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Slow release of NPK fertilizer using biodegradable porous carriers synthesized from agricultural waste

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Abstract

This study investigates the synthesis of porous biodegradable materials from rice bran and pineapple waste to determine their potential as carriers for slow-release NPK (Nitrogen, Phosphorus, Potassium) fertilizers. Through gel formation, solvent exchange, and carbonization; agro-waste gets converted into highly porous materials. A further examination of these materials demonstrates their adsorption capability and efficacy in progressive NPK fertilizer release. Experimental results show that both rice bran and pineapple waste-derived materials are effective slow-release fertilizer carriers. However, comparative investigation shows that rice bran-based material has better slow-release properties than its pineapple waste-derived counterpart. Here we also include the kinetic study of the release rate of NPK fertilizers which turned toward a Pseudo-zero order of release rate. This study emphasizes the necessity of repurposing agricultural byproducts for sustainable material synthesis, which contributes to the advancement of green chemistry and provides eco-friendly fertilizer delivery systems.

Keywords: Sustainable fertilizer; Porous material; Agro waste; NPK fertilizer; Rice bran; Pineapple waste

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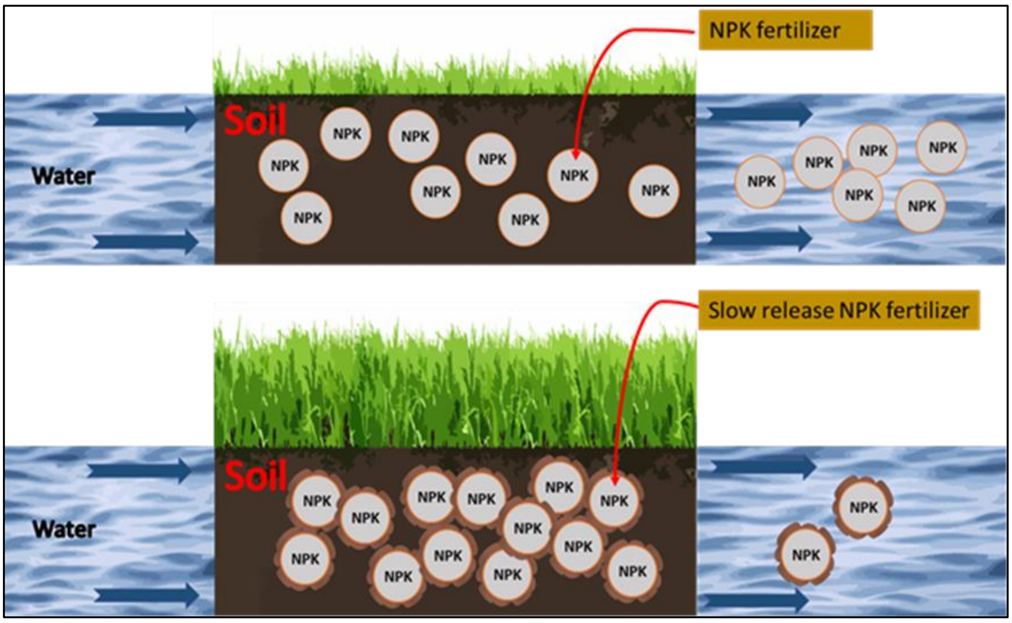
Graphical abstract



1. Introduction

Agriculture is the fundamental behind of human existence, providing food to civilizations throughout history. Crop production not only supplies vital nutrition but also benefits economies and cultures across the world. However, conventional techniques associated with modern agriculture, particularly the widespread use of chemical fertilizers, have inadvertently generated crucial environmental risks. Inadvertent use of chemical fertilizers has resulted in soil deterioration, water pollution, and negative effects on ecosystems, eroding the basic basis on which agriculture depends. Traditional fertilisers, however initially effective in increasing agricultural yields but eventually showed negative impacts on soil fertility and ecological wellness[1,2]. The easy release of nutrients into the soil leads to nutrient leaching, soil acidification, and negative effects on microbial populations. In addition, the discharge from these fertilizers adds to the pollution of water bodies, harming both aquatic life and human health. Hence, the use of chemical fertilizers has become more unsustainable, provoking a transition to more ecologically friendly alternatives[3].

With these problems, there is a growing acceptance of the need for sustainable agriculture methodologies that ensure food security while reducing pollution. This includes investigating novel techniques to regulate nutrients that maximize resource utilization while minimizing environmental impact. Slow-release fertilizers have emerged as an effective way to overcome the constraints of traditional fertilization processes. These fertilizers allow for the gradual release of nutrients by encapsulating them in porous matrices, enhancing nutrient efficiency, decreasing leaching, and limiting environmental pollution[4]. Slow-release fertilizers are a promising choice for sustainable agriculture, combining agronomic efficiency and concern for the environment. By utilizing highly porous biodegradable materials obtained from agro-waste, such as crop residues or organic by-products, these fertilizers not only offer necessary nutrients to crops but also help to waste valorization and retention of carbon[5].

