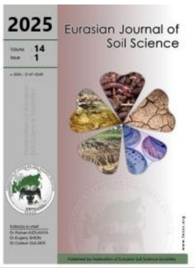
Eurasian Journal of Soil Science 2025, 14(1), 87 - 97

Eurasian Journal of Soil Science

Journal homepage : http://ejss.fesss.org



Zeolite-based nano phosphatic fertilizer for enhancing phosphorus availability in acidic soils of Assam, India

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Article Info
Received : 08.05.2024
Accepted : 11.11.2024
Available online: 14.11.2024

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Abstract

Considering the fixation and low availability of conventional phosphatic fertilizer in acidic soil, zeolite based nano phosphatic fertilizer was synthesized to investigate its release characteristics in acidic soil system via *invitro* studies. Result revealed that surface modification through a cationic surfactant improved the adsorption capacity of zeolite for phosphorus by 60%. Under the incubation study, the zeolite based nano phosphatic fertilizer sustained the release of phosphorous up to 90 days of incubation against 32 days under conventional SSP. The 100% replacement of RDP through nano fertilizer registered the maximum release of P in soil up to 9.36 mg/kg which was 23.80% higher than conventional SSP (7.56 mg/kg). The study release kinetics also revealed parabolic diffusion equation (3.012 µg/g/day) as the most suitable module for describing the P release as compared to other kinetic modules. Thus, zeolite can be used as carrier material for preparation of nano fertilizer for sustainable release of P for longer period of time under acidic soil.

Keywords: Zeolite, nano fertilizer, slow release, acid soil, parabolic diffusion, soil chemistry.

Introduction

Phosphorus, an essential macronutrient required for agricultural production (Wahid et al., 2020) is a principal component of cell membrane system, chloroplast, and mitochondria (Cordell et al., 2014). The requirement of phosphorous for various metabolic activities including growth of various plant parts of plant is already well established (Bindraban et al., 2020). Plants generally take up inorganic phosphorus ($H_2PO_4^-$ and HPO_4^{2-}) from soil solutions (Ibrahim et al., 2022), which accounts for about 35% to 70% of the total phosphorus present in soil system (Wilson et al., 2019). However, the movement of phosphorus in soil is subjected to different forms of losses, making it hurdle for a healthy growth of the crop. In acidic and highly weathered soils, 75-80% (Mahmood et al., 2021) of applied P is fixed onto the surfaces of Fe and Al oxides and hydroxides (Prüter et al., 2020) besides clay mineral lattices to form various complexes (Arai and Sparks, 2007), thereby reducing the available P concentration necessary for plant uptake. Leaching is another form of loss of P from the soil solution (Wakelin et al., 2017). Commercially available P sources, heretofore, are utilized to upgrade the agronomic production to meet the basic requirement (Sharpley et al., 2018). These sources contain water soluble phosphate salts which hardly provide 10-25% (Tarafdar et al., 2015) of P to the crops and the rest often wind up percolating to surface water bodies and coastal ecosystems through run-off or seepage, exacerbating the environmental degradation caused by

: https://doi.org/10.18393/ejss.1585148
: https://ejss.fesss.org/10.18393/ejss.1585148
Publisher : Federation of Eurasian Soil Science Societies
e-ISSN : 2147-4249

eutrophication (Conjin et al., 2018). Nano fertilizer shows promising outcomes to improve nutrient availability by exploring unique properties of nanoparticles (Poddar et al., 2018, Noruzi et al., 2023). They are nutrient carriers of dimensions ranging from 1-100 nm in size (Liu and Lal, 2014), having high surface area to volume ratio (Kumar et al., 2017). One of the major attributes is that they have small particle size (Chinnamuthu and Boopathi, 2009) which provides better penetration into the cell, activating plant and microbial functions for more plant nutrients uptake (Montalvo et al., 2015). Apart from increasing the yield and quality of agricultural produce, nano fertilizer improves the soil health creating favourable habitat for soil flora and fauna (Tarafdar et al., 2015).

The surface modified zeolite can be explored as one of the carrier options for preparation of zeolite based nano phosphatic fertilizer (Bhardwaj et al., 2014) which absorbs both positive (K^+, NH_4^+) and negative (NO_3^-, PO_4^{3-}) ions for its slow release to soil system (Solanki et al., 2015). Zeolites are alumino-silicate minerals, which have a molecular sieve action due to their open channel network; they are composed of SiO_4 tetrahedra linked with oxygen sharing the negative charge created by the presence of AlO_2^- which is balanced by cations that neutralize the charge deficiency (Jakkula and Wani, 2018). The preferential ion exchange property of zeolite (Wei et al., 2011) help the plants to utilize most of the nutrients by minimizing waste either through leaching (Subramanian and Thirunavukkarasu, 2017), volatilization or fixation in the soil (Dhansil et al., 2018). Therefore, the present investigation was carried out to study and analyse the feasibility of zeolite enabled phosphatic nano fertilizer for P availability in strongly acidic ($pH < 5.5$) environment. The nutrient uptake capacity of the synthesized nanofertilizer was studied, followed by comparative assessment of nutrient leaching patterns of P from nanofertilizer and conventional fertilizer. An evaluation of different reduced doses of nano fertilizer was also carried out to gauge the optimum dose economically and ecologically important for maintaining balanced crop nutrition.

Material and Methods

Fertilizer preparation

The synthesis of surfactant modified zeolite (SMZ) and zeolite based nano fertilizer for P was done following the standard procedure (Bansiwal et al., 2006). As shown in Figure 1, the synthesis of the nano fertilizer, Zeolite A (Sigma Aldrich), hexadecyltrimethylammonium bromide (HDTMABr) (Sigma Aldrich, ≥ 98%) were used 1:100 ratio. The mixture was stirred with 1M concentration of KH_2PO_4 solution for 8 hours. A 1:10 (solid to liquid) ratio followed by distillation and air drying. The dried sample was grounded to a finer particle size. Similarly, nutrient incorporation was carried out on unmodified zeolite to study the effect of surface modification on nutrient uptake capacity in comparison to surfactant modified zeolite.

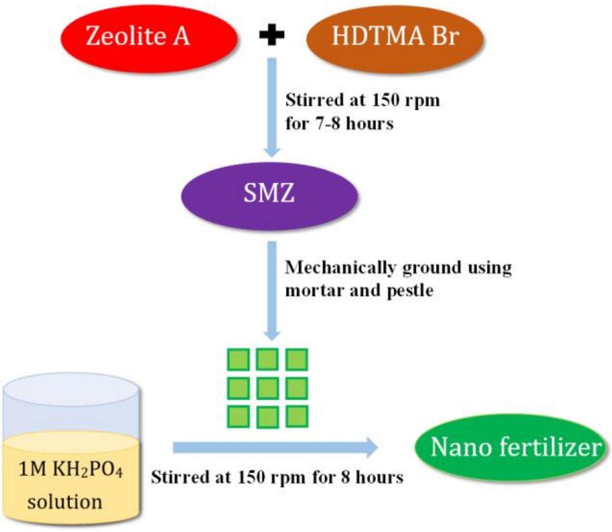


Figure 1. Schematic representation of preparation of Zeolite based nano P fertilizer

