

Research Article

Starch-Grafted Sodium Alginate-Modified Clay Composites as Environmentally Controlled-Release Materials for NPK Fertilizer

Nobert J. Jindor, Eric S. Agorku , and Anthony A. Adimado 

Department of Chemistry, College of Science, Kwame Nkrumah University of Science and Technology, PMB, Kumasi, Ghana

Correspondence should be addressed to Eric S. Agorku; esagorku.cos@knust.edu.gh

Received 7 May 2023; Revised 12 October 2023; Accepted 13 October 2023; Published 19 October 2023

Academic Editor: Annisa Utami Rauf

Copyright © 2023 Nobert J. Jindor et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In an effort to mitigate the harm caused by the irregular use of agrochemicals, a safer release system using biopolymers is promising due to their availability, biodegradability, and eco-friendliness. Herein, controlled-release materials for NPK fertilizer were formulated using clay-based graft biopolymer composites. The clay soil sample was collected and classified through Skempton's laboratory tests for soils and used as filler in starch-grafted sodium alginate (ST-g-SAG) with different percentages of clay. The clay-based graft biopolymer composites were synthesized via a microwave-assisted method. The biopolymer composites were characterized by FTIR, SEM, and EDS. The materials were loaded with NPK fertilizer, and a leaching test was conducted via a conductometric method to ascertain their release capacities. Biodegradation studies and the effect of humidity on the release of the NPK fertilizer were studied. Results of classification studies of the clay show Ca-montmorillonite (Ca-MMT) type. The average percent graft yield of starch-grafted sodium alginate/Ca-MMT (ST-g-SAG/Ca-MMT) was 83%. The results from FTIR and EDS showed that OH⁻, COO⁻, and CONH₂ were responsible for the absorption of water. The release profile of the active NPK in the biocomposites ranged from 1% to 103%. Biodegradation results also showed a significant breakdown in biopolymer structure and mass loss. The release of active NPK from the material was humidity-responsive.

1. Introduction

Agriculture production has been maximized as a result of the ongoing global demand for food caused by the growing global population. This necessitates the production of high-value crops and the application of herbicides, fertilizers, and high-tech machinery [1]. Agrochemicals are important in the effort to meet the rising demand for food from the expanding population [2]. Despite this, the negative impacts these chemicals have on human health and the environment place significant restrictions on their use [3].

Agrochemical is a catch-all term for the different chemical products used in agriculture, including insecticides, chemical fertilizers, manure, and other growth agents. For traditional formulations, the active ingredient is typically combined with other inert components for safer, simpler, more precise handling, and efficient field application. Traditional agrochemical formulations have the

potential to damage the environment, especially when intense cropping is used. To lessen pollution and health risks, controlled-release formulations of agrochemicals such as biopolymers are required [4].

The primary drawback of these traditional formulations is the quick release of active ingredients. As a result, these chemicals are quickly lost by leaching, volatilization, and other processes that take place after they are applied to the field. Below the minimum effective concentration needed to sustain biological efficacy, the concentration of active chemicals in the field falls off relatively quickly. As a result, agrochemicals must be applied repeatedly in order to keep the concentration of active molecules at the desired level, which causes several environmental and health issues [2].

Controlled-release fertilizers, which play a critical part in the sustainability of agriculture, have recently attracted growing interest. In general, crops require potassium (K) for the proper growth of the plant's main functions, phosphorus

(P) for the growth of roots, flowers, and fruit, and nitrogen (N) for the growth of leaves [5, 6]. Recently, novel formulations have been developed that may alter the performance of active ingredients with less negative environmental effects. These formulations produce a slow, steady release of the active ingredients [1]. Agrochemicals (such as chemical fertilizers) are incorporated into polymeric materials or inorganic hosts in controlled-release systems or controlled-release formulations. These systems are able to distribute active compounds to a specific target crop continuously and slowly for a longer period of time at the chosen rate [2].

Polymeric materials such as carboxymethyl cellulose, sodium alginate, and modified starch are already in use. However, most of these biopolymers tend to have poor mechanical properties, degrade faster, and do not respond to environmental conditions. This study, therefore, seeks to find headways to improve the aforementioned properties of biopolymer application in agriculture through grafting and composite formation with clay as filler, which is readily available, cheaper, and environmentally friendly.

2. Material and Methods

2.1. Materials. Afari (a Ghanaian community) clay was supplied by the Ceramics Department, KNUST, Ghana. Potato starch was obtained from VWR Chemicals, Prolabo. Sodium alginate was obtained from Qualikems Fine Chemical Pvt Ltd, India. NPK fertilizer (15:15:15) was obtained from Afcott Ghana Ltd.

2.2. Processing of Clay Soil. The clay soil from its natural ground was put into a mechanical device to remove foreign materials and compact it by rolling it into bars. The bars of clay were chopped into smaller units and air-dried. The dried units were milled into powder form by a mechanical miller.

2.3. Liquid Limit, Plastic Limit, and Plasticity Index Determination. The liquid limit (LL), plastic limit (PL), and plasticity index (PI) were determined by Atterberg's limit test method [7]. The plasticity index was calculated from the differences in liquid limit and plastic limit as follows:

$$PI = LL - PL. \quad (1)$$

2.4. Soil Particle Size Distribution Test. The soil particle size distribution test was determined by the hydrometer method [8].

2.5. Clay Soil Classification. The clay sample was classified according to the Skempton laboratory tests for soils [9]. The activity (Ac) of the clay was determined by using the following equation:

$$Ac = \frac{PI}{C}, \quad (2)$$

where PI is the plasticity index and C is the percent clay-size fraction, by weight.

2.6. Synthesis of Starch-Grafted Sodium Alginate/Ca-Montmorillonite (ST-G-SAG/Ca-MMT). ST-g-SAG/Ca-MMT was synthesized by the microwave-assisted method previously used by Sen et al. [10] with little modification. The details are as follows.

