Structure Regulation of Bentonite-Alginate Nanocomposites for Controlled Release of Imidacloprid

Haiyan Zhang, Yunsheng Shi, Xiafan Xu, Min Zhang, and Lin Ma*

ABSTRACT: To reveal the structure and release properties of bentonite-alginate nanocomposites, bentonite of different amounts was incorporated into alginate by the sol–gel route. The structure of the composites was characterized by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, and thermogravimetric analysis and related to the swelling property of the matrix and the release of imidacloprid. Bentonite was subject to exfoliation into nanosheetlets and combined into the polymeric network within alginate hydrogel, exhibiting profound effects on the structure features and release properties of the composites. Bentonite was of good compatibility with alginate due to the hydrogen bonding and the electrostatic attraction between them. The polymer chains were found to intercalate into the interlayer gallery of the clay. The high specific area of the nanoplatelets of bentonite benefited the intimate contact with alginate and reduced the permeability of the composites. However, in the composites with clay content of more than 10%, the polymer was insufficient to accommodate the silicate sheets completely. The aggregation of the platelets destroyed the structure integrity of the composites, facilitating the diffusion of the pesticide. The release of imidacloprid was greatly retarded by incorporating into bentonite-alginate composites and dominated by Fickian diffusion depending on the permeability of the matrix. The time taken for 50% of the active ingredient to be released, $T_{50}$, first increased and then decreased with increasing clay content in the composites, reaching a maximum around a weight percentage of 10%, at which the $T_{50}$ value for imidacloprid release was about 2.5 times that for the release from pure alginate formulation.

1. INTRODUCTION

The use of controlled release formulations (CRFs) is one of the best strategies to reduce the use and the impact of pesticides on the environment. To date, many types of CRFs of pesticides have been proposed, among which dispersion or dissolution of the active ingredient into the polymeric matrix is one of the most important technologies. Natural polymers such as starch, neem, cellulose, alginate, and their derivatives have been used as matrices for CRF due to their biocompatibility, biodegradability, and low cost.\(^1\)\(^{-5}\) Alginate, a water-soluble polysaccharide that is readily cross-linked in solutions by bivalent metal cations such as Ca\(^{2+}\) and Mg\(^{2+}\) to produce hydrogel, is widely used as a vehicle for controlled release of drugs and agrochemicals.\(^1\)\(^{-3}\),\(^6\)\(^{-9}\) However, the poor mechanical strength and extensive water uptake property resulted in uncontrolled and unpredictable release behavior of the active ingredients. Several methodologies have been established to improve the intermolecular interaction by increasing their cross-linking within the hydrogel structure through physical blending, interpenetrating networks, and incorporation of nanofillers.\(^1\)\(^{-3}\)

The combination of clay minerals and polymers at the nanometric level is an attractive method to develop nano-composites, providing distinct properties that are inherent to the two components.\(^10\) Bentonite, a natural silicate mineral containing montmorillonite (MMT) as a major constituent, is characterized by its lamellar structure and subject to exfoliation into nanoplatelets in an aqueous environment due to the strong hydration of the sorbed cations in the interlayer. Many works revealed that the use of MMT in hydrogel matrices induced higher mechanical and thermal properties of resultant nanocomposites and promoted drug encapsulation efficiency and sustained release properties when used as drug carriers.\(^1\)\(^{-3}\),\(^10\)\(^{-11}\) A recent study illustrated that MMT had profound effects on the structure and release property of the hydrogel matrix. The combination of MMT with urea/poly(ethylene oxide) (UPEO) generally resulted in an decreased water uptake of the composite and release rate of
sodium diclofenac. However, the water uptake of the composite and the release rate of sodium diclofenac increased with increasing MMT weight percentage from 1 to 20%.\textsuperscript{10}

