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Nano-potassium intercalated composted coir pith: A slow-release fertilizer suitable for laterite soils of humid tropics of India

Bhavishya[a,*], Kizhaeral Sevathapandian Subramanian[b], Murali Gopal[c], Ravi Bhat[c], Swapna Shanmukan Nair[d], Malavika Radhakrishnan[d], Muliyar Krishna Rajesh[a]

[a] *ICAR-Central Plantation Crops Research Institute, Regional Station, Vittal, 574 243, India*
[b] *Department of Nano Science and Technology, Tamil Nadu Agricultural University, Coimbatore, 641 003, India*
[c] *ICAR-Central Plantation Crops Research Institute, Kasaragod, 671 124, India*
[d] *Central University of Kerala, Kasaragod, 671320, India*

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ABSTRACT

High potassium (K)-demanding plantation crops are grown in laterite soils of the humid tropics of India; these soils generally contain low to medium K content. Nano-fertilizers offer an excellent alternative to conventional fertilizers as they release nutrients slowly for a longer period, enhancing their use efficiency. In this study, nano-zeolite based K fertilizer (NZK) was synthesized and intercalated into raw coir pith (CNZK) and composted coir pith (CCNZK). These were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), and UV–visible spectroscopy, and the intercalation of NZK was confirmed. The K content in CNZK and CCNZK was estimated to be 27.2% and 31.6%, respectively. Desorption studies indicated that nano-potassium fertilizer alone, and when intercalated into the composted coir pith, was found to release K slowly for a longer period (> 480 h) in the laterite soils. Our study suggests that nano-potassium intercalated composted coir pith can be synthesized for slow release of K in the laterite soils of the humid tropics of India.

Abbreviations

C: N	Carbon: Nitrogen
Ca	Calcium
CCNZK	Composted coir pith intercalated with nano-zeolite-based potassium fertilizer
CEC	Cation exchange capacity
CNZK	Coir pith intercalated with nano-zeolite-based potassium fertilizer
FTIR	Fourier transform infrared spectroscopy
FWHM	Full Width at Half Maximum
HA	Hydroxyapatite
K	Potassium
KCl	Potassium chloride
Mg	Magnesium

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* Corresponding author.
E-mail address: bhavishya@icar.gov.in (Bhavishya).

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Na	Sodium
NH^{4+}	Ammonium
NZ	Nano-zeolite
NZK	Nano-zeolite-based potassium fertilizer
OECD	The Organization for Economic Cooperation and Development
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
XRD	X-ray diffraction

1. Introduction

Potassium (K) is an essential element for plant growth and is a dynamic ion in the soil system. Of the major nutrient elements, K is usually abundant in soils (Reitemeier, 1951). However, the laterite soils (Ultisols) that predominate India's humid tropics are deficient in K (Badrinath et al., 1998; Wani et al., 2011) and poor in native soil fertility with abundant sesquioxides and low bases (Babu, 1981). These soils are well known for large-scale cultivation of plantation and fruit crops (Velayutham et al., 1999). The major problems associated with laterite soils are nutrient losses through runoff, leaching of basic cations like K and calcium (Ca) due to heavy rainfall during monsoon season (Badrinath et al., 1998), and poor nutrient retention due to low cation exchange capacity (3–14 c mol kg^{-1}) (Shivaprasad et al., 1998). Kaolinite is the dominant clay mineral in laterite soils, which is poor in K fixation. Moreover, recent studies have indicated an overwhelming level of K-mining in Indian soils, and the input is not commensurate to the extraction by intensive cropping, necessitating better K management strategies (Majumdar et al., 2017).

Coconut (*Cocos nucifera* L.), arecanut (*Areca catechu* L.) and cocoa (*Theobroma cacao* L.) are the important plantation crops grown in laterite soils of humid tropics of India which are heavy feeders of K (Manikandan et al., 1987; Khan et al., 2001; Bhat and Sujatha, 2007, 2012), and poor K nutrition is a limiting factor for their productivity (Nelliat, 1978). Since these are perennial crops, and growth and development occur throughout the year, the nutrients should be available longer. The soil constraints and crop nature necessitate effective nutrient management, mainly of K in sole and mixed cropping systems in laterite soil, for higher and sustained yield.

Nanotechnology is one of the emerging areas being exploited in a wide array of areas, such as electronics, energy, environment, medicine, and agriculture (Raliya et al., 2019). It deals with atomic manipulations resulting in precise processes and products, enabling improved use efficiencies due to the extensive surface area to mass ratio. Such a phenomenon is being used to design and fabricate nano-agri inputs, including nano-fertilizers, to improve use efficiency while reducing environmental hazards in soil and aquatic systems (Subramanian et al., 2015; Raliya et al., 2018). Nano-fertilizers improve the nutrient use efficiency of crops due to the unique properties of nanoparticles that provide extensive surface area for the exchange of nutrients (Guo et al., 2018). This approach assisted in improving the nutrient use efficiencies of nitrogen (Pereira et al., 2012; Wanyika et al., 2012; Manikandan and Subramanian, 2014), phosphorous (Mikhak et al., 2017), potassium (Subramanian and Rahale, 2013; Rady et al., 2023), sulfur (Li and Zhang, 2010) and zinc (Yuvaraj and Subramanian, 2018; Sheoran et al., 2021). Since these are designed to deliver the nutrients slowly over a long period, the nutrient loss is substantially reduced. Therefore, nano-based potassium fertilizers could offer an excellent alternative for K fertilization in plantation crops that are heavy and continuous feeders of this element and are predominantly cultivated in laterite soils of humid tropics, which are low in K. Heavy rainfall in these areas leaches out the externally added K; hence, nano-potassium could help in improving its use efficiency by reducing the loss of K by leaching.

