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Short Communication

Porous starch citrate biopolymer for controlled release of carbofuran in the management of root knot nematode *Meloidogyne incognita*

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ABSTRACT

The undesirable environmental impacts of inappropriate application of pesticides have brought about research into new matrices for controlled release of pesticides. Porous starch citrate biopolymer was designed for the release of carbofuran in this experiment and characterized using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Thermo-Gravimetric Analysis (TGA) for functional group, surface morphology and thermal stability properties respectively. The SEM revealed highly stabilized porous starch citrate biopolymers with porous structures and gradients suitable for controlled release studies. The transmittance bands at 3347, 1714 and 1073 cm^{-1} for OH, CO and COC—=—— stretching vibrations further confirms the successful synthesis of the biopolymer. TGA showed an increase in the thermal stability after citric acid modification with one-step decomposition from 290 °C to 500 °C. From Korsemeyer-Peppas model, the carbofuran-porous starch citrate (CBFN/PRS/STH/CTRT) followed a lower diffusion release model with gradual increment in all the quantity of carbofuran loaded. An accelerated rate of diffusion percentage was seen in direct application of carbofuran. Egg hatch and mortality of juveniles were recorded on daily basis for seven days. Direct application of carbofuran (CBFN/DRT) and carbofuran-porous starch citrate biopolymer gave the best results with significant ($p < 0.05$) reduction in egg hatch and higher percentage mortality. The rate of release of carbofuran from the starch citrate bio polymer matrix was significantly lower than the direct application, and in spite of the slow rate of release, higher juvenile mortality and reduction in egg hatch was achieved.

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1. Introduction

Plant parasitic nematodes are important soil borne pest in agriculture. The root-knot nematodes *Meloidogyne* spp are found worldwide [1,2], among the species, *Meloidogyne incognita* and *M. javanica* are the most important in terms of population and occurrence [3,4]. They have extensive host range which includes various crops and vegetables [5,6], and they form complexes with viruses, bacteria and fungi [7]. In Nigeria *Meloidogyne incognita* and *M. javanica* are the major root knot nematodes parasitizing various crops [8–11]. They are a significant serious threat to food security causing damages such as toppling, delayed maturity and reduction in yield and quality [12–14]. Control is achieved primarily with carbofuran, which is applied inappropriately (2, 3-dihydro-2, 2-dimethylbenzofuran-7-yl methylcarbamate) by illiterate farmers who can't read pesticide labels [15], thus the environment is polluted through excessive use of carbofuran and other agro chemicals [16,17]. Improper application of nematicides is a major factor which leads to pollution of groundwater [16,18,19]. The acute toxicity of carbofuran (LD_{50} 8 mg/kg) makes it a subject of environmental concern and it is widely known as a ground water contaminant [20–23]. Carbofuran residues have been identified in ground water samples [24]. The impact of nematicides in the environment can be reduced significantly by minimising the quantity applied while at the same time achieving the same optimally effective nematicidal result using controlled release (CR) formulations [25,48], which is a new alternative method to pesticide application. Pesticides are released from a matrix to the

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environment at controlled concentration. An effective concentration of pesticide is maintained with reduction in environmental pollution [25]. Starch is one of the most commonly used biopolymer in controlled release formulations [26–28]. The objective of this research is to develop controlled release formulations based on starch biopolymers and investigate their effectiveness on survival of *Meloidogyne incognita* juveniles and eggs.

2. Materials and Methods

2.1. Chemicals

Commercial grade carbofuran 3G was purchased from a chemical vendor in Ilorin metropolis. Corn starch MW 104–107 g/mol, citric acid, ammonium acetate, ethanol and methanol were obtained from Sigma Aldrich, USA.

2.2. Preparation of porous starch

Five hundred (500 g) grams of starch was weighed in to 10 litres of water in a glass reactor. The mixture was stirred at 90°C for thirty minutes for the starch to gelatinize. The starch gel obtained was frozen for twenty-four hours and was brought out to thaw and later refrozen and thawed again alternately for 1 week so as to break the gel bonds. The starch gel was then immersed in distilled ethanol for an hour, removed for drying for another one hour and again re-immersed in ethanol. This process was repeated thrice at 50°C before final drying at 90°C. The starch was grinded in a blender to homogenous particle size of 30/60 mesh.

2.3. Preparation of porous starch citrate

One gram (1 g) of ammonium acetate was added to 500 g of porous starch which was combined with a 10 % ammonia solution. The mixture was stirred and heated for 40 min and was thereafter allowed to cool. The solution was added to 300 mL of citric acid and dissolved in 400 mL of ethanol. The entire mixture was thoroughly stirred with a mechanical stirrer at 100°C for 30 min to remove all surface moisture. The temperature was increased to 120°C and the material was further allowed to react for 6 h. The porous starch citrate reaction product was stirred in water for 30 min, filtered and was air-dried overnight. The ammonium acetate is used to rapidly convert the citric acid to citric anhydride. The citric anhydride readily reacts with the hydroxyl groups of starch by an esterification reaction.

