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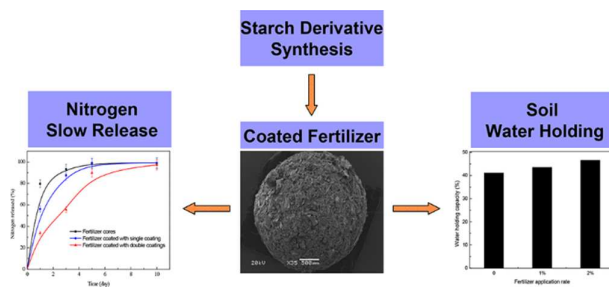
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Biomass based coated fertilizer was developed, which plays an important role in retarding nutrient release and holding water in soil.



ARTICLE

Synthesis of starch derivative and its application in fertilizer for slow nutrients release and water-holding

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With the increasing public concern toward human health, environmental protection, and natural resource sustainability, there is a shift toward the development of environmentally friendly fertilizers based on biomass. In the study, a coated fertilizer system based on starch acetate (SA) and weakly cross-linked carboxymethyl starch/xanthan gum (CMS/XG) was developed to improve biomass utilization efficiency and reduce environmental pollution. The coated fertilizer with the diameter in the range of 2.5-3.0 mm possesses low moisture content and high mechanical hardness. Nutrient nitrogen reached a steady state of releasing equilibrium within 20 days and the release behaviour depended on the coating thickness and the plasticizer content of SA film. Soil water-holding capacity determination showed that soil/coated fertilizer mixtures retained more water than the control soil, and the water content increased with increasing amount of the coated fertilizers in the soil. The experimental data indicated that the product based on starch derivatives as coating materials has preferable slow-release performance and the introduction of the natural polymers can improve biomass utilization efficiency, reduce nutrient loss and improve water use efficiency.

Introduction

The agricultural achievements of the past 50 years have been impressive. The doubling of agricultural food production was accompanied by greater input of fertilizer, water, new crop strains and pesticides, and other technologies of the “Green Revolution”^{1, 2}. Nitrogen is an essential plant nutrient and substantial nitrogen inputs are required for optimum plant growth and adequate food production. Developing countries now use more than 55 million metric tons of nitrogen fertilizer annually³. It is estimated that adequate production of food for present and future populations will not be achieved without external input of fertilizer nitrogen. However, increased awareness of ecological principles results in an improved understanding of the complex relationship between farming and ecosystems. It is now clear that large amounts of external nitrogen inputs with low nitrogen use efficiency have contributed to severe negative consequences, such as increased erosion, lower soil fertility, pollution of ground water, eutrophication of rivers and lakes, and impacts on atmospheric constituents and climate⁴⁻⁶.

Reconciliation of these two needs — increased world food production to meet rising demand with a decreasing impact on natural resources and the environment — presents a major challenge for scientists and policymakers. In the last several decades, slow/controlled release technology has emerged and

developed as an approach toward solving the problems associated with the application of conventional agrochemicals⁷⁻¹¹. Many efforts have been made by researchers toward obtaining novel slow/controlled release fertilizers. The most important groups of slow/controlled release fertilizers according to their production process are condensation products of urea and urea-aldehydes, and coated or encapsulated fertilizers. As a main product of urea-aldehydes, urea-formaldehyde based products have the largest share of the slow/controlled release fertilizers market. However, it appears that part of the nitrogen contained may be released to the soil extremely slowly or even not at all due to its low solubility. With regard to coated fertilizers, agents currently used for coating materials are sulphur, wax, rock phosphate, polyolefines and polyesters¹². In comparison to urea reaction products, coated fertilizers, particularly those coated with multi-layer coatings, may present more favourable economics.

Biomass used as coating materials have received considerable interest based on the characteristic properties of the polymeric molecules¹³⁻¹⁶. However, few examples of biomass applied in slow/controlled release fertilizers have been reported. Starch is renewable, biodegradable and relatively inexpensive, which make it attractive as an environmentally friendly polymer for general consumer applications¹⁷. Unfortunately, using starch for non-food use in its native form is often limited due to its poor solubility, low mechanical properties and instability at

high temperature and pH¹⁸. To overcome these shortcomings, many researches have been made to modify it to suit specific industrial process. Chemical modification of starch involves reaction of the hydroxyl groups in the anhydroglucose units¹⁹⁻²³. In this study, starch acetate (SA) with high degree of substitution was synthesized and used as a novel hydrophobic coating to allow for the slow release of the fertilizer nutrients. Carboxymethyl starch (CMS) and xanthan gum (XG) were used to prepare starch based absorbent material for improving water retention capacity of soil and water use efficiency. The introduction of these natural materials and their derivatives can induce biodegradability and full protection of the environment.

