

Research Article

Lauric Acid-Modified *Nitraria* Seed Meal Composite as Green Carrier Material for Pesticide Controlled Release

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To alleviate the adverse effects of pesticide residues on the environment, development of a more safe, economical, and reliable usage approach of pesticides is critically urgent. In the present study, a novel pesticide carrier LA-NSM (lauric acid-modified *Nitraria* seed meal) with controlled release property was prepared through grafting esterification of lauric acid onto *Nitraria* seed meal substrates. The structure of the obtained samples was characterized by Fourier-transform infrared spectroscopy, scanning electron microscopy, and contact angle measurements. The results indicated that LA-NSM products had a well-defined hydrophobic surface and irregular holes for efficient loading of pesticide molecules. Deltamethrin (DEL), a representative insoluble pyrethroid insecticide in water, was deliberately selected as the index pesticide to evaluate the loading and releasing efficiency of LA-NSM. The loading capacity of LA-NSM for DEL can reach about 1068 mg/g. pH, humidity of soil, and temperature had a significant influence on controlled release performance of LA-NSM@DEL. Moreover, the releasing kinetics of LA-NSM@DEL composites could be fitted well with the Higuchi model. Overall, the highly hydrophobic property, excellent loading, and controlled release ability of LA-NSM made it a promising candidate in agricultural applications.

1. Introduction

Pesticide residues, caused by conventional usage routes like customarily spraying or mixing them with soil, undoubtedly have received considerable attention in recent years because of their high toxicity to the ecosystem and human health [1, 2]. To solve this problem, some remedial measures, including natural degradation [3], biotreatment [4], ion exchange [5], and electrochemical and physical methods [6], have been proposed. Unfortunately, these treatments are inefficient, time-consuming, or high in cost. In other words, such strategies cannot effectively, economically, and radically mitigate the abovementioned drawbacks [7]. Therefore, the development and design of environmental-friendly and safe usage approaches are becoming extremely urgent for reducing the risk of

pesticide residues. Typically, controllable release of agrochemicals from various designed carriers has recently been put forward to replace the traditional treatment methods because of the facile preparation, low initial cost, and ease of operation. These strategies have been verified that they are able to serve as a superior technique for the remediation of environmental problems caused by pesticide residues [8, 9]. Up to date, various materials including clay minerals [10], montmorillonites [11], and starch [12–14] have been suggested to act as the scaffold for the controlled release of pesticides. In contrast, using alternative biomaterials as a vehicle has sparked another particular interest owing to their stable raw-material supply and low cost, renewable nature, nontoxicity, and biodegradable advantages [12, 15].

Nitraria, as an important economic crop belonging to the family Elaeagnaceae, is widely cultivated in East Asia,

North America, East Europe, and other areas in the world. Traditionally, the fruits of *Nitraria* are extensively used in pharmacy, brewing beer, and vinegar production [16]. In contrast, the residues of *Nitraria*, including seeds, pericarp, and roots, are often disposed as agricultural wastes. The common management options, such as discarding outside, burning, and burying, are harmful to groundwater resources, atmosphere, and the environment [17]. Therefore, effective utilization of discarded *Nitraria* residues still remains a challenge. *Nitraria* seed meals (NSMs) are the by-products of *Nitraria* seeds after oil extraction. Currently, a multitude of NSMs are used to be handled as agricultural wastes, which presents an obvious waste of resources. From the aspect of their microstructures, the residual NSMs are extremely rich in cellulose, oil body, and proteins since most of the oils of *Nitraria* seeds are mainly stored in tiny organelles (0.5–2.0 μm diameter) called oil body (OB) [17]. Hereby, it is inevitable that plenty of OB membranes and cellulosic substances would be left after oil expression. In terms of their chemical components, the oil-body membranes consist of approximately 50% phospholipids, 40% membrane proteins, and about 2–10% glycoproteins [18], which are abundant in various functional groups like acyl, long-chain alkyl, phosphate, carboxyl, and amidogen groups. The hydrophobic groups like long-chain alkyls endow NSMs with partial hydrophobicity and acquire the oily molecules voluntarily by absorptive function [19]. As a result, the NSMs display intrinsic positive sorption capacity for oily substances and consequently can be used as an ideal alternative base material for the fabrication of oleophilic carriers. However, to the best of our knowledge, there is no report on using NSMs as carriers for pesticide delivery.

Deltamethrin (DEL) is a water-fast pyrethroid insecticide that destroys the central nervous system of several insects [20, 21]. DEL pesticide has been extensively applied in the fields of agriculture, home pest control, and disease vector control [22] and achieves more effective insecticidal action compared with the common insecticides like dimethoate [23], carbofuran [24], and fenthion [25]. In practice, DEL is often utilized by spraying on the surface of emblems or mixing with soil into the roots of plants, which have brought about serious environmental issues. Hence, to alleviate the adverse effects of DEL residues on the environment, development of a more safe, economical, and reliable usage of DEL is critically urgent.

In the present study, a novel hydrophobic carrier LA-NSM, modified *Nitraria* seed meals with lauric acid, was fabricated through a facile chemical-surface modification route. The structure, surface wettability, and morphology of the obtained LA-NSM were characterized by Fourier-transform infrared spectroscopy (FT-IR), contact angle measurements (CAM), and scanning electron microscopy (SEM). Moreover, the degree of esterification and the influence of pH, temperature, and soil humidity on the release capacity of LA-NSM@DEL were also studied. Generally, the controlled DEL release of the LA-NSM platform not only enhanced the service efficiency of agrochemicals but also extended the utilization of waste *Nitraria* seeds.

2. Experimental Section

2.1. Materials. NSMs were obtained from the Delingha region (Qinghai, China). Lauric acid (LA) was obtained from Chengdu Kelong Chemical Reagent Factory (Chengdu, China). Deltamethrin (2.5 %) was supplied by Bayer Crop Science Co., Ltd. (Beijing, China). Absolute ethanol, hydrochloric acid (HCl), and sodium hydroxide (NaOH) were provided by Xian Chemical Reagent Corp. (Xian, China). The reagents used in this research were all of analytical grade and were used without further purification. Distilled water was used throughout the work.