2.4. Preparation of porous starch and porous starch citrate carbofuran formulations

Carbofuran was blended to powder and incorporated into the porous starch at 10 g, 20 g, and 30 g each. This was then added to 50 mL methanol in separate containers and the solution was stirred thoroughly. One hundred gram (100 g) each of the prepared porous starch and porous starch citrate was added to each of the carbofuran solutions separately. The entire mixture was stirred thoroughly and left to dry up for the carbofuran to be in contact with the porous-starch and porous starch citrate bio-polymer microspheres to give two different formulations of carbofuran-porous starch (CBFN/PRS/STH) and carbofuran-porous starch citrate (CBFN/PRS/STH/CTRT). The ordinary carbofuran was coded carbofuran (CBFN/DRT).

2.5. Carbofuran release studies

Known weight (5 g) of each carbofuran formulation of the porous starch and porous starch citrate were introduced into 5 by 5 cm semi-permeable parchment strips and placed at 2 cm depth in 50 mL of water. The carbofuran was released slowly from the bio-polymeric matrices and 5 mL solution was removed for analysis on the UV-spectrophotometer daily for six days at a wavelength of 360 nm. 5 mL of water was added back into the water to balance the 50 mL required volume. The percentage carbofuran released versus time was subjected to Korsemeyer-Peppas model to evaluate the type of diffusion release mechanism for the period of study.

3. Spectroscopy

The scanning electron microscopy (SEM) was recorded on JEOL 3010 model operating at 300 kV to observe the physical surface morphology of the biopolymers. Fourier transform infrared (FTIR) spectra were recorded on Brucker Equinox 55 Spectrophotometer (model 100). Each of the samples were finely ground and mixed with potassium bromide, KBr. The mixture was compressed into pellet form, FTIR spectral analysis was performed within the wave number range of 400-4000 cm^{-1} at a resolution of 4 cm^{-1}. The double beam of Hitachi (model 3000) ultraviolet/visible spectrophotometer was used for scanning the absorption spectra at λ max of 360 nm. Thermal gravimetric analysis (TGA) analysis of the starch materials was measured over time as temperature changes to check the thermal decomposition, absorption and desorption of the starch materials on Perkin Elmer TGA 8000.

3.1. Collection and extraction of inoculum

Galled roots of *Celosia argentea* infected with *Meloidogyne incognita* were collected from the vegetable garden of National Horticultural Research Institute (NIHORT) Ibadan, Nigeria. The roots were washed under running tap water to remove soil particles and were diced into small pieces of 1–2 cm pieces. Nematode eggs were extracted from the roots using the method of Hussey and Barker [29], by dissolving nematode egg masses with 0.4 % NaOCl while constantly shaking for 4 min. Eggs released into the solution were separated from roots and debris by sieving first through a 73 μm, 56 μm and lastly through a 25 μm aperture sieve in which the eggs were retained. The collected eggs were thoroughly rinsed and collected in a clean beaker. The number of nematode eggs per mL of water solution was evaluated by counting under a stereomicroscope (x10).

3.2. Egg hatch inhibition

Water suspension containing 50 *Meloidogyne incognita* eggs was dispensed using a pipette into individual glass blocks arranged on the laboratory bench. The experiment was in a completely randomized design (CRD) with three treatments carbofuran direct (CBFN/DRT), carbofuran porous starch citrate (CBFN/PRS/STH/CTRT) and carbofuran porous starch (CBFN/PRS/STH). Each treatment had three dosages of application and three replicates. Dosages consisted of the different 10, 20 and 30 % concentrations of each treatment. A pipette was used to apply 2 mL of each concentration per liquid to the glass blocks containing nematode eggs. The number of eggs that hatched into juveniles were counted daily for 7 days and recorded. Hatched juveniles were counted while viewing under a stereo microscope with a mechanical tally counter. The counts were used to calculate percentage egg hatch inhibition of the treatment materials.

3.3. Juvenile mortality test

The extracted egg-water suspensions were left in a beaker on the laboratory bench for 5 days to allow eggs to hatch into juveniles. The hatched juveniles were separated from unhatched

eggs using the extraction tray procedure [30]. The freshly hatched second stage juveniles were collected from the tray after 24 h. Nematode extract containing 50 juveniles were released into glass blocks arranged in a completely randomized design (CRD) with three replications. The different dosages were added to each glass block. *Meloidogyne incognita* juveniles were observed for mortality for 7 days during which dead nematodes were counted and removed from the treatments daily. The cumulative number of dead nematodes was used to calculate percentage mortality of *M. incognita* juveniles.

