DAP per unit weight of NCPC)

by immersing pre-weighed NCPCs in aqueous solution of DAP fertilizer solution for 24 hours to reach swelling equilibrium. Thereafter, the swollen products were dried at 60°C for 3 days. Finally, the dried products were milled, screened and stored for further analysis and use.

Soil

Two soil samples *viz.* Alfisol, *Typic Udorthents* (0-15 cm) from forest area of Purulia district, West Bengal, India (latitude 22°92'N, longitude 86°01'E) and Inceptisol, *Typic Haplustept* (15-30cm) from lawn of Division of Soil Science and Agricultural Chemistry, Indian Agricultural Research Institute, New Delhi, India (latitude 28°38'N, longitude 77°9'E) were collected for this study. The salient physico-chemical properties of soils are presented in table 1.

Test crop, location and climate

A greenhouse pot experiment was conducted with wheat (*Triticum aestivum L.*) [variety: HD 3059] as a test crop. The experiment was carried out in *rabi* season, December-March, 2014-15 at the ICAR-Indian Agricultural Research Institute, New Delhi, located at 28°38'N latitude and 77°9'E longitude, at an altitude of 228 m above sea level. The climate of the study area is semi-arid subtropical.

Experimental details

One kg of soil was filled in each pot and nitrogen and potassium were applied @ 80 mg N and 40 mg K_2O kg^{-1} of soil through urea and muriate of potash, whereas for P, DAP and modified NCPC loaded with DAP fertilizer were filled in nylon bags and applied to soils @ 40 mg P_2O_5 kg^{-1} soil after 7 days of seedling germination. Total three treatment combinations (control without P, conventional DAP fertilizer and DAP-loaded modified NCPC) in two types of soil was replicated thrice in a completely randomized design.

Sampling time

Soils were sampled thrice *i.e.* at crown root initiation (CRI), tillering and flowering stage. Thus 54 pots were required for this experiment. At each stage of sampling, shoots were cut, roots were separated from soil. Soils were mixed thoroughly and samples were taken for analysis. Moist soil sample was used for determination of available P and correction was done for moisture content.

Phosphorus content of soil

The soil samples were extracted with 0.5 M NaHCO₃; pH 8.5 (Olsen *et al.*, 1954). Phosphorus content in the extract was determined by ascorbic acid method (Watanabe and Olsen, 1965).

Phosphorus content of plant

A representative ground plant sample (0.5g) was taken for digestion. For pre-digestion in conical flask (100 ml) the plant samples were soaked overnight with 5ml of HNO₃ and finally digested in tri-acid mixture (HNO₃:HClO₄:H₂SO₄:: 9:3:1) on an electric hot plate following the procedure described by Piper (1967). The digested material was cooled, diluted with distilled water and filtered through Whatman No. 1 filter paper. The volume was made up to 100 ml in volumetric flask for further analysis. Phosphorus content in the acid extract was determined colorimetrically using vanadomolybdo yellow colour method in HNO₃ medium (Jackson, 1973).

Phosphorus content of nylon bag containing DAP and NCPC

Phosphorus content in NCPC and DAP in the soil-embedded nylon bag was determined after digestion of the material by the same process as in case of plant samples described earlier. The P content of nylon bag was then subtracted from total P added initially in nylon bag to get the actual amount of P released or sorbed to/from soil.

Determination of percent phosphorus fixation

Phosphorus fixation (%) was calculated based on different parameters as furnished in table 2.

$$\text{Phosphorus fixation (\%)} = \frac{((\text{P (control)} + (\text{P applied} - \text{P in nylon bag}) - \text{Phosphorus uptake by plant} - \text{available P}) / (\text{P (control)} + (\text{P applied} - \text{P in nylon bag})) * 100}$$

Where, P control = Phosphorus present in that soil where no fertilizer has been added

P applied = P applied through DAP and NCPC

P in nylon bag = P present in nylon bag at each sampling stage

Available P = Available P in soil at each stage which is determined by Olsen's reagent

Determination of phosphorus use efficiency (PUE)

Phosphorus use efficiency was calculated by using the formula as follows:

$$\text{PUE} = \frac{\text{P uptake by wheat (DAP/NCPC)} - \text{P uptake by wheat (control)}}{\text{Fertilizer P applied}}$$

RESULTS AND DISCUSSION

Available Phosphorus (P)