Characterization of the nano fertilizer

The unmodified zeolite and surfactant modified zeolite based nano phosphatic fertilizer were characterized by Powder X-ray diffractometer, Scanning Electron Microscope, Transmission Electron Microscope and Brunauer-Emmett-Teller adsorption isotherm. Crystal phase identification was conducted by powder X-ray diffraction. The powder X-ray diffractometer measurement was carried out on a Rigaku Ultima IV X-ray diffractometer of 2θ range using a Cu-Kα source of wavelength, $\lambda = 1.54$ Å. For examining the surface morphology, scanning electron microscopy images were acquired using a Carl Zeiss SIGMA scanning electron microscope. The compositional analysis of the synthesized nanoparticles was carried out by Energy Dispersive X-ray spectroscopy on an Oxford EDS attached to the same instrument. The particle size of the nano-fertilizer was assessed from the Transmission Electron Microscope images, which were recorded on a JEOL, JEM-2100 Plus Electron Microscope. Specific surface area, pore volume and pore diameter were analysed by Brunauer-Emmett-Teller surface area analyser on an Autosorb- iQ (Quantach – rome USA) adsorption analyser. The samples were degassed at 150ºC for 16 hours.

Collection and processing of soil for experimentation

The soil samples were collected from three different locations based on texture representing major soil orders of Assam, India. The vegetation cultivation area of Dhekorgorah block (Latitude: 26°82'18" N; Longitude: 94°31'53" E) of Jorhat district was taken for the soil order Inceptisols (silty clay loam). The rice cultivation area of Regional Agriculture Research Station (RARS), Titabar (Latitude: 26°34'51" N; Longitude: 94°10'50" E) was selected for soil order Alfisols (clay loam). The alluvium rich soil of Majuli (Latitude: 27°03'55" N; Longitude: 94°16'57" E) was taken for soil order Entisols (sandy clay loam). To conduct the incubation study, bulk surface soil samples (0-15 cm) from each site were collected and prepared following standard procedures. The analysis of initial soil parameters prior to application of fertilizers are given in Table 1.

Table 1. Initial physico-chemical properties of the soils

Parameters	Jorhat	Titabar	Majuli
Soil order	Inceptisol	Alfisol	Entisol
pH (soil:water :: 1:2.5)	5.34	5.07	5.53
Electrical conductivity (dSm^{-1})	0.02	0.03	0.03
Particle size distribution			
Sand (%)	19.00	42.00	60.00
Silt (%)	47.00	20.00	15.00
Clay (%)	34.00	38.00	25.00
Textural class	Silty clay loam	Clay loam	Sandy clay loam
Bulk density (g/cm^3)	1.35	1.32	1.39
Particle density(g/cm^3)	2.49	2.39	2.46
Moisture content at Field Capacity (%)	28.37	30.70	27.45
Organic carbon (%)	0.87	0.78	0.93
Available N (kg/ha)	347.61	298.70	361.70
Available P_2O_5 (kg/ha)	25.57	19.47	38.89
Available K_2O (kg/ha)	174.18	118.51	229.28
Exchangeable Ca^{2+}(cmol(p+)/kg)	1.87	2.73	3.21
Exchangeable Mg^{2+} (cmol(p+)/kg)	0.79	1.94	2.13
Cation Exchange Capacity (CEC)(cmol(p+)/kg)	8.19	8.22	7.23
Available S (mg/kg)	13.38	12.81	20.65

Incubation study

About 200 g of finely ground processed soil was placed in plastic containers of capacity 500 g and fertilizer was applied based on the recommended dose of fertilizer for maize (60:40:40 @ N: P_2O_5:K_2O kg/ha) before the incubation study. Recommended dose N and K remained constant throughout the treatments and P was supplied as per treatment mentioned below. Soils were incubated at room temperature (± 27°C) in the laboratory. A total of 10 sets were prepared for each periodical assessment for better results. The containers were partially closed for better gaseous exchange and limiting moisture loss. Soil moisture was maintained at field capacity during the entire period of experimentation. The loss in water content in soil was monitored at 3 days interval by addition of water as determined by the loss in weight of the containers.

Treatments included:

T_1 = Absolute control

T_2 = RDP through single superphosphate (SSP)

T_3 = RDP through nano fertilizer

T_4 = 2.5 times reduction of RDP from T_3

T_5 = 5 times reduction of RDP from T_3

T_6 = 10 times reduction of RDP from T_3

Samples were collected from the respective set at 0, 4, 7, 15, 22, 32, 44, 58, 74 and 90 days of incubation for analysis of the release pattern of P from the chemical and synthesized nano-fertilizer.

Kinetic equations

The rate kinetics of P was assessed based on first order, second order and parabolic diffusion as per the equations [3]:

First order : $\log C_t = \log C_o - kt$
Second order : $1/C_t = 1/C_o + kt$
Parabolic diffusion : $C_t/C_o = b + kt^{1/2}$

Where,

C_t = cumulative concentration of available P (μg/g)
C_o = concentration of P which can be released at equilibrium (μg/g)
k = rate constant
b = C_t/C_o when k = 0 or t = 0 (dimensionless)
t = time (days of incubation)

Statistical analysis

The data obtained under different treatments of each soil was statically analysed to see the significance of variance using Analysis of Variance (ANOVA) at 0.05 significance using IBM Statistical Package for Social Sciences (SPSS) Version 20. To compare the means post hoc analysis was done using Duncan's Multiple Range Test (DMRT).

Results and Discussion

Fertilizer characterization

The crystal phase of the synthesized nano P fertilizer was examined by the X–ray powder diffraction as displayed in Figure 2. The crystallinity of zeolite remained the same as diffraction peaks at 8.93° and 24.06° with indexes of (0 2 0) and (4 0 0) respectively, was seen in the spectrum, which is similar to parent zeolite (Mikhak et al., 2017). This suggests that there were no major structural changes in zeolite framework due to addition of HDTMABr surfactant except for minor changes in the intensity of the band's peak suggesting the retention of P ion within the porous structure of zeolite (Abdul Majid et al.,2018; Mir et al., 2020). The surface morphology of unmodified and modified zeolite was envisaged by scanning electron microscope as depicted in Figure 3. It was observed that the zeolite was of cubical geometry and the crystal lattice was mostly bound aggregates of small cubic particles. However, this was not clearly observed in case of modified zeolite. The particles of the modified zeolite appeared to have broken edges and corners possibly due to HDTMABr coverage on the external surface area of the crystal lattice, which also depicted the adsorption of P and other ion. Similar observations were also reported (Bansiwal et al., 2006; Yan et al., 2014).

