

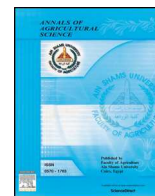
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Formulation of slow release NPK fertilizer (cellulose-graft-poly (acrylamide)/nano-hydroxyapatite/soluble fertilizer) composite and evaluating its N mineralization potential

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ARTICLE INFO

Keywords:

Nano-composite
Polymer hydrogel
Chemical interaction
Incubation experiment
Kinetics model

ABSTRACT

Polymer nano-composite fertilizer formulation has the potential to enhance nutrient use efficiency. Slow release fertilizer (SRF) composite was formulated by incorporating nano-hydroxyapatite (nano-HA) and water soluble fertilizers (urea, $(\text{NH}_4)_2\text{HPO}_4$ and K_2SO_4) into water hyacinth cellulose-graft-poly(acrylamide) polymer hydrogel. Fourier Transform Infra-red spectra revealed existence of chemical interaction between the monomer, cellulose, urea and nano-HA. The release of nutrients was assessed using laboratory incubation experiment. Significantly higher content of mineral nitrogen (MN) was observed in the first 4 weeks in conventional fertilizer (CF) compared to SRF treatments and the control. MN content in SRF treatments increased considerably between the 8th and 12th week, and declined in the 16th week. The values of potentially mineralizable N estimated using first order kinetics model related well to the observed cumulative MN at 16th week. No significant difference was observed between CF and SRF treatments for available P content in the 2nd week. Significantly higher P content was observed in CF compared to SRF treatment in the 4th week, whereas in the 8th week, some SRFs released significantly higher content than CF. Available P peaked in the 8th week in all the treatments and remained constant at 12th and 16th week. Availability of P in SRFs increased with increased content of soluble P and decreased content of nano-HA. Exchangeable K showed less variation during the incubation period, suggesting short release time. The data revealed reduced chances of leaching losses and toxic effect to the plant roots, as well as synchronized nutrient release and requirement by crops.

1. Introduction

Over the years, inherent soil fertility has declined in Kenyan farmlands (Kimetu et al., 2007; Mucheru-Muna et al., 2013) due to continuous cultivation and inadequate replenishment of nutrients, among other limiting factors. To increase and sustain crop yields, farmers apply conventional fertilizers such as diammonium phosphate (DAP), triple superphosphate (TSP), nitrogen, phosphorous and potassium (NPK), mono-ammonium phosphate (MAP), single super-phosphate (SSP), calcium ammonium nitrate (CAN), urea (Mathenge, 2009) and to some extent, organic manure, to supply the most limiting nutrients (NPK). However, use of considerable amounts of fertilizers in sub-humid zones result in low nutrient use efficiency (NUE) due to leaching. Split application by top-dressing is known to improve NUE, but small-scale poor-resource farmers consider it a luxury, or apply below recommended rates (Mucheru-Muna et al., 2013) leading to poor crop

performance. On the other hand, exclusive use of organic manure is limited by bulkiness, low nutrient quality, low nutrient mineralization (Makokha et al., 2001) and extra labour. The major constraint for usage of fertilizers and profitability to farming in Kenya has been high producer prices (Druilhe and Barreiro-Hurlé, 2012) and thus, alternative sources of cheaper fertilizers are being sought.

Of the amount of fertilizers applied to the farms, only a small percentage is utilized by plants, while the rest is eventually washed into water bodies (Tolescu et al., 2009) through leaching and surface runoff, or lost by volatilization under reduced conditions. About 40–70% N and 80–90% P of fertilizers applied in the farms is lost to the environment resulting not only in economic and resource losses, but also environmental pollution (Guo et al., 2005; Naderi and Danesh, 2013). Efforts have been made to minimize these challenges by developing new generation fertilizers, the so-called “smart” fertilizers. Among them, are slow or controlled release fertilizers (SRF) which contain at

Peer review under responsibility of Faculty of Agriculture, Ain-Shams University.

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<https://doi.org/10.1016/j.aoas.2018.11.001>

Received 26 July 2018; Received in revised form 27 August 2018; Accepted 2 November 2018

Available online 15 November 2018

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least one nutrient that either delays its availability and utilization processes, or is available to the plant for a longer period than the standard fertilizers which are considered “quickly available” (Zeroual and Kossir, 2012; Chen et al., 2013). The availability of nutrients is prolonged by either slowing the release or altering reactions leading to losses (Olson-Rutz et al., 2011). The enhancement of nutrient use efficiency (NUE) implies more efficient food production and reduced cost for environmental protection (Naderi and Danesh, 2013). Further, SRF can be applied as a pre-plant application and the need for split application is eliminated, reducing production costs (Chen et al., 2013).

In the face of resource scarcity and ever increasing population, development in agriculture can be achieved exclusively through effective use of modern technologies. To date, intensive research is directed towards integrating Nano-technologies into fertilizer development or formulation. Due to high surface area to volume ratio, Nano-fertilizers are expected to be more effective than polymer-coated conventional SRF as they enhance NUE, reduce toxicity and minimize the potential negative effects associated with excess application such as ground water pollution (DeRosa et al., 2010). Hydroxyapatite (HA) nano-particles are rated as one of the prominent candidates for potential agricultural nutrient sources (Kottegoda et al., 2011). However, much of the available data on HA is mainly focused on biomedical application (Mateus et al., 2007; Pang et al., 2010; Pataquiva-Mateus et al., 2013), while agricultural application is lacking.

More recently, there has been an increasing interest in the use of polymer hydrogels (PHG) in agricultural production. PHGs are macromolecular networks with the ability to swell or shrink in the presence or absence of water, due to hydrophilic groups and slightly cross-linked structure which resists dissolution (Sannino et al., 2009; Qiu and Hu, 2013). Polyacrylamide (PAM) is used as a chemical intermediate in the production of PHGs with high absorption capacity (super-absorbents) such as disposable diapers, medical and agricultural products, among others (Laftah and Hashim, 2014). High molecular weight PAM is added into the soil through irrigation water as anti-erosion additive (Charoenpanich, 2013) and it has been reported to be degraded by native soil bacterial species such as *Bacillus*, *Pseudomonas* and *Rhodococcus* among others, and also fungi (*Aspergillus*) which are capable of accessing N through amidase activity (Guezennec et al., 2015; Yu et al., 2015). Extracellular amidase enzyme catalyzes the hydrolysis of C-N bond of the amides, resulting in the generation of NH_3 , NH_4^+ and carboxylic acid group ($-\text{COOH}$). The production of NH_3 under moisture conditions contributes to mineral N in the soil, whereas carboxylic acid is further degraded by micro-organisms as source of carbon (energy) to CO_2 and H_2O , thus being environmental friendly. PAM-treated agricultural soil has been experimentally demonstrated by Kay-Shoemake et al. (1998) to exhibit higher bacterial counts, high inorganic N concentration and amidase activity, hence considered healthier soil than the untreated ones. In this study, cellulose grafted PAM polymer hydrogel was utilized in the formulation of slow release fertilizer composite and release of nutrients was assessed using laboratory incubation experiment.

2. Materials and methods

2.1. Materials

Swollen cellulose fibers were extracted from water hyacinth (*Eichhornia crassipes*) and Acrylic acid and *N,N*-methylene-bis-acrylamide, were obtained from ACROS Organics, Germany. Triton X-100 was obtained from Sigma Aldrich, while Ammonium persulphate, Calcium hydroxide and Phosphoric acid were from Loba Chemie, Mumbai, India. All other chemicals such as methanol, ammonia, ammonium acetate, potassium chloride, calcium chloride, hydrochloric acid, sulphuric acid, were analytical grade.

