

Phosphorus availability and adsorption kinetics of novel DAP encapsulated Nano clay polymer composites (NCPCs)

ABSTRACT

A controlled environment experiment involving maize, combined with a study on soil incubation, was executed to evaluate the impact of nanoclay polymer composites (NCPCs) loaded with DAP through in-situ and ex-situ polymerization reactions on phosphorus (P) availability and its adsorption kinetics. This research was conducted during the kharif season of 2023, spanning from July to September, at the Department of Soil Science and Agricultural Chemistry, Institute of Agricultural Sciences, B.H.U. Soil sub-samples were extracted and analysed at intervals of 5, 15, 30, 45, and 60 days post planting to assess P-availability. Concurrently, measurements were taken at 24, 72, 120, 168, and 240 hours to analyze P-adsorption kinetics. It was noted that the release of phosphorus was gradual in soil treated with encapsulated NCPC, particularly ex-situ NCPC, in contrast to conventional fertilizer. Moreover, phosphorus availability was found to be higher in NCPC-treated soil compared to conventional fertilizer, especially within the initial 45 days after sowing (DAS). The incubation experiment shed light on the dynamics of P-adsorption over a period of 240 hours. Greater adsorption was evident with 10 ppm solution in comparison to 20 ppm, while desorption was observed with 5 ppm solution initially. The peak adsorption occurred at 20 ppm, with levels stabilizing by the end of 240 hours. P-adsorption kinetics were more prominent in soil treated with phosphorus-loaded nanoclay polymer composite (NCPC) using the ex-situ method, as opposed to the in-situ method. Both first and second order kinetic models were found to be applicable for adsorption kinetics. Consequently, the experiment indicates that the ex-situ technique of fertilizer loading outperforms the in-situ method, possibly due to its capacity to enhance the polymerization of NCPC, leading to favorable results. The results imply that the integration of NCPC not only enhances crop growth but also contributes to the long-term sustainability of soil health through prolonged availability of nutrients.

Keywords: NCPC, in-situ and ex-situ polymerization, P-availability, P-adsorption kinetics

1. INTRODUCTION

Phosphorus (P) represents the second most crucial essential nutrient, serving as a catalyst in the regulation of diverse biochemical reactions associated with energy transfer within plants. Nevertheless, the distinct chemistry of phosphorus in the soil, characterized by its high reactivity and sluggish diffusion rate, leads to reduced utilization efficiency. Studies indicate that merely 15-30% of the phosphorus from applied fertilizers is absorbed by crops in the year of application (Syers et al., 2008). The application of phosphatic fertilizers to soil, owing to their high solubility, often results in fixation by soil components, leading to significant wastage and substantial economic losses of P. Diammonium phosphate (DAP) is widely utilized as a phosphorus fertilizer owing to its elevated nutrient concentration and advantageous

solubility properties. Nevertheless, traditional DAP fertilizers frequently encounter issues associated with phosphorus fixation, leaching, and runoff, resulting in diminished efficacy and environmental issues like water body eutrophication. In response to these challenges, recent progress in nanotechnology and material science has catalyzed the creation of novel fertilizer compositions designed to improve nutrient utilization efficiency and mitigate environmental impact.

Within this paradigm, NCPCs emerge as a pioneer and feasible alternative for the current fertilizer application methods, offering the potential to regulate the efficient supply of nutrients. Nano clay polymers exhibit promising potential for utilization in the field of agriculture in terms of providing nutrition and offering protection, owing to their small size, high surface-to-volume ratio, and distinctive characteristics. The global demand for fertilizers has been projected to show a continuous increase. Hence, there exists a pressing necessity to address the excessive utilization of both organic and synthetic fertilizers by exploring alternative approaches to the current deployment of fertilizers. Polymers demonstrate the ability to regulate the release of nutrients and function as vehicles for delivering nutrients. The potential applications of NCPCs in agriculture involve the encapsulation of materials at the nanoscale to achieve controlled release mechanisms (Brechet et al., 2001). According to multiple sources, the incorporation of clay into the polymeric framework enhances the cross-linking density, endowing NCPCs with a controlled-release capability that can be synchronized with crop growth stages (Verma et al., 2016). This will enhance biomass production, reduce nutrient loss, and improve nutrient uptake (Wu et al., 2008; Wang et al., 2009). The slow release characteristic of NCPC can be used to improve the efficiency of nutrient utilization.