Materials and methods

Materials

Native corn starch was supplied by Gansu Xuejing Biochemical Co., Ltd. (Gansu, China). CMS (viscosity of 19000 mPa·s in 4% aqueous solution, degree of substitution 0.91) was supplied by Tianqi Starch Company (Gansu, China). XG (viscosity of 800-1200 mPa·s in 1% aqueous solution) and trisodium trimetaphosphate (TSTP) were obtained from Aladdin Reagent Co., Ltd., (Shanghai, China). Triacetin was provided by Acros (New Jersey, USA). Natural attapulgite (APT, supplied by Gansu Haozhou APT Co., Baiyin, China) was milled and sieved through a 200-mesh screen before use.

Soil used in this study is a representative samples in Lanzhou, which lies in northwest China and is a dry, semidesert region with an average annual precipitation of 300 to 600 mm. Soil samples (0-10 cm in depth) were dried at room temperature for 2 weeks and then passed through a 26-mesh sieve. The soil texture is silt loam. The soil contains 9.27, 61.89 and 28.84% of clay, silt and sand, respectively. The pH and electroconductivity of the soil is 8.1 and 2150 μ s/cm, respectively.

Synthesis of starch acetate (SA)

A sample of 5 g of native corn starch was put into a 100 mL three-neck glass flask with a stirrer and a reflux condenser. The temperature of the bath was raised to 120 °C and 20 g of acetic anhydride was added. Then, 1.1 mL of sodium hydroxide (1%, v/v) was added dropwise over a period of 10 min. After 5 h, the remainder of the solution was precipitated with water, filtered, washed with excess distilled water. The solid was dried at 30 °C in a vacuum oven and then sieved.

Synthesis of cross-linked carboxymethyl starch/xanthan gum (CMS/XG) absorbent material

A series of CMS/XG absorbent material samples with different amount of CMS, XG, and cross-linker TSTP were prepared according to the following procedure. In a typical reaction, 13.3 g of XG and 6.7 g of CMS were dissolved in 1 L of distilled water under vigorous mixture. After 30 min, the cross-linking reaction was initiated by adding 0.1 g of NaOH and 0.6 g of TSTP. The reaction solution was poured into a container and

dried at 80 °C. The resultant dried CMS/XG absorbent material sample was milled and screened.

Preparation of double coated slow release fertilizer

Urea (600 g) and natural APT clay (500 g) was ground to powder and mixed well. Then, the mixture was fed into a rotating pan with urea granules (about 1.0-1.3 mm in diameter) in batches. During this step, the fertilizer cores with a desired range of sizes were obtained under water atomization. Subsequently, SA was dissolved in ethyl acetate followed by adding different amount of triacetin (0, 10% and 20%, $w_{\text{triacetin}}/w_{\text{SA}}$) as plastizer. The SA solution (3%, w/v) was stirred for 4 h prior to coating. Then, the coating solution was sprayed on the fertilizer cores to form the inner coating. The film-coating thickness was determined by the dry weight gain of the coated fertilizers. Finally, CMS/XG absorbent material powder (below 110 mesh) as the outer coating was coated on the surface of the fertilizer granules under rotation. The double coated urea fertilizer was fed into a dryer to remove excess water and to harden the granules.

Coating materials and coated urea fertilizer characterization

Fourier transform infrared (FTIR) spectroscopy of the native and acetylated corn starch, CMS, XG, and CMS/XG were obtained for the dried powder using a Nicolet NEXUS 670 FTIR spectrometer.

X-ray powder diffraction analysis of the native corn starch and SA were performed with a Panalytical X'Pert PRO diffractometer equipped with a monochromatic Co-K α radiation. Powder samples were tightly packed into rectangular aluminium cells and exposed to an X-ray beam with a voltage of 40 kV and a current of 100 mA. Data were collected from 2 θ of 5° to 40°.