2.2. Research methodology

2.2.1. Synthesis of hydroxyapatite (HA) nano-particles

The methodology used in the synthesis was adopted from Kottegoda et al. (2011) with some modifications. 7.716 g $\text{Ca}(\text{OH})_2$ was weighed into the beaker and 0.22 mM TX-100 (non-ionic surfactant) solution added to make a total volume of 100 mL and the mixture stirred for 30 min with a motorized stirrer. A 100 mL of 0.6 M H_3PO_4 was added into the suspension of $\text{Ca}(\text{OH})_2$, drop-wise (15 mLmin^{-1}) from the burette while stirring vigorously at 1000 rpm. After the reaction, the dispersion was stirred for 10 min and then allowed to age for 2 h. It was then oven-dried at 105°C to constant weight and then pulverized into fine powder. The surfactant was removed by washing the powder with methanol.

2.2.2. Synthesis of cellulose-g-poly(acrylamide)/nano-HA/soluble fertilizer composite

Thirty mL (predetermined volume containing 0.8 g dry weight) of cellulose fibers, 1.0 g nano-HA and varied amounts of soluble NPK fertilizer blend $(\text{NH}_4)_2\text{PO}_4$, urea and K_2SO_4 weight ratio 3:5:2, respectively, were transferred into a 3-necked flask. The flask was fitted with reflux condenser and nitrogen line, and then placed in a thermostated water bath equipped with a magnetic stirrer. Nitrogen gas was bubbled through the mixture for 10 min, as the temperature was gradually raised to 70°C . 0.1 g of ammonium persulphate (APS) was added into the mixture and stirred for 30 min to generate radicals. 2.7 mL of acrylic acid (AA), partially neutralized with NH_3 to 70% degree of neutralization and 0.25 g of *N,N*-methylene-bis-acrylamide (MBA) were mixed, stirred to dissolve and then introduced into the reaction mixture. The total volume of the reaction mixture was controlled at 40 mL. The mixture was stirred for an additional 1 min after which the reaction was allowed to proceed for 2 h. The reaction product was then cooled to room temperature, removed from the flask and then cut into regular pieces. 1:1 NH_3 solution was added drop-wise to adjust the pH to 8. Fertilizer composite was then oven dried at 60°C to constant weight and then pulverized to pass through a 1 mm sieve.

2.2.3. Chemical characterization of nano-HA and the fertilizer composite

Fourier Transform Infra-red spectrophotometer, Shimadzu IRAffinity-1S, was used to characterize nano-HA and cellulose-g-poly(acrylamide)/nano-HA/soluble fertilizer composite. The sample holder and the probe were cleaned and scanned in absence of the sample to collect the background spectrum. The finely ground sample was placed on the sample holder, pressed against the diamond using the probe and scanned between 4000 and 400 cm^{-1} . Field emission transmission electron microscope (Technai F20) was used to study the morphology of HA nano-particles and the fertilizer composite.

2.2.4. Soil sampling for incubation experiment

A field was identified at the College of Agriculture and Veterinary Science farm, University of Nairobi located in Kiambu County, Central Kenya, coordinates $1^\circ 15'\text{S}$ and $36^\circ 44'\text{E}$, and an altitude of 1940 m above sea level. The soils are very deep ($> 180 \text{ m}$), well-drained, dark red to dark reddish brown, friable clays (Kimetu et al., 2007; Karuku et al., 2012) with moderate to high inherent fertility (Mucheru-Muna et al., 2013) and are classified as Humic Nitisols (WRB, 2014). The site experiences a bi-modal rainfall distribution with long rains in mid March-May and short rains in October-December. The mean annual rainfall is about 1000 mm, and the average monthly maximum and minimum temperatures are 23.8 and 12.6°C , respectively. Crops grown in the area include; kales (*Brassica oleracea*), tomatoes (*Lycopersicon esculentum*), cabbage (*Brassica oleracea*), carrots (*Daucus carota*), onions (*Allium fistulosum*), beans (*Phaseolus vulgaris*), maize (*Zea mays*) and coffee (*Coffea Arabica*).

The surface litter that included leaves, sticks, stumps and other materials were removed gently to expose the surface soil. Soil samples

Table 1

The composition of the formulated fertilizer composite and the amounts of N, P and K, in the treatments.

Code	Composition of the Fertilizer Composite (% w/w)				Soil treatment (mg kg ⁻¹)		
	N-P ₂ O ₅ -K ₂ O	PHG	SF	Nano-HA	N	P ₂ O ₅	K ₂ O
T1	14: 0: 0	100	0	0	50	0	0
T2	13.8: 18.8: 4.6	68.8	16.0	16.0	50	68.1	16.6
T3	15.4: 20: 4.8	62.7	22.3	15.0	50	65.0	15.6
T4	16.8: 21.5: 6.2	57.7	28.5	14.3	50	64.0	18.4
T5	20: 24: 9.7	44.5	44.4	11.1	50	60.0	24.2
T6	21.3: 25.2: 11.6	25.0	66.0	9.0	50	58.5	27.2
T7	22: 24: 11	0	100	0	50	54.5	24.9

Legend: PHG = polymer hydrogel, SF = soluble fertilizer, nano-HA = nano-hydroxyapatite.

at a depth of 0–20 cm were randomly collected at selected points using a soil auger and bulked to make a composite sample. The composite sample was air-dried in the laboratory, crushed to pass through a 4 mm sieve to remove large pieces of surface materials. A portion of the composite sample was set aside for chemical characterization and the other portion for incubation experiments.

2.2.5. Soil characterization before onset of incubation experiment

Total nitrogen and mineral N were determined by micro-Kjedahl method (Bremner, 1996), available P with Mehlich 1 method (Mehlich, 1953) and exchangeable cations (Ca, K and Mg) by flame photometry after extraction with 1 M NH₄OAc. Soil pH was determined with glass electrode, 1: 2.5 soil to water (salt) ratio.

2.2.6. Fertilizer composite samples and laboratory incubation experiment

Table 1 shows the composition of the fertilizer composite and the amount of NPK added to the soil for incubation experiments. T1 is cellulose-g-poly(acrylamide) polymer hydrogel (PHG) and T2–T6 was formulated to contain cellulose-g-poly(acrylamide)/nano-HA/soluble fertilizer. The amount of soluble fertilizer (SF) in the composites increases from T2 to T6 with decrease in the content of PHG and nano-HA, whereas T7 represent conventional fertilizer.

The formulated fertilizer composite (< 1 mm) was added to the soil at the rate of 50 mg N kg⁻¹, thoroughly mixed and then put into plastic incubation bags. This corresponded to 100 kg N ha⁻¹, recommended for N application for maize in Kiambu County (planting, 250 kg/ha NPK 23:23:0; top dressing, 125 kg/ha CAN) (Ministry of Agriculture, 2014). The amount of the fertilizer added to 1 kg of soil include; T1 – 397 mg, T2 – 362 mg, T3 – 325 mg, T4 – 298 mg, T5 – 250 mg, T6 – 235 mg and T7 – 227 mg. The treatments were replicated three times, with untreated soil serving as the control. Distilled water was added to field capacity (30% w/w), bags were sealed and incubated in the dark at 20 °C for 16 weeks. The amount of mineral N (NH₄-N and NO₃-N), P and K were determined bi-weekly from the onset of incubation. Soil was kept moist at field capacity throughout the incubation period by adding distilled water where the feel method was used to establish the necessity. Aerobic conditions were maintained by opening plastic bags periodically to allow aeration. Each of the samples was divided into two portions at the time of sampling. For one portion, available N (NH₄-N and NO₃-N) was extracted and quantified. The other portion was air dried, before analyzing for total N, available P and K.