The last decade has thoroughly studied the use of agro-waste for sustainable slow-release fertilizer synthesis, with a focus on agricultural residues, agricultural byproducts, and biochar. These materials show ability as nutrient transporters, increasing soil fertility, crop yields, and ecological sustainability by lowering nutrient leaching and emitting greenhouse gases. Slow-release fertilizers obtained from agricultural waste provide a long-term option for enhancing crop yield while reducing the environmental effect[3,6]. These fertilizers, such as biochar-based slow-release fertilizers (BSRFs) and formulations made from garden plant waste, rice straw, wheat straw, sugarcane bagasse, and other organic materials, efficiently solve the nutrient loss difficulties associated with traditional fertilizers. These fertilizers aim foster sustainable agricultural practices by improving the qualities of the soil, retarding nutrient release, and improving plant nutrient absorption efficiency[7,8]. Granulation, coating, and secondary coating techniques are used to provide continuous and long-term nutrient release, hence enhancing fertilizer efficiency. Using waste materials not only decreases environmental impact but also delivers necessary nutrients to crops, making slow-release fertilizers from agro-waste an intriguing option for sustainable agriculture[5].

In this work, we propose the synthesis of highly porous materials using pineapple waste and rice bran residue to address the growing demand for organic farming practices. These materials will be used to adsorb NPK fertilizer, with additional investigation into the rate of release of the adsorbed fertilizer. We want to contribute to the development of effective slow-release fertilizer formulations by explaining the release behavior of NPK fertilizers from the synthesized materials, which will improve nutrient utilization efficiency while minimizing environmental impact.

2. Materials and Methods

2.1. Synthesis of porous materials

Pineapple waste was collected from a local fruit seller, carefully cleansed, and allowed to sun-dry over 2 to 3 days. It was then finely ground into a powder. Rice bran was collected from the local rice mill. Highly porous materials were synthesized using pineapple waste powder and rice bran residue. This process involved three steps: gelation, solvent exchange, and carbonization[9,10].

- Gelation: Pineapple waste powder was the basic raw material used to synthesize porous materials. In the initial phase of synthesis, gelation was carried out by mixing 10 g of pineapple waste powder with 100 ml of water at a 1:10 ratio. The mixture was rapidly agitated in a boiling water bath for one hour, followed by cooling at 50^{o}C in the freezer for 2-3 days until gel formation was seen.
- Solvent Exchange: The gel block undergoes solvent exchange to remove contamination and improve material stability. This procedure involves swirling the gel block with ethanol for one hour, followed by cooling for two days. The solvent was then decanted, and the resulting starch material was washed three times with ethanol for 10 minutes each. The wet starch following solvent exchange was then dried in the sunlight for 2-3 days until it reached an appropriate consistency.
- Carbonization: After synthesis, the dried material was carbonized using a temperature cycle up to 250°C. The method converted the material into a highly porous structure known as ‘starbon’[9]. The same synthesis technique was used for rice bran powder to produce extremely porous materials

2.2. Loading NPK Fertiliser on Porous Materials:

The slow-release behavior of the synthesized porous materials was evaluated using NPK fertilizer as a model fertilizer. At first, 0.5 g of NPK was dissolved in 10 ml of water. Then, 1 g of measured porous material was added to the NPK solution. The suspension was then stirred at room temperature for 3 hours at 100 rotations per minute (rpm) to achieve total blending and equilibrium. Following stirring, the suspension was filtered under a vacuum to get out the loaded porous material from the solution. The filtrate was eliminated and the loaded material was dried for three hours at temperatures ranging from 50 to 60°C to eliminate any remaining moisture.

To determine loading efficiency, the porous materials were precisely weighed before and after loading with NPK. Notably, there was a significant difference in weight between materials derived from pineapple waste powder and rice bran powder before and after NPK loading. Specifically, the weight of pineapple waste increased from 1 g to 1.21 g, while rice bran increased from 1 g to 1.35 g.

2.3. Calibration of NPK fertilizer

The standardization of NPK fertilizer was conducted through the utilization of various concentrations of NPK solutions against absorbance measurements. Concentrations ranging from 20 mg/liter to 200 mg/liter were selected for this purpose. These solutions were analyzed for their absorbance using a UV-spectrophotometer, thus facilitating the construction of a calibration curve as shown in Figure 1. This graph serves as a crucial reference point for the subsequent analysis of the slow-release behavior of NPK fertilizer[11,12].