The acetyl content and degree of substitution (DS) of SA were determined according to a reported procedure²⁴. Briefly, a sample of 0.5 g of SA was added to 25 mL of 75% (v/v) ethanol solution. After stirring at 50 °C for 30 min, the slurry was cooled to room temperature and 20 mL of KOH solution (0.5 mol/L) was added. The slurry was stirred for 72 h at room temperature. Then, the excess of alkali in the solution was titrated with 0.5 mol/L HCl. The DS of SA was calculated according to the following equations:

$$\text{Acetyl content (\%A)} = [(V_0 - V_n) \times N \times 43 \times 10^{-3} \times 100] / M \quad (1)$$

$$\text{DS} = 162 \times \%A / (43 \times 100 - 42 \times \%A) \quad (2)$$

where V_0 is consumption of HCl for blank value (mL), V_n is volume of HCl used to titrate sample (mL), N is the concentration of HCl, 43 is molar mass of acetyl group, and M is weight of SA, respectively. In this study, The DS of the SA prepared was determined to be 2.87.

The content of nitrogen in the coated fertilizer was determined by an elemental analysis instrument (Germany Elemental Vario EL Corp., model 1106).

The average crushing strength was measured using a compressing equipment for 30 fertilizer granules (2.7 ± 0.3 mm in diameter).

The moisture content of the coated fertilizer was determined by drying 10 g of the product in a vacuum drying chamber at $50 \pm 2^\circ\text{C}$ until there was no change in the mass of the sample.

The surface morphology of the coated and uncoated fertilizer granules was examined with scanning electron microscopy (SEM) (Hitachi, model S-4800, Japan).

Measurement of water absorbency of the CMS/XG absorbent material

The accurately weighed CMS/XG absorbent material (0.5 g, 40–90 mesh) was immersed into 100 ml of tap water and allowed to soak at ambient temperature for 2 h. The swollen polymers were filtered and weighed. All experiments were done in triplicate. The water absorbency (WA) is the swelling ratio of the absorbent material in water, which was calculated using eq 3:

$$WA = (M - M_0) / M_0 \quad (3)$$

where M and M_0 refer to the weight of the swollen and dried absorbent material, respectively.

Soil release kinetics of the coated fertilizers

A preweighed sample of fertilizer (1 g) was enclosed in a nylon screen bag, which was buried approximately 6 cm below the surface of 200 g of dry soil (below 26 mesh). Then they were kept in a 200 mL glass beaker that was properly covered and incubated for different periods of time at room temperature. The moisture content of the soil was kept at 20% throughout the experiment. At fixed time intervals, the screen bags were withdrawn and dried. The total nitrogen content released in soil was determined by the difference between the initial nitrogen content in the fertilizer granules and the amount remaining when the release experiment finished. Values reported for the release percentage were average of three experiments.

Effect of the coated fertilizers on water-holding capacity of soil

The effect of the CMS/XG coating material on water-holding capacity of soil was determined according to previously reported methods slightly modified^{25, 26}. A 4.5 cm diameter polyvinyl chloride tube containing 200 g of dry soil (below 26 mesh) was used. Different amount of the double coated fertilizers (0, 2 and 4 g) were placed 6 cm beneath the surface of the soil in the form of a spot application. The bottom of the tube was sealed with nylon fabric and weighed (marked W_1). The soil was slowly drenched by tap water from the top of the tube until water seeped out from the bottom. When no water seeped at the bottom, the tube was weighed again (marked W_2). A control experiment without the coated fertilizers was also carried out. Two fertilizer application rates (1 and 2%) were examined. All experiments were done in triplicate. The water-holding capacity (WH %) of the soil was calculated from eq 4:

$$WH \% = (W_2 - W_1) \times 100 / 200 \quad (4)$$

Results and discussion

Morphology and characteristics of the coated fertilizers

Figure 1 shows the morphology of the fertilizer core (a, d), fertilizer core with the inner coating SA (b, e), the final product with the inner coating SA and outer coating CMS/XG absorbent material (c, f). As can be seen from Figure 1b and e, the surface of the fertilizer is smooth due to the SA film, which could prevent the moisture permeating through it into the fertilizer cores. Figure 1c and f show that fine particles of CMS/XG absorbent material covered the surface of the fertilizer. The characteristics of the coated fertilizers are presented in Table 1.