5 g of soluble potato starch was weighed using an analytical balance and transferred into a 250 ml beaker. 100 ml of distilled water was added to the content in a beaker. The solution was heated using a hot plate while stirring with a stirring rod to obtain a homogenous 5% w/v starch solution.

Thereafter, 5 g of sodium alginate was weighed and transferred into a separate 250 ml beaker. 100 ml of distilled water was added, and the content in the beaker was thoroughly stirred while heating to obtain a homogenous 5% w/v sodium alginate solution.

To synthesize ST-g-SAG (Figure 1), the starch solution was added to the sodium alginate solution and thoroughly mixed. The resulting mixture was transferred into the reaction vessel which was placed on the turntable of a microwave (with input and output power of 1350 W and 800 W, respectively). Microwave irradiation with pause ablation for 30 sec was performed for 4 min. The reaction content was periodically cooled by placing the reaction vessel on ice. The ST-g-SAG/Ca-MMT was synthesized similarly by adding 0.30 g, 0.50 g, and 1.00 g of Ca-MMT to the starch/sodium alginate mixture prior to microwave irradiation. The reaction vessel and its contents were finally kept undisturbed for 24 hrs to complete the grafting reaction. After 24 hrs of undisturbed reaction, further heating and cooling were made in an oven at 60°C to 70°C to separate the precipitates from the supernatant. The precipitates were filtered using filter paper of diameter 125 mm and heated to dryness in an oven.

The percentage yield of grafting (% yield of grafting) was calculated using the following equation:

$$\text{The percentage yield of grafting} = \frac{\text{mass of graft yield (MG)}}{\text{total mass used for grafting (MT)}} \times 100. \quad (3)$$

2.7. Loading of NPK Fertilizer onto ST-G-SAG/Ca-MMT. A 3 g of NPK fertilizer (15:15:15) was solubilized in 50 ml of distilled water and acidified with 1 ml of HCl to promote greater solubility of the NPK. The solution was added to the

ST-g-SAG/Ca-MMT composites and left for 24 hrs for the NPK to get soaked into the biopolymer chains as the biopolymer composites swell and expand in size. The resulting ST-g-SAG/Ca-MMT composites with different percentages

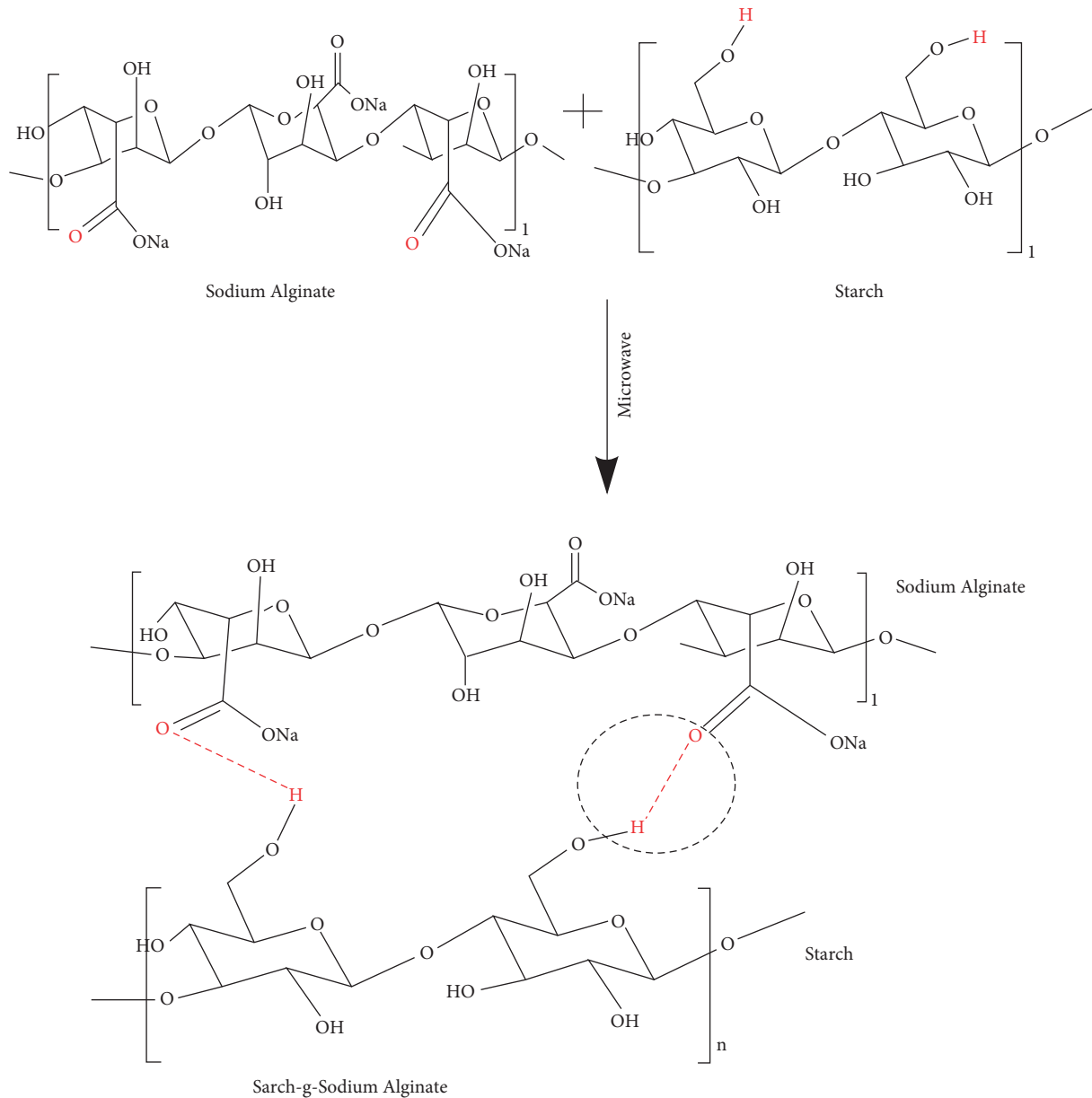


FIGURE 1: Diagrammatic representation of the synthesis of ST-g-SAG.

of clay filler were dried in an oven at 70°C until a constant weight was obtained.