Addition of P loaded NCPC and conventional DAP maintained higher available P at different growth stages of wheat as compared to control in Alfisol (Table 3 a). There was a significant increase in available P from 1.85 (DAP) to 4.20 mg kg⁻¹ of soil (NCPC) at CRI stage. At tillering stage also available P was more in case of NCPC and again rose significantly from 3.38 (DAP) to 6.51 mg kg⁻¹ of soil (NCPC) at flowering stage. Overall, the mean value of available P was higher in case of NCPC as compared to DAP. Significant ($p < 0.05$) interaction effect between different fertilizer treatments and growth stages were found. It may be attributed to controlled release property of NCPCs as it maintained P supply over a longer period of time preventing build-up of high P concentration in soil. In case of NCPCs, introduction of clay in polymeric network results in more cross linking density reducing water absorbency or permeability and nutrient release (Zhang and Wang, 2007; Liang and Liu, 2007). Mikkelsen *et al.* (1994) also reported an improvement in chemical properties of soil when controlled release fertilizers were applied as compared to conventional fertilizers. Similar results were reported by Mandal *et al.* (2015) where zincated NCPCs recorded slower release of zinc as compared to conventional zinc sulphate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$).

Similar results were reported in Inceptisol also where NCPC application maintained higher available P over DAP irrespective of growth stages of crop. DAP resulted in an increase in available P throughout the growth stage of crop over control where no P was applied (Table 3 b). However, amount of available P was still lesser (4.73 mg kg⁻¹ of soil) than in case of NCPC (9.52 mg kg⁻¹ of soil). The interactive effect of growth stage and treatment was also found to be significant.

However, available P was higher in case of Inceptisol as compared to Alfisol. It was due to high P fixation by Al and Fe as the pH of Alfisol was 5.52 at which high P fixation occurs reducing its availability. The pH of 8.31 in Inceptisol resulted in medium P fixation by Ca and thus more availability of P. It has been reported by many researchers that P fixation in acid soils occurs

mainly due to its precipitation as Fe and Al phosphate (Chandler, 1941; Metzger *et al.*, 1941). Further, Ghani and AJeern (1943) conclusively proved that P accumulation in acid soil occurs mainly in form of iron and aluminum phosphate.

Phosphorus concentration in nylon bag

Results of the experiment showed P concentration in nylon bag was significantly affected by different treatments in Alfisol (Table 4 a). In case of DAP a continuous decrease was found from 0.20 to 0.06 mg kg⁻¹ throughout the crop growth stages whereas in NCPC it increased from 0.48 mg kg⁻¹ at CRI to 0.60 mg kg⁻¹ at tillering and again decreased to 0.39 mg kg⁻¹ at flowering. The reason behind this may be explained as once, P released from nylon bag, if not taken by crop, could be resorbed by NCPC in nylon bag, thus avoiding high build-up of P. In case of DAP, such

phenomenon was not possible. On an average, NCPC maintained a significantly higher P concentration over DAP irrespective of crop growth stage. Effect of treatments, growth stage and their interactive effect was found to be significant on P concentration in nylon bag.

NCPC also maintained a significantly higher P concentration at each growth stage (0.79, 0.76 and 0.64 mg kg⁻¹ of soil at CRI, tillering and flowering respectively) over DAP (0.23, 0.18 and 0.08 mg kg⁻¹ at CRI, tillering and flowering) in Inceptisol but considering the interaction effect, no significant differences were observed (Table 4 b).

Phosphorus uptake by plant

Phosphorus uptake by wheat increased significantly ($p < 0.05$) with application of fertilizers over control (Figure 2 a) in Alfisol. Significantly