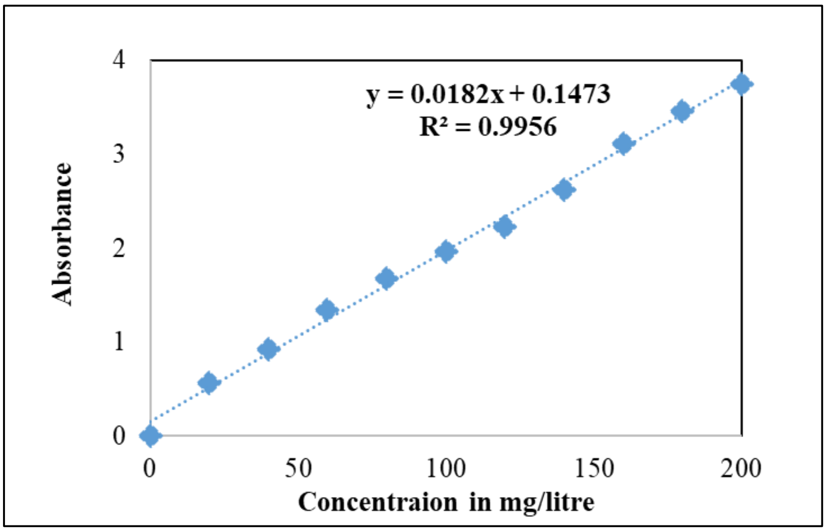


Figure 1 Calibration curve of NPK fertilizer

2.4. Slow-release behaviour of NPK fertilizer loaded on highly porous materials

To evaluate the release behaviour of NPK fertilizer incorporated into porous materials synthesized from rice bran residue and pineapple waste, 1 gram of each synthesized material was accurately measured. The rice bran-derived material contained 0.35 grams of NPK fertilizer, while the pineapple waste-derived material contained 0.21 grams. These materials were placed in separate glass columns. The urea release profile was analyzed using both continuous and batch methods. The columns were consistently maintained with just enough distilled water to ensure complete saturation. For each measurement, 5 ml of distilled water was added to the column, and 5 ml of the eluate was collected at various time intervals. Three distinct types of studies were conducted to analyze the release behaviour[11,13,14].

- Continuous elution method
- After six hours' elution method
- After 24 hours' elution method

2.5. Characterization of Porous Materials

The morphology of the materials was examined through scanning electron microscopy (SEM) employing a Tescan Vega3 model, operating at an accelerating voltage of 20 kV. Fourier transform infrared (FTIR) spectroscopy was utilized to identify surface functional groups within the porous material. FTIR analysis was conducted using a PerkinElmer FTIR spectrometer, covering a range from 400 to 4000 cm^−1, employing the KBr pellet method. UV spectrophotometer was used to the find out concentration of NPK fertilizer while studying slow release behaviours of NPK fertilizer when adsorbed on highly porous materials which we synthesized

3. Result and Discussion

3.1. SEM micrographs

Scanning electron microscopic (SEM) analysis was conducted to examine the morphology of porous materials derived from selected agro-wastes. In the case of porous material derived from pineapple waste (Figure 2 A, B), distinct microporous structures were observed. Micrographs in Figure 2 C, D depict the NPK-loaded porous material derived from pineapple waste, clearly illustrating the presence of NPK fertilizer particles. Conversely, for porous material derived from rice bran residue (Figure 3 A, B), similar microporous features were observed. The SEM images in Figure 3 C, D reveal the presence of NPK fertilizer loaded onto the material. The SEM images exhibited well-defined micropores in the unloaded material with some flex formation, while the loaded material efficiently displayed adsorbed fertilizer within these pores[11,15].