2.2.7. Nitrogen mineralization potential, N₀

Several models have been proposed to simulate N-mineralization dynamics during long-term aerobic incubation. Simulation models widely employed include; single first-order kinetics model, double first-order kinetics model, and mixed first-order and zero-order kinetics model (Zhang et al., 2017). Potentially mineralizable-N (N₀), which is

the fractional quantity N susceptible to mineralization, was estimated using single first order kinetics employed by Stanford et al. (1974) and later adopted by Karuku (1989), and Karuku and Mochoge (2018), Eq. (1).

$$\frac{dN}{dt} = -kN \quad (1)$$

Integration gives Eq. (2),

$$\text{Log}(N_0 - N_t) = \text{log}N_0 - kt/2.303 \quad (2)$$

Where, N_t is the cumulative N mineralized at time t (days), N₀ is the amount of potentially mineralizable N and k is the first order rate constant (day⁻¹). Stanford et al. (1974); Karuku and Mochoge (2018) found the rate constant k, to be reasonably equal for large number of soils and a period of 2 weeks incubation following a short term pre-incubation was sufficient to estimate mineralization potential (N₀) using simplified Eq. (3).

$$N_0 = 9.77N_t \quad (3)$$

Where, N₀ is nitrogen mineralization potential and N_t is nitrogen mineralized in 2 weeks.

2.2.8. Statistical analysis

The data from the incubation experiment was subjected to ANOVA, using IBM SPSS Statistics Version 20. Tukey honest significant difference (HSD) post hoc test was used to compare and assess the significance of the mean values. The main effects; time (within-subject factor) and treatment (between-subject factor) were considered significant at a probability level, p ≤ 0.05.

3. Results and discussion

3.1. Fourier Transform Infra-red spectroscopic analysis of SRF and Nano-HA

The Fourier Transform Infra-red (FTIR) spectrum of HA nano-particles is shown in Fig. 1. The absorption bands at 1419 and 875 cm⁻¹ correspond to CO₃²⁻ ions, attributed to the physical interaction of HA with CO₂ during the synthesis at ambient conditions (Iyyappan and Wilson, 2013). The spectrum observed in the study is similar to that of Costescu et al. (2010), who reported decreased intensity of the peaks related to CO₃²⁻ at high calcination temperatures of 600 and 1000 °C. The broad and weak band at 3600–3000 cm⁻¹ and 1635 cm⁻¹ correspond to H–O–H of lattice water, which also diminish on heating. The characteristic bands for PO₄³⁻ group appear at 1022 and 964 cm⁻¹ due to stretching vibrations and, 601 and 563 cm⁻¹ corresponding to the bending vibrations. The bands characteristic of C–H stretch at 2928 and 2856 cm⁻¹ due to –CH₃ and –CH₂ respectively, were found to be

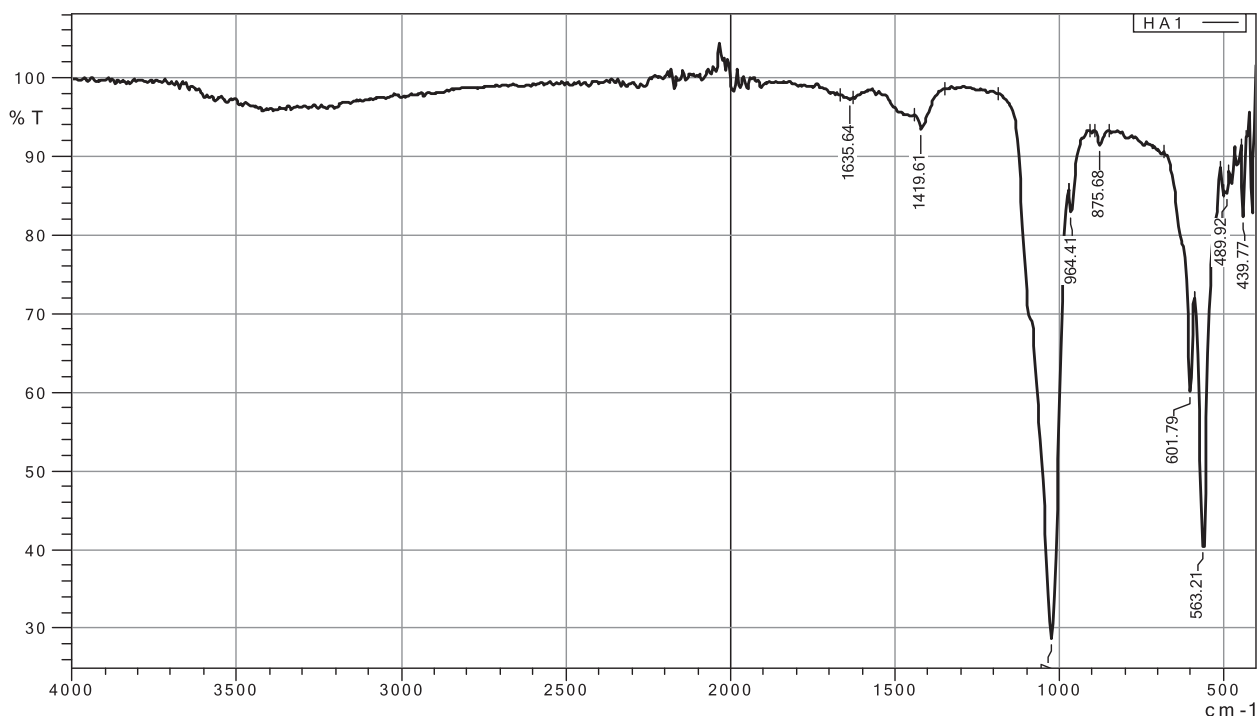


Fig. 1. FTIR spectrum of hydroxyapatite nano-particles.