In our previous work, organobentonites with quaternary ammonium surfactants were used as modifying agents in the alginate-based CRF to provide an effective delay of the release of imidacloprid \([1\text{-}(6\text{-chloro-3-pyridylmethyl})\text{-}N\text{-}\text{nitro-imidazolidin-2-ylideneamine}]\), a typical member of neonicotinoids that has been widely used as an agricultural insecticide. The results also showed that the combination of bentonite (weight percentage of 50\%) increased the release of imidacloprid from alginate beads.\textsuperscript{12} A further study from our laboratory indicated that the release of imidacloprid from bentonite-alginate composite hydrogel could be reduced by a small quantity of bentonite, similar to the release of sodium diclofenac from the MMT-UPEO composite,\textsuperscript{10} suggesting a possibility of structure regulation of the bentonite-alginate composite for controlled release. Unfortunately, the structure features of the bentonite-alginate composite and its effects on the release properties remained unclear. In this work, bentonite-alginate composites with different clay loading were prepared and used as carriers for imidacloprid. The structure of the composites was characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermogravimetric (TG) analysis, and the swelling property was investigated. The results were utilized to reveal the effects of bentonite loading on the release behavior of imidacloprid from the composite as well as its mechanism.

### 2. RESULTS AND DISCUSSION

#### 2.1. Preparation of Bentonite-Alginate Composites

Bentonite-alginate composite hydrogel beads containing different amounts of bentonite were prepared by cross-linking with Ca\(^{2+}\). Characteristics of the composite beads with and without imidacloprid are presented in Table 1. Typical photographs of imidacloprid-loaded composite beads of different clay contents are shown in Figure 1. The beads obtained were generally spherical in shape and the size varied in the range from 1.28 to 1.48 mm for the composites without imidacloprid. The incorporation of the pesticide led to a slight increase in the size of the beads, ranging from 1.56 to 1.76 mm, maybe due to the enhanced viscosity of the mixture. Owing to the water solubility of imidacloprid, the encapsulation efficiency of the pesticide in the composite beads was low and the content was between 34.3 and 41.7 mg g\(^{-1}\).

#### 2.2. FTIR

The FTIR spectra of bentonite-alginate and imidacloprid-bentonite-alginate composites are presented in Figure 2. Alginate was characterized by a strong asymmetric peak at 10069

### Table 1. Formulation and Characteristics of Bentonite-Alginate Composite Beads with and without Imidacloprid

| formulation | imidacloprid percentage (%) | alginate percentage (%) | bentonite percentage (%) | water percentage (%) | imidacloprid content (mg g\(^{-1}\)) | average diameter (mm) |
|-------------|-----------------------------|-------------------------|--------------------------|----------------------|--------------------------------------|-----------------------|
| A           | 2.00                        | 0                       | 98.0                     | 1.28 ± 0.03          |                                      |                       |
| AB\(_{2.5}\) | 1.95                        | 0.05                    | 98.0                     | 1.36 ± 0.02          |                                      |                       |
| AB\(_{5}\)  | 1.90                        | 0.10                    | 98.0                     | 1.32 ± 0.04          |                                      |                       |
| AB\(_{10}\) | 1.80                       | 0.20                    | 98.0                     | 1.41 ± 0.01          |                                      |                       |
| AB\(_{20}\) | 1.60                       | 0.40                    | 98.0                     | 1.35 ± 0.02          |                                      |                       |
| AB\(_{30}\) | 1.40                       | 0.60                    | 98.0                     | 1.48 ± 0.02          |                                      |                       |
| IA          | 0.20                       | 2.00                    | 0                       | 97.8                 | 34.3 ± 1.5                           | 1.66 ± 0.05           |
| IAB\(_{2.5}\)| 0.20                       | 1.95                    | 0.05                    | 97.8                 | 41.7 ± 0.8                           | 1.56 ± 0.01           |
| IAB\(_{5}\) | 0.20                       | 1.90                    | 0.10                    | 97.8                 | 37.3 ± 1.0                           | 1.72 ± 0.03           |
| IAB\(_{10}\)| 0.20                       | 1.80                    | 0.20                    | 97.8                 | 43.7 ± 1.3                           | 1.61 ± 0.02           |
| IAB\(_{20}\)| 0.20                       | 1.60                    | 0.40                    | 97.8                 | 39.7 ± 1.6                           | 1.76 ± 0.02           |
| IAB\(_{30}\)| 0.20                       | 1.40                    | 0.60                    | 97.8                 | 37.8 ± 2.2                           | 1.58 ± 0.03           |