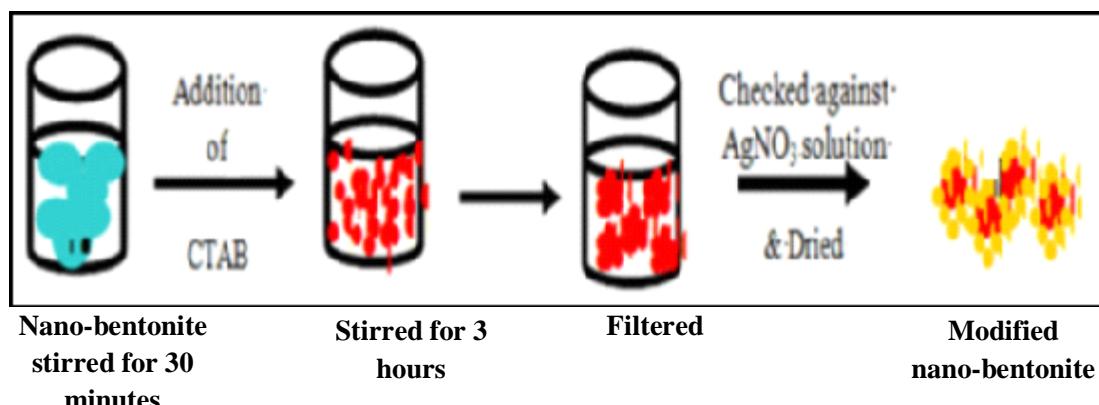


Fig. 1: Schematic process diagram of organo-clay preparation

Table 1. Some important physico-chemical properties of the experimental soils

Parameter	Inceptisol (IARI, New Delhi)	Alfisol	Reference (Purulia, WB)
pH _{1:2.5}	8.31	5.52	Jackson (1973)
EC _{1:2.5} (dS m ⁻¹)	0.24	0.12	Jackson (1973)
Mechanical composition			
Sand(%)	61.0	78.5	
Silt(%)	23.9	12.2	
Clay(%)	15.1	9.3	
Soil texture	Sandy loam	Sandy loam	Bouyoucos (1962)
Organic C (%)	0.18	0.48	Walkley and Black (1934)
Available N (kg ha ⁻¹)	90	240	Subbiah and Asija (1956)
Available P (kg ha ⁻¹)	13.4	2.21	Olsen <i>et al.</i> (1954)
Available K (kg ha ⁻¹)	79.3	43.5	Hanway and Heidel (1952)
Available Zn (mg kg ⁻¹)	4.87	2.74	Lindsay and Norvell (1978)

more P uptake was found in case of NCPC (4.81 mg kg^{-1}) over conventional DAP fertilizer (2.35 mg kg^{-1}). Phosphorus uptake increased significantly with growth stages irrespective of treatments. On an average, it increased from 0.86 at CRI to 4.20 mg kg^{-1} at flowering stage. The interactive effect of treatment and growth stages was significant.

In case of Inceptisol also, pots treated with NCPC resulted in significantly higher P uptake (6.34 mg kg^{-1}) over DAP (2.91 mg kg^{-1}). Effect of treatments, growth stage and their interactive effect was found to be significant (Figure 2 b).

This may be attributed to more nutrient availability in case of NCPC at critical growth stages of wheat and P uptake rate is proportional to P concentration in soil solution near root surface. Harring and Harrington (1993) reported that release of P from controlled release fertilizers took place at a rate that allowed growing plant to maintain maximum expression of their genetic capability. Moreover, the reduced P fixation as a result of slow release from NCPC might have resulted in its increased availability to crop (Bolan *et al.*, 1993). Similar results were reported by Chen *et al.* (2008) where application of controlled release fertilizer

resulted in improved nutrient uptake by crop at critical growth stages due to long term release of nutrient. Higher biomass yield as well as nutrient uptake was also reported by Sarkar *et al.* (2014) in case of pearl millet. Mukhopadhyay and De (2015) also reported that application of NCPC along with FYM resulted in higher biomass yield of lentil under rainfed condition due to more moisture retention and nutrient availability.

Percent P fixation

NCPC resulted in significant decrease in percent P fixation at each crop growth stage. At CRI stage, it was 83.3 in case of DAP whereas in case of NCPC it was 69.9. At tillering stage also, P fixation was less in case of NCPC but the decrement was less as compared to CRI. At flowering state, NCPC reduced P fixation to 19.1 from 60.6%. Overall, on an average NCPC resulted in less fixation of P in Alfisol (Figure 3 a).