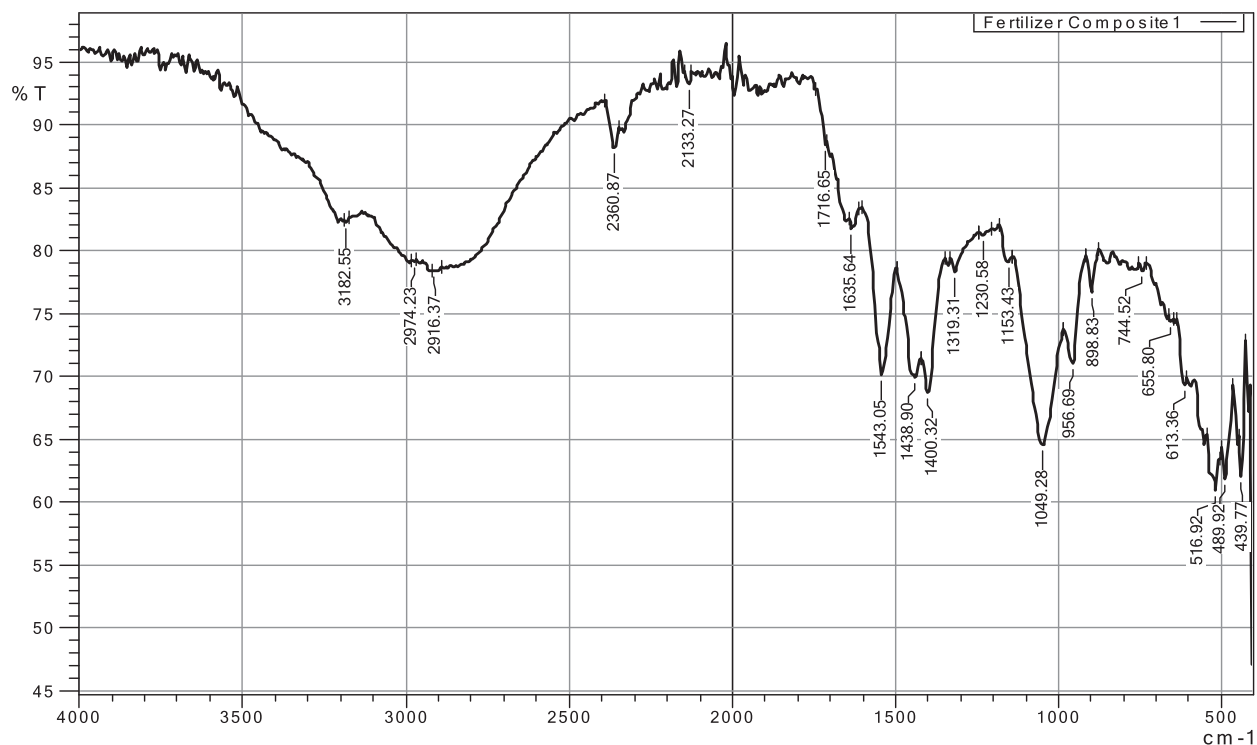


Fig. 2. FTIR spectrum of cellulose-g-poly(acrylamide)/nano-HA/soluble fertilizer composite.

absent in the FTIR spectrum. This confirms complete removal of T-X 100 upon washing HA nano-particles with methanol.

FTIR spectrum of the fertilizer composite is shown in Fig. 2. The broad and strong band at $2500\text{--}3500\text{ cm}^{-1}$ can be assigned to O–H stretch due to carboxylic acid (acrylic acid) and alcoholic group (cellulose), and also, N–H for amide group (acrylamide). The bands at

3182 and 1543 cm^{-1} are assigned to N–H stretching vibration for primary amide (Bundela and Bajpai, 2008).

Eritsyian et al. (2006) and Fernandes et al. (2015) proposed radical polymerization reaction mechanism between acrylic acid and urea via the carbonyl carbon reaction scheme (a). According to these authors, the moderately strong band at 1635 cm^{-1} (Fig. 2) is assigned to

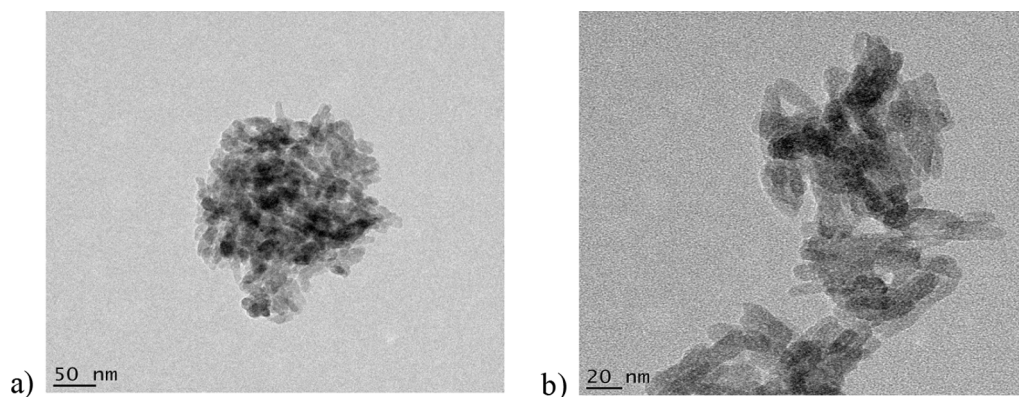
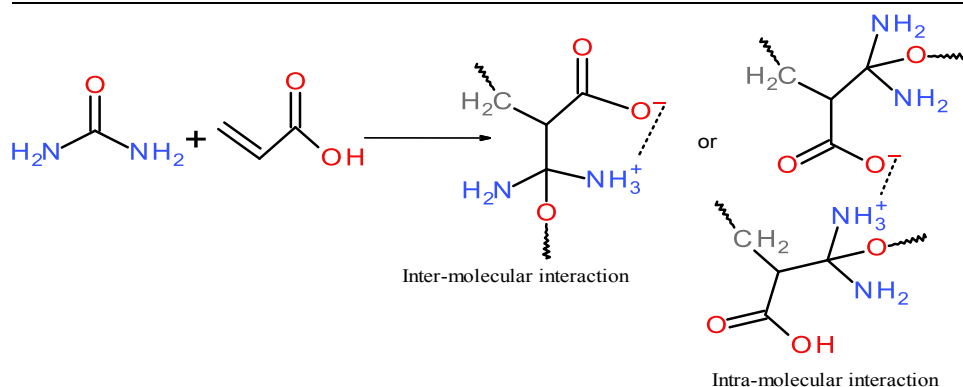


Fig. 3. TEM images of rod-shaped agglomerates of HA nano-particles at 50 and 20 nm scales.

adsorption of NH_3^+ and COO^- groups as a result of intra- and inter-molecular interactions between $-\text{COOH}$ and $-\text{NH}_2$ which lead to the formation of a salt. Since acrylic acid was partially neutralized with

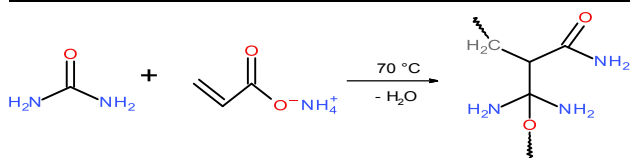
(Fig. 2) corresponds to O–H bending vibration for carboxylic acid, revealing incomplete neutralization of acrylic acid. Spectral bands at 1153 to 1049 cm^{-1} are assigned to C–O–C bridging resulting from the



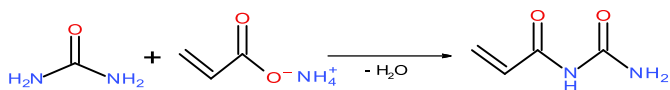
Reaction Scheme (a): Radical polymerization between urea and acrylic acid

NH_3 , it therefore implies that ammonium acrylate could react the same way according to reaction scheme (b). Alongside radical polymerization, condensation reaction between urea and acrylic acid may also occur (Fernandes et al., 2015), yielding a branched co-polymer according to reaction scheme (c). The strong band at 1438 – 1400 cm^{-1}

reaction between ammonium acrylate (monomer) and the $-\text{OH}$ group of cellulose. The band at 898 cm^{-1} is assigned to C–O–C stretch of glucosidic bonds for amorphous cellulose (Synytsya and Novak, 2014). The FTIR peaks from 1049 to 920 cm^{-1} are assigned to P–O–C (Fig. 2), suggesting an overlap between bands attributed to C–O–C and P–O–C