4. Results and Discussion

The Fourier Transform Infra-Red (FTIR) spectra shows the vibrational frequencies of the starch, porous starch and porous starch citrate biopolymers respectively (Figs. 1, 2 & 3). The O—H, C–H and COC—— stretching frequencies of the glucopyranosic rings were confirmed at 3268, 2829 and 1077 cm-^{1} respectively. The bending vibrations of C–H and OH— were seen at 1338 and 1420 cm-^{1}. The FTIR further shows various assymetric C—C polymeric bands at 928, 760 and 704 cm-^{1} respectively (Fig. 1). The successful citric acid modification was established by the FTIR figure shown above (Fig. 2). A steep band at 1714 cm-^{1} confirmed the citrate ester functional group inserted. The overall surface negative charge effect caused increase in the overall wave numbers and O—H, C–H wave numbers were seen at 3347 and 2922 cm-^{1} respectively. The C–H and CC— out of plane bends were seen at 935, 861, 760 cm-^{1} respectively. The citric acid modification causes little shift of the starch C—OC— glucopyranosic bond to 1073 cm-^{1}. The porous starch had its corresponding C–H and OH— at higher wave numbers 2926 and 3272 cm-^{1}. Although, the C—OC— glucopyranosic bonds at 1077 cm-^{1} remains unshifted to show that the freeze-thawing process which created the porous design did not disrupt the polymeric bond profiles of the starch biopolymer. C–H scissoring and out of plane bending vibrations were captured at 931, 879, 857, 760 and 704 cm-^{1} respectively (Fig. 3). The surface morphology and shape of the starch biopolymer is shown in Plate 1 a & b. The scanning electron microscopy (SEM) showed starch particles with rhombohedra and hexagonal crystal with smooth surfaces open for modifications. They are aggregated together to form half-micelles in the 50 and 80 μm range. The porous starch formed contains areas with pores and some other sections without pores (Plate 2 a & b). The presence of pores shows that the process of successive freezing and thawing on the ordinary starch biopolymer was successful. The porous channels created can therefore be harnessed for the release of incorporated pesticides. The SEM image of the porous starch citrate (Plate 3 a & b) further reveals the pores and the gradient surface of the highly stabilized polymeric material formed. The surface morphology confirms the suitability of the modified biopolymer in controlled release studies and the cyclically patterned pores is in tandem with the requirements to deliver large molecular pesticides like carbofuran without a premature release effect. The result of the thermo gravimetric analysis for starch and starch citrate is shown in Figs. 4a and b. It depicts the level of stability of the biopolymer within the temperature range of 30°C to 900°C. The thermal decomposition starts at 270°C and ends at 530°C with about 84 % of the bulk porous starch decomposed. The one step decomposition curve indicates the successful synthesis of a pure porous starch biopolymer. The thermal stability increased after citric acid modification with a thermal decomposition from 290°C to 500°C with 76 % decomposition. The steepness of the decomposition curve reduced and this further confirmed the superior thermal stability after the citric acid modification. As shown by FTIR, SEM and TGA, in general, the chemical modification introduced surface active charges and therefore increased the crosslinking within the chains of the porous starch thereby creating a significant structural and morphological stability towards heat. This shows that porous starch citrate can survive pesticide release in both hot and cold weather conditions and can help to regulate diffusion based delivery of the carbofuran pesticide. The percentage cumulative release from the 10, 20 and 30 g formulations of carbofuran in the space of six days is shown in Figs. 5, 6 & 7 . The porous starch citrate had the best performance among the two biopolymers evaluated. In the 10 g formulation, at day 1 there was 11 % release from (CBFN/PRS/STH) carbofuran porous starch and (CBFN/PRS/STH/CTRT) carbofuran starch citrate. The 10 and 20 g quantity of carbofuran rose from an initial 10 % to 20 % (Fig. 6), while that of the 30 g was from 30 % and rose to 70 % (Fig. 7) over the numbers of days of the experiment (Figs. 8, 9 & 10). However, the cumulative release of the two biopolymers was between 11–20 % which remained constant over six days of the experiment. For the 10 g carbofuran based formulation, the 'n' value was 0.3, 0.4 and 0.7 for the three matrices involved (CBFN/PRS/STH/CTRT, CBFN/PRS/STH and CBFN/DRT). The value of n equals 0.4 shows that carbofuran porous starch citrate (CBFN/PRS/STH/CTRT) release is Fickian diffusion controlled

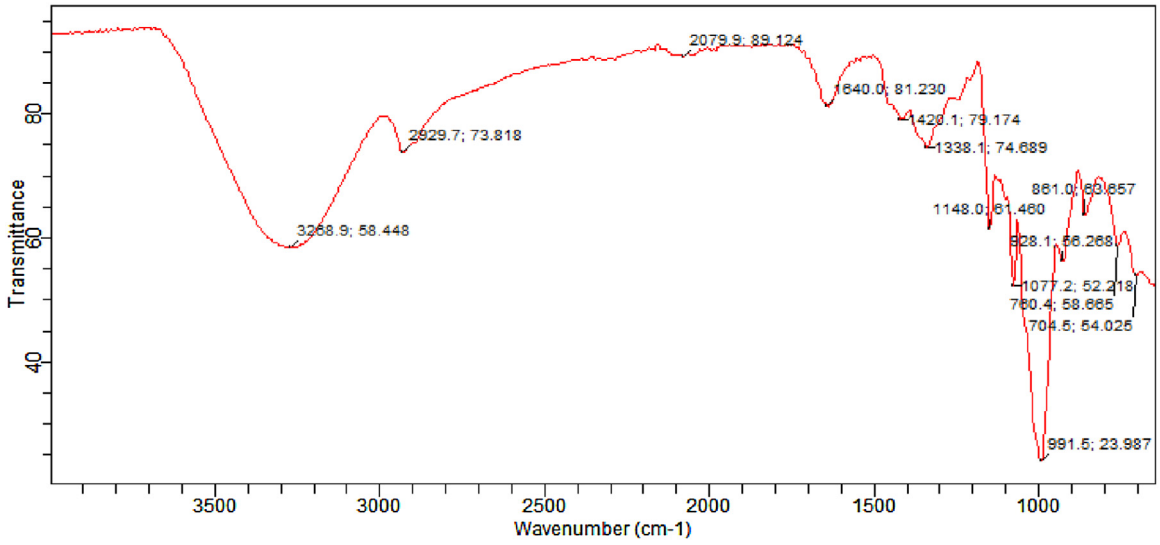


Fig. 1. Starch.