The polymers exert a notable influence on the adsorption and desorption kinetics of nutrients in soil. Their contribution lies in enhancing adsorption through the provision of binding sites for nutrients, consequently improving retention and reducing leaching (Smith et al., 2020). Moreover, polymers have the capability to delay the desorption process by establishing a barrier that obstructs nutrient release (Johnson et al., 2018). This controlled nutrient release mechanism proves desirable for plant uptake. In essence, polymers serve as regulators of nutrient kinetics, thereby optimizing nutrient availability for plants, enhancing efficiency, and minimizing nutrient loss—a critical aspect in the realms of sustainable agriculture and environmental conservation.

Thus, understanding the kinetics governing the adsorption and release of phosphorus by NCPC is essential for comprehending its mechanism. However, various P intensity, quantity and buffering capacity indices have been used to predict the P release in soil, little information exist on the relation between P release rate parameters and order of kinetics governing the release of P in soil by NCPC especially, the encapsulated NCPC. Therefore, in order to grasp the aforementioned assertions, the aims of this research paper are as follows: i.) to compare the impact of conventional fertilizer and novel DAP loaded encapsulated NCPC on available phosphorus ii.) To evaluate the phosphorus adsorption kinetics of novel DAP loaded encapsulated NCPC in incubation.

2. MATERIAL AND METHOD

2.1. Synthesis and loading of Nanoclay polymer composite (NCPCs) with phosphorus

The bottom up method was used in synthesis of the unique encapsulated DAP loaded nanoparticles. With a few modifications, NCPCs were synthesized using the methods outlined by Liang and Liu (2007). Two different methods—in-situ and ex-situ loading—were used to integrate phosphorus into NCPC. In the first technique, a measured quantity of KH_2PO_4 and DAP was introduced during the polymerization process. While in the second approach, a specified amount of an aqueous solution containing KH_2PO_4 and DAP in distilled water was prepared. Once equilibrium was reached, pre-weighed dry NCPC samples were submerged in this solution.

2.2. Phosphorus kinetics study

2.2.1. Pot experiment

A greenhouse pot experiment was carried out in kharif season of 2023, July to September, at Department of Soil Science and Agricultural Chemistry, Institute of Agricultural Sciences, B.H.U. Varanasi, U.P. An alluvial soil with predominance of illite, quartz and feldspars minerals was collected from the farm of BHU for pot experiment. Maize (*Zea mays* L.) was grown in 10 kg capacity pots under 10 treatments with 4 replications. Prior to sowing, fertilizers and NCPC were added in accordance with the treatment plan. Fertilizer sources including 100% potassium and phosphorus and 50% urea were administered as the basal dose while other 50% urea was added as top dressing. Soil samples were drawn at 5, 15, 30, 45 and 60 days after planting to study the phosphorus availability.

2.2.2. Treatment details

Table 1: Details of treatments used in pot experiment:

Treatments notation	Description of treatments
T0	Recommended Dose of Fertilizer 120:60:40 Kg ha ⁻¹ (N ₂ :P ₂ O ₅ :K ₂ O)
T1	0 ppm DAP loaded NCPC, urea =77.64 ppm, MOP=22.30 ppm
T2	10 ppm DAP loaded NCPC, urea =73.70 ppm, MOP=22.30 ppm
T3	20 ppm DAP loaded NCPC, urea =69.80 ppm, MOP=22.30 ppm
T4	0 ppm DAP loaded NCPC-in-situ, urea =77.64 ppm,

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	MOP=22.30 ppm
T5	10 ppm DAP loaded NCPC-in-situ, urea =73.70 ppm, MOP=22.30 ppm
T6	20 ppm DAP loaded NCPC-in-situ, urea =69.80 ppm, MOP=22.30 ppm
T7	0 ppm DAP loaded NCPC-ex-situ, urea =77.64 ppm, MOP=22.30 ppm
T8	10 ppm DAP loaded NCPC-ex-situ, urea =73.70 ppm, MOP=22.30 ppm
T9	20 ppm DAP loaded NCPC-ex-situ, urea =69.80 ppm, MOP=22.30 ppm
T10	100% of N and K and 50% P through conventional fertilizer+ 50% P through 10ppm DAP loaded NCPC-in-situ
T11	100% of N and K and 50% P through conventional fertilizer+ 50% P through 10ppm DAP loaded NCPC-ex-situ

2.2.3. Incubation

For incubation study 100g of same soil as taken for pot experiment was taken in a plastic bottle and sub-samples were drawn to study the phosphorus adsorption kinetics at 24hrs, 72hrs, 120hrs, 168hrs and 240hrs. The soil sample were treated with different conventional and DAP loaded encapsulated NCPC treatments and data were recorded.