2.2. Preparation of LA-NSM. NSMs were modified according to a previous method [26]. Raw waste *Nitraria* seeds were first dried and pulverized to obtain NSMs with suitable size for blending. Next, the pieces were washed with NaOH (2% w/w) as well as distilled water to remove the adhering substances and then dried at 60°C for 1.0 h. After that, 20.0 g of dried NSM powder was suspended in 400 mL of lauric acid solution (1.0 M). The mixture was stirred gently for 6 h at desired temperature (90°C–140°C). Finally, the reaction products were centrifuged, washed with *n*-hexane three times, and dried to yield LA-NSM carriers.

2.3. Characterization. Fourier-transform infrared spectroscopy (FT-IR) was performed using a Perkin Elmer FT-IR System 2000 from 400 to 4000 cm^{-1} range via KBr pellets. Scanning electron microscopy (SEM) images were recorded using a Hitachi S-4800 microscope. The contact angle measurement was evaluated by Dataphysics OCA15 (Germany) equipment at ambient temperature. Liquid droplets ($\sim 6 \mu\text{L}$) were dropped carefully onto the surface of the products, and the average contact angle was determined by five parallel experiments at different positions on the same samples.

2.4. Determination of the Degree of Esterification. The degree of esterification (DE) was ascertained using the titration method reported by Chiou et al. [27]. Specifically, 1.0 g of LA-NSM was suspended in 50 mL of 75 % ethanol solution. The mixture was kept in a water bath (50°C) for 30 min under stirring, and 30 mL of NaOH solution (0.5 M) was then added to saponify the ester. The reaction was maintained for 72 h with continuous agitation at room temperature. The excess alkali was titrated by 0.5 M HCl using phenolphthalein as the indicator. Reference and duplicate samples were treated in a similar way. The DE was calculated according to the following equation [28, 29]:

$$\text{DE}(\%) = \frac{(V_0 - V_n) \times N \times 199 \times 10^{-3} \times 100}{W}, \quad (1)$$

where V_0 and V_n (mL) are the volumes of HCl used to titrate the blank and the sample, respectively. N is the normality of used HCl. W (g) is the weight of the dry sample. 199 is the molecular weight of the lauric acid ester group.

2.5. Loading Capacity of LA-NSM. The loading capacity of LA-NSM was determined by a gravimetric method [30]. A small amount of weighed dried samples (m_0) was immersed into DEL (2.5%) and withdrawn at regular time intervals (t) and weighed (m_t). The loading capacity (q_e , $\text{mg}\cdot\text{g}^{-1}$) of LA-NSM was calculated according to the equation [31]:

$$q_e = \frac{m_t - m_0}{m_0} \times 1000, \quad (2)$$

where m_t (g) is the quantity of carriers after loading and m_0 (g) is the initial weight of carriers, respectively.

2.6. Controlled Release Experiments. Controlled release of DEL-loaded LA-NSM was carried out in several 250 mL beakers containing different soils. The soils were employed as a medium to release DEL [32, 33]. The soil humidity and temperature were determined by soil moisture sensors (TRIME-PICO32, Germany). Specifically, 1.0 g LA-NSM@DEL was put into the dissolution medium under stirring (100 rpm). Every 10 min, 2.0 mL of the mixture was collected and assayed spectrophotometrically. After that, the analyzed samples were returned to the system to maintain a constant volume of the surrounding release medium. To verify the effect of pH on the release performance of LA-NSM@DEL, solutions with pH 3–10 were adjusted by dilution with HCl (pH 1.0) or NaOH (pH 13.0). The pH values were accurately measured with a pH meter (PHS-25, China). All experiments were conducted in triplicate, and the results were averaged. The accumulative release was calculated according to the following equation [33]:

$$\text{accumulative release (\%)} = \frac{(W_t)}{W_e} \times 100, \quad (3)$$

where W_e and W_t are the masses of the pesticide entrapped in LA-NSM carriers at the equilibrium state and released from pesticide-loaded LA-NSM at time t during the release process, respectively.

For further exploring the potential mechanism behind the slow release of LA-NSM@DEL, evaluating the release kinetics is particularly necessary. In this section, the experimental data were then fitted to the first-order, Higuchi, and Weibull models.

First order model:

$$\ln(Q_e - Q_t) = k_1 t + L. \quad (4)$$

Higuchi model:

$$\frac{Q_t}{Q_e} = k_2 t^{1/2}, \quad (5)$$

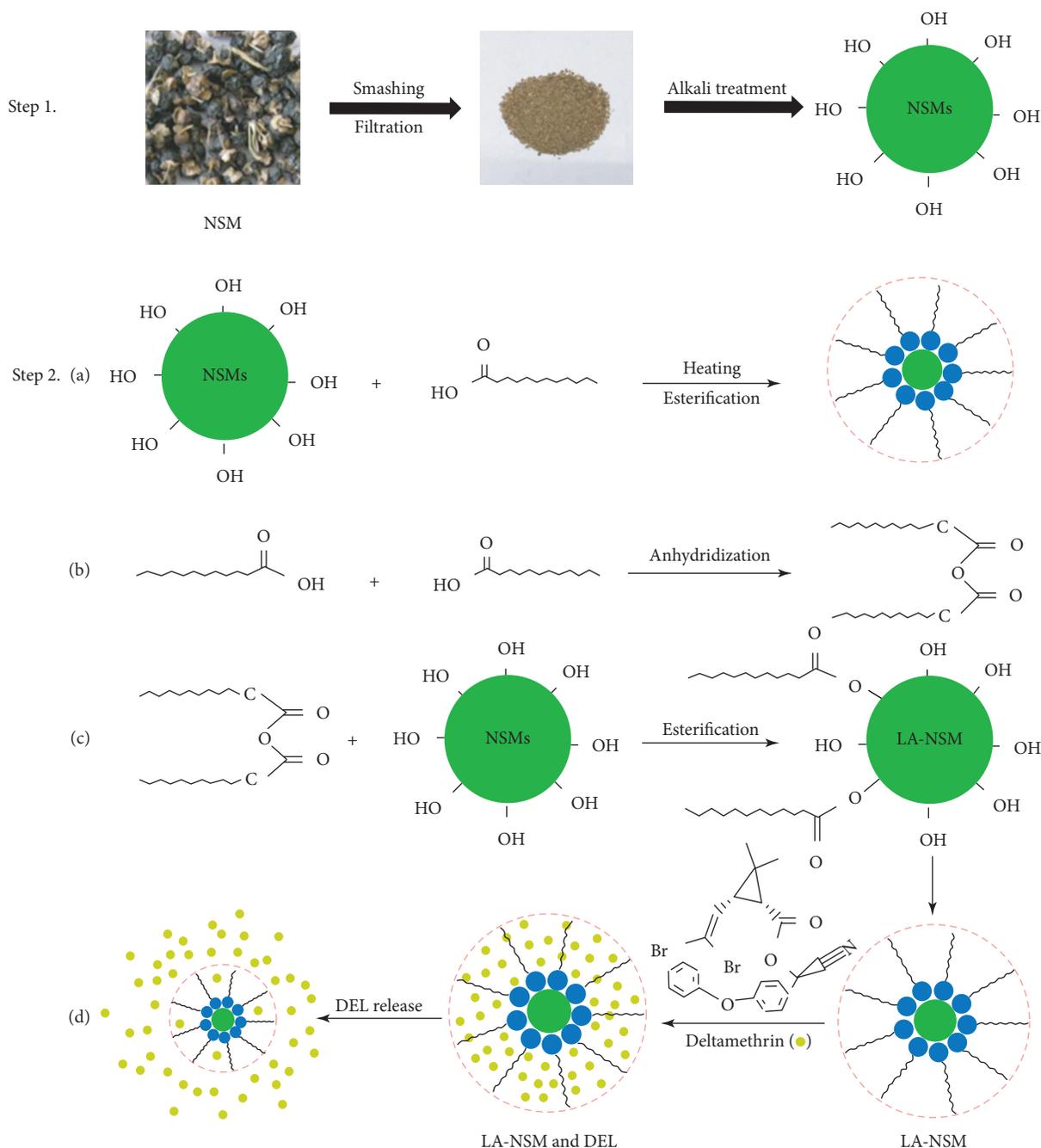
where Q_e and Q_t are the equilibrium loading amount (mg/g) and release amount at any time, respectively. k_1 , and k_2 are the rate constants, t is the release time (h), and L is the intercept (mg/g).

3. Results and Discussion

3.1. Formation and Characterization of LA-NSM. The detailed functionalization and fabrication processes of

LA-NSM composites are schematically illustrated in Scheme 1. As stated earlier, the surface of NSMs is covered by a number of inborn waxes, oils, and other impurities [19], making it difficult to be directly modified and to graft some new groups. Herein, we proposed a simple alkali-pretreatment method to remove these impurities and make the hydroxyl groups of NSMs exposed [34]. As a result, the surface of the alkali-pretreated NSM was inevitably equipped with abundant $-\text{OH}$ groups in comparison with the naked NSM substrates, making the further surface functionalization of the NSM substrate easy to occur. Afterward, the pretreated NSMs were immersed into lauric acid methanol solutions, and the grafting esterification reaction between lauric acid molecules and the NSM substrate occurred, making a lauric acid layer attach to the surface of the NSM substrate tightly and uniformly (denoted here as LA-NSM) [35]. The details of the grafting esterification reaction are as follows: the carboxylic acid groups on two lauric acid molecules were first dehydrated to yield a longer chain anhydride under heating conditions [36] (step 2a). The reactive anhydride subsequently reacted with hydroxyl groups on the NSMs to form an ester linkage [37] (step 2b), resulting in the successful anchoring of the lauric acid layer on the NSM substrate. Owing to the oleophilic groups and hydrophobic active sites of the lauric acid layer, LA-NSM can provide more superior sites for higher loading of DEL molecules (step 3).

Predicting from their structure, the as-prepared LA-NSM with a denser hydrophobic lauric acid coating could be very valuable and notable for the development of biodegradable superabsorbent composites for water holding and sustained release of fertilizers in potential agriculture applications. First, the NSM particles have an outstanding adsorption ability for DEL molecules through a strong hydrogen bond interaction due to their plentiful long-chain alkyls and nonpolar hydrocarbon groups [38] arising from the phospholipid monolayers, membrane proteins, and glycoproteins in the oil-body membranes. What is more, the NSM substrates preserve lots of inherent pores in the oil body after oil extraction [39]. Just like a mini warehouse, these inner pores of the NSM matrix could efficiently improve the loading of the DEL pesticide, and the semi-permeable property of tiny organelles in the oil body allows the loaded DEL molecules to slowly release into the environment. Second, the lauric acid molecules used as modifiers are natural and environmentally friendly. They offer a large number of active sites (long-chain alkyls and nonpolar hydrocarbon groups) for binding DEL molecules, which significantly improves the loading performance of the LA-NSM composite. Concurrently, the lauric acid layer was densely anchored on the NSM surface, which resembled a diffusion barrier to weaken the unexpected leakage of the agricultural insecticide, protect the insecticide loaded on the LA-NSM from burst release, and regulate the release behavior to a sustainable release. From these points of view, this intriguing and economical strategy opens up a suitable route to prepare a novel insecticide-loading system with an improved loading capacity and a sustainable release behavior by using the abundance, biodegradability, and renewability traits of the by-products of *Nitraria* seeds.



SCHEME 1: The formation mechanism of LA-NSM and controlled release of DEL-loaded LA-NSM.

To verify the successful modification of NSMs, FT-IR was employed to monitor the chemical bond transformation of parallel NSMs and LA-NSMs (Figure 1). In Figure 1(a), the absorption peaks observed at 2927 and 2854 cm^{-1} are due to the asymmetric and symmetric methylene groups in lauric acid [40, 41], respectively. The peaks at 1722, 1415, 1313, and 995 cm^{-1} are assigned to C=O stretching vibrations in carboxylic acid groups, CH_2 bending vibrations caused by C=O, C-O in carboxylic acid groups, and ethyl group in alkyl chain, respectively [42–44]. The absorption band near 3440 cm^{-1} in the spectrum of NSMs (Figure 1(b)) is related to the stretching vibrations of the hydroxyl group