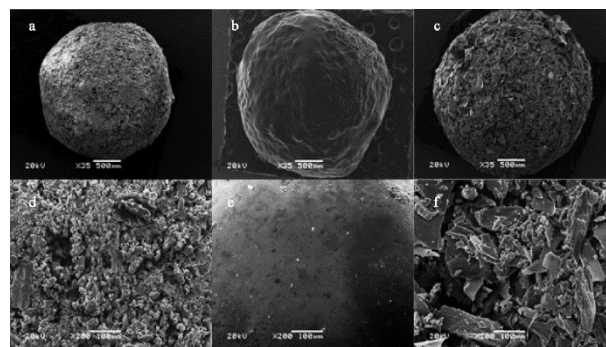


Figure 1. Morphology of the fertilizer core (a, d), fertilizer core with the inner coating SA (b, e), the final product with the inner coating SA and outer coating CMS/XG absorbent material (c, f). Scale bar: 500 μm (a, b and c), 100 μm (d, e and f).

Table 1. Characteristics of the double coated urea fertilizer.

Characteristics	Value
Diameter of dry sample	2.5-3.0 mm
Nitrogen content	21.4%
SA content	9%
Plasticizer content	20%
CMS/XG content	11.3%
Average moisture content	2.6%
Average crushing strength	25.7 N

Characterization of SA

The FTIR spectra of native corn starch and SA are shown in Figure 2A. In the spectrum of native corn starch (Figure 2A (a)), there are several peaks at 1018 cm^{-1} , 1080 cm^{-1} , and 1157 cm^{-1} , which are attributed to the C–O stretching vibration. Other characteristic absorption peaks are observed at around 1640 cm^{-1} and 3450 cm^{-1} , corresponding to the tightly bond water in the starch and the vibration of the hydroxyl group, respectively. After acetylation (Figure 2A (b)), new absorption peaks appear at 1750 cm^{-1} , 1373 cm^{-1} , and 1240 cm^{-1} , assigned to C=O stretching vibration of ester, CH_3 flexural vibration, and C–O stretching vibration of ester, respectively²⁷. These new absorption peaks suggest that the ester carbonyl groups were formed during the esterification process in starch, namely, the SA product synthesised successfully.