Table 2: Details of treatments used in incubation:

Treatments notation	Description of treatments
T1	5 ppm DAP
T2	10 ppm DAP
T3	20 ppm DAP
T4	5 ppm DAP NCPC-in-situ
T5	10 ppm DAP NCPC-in-situ
T6	20 ppm DAP NCPC-in-situ
T7	5 ppm DAP NCPC-ex-situ
T8	10 ppm DAP NCPC-ex-situ
T9	20 ppm DAP NCPC-ex-situ

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2.2.4. First and second order kinetic of P

The release of P from each soil i.e., from both pot experiment and incubation, was then performed by successive extraction of P from a 2.5 g soil subsample with 40 ml 0.01 M CaCl₂ solution on an orbital shaker at 25°C from 0.25 to 72 h. The experiment was carried out in duplicate and a few drops of toluene were added to inhibit microbial growth. The suspensions were then centrifuged at 3000 rpm for 15 minutes, the supernatants were filtered and analyzed for total P according to Murphy and Riley (1962). The cumulative released P was plotted against time for each soil and different kinetic equations were fitted to the data.

The rate of P release from the soil sample is analyzed by the kinetic equations that are given in Table 3. The goodness of fit of each kinetic equation was assessed using the coefficient of determination (R²).

Table 3: Equations tested to describe P release kinetic data (Dang et al., 1994)

Kinetic equation	Parameters
First order: $\ln Q_t = \ln Q_e - k_1 t$	k_1 , first-order rate constant (h^{-1})
Second order: $1/Q_t = 1/Q_e + k_2 t$	k_2 , second-order rate constant [$(\mu g P g^{-1})^{-1}$]

Q_t ($\mu g P g^{-1}$) is the amount of P released after t hours, Q_e ($\mu g P g^{-1}$) is the amount of P release at equilibrium.

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3. RESULTS AND DISCUSSION

3.1. Impact of P loaded NCPC on available phosphorus in soil

Following the application of treatments to the soil, the quantity of available phosphorus was measured at 5, 15, 30, 45, and 60 days (Fig. 1). The lowest amount of Olsen-P were recorded in treatment T1, T4 and T7 where no P was added compared to treatments receiving P-fertilization, irrespective of sampling period. Regardless of fertilizer treatments, the availability of P generally declined steadily throughout the course of the sampling periods; however, the rate of decrease was significantly faster under RDF treated soils than that in NCPC treated soils whether it is in-situ or ex-situ, particularly during the early sampling periods. Furthermore, under equivalent fertilizer dosages, the P-availability was greater in NCPC-treated soil than in soil treated with conventional fertilizer, at least up to 45 days after sowing (DAS). Similar findings were documented by Sarkar et al. (2014). They observed a gradual availability of phosphorus and mineral-N in soil treated with NCPC in comparison to soil treated with conventional fertilizer. The slow release of phosphorus, observed in treatments T2 to T11 except T4 and T7 where P is 0ppm, can be attributed to the application of phosphorus via nanoclay polymer composite (NCPC). This unique delivery system appears to have resulted in a consistent presence of phosphorus throughout the entire growth period, as evidenced by the decreasing trend in phosphorus levels from 5 days to 60 days. The persistent discharge could potentially be attributed to the controlled and sustained release mechanism of the NCPC, guaranteeing an uninterrupted provision of phosphorus to the plants across an extended duration (Smith