Reaction Scheme (b): Radical polymerization between urea and ammonium acrylate



Reaction Scheme (c): Condensation reaction between urea and acrylic acid

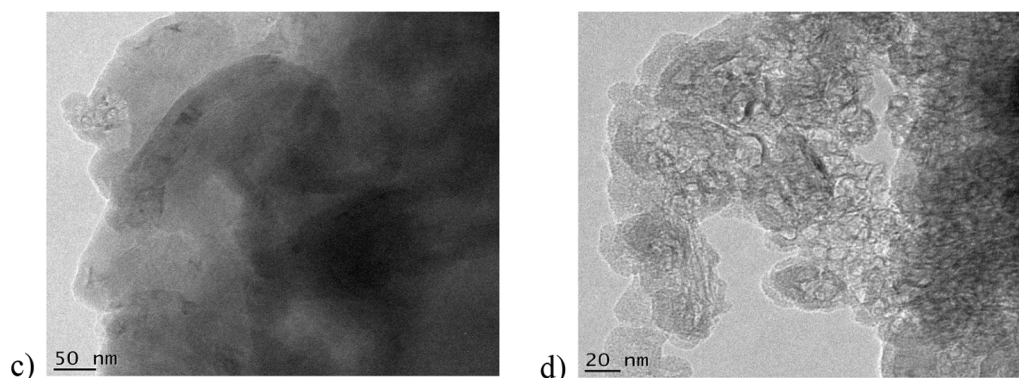


Fig. 4. TEM images of cellulose-g-poly(acrylamide)/nano-hydroxyapatite/soluble fertilizer composite at 50 and 20 nm scales.

groups. The peaks at 1049 and 956 cm^{-1} are assigned to P–O–C stretching vibrations, indicating the reaction between –OH groups at the surface of HA nano-particles and the monomer. The bands at 1319 and 516 cm^{-1} (Fig. 2) are attributed to P=O stretching vibrations for the PO_4^{3-} ion, whereas the bands at 613 and 439 cm^{-1} corresponds to SO_4^{2-} ion for the inorganic salts i.e., $(\text{NH}_4)_2\text{HPO}_4$ and K_2SO_4 .

From FTIR spectrum of the fertilizer composite, there is an indication of the existence of chemical interactions between (a) the monomer, cellulose and nano-HA, and (b) monomer and urea molecules towards the formation of 3-D network structure. Additionally, due to large surface area of HA nano-particles, Kottegoda et al. (2011, 2017) associated the formation of urea-HA Nano-hybrid (molar ratio, 6:1) to the existence of H-bonds between –OH group on the surface of HA and – NH_2 group of urea.

3.2. Transmission electron microscopy

Figs. 3 and 4 show transmission electron microscopy (TEM) images of HA nano-particles and cellulose-g-poly(acrylamide)/nano-hydroxyapatite/soluble fertilizer composite. The images of nano-HA displayed rod-shaped nano-particle agglomerates with particle size of less than 50 nm (Fig. 3). The TEM images of the fertilizer composite (Fig. 4) showed dispersion of the HA nano-particles and the salt crystals.

3.3. Chemical characteristics of soil at the onset of the experiment

Table 2 shows salient characteristics of the soil used in the study. The soils at the site were acidic with low available P content. The soil acidity could be attributed to the humid conditions in central highlands which lead to the leaching of Ca, Mg and K, and other basic cations. Low amounts of available P could be attributed to soil acidity which renders P unavailable through fixation and also, continuous removal by crops.

Table 2
Some salient chemical characteristics of soil used in incubation experiment.

Parameter	Units	Value
pH (soil: H_2O , 1: 2.5)	–	5.25
pH (CaCl_2 : 1: 2.5)	–	4.50
Electrical conductivity	ds/m	0.26
Cation exchange capacity	C mol kg^{-1}	15.62
N	%	0.29
Available P	ppm	8.50
Exchangeable K	C mol kg^{-1}	1.10
Ca	C mol kg^{-1}	8.51
Mg	C mol kg^{-1}	4.26

3.4. Nitrogen mineralization

The content of mineral N ($\text{NH}_4\text{-N} + \text{NO}_3\text{-N}$) during 16 weeks incubation period is shown in Table 3. The results revealed low content of MN in the initial stages of incubation with some decrease in the 4th week, followed by significant increase through the 8th week and a peak at the 12th week then a decline in the 16th week. Low mineralization of N in the initial stages of incubation reflects the lag phase (Deenik and Yost, 2008) associated with immobilization of nutrients by micro-organisms to nourish and increase their biomass (Karuku and Mochoge, 2016; Tambone and Adani, 2017). Micro-organisms require sufficient water, inorganic nutrients, carbon sources and trace elements for maintenance and growth. The period between the 4th and 12th week relates to microbial exponential growth phase and the microbes have proliferated hence able to act on the substrate. Although they are well satiated, more are left for mineralization process and the rate of mineralization is much higher than immobilization. The decline in MN content beyond the 12th week is attributed to depletion of mineralizable substrate. Also, the microbes may have passed the stationary phase and had entered the endogeneous growth phase, leading to decline in immobilization. Low N mineralization observed within the treatments up to 4 weeks might favour annual crops such as maize, because the uptake of N is slow at establishment, faster at development and reproductive phases, and declines at maturity.

The release of N from the SRF composites T2 to T6 (cellulose-g-poly (acrylamide)/nano-HA/soluble fertilizer composite) occurred in two phases: i) diffusion of urea-N and $\text{NH}_4\text{-N}$ and ii) hydrolysis of amide-N (Liu et al., 2007). The highest content of MN in the first 4 weeks was

Table 3
Concentrations of Mineral N ($\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$) during 16 weeks incubation period.

Treatment	Incubation period (weeks)					Cumulative MN at 16th wk
	2	4	8	12	16	
Cntrl	43.6a	24.2 a	107.2 a	145.8a	85.1 a	405.8 a
T1	50.8ab	33.0 b	152.9 b	176.6ab	117.9 b	531.1 b
T2	59.0abc	44.1 cd	176.4 c	200.1bc	128.4 cd	608.0 cd
T3	55.0abc	41.5 c	189.5 cd	192.2bc	119.3 b	597.4 c
T4	55.3abc	46.0 cd	205.1 de	266.1e	139.1 e	711.7 e
T5	63.5bc	42.9 c	190.1 cde	210.6 cd	124.7 bcd	631.8 cd
T6	58.3abc	48.8 cd	211.7 e	242.1de	131.2 de	692.1 e
T7	73.2c	51.7 d	184.9 cd	207.5bc	129.6 d	646.9 d

Notes; different letters in the same column are significantly different ($p \leq 0.05$ level). Cntrl = No treatment, T1 = 14: 0: 0, T2 = 13.8: 18.8: 4.6, T3 = 15.4: 20: 4.8, T4 = 16.8: 21.5: 6.2, T5 = 20: 24: 9.7, T6 = 21.3: 25: 11.2, T7 = 24: 22: 11.

observed in conventional fertilizer T7 which was attributed to the hydrolysis of urea-N and release of $\text{NH}_4\text{-N}$ from DAP. However, no significant difference was observed between T7 and T2, T3, T4, T5 and T6 in the 2nd and the 4th week of incubation. This insignificant difference may be attributed to small particle sizes of SRF composite (< 1 mm) which enabled faster diffusion of the soluble fertilizer into the soil, and thus slow release of N might be enhanced by increasing the particle size of the fertilizer composite. Significant higher content of N observed in T6 in the 8th and 12th week and T4 in the 12th and 16th week relative to T7, may be attributed to early exposure of $\text{NH}_4\text{-N}$ (in case of T7) to exchangeable sites in the soil and possibility of immobilization through fixation. NH_4^+ fixation occurs in soils with clay minerals of the type 2:1 such as illite and vermiculite, due to the formation of NH-O bond in the hexagonal holes and the balancing of positive charge deficiency which arises from isomorphous substitution of Si^{4+} and Al^{3+} ions (Chen, 1997). Among the factors which have been found to enhance fixation are increased concentration and contact time (Kissel et al., 2008). No significant difference was observed in the 12th week between T7 and T1, T2 & T3, indicating considerable mineralization of N in SRF treatments. The observed increase in MN contents between the 8th and 16th week in SRF T1 to T6 may be attributed to the release (hydrolysis) of amide-N.