[45, 46]: 2940 and 1535 cm^{-1} (C-H stretching vibrations in CH_2 and CH_3) [6, 47, 48], 1733 and 1649 cm^{-1} (C=O stretching vibrations in lignin), and 1242 cm^{-1} (ring vibrations in β -1, 4-glycosidic bonds) [49, 50], separately. These peaks belong to the characteristic absorption bands of the NSMs. After modifying NSM with lauric acid, significant changes occur in its FT-IR spectra (Figure 1(c)). For example, the peak at 3440 cm^{-1} shifts to 3300 cm^{-1} and exhibits a slight weaker intensity, proving the participation of hydroxyl groups of NSMs in the modification process. Furthermore, the intensive absorption bands appearing at 1655 and 1242 cm^{-1} were due to the C=O stretching

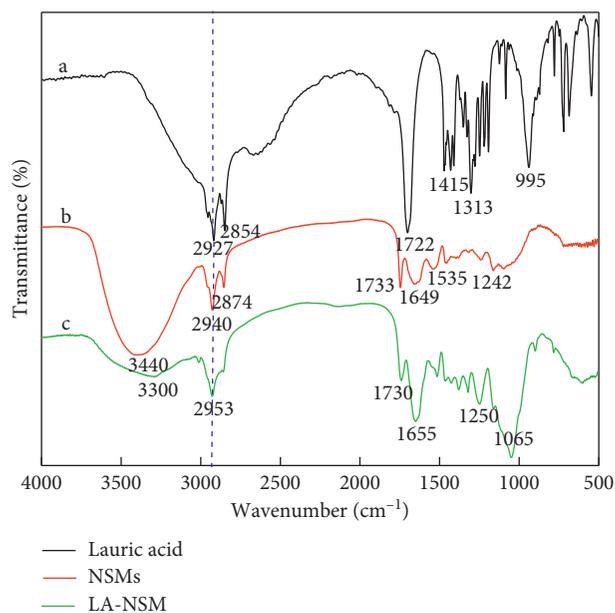


FIGURE 1: FT-IR spectra of lauric acid (a), NSMs (b), and LA-NSM (c).

vibrations in the ester group, further demonstrating the introduction of additional carbonyl groups onto the NSM surface during the esterification with lauric acid. Besides, a new absorption peak emerges at 1065 cm^{-1} , which corresponds to C–O–C vibrations, further verifying the successful modification of NSMs. On the whole, we conclude that the NSM surface has been successfully modified by lauric acid through reaction between hydroxyl and carboxyl groups, leading to the formation of a dense lauric acid coating outside the NSM surface.

SEM micrographs of the native NSM before and after modification with lauric acid (as illustrated in Figure 3) give further insight into NSM morphology and its modification during the treatment. In Figure 2(a), it was visible that there were lots of wrinkles and abundant pores with diverse diameters on the surface of the native NSM, which contributed to the relatively large specific surface area of the NSM substrate. Such surface morphology with a high surface area and irregular pores endowed the NSM material with abundant DEL-absorbing sites, and this was beneficial for pesticide molecules to penetrate into the internal oil-body structure. The inset image in the top right corner of Figure 2(a) is the optical photograph of the pure WH scaffold, exhibiting a distinct dark coffee-like skin. Furthermore, the light yellow LA-NSM powder in the inset image of Figure 2(b), in comparison with the dark green powder of the pure NSM substrate, provided assertive evidence that the LA layer had spontaneously deposited on the NSM scaffold, thereby leading to an alteration of appearance of color. Such differences of the color with and without modification further indicated that the $-\text{COOH}$ groups of lauric acid had reacted with free $-\text{OH}$ groups of the NSM matrix via esterification and that a denser lauric acid layer was formed on the surface to adsorb DEL molecules. Nevertheless, as seen from the surface morphology of LA-NSM, the porous structure and the rough surface of the

parent NSM scaffold have still been maintained after LA modification, which should favor the adsorption of DEL molecules and enhance their loading capacity [33].

The surface modification of NSMs with lauric acid inevitably also led to a change in the surface wettability. To investigate the surface wettability of LA-NSM, contact angle measurements (CAM) were further performed on the substrate-air interface at ambient temperature, and the results are presented in Figure 3. Figures 3(a) and 3(b) show the images of water droplet ($\sim 6\ \mu\text{L}$) on NSMs and LA-NSM surfaces captured at predetermined time intervals. The contact angles of the water droplets placed on the surfaces of NSMs and LA-NSM are $120 \pm 2^\circ$ and $142 \pm 2^\circ$, respectively. After 6 s, the water drop sinks rapidly into the NSMs. But, the water droplet on the LA-NSM surface still maintains a larger contact angle of $104 \pm 2^\circ$ after 60 s, definitely indicating the low energy and hydrophobicity of the LA-NSM surface [51]. In contrast, a drop of ethyl acetate ($\sim 6\ \mu\text{L}$) can quickly spread over the LA-NSM surface and permeate thoroughly in less than 0.5 s (Figure 3(c)) [52]. Meanwhile, the contact angle of ethyl acetate is measured to be 0° , indicating the excellent lipophilicity of LA-NSM. This phenomenon can be attributed to the smaller surface tension of ethyl acetate (26.29 mN/m) in comparison with water (72.75 mN/m). Theoretically, when the surface tension of the substrate lies between water and oil, hydrophobicity and oleophilicity can be achieved [53]. Consequently, the synthesized LA-NSM carriers modified with lauric acid hold a highly hydrophobic and oleophilic property.

The esterification degree (DE) was the percentage of the reacted carboxyl groups relative to the total initial carboxyl groups of lauric acid, which can be determined by a titration method. We have ascertained that the loading of LA-NSM for DEL could be accurately controlled by the esterification degree (DE) between the hydroxyl groups in NSMs and carboxyl groups in lauric acid. Specifically, the degree of esterification can be adjusted by changing the reaction temperature on purpose, and the experimental results are shown in Figure 4.