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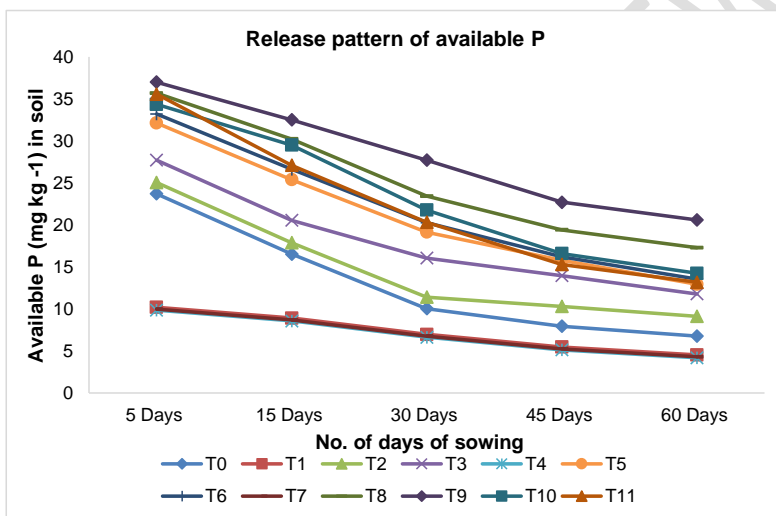
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et al., 2020). Similarly, treatments T5, T6, T8, T9, T10 and T11 exhibit a sustained slow release of phosphorus. This prolonged phosphorus availability is crucial for crop growth because it promotes higher nutrient uptake over time, which may enhance plant development, health, and yield. The experiment's findings indicated that using nanoclay polymer composite as a phosphorus carrier can be a useful strategy for long-term nutrient management, giving crops a steady supply of phosphorus over a longer growing season. These results showed promise for enhancing nutrient utilization in crop production and for sustainable agriculture.

Fig. 1: Effect of P loaded NCPC on slow release of plant available phosphorus (mg kg^{-1}) in soil



3.2. Comparison of kinetic equations to describe P adsorption kinetics

The adsorption of phosphorus (P) from various soil treatments exhibited rapid initial uptake within the first few hours, followed by a gradual slowdown until reaching a state of apparent equilibrium. The reduction in surface charge and consequent decline in interaction between the absorbed phosphorus ions likely contributed to the steady decrease in the rate of P release over time as the adsorption reaction advanced (Kuo and Lotse, 1974). McDowell and Sharpley (2003) suggested that the processes limiting the rate of short- and long-term phosphorus release reactions were probably P desorption and diffusion from within the soil particles. Desorption and diffusion-dissolution reactions were also associated with the initial rapid and subsequent slow phosphorus release processes (Smet et al., 1998). The adsorption kinetics (Fig.2) in soil treated with nanoclay polymer composite loaded with different sources of phosphorus were monitored on 24hrs, 72hrs, 120hrs, 168hrs and 240hrs for three different concentration of phosphorus (5, 10 and 20 ppm). The study investigated P adsorption dynamics for 10 days or 240 hrs.

Initially, higher adsorption occurred with 10 ppm compared to 20 ppm solutions, while desorption was evident with 5 ppm. By 72 hrs, maximum adsorption was seen with 20 ppm, followed by 10 ppm and 5 ppm. Adsorption increased over time, however with the rate declining gradually. 5 ppm DAP NCPC in-situ shows desorption dynamics within 24hr of incubation, but adsorption was observed thereafter. The adsorption was rapid initially, slowing after 120 hours, indicating nearing equilibrium for encapsulated DAP NCPC. The DAP NCPC ex-situ showed delayed but efficient adsorption, likely due to material characteristics. By the end of 240 hrs, adsorption reached a plateau, indicating maximum capacity.

The rate constants and coefficients of determination (R^2) obtained from these equations are presented in Table 4, respectively. Phosphorus sorption exhibited greater prominence in the soil subjected to treatment with a nanoclay polymer composite (NCPC) containing phosphorus via the ex situ technique as opposed to the in situ approach. This discrepancy can be ascribed to the impact of the trapped compound (KH_2PO_4 or DAP) on the process of polymerization and the structure of the polymer. In the in situ approach, the polymerization process might also have negative repercussions on the trapped compound (Liang et al., 2007). As a result, it can be inferred that a higher number of sorption sites were accessible in the NCPC generated through the ex situ method, despite the application of a lower phosphorus content, when compared to the in situ method utilizing a relatively higher phosphorus content. In the conducted experiment, observations revealed a gradual decline in the percentage of P adsorption with an increase in the levels of added P. This decline was expected due to the decrease in electric potential of the reactive surfaces caused by the introduction of additional P fertilizer, rendering them less favorable for subsequent P adsorption. First order (Fig.3.) and second order kinetics models (Fig.4.) were found to be applicable when R^2 values from different plots fitting the data from the adsorption experiment were compared to each other. In most instances, the second-order equation offered a more accurate depiction of the reaction rate, according to the R^2 values.