The cumulative MN in SRF treatments generally increased from T1 to T6, reflecting increased amount of soluble fertilizer and decreased content of nano-HA incorporated into the PHG. Since N mineralization is a biological process, the release of N depends on the chemical constituent of the fertilizer such as N content and C:N ratio (Masunga et al., 2016) among other factors. The C:N ratio influences mineralization rate, as microorganisms immobilize N to break carbon bonds/chains in the organic material for their energy requirement (Dong et al., 2012; Karuku and Mochoge, 2016; Tambone and Adani, 2017). The significant difference observed in SRF T1 {cellulose-g-poly(acrylamide)} MN content compared to T2, T3, T4, T5 and T6, from the 4th to the 16th week, could be related to the carbon content. Slow mineralization of N may have been contributed by higher C content in T1 (i.e., 14% N, the rest being carbonaceous material of acrylic and complex cellulose chains), compared to T2 to T6 of which the C content decreased on incorporating soluble fertilizer and nano-HA.

Nevertheless, significantly higher MN content in T1 compared with the control indicates substantial hydrolysis of the amide-N within the incubation period. Cellulose chains being part of the polymer composite provide easily degradable-C to the microorganisms, enhancing breakdown of the copolymer and hence N release. Addition of organic material to PAM-amended soil has been reported to effect degradation through increased microbial activity. Higher amounts of soil aggregating fungi was reported by TonThat et al. (2008) in macro-aggregates generated from PAM-wheat residue amended soil compared to the control. Award et al. (2012) also reported stimulating effect of synthesized PAM biopolymer (BP) and biochar (BC) on the decomposition of soil organic matter and maize residue. Higher enzymatic activities were observed in both BP and BC amended soil compared to the control and, fungi contributed highly to plant residue decomposition. Watson et al. (2016) observed stimulation of nitrification and C-mineralization in maize straw-amended soil conditioned with PAM, a phenomenon attributed to improved microbial conditions and partial utilization of PAM as a substrate.

Addition of MN from inorganic source to organic fertilizer enhances decomposition of organic material (Abbasi and Khaliq 2016). Further, cultures of bacteria derived from agricultural soils have been reported to utilize PAM as N source (Kay-Shoemake et al., 1998). Bacterial strain (*Pseudomonas putida* H147) studied by Yu et al. (2015) showed 31.1% degradation efficiency of PAM in 7 days and exceeded 45% under optimum culture conditions. Degraded PAM showed low molecular weight oligomer derivatives while acrylamide monomers did not accumulate. The observed increase in the content of MN in SRF treatments T2 to T6, could be attributed to increased amount of soluble N

Table 4Concentrations of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ during 16 weeks incubation period.

Treatment	Incubation Period (weeks)					Cumulative MN at 16th wk
	2	4	8	12	16	
<i>NH₄-N</i>						
Cntrl	29.4 a	17.1 a	72.5 a	87.0 a	53.3 a	259.0 a
T1	34.0 ab	24.5 b	83.0 ab	99.6 ab	69.3 b	310.3 b
T2	38.8 c	26.8 b	97.4 bc	116.8 bc	78.9 cd	358.7 cd
T3	34.0 ab	25.0 b	95.4 bc	114.5 bc	73.6 bc	342.5 bc
T4	35.1 ab	29.3 b	109.8c	131.7 c	86.4 d	392.3 bc
T5	35.8 ab	23.5 ab	86.29 ab	103.5 ab	78.9 cd	328.0 bc
T6	38.8 c	28.3 b	113.7 c	136.4 c	78.9 cd	396.1 d
T7	38.8 c	27.9 b	89.5 ab	107.4 ab	73.6 bc	342.6 c
<i>NO₃-N</i>						
Cntrl	14.2 a	7.2 a	34.6 a	58.8 a	31.7 a	146.5 a
T1	16.8 ab	8.7 b	69.9 b	77.0 ab	48.5 b	220.8 b
T2	20.2 abc	17.2 cd	79.1 c	83.3 bc	49.5 cd	249.2 c
T3	20.9 abc	16.5 c	94.1 cd	77.7 bc	45.7 bc	254.9 c
T4	20.2 abc	16.7 c	95.4 de	134.4 e	52.7 e	319.3 d
T5	27.6 bc	19.5 c	103.9 cde	107.1 cd	45.7 bcd	303.8 d
T6	19.4 bc	20.5 cd	98.1 e	105.7 de	52.3 de	295.9 d
T7	34.3 c	23.8 d	95.4 cd	100.1 bc	56.0 d	309.7 d

Notes; different letters in the same column are significantly different ($p \leq 0.05$ level). Cntrl = No treatment, T1 = 14: 0: 0, T2 = 13.8: 18.8: 4.6, T3 = 15.4: 20: 4.8, T4 = 16.8: 21.5: 6.2, T5 = 20: 24: 9.7, T6 = 21.3: 25: 11.2, T7 = 24: 22: 11.

from DAP and easily hydrolysable N from urea. The microbes were provided with easy source of N and to acquire energy (carbon), the polymer has to be degraded. Polymer medium supplemented with mineral N, liquid paraffin and sucrose has been shown to contribute to PAM degradation and microbial biomass compared to the control (Yu et al., 2015). The significantly ($p \leq 0.05$) lower content of MN observed in SRF treatment T5 relative to T4 and T6 could be attributed to the experimental errors.

Table 4 shows the contents of ammonium-N and nitrate-N during different incubation stages. The $\text{NH}_4\text{-N}$ content in T7 was significantly higher ($p \leq 0.05$) than T1, T2, T4 & T5 in the 2nd week, whereas for $\text{NO}_3\text{-N}$, T7 showed significantly higher value than T1, T3, T4 & T5 in the 4th week of incubation. No significant difference in both $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ content was observed between T7 and SRF T2, T3 and T5 in the 8th, 12th and 16th week, but significantly higher values were observed in T4 and T6 compared to T7. Significantly higher N content in T7 at early stages of incubation (2nd & 4th week) reveals availability of N which crops may not fully utilize as it may be lost through leaching or fixation by clay minerals, while in SRFs it may be preserved for future use and hence better synchronization. From the 8th to the 16th week, both T7 and SRF showed nearly equal N content, implying that the plant can utilize N released by SRF more efficiently than T7 which might get depleted sooner due to earlier losses.

