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Preparation and characterization of controlled-release fertilizers coated with marine polysaccharide derivatives*

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Abstract Encapsulation of water-soluble nitrogen fertilizers by membranes can be used to control the release of nutrients to maximize the fertilization effect and reduce environmental pollution. In this research, we formulated a new double-coated controlled-release fertilizer (CRF) by using food-grade microcrystalline wax (MW) and marine polysaccharide derivatives (calcium alginate and chitosan-glutaraldehyde copolymer). The pellets of water-soluble nitrogen fertilizer were coated with the marine polysaccharide derivatives and MW. A convenient and eco-friendly method was used to prepare the CRF. Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) were used to characterize the morphology and composition of the products. The nitrogen-release properties were determined in water using UV-Vis spectrophotometry. The controlled-release properties of the fertilizer were improved dramatically after coating with MW and the marine polysaccharide derivatives. The results show that the double-coated CRFs can release nitrogen in a controlled manner, have excellent controlled-release features, and meet the European Standard for CRFs.

Keyword: marine polysaccharide; microcrystalline wax; double-coating; controlled-release; water-soluble fertilizer

Abbreviation: CA: calcium alginate; CGC: chitosan-glutaraldehyde copolymers; CRF: controlled-release fertilizer; DPF: derivative of polysaccharide coated fertilizer; FTIR: Fourier transform infrared spectroscopy; MDPF: microcrystalline wax derivative of polysaccharide coated fertilizer; MW: microcrystalline wax; MW-70: microcrystalline wax in freezing point of 70°C; MW-80: microcrystalline wax in freezing point of 80°C; MW70A: inner coat CGC prepared from 20 μL glutaraldehyde, outer coat MW-70; MW70B: inner coat CGC prepared from 30 μL glutaraldehyde, outer coat MW-70; MW70C: inner coat CGC prepared from 40 μL glutaraldehyde, outer coat MW-70; MW70D: inner coat CGC prepared from 50 μL glutaraldehyde, outer coat MW-70; MW80A: inner coat CGC prepared from 20 μL glutaraldehyde, outer coat MW-80; MW80B: inner coat CGC prepared from 30 μL glutaraldehyde, outer coat MW-80; MW80C: inner coat CGC prepared from 40 μL glutaraldehyde, outer coat MW-80; MW80D: inner coat CGC prepared from 50 μL glutaraldehyde, outer coat MW-80; MW70CA: inner coat CA, outer coat MW-70; MW80CA: inner coat CA, outer coat MW-80; MW70SA: inner coat SA, outer coat MW-70; MW80SA: inner coat SA, outer coat MW-80; SA: sodium alginate; SEM: scanning electron microscopy

1 INTRODUCTION

Fertilizers provide plants with nutrients for growth, including nitrogen, phosphorus, and potassium. However, traditional fertilization methods may produce high waste and have low efficiency. They

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** Corresponding author: pcli@qdio.ac.cn may even have adverse effects on the environment, such as nocuous gas emissions and water eutrophication (Shaviv and Mikkelsen, 1993). To increase efficiency, researchers have attempted to find solutions to increase the utilization of fertilizers and minimize environmental pollution (Chien et al., 2009).

Slow-release fertilizers provide a good solution (Mohammadi-Khoo et al., 2016), in which fertilizer components (nutrients) are released slowly to improve their utilization (Shaviv, 2001). The use of slow-release fertilizers can enhance efficiency and minimize environmental pollution. Moreover, the rate of release of a specific formulation can be controlled or programmed. A new-type of CRF has been developed, whereby a fertilizer is capsulated with a physical barrier to control the dissolution rate of the nutrients, of which water-soluble nitrogen fertilizer particles are encapsulated in hydrophobic membranes such as polymer coatings (Shavit et al., 1997; Shaviv, 2001; Azeem et al., 2014). According to the European Standard EN 13266 issued by the European Committee for Standardization, a fertilizer is commonly referred to as a slow- or controlled-release fertilizer if the following requirements are met: no more than 15% of the nutrients are released within 24 h, and no more than 75% of the nutrients are released within 28 days (European Standard EN 13266, 2001). Polymer-coated CRFs have shown promise for widespread use in agriculture. They can be designed to release nutrients in a well-controlled manner as a result of fast advances in polymer applications in recent years.