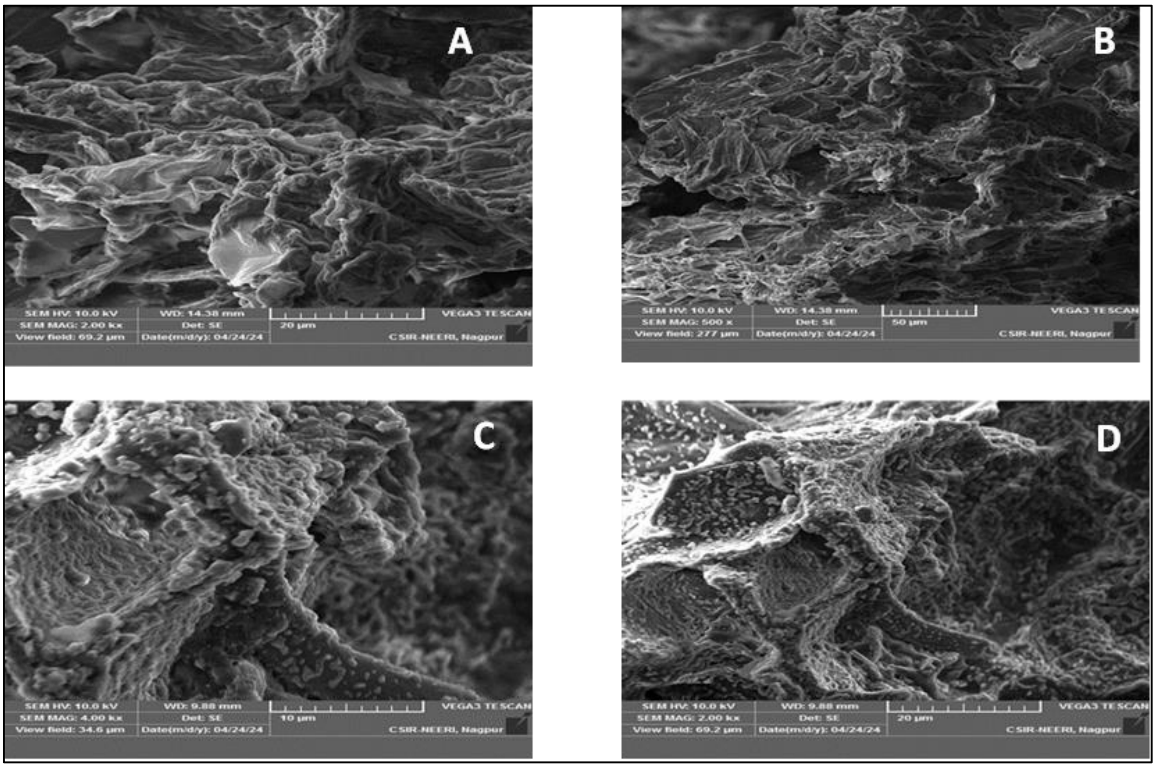


Figure 2 SEM images of (A, B) porous material derived from pineapple waste before NPK loading (C, D) porous material derived from pineapple waste after NPK loading

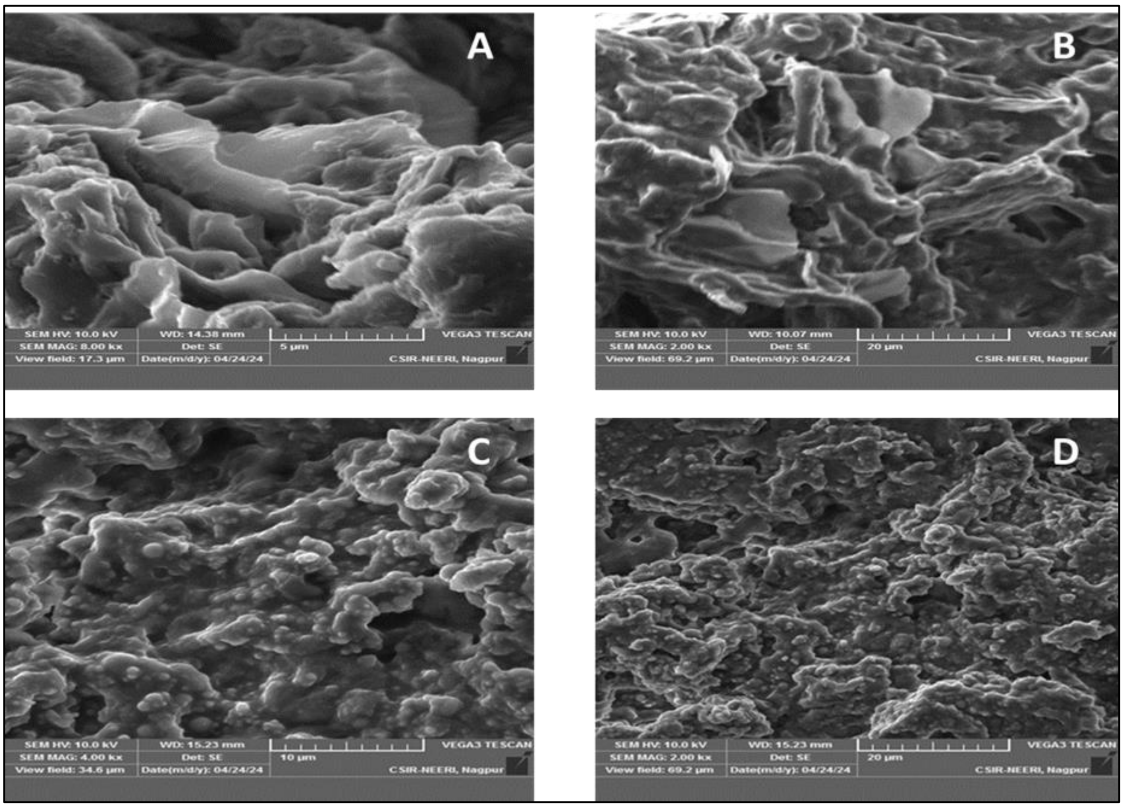
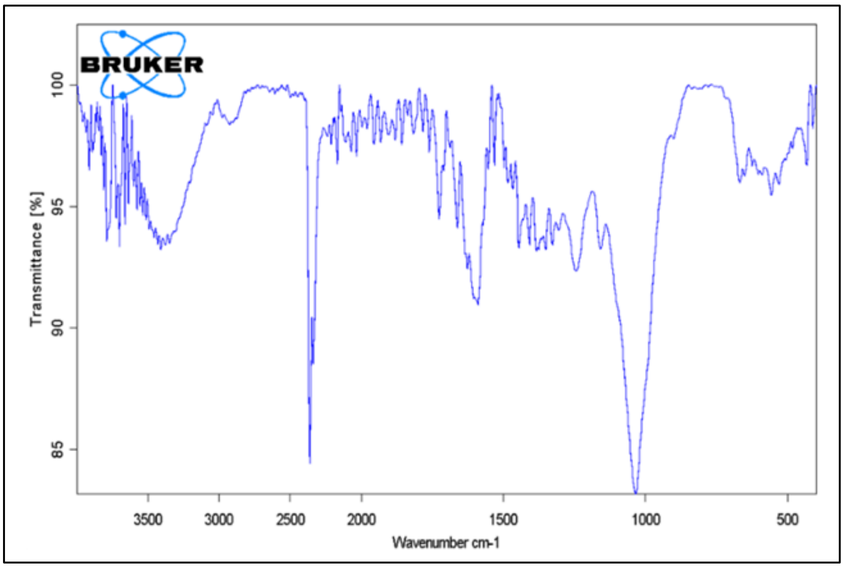