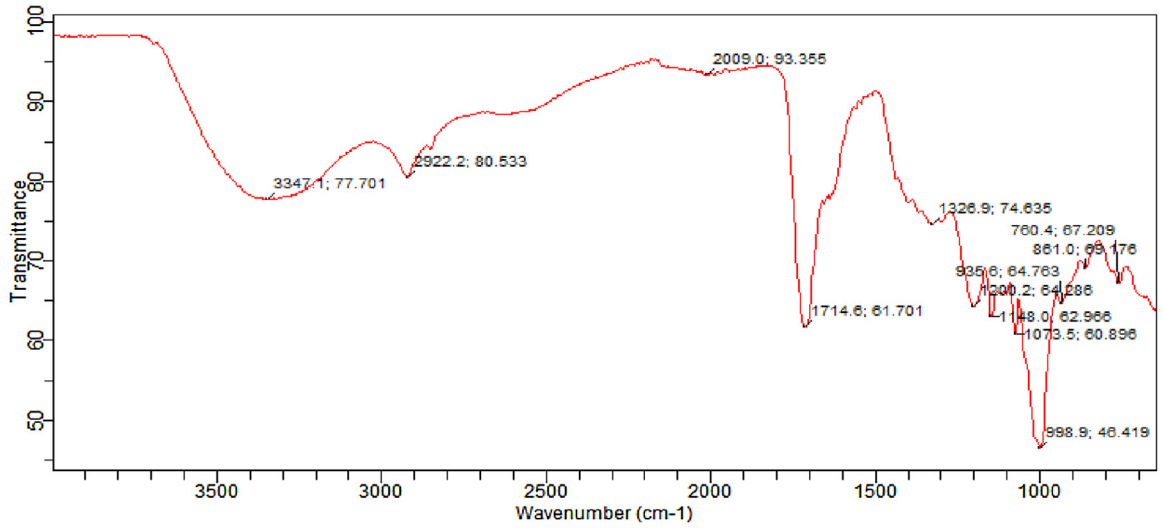


Fig. 2. Starch Citrate.

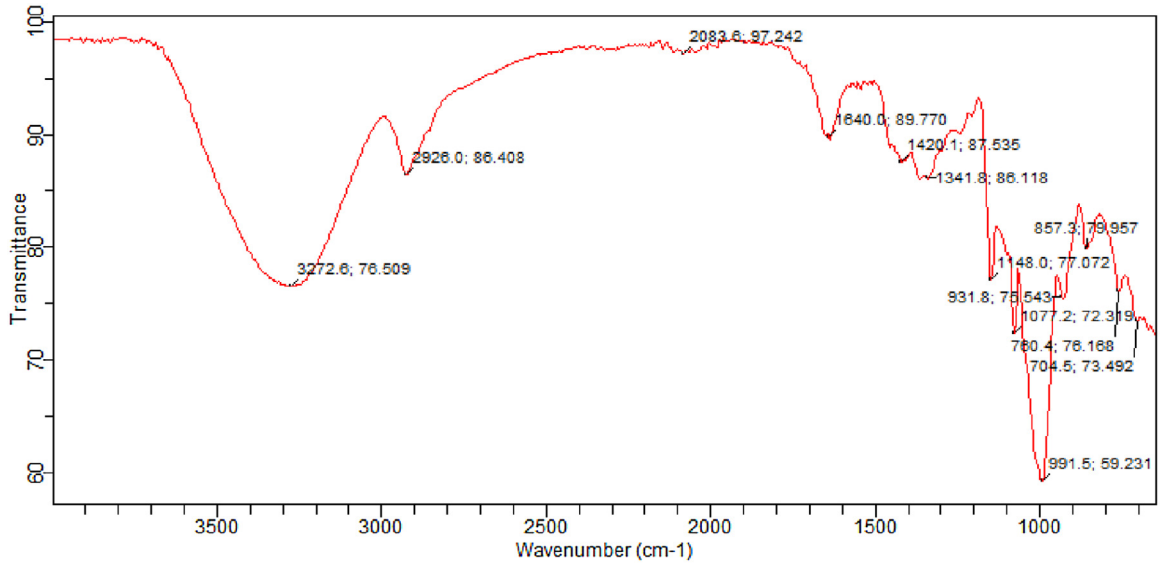


Fig. 3. Porous Starch.