Figure 1. Typical photographs of imidacloprid-loaded bentonite-alginate composite beads (A–C) before and (a–c) after drying. Clay content: (A, a) 0\%, (B, b) 5\%, and (C, c) 20\%.
The addition of bentonite had little in-
crease in the intensity of the bending (1633 cm−1) of bentonite, which was con-
tracted with the stretching vibration of the structural −OH (Si−OH and Al−OH) at 3630 cm−1.1,2 The addition of bentonite had little influence on the peak position of the characteristic absorption of alginate. However, a decrease in the intensity of the stretching of carboxylate (1600 and 1430 cm−1) was observed, accompanying an increase in the intensity of −CH2 bending around 1028 cm−1, which was overlapped with Si−O stretching of bentonite. The overlapping of the stretching of structural −OH (3626 cm−1) of bentonite, stretching (3406 cm−1), and bending (1633 cm−1) of water adsorbed with the stretching of −OH (3365 cm−1) and carboxylate (1600 cm−1) of alginate was also observed. To determine the possible interaction between bentonite and alginate, the relative intensity of the absorption at 3626, 3406, and 1633 cm−1 was calculated for bentonite-alginate composites based on the absorption of carboxylate at 1600 cm−1, at which the absorption of bentonite was fairly weak (Figure 2). Without considering the interaction between the two components, the addition of bentonite would result in an increase in the relative intensity of the absorption of the composites at 3626, 3406, and 1633 cm−1. However, the relative intensity exhibited a “Z”-type behavior with increasing bentonite content in the composites (Figure 3). The drop of the relative intensity of the absorption of the composites with increasing bentonite content from 5 to 20% indicated a possible hydrogen bond between the carbonyl groups of alginate and hydroxyl groups of bentonite and that between hydroxyl groups of alginate and SiO4 geometry of bentonite, leading to a reduction of water adsorbed on the surface of bentonite. The results were quite consistent with the study by Abdollahi et al.13

For all formulations with imidacloprid, the characteristic vibration of N−N stretching was clearly observed around 1558 cm−1. The relatively weak absorption around 3347 and 1220 cm−1 was assigned to the stretching and bending vibration of N−H.14 However, no significant alteration of the characteristic vibration of imidacloprid was found when incorporating into the bentonite-alginate composite due to the overlapping with stretching vibration of carboxylate and −OH of alginate (Figure 2B).

2.3. XRD. The influence of bentonite loading on the structural characteristic of bentonite-alginate composites was investigated by XRD (Figure 4A). The XRD pattern of bentonite was characterized by the (001), (003), and (110) diffractions around 2θ = 5.9°, 17.6°, and 19.9°, respectively. The basal spacing d001, estimated by the Bragg equation, was 1.49 nm, agreeing well with the typical value of Ca2+-bentonite in the literature.15 Due to the presence of clay and nonclay impurities, several weak diffractions were observed around 8.7° (illite), 12.4° (kaolinite), 20.9° (quartz), and 26.7° (dolomite).16,17 When incorporating into alginate hydrogel, the (001) peak of bentonite slightly shifted toward a lower angle. The 2θ value for the (001) peak of bentonite in composite AB5 was around 5.6° (corresponding d001 = 1.59 nm), indicating that the polymer chains of alginate had intercalated into the interlayer gallery and led to an increase in the interlayer spacing of bentonite. An approximation of the platelets would be expected due to the decrease of alginic. As shown in Figure 4A, the diffraction of the (001) plane of bentonite slightly increased with increasing bentonite content in the composites. The 2θ value for AB30 was almost the same as that of pure bentonite, suggesting a possible aggregation of the platelets of bentonite, which was confirmed by SEM analysis in the following section.