Table 4.a. Rate constant of first order kinetics equation (K_1 and R^2 values) fitted to phosphate sorption data in different treatment of soil

Treatment	5 ppm		10 ppm		15 ppm	
	K_1	R^2	K_1	R^2	K_1	R^2
T0	0.007	0.869	0.0054	0.902	0.0083	0.842
T1	0.0027	0.669	0.0053	0.931	0.0055	0.979
T2	0.0034	0.816	0.007	0.773	0.0052	0.804
T3	0.0052	0.769	0.0056	0.934	0.0045	0.933

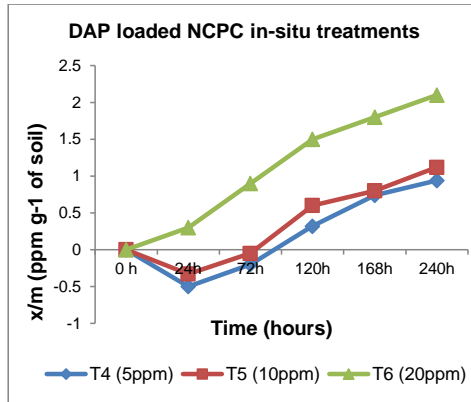
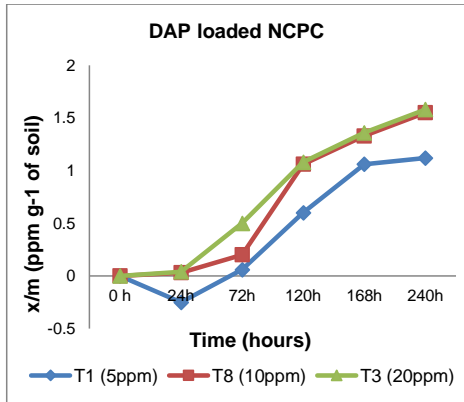
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T4	0.0031	0.814	0.0045	0.756	0.0042	0.895
T5	0.0021	0.894	0.0057	0.935	0.0049	0.924
T6	0.0061	0.908	0.0055	0.933	0.0052	0.757
T7	0.0042	0.769	0.0056	0.934	0.0045	0.933
T8	0.0026	0.879	0.0041	0.0942	0.004	0.828

Table 4.b. Rate constant of second order kinetics equation (K_2 and R^2 values) fitted to phosphate sorption data in different treatment of soil

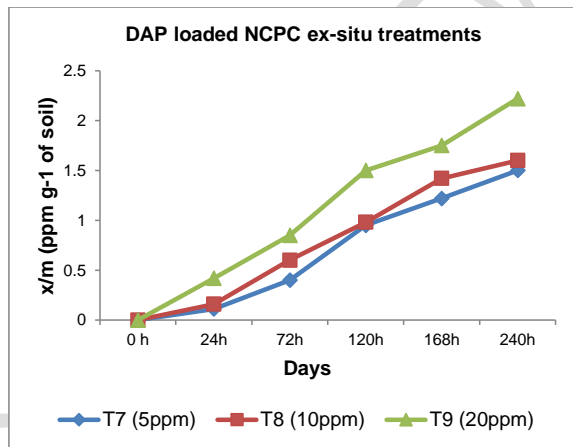
Treatment	5 ppm		10 ppm		15 ppm	
	K_1	R^2	K_1	R^2	K_1	R^2
T0	-0.0008	0.893	-0.0006	0.945	-0.0004	0.938
T1	-0.0004	0.7951	-0.0006	0.841	-0.0004	0.915
T2	-0.0002	0.621	-0.0004	0.932	-0.0003	0.978
T3	-0.0005	0.91	-0.0004	0.993	-0.0005	0.942
T4	-0.0003	0.821	-0.0006	0.839	-0.0004	0.825
T5	-0.0002	0.894	-0.0001	0.843	-0.0003	0.798
T6	-0.0004	0.875	-0.0003	0.694	-0.0004	0.782
T7	-0.0002	0.621	-0.0004	0.832	-0.0003	0.878
T8	-0.0002	0.881	-0.0003	0.949	-0.0002	0.843