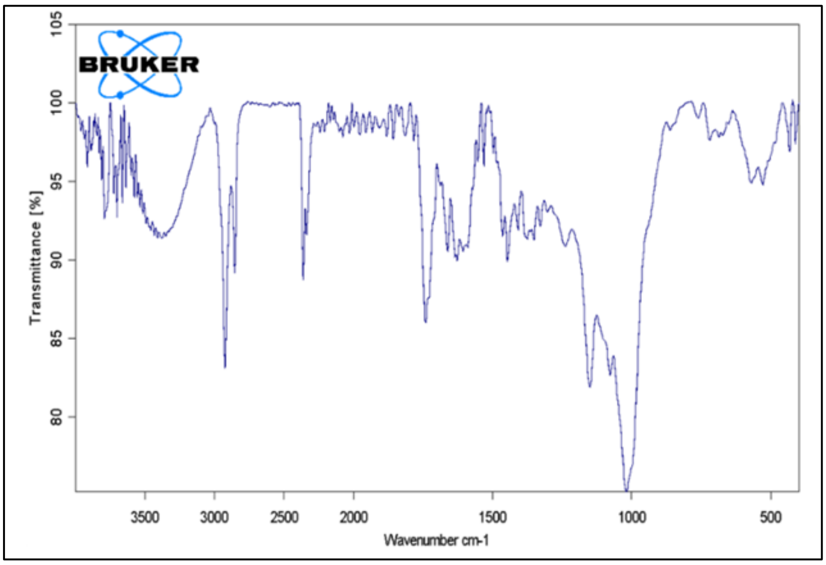
Figure 3 SEM images of (A, B) porous material derived from rice bran residue before NPK loading (C, D) porous material derived from rice bran residue after NPK loading

3.2. FTIR spectroscopy

The porous materials and their NPK-loaded analogues were characterized using FTIR spectroscopy to identify compositional changes after synthesis. Figure 4 (A) shows the FTIR spectra of a porous material generated from pineapple waste before NPK addition. Signals between 2300-2500 cm^{-1} possibly indicate C-H stretching vibrations in aliphatic molecules like lipids or the presence of adsorbed ambient carbon Signals in the 1000-1100 cm^{-1} range indicate the presence of carbohydrates and organic acids in pineapple waste. Peaks between 1500 and 1700 cm^{-1} indicate stretching vibrations of carbonyl groups commonly found in sugars, organic acids, and related substances. Figure 4 (B) shows the FTIR spectra of porous material formed from rice bran residue, which display distinct peaks indicating diverse functional groups within the sample. Peaks seen between 2200-2350 cm^{-1} indicate the presence of C≡C stretching vibrations, present in alkenes and alkynes[16]. Signals between 2850-3000 cm^{-1} reveals the C-H stretching vibrations in organic compounds like fatty acids and proteins. Peaks in the 1000-1100 cm^{-1} range reveal C-O stretching vibrations, indicating the presence of polysaccharides and carbohydrates. Peaks in the 1600-1700 cm^{-1} range imply C=O stretching vibrations, which are typically seen in fatty acids and proteins[17].



(A)



(B)

Figure 4 IR spectra of (A) Porous material derived from Pineapple waste material (B)) Porous material derived from Rice bran residue

3.3. Analysis of slow release of NPK through porous materials

The analysis of the slow release of NPK through porous materials involved the investigation of release behavior using three distinct methodologies where we used three different columns filled with accurately weighed SRF material as we discussed earlier, for both materials rice bran material with NPK fertilizers and pineapple waste material with NPK fertilizers. Continuous evaluations were conducted wherein eluates were collected at one-minute intervals from the porous material bed column. In the case of six hours method, eluates were collected at six-hour intervals, providing periodic assessments of the release process and in the last methodology, eluates were collected after a 24-hour duration, representing a daily evaluation of NPK release.

3.3.1. Continuous elution method

In the continuous elution method, two separate columns were filled with pineapple waste material and rice bran residue material, both loaded with NPK fertilizers. The total weight of the materials was 1.21 grams and 1.35 grams respectively. Distilled water was then used to fill the columns, and elution samples of 5 ml were collected after each minute for both columns. Initially, the concentration of NPK fertilizer in the elution was high, gradually decreasing up to the 20th elution in both cases. However, it was noted that in the case of rice bran material, the concentration remained higher compared to the pineapple material. Specifically, after the 14th elution, the release concentration of NPK fertilizers slowed down in the rice bran material, and similar readings were observed thereafter as shown in Figure 5 A. As a result, the adsorption capacity observed in the rice bran material was found to be slightly higher than that of the pineapple material. This indicates that rice bran material serves as an efficient carrier for slow-release fertilizer applications[16].