The addition of bentonite had an impact on the interaction among the polymer chains of alginate within the hydrogel structure. Alginate presented a broad diffraction from 10° to

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**Figure 2.** FTIR spectra of (A) bentonite-alginate composites and (B) imidacloprid-loaded composites.

**Figure 3.** Relative intensity of IR absorption of bentonite-alginate composites against the weight percentage of bentonite.

![FTIR spectra](https://dx.doi.org/10.1021/acsomega.0c00610)
20°, indicating an amorphous structure. The diffraction patterns of the composites showed an antagonistic effect with increasing bentonite loading. The decrease in the diffraction intensity of alginate in the composites with increasing bentonite loading up to 10% suggested a possible interaction between alginate and bentonite, which interfered with the cross-linking between the polymer chains by Ca2+.

XRD patterns of imidacloprid-loaded bentonite-alginate composites were also recorded to reveal the possible influence of imidacloprid on the structure of the composites (Figure 4B). Crystalline imidacloprid presented narrow and well-defined diffraction peaks at 13.9°, 15.12°, 16.5°, 18.54°, 19.0°, and 22.18°. However, no diffraction features of imidacloprid were observed in the XRD profiles of imidacloprid-loaded composites, suggesting that the pesticide was dispersed in the composites in molecular form, maybe due to the electrostatic attraction of the positively charged imidacloprid with the negatively charged surface of the clay and the carboxyl group of alginate. In the composites, the carboxyl groups in l-guluronic acid units of alginate interacted with Ca2+ to form a cross-linked network. Thus, competition binding with the carboxyl groups by imidacloprid would reduce the cross-linking between the polymer chains, leading to a decrease in diffraction intensity of alginate around 15°, as compared with the composites without imidacloprid (Figure 4A).

2.4. SEM. One of the most important parameters affecting the release behavior of the drug is the surface of the carrier. SEM was used to reveal the influence of bentonite loading on the surface morphology of bentonite-alginate composites. No significant change in surface morphology of the composites was observed upon the incorporation of imidacloprid. Thus, only the results for bentonite-alginate composites were presented (Figure 5). Pure alginate hydrogel displayed a smooth and homogeneous surface, showing an almost amorphous structure, in accordance with XRD analysis. The
addition of bentonite had little influence on the surface integrity of the composites at a loading level less than the weight percentage of 10%. However, the rougher surface of the composite verified the presence of clay platelets. Particles and cracks were clearly observed on the surface of the composites and the size increased with increasing clay content above 10%, suggesting that alginate was insufficient to accommodate the clay platelets. The aggregation of the clay platelets weakened the cross-linking within the polymeric network and destroyed the integrity of the matrix, which was consistent with XRD analysis (Figure 4).

2.5. TG and DTG. TG and DTG curves of bentonite-alginate composites are presented in Figure 6. In general, the thermal decomposition of polysaccharides involved desorption of adsorbed water, dehydration, depolymerization, and finally the formation of polynuclear aromatic and graphitic carbon structures. In the present work, the mass loss in the temperature range between 40 and 160 °C corresponded to the removal of different kinds of water molecules depending on the interaction with the polysaccharides. The actual decomposition of alginate started from 171 °C and the maximum rate of mass loss appeared at 188 °C (Figure 6). Due to the high thermal stability of mineral clay, it was generally believed that the introduction of mineral clay into organic materials could improve their thermal stability. However, the decrease in thermal stability of poly(lactic acid), polyester, and starch was also found in nanocomposites with MMT, which was attributed to the interaction between the clay and polymer matrix. Singh et al. reported an increase in the initial decomposition temperature of alginate-neem composites induced by the addition of MMT and kaolinite at a weight percentage of 20−50%; however, they also observed a decrease in the thermal stability of alginate-starch composites at lower clay loading (weight percentage of 7−24%). Similar to the studies by Singh et al., a slight decrease in the initial decomposition temperature of alginate was observed in the composites with a small amount of bentonite up to a weight percentage of 10%, opposite to the behavior of the composite with higher clay loading (Figure 6). The results indicated that bentonite had antagonistic effects on the thermal stability of composites, which were related to the thermal stability of the clay and its interaction with alginate.