In Inceptisol also, NCPC resulted in reduced P fixation. At CRI stage, it was 75.9% in DAP and reduced to 52.3% whereas at flowering stage NCPC resulted in no fixation. It was 50.1% in case of DAP which was reduced to 0.02% in NCPC. Also a significant effect of treatment as well as

Table 2. Values of different parameters used for calculating percent P fixation at critical growth stages of wheat in Alfisol and Inceptisol

Parameters	CRI	Alfisol		Inceptisol	
		Tillering	Flowering	CRI	Tillering
P control (mg kg^{-1})	0.69	0.52	0.43	2.99	2.65
P applied (mg kg^{-1})	17.46	17.46			
P in nylon bag (mg kg^{-1})	DAP	0.20	0.10	0.23	0.18
	NCPC	0.48	0.60	0.79	0.76
P uptake (mg kg^{-1})	DAP	1.16	2.57	1.09	3.17
	NCPC	1.32	4.40	8.71	4.45
Available P (mg kg^{-1})	DAP	1.85	3.38	3.78	5.18
	NCPC	4.20	6.51	8.09	9.42
					5.25
					10.8

Table 3 a. Effect of P loaded NCPC over conventional DAP on available P (mg kg^{-1}) in Alfisol

Treatment (T)	Growth stage (S)			Mean
	CRI	Tillering	Flowering	
Control	0.69	0.52	0.43	0.55
DAP	1.85	3.38	3.71	2.98
NCPC	4.20	6.51	8.09	6.27
Mean	2.25	3.47	4.08	
LSD ($P = 0.05$)	T = 0.36	S = 0.36	T×S = 0.62	

Table 3 b. Effect of P loaded NCPC over conventional DAP on available P (mg kg^{-1}) in Inceptisol

Treatment(T)	Growth stage (S)			Mean
	CRI	Tillering	Flowering	
Control	2.99	2.65	2.07	2.57
DAP	3.78	5.18	5.25	4.73
NCPC	8.38	9.42	10.8	9.52
Mean	5.05	5.75	6.03	
LSD ($P = 0.05$)	T = 0.20	S = 0.20	T×S = 0.35	

growth stages was found in this case (Figure 3 b). It can be explained by the fact that application of NCPC prevented build of high P concentration in soil by regulating its supply. Thus in NCPC treated soils, P concentration did not exceed fixation threshold level by a great margin. Hence, P fixation was lower than DAP treated soil. There are reports that P fixation from labile to non-labile pool occurred only when P concentration exceeded the fixation threshold level whereas its release from non-labile

pool to labile pool occurred at a concentration below the release threshold level (Datta, 2006). This implies that single application of phosphatic fertilizer due to their high solubility results in rapid reduction of available P (Barber 1985; Schnek 1987; Shaviv and Schnek, 1989). However, in case of NCPCs introduction of clay in polymeric network resulted in more cross linking density reducing water absorbency or permeability and nutrient release (Zhang and Wang, 2007; Liang and Liu,

Table 4 a. Effect of P loaded NCPC over conventional DAP on P concentration (mg kg^{-1}) in nylon bag in Alfisol

Treatment (T)	Growth stage (S)			
	CRI	Tillering	Flowering	Mean
DAP	0.20	0.10	0.06	0.12
NCPC	0.48	0.60	0.39	0.49
Mean	0.34	0.35	0.22	
LSD ($P = 0.05$)	$T = 0.03$	$S = 0.04$	$T \times S = 0.06$	

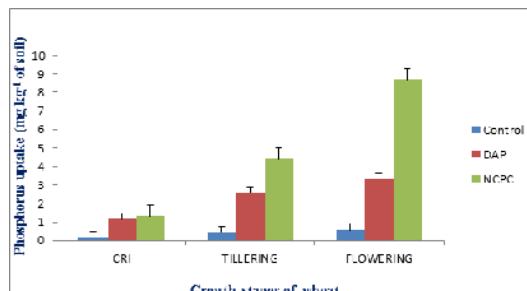


Fig. 2 a. Effect of P loaded NCPC over DAP on P uptake (mg kg^{-1} of soil) by wheat in Alfisol
Error bar represents the least significant difference (LSD, $P = 0.05$) between the three treatments

Table 4 b. Effect of P loaded NCPC over conventional DAP on P concentration (mg kg^{-1}) in nylon bag in Inceptisol

Treatment (T)	Growth stage (S)			
	CRI	Tillering	Flowering	Mean
DAP	0.23	0.18	0.08	0.16
NCPC	0.79	0.76	0.64	0.73
Mean	0.51	0.47	0.36	
LSD ($P = 0.05$)	$T = 0.04$	$S = 0.05$	$T \times S = \text{NS}$	