2.8. Leaching Test. 1 g each of ST-g-SAG/NPK, ST-g-SAG/Ca-MMT/NPK, and Ca-MMT/NPK and pure NPK samples were immersed in 100 ml of distilled water to stimulate the action of the water in the leaching of the active NPK. Periodically, a 10 ml syringe was used to withdraw the solution for measurement of conductivity using the pH/mV/conductivity/°C/F° meter (model: PC 700) for time intervals of 0 hrs, 24 hrs, 48 hrs, 72 hrs, and 96 hrs. 10 ml of distilled water was added to the solution to restore the initial volume. The percentage (%) of NPK fertilizer released was calculated using the following equation:

$$Ar = \frac{Vs \sum_i^{n-1} Ci + VoCn}{VoCt} \times 100, \quad (4)$$

where Ar is the percentage (%) of fertilizer released, Vs is the sample volume (ml), Vo is the initial test volume (ml), Ci and Cn are the conductivities of the samples (mSml⁻¹) at the time i through n, and Ct is the theoretical total conductivity (mSml⁻¹) which is based on the free NPK content released.

2.9. Biodegradation Test. The ST-g-SAG/Ca-MMT/NPK composites were moulded into pellets using a mechanical press. A simulated soil was prepared by mixing equal parts of humus soil, anthill soil, and powdered dried cow dung. After these preparations, a biodegradation test in the simulated

soil was performed through the buried and exhumed method (ASTM G 160–03 standard). The exhumed pellets were cleaned, dried, and weighed to measure the mass loss. The pellets were also analyzed by FTIR spectroscopy to ascertain any change in functional groups. The degree of degradation of the specimens was determined by the differences in weight ($M_o - M_i$). The percentage (%) degradation was evaluated according to the following equation:

$$\% \text{ Degradation} = \frac{M_o - M_i}{M_o} \times 100, \quad (5)$$

where M_o is the mass of the pellet before burial and M_i is the mass of exhumed pellet after the biodegradation period.

2.10. Characterization of Materials. The materials were characterized using a Fourier transform infrared (FTIR) spectrometer (Alpha II Platinum ATR, Bruker Daltonik GmbH, Germany). In order to investigate the surface morphology of the powders, SEM (Zeiss EVO MA15, UK) was used. The electron dispersive spectroscopy (EDS) attached to the SEM was used for elemental identification and distribution.

3. Results and Discussion

3.1. Soil Classification Test. The plasticity index may be considered as a measure of the cohesion possessed by a soil. From Table 1, the plasticity index of the Afari clay soil sample was 36%. The particle size distribution results revealed that the clay component was 22%.

The activity of the clay sample was calculated based on the plasticity index and percentage of clay components. From Table 2, the clay sample was classified using activity values recorded in comparison with the theoretical range of activity values for the classification of clay. This classification was based on the minerals present in the clay soil and the activity level. The activity level for the Afari clay was 1.65 and accordingly classified as active calcium montmorillonite clay. The active clay has a high ion exchange capacity and is less stable. The plasticity index of clay is directly proportional to its activity [11].

3.2. FTIR Results. Figure 2 shows the FTIR spectra for the polymer composites. Pure starch (ST) (a) showed peaks at frequencies corresponding to various functional groups within its structure. Peaks at 3269 cm^{-1} (broad) and 2925 cm^{-1} are assigned to hydroxyl (OH^-) stretch and methylene C-H asym/sym stretch. Also, 1334 cm^{-1} and 1076 cm^{-1} peaks are characteristic of 1° or 2° , OH^- -in-plane bends and cyclic ethers C-O stretch. In addition, the peak at 992 cm^{-1} and peaks from 859 cm^{-1} to 760 cm^{-1} were signatures of vinyl C-H out-of-plane bend and skeletal C-C vibrations [12, 13].

Bare sodium alginate (SAG) (b) showed peaks at 3292 cm^{-1} (broad) and 2920 cm^{-1} which are an indication of hydroxyl (OH^-) stretch and methylene C-H asym/sym stretch. Moreover, peaks from 1590 cm^{-1} to 1409 cm^{-1} are characteristic of carboxylate (COO^-) stretch. Peaks at

1320 cm^{-1} and 1100 cm^{-1} are assigned to 1° or 2° , OH-plane bend and cyclic ethers, and C-O stretch, respectively [10].

Moreover, nitrogen phosphorus potassium (NPK) fertilizer (c) showed peaks from 3023 cm^{-1} to 1397 cm^{-1} which can be assigned to ammonium ion. Peaks at 1655 cm^{-1} and 1072 cm^{-1} are attributed to amide and 1° amine C-N stretch. Peaks between 1072 cm^{-1} and 1019 cm^{-1} can be assigned to phosphate ion [13].

The FTIR data for ST-g-SAG/NPK (d) show successful grafting and loading, respectively. This is because there was an overlap of peaks and shifts in wavenumbers generally across the spectra. Thus, OH^- stretch at 3269 cm^{-1} in starch and at 3292 cm^{-1} in sodium alginate has overlapped to form a single peak with wavenumber shifting to 3237 cm^{-1} in the grafted biocomposites (Figure 1). A similar trend was observed with carboxylate COO^- stretching from 1590 cm^{-1} to 1409 cm^{-1} in sodium alginate overlapping to form a single peak in biocomposites. The wavenumbers correspondingly shifted to 1631 cm^{-1} [10]. These results compare with similar results reported by Couto *et al.* (2015) [14]. The bands at 3280 cm^{-1} , 3307 cm^{-1} , and 1659 cm^{-1} correspond to the hydroxyl groups present in the starch, absorption of water, and the presence of acidic functional groups, respectively.