Fig. 2. Effect of NCPC on P adsorbed per unit mass of adsorbent(x/m) vs Time (hours)



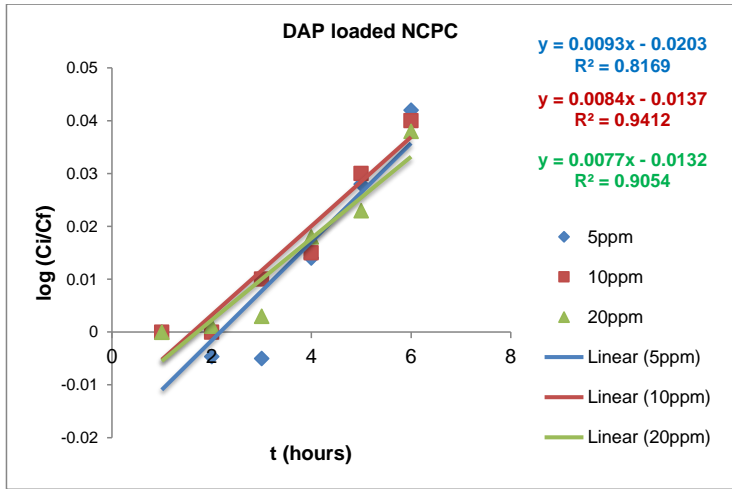
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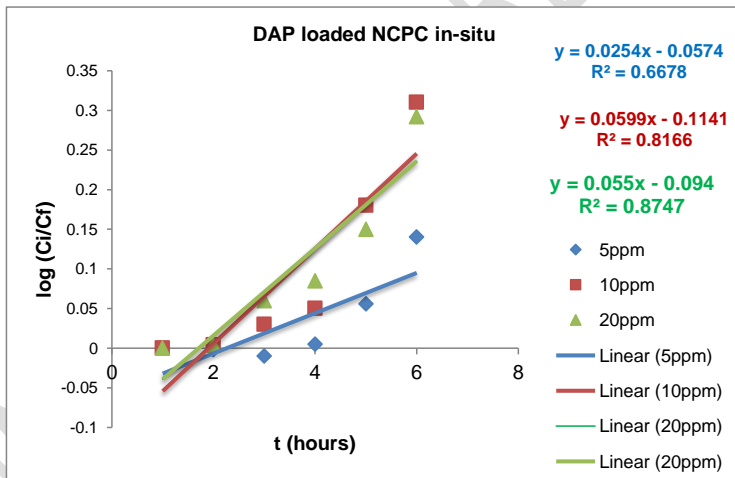


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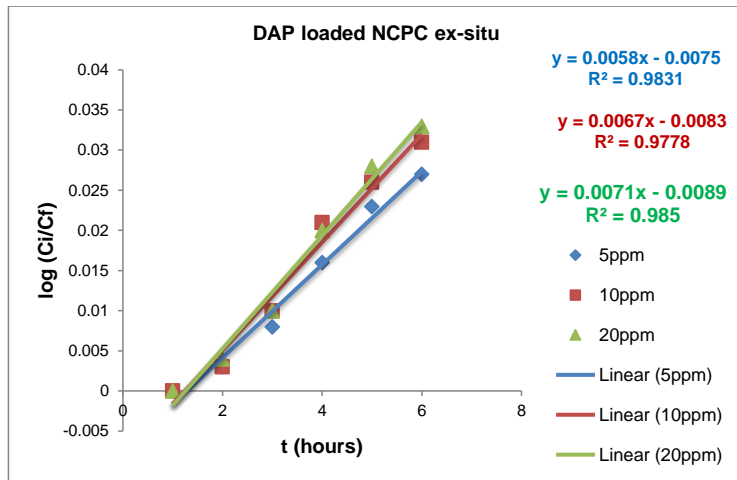
Fig.3. Plot of first order kinetic equation for P sorption