To develop nano-fertilizers, several substrates such as clays and zeolites are used to exploit their large surface area, and it gets increased many-fold when they are reduced to nano-dimension using high-energy ball milling (Subramanian et al., 2015). Zeolite is the most commonly used adsorbent in synthesizing nano-fertilizers due to its honeycomb structure, which facilitates nutrient adsorption on both internal and external surfaces. They are abundant in nature and are useful in agriculture because of their large porosity, high cation exchange capacity (CEC), and physical stability (Ramesh et al., 2010). Zeolite has many negatively charged cavities, constituting up to 34% of zeolite volume (Boettinger and Ming, 2002). Because of this structure and sorption and ion exchange properties, zeolite can be used as a slowly releasing carrier of nutrients (Dwairi, 1998; Gul et al., 2005; Bansiwal et al., 2006; Iskander et al., 2011; Jaskunas et al., 2015). Because of the density of the negative charges in the structure and dimension of the interior channels, they are selective for K^+ and ammonium (NH^{4+}) rather than Ca^{2+} and magnesium (Mg^{2+}) (Ming and Mumpton, 1989). Hence, K can be impregnated into zeolite to synthesize slowly releasing K fertilizer (Allen and Ming, 1995; Pino et al., 1995; Li et al., 2013; Lateef et al., 2016). More importantly, K uptake is inversely proportional to the particle size of zeolite, indicating that the adsorption of K is higher when the size of zeolite particles is smaller (Jaskunas et al., 2015). This shows that reducing the size of zeolite to nanoscale by top-down approach could increase nutrient adsorption (Subramanian et al., 2015) due to higher adsorptive surface area, shorter diffusion path lengths, and higher CEC (Ramesh et al., 2010; Manikandan and Subramanian, 2014). Because of these properties, nano-zeolite could be an excellent carrier of nutrients (Ramesh et al., 2010; Lateef et al., 2016).

While developing nano-products in agriculture, including nano-fertilizers, the safety of the nano-products is to be tested at various trophic levels, namely soil microbes, beneficial insects (predators, parasites, and honey bees), earthworms, fish, and humans as per OECD stipulated guidelines (Subramanian and Rajkishore, 2018). In 2019, a draft guideline was developed by the Department of Biotechnology, Government of India, for the evaluation of nano-agri inputs and nano-agri products for use in India (http://dbtindia.gov.in/sites/default/files/DBT_Draft1-Nano-Agri_Input_nd_Nano Agri_Products.pdf). Several steps have been considered to minimize the damage to the agri-food chain while exploiting the unique properties of nano-products. Inhalation is an important route of nanoparticle exposure, as they can travel great distances in the air by Brownian diffusion (Oberdorster et al., 2005). Kottegoda et al. (2011) successfully encapsulated urea-modified hydroxyapatite (HA) nanoparticles into microporous cavities of the young stem of *Glyricidia sepium,* which showed a significant degree of slow and sustained release of urea. The coir pith, which is plenty but has limited utilization, could also be used as a carrier as the porosity and absorptivity are more due to vacant spaces in the dead cells of the coir pith. Coir pith is a lignocellulosic by-product generated during the separation process of coir fibre from coconut husk. The peculiar porous microstructures of coir pith make it potential for the slow release of agrochemicals (Pavithran, 1993). High CEC (38.9–60 meq/100 g) (Evans et al., 1996) and porosity (94.1–98.3% by volume) (Abad et al., 2005) enable it to retain large amounts of nutrients. Moreover, the adsorption complex has high contents of exchangeable K, sodium (Na), Ca, and Mg (Verhagen and Papadopoulos, 1997). Applying coir pith blended with muriate of potash has been reported to enhance K use efficiency in rice (Ammal and Durairajamuthiah, 1996). Thus, raw coir pith has been considered a composite material for intercalating plant nutrients. However, composted coir pith has so far not been attempted to be used as an intercalating sub-composite for loading nano-fertilizers. It has been reported that composting of coir pith results in higher pore space apart from reducing the C: N ratio (Padmadevi et al., 2016). Moreover, it possesses higher macro and micronutrients than raw coir pith (Thomas et al., 2013). These properties can make composted coir pith an excellent carrier of agrochemicals, including nano-fertilizers. Among several technologies to convert coir pith to useful fertilizer, composting using urea + *Pleurotus sajor-caju* ('PITHPLUS') (Ravindranath, 2008), co-composting using poultry manure (Thomas et al., 2013) and biodegradation (Padmadevi et al., 2016) are some of the popular ones in India.

Therefore, considering the requirement of continuous and copious quantities of K nutrition in plantation crops, it was hypothesized that nano-zeolite based potassium fertilizer could be synthesized and intercalated with coir pith for use in laterite soils of humid tropics, which is poor in potassium content. Such nano-fertilizers could release K slowly in a regulated pattern that may assist in improving the availability of nutrients for longer periods with minimum loss. With this background, an experiment was carried out to synthesize nano-potassium intercalated composted coir pith and study the K release pattern in laterite soil commonly found in India's humid tropics.

2. Materials and methods

2.1. Composting of coir pith

Raw and poultry manure-based co-composted coir piths available at the Microbiology Section of ICAR-Central Plantation Crops Research Institute (ICAR-CPCRI), Kasaragod, India, were used for preparing the nano-potassium intercalated coir pith fertilizer. Coir pith was composted following the method of co-composting using poultry manure developed at ICAR-CPCRI (Thomas et al., 2013). The procedure involves admixing 90 kg of coir pith with 10 kg of good quality poultry manure along with 0.5 kg of lime and 0.5 kg of rock phosphate. The mixed substrate is spread evenly into a heap on a cement floor or tarpaulin sheet after being adequately mixed with water. Layer by layer, a large 500–600 kg heap is prepared. The heap is then kept sufficiently moist by sprinkling water regularly and covered with gunny bags or a tarp to undergo aerobic composting. Turning is required once every 15 days till 45–60 days when the coir pith becomes dark brown to black (Gopal et al., 2016).

2.2. Synthesis of nano-zeolite (NZ)

The initial dimension of the natural zeolite (clinoptilolite) was 1–2 μm in size. Nano-zeolite was synthesized using a high energy ball milling (Fritsch Planetary Micro Mill Pulverisette 7, Germany). In this study, the optimal milling speed, duration, and balls-to-powder ratio were set as 600 rpm, 6 h, and 1:10, respectively (Subramanian and Rahale, 2013). About 5 g of adsorbent (zeolite) was put into two grinding cups and ground for 6 h at 600 rpm using 6 balls of 8 g weight.

2.3. Sorption of potassium on nano-zeolite

To study the sorption behavior of potassium on nano-zeolite (NZ), 2.5 g of nano-zeolite and 25 mL of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5 M of potassium chloride (KCl) solution was added to 100 mL plastic bottles and were shaken in an orbital shaker for 24 h at 150 rpm (Rahale, 2010) and 65 °C (Jaskunas et al., 2015). The mixtures were then centrifuged at 12000 rpm for 10 min, and the solution was filtered using Whatman no. 42 filter paper. The potassium concentration in the leachate was determined by flame photometry. The potassium uptake (q) was calculated by the increase or decrease of their respective concentration in the liquid phase according to the equation below:

$$q\,(\mathrm{mg/g}) = \frac{(C_0 - C_1).\mathrm{V}}{\mathrm{m}}$$

Where C_0 and C_1 are the initial and final concentrations of cation (mg mL^{-1}), respectively, in the solution; V is the volume of the solution (mL), and m is the mass of zeolite (g).