Figure 3(a) shows EDS spectrum for ST-g-SAG/Ca-MMT(5%)/NPK composite. The elemental composition of the ST-g-SAG/Ca-MMT/NPK provided both quantitative and qualitative information on the synthesized composites. The elemental profile of the composites revealed the presence of mostly macro (major) essential plant nutrients in significant amounts. The essential elements such as N (12.14%), P (2.71%), K (3.68%), S (6.35%), Ca (2.90%), O (46.23%), C (17.53%), and Na (5.90%) were present in significant amounts compared to similar results reported by other researchers [15], with N (1.66%), P (0.85%), and K (1.41%) in their study involving polymer modified-bentonite systems. Cl (2.57%) was also present in the composites.

Figure 3(b) shows SEM micrograph of ST-g-SAG/Ca-MMT(5%)/NPK composite. The micrograph showed agglomeration in the composite.

3.3. Leaching Test Results. Figure 4 shows the conductivity of NPK-loaded composites in water. The conductivity is linked directly to the release of soluble ions. The conductivity increased generally from 0 hour to a maximum of 48 hours, after which the conductivity decreased. This trend was so because, as the hydrogel composites were soaked in water, they quickly expanded in size and consequently released trapped soluble NPK ions into the water for conductivity. The hydrogel composites continue to expand in size as they absorb water and get to a maximum expansion where further absorption of water yields no expansion in size and, hence, decreases the release of soluble ions [16–20]. This might have accounted for the general decrease in conductivity after 48 hours (Figure 5). However, the conductivity of pure NPK ions was the highest and on a decreasing trend from 0 to 96 hours.

TABLE 1: Summary of classification test results.

Sample ID	Specific Gravity	Atterberg limits (%)			Particle size distribution (%)				Soil type
		LL	PL	PI	Clay	Silt	Sand	Gravel	
Afari	2.29	60.20	24.00	36.20	22.00	38.00	40.00	0.00	Clayey, silty, and sand

LL: liquid limit, PL: plastic limit, and PI: plasticity index.

TABLE 2: Mineral and activity classification of clay sample.

Sample ID	Activity value	Mineral present	Classification
Afari	1.65	Ca-montmorillonite	Active clay

TAV: theoretical activity values [9]; SAV: sample activity values.

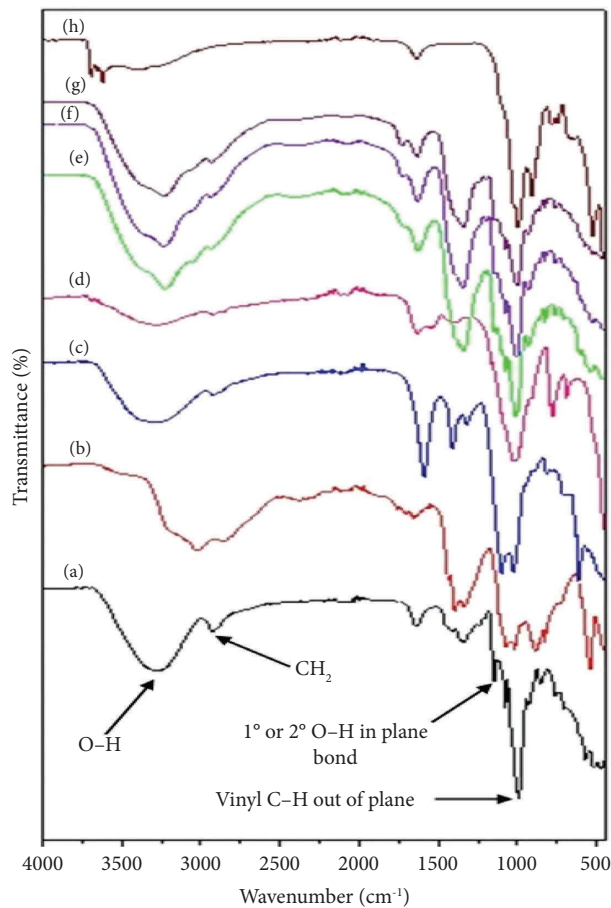


FIGURE 2: FTIR spectra of pure starch (a), pure sodium alginate (b), pure NPK (c), ST-g-SAG/NPK (d), ST-g-SAG/Ca-MMT(3%)/NPK (e), ST-g-SAG/Ca-MMT(5%)/NPK (f), ST-g-SAG/Ca-MMT(10%)/NPK (g), and pure Ca-MMT (h).

The conductivity trend was NPK > ST-g-SAG/10%Ca-MMT/NPK > ST-g-SAG/NPK > ST-g-SAG/5%Ca-MMT/NPK > ST-g-SAG/3%Ca-MMT/NPK > Ca-MMT/NPK.

Figure 6 shows the percentage of active NPK released over the entire time frame from 0 to 96 hours. The percentage of active NPK released was observed to be constantly decreasing with time. The total percentage of active NPK released ranges from 1% to 103%. The trend in the percentage of active NPK released was again observed to be NPK > ST-SAG/10%Ca-

MMT/NPK > ST-g-SAG/NPK > ST-g-SAG/5%Ca-MMT/NPK > ST-g-SAG/3%Ca-MMT/NPK > Ca-MMT/NPK.