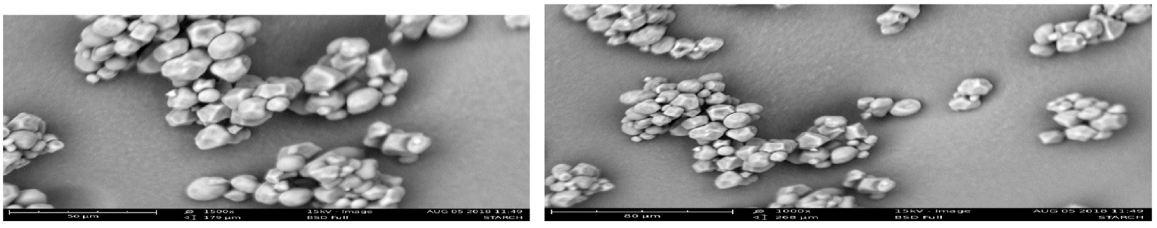


Plate 1. a &b: SEM Image Showing Surface Morphology of Starch at 50 and 80 μm.

type of release. The n equals 0.7 for carbofuran without a polymer matrix (CBFN/DRT) shows that there is an acceleration of the release in time and a higher release rate, while n equals 0.3 for porous starch (CBFN/PRS/STH) formulation reveals that the carbofuran is released by a poly dispersed route. This release profile was maintained for the 20 and 30 g carbofuran based formulation (Figs. 8, 9 & 10). Fig.11 shows the percentage juvenile mortality over a seven-day period. The treatments significantly $P < 0.01$ induce juvenile mortality. There was no significant difference among the treatments in the first two days of treatment application. At day seven, the direct application of carbofuran (CBFN/DRT) had the highest percentage juvenile mortality, with two out of fifty juveniles alive, which corresponds to 96 percent mortality. Carbofuran starch citrate (CBFN/STH/CTRT) had 66 % mortality with 17 out of 50 juveniles alive after seven days of treatment application. Percentage mortality was significantly low

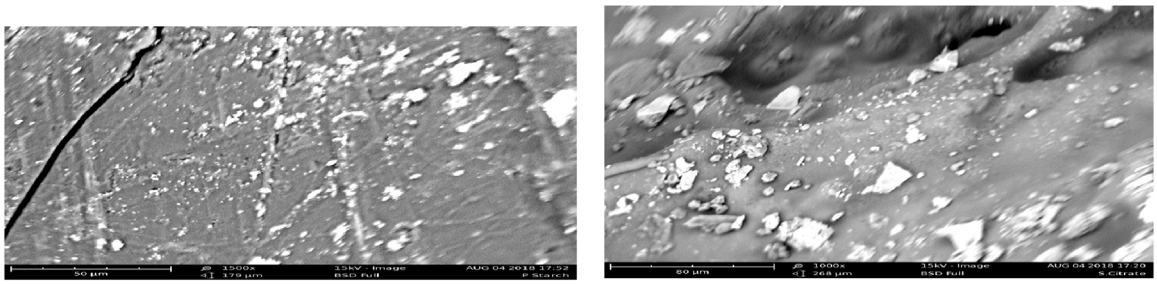


Plate 2. a &b: SEM Image Showing Surface Morphology of Porous Starch at 50 and 80 μm.

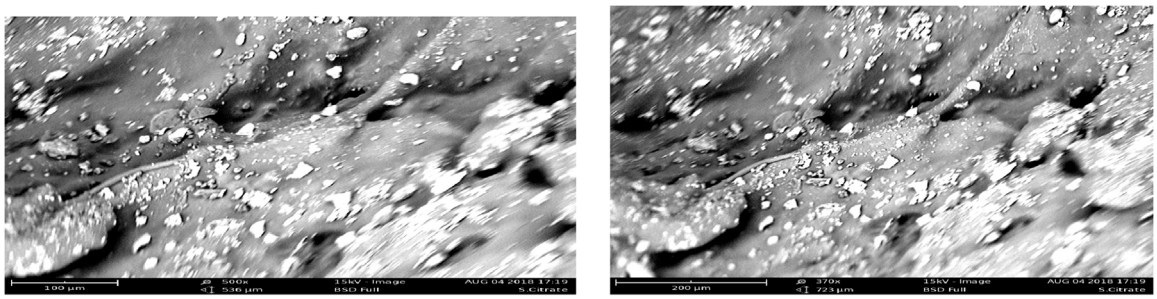


Plate 3. a &b: SEM Image Showing Surface Morphology of Starch Citrate at 50 and 80 μm.