2.4. Preparation of nano-potassium fertilizer (NZK)

About 2.5 g of NZ was taken in a 100 mL plastic bottle, and to that, 25 mL of 4.0 M KCl solution was added and shaken in an orbital shaker for 24 h at 150 rpm and 65 °C. It was then centrifuged at 12000 rpm for 10 min to separate the solid particles, filtered, and oven-dried at 105 °C to obtain nano-zeolite K fertilizer (NZK).

2.5. Preparation of nano-potassium intercalated coir pith fertilizer

To prepare nano-potassium intercalated coir pith fertilizer, the coir piths (raw and composted) were washed thrice with demineralized water, air dried, ground, and sieved. Different proportions (1:1, 2:3, 1:2, 1:5, and 1:10) of NZK and coir pith were used to study the maximum loading/intercalation of NZK into the coir pith. They were added to 50 mL of 4.0 M KCl solution and then shaken using an orbital shaker at 150 rpm and 65 °C for 24 h, centrifuged at 12000 rpm for 10 min, and the solid material was dried to get nano-potassium intercalated coir pith fertilizer (CNZK) and nano-potassium intercalated composted coir pith fertilizer (CCNZK).

2.6. Characterization of NZ, NZK, CNZK and CCNZK

The particle size analysis of nano-zeolite (NZ) before and after impregnation with K was done using a Particle Size Analyzer (Horiba, SZ-100, Japan). Accurately, 0.5 mg of the sample was dispersed in 10 mL distilled water and sonicated using a QSonica sonicator for 32 min at four lapses of 8 min. Immediately, the sample was taken in a glass cuvette and observed in a particle size analyzer at 90° angle and 25 °C. The crystal structure and associated parameters were elucidated via X-ray diffraction, employing the Rigaku Miniflex instrument with Cu Kalpha radiation ($\lambda = 1.5406$ nm). Approximately one gram of sample (NZ, NZK, and CCNZK) was dusted on a glass substrate and mounted on the sample stage, and diffraction was measured. UV–Vis spectroscopy with the Agilent Cary 4000 spectrometer was used to determine the optical absorption maxima and bandgap characteristics.

Furthermore, excitation profiles were analyzed with the same Agilent Cary instrument. Conjugation mechanisms were investigated and recorded *via* FTIR spectroscopy within the 400 cm^{-1} - 4000 cm^{-1} wavenumber range. SEM images of the samples were taken in FEI QUANTA 250 (FEI, Hillsboro, OR, USA). The dried sample was dusted on the carbon conducting tape. Then, the tape was mounted on the sample stage, and the images were taken at 400-16000x magnification. TEM images of NZ and NZK were taken in FEI Technai, USA. About 0.5 mg of sample was taken in a beaker, and 10 mL of ultra-pure water was added and sonicated for half an hour using an ultra sonicator. It was loaded into the dark side of the 300-mesh lacy carbon-coated copper grid using a syringe, dried, and images were taken.

2.7. Desorption of potassium from NZK, CCNZK, and KCl in laterite soil

The percolation unit for the desorption study was set up according to Bansiwal et al. (2006). The unit consisted of three glass cylinders with an internal diameter of 1.5 cm and 25 cm height with four small holes. From the top of the glass cylinder, ultrapure water was made to drip at the rate of 1.5 mL h^{-1}. The experiment was conducted at ambient temperature. About 0.5 g potassium equivalent of each fertilizer (NZK, CCNZK, and KCl) was taken, homogenized with 30 g of soil (pH 5.90), and placed in the glass cylinder. Ultrapure water (30 mL) was added daily, the leachate was collected once in two days, and the K content was determined using a flame photometer.

3. Results

3.1. Particle size of zeolite

The size of the zeolite after ball milling for 6 h was measured in a particle size analyzer, and the data is presented in Table 1. The average dimension of the nano-zeolite particles was 81.40 nm. The distribution of the particles suggested that more than 74.46% of the particles were below 100 nm in size. It was also found that ball milling for a longer period (>6 h) would cause agglomeration of the particles and change the colour of the adsorbent.

Table 1
Particle size distribution of nano-zeolite.

No.	Diameter	Frequency	Cumulation	No.	Diameter	Frequency	Cumulation	No.	Diameter	Frequency	Cumulation
1	1.02	0.000	0.000	21	11.68	0.000	0.000	41	134.16	4.834	95.263
2	1.15	0.000	0.000	22	13.20	0.000	0.000	42	151.57	4.101	99.364
3	1.30	0.000	0.000	23	14.91	0.000	0.000	43	171.25	0.636	100.000
4	1.47	0.000	0.000	24	16.84	0.000	0.000	44	193.48	0.000	100.000
5	1.66	0.000	0.000	25	19.03	0.000	0.000	45	218.60	0.000	100.000
6	1.87	0.000	0.000	26	21.50	0.000	0.000	46	246.98	0.000	100.000
7	2.11	0.000	0.000	27	24.29	0.000	0.000	47	279.04	0.000	100.000
8	2.39	0.000	0.000	28	27.45	0.000	0.000	48	315.27	0.000	100.000
9	2.70	0.000	0.000	29	31.01	0.000	0.000	49	356.20	0.000	100.000
10	3.05	0.000	0.000	30	35.03	0.000	0.000	50	402.44	0.000	100.000
11	3.45	0.000	0.000	31	39.58	0.000	0.000	51	454.69	0.000	100.000
12	3.89	0.000	0.000	32	44.72	0.000	0.000	52	513.71	0.000	100.000
13	4.40	0.000	0.000	33	50.53	1.854	1.854	53	580.41	0.000	100.000
14	4.97	0.000	0.000	34	57.09	11.278	13.132	54	655.76	0.000	100.000
15	5.61	0.000	0.000	35	64.50	14.853	27.985	55	740.89	0.000	100.000
16	6.34	0.000	0.000	36	72.87	16.436	44.421	56	837.07	0.000	100.000
17	7.17	0.000	0.000	37	82.33	19.573	63.994	57	945.74	0.000	100.000
18	8.10	0.000	0.000	38	93.02	9.958	73.952	58	1068.52	0.000	100.000
19	9.15	0.000	0.000	39	105.10	9.521	83.473	59	1207.24	0.000	100.000
20	10.34	0.000	0.000	40	118.74	6.956	90.429	60	1363.97	0.000	100.000

3.2. Potassium sorption

The nano-zeolite was loaded with KCl of different molar concentrations varying from 0.5 to 4.5 M. The K sorption on nano-zeolite showed that the amount of adsorbed-K increased with the increase in K concentration (Fig. 1). The adsorption pattern of K on nano-zeolite was almost linear with small curves, with a steep increase in K sorption with an increase in K concentration from 0.1 M to 2.0 M. Thereafter, it increased gradually up to 3.0 M, but it increased greatly at 3.5 M and 4.0 M concentrations, and marginally thereon.