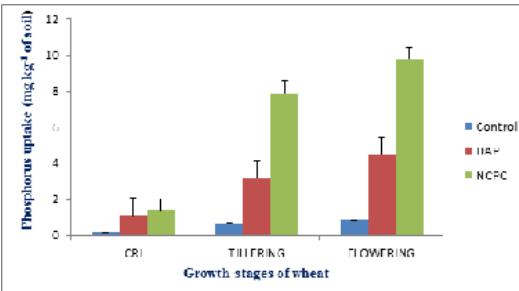


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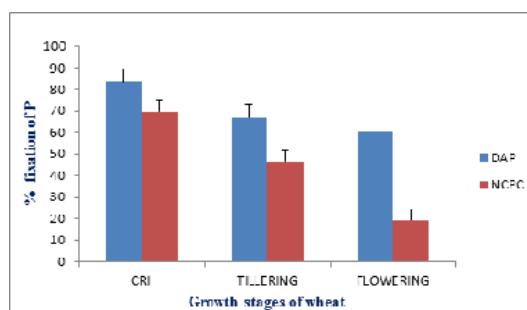


Fig. 3 a. Effect of P loaded NCPC over DAP on % fixation of P in Alfisol
Error bar represents the least significant difference (LSD, $P = 0.05$) between the two treatments

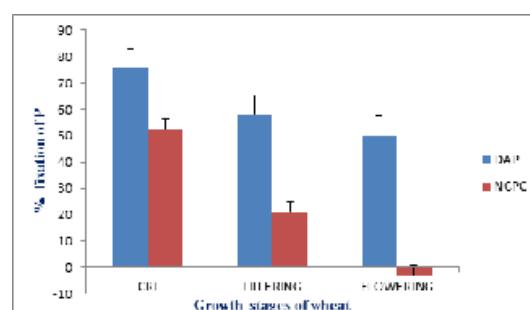


Fig. 3 b. Effect of P loaded NCPC over DAP on % fixation of P in Inceptisol
Error bar represents the least significant difference (LSD, $P = 0.05$) between the two treatments

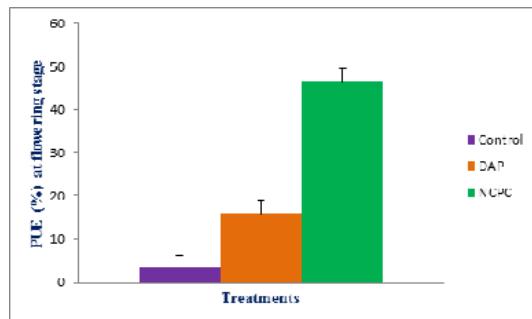


Fig. 4 a. Effect of P loaded NCPC over DAP on PUE (%) in wheat in Alfisol
Error bar represents the least significant difference (LSD, $P = 0.05$) between the three treatments

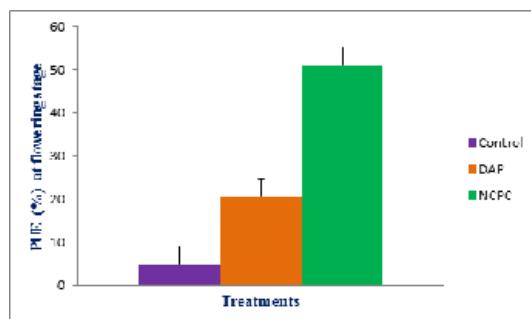


Fig. 4 b. Effect of P loaded NCPC over DAP on PUE (%) in wheat in Inceptisol
Error bar represents the least significant difference (LSD, $P = 0.05$) between the three treatments

2007). This reduction of fixation was less in case of Alfisol than Inceptisol due to presence of high content of Fe and Al in Alfisol at pH 5.52.

Fertilizer P use efficiency

Fertilizer P use efficiency increased from 16 to 47% by changing P application from DAP to P-loaded NCPC in case of Alfisol and the corresponding increase in efficiency in Inceptisol was from 21 to 51% at flowering stage (Figure 4a and 4 b). Hence, use of P loaded organically modified NCPC can be a promising option in reducing P-fixation and increasing PUE over DAP fertilizer.

CONCLUSIONS

Nanoclay-polymer composite prepared from CTAB-treated modified nanoclay resulted in more nutrient retention and optimum release rate properties in response to plants demand as compared to those from conventional DAP fertilizer. Therefore, use of organically modified NCPCs as a fertilizer carrier would be a promising option to increase nutrient use efficiency especially in P deficient soils.

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