Polysaccharide-based compounds are a new category of environmentally safe materials because of their nontoxicity, biocompatibility, and biodegradability (Xing et al., 2009). Therefore, the potential applications of polysaccharides are very promising. Sodium alginate (SA) is a natural anionic polymer composed of different proportions of poly-β-1,4-D-mannuronic acid and α-1,4-L-guluronic acid joined by 1-4 linkages. The combined use of SA with other polymers for making special membranes has been explored recently in the fertilizer and pharmaceutical industries (Li et al., 2012). For example, by mixing SA aqueous solution with calcium chloride ($CaCl_2$) solution, cross-linked hydrogel beads are formed and can be used as a purely natural coater (Wang et al., 2012). Another feasible way is to entrap bacterial fertilizer into modified calcium alginate (CA) capsules (Liu et al., 2008).

Chitosan obtained through the hydrolysis of chitin is another natural substance common in crustacean (shrimp and crab) shells. Chitosan can be dissolved in an acidic aqueous solution, such as acetic acid, owing to the protonation of the amino group (Ravi Kumar, 2000; Melaj and Daraio, 2013), and shows great potential for the development of drug delivery systems because of its gelating and film-forming ability (Teixeira et al.,1990). However, chitosan as a single polymer could not be applied satisfactorily in such a delivery system (Melaj and Daraio, 2014). Crini and Badot (2008) reported that cross-linking of chitosan with glutaraldehyde afforded a copolymer material with a porous network with improved adsorption properties. By optimizing the proportion of chitosan and glutaraldehyde, the chitosan structure can be modified by forming chitosan-glutaraldehyde copolymers (CGC) in various forms, such as hydrogels, powders, or membranes.

Biocompatible and biodegradable materials, such as cellulose, chitosan, CA, and starch can be used directly or modified as coating materials for encapsulating fertilizer pellets. However, when these materials are used for coating fertilizers, efficiency in long-lasting release of nutrient is limited (Fernández-Pérez et al., 2008; Han et al., 2009; Ni et al., 2011; Zhong et al., 2013). Therefore, there is great demand for the development of new materials that can be used for controlled-release of nutrients in fertilizer (Yang et al., 2013). As a nontoxic food-grade coating material, MW is more feasible than paraffin wax because of its higher melting point. In addition, it has super hydrophobic properties and can be coated on fertilizer pellets, which not only insulates the pellets from the surrounding water but can also keep the pellets separated from each other (Rindt et al., 1968; Qiu et al., 2013).

In this study, CA, CGC, and MW were characterized and evaluated as candidates for use in CRFs. The combination of these materials as coating materials for agricultural use has not been reported. We developed a convenient and eco-friendly method to formulate a nitrogen (in the form of ammonium) CRF, in which water-soluble nitrogen fertilizer pellets are double-coated with CGC or CA and MW. The results show that the double-coated CRFs can release nitrogen in a desired manner and have excellent controlled-release properties. Therefore, such CRFs could have practical applications in agriculture and horticulture.

2 MATERIAL AND METHOD

2.1 Material

The water-soluble nitrogen fertilizer used in the study was in industrial grade and manufactured by Yantai Wuzhou Shidefu Fertilizer Company, in which nitrogen was borne in ammonium and the content of total water-soluble nitrogen was 18.87%. Chitosan was in 85% of deacetylation and average-molecular weight of 1 800 kDa produced by Qingdao Baicheng Biochemical Corporation. Glutaraldehyde (50%, w/w) in water, SA, $CaCl_2$, and glacial acetic acid were purchased from Shanghai Chemical Reagent Company. Food-grade MWs with freezing point of 70°C or 80°C were supplied by China Petroleum & Chemical Corporation. Other chemical reagents were acquired from Shanghai Chemical Reagent Company. All of the water used was deionized. All other chemicals were of analytical grade.