The nano-zeolite was loaded with K using KCl to synthesize nano-potassium fertilizer. It was then impregnated into the coir pith in the K-rich solution. Among different proportions of NZK and coir pith, the highest concentration of 31.6% and 27.2% K was obtained in a 1:2 ratio of NZK and coir pith (composted and raw, respectively). The CCNZK contained higher macro and micronutrients than CNZK (Table 2). Since NZK was impregnated into coir pith in a K-rich solution, the total K in CNZK and CCNZK was higher than NZK.

3.3. Characterization of nano-fertilizer and composites

The NZK, CNZK and CCNZK were characterized using SEM, XRD, FTIR and UV–Vis spectroscopy. The morphological changes in the nano-zeolite before and after the loading of K were assessed through SEM and TEM studies. We observed that the nano-zeolites were cubical (Fig. 3A), and there was no profound change in the surface morphology after impregnating K except for slight irregularity in the shape (Figs. 3B and 4). Among the two types of coir piths studied, composted coir piths showed higher K content (31.6%). SEM images of the coir pith composted using poultry manure showed plenty of open cells with large empty cavities (Figs. 2 and 3C). The SEM image of the cross-sectioned CCNZK fertilizer showed the presence of NZK in the cavities of the coir pith (Fig. 3D). They entered the micro-pores of the coir pith; however, the particles were found agglomerated.

The specific X-ray diffraction (XRD) patterns for pure zeolite and nano-zeolite-based potassium fertilizer (NZK) are provided in Fig. 5. It is evident from these patterns that the K-enriched nano-zeolites exhibit XRD patterns similar to that of the pure zeolite sample, with a slight shift in Full Width at Half Maximum (FWHM) values. Notably, the peaks corresponding to 2θ values of 28.030, 40.470, 50.12, and 66.670 exhibits higher intensity in the K-fortified samples than the pure zeolites. This intensity variation and the observed shift in FWHM values could be attributed to the K enrichment achieved through KCl. The XRD pattern indicated little changes in the zeolite structure as the adsorption occurred through cation exchange. Even in CCNZK, similar peaks were also observed (Fig. 6). However, their intensity varied widely from NZ and NZK. Peaks corresponding to K were also observed to be similar to NZK, but their intensities were very high. Conversely, in the case of CCNZK and CNZK (Fig. 6) samples, the peak intensity decreased, suggesting a reduction in crystallinity following the intercalation with the coir pith. The absence of extra peaks in the XRD patterns indicates that the CCNZK and CNZK samples retain their purity. The observed variations in peak intensity and FWHM values indicate the impregnation of nano-potassium into composted coir pith and raw coir pith. In the case of CCNZK and NZK, a large amount of KCl

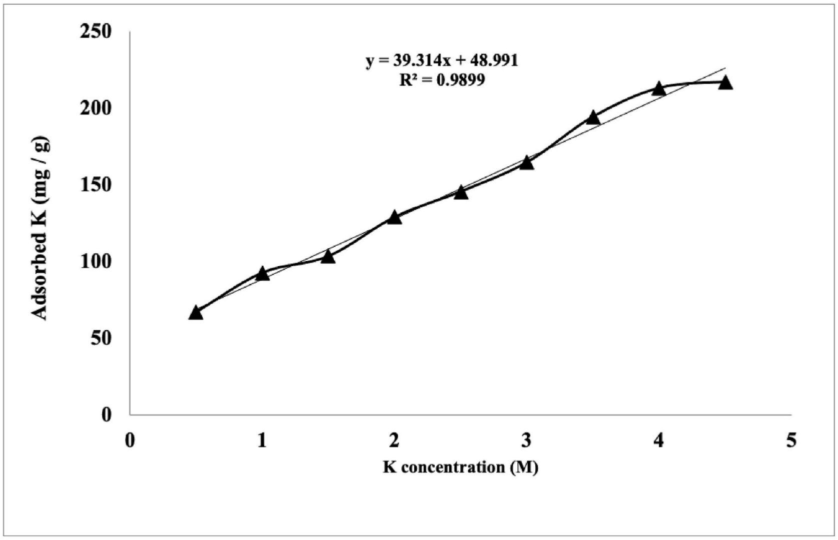

Fig. 1. Sorption of potassium on nano-zeolite under varying molar concentrations of potassium chloride.

Table 2
Nutrient status (mg kg^{-1}) of laterite soil, nano-potassium intercalated raw coir pith (CNZK) and composted coir pith (CCNZK) fertilizers.

	K	N	P	Ca	Mg	Fe	Mn	Cu	Zn
Soil	183	204	14.4	830	146	112.0	78.0	4.7	18.1
CNZK	27.2%	0.38%	0.08%	0.18%	0.12%	218.3	4.9	14.8	22.1
CCNZK	31.6%	0.69%	0.22%	0.27%	0.15%	512.7	31.5	25.6	69.8

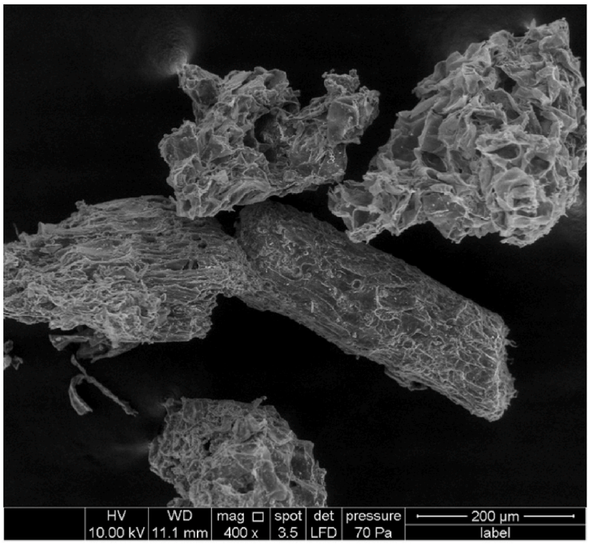

Fig. 2. SEM image of composted coir pith showing micro-porous cavities.

was also impregnated into the micro-pores of composted coir pith, resulting in higher intensity of 2θ values corresponding to K than NZK.