Total percentages of active NPK released after 24 hours were 47.2, 10.3, 9.9, and 0.5 for NPK, ST-g-SAG/NPK, ST-g-SAG/5% Ca-MMT/NPK, and Ca-MMT/NPK, respectively. Daitx et al. reported similar results on the percentage of active NPK released after 24 hours as 44%, 19%, and 6% for pure NPK, pure polymer, and polymer/5% bentonite, respectively, in their study involving

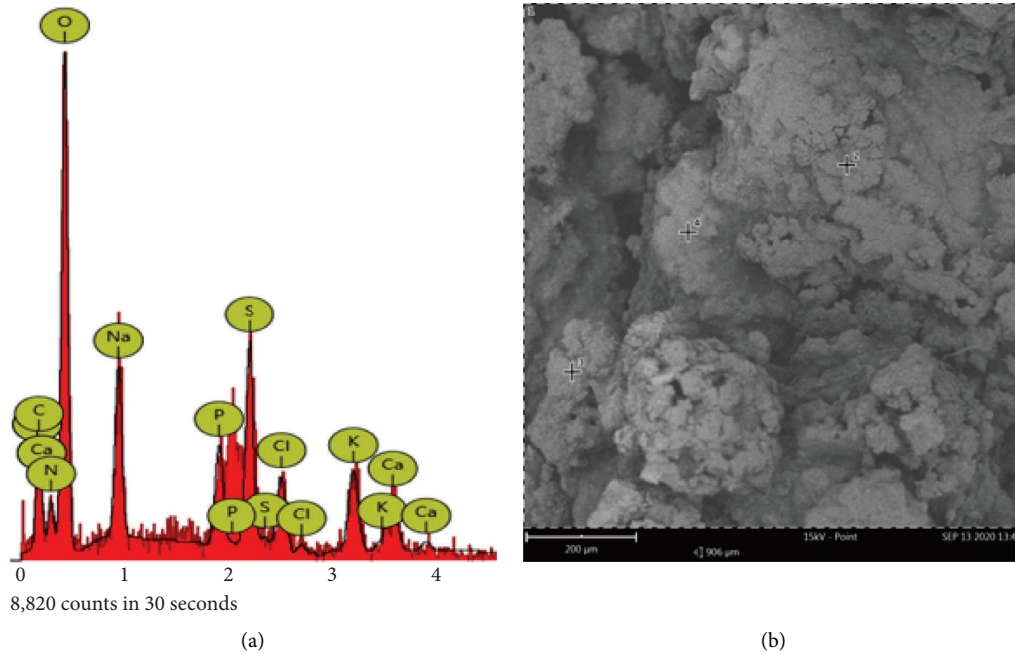


FIGURE 3: EDS spectrum (a) and SEM monograph (b) of ST-g-SAG/Ca-MMT(5%)/NPK composite.

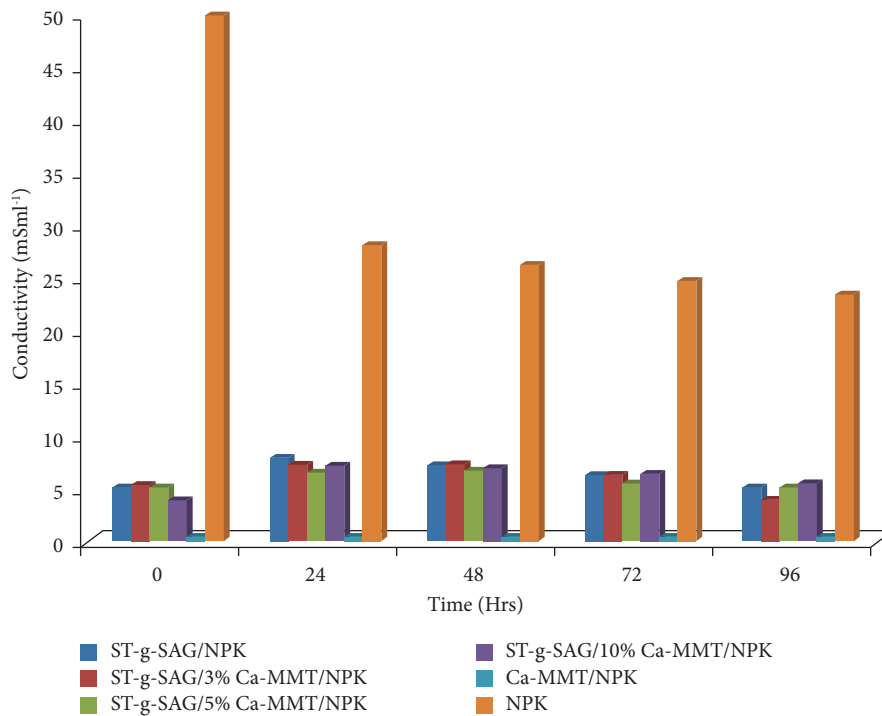


FIGURE 4: Conductivity of active NPK with time.

polymer/clay systems [15]. A large percentage of NPK released in this research accounted for why the immediate release of active NPK is the main drawback associated with these conventional NPK formulations. This could lead to leaching, posing various environmental problems and economic burdens on the users [2]. Moderate NPK

release was recorded when NPK was incorporated into the pure polymer, and polymer-clay systems, and extremely low release was recorded in pure clay systems. These systems are capable of delivering active compounds slowly and continuously for a longer duration to a specified target crop at a desired rate [2].