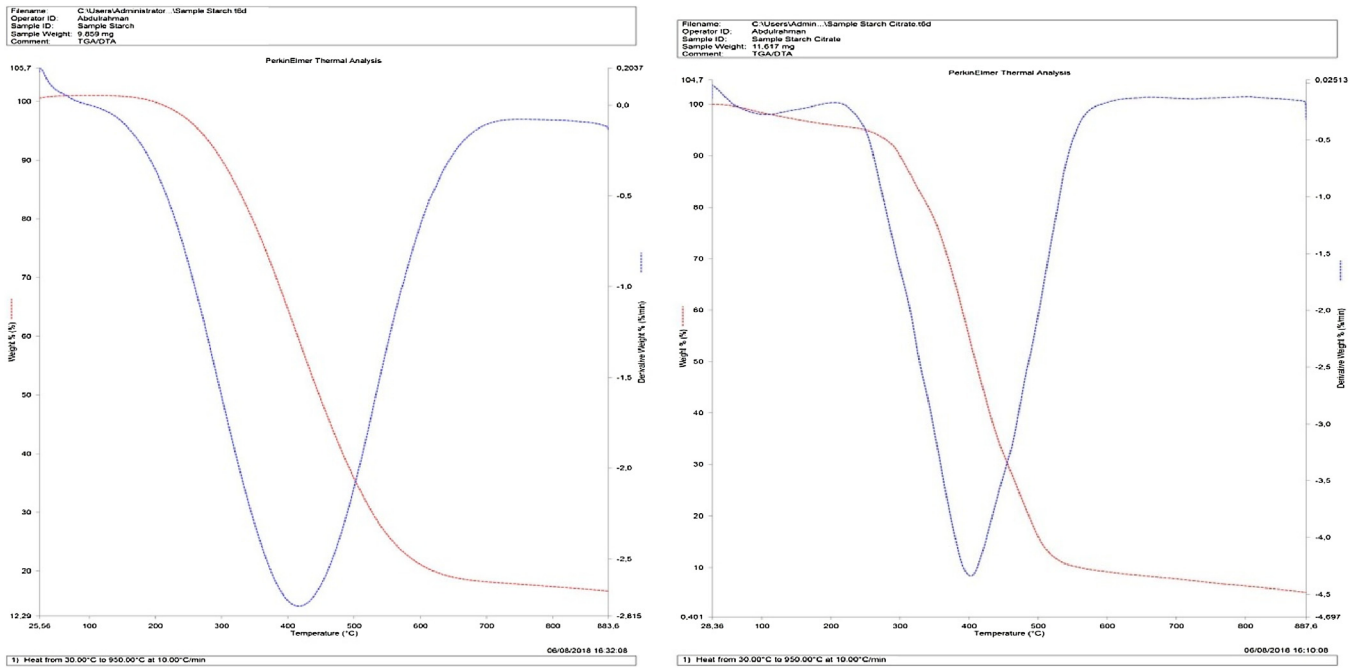


Fig. 4. a & b: Thermo Gravimetric Analysis for Porous Starch.

in porous starch. 35 juveniles were alive which corresponds to 30 percent mortality. Significantly low juvenile mortality was observed in the control. The effect of dosages of application is depicted in Fig. 12. There was no significant difference in the effect of the dosages in the first six days of treatment application. At day 7, the highest dosage of application was significantly more effective with the lowest number of live juveniles. A total of fifteen juveniles were alive which represented 71 percent, while the second and third dosage of application recorded 19 juveniles which is equivalent to 62 percent mortality. There was no significant difference in the effect of carbofuran starch citrate and carbofuran direct. They both recorded 100 percent egg hatch inhibition, while carbofuran porous starch had significantly higher percentage of egg hatch, a hundred percent egg hath was recorded in the control experiment (Fig. 13). There was an overlap in the effect of dosage one and dosage two, however a slight difference was seen in the third dosage of application at day seven Fig. 14.

5. Discussion

The hazards caused by crop protection chemicals in the environment can be minimised by the use of controlled release

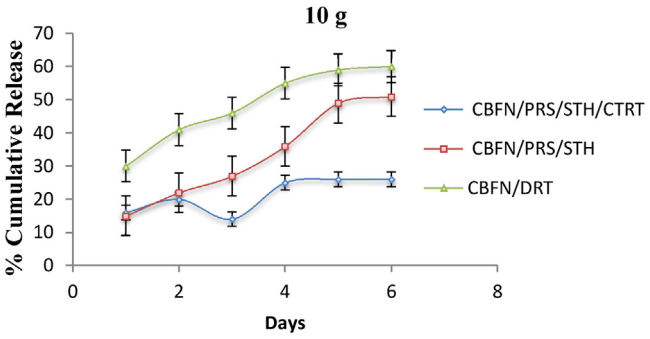


Fig. 5. Cumulative release plot for 10 g carbofuran based formulations.

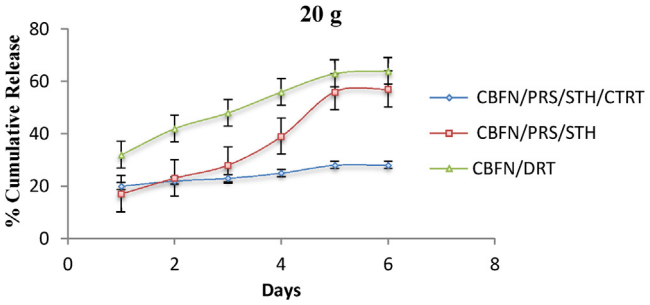


Fig. 6. Release cumulative release plot for 20 g carbofuran based formulations.

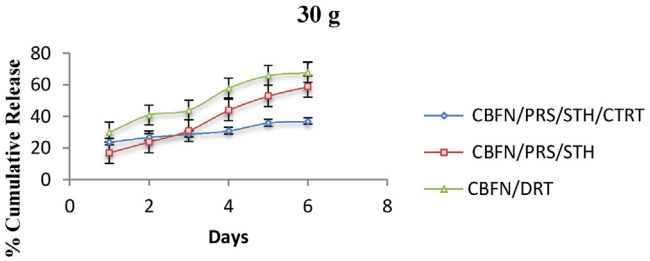


Fig. 7. Cumulative release plot for 30 g carbofuran based formulations.

systems. Conventional application of pesticides is characterised by injection of a high initial dose of active ingredient into the environment, which later drops rapidly below effective level, while a controlled release maintains an effective level for a long time [31,32]. Starch are known to provide good and effective release profile [28,33], and are mostly employed in pesticide release systems [34,35].