Figure 6 also shows the thermal profiles of nature bentonite. Bentonite presented a weight loss of 6% after exposure, which can be ascribed to the desorption of physically adsorbed water. The maximum rate of water removal from bentonite occurred around 66 °C, much lower than that from alginate hydrogel (81 °C), indicating a lower affinity of bentonite toward water. However, the temperature of maximum rate of water removal from the composites first increased and then decreased with increasing bentonite content, which may be related to the structure change of the composite and the interaction between the two components. Bentonite is a silicate mineral with a lamellar structure, with Si−OH and Al−OH on the surface, which is negatively charged, arising from isomorphous substitutions of certain atoms in their structure for other atoms of different valence, and compensated by the adsorption of cations such as Na+, Ca2+, Mg2+, etc. Alginate is a polysaccharide consisting of D-mannuronic acid and L-guluronic acid units. The large quantity of hydroxyl and carboxyl groups facilitated the interaction with bentonite via hydrogen binding and electrostatic attraction. Moreover, the polymer chains of alginate intercalated into the interlayer galleries of bentonite. The high specific area of the nanoplatelets benefited the intimate contact with alginate and reduced the diffusion of water molecules in the composite. On the other hand, it should be noticed that the interaction with bentonite decreased the cross-linking within the hydrogel structure, as illustrated by XRD analysis (Figure 4). Meanwhile, the aggregation of platelets of bentonite and the disruption of the structure of the composites with high bentonite loading resulted in enhanced diffusion of water molecules through the interlayer space of bentonite and the defects in the composites (Figure 5).

2.6. Water Uptake. The kinetics of water uptake by bentonite-alginate composites are presented in Figure 7. A
slight decrease was observed after the initial water uptake in all of the cases. Such shrinkage was also observed for carboxymethylcellulose hydrogel cross-linked by Fe$^{3+}$, which was attributed to the particular core–shell structure of hydrogel beads fabricated by chemical cross-linking with multivalent cations. It was suggested that the cationic ions enriched in the shell might further penetrate into the core and more macromolecules were cross-linked to form a thicker shell layer, in which the irreversible network structure constrained their swelling.4

Water uptake by bentonite-alginate composites was totally a fast process, reaching equilibrium within 30 min. Maybe due to the lower affinity of bentonite toward water (as illustrated by thermal analysis in Figure 6) and the interaction between bentonite and the polymer, which hindered the water swelling process, water uptake by the composites decreased with increasing bentonite content up to 10%. However, a further increase of bentonite led to enhancement of water uptake, indicating the increased porosity of the composites, which was consistent with SEM analysis (Figure 5).

2.7. Release Studies. The cumulative release of imidacloprid from bentonite-alginate beads and the dissolution profile for the technical grade imidacloprid are shown in Figure 8. The data were fitted to the empirical equation proposed by Rigter and Peppas:28,29

$$\frac{M_t}{M_0} = kt^n$$

where $M_t/M_0$ is the fractional amount of active ingredient released at time $t$, $k$ is a characteristic constant of the system, and $n$ is the diffusional exponent to describe the kinetics and the release mechanism. The values of $k$ and $n$ were obtained by a nonlinear fit, from which the time taken for 50% of the active ingredient to be released, $T_{50}$, was calculated (Table 2). The technical grade imidacloprid was dissolved completely within 5 h and could not be fitted well to the Rigter–Peppas equation. The $T_{50}$ value for imidacloprid dissolution was then estimated by an interpolation method and found to be 0.71 h. The release of imidacloprid was retarded by incorporating into bentonite-alginate composites, of which the $T_{50}$ value was 1.7–4.1 times that for imidacloprid dissolution, depending on the clay loading in the formulations (Table 2).