It can be seen from Figure 4 (left axis) that the DE increases with increasing the temperature from 90°C to 110°C . The cause lies in that a high temperature provides a stronger driving force to the modification and cross-linking between NSMs and lauric acid. Nevertheless, as the temperature goes higher than 110°C , the DE between the hydroxyl group on NSMs and carboxyl groups of lauric acid exhibits a decreasing trend. This can be ascribed to that too higher temperatures produce a crucial restraining effect on the exothermal esterification [54], resulting in a lower DE. Due to the difference of the DE value of LA-NSM prepared at various temperatures, the LA-NSM showed different loading performances for DEL. Thus, the DEL-loading capacity at various temperatures was investigated. As depicted in Figure 4 (right axis), an increasing number of DEL molecules were loaded into the LA-NSM carriers with the temperature increasing from 90°C to 110°C , but an abrupt decrease occurs when the synthesis temperature goes higher from 110°C to 140°C . This decrease can be attributed to the decreasing DE between the hydroxyl group of NSMs and carboxyl groups of lauric acid. Considering its exothermic feature, esterification reaction can be promoted by increasing the reaction

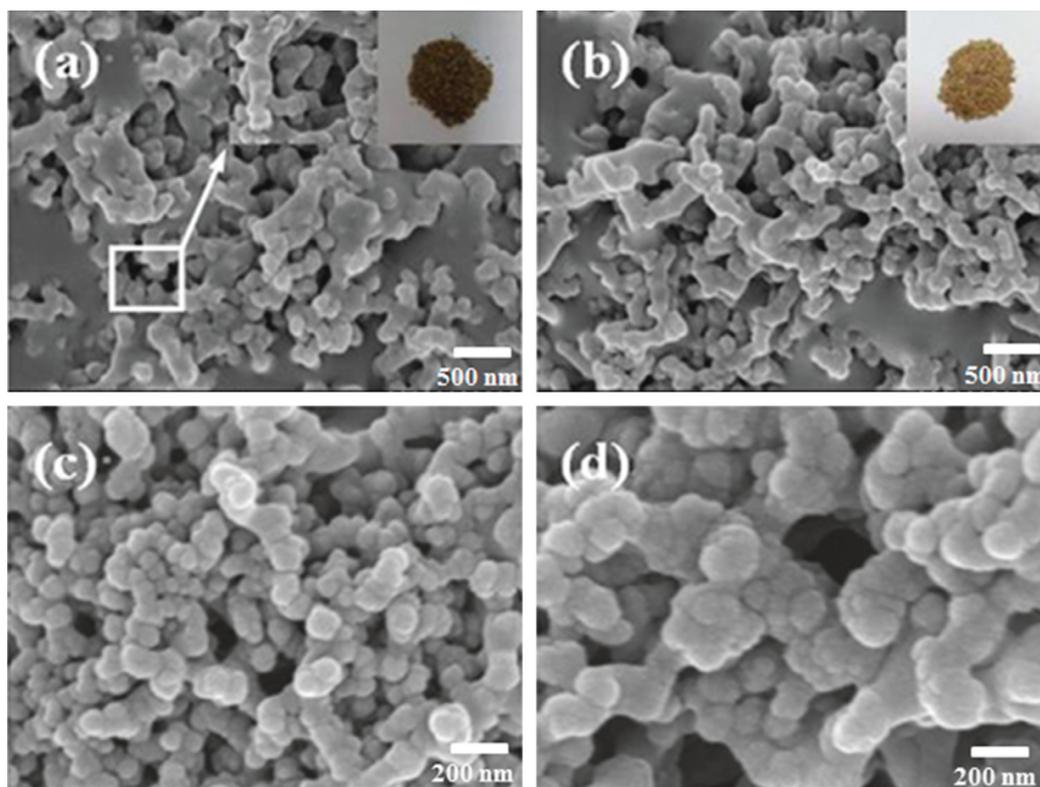


FIGURE 2: SEM images of NSM (a) and LA-NSM (b-d).

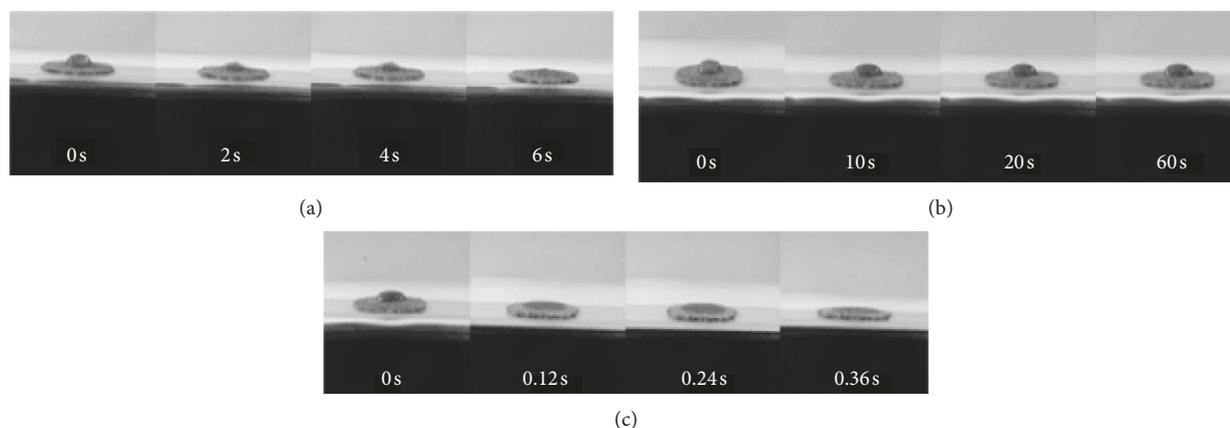


FIGURE 3: The images of a water droplet placed on NSMs (a) and water drop (b) and ethyl acetate (c) on LA-NSM.

temperature. But, too high temperatures may exert an intense restraining effect on the esterification, resulting in a lower degree of esterification [55]. Correspondingly, the loading amount of LA-NSM for DEL decreases.