$\text{NH}_4\text{-N}$ content was higher than $\text{NO}_3\text{-N}$ throughout the incubation. Subsequently, the cumulative $\text{NH}_4\text{-N}$ content at the end of incubation period recorded higher values than $\text{NO}_3\text{-N}$ content and generally increased from T1 to T6. No significant difference was observed in cumulative $\text{NH}_4\text{-N}$ content between T7 and SRF T2, T3, T4 & T5, and also, in the cumulative $\text{NO}_3\text{-N}$ between T7 and SRF T4, T5 & T6. The higher $\text{NH}_4\text{-N}$ content compared to $\text{NO}_3\text{-N}$ may be attributed to the acidity of soil which could have inhibited the growth and activities of nitrifying bacteria. The pH of soil during the incubation period showed some increase in the 12th and 16th week, particularly in SRF T2 to T6, though not significant among the treatments (Table 5). The lowest pH value was 5.15 recorded in the 2nd week, while the highest value was 5.97 recorded in the 16th week. Nitrification process which is a biological oxidation of NH_4^+ to NO_3^- has been found to occur in soil pH values ranging between 5.5 and 10.0 (Sahrawat, 2008) with an

Table 5
Soil pH during the incubation period.

Treatment	Incubation period (weeks)				
	2	4	8	12	16
Cntrl	5.34 a	5.60 a	5.53 a	5.33 a	5.42 a
T1	5.31 a	5.54 a	5.43 a	5.66b	5.71b
T2	5.28 a	5.23 a	5.56 a	5.74b	5.76 bc
T3	5.21 a	5.69 a	5.30 a	5.63 ab	5.67b
T4	5.33 a	5.46 a	5.36 a	5.68b	5.83 bc
T5	5.15 a	5.47 a	5.44 a	5.59 ab	5.71 bc
T6	5.28 a	5.80 a	5.34 a	5.47 ab	5.92c
T7	5.24 a	5.65 a	5.23 a	5.52 ab	5.68b

Notes; different letters in the same column are significantly different ($p \leq 0.05$ level). Cntrl = No treatment, T1 = 14: 0: 0, T2 = 13.8: 18.8: 4.6, T3 = 15.4: 20: 4.8, T4 = 16.8: 21.5: 6.2, T5 = 20: 24: 9.7, T6 = 21.3: 25: 11.2, T7 = 24: 22: 11.

optimum pH value of about 8.5, while the process is inhibited at pH less than 5 and optimal at pH greater than 6. Higher content of $\text{NH}_4\text{-N}$ than $\text{NO}_3\text{-N}$ was observed by Omar and Ismail (1999) in soil treated with a mixture of urea and Ca_2Cl_2 or K_2SO_4 . The population of bacteria and fungi decreased in urea treatments except cellulolytic fungi, and the same decrease in microbial population was also observed in Ca_2Cl_2 or K_2SO_4 soil amendments. Soil pH increased in urea amendment, but was decreased in inorganic salts amendments to values lower than that of the control. The toxic effect of urea and inorganic salts reduced when they were applied as a mixture. Giroto et al. (2017) observed higher pH values (6.3–7.9) after 42 days of aerobic incubation of soil amended with urea/HA and thermoplastic starch urea/HA amendments compared to untreated soil, whereas the pH of soil amended with HA and SSP remained close to the pH of the control (≈ 5). The increase in pH in Nano-composite amendments was attributed to high hydrolysis of urea in the soil with low CEC and buffering capacity. The existence of more of MN in the form of $\text{NH}_4\text{-N}$ is beneficial because it is not susceptible to leaching losses.

Table 6 shows N mineralization potential (N_0), mineralization rate constant (K), coefficient of determination (R^2) and time taken for 50% of potentially mineralizable N ($t_{1/2}$), to be mineralized.

T7 had the highest potentially mineralizable nitrogen (N_0) compared to all other treatments though not significantly different from T2, T3, T4, T5 and T6. The low N mineralization observed in SRF treatments may be attributed to slow release of nutrients in the initial stages of incubation. N_0 related well to the observed cumulative mineral N as at 16th week of incubation. However, no significant difference was observed for cumulative MN between T7, T2 and T5 at 16th week of incubation, implying that incorporation of soluble fertilizer into the

Table 6
Nitrogen mineralization potential (N_0), mineralization rate constant (K), half-life ($t_{1/2}$) and cumulative MN.

Treatment	N_0	R^2	K (week ⁻¹)	$t_{1/2}$ (wks)	Observed cumulative MN at 16 wk
Cntrl	425 a	0.903	0.052	13.3	405 a
T1	495 ab	0.917	0.051	13.6	531 b
T2	576 abc	0.829	0.059	11.7	608 cd
T3	536 abc	0.716	0.051	13.6	597 c
T4	539 abc	0.865	0.056	12.4	712 e
T5	619 bc	0.742	0.060	11.6	632 cd
T6	569 abc	0.910	0.053	13.1	692 e
T7	714 c	0.831	0.057	12.2	647 d

Legend: N_0 = Nitrogen Mineralization Potential, K = Mineralization rate constant and $t_{1/2}$ = Time taken for 50% of potentially mineralizable nitrogen to be mineralized. Cntrl = No treatment, T1 = 14: 0: 0, T2 = 13.8: 18.8: 4.6, T3 = 15.4: 20: 4.8, T4 = 16.8: 21.5: 6.2, T5 = 20: 24: 9.7, T6 = 21.3: 25: 11.2, T7 = 24: 22: 11.

Table 7
Content of available P (ppm) at different incubation times (weeks).

Treatment	Incubation period (weeks)				
	2	4	8	12	16
Cntrl	21.0 a	10.4 a	25.3 a	23.9 a	26.1 a
T1	24.1 ab	12.9 abc	25.9 a	26.3 a	28.5 a
T2	24.1 ab	12.5 ab	39.3 b	37.8 b	41.1 b
T3	22.3 ab	13.6 abc	46.5 bc	46.6 c	46.2 bc
T4	26.1 ab	14.4 bc	55.2 cd	54.3 d	51.6 cd
T5	25.6 ab	16.3 cd	63.5 d	66.2 e	66.2 e
T6	27.4 ab	16.3 cd	76.3 e	80.4 f	76.6 f
T7	27.8 b	19.6 d	54.2 cd	53.7 d	54.3 d

Notes; different letters in the same column are significantly different ($p \leq 0.05$ level).

Legend: Cntrl = No treatment, T1 = 14: 0: 0, T2 = 13.8: 18.8: 4.6, T3 = 15.4: 20: 4.8, T4 = 16.8: 21.5: 6.2, T5 = 20: 24: 9.7, T6 = 21.3: 25: 11.2, T7 = 24: 22: 11.

polymer composite enhances mineralization of N. Thus, the significantly higher ($p \leq 0.05$) MN values observed in T4 and T6, relative to T7 may be attributed to improved mineralization leading to release of higher amounts of MN in the later stages of incubation.

The coefficient of determination, R^2 ranged from 0.742 to 0.917, indicating a good fit of the experimental data to the single order kinetics model. The mineralization rate constant ranged from 0.051 to 0.056 week⁻¹ which resulted in half-life time ($t_{1/2}$) ranging from 11.6 to 13.6 weeks, suggesting that mineralization of most of the N would occur within the growing period of most annual crops of about 20 weeks. The $t_{1/2}$ values obtained in the experiment were similar to the average value of 12.8 weeks reported by Stanford and Smith (1972) on evaluating N_0 of 39 soil types in the USA. Since there was less variation in the $t_{1/2}$ among the treatments, the advantage of SRF over T7 could be attributed to the slow initial N mineralization, leading to release of significantly ($p \leq 0.5$) higher amounts in the later stages of incubation. The incubation experiment was however carried out at optimal conditions of moisture, temperature and aeration, for the growth and activity of soil microbes and hence N-mineralization rate might be lower/higher in the field than in the laboratory due to varying conditions that could affect the performance of micro-organisms.