2.2 Preparation of coating material

The water-soluble nitrogen fertilizer was prepared as a pellet with a diameter of 2–3 mm. SA was employed to prepare the polysaccharide coating. The SA solution (2%, w/v) was prepared by dissolving 1.00 g of SA in 50 mL of water. The solution was stirred until a transparent sticky solution formed. A solution of $CaCl_2$ (5%, w/v) was prepared by dissolving 5.00 g of $CaCl_2$ in 100 mL of water by continuous stirring.

Chitosan (0.60 g) was dissolved in 30 mL of aqueous acetic acid (2%, v/v) in four replicates. Four glutaraldehyde solutions (50%, w/w) of 20, 30, 40, and 50 μL were diluted by the addition of 10 mL (2%, v/v) aqueous acetic acid. The four diluted glutaraldehyde solutions were added to the four chitosan solutions and stirred for 12 h at 20°C. Yellow and sticky CGC solutions were obtained, which were then used as the inner coating materials (Poon et al., 2014). The degree of cross-linking between chitosan and glutaraldehyde was controlled by changing the quantity of glutaraldehyde. The prepared CGC solutions were labeled A, B, C, and D, corresponding to the initial glutaraldehyde amounts of 20, 30, 40, and 50 μL, respectively.

2.3 The inner coating for fertilizer pellets

The water-soluble nitrogen fertilizer pellets were coated with an inner coating of CA or CGC using the immersion method, in which the pellets were immersed in the previously prepared polymeric CGC solutions. The coated fertilizers were gently spread apart and dried at 60°C to evaporate the solvent residues. Next, the coated pellets were immersed in the SA solution and then added into the $CaCl_2$ solution as drops. The drops quickly turned into beads because the SA in the drops immediately cross-linked with Ca^{2+}. These pellets were again spread gently and dried at 60°C to evaporate the solvent.

2.4 The outer coating for fertilizer pellets

The outer coating was formed by a phase-inversion technique using water in a precipitation bath. MW-70 (MW with a freezing point of 70°C) or MW-80 (MW with a freezing point of 80°C) were melted to liquids in a water bath at 90°C. The derivative of polysaccharide coated fertilizer (DPF) was added into molten MW-70 for 10 s. The DPF covered with MW-70 was then dropped into the precipitation bath to start the gelation process. In this way, MW70A, MW70B, MW70C, and MW70D were prepared with an inner coating from CGC solutions A, B, C, and D, respectively, and an outer coating of MW-70. MW80A, MW80B, MW80C, and MW80D were prepared and named using the same nomenclature, in which MW-80 was used to replace MW-70 as the outer coating. The CA-coated single-layered fertilizer was added to molten MW-70 or MW-80 to obtain MW70CA or MW80CA, respectively. MW70SA and MW80SA were also prepared, in which SA was used instead of CA as the inner coating.

2.5 Characterization

The chemical components of different coating materials were analyzed with NicoletTM iS10 FTIR spectrometer (Thermo Fisher Scientific). The samples of chitosan, CGC, SA, and CA were mixed with dried KBr powder, respectively. The KBr disks were dried again for the FTIR analysis. The pellets of water-soluble nitrogen fertilizer, DPF, and microcrystalline wax derivative of polysaccharide coated fertilizer (MDPF) were taken for SEM imaging. The samples were gold-coated and observed with S-3400N scanning electron microscpoe (Hitachi High-Technologies). The content of water-soluble total nitrogen was determined using TU-1810 UV-Vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.). Origin7.0 software was used to present experimental results of nitrogen release and FTIR analysis on coating materials.

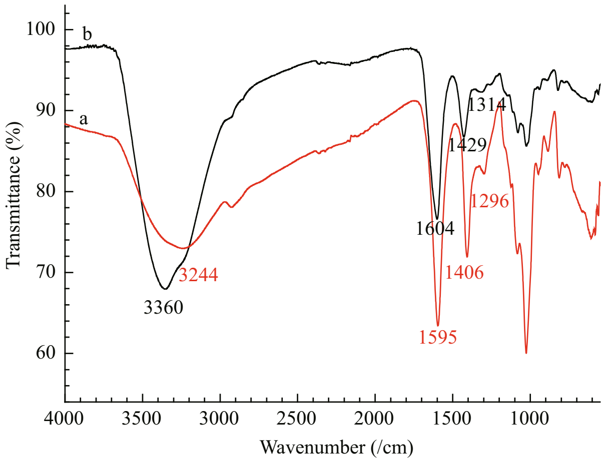

Fig.1 FTIR spectra of coating materials

a. SA; b. CA.