3.2. Controlled Release Performance of the DEL Pesticide. DEL is one of the most widely used pesticides in agriculture. Unfortunately, approximately only 30–60% of DEL pesticides can be absorbed into plant bodies by spraying on

the emblem surface or mixing with soil [22]. A vast majority of DEL molecules evaporate into atmosphere and get into groundwater and other botanic interiors. Therefore, to find an environmental-friendly and safe usage approach is extremely urgent for reducing the risk of DEL pesticide residues. Thus, the controlled release of DEL was proposed in the succeeding section. It is believed that such tactics through a controlled release approach not only can alleviate the adverse effects of DEL residues on the environment strongly but also can promote the assimilation of DEL

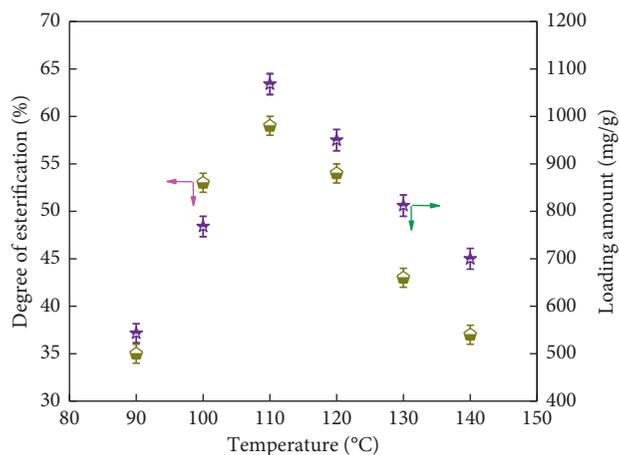


FIGURE 4: The effect of temperature on degree of esterification and loading amount of DEL.

pesticides by plants effectively [8, 9]. More importantly, the release behavior of DEL pesticides can be controlled by adjusting the environmental factors. Typically, the influence of pH, temperature, and soil humidity on controlled release of LA-NSM@DEL composites was evaluated.

3.2.1. pH-Dependent DEL Release. For pesticide delivery systems, the level of acidity or alkalinity of soil, which could have an impact on the degree of speciation of pesticide carriers, is one of the most significant factors influencing the whole release process. Thus, the effects of soil pH on the release behavior of NSMs and LA-NSM carriers were studied, as shown in Figure 5.

As seen in Figure 5, for NSMs without LA modification, an obvious burst release phenomenon was observed, and more than 80% of DEL diffuses quickly into the surrounding medium within 24 h. In contrast, the release amount of DEL from the LA-NSM@DEL was less than 12% within the same time under the same condition. The different release behaviors could be ascribed to the hydrophobic groups and diffusion barrier formed by lauric acid on the surface of LA-NSM particles. The intensive lauric acid layer could efficiently set up a barrier on the pathway of DEL diffusion from inside the LA-NSM@DEL to the soil, which could effectively reduce the diffusion rate and protect DEL molecules from unexpected leakage or burst release. Moreover, the release of DEL could be dramatically increased by adjusting pH values. For example, changing the acidification of soils from pH 8.5 to pH 6.0 and 3.8 gave rise to an increased release for DEL to 37.5% and 85.2%, respectively. The variation may be attributed to the degree of esterification on the LA-NSM surface. In theory, most ester groups fixed on the structure of LA-NSM carriers could combine with hydrogen ions (H^+) in strong acidic media ($3 < pH < 6$) to form hydrophilic carboxyl groups ($-COOH$) [56], decreasing the oleophilic and hydrophobic action. Thus, the attraction between the LA-NSM and DEL molecules would be weakened [15], strongly facilitating the DEL molecules to quickly diffuse into the surrounding medium. When the pH was higher ($pH > 6$), the carboxyl groups were deprotonated under

alkaline conditions and a limited amount of DEL molecules was released from the LA-NSM composites. The higher the pH value of the incubation medium, the higher the number of carboxyl groups which were deprotonated, but the strong hydrogen bonds between the LA-NSM and DEL molecules would dominate the release efficiency, which largely restricted the release of DEL molecules into the external media. Therefore, the LA-NSM composites gave a major push to sustained release due to the pH-responsive property of carbonyl and ester groups [56], and the release behavior could be easily managed via controlling the environment pH values.

3.3. Temperature-Dependent DEL Release. The release profiles of DEL were exploited at various temperatures ($10^\circ C$, $20^\circ C$, and $30^\circ C$) to evaluate the temperature stimuli responsiveness of the pesticide-loaded carrier. As we can see from Figure 6, the curves for the NSM@DEL without LA modification exhibited a classical cumulative release mode consisting of three stages, including an initial burst release (more than 77.4% at $10^\circ C$) followed by a slow release and a plateau in the range of temperature from $20^\circ C$ to $30^\circ C$. In comparison, the DEL release from LA-NSM@DEL is dependent on the temperature of the surrounding environment. The release rate of DEL initially increased from $\sim 13.5\%$ at $10^\circ C$ to $\sim 40\%$ at $20^\circ C$ and then, a further increase in temperature from $20^\circ C$ to $30^\circ C$ caused a sharp increase in DEL release efficiency. This suggests that the DEL escape from LA-NSM@DEL is favored at higher temperatures within the appropriate temperature range and the release process is endothermic in nature. The causes of temperature-dependent release behavior lied in that, at lower temperatures, kinetic energy of the solid-liquid interface was relatively low and DEL molecules could not get enough driving force to quickly escape from the LA-NSM@DEL carriers, leading to a mild release of DEL. Also, the superoleophilic surface of LA-NSM acted as a positive diffusion barrier and suppressed the diffusion of DEL into the external medium. As the temperature increased, the mobility of DEL molecules is significantly enhanced and more energy was imparted into the system. Thus, the link between the DEL molecules and the hydrophobic groups in the LA-NSM composites was easy to break at higher temperatures, facilitating the DEL molecules to quickly diffuse into the surrounding medium [57]. It should be noted that the slow-release efficiency cannot reach 100% since some DEL molecules might be trapped in the pores of LA-NSM, and these remaining pesticides will be fully released with the continuous degradation of NSM matrices.

3.3.1. Soil Humidity-Dependent DEL Release. In addition to the temperature-sensitive property, the releasing capability of LA-NSM@DEL was also dependent on the soil humidity. To further confirm its soil humidity-sensitive property to trigger the DEL release, LA-NSM@DEL was immersed into soils of different humidity, and the results are depicted in Figure 7.