3.3.2. After 6 hours' elution method

In this method, we conducted experiments mirroring the continuous method, with the sole variation being elution extraction every 6 hours. This enabled us to observe a gradual and consistent release profile of NPK fertilizer in both materials. Notably, our findings revealed a more efficacious release profile of NPK fertilizer in rice bran material compared to pineapple waste material, as depicted in Figure 5 B.

3.3.3. After 24 hours Elution method

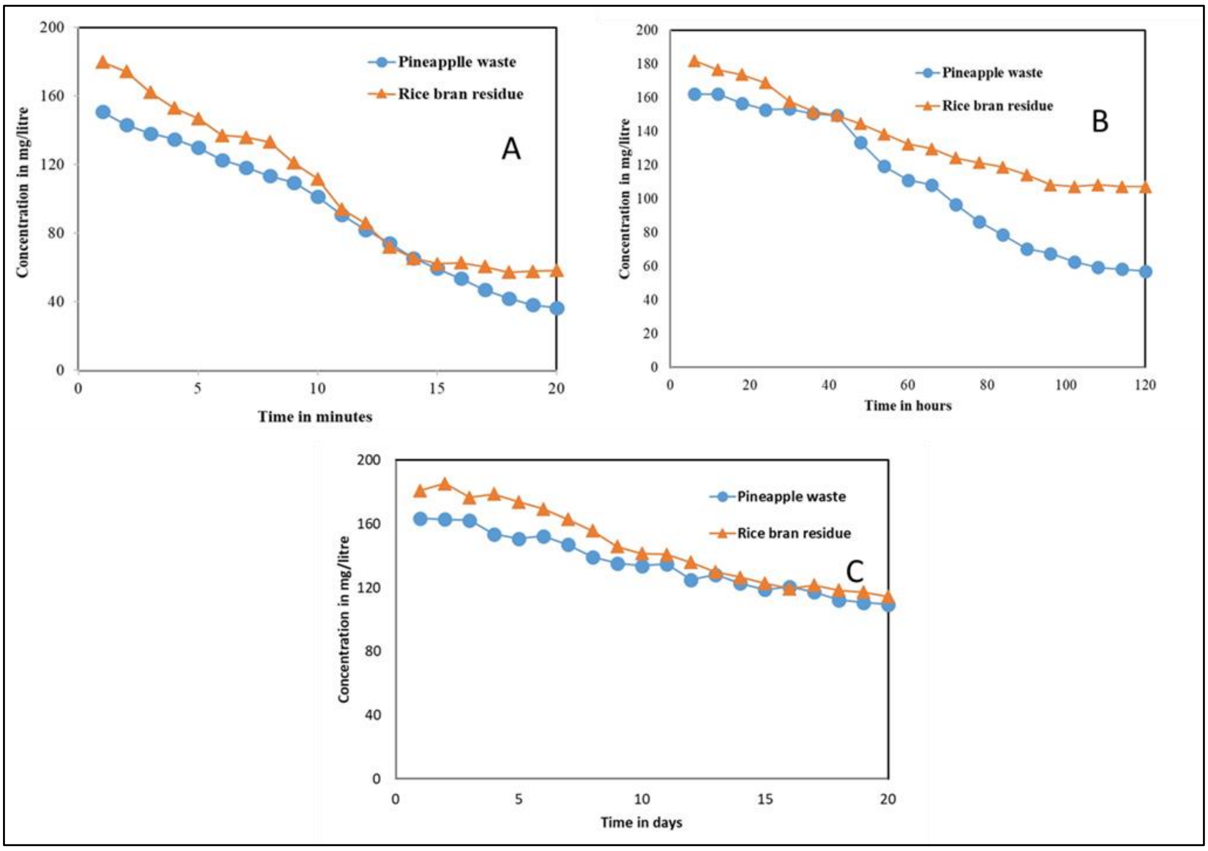


Figure 5 Concentration of NPK fertilizer during A. Continuous elution method B. 6 hrs elution method C. 24 hrs elution method