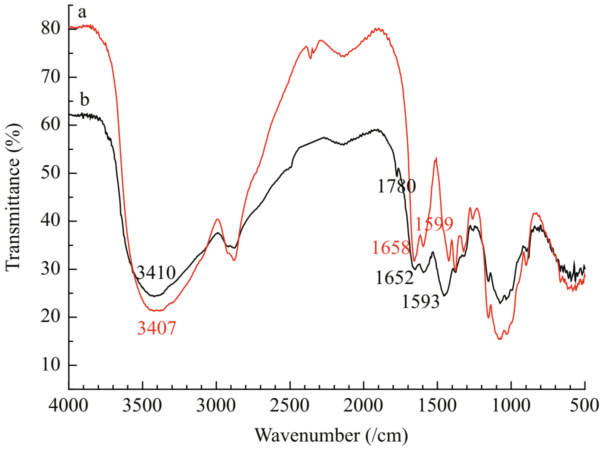

Fig.2 FTIR spectra of coating materials

a. chitosan; b. CGC.

2.6 Release of CRF in water

The nitrogen released from the prepared fertilizers in water was determined using the following procedure: Approximately 1.00 g of the products was weighed and the reading of the accuracy was rounded down. The pellets were then enclosed in nylon bolting cloth bags. The bags were placed in sealed beakers with 40 mL of deionized water and kept in an incubator at 25±0.5°C in triplicates. The aqueous solution was removed completely at various time intervals (1, 3, 5, 10, 15, 22, and 30 days) and the same volume of deionized water was added into the beakers. Alkaline persulfate digestion was monitored using a UV-Vis spectrophotometer to determine the total amount of nitrogen that was released in the aqueous samples according to the method reported by Kroon (1993).

3 RESULT AND DISCUSSION

3.1 FTIR analysis on the coating materials

FTIR analysis was used to confirm the structures of the coating materials (Fig.1). The absorption of the hydroxyl group shifted from 3 244/cm to 3 360/cm because of the weakening of the hydrogen-bond interactions of the hydroxyl groups as a result of chelation between the Ca^{2+} and OH groups. Similar observations have also been reported by Jin et al. (2013). The absorption at 1 595/cm reflects the vibration of C=O bond stretching, and those at 1 406 and 1 296/cm indicate the presence of a carboxyl group. The above information indicates that when the intensity of some characteristic adsorptions increases, chelation between Ca^{2+} and OH groups occurs.

Moreover, as shown in the spectrum of chitosan (Fig.2a), the absorption at 3 407/cm is indicative of the stretching vibration of the hydroxyl group. The troughs at 1 658 and 1 599/cm are the absorptions of amide I and amide II (Yang et al., 2001; Duan et al., 2009; Tao et al., 2012). Comparing the spectra of chitosan (Fig.2a) with CGC (Fig.2b), the small peak at 1 780/cm was attributed to the C=N stretching vibration. The absorption at 3 410/cm was weakened. Furthermore, the troughs at 1 652 and 1 593/cm were attributed to the absorptions of amide I and amide II, which also decreased in intensity. The above data supported the successful preparation of CGC, which was in line with the sorption properties of CGC reported recently by Poon et al. (2014).