We observed a broad and less intense absorption peak at a wavelength of 273 nm (Fig. 7). It is a common characteristic of nano-zeolites to possess a wide band gap and absorption maxima in the ultraviolet (UV) region. The band gap of pure zeolite was measured at 4.87 eV. In the case of K-fortified nano-zeolites, the band gap increased to 4.95 eV, which suggests a reduction in particle size. Furthermore, the band gap for nano-zeolites incorporated into raw and composted coir piths was determined to be 4.86 eV and 4.82 eV, respectively (Table 3).

The FTIR spectra for both pure and K-fortified nano-zeolites are illustrated in Fig. 8. Additionally, the IR spectra for NZK incorporated into raw and composted coir pith are provided in the same figure. The peaks at wavenumbers 964 cm^{-1}, 662 cm^{-1}, 545 cm^{-1}, and 453 cm^{-1} correspond to asymmetric stretching, symmetric stretching, double six-member ring vibrations, and bending vibrations of the Al–O/Si–O bonds. A narrow peak observed at 1649 cm^{-1} is attributed to the water deformation mode (Fig. 8).

3.4. Slow release of potassium

The release pattern of K from potassium chloride (KCl) and synthesized potassium fertilizers (NZK and CCNZK) in laterite soil was studied using a percolation reactor. The pH of the soil was 5.90. The data on available soil nutrients is given in Table 2. It was observed that, initially, there was a burst release of nutrients, irrespective of fertilizers (Fig. 10). However, a maximum concentration of 82 mmol L^{-1} of K was leached from KCl followed by CCNZK (59 mmol L^{-1}), and NZK (46 mmol L^{-1}). The data revealed that K release from KCl continued at a greater pace. About 87% of available K was desorbed after 240 h, beyond which the concentration of K in the leachate was very low (Fig. 10). However, K was released gradually from NZK and CCNZK with 54.6% and 57.3% release, respectively, in 240 h. Higher initial K release from CCNZK may be from the KCl present in the micropores, after which it exhibited very slow release up to 384 h, and thereon, it attained a static phase. Interestingly, K release continued even after 480 h, with a concentration of 9 mmol L^{-1} and 8 mmol L^{-1} in CCNZK and NZK, respectively. This result clearly demonstrated a slow and steady release of K from NZK and CCNZK.

4. Discussion

Zeolite is employed to retain nutrients and improve long-term soil quality by enhancing its adsorption ability and enabling slow nutrient release. This, in turn, leads to improved nutrient use efficiency. If the size of zeolite is reduced to nanoscale, it can adsorb more cations in its crystalline network due to its higher surface area and CEC (Manikandan and Subramanian, 2014; Ramesh et al., 2010). Hence, in the current study, natural zeolite with 1–2 μm particle size was reduced to a nano-dimension by high-energy ball milling. The size of the particles was observed to range from 50.53 to 171.25 nm. Such a variation in the particle size is a snag of ball milling. Subramanian et al. (2015) opined that the physical nanoparticle synthesis method is very simple, but the product is heterogeneous, and particles often get agglomerated. Conversion of flaky zeolite to separated agglomerate particles of less than 100 nm size with spherical, elliptical, or irregular shapes using a ball mill has been well documented for nanoparticle preparation (Nezamzadeh-Ejhieh and Tavakoli-Ghinani, 2014).

The adsorption of K in a potassium-rich solution directly depends on the K concentration in the liquid phase (Rezaei and MovahediNaeini, 2009). Moreover, the K adsorption is inversely proportional to the particle size of zeolite (Jaskunas et al., 2015). Nano-zeolites, which are characterized by smaller particle sizes, exhibit greater K adsorption capacity than zeolites possessing larger particle sizes (Mondal et al., 2021). Initially, K^+ adsorption increased steeply but levelled off marginally after reaching a concentra-

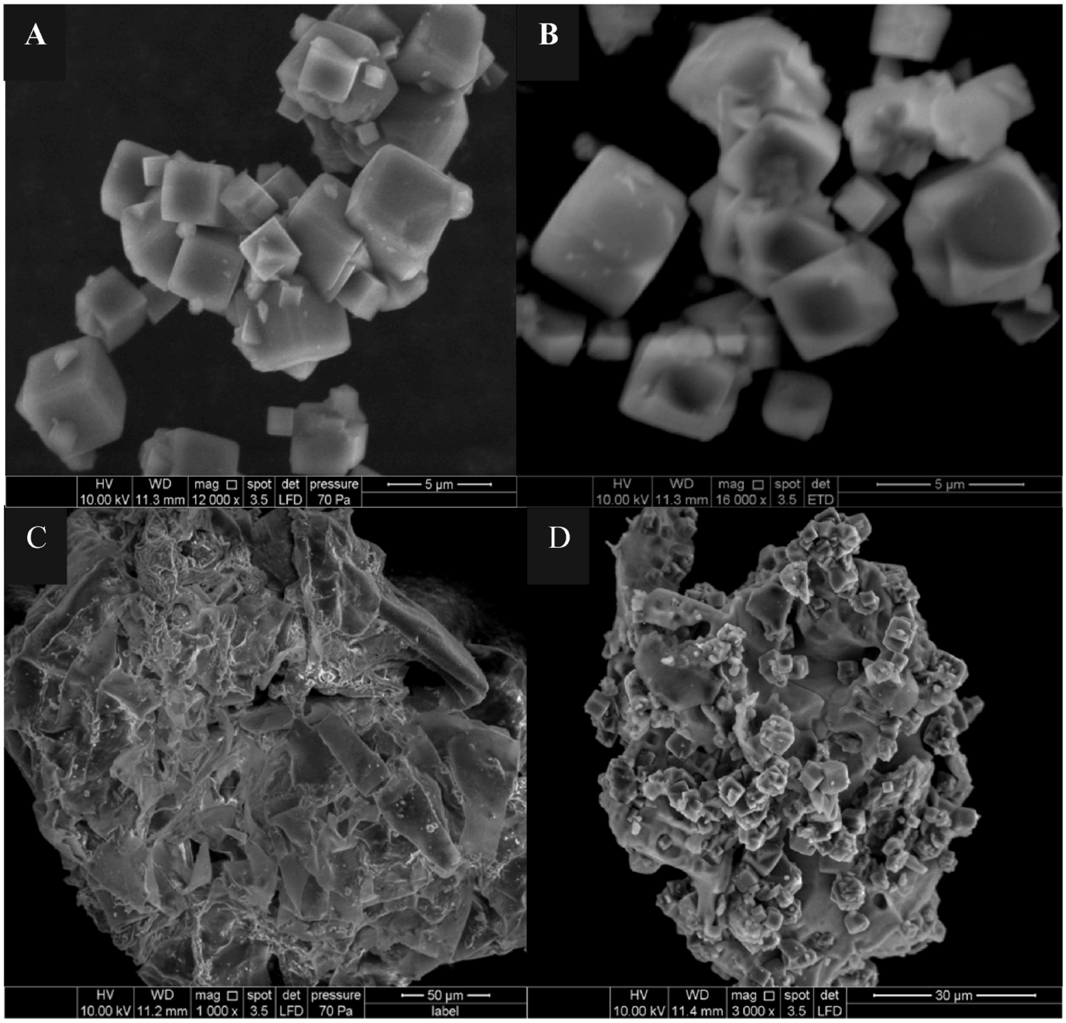

Fig. 3. SEM image of nano-zeolite (A), potassium-impregnated nano-zeolite (B), composted coir pith (C) and nano-potassium intercalated composted coir pith (D).