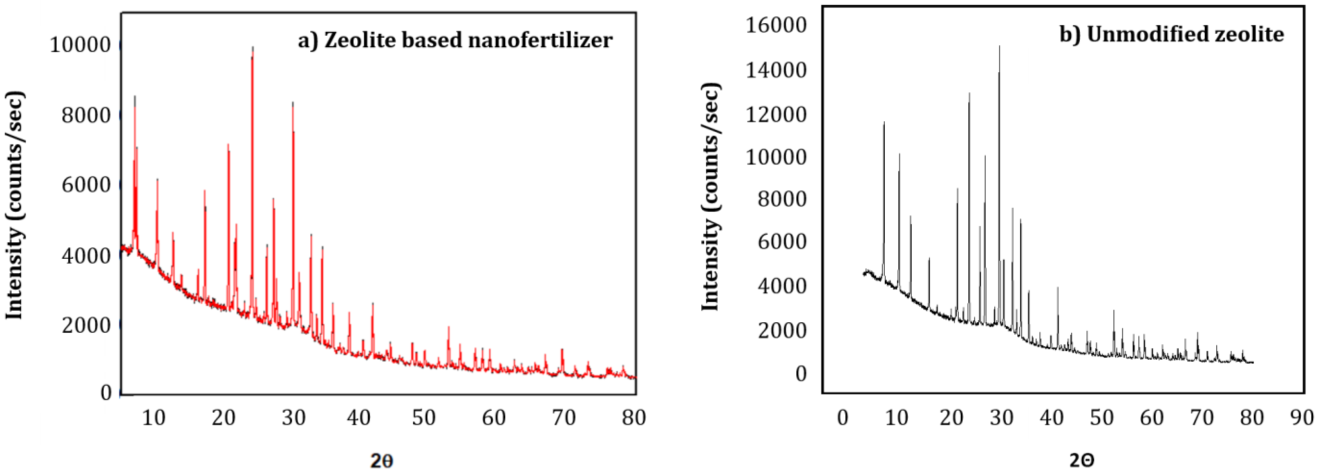


Figure 2. XRD (Powder X-ray diffractometer) patterns of (a) synthesized nano phosphorus fertilizer and (b) parent zeolite (for reference)

The elemental composition of the nano-fertilizer was acquired from the EDX pattern which established the existence of C, N, O, Al, Si, Br, Na, P and K in the compound. During the EDX measurement, different areas were focused, and the corresponding peaks are shown in the figure 4. The addition of surfactant greatly increased adsorption of added P upto 7.4% in nano fertilizer which was 60% greater than the unmodified zeolite. This implies that the surface modification altered the surface charge on zeolite which led to better adsorption of the anion (Akrami et al.,2019). Adsorption of K was also noted from the spectrum of the sample, probably due to presence of available exchange sites inside the crystal lattice of zeolite. Therefore, stacking of positively charged ions such as K in the pores can be attained together with the negatively charged ions such as P on their surface (Singh et al., 2018; Hagab et al .2018).

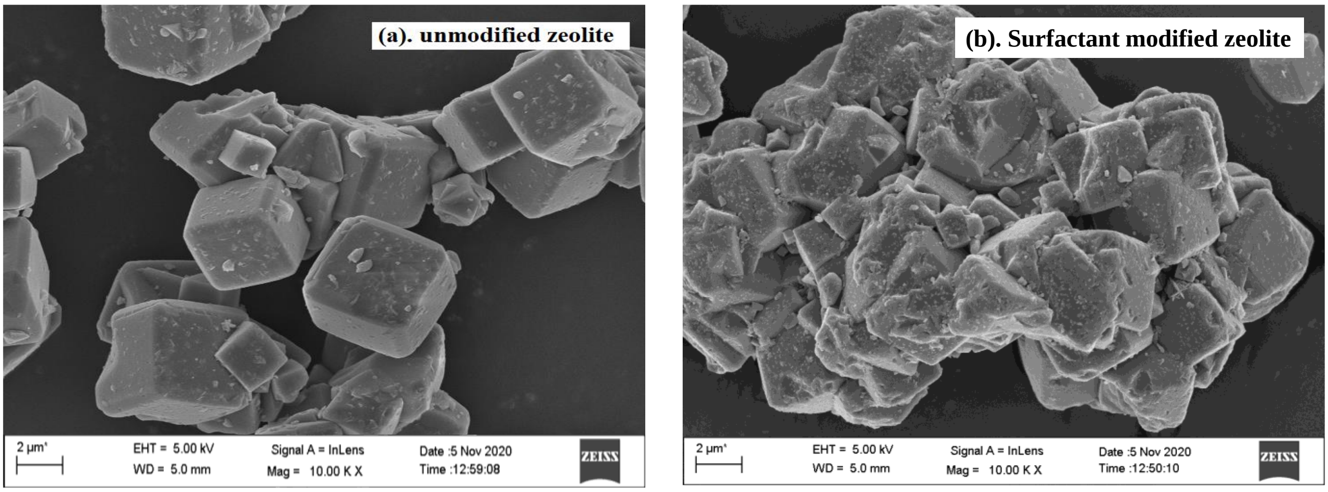
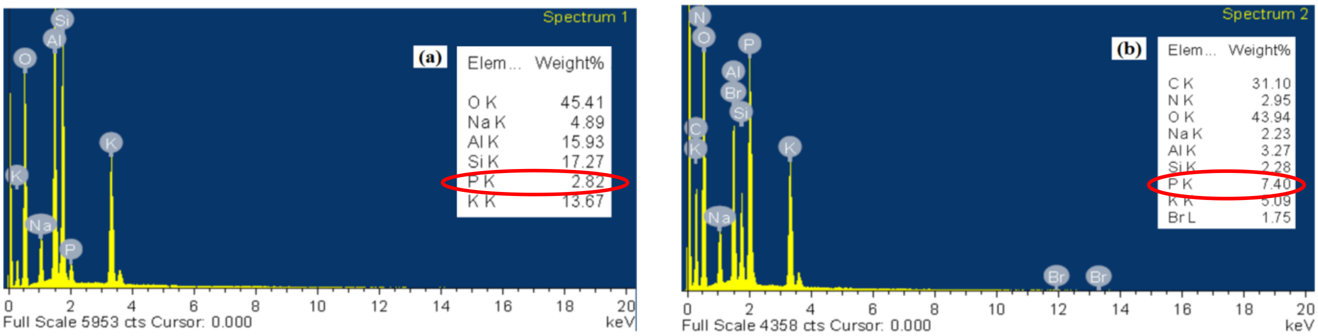


Figure 3. SEM images of (a) unmodified zeolite and (b) modified zeolite fertilizer



Elem...	Weight%
O K	45.41
Na K	4.89
Al K	15.93
Si K	17.27
P K	2.82
K K	13.67

Elem...	Weight%
C K	31.10
N K	2.95
O K	43.94
Na K	2.23
Al K	3.27
Si K	2.28
P K	7.40
K K	5.09
Br L	1.75

Figure 4. EDX pattern of the nano-fertilizer; (a) spectrum of unmodified zeolite loaded with phosphorus and (b) spectrum of surfactant modified zeolite loaded with phosphorus

From the figure 5, it can be seen that average particle size of zeolite based nano P fertilizer < 100 nm which clearly falls within the nanoparticle range of 1-100 nm (Liu and Lal, 2014; Montalvo et al., 2015). The small black dots observed in the images (Fig. 5a & 5b) were most probably the nutrient particles. As seen in the Figure 5(a), the channel like structures depicted the pores of the nano zeolite particles. In the closer resolution of the sample clear lattice fringes were seen which assured high crystallinity of the nanostructure (Figure 5c). Almost all the particles had been converted to nano zeolite particles as evident from the small black dots found in the images.