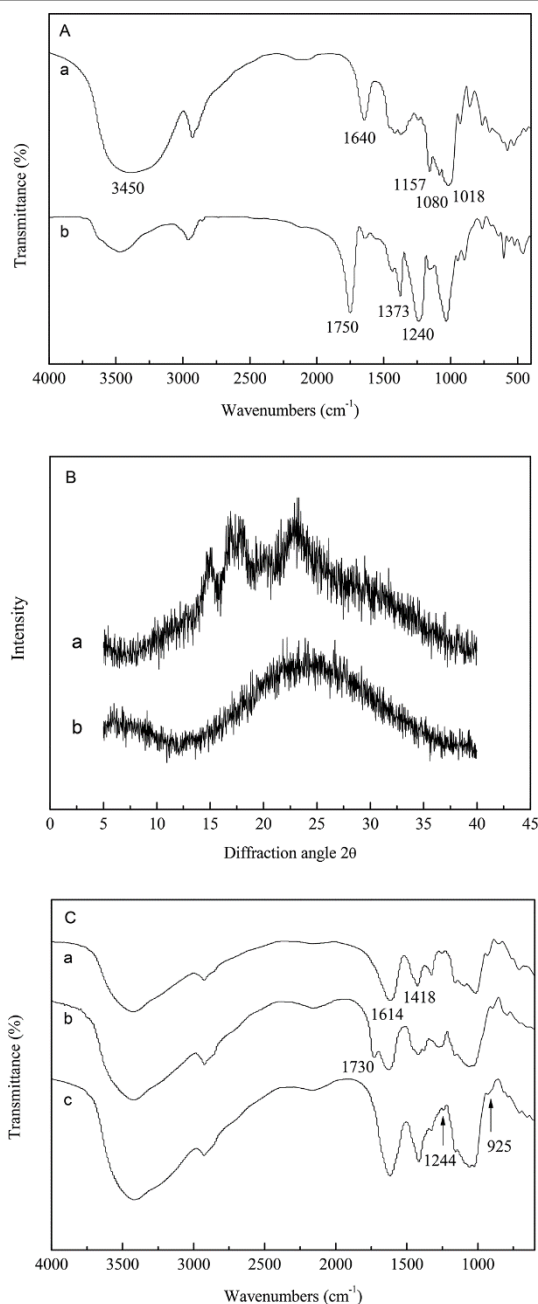


Figure 2. (A) FTIR spectra of native corn starch (a) and SA (DS = 2.87) (b); (B) Wide angle X-ray diffraction pattern of native corn starch (a) and SA (DS = 2.87) (b); (C) FTIR spectra of CMS (a), XG (b), and CMS/XG absorbent material (c).

X-ray powder diffraction measurements were performed to further investigate the effect of the modification on the crystalline structure of starch. As indicated in Figure 2B, native corn starch (Figure 2B (a)) has a typical A-type pattern structure, with the sharp diffraction peaks at 15°, 17°, 18°, and 23°. For SA (Figure 2B (b)), even though the similar type of diffraction pattern is observed, the XRD spectrum has a broad peak and the intensity of the peaks reduces significantly, which suggest that the ordered crystalline structure of the native starch was destroyed in the esterification process.

Characterization of CMS/XG

Figure 2C presents the FTIR spectra of CMS (a), XG (b), and CMS/XG cross-linked with 3% TSTP (c). The spectra of CMS and XG both display the typical peaks of polysaccharides in the range of 980-1200 cm⁻¹, which are attributed to the C–O stretching vibration. The peaks at 1614 and 1418 cm⁻¹ in the spectrum of CMS are attributed to the –COO⁻ asymmetric and symmetric stretching vibration, respectively²⁸. The peak at 1730 cm⁻¹ in the spectrum of XG is ascribed to the C=O stretching vibration of acetyl and carboxyl. Two new small peaks appear at 1244 and 925 cm⁻¹ in the spectrum of CMS/XG are assigned to the characteristic bonds of P=O and P–O vibration in the cross-linked polysaccharides, respectively. Figure 3 shows the cross-linking reaction scheme of CMS and XG with TSTP.

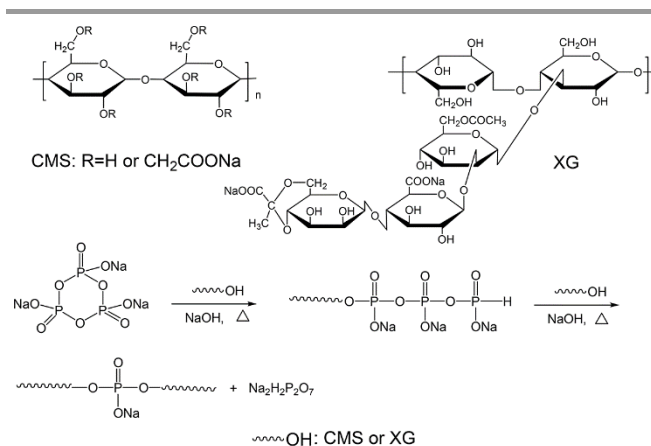


Figure 3. Schematic representation of cross-linking reaction of CMS and XG with TSTP.

Effect of the reaction parameters on water absorbency of CMS/XG absorbent material

Using polymer-based absorbent materials to improve the water and nutrient supplying capacity of soil has attracted considerable attention in the last several years. Cross-linked synthetic polymers such as polymethacrylates, polyacrylates, and polyacrylamides have been reported to produce superabsorbents^{7, 26, 29}. Due to environmental issues, growing efforts have been made to develop natural polymer-based materials that guarantee degradability. In this study, CMS and XG were used to synthesize a novel absorbent material. CMS and XG are water-soluble polysaccharides and hydrophilic backbone brings a considerable contribution to the swelling capacity because of the high affinity between polymer chains and water^{30, 31}. In addition, the presence of fixed negative charges on polymer chains enhances the water absorbency of the material due to Donnan equilibrium established between the polymeric network and the external solution. To improve the water absorbency of CMS/XG, the reaction parameters were optimized. The water absorbency in tap water as a function of XG/CMS weight ratio is shown in Figure 4A. It can be seen that the water absorbency increases when the ratio of XG/CMS is

lower than 2:1 and decreases with the larger ratio. CMS is less sterically hinder than XG and can react with TSTP easily than XG (see Figure 3). When the CMS content is high, the cross-linking density of the absorbent material is high, which results in the decrease of water absorbency. When the ratio of XG/CMS is larger than 2:1, a further increase in the XG content results in the cross-linking degree decreasing. Meanwhile, the viscosity of the reaction mixture increases dramatically, which hinders the movement of the reactants. Thus, the soluble materials increase, resulting in a decrease in water absorbency.