A constant release of active ingredient was achieved at a smaller dosage in this study. There was no difference in the rates of release of all the quantity of carbofuran incorporated into the polymer, while there was a fast release of commercial carbofuran 3 G with a rising concentration of the active ingredient which showed drastically after the maximum release on day 1 after treatment. In the same vein Choudhary et al., [36], in their study with rosin yellow, rosin black, kaolinite, bentonite and fullers earth as polymeric controlled release formulations observed a sharp release of the commercial carbofuran and a drop in the concentration of active ingredient after fourteen days, while the polymeric substances released slowly the active ingredient over a much longer period with maximum concentration of active ingredient.

This is in line with the fact that controlled release could be used where the protection of crops from pest like *M. incognita* is required for a long period of time [37], thus providing better control. Kumar et al. [38], reported 75 % effective control of weeds with controlled release of metribuzin as against 57 % obtained with the direct application. Similarly, Li [39], achieved the slow release of nitrate from nitrate fertilizers using surfactant modified zeolite, the unnecessary release of nitrate and other anions was reduced. The mobility of imidacloprid in soil was reduced by alginate controlled release systems to 44.7 % in soil, while 82.3 % of the insecticide was observed with direct application [40].

The n value obtained for carbofuran-porous starch citrate was 0.4, which establishes that the release is controlled by mechanism of diffusion. This corroborates the findings of Ritger and Peppas, [41]. They reported that n values close to 0.5 confirm the existence of a diffusion mechanism in the matrix. Grillo et al. [42], and Campos et al. [43], equally affirmed that release of active ingredients from controlled systems is governed by the mechanism of diffusion. The SEM result confirmed the smoothness and nonporous nature of the polymeric material formed in the porous starch citrate, thus corroborating the reports of Kulkarni et al., [37],Pourjavad et al. [44], and Cea et al., [45], who employed FTIR, SEM and TGA to ascertain the functional group, and stability of biopolymers.

Effective control of *Meloidogyne incognita* can be achieved with the ability to control the rate of active ingredient released into the environment. This was demonstrated in this study, 66 percent juvenile mortality was recorded with the starch citrate and porous starch had 30 percent mortality. Egg hatch was totally inhibited in starch citrate and this was comparable to the result obtained for direct application of commercial carbofuran. Hypothetically, the citrate starch controlled release formulation could achieve a hundred percent (100 %) mortality if the number of days of observation had been longer than seven days. Choudhary et al., [36] recorded effective control and reduction in nematode population with controlled release formulations as against the commercial formulation.

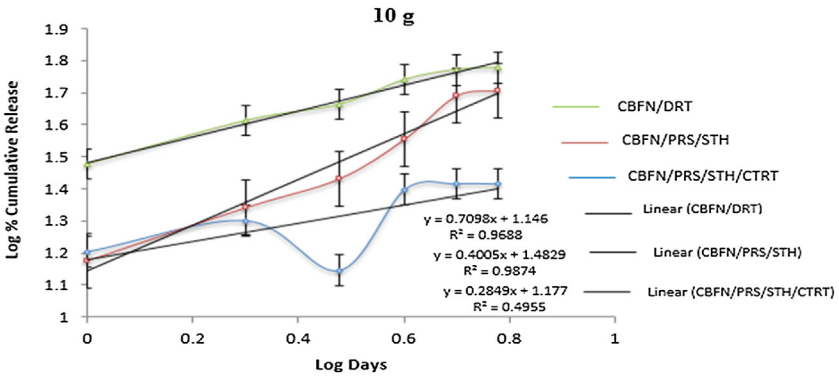


Fig. 8. Cumulative release log for 10 g carbofuran.

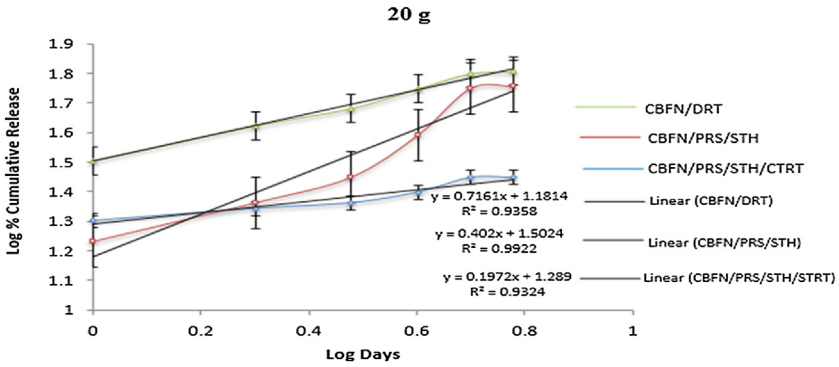


Fig. 9. Cumulative release log for 20 g carbofuran.