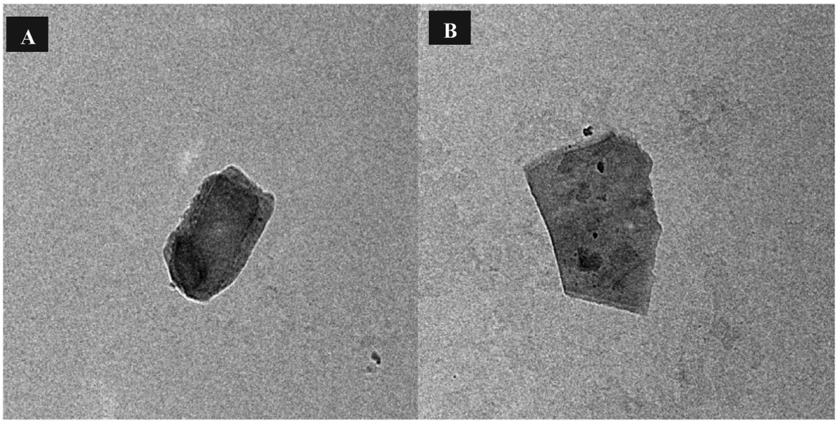

Fig. 4. TEM image of nano-zeolite (A), potassium-impregnated nano-zeolite (B).

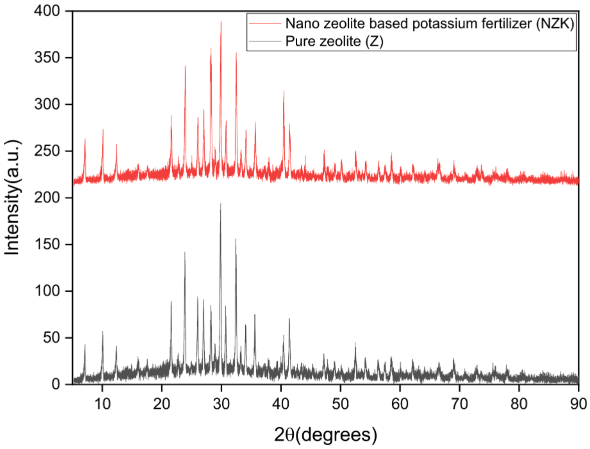

Fig. 5. X-ray diffraction (XRD) patterns for pure zeolite and nano-zeolite-based potassium fertilizer (NZK).

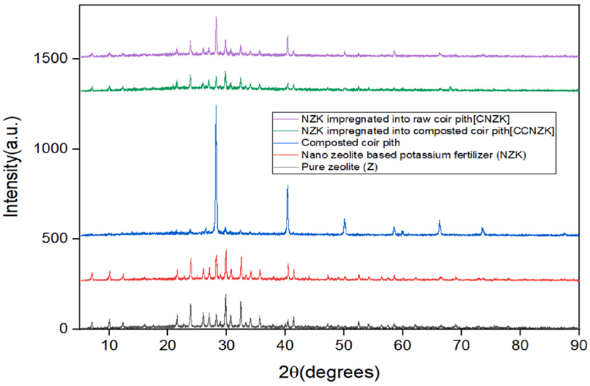

Fig. 6. XRD spectrum of pure zeolite, nano-zeolite, composted coir pith, NZK impregnated into coir pith, and NZK impregnated into composted coir pith.

tion of 4.0 M. This is attributed to the initial adsorption of K^+ in pores near the zeolite-solution boundary, followed by further adsorption in deeper pores, ultimately leading to a diffusion-controlled process (Jaskunas et al., 2015; Pérez-Botella et al., 2022). Therefore, the concentration of K in the solution emerges as a crucial factor during the sorption of K on zeolites.

The nano-K fertilizer synthesized in the current study was characterized using XRD, SEM, TEM, FTIR, and UV-Spectroscopy before and after impregnating into coir pith. Our observation of minor morphological changes in the XRD patterns of K-loaded nano-zeolite *vs*. nano-zeolite finds support in the report of Jaskunas et al., (2015), who found that impregnation of K did not tangibly alter the surface of zeolite because it is mainly adsorbed by ion exchange with Ca and Na. It is immobilized onto nano-zeolites through the formation of hydrogen bonds. The new peaks that appeared in the NZK (Fig. 5) belong to the K incorporated from KCl. Analysis of the FTIR spectrum revealed a discernible shift towards the lower wavenumber region, signifying the successful binding of K fertilizer with the nano-zeolite substrate (Fig. 9). This observed wavenumber shift can be attributed to the increase in the overall molecular mass following the binding event. The phenomenon is consistent with the established principle that vibrational frequencies in FTIR spectroscopy are inversely proportional to the mass of the vibrating species. The peak shift towards lower wavenumbers corroborates the structural modification due to the attachment of the fertilizer (Lateef et al., 2016). It underpins the significance of this interaction in the context of zeolite-based agricultural applications.