It has been suggested that the exponent $n$ is characterized by the values of 0.5, 0.45, and 0.43, respectively, for the release from a slab, cylinder, and sphere swelling-controlled release system via the Fickian diffusion mechanism. In the case of non-Fickian release, a “case II transport” mechanism is proposed to be of $n$ values of 1.0, 0.89, and 0.85, respectively. Other values for $n$ indicate a combined mechanism of pure diffusion and a case II transport.28,29 The diffusional exponent $n$ for imidacloprid release from bentonite-alginate composites ranged from 0.29 to 0.39, indicating that the release was predominated by Fickian diffusion.

The release of pesticide from CRFs was usually understood from the adsorption capability and the permeability of the matrix. A higher adsorption capability and lower permeability of the matrix would result in a slower release.30,31 XRD and TG analysis indicated an interaction between alginate and imidacloprid (Figure 4B). A previous study also illustrated a weak adsorption capability of bentonite toward the pesticide.12 However, the $T_{50}$ value for imidacloprid release was found to increase first and then decrease with increasing bentonite loading in the composite. The combination of bentonite at a weight percentage of 10% provided the most efficient retention of the pesticide, of which the $T_{50}$ value was about 2.5 times that for the release from pure alginate beads (Table 2), suggesting a possible alteration of matrix permeability.

As illustrated in Figure 8, a decline in the release of imidacloprid over time was observed for all formulations, probably due to an increase in the distance where dissolved molecules had to diffuse as the depleted zone advanced to the center of the matrix. In diffusion-controlled matrix systems, this usually means that the release is proportional to the square root of time.12 The formulations of this research could be considered as spherical monolith systems containing solute molecules dispersed within the matrix phase, from which the release via Fickian diffusion could be described by the Higuchi equation33

8. The data were fitted to the empirical equation proposed by Rigter and Peppas:28,29

$$Q_t = \frac{Q_0}{1 + t^{1/n}}$$

The cumulative release of imidacloprid from bentonite-alginate composite beads in water.

Table 2. Parameters Obtained from the Rigter–Peppas Equation and Higuchi Equation for Imidacloprid Release from Bentonite-Alginate Composites

| sample | Rigter–Peppas | Higuchi |
|--------|---------------|---------|
|        | $K$ (h$^{-1}$) | $n$     | $R^2$ | $T_{50}$ (h) | $K_{H} \times 10^3$ (h$^{-1/2}$) | $P \times 10^5$ (h$^{-1}$-mm$^2$) | $R$ |
| control | 0.71 | | | | | | |
| IA | 47.7 ± 4.0 | 0.29 ± 0.04 | 0.951 | 1.18 | 1.30 ± 0.05 | 1.58 | 0.998 |
| IAB,5 | 43.2 ± 3.2 | 0.34 ± 0.04 | 0.971 | 1.55 | 1.14 ± 0.03 | 1.32 | 0.999 |
| IAB,10 | 41.8 ± 2.9 | 0.32 ± 0.03 | 0.971 | 1.75 | 1.02 ± 0.03 | 1.13 | 0.998 |
| IAB,20 | 32.9 ± 3.5 | 0.39 ± 0.05 | 0.957 | 2.93 | 0.93 ± 0.04 | 0.97 | 0.996 |
| IAB,20 | 38.2 ± 3.0 | 0.35 ± 0.04 | 0.970 | 2.15 | 0.99 ± 0.03 | 1.21 | 0.998 |
| IAB,10 | 45.3 ± 2.6 | 0.38 ± 0.04 | 0.980 | 1.30 | 1.33 ± 0.04 | 1.67 | 0.998 |

ACS Omega 2020, 5, 10068–10076
where \( M_t/M_0 \) is the fraction of the active ingredient released at time \( t \) and \( K_H \) is a constant depending on the radius of the sphere \( (r) \), the initial concentration of the active ingredient \( (C_0) \), and the permeability of the matrix \( (P) \)

\[
K_H = \left[ \frac{P}{(C_0 r^2)} \right]^{1/2}
\]