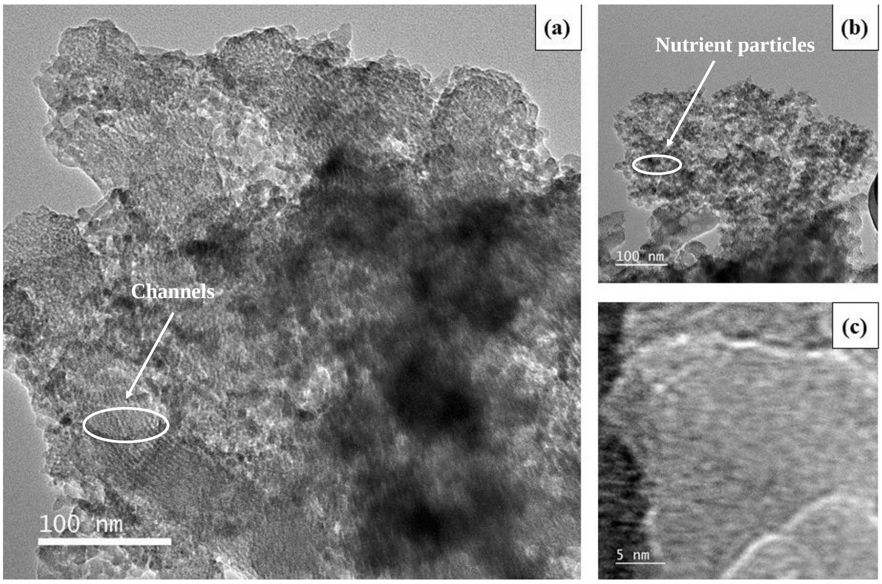


Figure 5. TEM image of the synthesized nano fertilizer

The data presented on Table 2 clearly illustrated that the specific surface area of the modified nano zeolite fertilizer comparatively less (90.07 m^2/g) than the unmodified zeolite (262.72 m^2/g). The specific surface area of zeolite was reduced due to surface modification and subsequent phosphorus loading (Salako et al., 2020). This means that in the pore space of zeolite, P had been loaded which had decreased the pore diameter. Hence, there was overall reduction of surface area of the fertilizer. The pore size was found to be microporous (< 20 nm) in diameter.

Table 2. Surface area, Pore volume and Pore diameter of unmodified and modified zeolite

Sl. No.	Parameters	Unmodified zeolite	Nano P fertilizer
1.	Surface area (m^2/g)	262.72	90.07
2.	Pore volume (cm^3/g)	0.129	0.016
3.	Pore diameter (nm)	6.2	1.2

Release pattern of P

The release pattern of P presented in Figure 6 clearly illustrated that incubation days and clay proportion of the soils played a significant role on release of P in the soil environment and showed a strong and positive interaction between level of treatments and days of incubation. The mean P concentration in control was seen to be declining from 0 to 22 days, then rising from 22 to 44 days, and again decreasing from 44 to 74 days with a slight increase from 74 to 90 days. The overall P level indicated that it was in well maintained equilibrium with respect to the initial P concentration of the soil. The P concentration in T_2 was observed to decrease from 0 to 7 days, with increase from 7 to 32 days. The maximum peak of P release was obtained on 32 days of incubation, after which there was a sharp decline in the release trend which continued up to 90 days of incubation. This might be attributed to low nutrient use efficiency (10-25%) of conventional phosphatic fertilizer (Tarafdar et al., 2015) where about 75-80% of the applied P is fixed by soil solids (Mahmood et al., 2021). Similarly, Dhansil et al. (2018) also reported that in case of chemical fertilizer, the availability of phosphorus greatly increased up to 30 days of incubation and declined afterwards.

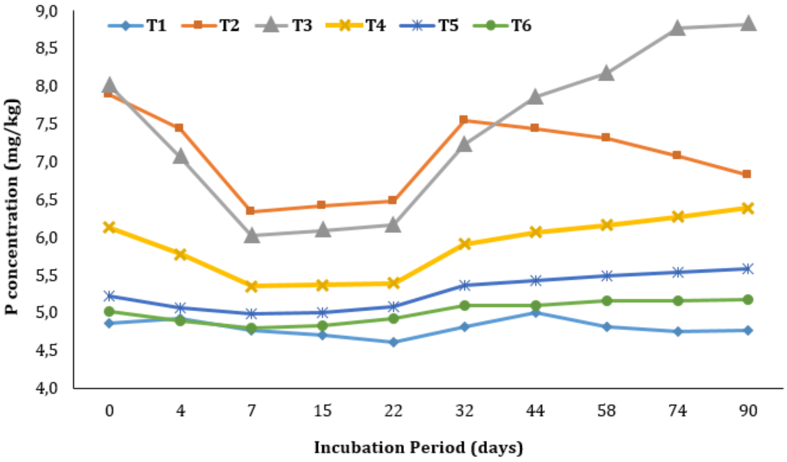


Figure 6. Release of P (mg/kg) as influenced by different levels of treatment over days of incubation (T1= Absolute control, T2 = RDP through single superphosphate, T3= RDF through nano fertilizer, T4 = 2.5 times reduction of RDP from T3, T5 = 5 times reduction of RDF from T3, T6 = 10 times reduction of RDP from T3) Error bars: standard deviation, N = 46

On the contrary, the release of phosphorus from nano fertilizer, showed a gradual increase after 22 days of incubation which was sustained throughout the investigation period. Similar observations have been reported through investigation of nano P formulations in acidic culture media (Mahmood et al., 2021). The release pattern was also similar for the reduced dosages of nano fertilizer applied in the different soil types. The maximum value was recorded on 90 days of incubation with further increasing trend as seen from the Figure 6. T_3 showed the highest increase in mean P levels compared to the other treatments. The slow release of nano-fertilizer might be attributed to the porous structural framework of the zeolite carrier (Singh et al., 2018). The phosphorus adsorbed onto the crystal lattice of zeolite most probably had undergone interaction between the surfaces inside the pores as well as surfaces outside the pores. The loosely bound elements and/or compounds from the top of the surface would release first, then the second layer would contribute and thereafter layer by layer the adsorbed phosphorus would be released by the nano-fertilizer. The influence of several biotic and abiotic factors of soil environment such as soil pH, temperature, humidity, etc., on the fertilizer allowed the zeolite to slowly detach nutrients from its structure (Bharadwaj et al., 2014)

Table 3: Effect of different fertilizer levels on P release in different soil types

Soil type	Treatment	P release
Sandy Clay Loam	T_1	7.51 ± 0.11a
	T_6	7.82 ± 0.25b
	T_5	8.03 ± 0.21b
	T_4	8.64 ± 0.37c
	T_2	9.91 ± 0.49d
	T_3	10.28 ± 1.04e
Silty Clay Loam	T_1	4.81 ± 0.11a
	T_6	5.07 ± 0.21b
	T_5	5.28 ± 0.22b
	T_4	5.88 ± 0.38c
	T_2	7.08 ± 0.52d
	T_3	7.42 ± 1.04e
Clay Loam	T_1	3.70 ± 0.94a
	T_6	3.99 ± 0.14b
	T_5	4.22 ± 0.22b
	T_4	4.79 ± 0.37c
	T_2	5.93 ± 0.58d
	T_3	6.17 ± 1.02d

Means under the same letter in a column are not significantly different at $p \leq 0.001$
*Average ± standard error, treatment has been arranged as descending order.