The SEM imaging of NZ and NZK showed that they were cubical (Fig. 3A and B), with few morphological changes. This is because the adsorption of K on zeolite takes place with the ion exchange. The net negative charge arising from the isomorphous substitution of Al^{3+} for Si^{4+} is balanced most commonly by K^+, Na^+ and Ca^{2+} within the existing pores (Sparks and Huang, 1985), and the selectivity of ion exchange on zeolite was determined in order of $K^+ > NH^{4+} > Na^+ > Ca^{2+} > Mg^{2+}$ (Ames, 1960; Guo et al., 2008). The K^+ adsorption occurs *via* ion exchange with Ca^{2+}, Na^+ and Mg^{2+}. The SEM imaging of the coir pith showed the presence of micro-porous structures (Fig. 2). Such open cells with large cavities were earlier reported in coir pith, which was proposed to act as capillaries for water adsorption (Idiculla et al., 1983). These cavities could also work similarly for the sorption and storage of nutrients such as potassium (Pavithran, 1993; Krishnan and Haridas, 2008). Coir pith has CEC ranging between 39 and 60 meq 100 g^{-1} (Evans et al., 1996), which offers a good scope for retaining large amounts of nutrients, particularly the cations. Coir pith, thus, is an effective adsorbent or bio-sorbent for cations like nickel, copper, zinc (Swarnalatha and Ayoob, 2016) and cobalt (Parab et al., 2010). Composting of the coir pith improves the CEC value up to 80 meq 100 g^{-1} (http://www.ccriindia.org/c_pom.html), which can be safely assumed to become a more effective adsorbent matrix compared to raw coir pith. Li et al. (2014) reported that the zeta potential of the

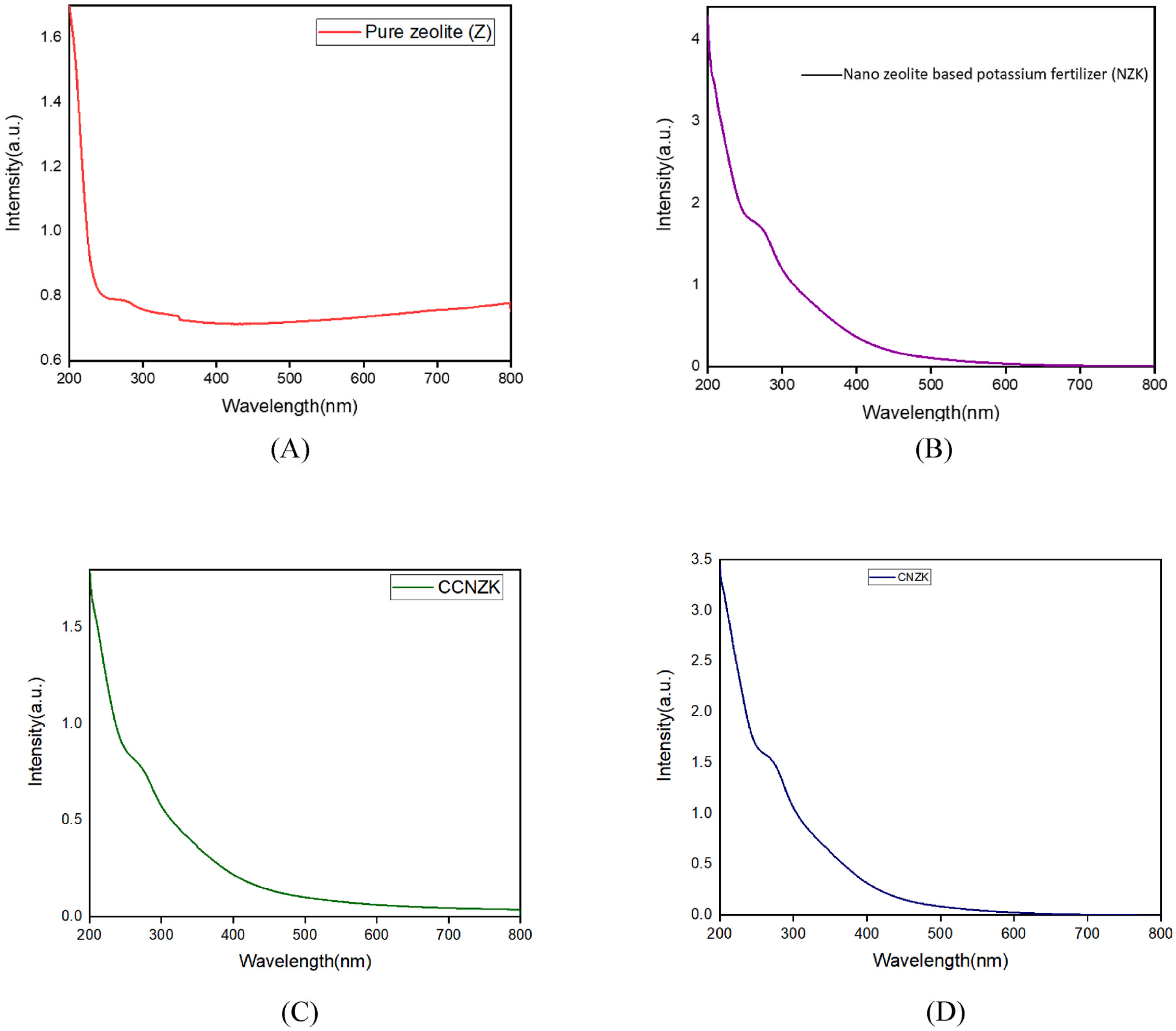

Fig. 7. UV–Vis absorption spectra of pure zeolite (A), nano-zeolite-based potassium fertilizer (B), NZK-impregnated composted coir pith (C), and NZK-impregnated raw coir pith (D).

Table 3
Band gap values of pure-zeolite, NZK, CNZK and CCNZK.

Sample	Band gap (eV)
Pure Zeolite	4.87
NZK	4.95
CNZK	4.86
CCNZK	4.82

rice straw increased with the decomposition period, and it could adsorb more K ions. Furthermore, enhanced pore space and physico-chemical properties in composted coir pith compared to raw coir pith were observed by Padmadevi et al. (2016), which might have contributed to higher K in CCNZK than CNZK. The other mineral nutrients were also higher in CCNZK as the coir pith was composted using poultry manure.

In the humid tropics of India, coconut, arecanut, and cocoa are primarily cultivated in laterite soils; this soil type is characterized by low K. These crops, therefore, require higher amounts of this nutrient. Using slow-release K fertilizers is more beneficial, as they can gradually release the nutrient over an extended period. This extended-release enhances nutrient availability, ultimately improving K-use efficiency in growing these crops in laterite soils. The release of K from zeolite is slow (Pino et al., 1995) because it occurs through the process of dissolution and ion exchange reactions (Allen and Ming, 1995). Initially, K present in the fertilizer form will be released from the zeolite pores into the soil solution due to diffusion (Jaskunas et al., 2015), which may add to the initial burst release

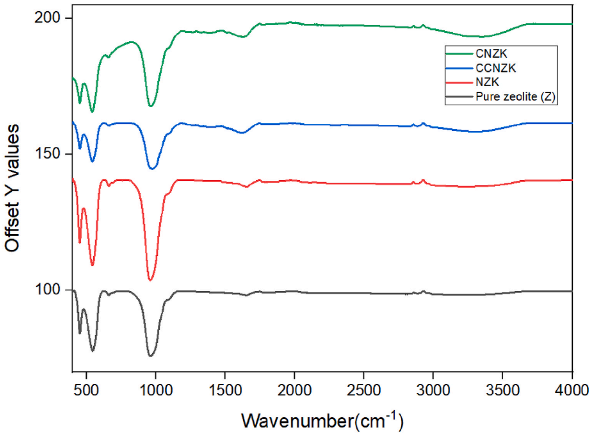

Fig. 8. FTIR spectra of pure zeolite, NZK, CCNZK, and CNZK.