\( K_H \) values were obtained by a nonlinear fit using a least-square method and constant \( P \) was derived (Table 2). Right opposite to \( T_{50} \) values for imidacloprid release, the permeability of the composites toward the pesticide first decreased and then increased with increasing bentonite content, with a minimum at a weight percentage of about 10%. A further comparison showed that the bentonite loading had the same impact on the permeability and water uptake of the composites (Figure 7), indicating that the release of imidacloprid was controlled by the diffusion of the active ingredient and was dependent on the microstructure of the matrix. Good dispersion of the silicate platelets of bentonite in the polymeric network and the interaction with alginate played key roles in the sustained release from the composites, suggesting the feasibility of highly controllable release of pesticide by regulating the structure features of the bentonite-alginate composite.

3. CONCLUSIONS

Bentonite, a silicate mineral clay with a lamellar structure and of excellent swelling property, was subject to exfoliation into nanoparticles in an aqueous environment and combined into the polymeric network within alginate hydrogel prepared by the sol–gel route. A combinational study of FTIR, XRD, SEM, and TG analysis illustrated that bentonite was of good compatibility with alginate due to the hydrogen bonding and the electrostatic attraction between them. The polymer chains intercalated into the interlayer gallery of the clay. The high specific area of the nanoparticles of bentonite benefited the intimate contact with alginate and reduced the permeability of the composites. However, the interaction with bentonite decreased the cross-linking within the hydrogel structure. In the composites with clay content of more than 10%, the polymer was insufficient to accommodate the silicate sheets completely. The aggregation of the platelets destroyed the structure integrity of the composites, facilitating the diffusion of the pesticide.

The release of imidacloprid was greatly retarded by incorporating into the bentonite-alginate composite and predominated by the Fickian diffusion mechanism depending on the permeability of the matrix. The time taken for 50% of the active ingredient to be released, \( T_{50} \), first increased and then decreased with increasing clay loading in the composites. The composite with a weight percentage of clay of about 10% presented the most prominent efficiency to sustain the release of imidacloprid, of which the \( T_{50} \) value was about 2.5 times that for the control formulation without bentonite. The results from this work illustrated an efficient strategy to control the release of pesticide from polymer-based formulations by combining natural clay minerals, which was of significance to explore CRFs of pesticides to fulfill the requirement of agricultural practice.

4. MATERIALS AND METHODS

4.1. Materials. Ca-bentonite, with a cation exchange capacity of 0.82 mmol g\(^{-1}\), was obtained from Guangxi Ninning Minerals Co. (China). Analytical grade disodium ethylenediamine tetraacetic acid (EDTA) from Sinopharm Chemical Reagent Ltd. (China) and chemical pure sodium alginate (viscosity of \( \geq 2000 \) cps for a 2% solution at 25 °C) from Sigma Co. (USA) were used as received. Technical grade imidacloprid (96.3%, HPLC) was kindly supplied by Guangxi Tianyuan Biochemical Ltd. (China). Deionized water was used throughout the experiments.

4.2. Methods. 4.2.1. Preparation of Bentonite-Alginate Composites. Bentonite-alginate composites with and without imidacloprid were prepared following a common procedure. Different amounts of imidacloprid (I), sodium alginate (A), and bentonite (B) were added in 50 mL of water (formulations are shown in Table 1) and stirred slowly to form homogeneous mixtures. The mixtures were added dropwise using a 50 mL syringe (needle size, 1.2 mm) into 100 mL of CaCl\(_2\) solution (0.1 M) under constant stirring. The resulting beads were allowed to gel for 20 min, filtered, and then dried to constant weight at 45 °C. The products obtained were labeled as A and AB\(x\), for pure alginate hydrogel and the composites without imidacloprid, respectively, and IA and IAB\(x\), for those with imidacloprid, whereas \( x \) was the weight percentage of bentonite.

4.2.2. Dynamic Light Scattering for Diameter Measurement. The average diameter of bentonite-alginate composite beads was determined on a Malvern Mastersizer 3000 dynamic scattering spectrometer (U.K.), using water as dispersant. The measurement was performed at least three times.