3.2 Morphological analysis

SEM images of the water-soluble nitrogen fertilizers DPF and MDPF were obtained to study their morphology (Fig.3). Clearly, the surface of the fertilizer was rough (Fig.3a, b), whereas that of the CGC coating was smoother (Fig.3c, d) and its surface was porous and wrinkly with the presence of some pinholes. The surface of the CA coating (Fig.3e, f) was porous with some openings and rougher than that of the CGC coating. Therefore, when water passes through the CA coating, it would be absorbed and result in swelling of the fertilizer and the formation of a CA hydrogel. The hydrogel coating could prevent water from reaching the inner core and slow down the leaching of the nutrients from the fertilizer (Noppakundilograt et al., 2015). The outer coating of the MW-coated fertilizer (Fig.3g) was shiny and smooth. The cross-section image (Fig.3h) clearly shows a tightly bound two-layered coating. The thickness of the inner coating was 40–60 μm, which

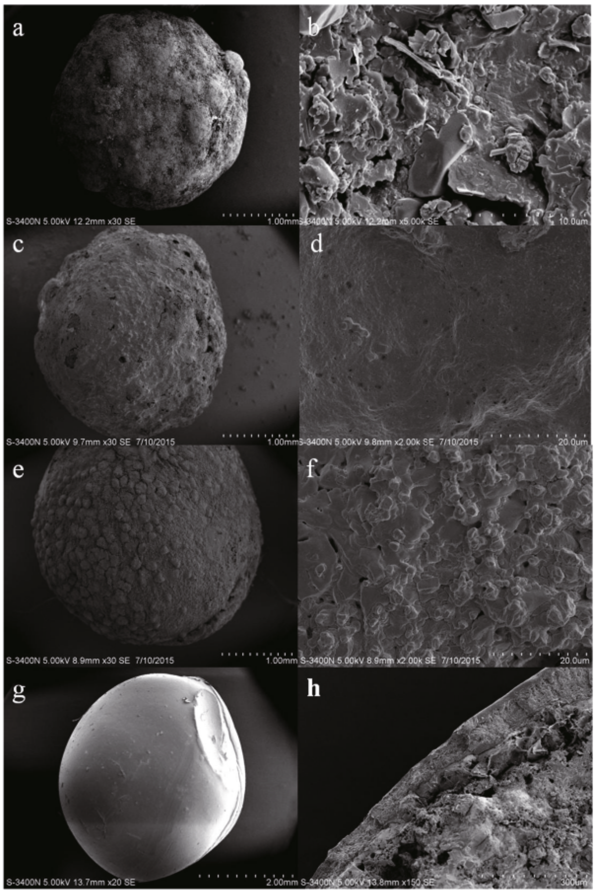

Fig.3 SEM images of the surface and cross-section of different materials

a and b. the water-soluble nitrogen fertilizer magnified 30 times (left) and 5 000 times (right); c and d. DPF (CGC as membrane material) magnified 30 times (left) and 2 000 times (right); e and f. DPF (CA as membrane material) magnified 30 times (left) and 2 000 times (right); g and h. MDPF magnified 20 times (left) and its cross-section magnified 150 times (right).

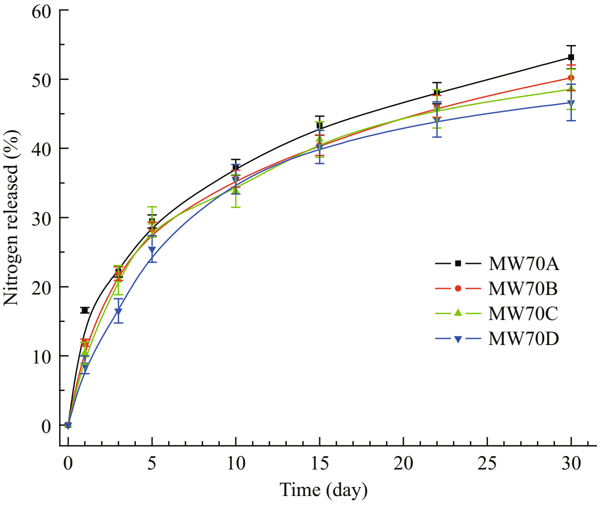

Fig.4 Curves of nitrogen release from CRF (inner coating CGC, outer coating MW-70) under 25°C in water