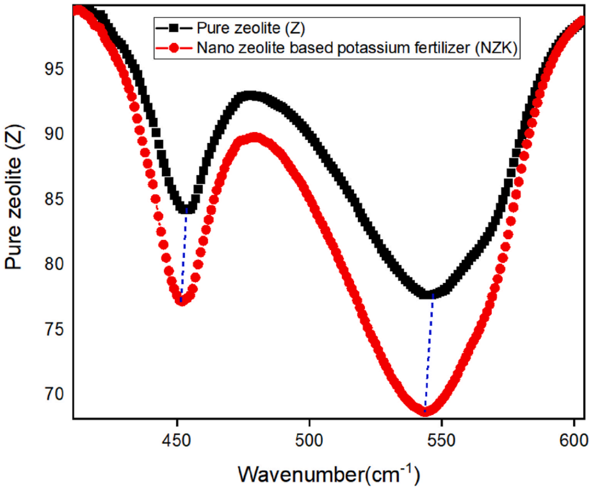

Fig. 9. Shift towards the lower wavenumber region, signifying the successful binding of K fertilizer with the nano-zeolite substrate.

of K from NZK. In this study, the initial K release was higher in KCl, followed by CCNZK and NZK. Apart from NZK, even KCl was also present in the microporous cavities of composted coir pith. This could have contributed to a higher initial K release from CCNZK than NZK. However, after 96 h, there was a steady release of K from CCNZK. It released 9 mmol L^{-1} of K even after 480 h. This indicates that K-release will be slower when nano-zeolite based fertilizer is impregnated into composted coir pith. This makes it an excellent carrier of nano-potassium fertilizer. Our results confirm the earlier report of the slow and steady release of major and minor nutrients from nano-zeolite composite and improved nutrient use efficiency (Lateef et al., 2016). Significantly, this slow release of nutrients from nano-fertilizers results in higher nutrient use efficiency (Subramanian et al., 2015) apart from possible reduction in environmental pollution. Care should be taken when applying fertilizers in the nano form, as they can travel greater distances due to Brownian diffusion. However, the size of the composite after impregnating nano-K into the composted coir pith was 1–3 mm. This makes the application easier and could reduce exposure to nanoparticles at the time of application.

5. Conclusions

The laterite soils of the humid tropics of India are low to medium in K. High K-demanding plantation crops are grown in this region. Moreover, leaching losses are high due to heavy rainfall during monsoon and inherent soil constraints. Hence, K should be released slowly for a longer period. Zeolite based nano-fertilizers offer a significant advantage in achieving this slow nutrient release. Therefore, we synthesized nano-zeolite based potassium fertilizer (NZK). Since inhalation is an important route of nanoparticle exposure, we impregnated the nano-K fertilizer into raw and composted coir pith to get CNZK and CCNZK, respectively. The K content in CNZK and CCNZK was 27.2% and 31.6%, respectively. They were characterized using XRD, UV–Vis, FTIR, and SEM, and the intercalation of NZK was confirmed.

The release of K from NZK, CCNZK, and KCl was studied in the laterite soil. It indicated that both NZK and CCNZK exhibited a prolonged release of K, surpassing 480 h. This extended-release is particularly beneficial in acidic laterite soils of the humid tropics of India, where leaching losses are high. The data strongly suggests that zeolite of nano dimension will be very effective in improving the

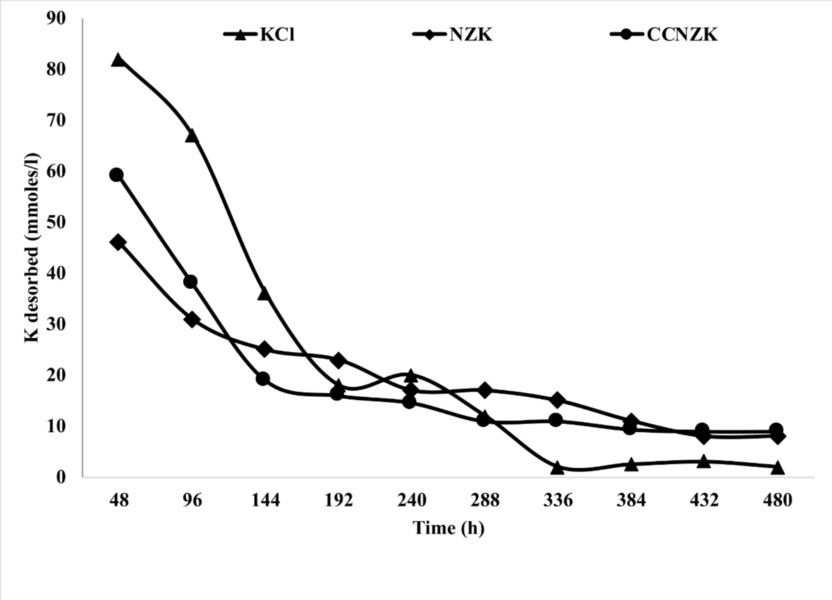

Fig. 10. Desorption of potassium from NZK, CCNZK and KCl.

use efficiency of K and more so when it is intercalated with composted coir pith. Importantly, this slow release of K from NZK and CC-NZK could lead to a possible reduction in environmental pollution.

Our work presents a novel approach of using the composted coir pith as a carrier material for nano-fertilizer as it not only contains higher K than NZK but also releases K slowly for a longer period, making it an excellent carrier of nano-zeolite based K fertilizer. This is the first report of using composted coir pith as a carrier of nano-fertilizer.

CRediT authorship contribution statement

Bhavishya: Writing – original draft, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Kizhaeral Sevathapandian Subramanian:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation. **Murali Gopal:** Writing – review & editing, Resources, Methodology, Investigation. **Ravi Bhat:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Data curation, Conceptualization. **Swapna Shanmukan Nair:** Writing – review & editing, Visualization, Methodology, Formal analysis, Data curation. **Malavika Radhakrishnan:** Writing – review & editing, Visualization, Methodology, Investigation, Formal analysis. **Muliyar Krishna Rajesh:** Writing – review & editing, Visualization, Resources, Project administration, Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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