The P release pattern from the sandy clay loam textured soil presented in Figure 7a revealed highest P concentration in RD of P was applied through nano-fertilizer (10.28 ± 1.04) at 90 days of incubation, which was statistically higher than P released from SSP fertilizer (9.91 ± 0.49). Similarly, in silty clay loam textured soil (Figure 7b) and clay loam textured soil (Figure 7c) the mean P level of T_3 (7.42 ± 1.04; 6.17 ± 1.02, respectively) was found to be highest amongst all the treatment levels.

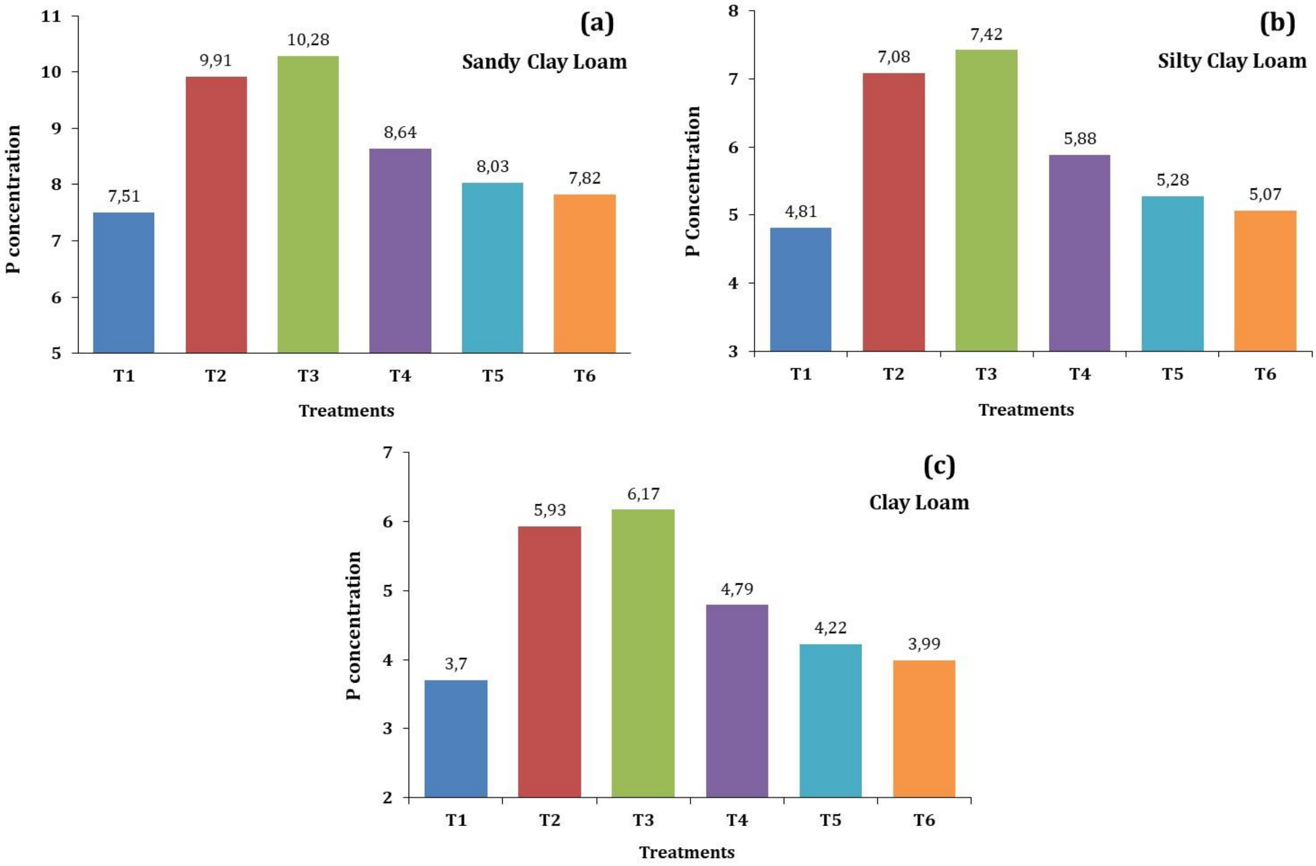


Figure 7. Phosphorus release pattern from different soil due to different treatment levels

The variation in clay content affects the P release pattern in different types of soil as shown in Figure 8. The phosphorus release followed the sequence: sandy clay loam > silty clay loam > clay loam. This might be due to presence of higher content of clay, organic carbon and free oxides of Fe and Al in clay loam textured soil as compared to the other soils, which resulted in more adsorption of P by soil matrix. In contrast, the sandy clay loam textured soil contained lesser amount of clay, organic carbon and free oxides of Fe and Al, thereby more available phosphorus concentration was being released into the soil solution. Similar observations were reported during other investigations (Prakash et al., 2017; Gupta et al., 2020).

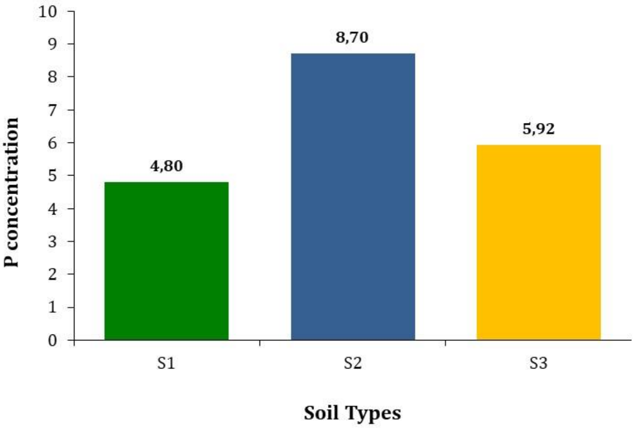


Figure 8. Differences in clay content influence the release of P in soil: sandy clay loam (S2) > silty clay loam (S3) > clay loam (S1)

Kinetics of Phosphate release in soil

The first order kinetic constant was found to increase from T_2 to T_6 in all the three types of soil as noted from Tables 4, 5 and 6. This might be due to less fixation of phosphorus by the sesquioxides content of the soil. The first order kinetic model was unable to describe the P release in soil, due to the uncertainty of the model to explain the concentration of P in soil – water system, whether the contribution of P was from the soil solution or the exchange sites on the clay surfaces (Sparks, 2003). In case of second order kinetics, there was a decrease in rate constant (KcII) value which probably meant that there was increase in the release of P which is dependent upon both soil solution and soil matrix (Sanyal, 2018). The presence of negative sign indicates that as it is inverse of cumulative concentration of available phosphorus ($1/C_t$), while plotting the graph, the slope is from left to right in descending order as depicted in Figure 9. Lower values of correlation coefficients in second order kinetic constants than first order in all the treatments might be due to involvement of solid matrix in regulating equilibrium P concentrations in solution (Medhi et al., 2012).