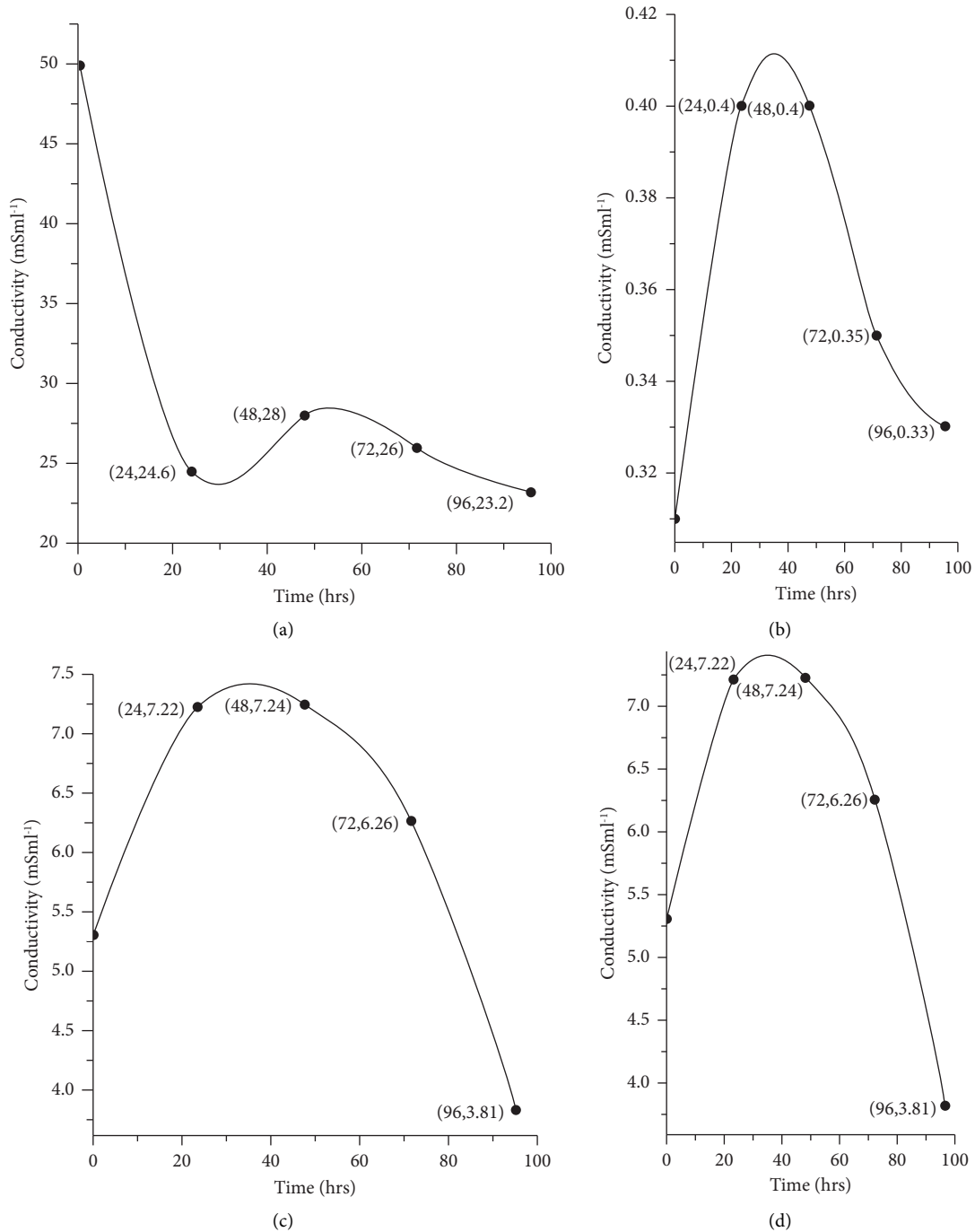


FIGURE 5: Conductivity of active NPK with time for NPK (a), Ca-MMT/NPK (b), ST-g-SAG/NPK (c), and ST-g-SAG/Ca-MMT(5%)/NPK (d).

Scaffaro et al. [5] using *Opuntia Ficus Indica*-based green composites for NPK fertilizer showed a release rate of up to 30 days. Białkowska and coworkers also used polyacrylamide and polyvinyl alcohol as a slow-release system for NPK fertilizer. They demonstrated that the degree of absorption increases with bead immersion time (up to 12 hours) [6].

The release of NPK in polymer/NPK, polymer/clay/NPK, and clay/NPK formulations will have a less harmful impact on the environment and reduce the economic burden on the users [1, 16]. The clay/NPK formulations will be especially good for crops in waterlogged areas.

3.4. Biodegradation Studies. The percentage degradation (%D) of ST-g-SAG/Ca-MMT/NPK composites (Figure 7) ranged from 56% to 98% with the latter three months recording high percentages. This is because microorganism attack on the composites increases with time as a result of chemical degradation (hydrolysis reactions) occurring concurrently with degradation [14]. During the biodegradation process, microorganisms' attack could have been facilitated by the breakdown of the chemical bonds in the molecules caused by hydrolysis due to the absorption of water. The ST-g-SAG/Ca-MMT/NPK composite can be considered

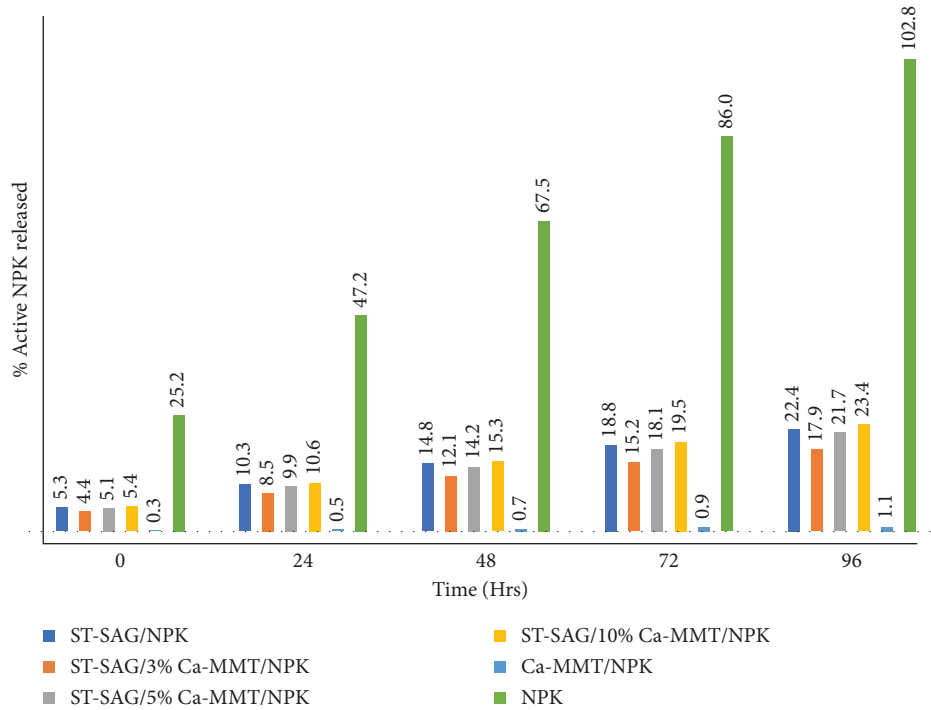


FIGURE 6: Percentage of active NPK released with time.