4.2.3. FTIR. Homogeneous mixtures containing imidacloprid, sodium alginate, and bentonite were prepared following the procedure described in Section 4.2.1 and casted into Petri plates. A solution containing CaCl\(_2\) (0.1 M) was added carefully and kept for 20 min. Resulting hydrogel films were dried to constant weight at 45 °C. The FTIR spectra were recorded from 500 to 4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) on a PE Frontier FTIR spectrometer (USA) equipped with an ATR accessory.

4.2.4. XRD. XRD patterns of bentonite-alginate composite films with and without imidacloprid, prepared following the procedure described in Section 4.2.3, were obtained by a Rigaku SmartLab3KW diffractometer (Japan). The Ni-filtered Cu-K\(_{\alpha}\) radiation \((\lambda = 1.5405 \text{ Å})\) was used as an X-ray source. All scans were performed in the range of 2θ = 3°–30° at a speed of 10°·min\(^{-1}\), with a step size of 0.02°. The basal spacing of bentonite was calculated from the 2θ value of the (001) plane using the Bragg equation.

4.2.5. SEM. The surface morphology of bentonite-alginate composite films was examined using a PHENOM F16502 electronic scanning microscope (Netherlands). Prior to the performance, the samples were attached to metallic stubs and coated with gold for 20 s in a TRP450 magnetron sputtering coating system (SKY Technology Development Co., Ltd., CAS, China).

4.2.6. TG Analysis. Thermogravimetric analysis was carried out on a NETZSCH STA 449 F3 thermal analysis instrument (German). TG and DTG thermograms of bentonite-alginate composites were recorded from room temperature to 350 °C at a heat rate of 10 °C·min\(^{-1}\) under nitrogen flow.
4.2.7. Water Uptake. The measured amount of dry composite beads (about 0.4 g) was immersed in water and kept in a thermostatic bath at 25 ± 1 °C. The samples were removed at preset time intervals. After the excess water on the surface was blotted by using filter paper, the beads were weighted to obtain the water uptake. The test was carried out in duplicate.

4.2.8. Imidacloprid Content Determination. The measured amount of imidacloprid-loaded composite beads (ca. 0.1 g) was disintegrated in 10 mL of EDTA solution (100 g L⁻¹) and then extracted three times by 10 mL of methanol. The extract was collected and analyzed by HPLC to evaluate the actual content of imidacloprid in the products. The measurement was carried out in duplicate.

4.2.9. HPLC Analysis of Imidacloprid. The concentration of imidacloprid in the solutions was determined on a Shimadzu SPD-10A high-performance liquid chromatograph (Japan) equipped with a UV–vis detector set at 254 nm. The column was a Hypersil ODS column (250 mm × 4.6 mm, 5 μm). The mobile phase was a methanol–water mixture (90:10) at a flow rate of 1.0 mL min⁻¹. Solutions containing imidacloprid were passed through nylon filters of 0.22 μm in pore diameter before the performance.

4.2.10. Imidacloprid Release in Water. Accurately weighted composite beads containing about 4 mg of the active ingredient for each sample were added to 100 mL of water (ca. pH 6.5) in stopped conical flasks and kept at 25 ± 1 °C in an overhead shaker. At preset time intervals, aliquots of the 2 mL supernatant were removed and equivalent fresh water was added. The supernatant collected was analyzed by HPLC and the amount of the released active ingredient was calculated to obtain the cumulative release profile. Experiments were run in duplicates.

AUTHOR INFORMATION

Corresponding Author
Lin Ma — School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, P. R. China; Phone: +86-771-3233718; Email: malinzju@163.com; Fax: +86-0771-3233718

Authors
Haiyan Zhang — School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, P. R. China
Yunsheng Shi — School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, P. R. China
Xiafan Xu — School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, P. R. China
Min Zhang — School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c00610

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Scientific Research and Technology Development Program of Guangxi Province of China (no. 1898025-17).

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