a

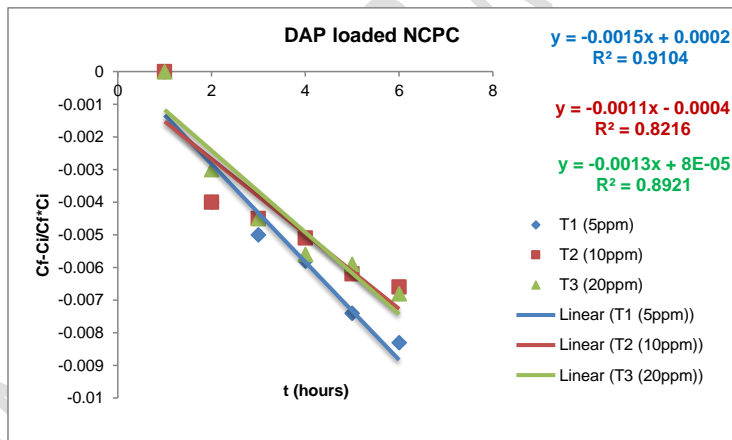


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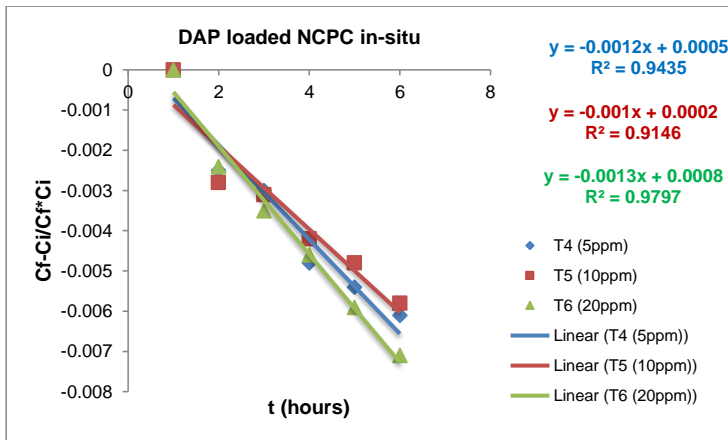


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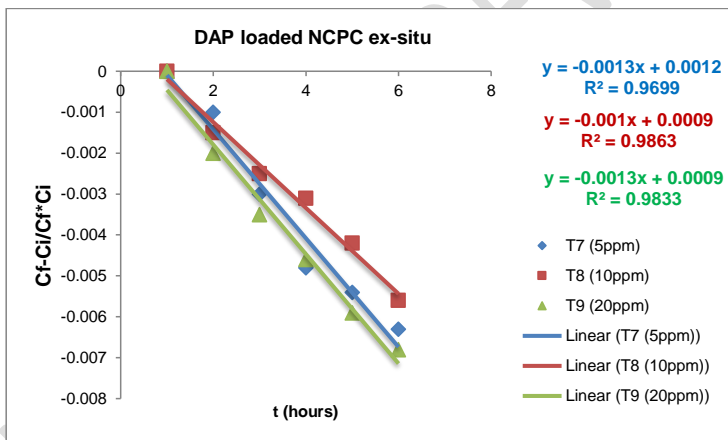
Fig.4. Plot of second order kinetic equation for P sorption



a



b



c

4. Conclusion

Upon comprehensive analysis of the effects of DAP-loaded nanoclay polymer composite (NCPC), it becomes apparent that employing the complete recommended dose of KH_2PO_4 and DAP embedded in NCPC via the ex-situ method stands out as the most appropriate approach for crop cultivation and enhancing phosphorus utilization efficiency. This approach guarantees prolonged phosphorus availability, rendering it a preferable option. Remarkably, even utilizing half of the recommended phosphorus dosage in conjunction with NCPC yields favorable outcomes. It can be concluded that the ex-situ method of fertilizer loading surpasses the in-situ method, likely due to its ability to facilitate enhanced polymerization of NCPC, resulting in favorable outcomes.

The results imply that the application of NCPC not only enhances crop growth but also plays a part in the comprehensive maintenance of soil quality through the assurance of extended fertilizer presence. This highlights the importance of adopting new technologies as they are crucial in promoting sustainable and efficient agriculture practices while protecting soil integrity.

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