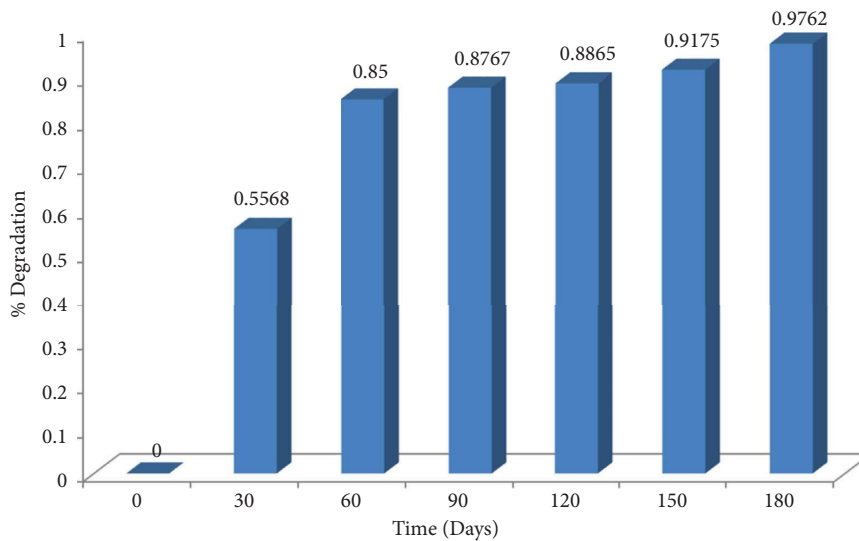


FIGURE 7: Percentage degradation of ST-g-SAG/Ca-MMT/NPK with time.

a biodegradable material due to a great deal of mass loss the polymer suffered during burial in simulated soil.

Figure 8 shows the FTIR spectra for 180 days (6 months) of biodegradation of ST-g-SAG/Ca-MMT/NPK composite. The hydroxyl (OH) group at 3237 cm^{-1} , methylene (CH_2) group at 2931 cm^{-1} , carboxyl (COO^-) group at 1631 cm^{-1} , and amide (CONH_2) group at 1341 cm^{-1} were associated with the ST-g-SAG/Ca-MMT/NPK composite before biodegradation (a). The FTIR spectra showed that samples suffered degradation during burial in the soil. This was

demonstrated by the shifts in wavenumbers from 3237 cm^{-1} to 3275 cm^{-1} for hydroxyl (OH) groups and 2931 cm^{-1} to 2908 cm^{-1} for the methylene (CH_2) group. There were also significant shifts in wavenumbers from 1631 cm^{-1} to 1636 cm^{-1} for the carboxyl (COO^-) group and from 3237 cm^{-1} to 3797 cm^{-1} for the nonbonding hydroxyl (OH) group due to the absorption of water. In addition, some groups (peaks) completely disappeared while others significantly reduced in intensity. This is an indication of mass loss during the biodegradation process [14].

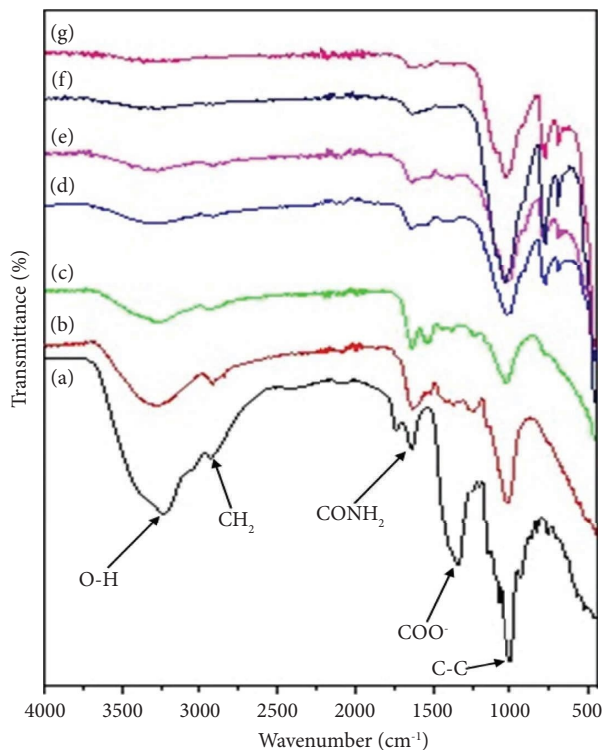


FIGURE 8: FTIR spectra of biodegradation of ST-g-SAG/Ca-MMT/NPK for 0 month (a), 1 month (b), 2 months (c), 3 months (d), 4 months (e), 5 months (f), and 6 months (g).

4. Conclusions

In this study, clay samples were obtained from Afari (Ghanaian community) and classified according to Skempton's method and thereafter dispersed in starch-grafted sodium alginate (ST-g-SAG) for slow release of NPK application. The ST-g-SAG was synthesized by the microwave-assisted method. Results of classification studies of the clay show Ca-montmorillonite (Ca-MMT) type. The Ca-MMT clay was dispersed in the grafted biopolymer with different percentages of clay, and the materials were loaded with NPK fertilizer. The materials were characterized by FTIR, SEM, and EDS. A biodegradation study was performed on the polymer/clay/NPK composites to ascertain their stability in the environment. Leaching tests were also performed to determine the potential use of the materials as a slow-release system for NPK fertilizer.