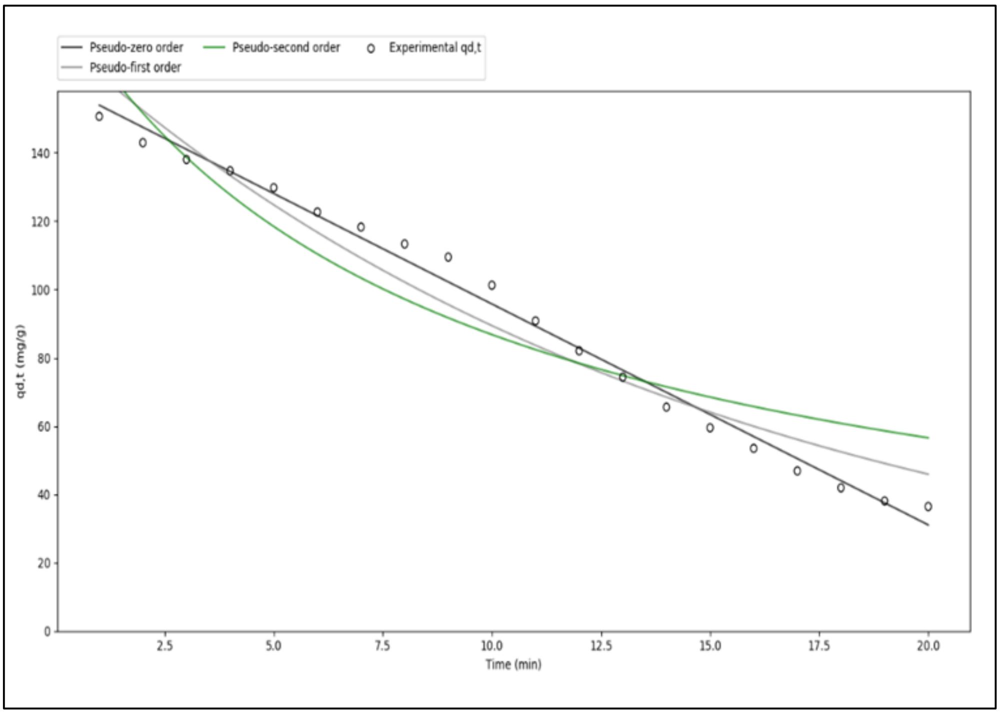
In this methodology, our experimental procedures were conducted by the continuous method, with the sole deviation being the extraction of eluates every 24 hours. Through this approach, we scrutinized the release profiles of both materials and observed a nearly identical trend. Initially, the concentration of NPK fertilizer in the rice bran material exhibited a higher concentration as shown in Figure 5 C. However, by the 12th day of experimentation, we noted a convergence in the release of NPK fertilizer from both materials, displaying a gradual and consistent pattern.

The continuous elution method, involving one-minute interval collections, revealed that the rice bran material exhibited a higher initial concentration and a more sustained release of NPK compared to the pineapple waste material. This was evident from the 14^{th} elution onward, where the release rate in the rice bran column showed a slower decline, indicating a superior adsorption capacity. Consequently, rice bran material demonstrated its potential as a more efficient carrier for slow-release fertilizer applications, maintaining higher nutrient availability over time[18].

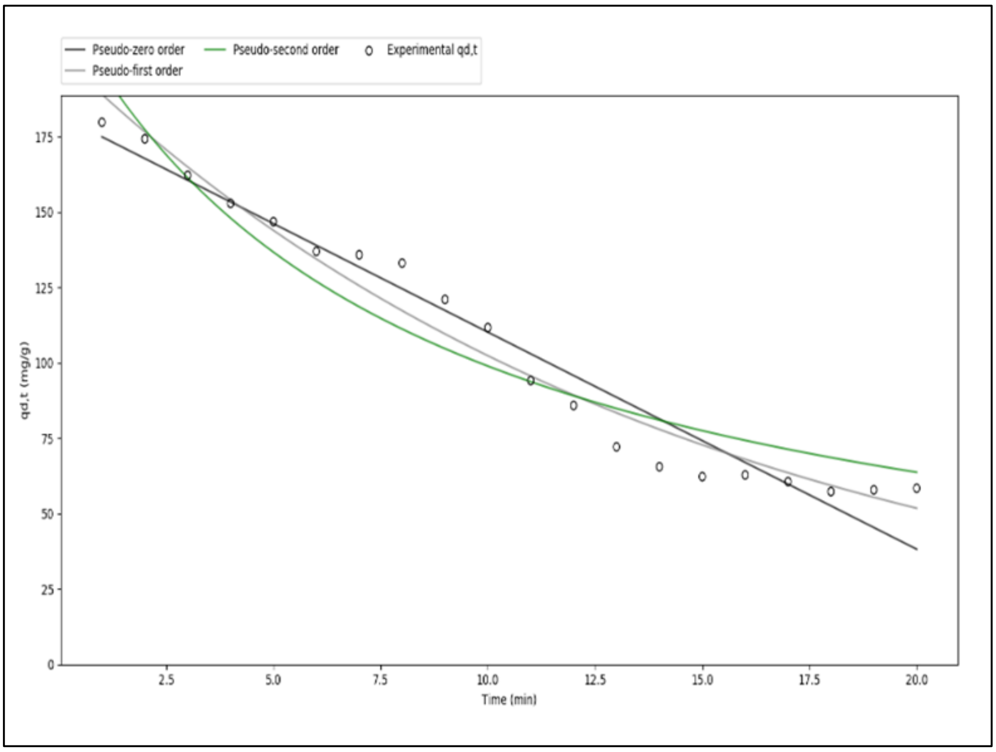
Further assessments using six-hour and 24-hour elution methods reinforced these findings. Both methods highlighted a more gradual and consistent release profile in rice bran material. Specifically, the six-hour interval collection showed a pronounced efficacy in nutrient release from rice bran, while the 24-hour method revealed that although the initial concentrations were higher in rice bran, the release profiles of both materials converged by the 12^{th} day, displaying a uniform pattern. These results underscore the advantage of rice bran as a sustainable and efficient medium for slow-release fertilizers, promoting prolonged nutrient availability and reduced environmental impact, thereby offering a viable solution for enhanced agricultural productivity[3].