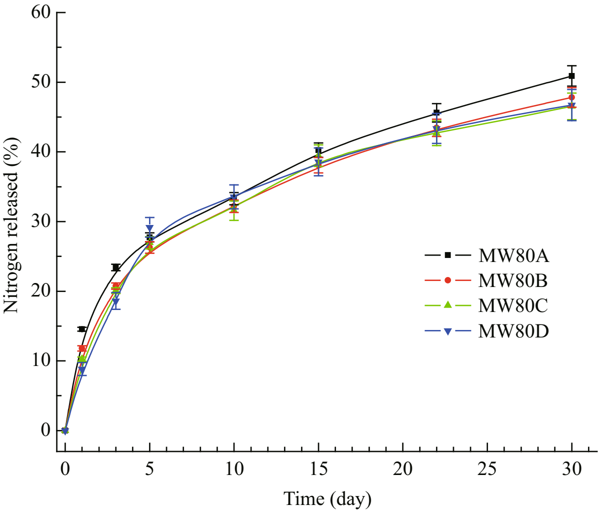

Fig.5 Curves of nitrogen release from CRF (inner coating CGC, outer coating MW-80) under 25°C in water

effectively reduces the penetration of water into the core and the diffusion of nutrients from the core. The thickness of the outer coating was 60–100 μm, which provides the hydrophobic MDPF with good controlled-release properties.

3.3 Controlled-release nature of CRF in water

The controlled-release nature of CRFs favors efficient nutrient delivery (Zhang et al., 2014). Figure 4 shows the relationship between nitrogen-release and time for MW70A, MW70B, MW70C, and MW70D. Approximately 16.60%, 11.89%, 10.38%, and 8.70% of nitrogen was released from MW70A, MW70B, MW70C, and MW70D in one day, respectively. Among them, the amount of nitrogen released by MW70D was also the lowest (46.63%) after 30 days. The degree of cross-linking between chitosan and glutaraldehyde increased in the order MW70A < MW70B < MW70C < MW70D. Therefore, the controlled-release properties of the nutrients were enhanced with increasing degree of cross-linking.

This is mainly because the inner CGC coating of the CRF prevents the exterior water from entering the inner core. The nutrient release from the coated pellets decreased with the decrease in porosity of the coating. The porosity of the coating was decreased with the increase in the degree of cross-linking between chitosan and glutaraldehyde. Therefore, the controlled-release properties were enhanced as the degree of cross-linking increased.

The plot of nitrogen release versus time for MW80A, MW80B, MW80C, and MW80D is presented (Fig.5). 14.55%, 11.80%, 10.24%, and

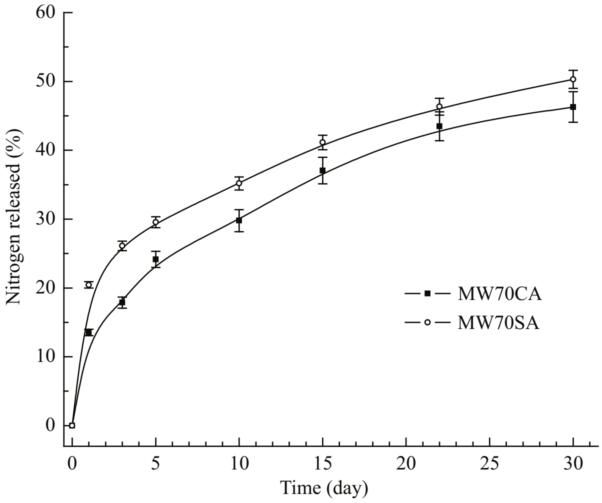

Fig.6 Curves of nitrogen release from CRF (inner coating CA or SA, outer coating MW-70) under 25°C in water