The leaching test results showed that the ST-g-SAG and ST-g-SAG/Ca-MMT/NPK were very sensitive to changes in moisture (humidity) and responded exceptionally in terms of active NPK released. The total percentage of active NPK released ranged from 1% to 103%. The release was in the order: NPK > ST-SAG/10%Ca-MMT/NPK > ST-g-SAG/NPK > ST-g-SAG/5%Ca-MMT/NPK > ST-g-SAG/3%Ca-MMT/NPK > Ca-MMT/NPK. This makes the materials practically applicable in several fields since humidity is easily achieved in the environment. The biopolymers and biocomposites responded to changes in humidity with time which enhanced the slow release of the NPK

fertilizer. The percentage degradation for ST-g-SAG/Ca-MMT/NPK composites ranged from 56% to 98%.

Data Availability

The data used in this research article came from our experiments. The data used to support the study's findings are included in the article and can also be obtained upon request from the corresponding author.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors wish to express their profound gratitude to the Chemical Engineering Department of the Kwame Nkrumah University of Science and Technology (KNUST), Kumasi, Ghana, for the leaching test determination.

References

- [1] E. V. R. Campos, J. L. de Oliveira, and L. F. Fraceto, "Applications of controlled release systems for fungicides, herbicides, acaricides, nutrients, and plant growth hormones: a review," *Advanced Science, Engineering and Medicine*, vol. 6, no. 4, pp. 373–387, 2014.
- [2] E. V. R. Campos, J. L. de Oliveira, L. F. Fraceto, and B. Singh, "Polysaccharides as safer release systems for agrochemicals," *Agronomy for Sustainable Development*, vol. 35, no. 1, pp. 47–66, 2015.
- [3] P. C. Abhilash and N. Singh, "Pesticide use and application: an Indian scenario," *Journal of Hazardous Materials*, vol. 165, no. 1–3, pp. 1–12, 2009.
- [4] A. T. Albuquerque, J. S. Rodrigues, A. S. de Freitas, G. T. Machado, and V. R. Botaro, "Renewable source hydrogel as a substrate of controlled release of NPK fertilizers for sustainable management of eucalyptus urograndis: field study," *ACS Agricultural Science & Technology*, vol. 2, no. 6, pp. 1251–1260, 2022.
- [5] R. Scaffaro, M. C. Citarrella, and E. F. Gulino, "Opuntia Ficus Indica based green composites for NPK fertilizer controlled release produced by compression molding and fused deposition modeling," *Composites Part A: Applied Science and Manufacturing*, vol. 159, Article ID 107030, 2022.
- [6] A. Białkowska, B. Borycka, M. Bakar, and A. Rzany, "Innovative NPK fertilizers based on polyacrylamide and polyvinyl alcohol with controlled release of nutrients," *Polish Journal of Chemical Technology*, vol. 24, no. 3, pp. 14–18, 2022.
- [7] Geotechnical Test Method, "7 Test method for liquid limit, plastic limit, and plasticity," *Geotechnical Engineering Bureau*, vol. 2, p. 1, 2015.
- [8] M. C. Laker and C. C. Du Preez, "An investigation into the accuracy of hydrometers for soil particle size determinations," *Agroplantae*, vol. 14, pp. 17–22, 1982.
- [9] A. W. Skempton, *The Colloidal Activity of Clays. Selected Papers on Soil Mechanics*, Thomas Telford Ltd, London, UK, 1953.
- [10] G. Sen, R. P. Singh, and S. Pal, "Microwave-initiated synthesis of polyacrylamide grafted sodium alginate: synthesis and characterization," *Journal of Applied Polymer Science*, vol. 115, no. 1, pp. 63–71, 2010.

- [11] F. Uddin, *Montmorillonite: An Introduction to Properties and Utilization*, IntechOpen, London, UK, 2018.
- [12] A. Bashir, R. Malviya, and P. K. Sharma, "Microwave assisted grafting of natural polysaccharides," *Journal of Chronotherapy and Drug Delivery*, vol. 6, pp. 79–92, 2015.
- [13] R. C. Bhatt, T. C. Ghany, Y. F. Yueh, P. J. Singh, and L. D. McIntyre, "Laser-induced breakdown spectroscopy: advanced analytical technique," *JPS Advance Technology*, vol. 12, p. 265, 2018.
- [14] O. D. L. Couto, O. D. L. Paiva, C. M. Lyra, D. A. C. A. Costa, and M. A. C. M. Leite, "Microbiological degradation of starch based films: preparation, properties and evaluation of biodegradation," *International Journal of Scientific Research*, vol. 3, p. 10, 2015.
- [15] T. S. Daitx, M. Giovanela, L. N. Carli, and R. S. Mauler, "Biodegradable polymer/clay systems for highly controlled release of NPK fertilizer," *Polymers for Advanced Technologies*, vol. 30, no. 3, pp. 631–639, 2019.
- [16] H. B. Scher, *Controlled-release Delivery Systems for Pesticides*, CRC Press, Boca Raton, FL, USA, 1999.
- [17] X. Wang, X. Hou, P. Zou, A. Huang, M. Zhang, and L. Ma, "Cationic starch modified bentonite-alginate nanocomposites for highly controlled diffusion release of pesticides," *International Journal of Biological Macromolecules*, vol. 213, pp. 123–133, 2022.
- [18] X. Sun, H. Fu, M. Bao et al., "Preparation of slow-release microencapsulated fertilizer—biostimulation remediation of marine oil spill pollution," *Journal of Environmental Chemical Engineering*, vol. 11, no. 2, Article ID 109283, 2023.
- [19] Y. He, Z. Wu, L. Tu, Y. Han, G. Zhang, and C. Li, "Encapsulation and characterization of slow-release microbial fertilizer from the composites of bentonite and alginate," *Applied Clay Science*, vol. 109, pp. 68–75, 2015.
- [20] H. S. Samanta and S. K. Ray, "Synthesis, characterization, swelling and drug release behavior of semi-interpenetrating network hydrogels of sodium alginate and polyacrylamide," *Carbohydrate Polymers*, vol. 99, pp. 666–678, 2014.