As can be perceived, at the initial stage, the releasing efficiency of NSMs@DEL presented a dramatic increase and up to 57.3% within 24 h, while the amount of DEL from LA-NSM was essentially negligible ($\sim 10\%$ within 24 h). The reason

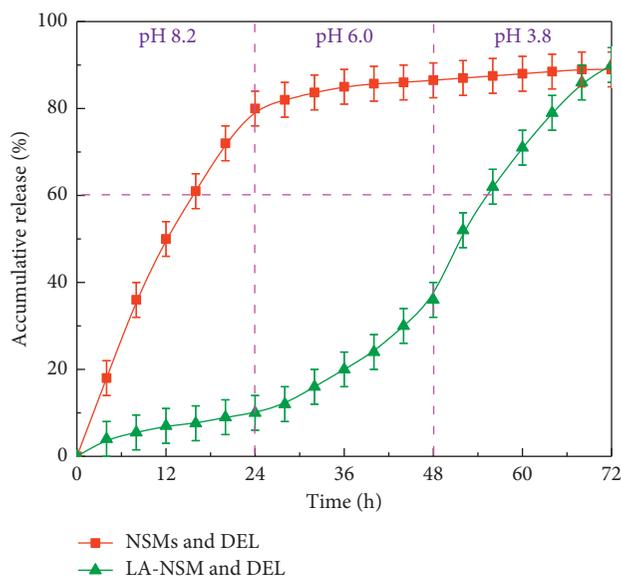


FIGURE 5: DEL-release profiles from LA-NSM and NSMs at different pH values in soils.

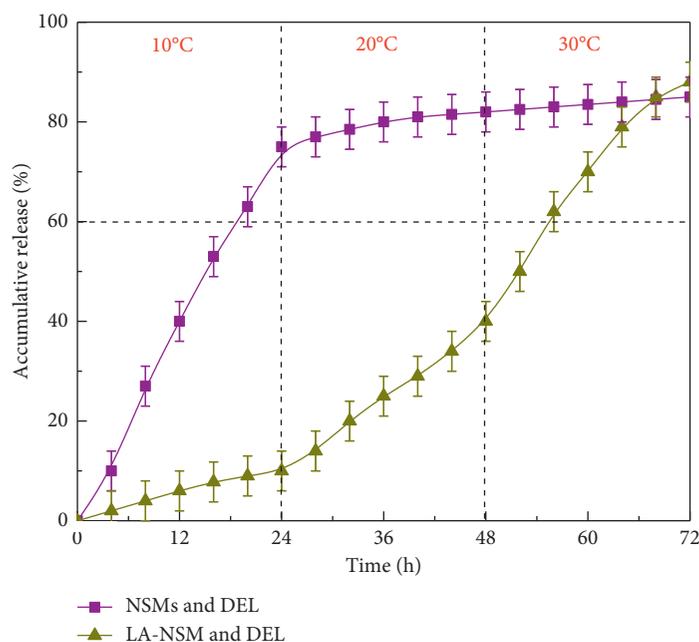


FIGURE 6: DEL release profiles from LA-NSM and NSMs at different temperatures in soils.

for this phenomenon was that the superhydrophobic surface on the LA-NSM carrier can indeed act as a diffusion barrier during the molecular diffusion between the LA-NSM domains and the soil environment. The superhydrophobic barriers will separate the internal domain of LA-NSM and the external soil environment, terminating transport of most of the molecules across the boundaries of the LA-NSM and thus significantly suppressing the diffusion rate of the DEL molecules. Nevertheless, NSMs would fail in preventing DEL molecules' diffusion at the beginning because of the weaker hydrophobicity of pristine-NSM surfaces, leading to a burst increase of releasing efficiency, up to 57.3% within 24 h. With the decrease of humidity, the amount of water molecules in the soil

decreased, which could enhance the difference of osmotic pressure between the carrier interior and surrounding media, consequently expediting the release of DEL from LA-NSM. In contrast, there was a slight increase for NSMs@DEL, and it was attributed to the decrease of DEL entrapped inside the NSMs. It could be inferred hereby that the LA-NSM could be a valuable pesticide manager to efficaciously slow down the release of the pesticide into soil for plants and avoid excessive pesticide consumption in agriculture application.

3.3.2. Release Kinetics of DEL Pesticides through LA-NSM. Figure 8 shows the release profiles of DEL from LA-NSM@DEL with different esterification temperatures from 90°C to

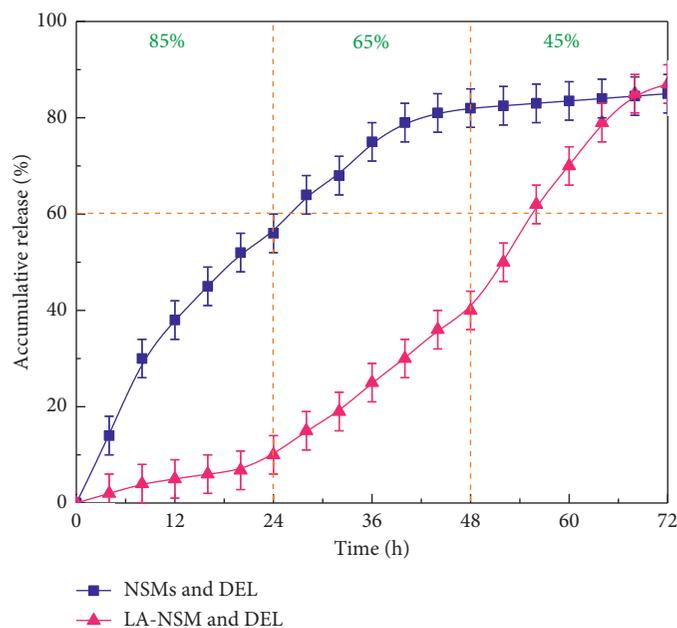


FIGURE 7: DEL release profiles from LA-NSM and NSMs at different humidity in soils.

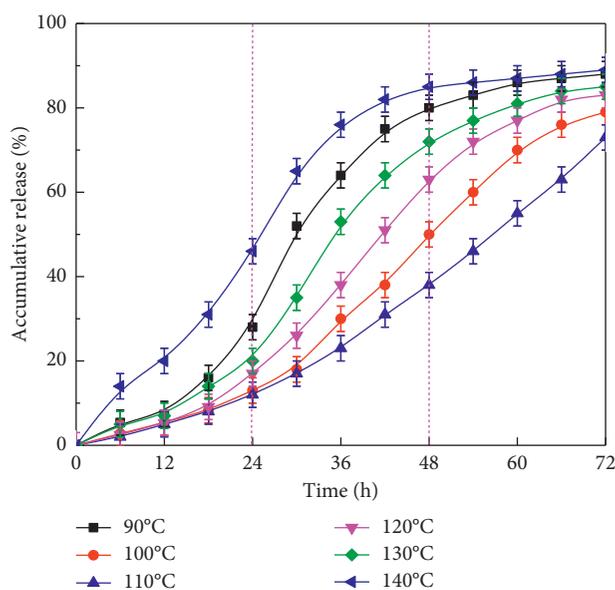


FIGURE 8: Release kinetic curves of LA-NSM@DEL with different esterification temperatures.