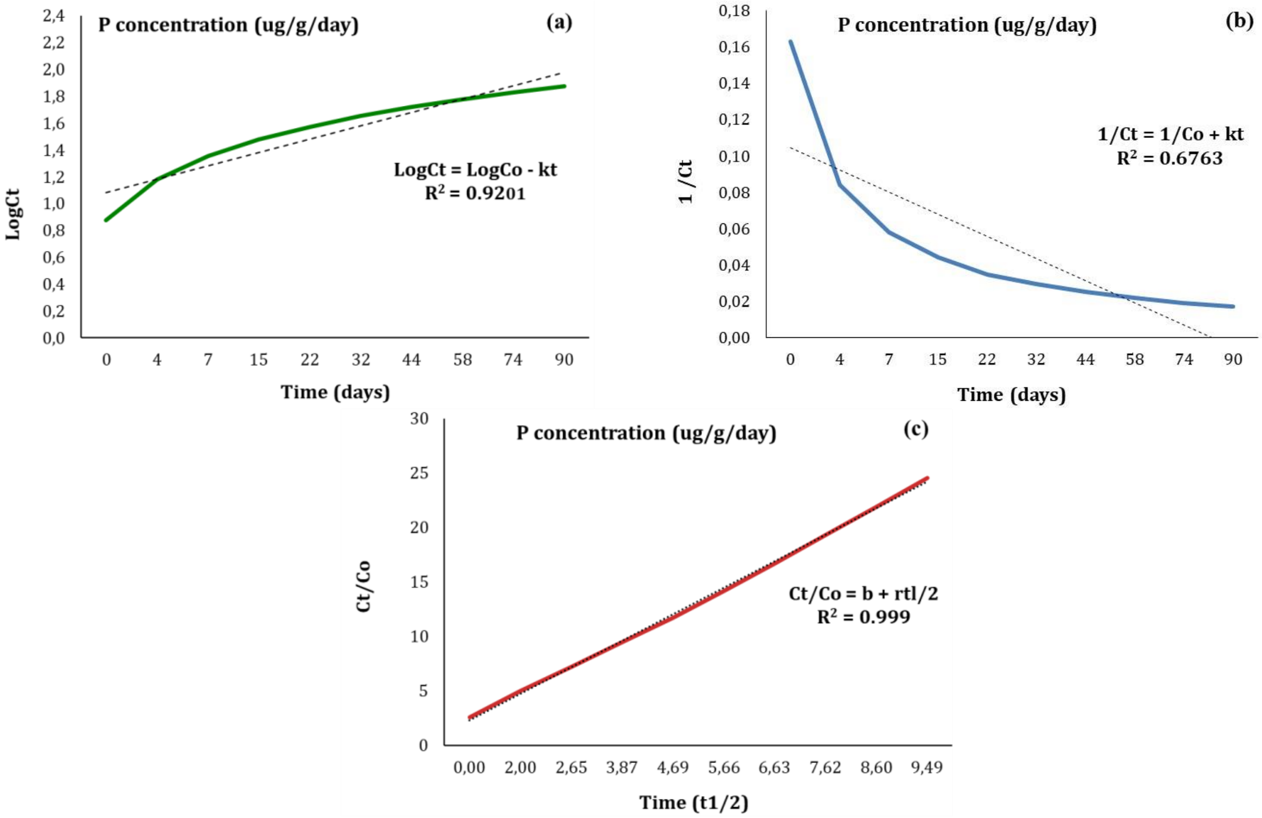


Figure 9. Kinetics of P release in soil system: (a) first order kinetic model, (b) second order kinetic model and (c) parabolic diffusion kinetic model

Table 4. Kinetic parameters from linear regression analysis of first order, second order and parabolic diffusion kinetic models of P release in sandy clay loam soil

Treatments	P release kinetics								
	First order			Second order			Parabolic diffusion		
	Equation	KcI ($\mu g\ g^{-1} day^{-1}$)	R^2	Equation	KcII ($g\ \mu g^{-1} day^{-1}$)	R^2	Equation	Kcp ($\mu g\ g^{-1} day^{-1}$)	R^2
T_1=Absolute control	$\log C_t=0.099t+0.793$	0.099	0.906	$1/C_t=-0.015t+0.143$	-0.015	0.654	$C_t/C_o=2.010t^{1/2}+0.040$	2.010	1
T_2=RDF through SSP	$\log C_t=0.096t+0.985$	0.096	0.920	$1/C_t=-0.009t+0.091$	-0.009	0.681	$C_t/C_o=2.909t^{1/2}+0.245$	2.909	0.999
T_3=RDF through nano fertilizer	$\log C_t=0.097t+0.971$	0.097	0.939	$1/C_t=-0.009t+0.091$	-0.009	0.705	$C_t/C_o=3.012t^{1/2}+0.357$	3.012	0.994
T_4=2.5 times reduction of RDF from T_3	$\log C_t=0.098t+0.876$	0.098	0.920	$1/C_t=-0.012t+0.116$	-0.012	0.676	$C_t/C_o=2.432t^{1/2}+0.114$	2.432	0.999
T_5=5 times reduction of RDF from T_3	$\log C_t=0.101t+0.812$	0.101	0.916	$1/C_t=-0.014t+0.135$	-0.014	0.666	$C_t/C_o=2.210t^{1/2}+0.220$	2.210	0.999
T_6=10 times reduction of RDF from T_3	$\log C_t=0.100t+0.797$	0.100	0.913	$1/C_t=-0.014t+0.140$	-0.014	0.664	$C_t/C_o=2.102t^{1/2}+0.127$	2.102	0.999

Table 5. Kinetic parameters from linear regression analysis of first order, second order and parabolic diffusion kinetic models of P release in silty clay loam soil

Treatments	P release kinetics								
	First order			Second order			Parabolic diffusion		
	Equation	KcI ($\mu g\ g^{-1} day^{-1}$)	R^2	Equation	KcII ($g\ \mu g^{-1} day^{-1}$)	R^2	Equation	Kcp ($\mu g\ g^{-1} day^{-1}$)	R^2
T_1=Absolute control	$\log C_t=0.099t+0.793$	0.099	0.906	$1/C_t=-0.015t+0.143$	-0.015	0.654	$C_t/C_o=2.010t^{1/2}+0.040$	2.010	1
T_2=RDF through SSP	$\log C_t=0.096t+0.985$	0.096	0.920	$1/C_t=-0.009t+0.091$	-0.009	0.681	$C_t/C_o=2.909t^{1/2}+0.245$	2.909	0.999
T_3=RDF through nano fertilizer	$\log C_t=0.097t+0.971$	0.097	0.939	$1/C_t=-0.009t+0.091$	-0.009	0.705	$C_t/C_o=3.012t^{1/2}+0.357$	3.012	0.994
T_4=2.5 times reduction of RDF from T_3	$\log C_t=0.098t+0.876$	0.098	0.920	$1/C_t=-0.012t+0.116$	-0.012	0.676	$C_t/C_o=2.432t^{1/2}+0.114$	2.432	0.999
T_5=5 times reduction of RDF from T_3	$\log C_t=0.101t+0.812$	0.101	0.916	$1/C_t=-0.014t+0.135$	-0.014	0.666	$C_t/C_o=2.210t^{1/2}+0.220$	2.210	0.999
T_6=10 times reduction of RDF from T_3	$\log C_t=0.100t+0.797$	0.100	0.913	$1/C_t=-0.014t+0.140$	-0.014	0.664	$C_t/C_o=2.102t^{1/2}+0.127$	2.102	0.999