3.5. Available phosphorous

Available P at different incubation times are shown in Table 7. The lowest P values were recorded in the 4th week, highest in the 8th week and remained nearly constant in the 12th and 16th week of incubation. The decline in P content between the 2nd and 4th week could be attributed to microbial immobilization and adsorption of soluble P into the soil. The increased P availability after 4 weeks in all SRF treatments may be attributed to its release through microbial solubilization of nano-HA and degradation of the copolymer. Insoluble phosphates such as apatite have been shown to be solubilized by native soil micro-organisms. Phosphate solubilizing bacteria (*Pseudomonas*, *Enterobacter*, *Anthrobacter*) and fungi (*Aspergillus*, *Penicillium*) present in the soil and the rhizosphere have been reported to hydrolyze insoluble P by secreting low molecular mass organic acids, to chelate mineral ions or lower the pH (Khan et al., 2014; Alori et al., 2017). Besides organic acids, mineral acids such as HCl, HNO_3 and H_2SO_4 produced by chemoautotrophs and H^+ pump, for instance in *Penicillium rugulosum* has been reported to solubilize P (Khan et al., 2014). Soil fungi such as mycorrhizae have been shown to better solubilize P than bacteria as they traverse longer distances within the soil and also, produce and secrete more acids such as gluconic, citric, lactic, 2-ketogluconic, oxalic, tartaric and acetic acid (Alori et al., 2017). Additionally, assimilation of NH_4^+ within microbial cells release H^+ that solubilize P without production of organic acids. Acidification of microbial cells and

Table 8
Concentrations of exchangeable K (C mol kg⁻¹) at different incubation times (weeks).

Treatment	Incubation period (weeks)				
	2	4	8	12	16
Cntrl	1.63 a	1.70 a	1.87 a	1.58 a	1.70 a
T1	1.75 ab	1.85 ab	1.90 ab	1.85 a	1.80 a
T2	1.87 ab	1.83 ab	1.98 bc	2.05 b	2.08 b
T3	2.00 ab	1.92 ab	1.90 c	2.06 b	2.18 c
T4	2.05 ab	2.05 bc	1.95 d	2.00 c	1.95 d
T5	2.10 ab	2.10 bc	2.05 d	2.10 d	2.37 e
T6	2.17 ab	2.13 bc	2.25 e	2.17 e	2.27 e
T7	2.10 b	2.07 bc	2.30 d	2.37 c	2.28 d

Notes; different letters in the same column are significantly different ($p \leq 0.05$ level).

Legend: Cntrl = No treatment, T1 = 14: 0: 0, T2 = 13.8: 18.8: 4.6, T3 = 15.4: 20: 4.8, T4 = 16.8: 21.5: 6.2, T5 = 20: 24: 9.7, T6 = 21.3: 25: 11.2, T7 = 24: 22: 11.

their surroundings release P through substitution of H⁺ for Ca²⁺ ions. The release of Ca²⁺ ions into the soil could be the reason for the observed increase in soil pH towards the end of the incubation period (Table 5). Ca²⁺ ions are bases and have the effect of neutralizing soil acidity (Mucheru-Muna et al., 2013).

No significant difference was observed in the 2nd week between T7 and SRF T1 to T6, while in the 4th week T1 to T4 recorded significantly lower P content compared to T7. From the 8th to 16th week, highest P value was observed in T6 which was also significantly different from all the treatments. The observation could be attributed to solubilization of nano-HA and release of soluble P which was physically protected by composite from adsorption into the soil in the initial stages of incubation.

Fertilizer composites were quantified to deliver a specific amount of N (50 mg N kg⁻¹ of soil) into the soil regardless of NPK formulae, hence the amount of P in the amendments varied as: T2 = 68.1 mg kg⁻¹, T3 = 65 mg kg⁻¹, T4 = 64 mg kg⁻¹, T5 = 60 mg kg⁻¹, T6 = 58.5 mg kg⁻¹ and T7 = 54.5 mg kg⁻¹. The available P increased significantly ($p \leq 0.05$) from T2 to T6, an observation attributed to increased content of soluble P and decreased content of hydroxyapatite. No significant difference was observed between T7 and T4, except in the 4th week, a fact attributed to the balance between the amount of P in the treatment (T7 < T4) and availability in the soil. Nitisols are strong P sorbing soils (WRB, 2014) and hence, lower content of P observed in T7, relative to T5 and T6 could be attributed to soil retention capacity which increases with contact time (Naima et al., 2015; Giroto et al., 2017). Slow microbial solubilization of nano-HA and encapsulation by the copolymer composite could have reduced available P time of contact in T5 and T6. No significance difference was observed between the control and T1 since they did not contain P in the shipments. Due to varied content of P in the amendments it was impossible to ascertain the optimum amount to be incorporated into the fertilizer composite.

3.6. Exchangeable potassium

Exchangeable K at different incubation times are shown in Table 8. The K content showed less variation during the incubation period suggesting a short release time. The small particle size of SRF composite and high water solubility of the K₂SO₄ salt could have enabled faster diffusion of K into the soil. No significant difference ($p \geq 0.05$) was observed between T7 and SRF T1 to T6 in the first 4 weeks, but significant difference was observed between them from the 8th to the 16th week. The control did not differ significantly from T1 throughout the incubation period and this was expected as K was not included in the shipment. The contents of K in the shipments were different (Table 1)

and hence, just like in P, it was impossible to ascertain the optimum amount to be incorporated into the fertilizer composite.

4. Conclusion and recommendations

A SRF composite has been formulated and assessed for release of nutrients using laboratory incubation experiment. Characterization by FTIR spectroscopy revealed synthesis of nano-HA and existence of chemical interaction between the monomer, cellulose, nano-HA and urea molecules. The incubation experiment revealed low MN content in the first 4 weeks and a peak at the 12th week corresponding to the most active and nutrient demand stages of development and reproduction of most crops, hence proper synchronization of SRF. The highest MN content was observed in T7 in the first 4 weeks, whereas between the 8th and 16th week, both T7 and SRF showed similar MN content with some SRFs, for instance T4 and T6, releasing significantly higher amounts. Single order kinetics model predicted well N mineralization and the half-life time ($t_{1/2}$) showed less variation among the treatments. Low contents of P were observed in the first 4 weeks, increased to the maximum in the 8th week and remained constant thereafter. Availability of P increased significantly in SRF with increased content of soluble P and decreased content of nano-HA. The specific objective of the study was achieved and SRF T5 & T6 could provide synchronized release N & P, although the release of K was almost immediate. The SRF composite would be more suitable for use in annual crops and should be applied during planting, so as to match nutrient release with crop uptake. However, the findings were based on laboratory incubation experiments and evaluation should be done under field conditions before they can be recommended with confidence.

Acknowledgements

The authors acknowledge DAAD for the scholarship award, National Research Fund (NRF) for financial assistance and University of Nairobi technical staff, Mr. Kimotho and Mr. Anyika for their assistance.

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