140°C. As seen in the picture, in all cases, there were no significant differences in the release tendency of DEL. At the beginning phase, the release efficiency increases gradually and then quickly after 24 h. This phenomenon could be ascribed to the esterification degree of LA-NSM. At lower and higher temperatures, the degree of esterification between hydroxyl functional groups on NSMs and carboxyl groups in lauric acid was lower, which could reduce loading active sites for binding DEL molecules via π - π stacking and electrostatic attraction, allowing DEL molecules to separate from LA-NSM@DEL. Nevertheless, at an excellent degree of esterification (\sim 110°C), only a slow release rate of DEL was observed from the LA-NSM@DEL. The sluggish release

capacity may be due to maximization of the degree of esterification, strengthening the attraction between the DEL molecules and LA-NSM. With time prolonging, there were less DEL molecules entrapped inside the LA-NSM, resulting in a slight increase of DEL release.

Data obtained from the release studies were calculated by the first-order and Higuchi models [58, 59], and the corresponding parameter values are listed in Table 1. From Figure 9 and the obtained correlation coefficients (R_2) in Table 1, it is evident that the release of DEL from LA-NSM@DEL composites could be better described by the Higuchi model than the first-order model. It signified that the DEL release from LA-NSM@DEL was controlled by a relatively strong physical

TABLE 1: DEL-releasing coefficients calculated with the two models.

	Temperature (°C)	Equations		R^2	
		First order	Higuchi	First order	Higuchi
LA-NSM@DEL	90	$y = -0.058x + 5.072$	$y = 1.22x - 0.358$	0.958	0.981
	100	$y = -0.0295x + 4.87$	$y = 1.23x - 9.769$	0.883	0.988
	110	$y = -0.0205x + 4.75$	$y = 1.03x - 8.329$	0.858	0.992
	120	$y = -0.0383x + 4.97$	$y = 1.36x - 8.601$	0.913	0.984
	130	$y = -0.0442x + 4.96$	$y = 1.39x - 4.285$	0.944	0.997
	140	$y = -0.0653x + 4.94$	$y = 1.31x - 11.945$	0.975	0.987

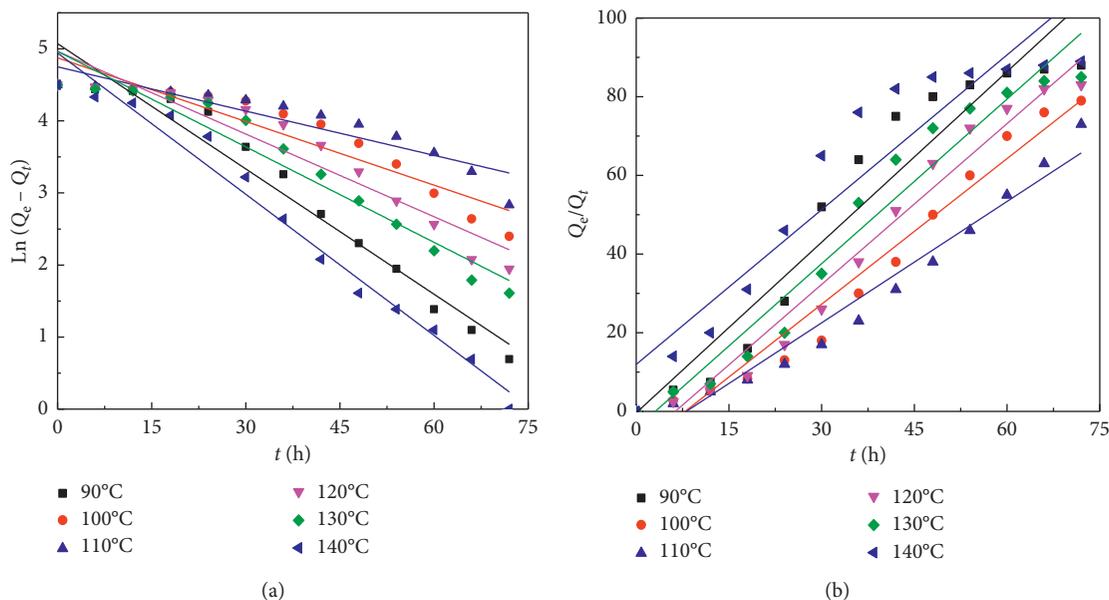


FIGURE 9: Release profiles of LA-NSM@DEL with different esterification temperatures: (a) first-order model and (b) Higuchi model.

process instead of a common chemical one. Also, the model revealed the release boundaries of LA-NSM@DEL carriers moved inward as the DEL was gradually released into the surrounding medium [60]. In other words, the release process of LA-NSM@DEL had a “moving boundary”. Moreover, the regression of Q_t/Q_e versus $t_{1/2}$ for the intraparticle diffusion model is found to be linear, and the linear plots do not pass through the origin point (Figure 9(b)). This phenomenon demonstrated that the pore diffusion was also a rate-controlling step during the pesticide-releasing process.

4. Conclusions

In summary, an environmentally friendly LA-NSM carrier was successfully prepared through modifying waste NSMs with lauric acid. FT-IR, SEM, and CAM analyses confirmed the reaction between hydroxyl groups of NSMs and carboxyl groups of lauric acid. The loading experimental results indicate that the equilibrium loading capacity of DEL into the LA-NSM carrier can reach about 1068 mg/g. The pH of soil, environmental temperature, and soil humidity have an obvious influence on the releasing property of LA-NSM@DEL. Moreover, the release process was fitted well to the Higuchi model. Of particular interest regarding this technology that

deserves to be mentioned is that the present route not only makes good use of natural waste resources but also can significantly address and reduce multiple issues created by pesticides, in view of their handy, convenient, and inexpensive fabrication method.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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