Table 6. Kinetic parameters from linear regression analysis of first order, second order and parabolic diffusion kinetic models of P release in clay loam soil

Treatments	P release kinetics								
	First order			Second order			Parabolic diffusion		
	Equation	KcI ($\mu g\ g^{-1} day^{-1}$)	R^2	Equation	KcII ($g\ \mu g^{-1} day^{-1}$)	R^2	Equation	Kcp ($\mu g\ g^{-1} day^{-1}$)	R^2
T_1=Absolute control	$\log C_t=0.1t+0.684$	0.1	0.907	$1/C_t=-0.019t+0.184$	-0.019	0.653	$C_t/C_o=1.595t^{1/2}+ 0.013$	1.595	0.999
T_2=RDF through SSP	$\log C_t=0.096t+0.804$	0.096	0.934	$1/C_t=0.011t+0.108$	-0.011	0.710	$C_t/C_o=2.445t^{1/2}+0.014$	2.445	0.998
T_3=RDF through nano fertilizer	$\log C_t=0.096t+0.798$	0.096	0.947	$1/C_t=-0.011t+0.108$	-0.011	0.725	$C_t/C_o=2.500t^{1/2} +0.311$	2.500	0.992
T_4=2.5 times reduction of RDF from T_3	$\log C_t=0.098t+0.691$	0.098	0.923	$1/C_t=-0.014t+0.142$	-0.014	0.679	$C_t/C_o =1.983t^{1/2}+ 0.076$	1.983	0.998
T_5=5 times reduction of RDF from T_3	$\log C_t=0.101t+0.607$	0.101	0.918	$1/C_t=-0.018t+0.171$	-0.018	0.668	$C_t/C_o =1.780t^{1/2}+ 0.248$	1.780	0.999
T_6=10 times reduction of RDF from T_3	$\log C_t=0.101t+0.690$	0.101	0.915	$1/C_t=-0.019t+0.179$	-0.019	0.665	$C_t/C_o=1.682t^{1/2} + 0.167$	1.682	0.999

In parabolic diffusion kinetic model, strong and significant positive correlation between cumulative P desorbed and $t^{1/2}$ reflected that rate of release of P is synchronizing with time or rather a good state of equilibrium is achieved (Medhi et al., 2012). The rate constant of parabolic diffusion (Kcp) equation was the highest in treatment receiving nano-fertilizer (T3) in all the three types of soil, which indicated that there was sustained release of P as well as longevity of the fertilizer. The coefficient of determination was highest for the parabolic diffusion kinetic equation as compared to the other two kinetic models. Several authors have reported similar findings that parabolic diffusion was the best fit ($R^2 > 0.95$) to describe the release of phosphorus in soil which is a diffusion-controlled process rather than mass flow or root interception (Islas-Espinoza et al., 2014; Singh and Prakash, 2014; Azadi and Baghernejad, 2019) .

Conclusion

The modified zeolite framework witnessed adsorbing both positive and negative ions for its slow release into the soil system throughout the incubation period which may likely be the solution to the major problem of phosphorus fertilization in acid soil which arises due to fixation by sesquioxides. The highest rate constant of parabolic diffusion model was found for the treatment receiving nano-enabled recommended P, which further emphasizes on the sustained release of phosphorous into the soil solution.

Hence, it can be concluded that nutrient use efficiency of phosphatic fertilizers can be significantly improved by nano phosphorus. Zeolite could potentially and simultaneously adsorb both negative and positively charged ions that might possibly be explored as good source of nano carriers for preparation of nano-enabled fertilizers having both positive and negative charged ions. Thus, conventional chemical fertilizers (SSP) can be effectively supplemented by nano phosphatic fertilizer in acidic soil environment.

References

Abdul Majid, S., Ahmad Mir, M., Mir, J.M., 2018. Nitrate and phosphate sorption efficiency of mordenite versus zeolite-A at the convergence of experimental and density functionalized evaluation. *Journal of the Chinese Advanced Materials Society* 6(4): 691-705.

Akrami, Z., Norouzi, S., Bagherzadeh, M., 2019. Immobilization of modified zeolite on polyethylene surface: characterization and its application towards phosphate removal and microalgae growth. *SN Applied Sciences* 1(10): 1183.

Arai, Y., Sparks, D.L., 2007. Phosphate reaction dynamics in soils and soil minerals: a multiscale approach. *Advances in Agronomy* 94: 135-179.

Azadi, A., Baghernejad, M., 2019. Application of kinetic models in describing soil phosphorus release and relation with soil phosphorus fractions across three soil toposequences of calcareous soils. *Eurasian Soil Science* 52(7): 778-792.

Bansiwal, A.K., Rayalu, S.S., Labhasetwar, N.K., Juwarkar, A.A., Devotta, S., 2006. Surfactant modified zeolite as a slow release fertilizer for phosphorus. *Journal of Agricultural and Food Chemistry* 54(13): 4773-4779.

Bhardwaj, P., Sharma, M., Sharma, M., Tomar, R., 2014. Removal and slow release studies of phosphate on surfactant loaded hydrothermally synthesized silicate nanoparticles. *Journal of the Taiwan Institute of Chemical Engineers* 42(5): 2649-2658.

Bindraban, P.S., Dimkpa, C.O., Pandey, R., 2020. Exploring phosphorus fertilizers and fertilization strategies for improved human and environmental health. *Biology and Fertility of Soils* 56(3): 299-317.

Chinnamuthu, C.R., Boopathi, P.M., 2009. Nanotechnology and agroecosystem. *Madras Agricultural Journal* 96(1/6): 17-31.

Conijn, J.G., Bindraban, P.S., Schröder, J.J., Jongschaap, R.E.E., 2018. Can our global food system meet food demand within planetary boundaries? *Agriculture, Ecosystems & Environment* 251: 244-256.

Cordell, D., Neset, T.S.S., 2014. Phosphorus vulnerability: a qualitative framework for assessing the vulnerability of national and regional food systems to the multi-dimensional stressors of phosphorus scarcity. *Global Environmental Change* 24: 108-122.

Dhansil, A., Zalawadia, N.M., Prajapat, B.S., Yadav, K., 2018. Effect of nano phosphatic fertilizer on nutrient content and uptake by pearl millet (Pennisetum glaucum L.) crop. *International Journal of Current Microbiology and Applied Sciences* 7(12): 2327-2337.

Gupta, A.K., Maheshwari, A., Khanam, R., 2020. Assessment of phosphorus fixing capacity in different soil orders of India. *Journal of Plant Nutrition* 42(15): 2395-2401.

Hagab, R.H., Kotp, Y.H., Eissa, D., 2018. Using nanotechnology for enhancing phosphorus fertilizer use efficiency of peanut bean grown in sandy soil. *Journal of Advanced Pharmacy Education and Research* 8(3): 59-67.