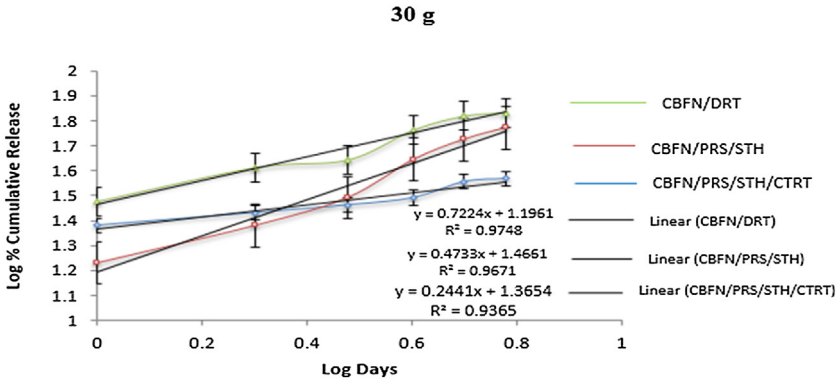


Fig. 10. Cumulative release log for 30 g carbofuran.

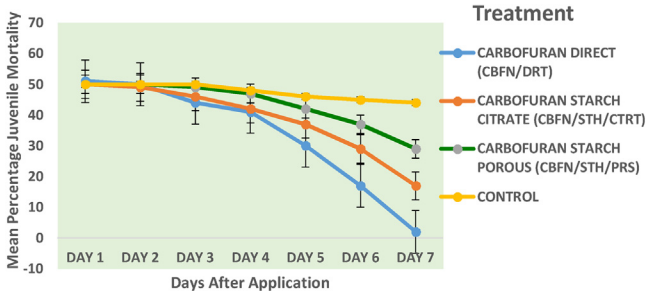


Fig. 11. Effect of Treatment Application on Percentage Juvenile Mortality.

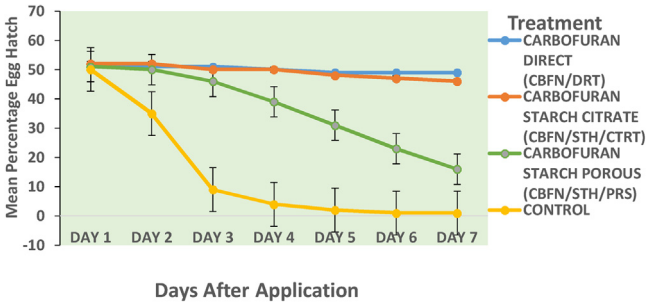


Fig. 13. Effect of Treatment Application on Percentage Egg Hatch.

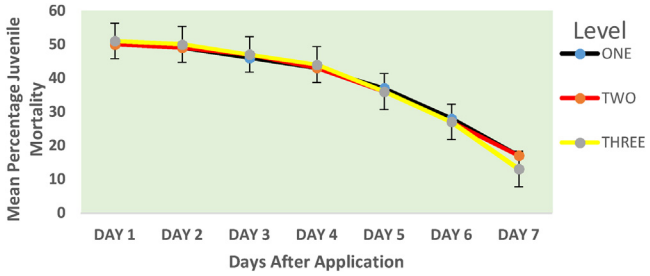


Fig. 12. Effect of Dosages of Application on Percentage Juvenile Mortality.

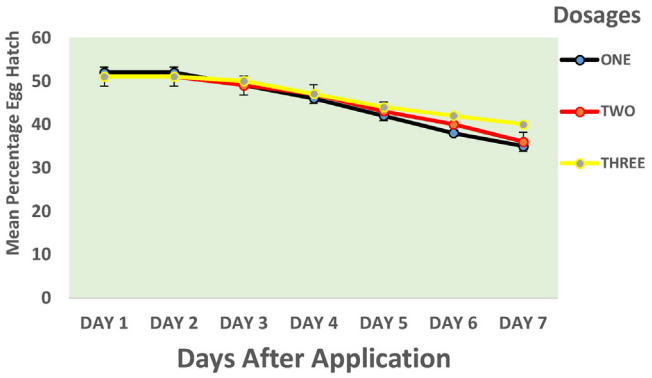


Fig. 14. Effect of Dosages of Application on Percentage Juvenile Mortality.

The slow release mechanism of the citrate starch could be associated with particle size and pore spaces and porous channel available in the biopolymer. Biopolymers with large particle sizes and pore spaces are known to release slowly. This finding is in line with the report of Garrido-Herrera et al., [46], who confirmed that

larger particles provide slow release. Addition of citric acid may have assisted the biopolymer to release the active ingredient in a controlled manner better than the ordinary porous starch. This is supported by the findings of Rashidzadeh et al., [47], they reported that acrilic acid-co acrylamaid enhance a more controlled release than ordinary hydrogels. The impact of pesticide in the environment can be drastically reduced with the use of controlled formulations of pesticides application, with the assurance that the active ingredient will be delivered to their targets precisely with the required optimum quantity without health hazards.

6. Conclusion

Slow release methods allow the use of small quantities of active ingredient with concomitant optimal effective nematicidal activity. This approach reduces the cost of production to farmers, while at the same time minimising environmental toxicity that might accompany application of the nematicide. More importantly, the technology can be a spring board to further improvements in integrated pest control. Ultimately, the results obtained from this study contribute significantly towards global effort at ensuring food security. Finally, the use of starch matrix in controlled release systems has unique advantage because of its ready availability and comparatively low cost.

Declaration of Conflict of Interest

This is to state clearly that, there is no conflict of interest among all the authors who have participated in putting together the content of this manuscript.

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