3.4. Release kinetics of NPK fertilizers

In this investigation, we rigorously analyzed the release kinetics of NPK fertilizers from biodegradable porous materials derived from rice bran and pineapple waste using four distinct models: Pseudo Zero Order, Pseudo First Order, Pseudo Second Order, and the Weber Morris Model. Employing the CAVS software for kinetic modeling, we sought to determine the most accurate model describing the release profiles observed. Our findings revealed that the Pseudo Zero Order kinetic model best matched the release rate data for the ZA-HA sample. This indicates a constant release rate independent of the fertilizer concentration, suggesting that the release mechanism is predominantly governed by steady-state diffusion through the porous matrix of the rice bran materials[11,19,20].



(A)



(B)

Figure 6 Release kinetics of NPK fertilizers with Pseudo zero order, Pseudo first order, Pseudo second order and Weber Morris desorption kinetics by using CAVS A. SRF derived from Pineapple Waste B. SRF derived from Rice bran

Conversely, the pseudo-first-order and pseudo-second-order models, which assume release rates proportional to the concentration and the square of the concentration of the fertilizer, respectively, did not align well with our experimental data. These models failed to accurately capture the initial high release rates followed by a more gradual, sustained release phase[21]. Additionally, the Weber-Morris Model, which considers both external mass transfer and intra-particle diffusion, provided insights into the diffusion-controlled aspects of the release but was less effective in describing the overall kinetics. The superior fit of the Pseudo Zero Order model underscores the efficacy of rice bran material in facilitating a controlled, consistent release of NPK fertilizers, highlighting its potential for optimizing nutrient delivery in agricultural applications while mitigating environmental impacts[22,23].

3.5. Comparative Study with Conventional Method

Nitrogen, Phosphorus, and Potassium, or NPK, fertilizers are extensively utilized for a wide range of crops, including fruits, vegetables, cereals (such rice, wheat, and corn), and cash crops like cotton and sugarcane. The type of crop and the soil conditions affect the amount and timing of NPK treatment[14,24]. NPK fertilizers are normally administered using traditional methods at concentrations between 100 and 200 kg/ha, and because of nutrient leaching and runoff, they need to be repeated every few weeks. As a result, there are large nutrient losses, destruction of the environment, and inefficient fertilizer use. On the other hand, slow-release fertilizers made from pineapple waste and rice bran show promise as a substitute, especially for crops that benefit from steady nitrogen availability[13,25]. With a constant and continuous release rate of 115 ppm, the maximum observed release rate in our investigation was 182 ppm. For crops like rice, maize, and wheat, which need consistent nutrient availability throughout their growth cycles, this regulated release is quite advantageous[26,27]. The slow-release capabilities minimize environmental effects by improving fertilizer use efficiency and reducing nutrient runoff[8,28]. These slow-release fertilizers may significantly improve crop yields and nourish the soil in areas with intense agriculture, such as Southeast Asia for rice or the Midwest of the United States for maize[18,20]. By ensuring a consistent supply of vital nutrients to crops, the constant release of 115 ppm enhances crop growth and minimizes the need for recurrent fertilizer applications. This is particularly beneficial in places that get a lot of rain since traditional fertilizers get washed away and cause the soil to end up depleted of nutrients. When all factors are considered, applying slow-release NPK fertilizers made from agro-waste aligns with ecologically conscious agriculture and encourages the development of environmentally friendly farming practices in a variety of crop and geographic contexts[8,29,30].

4. Conclusion and Future Prospective

This work effectively illustrates the synthesis of extremely porous, biodegradable polymers from pineapple waste and rice bran that are specifically designed to act as carriers for slow-release NPK fertilizers. A number of procedures, such as gel formation, solvent exchange and carbonization; were used to create the materials. According to our study, materials made from rice bran and pineapple waste have considerable adsorption capacities for NPK fertilizers, with materials made from rice bran displaying better slow-release qualities. The porous structure of the synthesized materials was confirmed by scanning electron microscopy (SEM) images, and the chemical integrity and anticipated functional groups of the materials were validated by Fourier transform infrared spectroscopy (FTIR) data. A pseudo-zero order release rate was identified by the kinetic analysis, highlighting the materials' capacity for a steady and reliable nitrogen release a critical component of efficient fertilizer application in agriculture.

To further improve the porosity and adsorption effectiveness of biodegradable materials, future research should concentrate on streamlining the synthesis procedure. The spectrum of raw materials for sustainable fertilizer carriers should be increased by investigating additional agro-waste sources, which may produce materials with even better performance characteristics. Furthermore, field tests must be carried out to evaluate the feasibility and ecological consequences of these slow-release fertilizers in diverse soil kinds and farming environments. To guarantee these materials' viability as environmentally friendly alternatives, it will also be crucial to look into their long-term biodegradability and environmental safety. By incorporating these discoveries into large-scale farming operations, fertilizer application could be revolutionized, thereby furthering green chemistry principles and sustainability in the agricultural industry.

Compliance with ethical standards

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Disclosure of conflict of interest

No potential conflict of interest was reported by the author(s)

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