Ibrahim, E.A., El-Sherbini, M.A.A., Selim, E.M., 2022. Effects of biochar on soil properties, heavy metal availability and uptake, and growth of summer squash grown in metal-contaminated soil. *Scientia Horticulturae* 301: 111097.

Islas-Espinoza, M., Solís-Mejía, L., Esteller, M.V., 2014. Phosphorus release kinetics in a soil amended with biosolids and vermicompost. *Environmental Earth Sciences* 71: 1441-1451.

Jakkula, V.S., Wani, S.P., 2018. Zeolites: Potential soil amendments for improving nutrient and water use efficiency and agriculture productivity. *Scientific Reviews & Chemical Communications* 8(1): 119.

Kumar, K., Smita, L., Cumbal., Debut, A., 2017. Green synthesis of silver nanoparticles using Andean blackberry fruit extract. *Saudi Journal of Biological Sciences* 24(1): 45-50.

Liu, R., Lal, R., 2014. Synthetic apatite nanoparticles as a phosphorus fertilizer for soybean (Glycine max). *Scientific Reports* 4: 5686.

Mahmood, M., Tian, Y., Ma, Q., Hui, X., Elrys, A.S., Ahmed, W., Mehmood, S., Wang, Z., 2021. Changes in phosphorus fractions in response to long-term nitrogen fertilization in loess plateau of China. *Field Crops Research* 270: 108207.

Medhi, B.K., Ruhal, D.S., Singh, C.P., Grover, D.K., Sarma, A., 2012. Effect of levels of phosphate and organic manures on phosphate supplying capacity and P-kinetics in wheat grown in a TypicHaplustept soil. *Crop Research* 44(1&2): 20-25.

Mikhak, A., Sohrabi,A., Kassaee, M.Z., Feizian, M., 2017. Synthetic nanozeolite/nanohydroxyapatite as a phosphorus fertilizer for German chamomile (Matricariachamomilla L.). *Industrial Crops and Products* 95: 444-452.

Mir, J.M., Ahmad Mir, M., Abdul Majid, S., 2020. Molecular electron density and nitrate-phosphate sorption efficiency of zeolite-A: physico-chemical and DFT analyses. *Indian Journal of Chemistry* 59A: 939-947.

Montalvo, D., Mclaughlin, M.J, Degryse, F., 2015. Efficacy of hydroxyapatite nanoparticles as phosphorus fertilizer in andisols and oxisols. *Soil Science Society of America Journal* 79: 551-558.

Noruzi, M., Hadian, P., Soleimanpour, L., Ma'mani, L., Shahbazi, K., 2023. Hydroxyapatite nanoparticles: an alternative to conventional phosphorus fertilizers in acidic culture media. *Chemical and Biological Technologies in Agriculture* 10(1): 71-76.

Poddar, K., Vijayan, J., Ray, S., Adak, T., 2018. Nanotechnology for sustainable agriculture. In: Biotechnology for Sustainable Agriculture : Emerging Approaches and Strategies. Singh, R.L., Mondal, S. (Eds.). Woodhead Publishing, pp.281-303.

Prakash, D., Benbi, D.K., Saroa, G.S., 2017. Clay, organic carbon, available P and calcium carbonate effects on phosphorus release and sorption-desorption kinetics in alluvial soils. *Communications in Soil Science and Plant Analysis* 48(1): 92-106.

Prüter, J., Leipe, T., Michalik, D., Klysubun, W., Leinweber, P., 2020. Phosphorus speciation in sediments from the Baltic Sea, evaluated by a multi-method approach. *Journal of Soils and Sediments* 20: 1676-1691.

Salako, O., Kovo, A.S., Abdulkareem, A.S., Yusuf, S.T., Afolabi, E.A., Auta, M., 2020. The effect of synthesized NPK loaded surfactant modified zeolite A based fertilizer in tomato (Lycopersycum esclentum) cultivation. *Journal of Nigerian Society of Chemical Engineers* 35(1): 50-63.

Sanyal, S.K., 2018. A textbook of soil chemistry. Astral International Pvt. Limited, India. 306p.

Sharpley, A., Jarvie, H., Flaten, D., Kleinman, P., 2018. Celebrating the 350th anniversary of phosphorus discovery: A conundrum of deficiency and excess. *Journal of Environmental Quality* 47(4): 774-777 .

Singh, D.J.. Sarkar, S.D., Mittal, S., Dhaka, R., Maiti, P., Singh, A., Raghav, T., Solanki, D., Ahmed, N., Singh, S.B., 2018. Zeolite reinforced carboxymethyl cellulose-Na+-g-cl-poly(AAm) hydrogel composites with pH responsive phosphate release behaviour. *Journal of Applied Polymer Science* 136(15): 47332.

Singh, P., Prakash, D., 2014. Phosphorus dynamics in soils as influenced by the application of organic sources: A review. *Indian Journal of Fertilisers*. 10(10): 16-26.

Solanki, P., Bhargava, A., Chhipa, H., Jain, N., Panwar, J. 2015. Nano-fertilizers and their smart delivery system. In: Nanotechnologies in food and agriculture. Rai, M., Ribeiro, C., Mattoso, L., Duran, N. (Eds.). Springer, Cham. pp. 81-101.

Sparks, D.L., 2003. Environmental soil chemistry. Elsevier, 352p.

Subramanian, K.S., Thirunavukkarasu, M., 2017. Nano-fertilizers and nutrient transformations in soil. In: Nanoscience and Plant–Soil Systems. Ghorbanpour, M., Manika, K., Varma, A. (Eds.). Springer Cham. pp. 305-319.

Tarafdar, J.C., Rathore, I., Thomas, E., 2015. Enhancing nutrient use efficiency through nano technological interventions. *Indian Journal of Fertilizers* 11(12): 46-51.

Wahid, F., Fahad, S., Danish, S., Adnan, M., Yue, Z., Saud, S., Siddiqui, M.H., Brtnicky, M., Hammerschmiedt, T., Datta, R., 2020. Sustainable management with mycorrhizae and phosphate solubilizing bacteria for enhanced phosphorus uptake in calcareous soils. *Agriculture* 10(8): 334.

Wakelin, S.A., Condron, L.M., Gerard, E., Dignam, B.E.A., Black, A., O'Callaghan, M., 2017. Long-term P fertilisation of pasture soil did not increase soil organic matter stocks but increased microbial biomass and activity. *Biology and Fertility of Soils* 53: 511-521.

Wei, Y.X., Ye, Z.F., Wang, Y.L., Ma, M.G., Li, Y.F., 2011. Enhanced ammonia nitrogen removal using consistent ammonium exchange of modified zeolite and biological regeneration in a sequencing batch reactor process. *Environmental Technology* 32(12): 1337–1343.

Wilson, J.. Elliott, J., Macrae, M., Glenn, A., 2019. Near-surface soils as a source of phosphorus in snowmelt runoff from cropland. *Journal of Environmental Quality* 48(4): 921-930.

Yan, Z., Lin, Z., Kai, M., Guozhu, M., 2014. The surface modification of zeolite 4A and its effect on the water-absorption capability of starch-g-poly (acrylic acid) composite. *Clay and Clay Minerals* 62(3): 211-223.