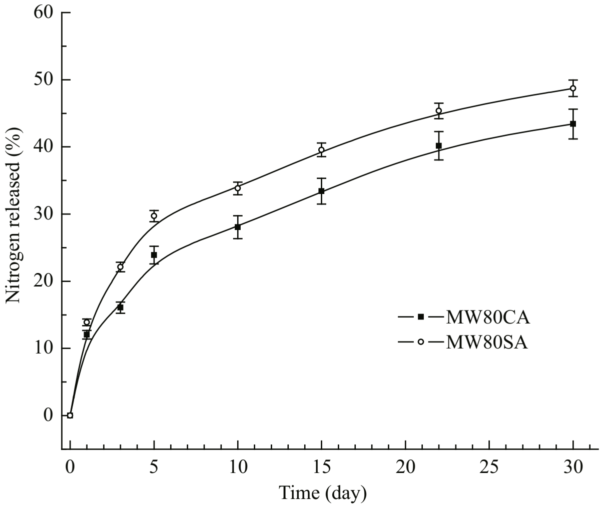

Fig.7 Curves of nitrogen release from CRF (inner coating CA or SA, outer coating MW-80) under 25°C in water

8.83% of nitrogen was released from MW80A, MW80B, MW80C, and MW80D in one day, respectively. The amount of nitrogen released after 30 days was the lowest (46.72%) for MW80D, although the tendency is the same for all MW-80s, indicating that the controlled-release characteristics increase with the increase in the degree of CGC cross-linking. Moreover, the fertilizer pellets with an MW-80 outer coating displayed better controlled-release properties in water than the MW-70 samples.

The nitrogen release of the double-coated fertilizers shows that 13.54% and 20.44% of nitrogen was released from the MW70CA and MW70SA, respectively, in one day (Fig.6). MW70CA showed better performance (46.28%) after 30 days. The chelation between Ca^{2+} and the OH groups decreases the water solubility of the coated fertilizers. The inner coating of CA could swell after water absorption and form a hydrogel crust. The hydrogel crust could then prevent water from further penetration into the core. In contrast, the inner coating of SA could not form a hydrogel. Therefore, the CA inner coating is better for the controlled-release of nutrients in water.

The nitrogen release of MW80CA and MW80SA showed that approximately 12.05% and 13.89% of nitrogen was released in one day, respectively (Fig.7). The release of MW80CA was slower after 30 days (43.42%), although the tendency of both MW-80 and MW-70 outer coatings was the same. It is clear that the CA inner coating was better than the SA inner coating at preventing the release of nutrients in water, and that the MW-80 outer coating had better thermal resistance than the MW-70 outer coating.

Wu and Liu (2008), Wu et al. (2008), and Noppakundilograt et al. (2015) have investigated the nutrient release mechanism, which is similar to our observations in this study. Briefly, the outer MW coating creates a superhydrophobic mini-environment for insulating water. Over time, a dynamic exchange develops between the free water in MW and ambient water. Once the water in the MW crust enters the inner CGC coating, the water-soluble nitrogen fertilizer in the core is dissolved. However, in the case of the CA inner coating, water is absorbed and the encrusted particle swells slowly and transforms into a hydrogel shell. Nitrogen in the core of the MDPF could be dissolved and released slowly in such a swollen hydrogel network and taken by the plant roots during water exchange.

The above results illustrate that the fertilizer encapsulated by CGC or CA with MW as a coating material can be used to control the release of nutrients and enhance the utilization of the fertilizer. The data show that <15% of nitrogen of the double-coated CRFs was released within 24 h. In addition, the long-term nitrogen release after 28 days was <75%. The nitrogen release meets the European standard for CRFs, which is consistent with a previous study (Lubkowski et al., 2015). However, the reasons why the MW-80 outer coating had better controlled-release properties in water than MW-70 remain unclear and need to be explored further. Future research will focus on the dynamic release mechanism of double-coated CRFs, the application of the double-coated CRFs to plants, and synthesis of new marine polysaccharide derivatives as coating materials.

4 CONCLUSION

Double-coated CRFs were realized by encapsulating water-soluble nitrogen fertilizer pellets with an inner coating of CGC or CA, and an outer coating of MW-70 or MW-80. SEM observations of the microtexture and FTIR analysis of the chemical composition revealed that this double-coating provided a convenient and eco-friendly method for the preparation of MDPF. The combination of CGC or CA with MW as a coating material results in controllable and efficient release of the encapsulated nutrients and shows potential for the use of natural resources such as CGC and CA in the fertilizer industry. The nitrogen release meets the requirements of the European standards for CRFs. Therefore, the technology could be used in industry for agricultural and horticultural applications.

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