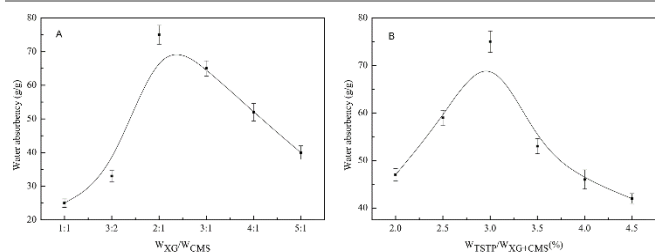


Figure 4. (A) Effect of CMS and XG content on water absorbency of the CMS/XG absorbent material (reaction conditions include the total polymer concentration, 2 wt%; TSTP content, 3 wt%; and reaction temperature, 80 °C); (B) Effect of TSTP content on water absorbency of the CMS/XG absorbent material (reaction conditions include the total polymer concentration, 2 wt%; ratio of XG/CMS, 2:1; and reaction temperature, 80 °C).

Cross-linking is a common approach to prepare materials with network structures for various applications. However, the chemicals used for cross-linking reaction are usually relatively toxic and expensive. TSTP is a solid of low toxicity with no reported adverse effects on humans and is an effective cross-linking agent at warm temperature with hydrated starch in aqueous slurry³². In this study, TSTP was used as a cross-linker in the synthesis of CMS/XG absorbent material. The effect of the TSTP content on water absorbency of the polysaccharide based absorbent material is shown in Figure 4B. As we can see from the figure, the water absorbency decreases when the TSTP content is lower than 3 wt%. This is because the cross-linking reaction between the polymer chains of CMS and XG does not occur effectively, leading to an increase in soluble materials. When the cross-linker content is larger than 3 wt%, the cross-linking density increases and the average molecular weight between two cross-linking points decreases, which results in an increase of the network elastic response to swelling. This obviously restricts relaxation of network chains, thus resulting in a fall in the water absorbency of the material.

Effect of the SA and CMS/XG double coatings on nitrogen release behaviour

Urea is the major nitrogen fertilizer. When urea is applied to the soil, it hydrolyzes to form ammonium carbonate, which is an unstable compound and decomposes to ammonia and dioxide. The process is greatly enhanced in the presence of the enzyme urease. More than 20 % of urea is lost due to the high solubility and ammonia volatilization³³.

In this study, a slow release system based on SA and CMS/XG double coatings was developed to alleviate the nitrogen loss.

The effects of the coatings, coating thickness, and the plasticizer content of SA film on urea release behaviour of the product were evaluated in soil. Figure 5A shows the release profiles of fertilizer cores, fertilizer coated with SA, and fertilizer coated with SA and CMS/XG double coatings, respectively. As shown in the figure, uncoated product shows a rapid release. The release rate of nitrogen is up to 79.7% for one day. When the fertilizer cores were coated with SA, the release rate of nitrogen decreased: about 56.2% for one day, and it reaches release equilibrium on the 5th day. This is mainly due to the diffusion barrier of hydrophobic SA film. When the fertilizer cores were coated with SA and CMS/XG double coatings, the nutrient nitrogen reaches release equilibrium on the 10th day. CMS/XG can absorb part of the urea and then the nutrient releases in soil through the dynamic exchange of free water. It is obvious that the double coatings play an important role in retarding the nutrient release although there is a burst release of nitrogen within the first day, which is most likely because that the thickness of SA film is too small to allow for establishing homogenous films and prevent the component being released.

The effect of thickness of SA coating film on nitrogen release behaviour was investigated and shown in Figure 5B. As expected, the release rate decreases with the thickness of SA coating increasing. When the SA content is 5%, the nitrogen release percentage is up to 33.6% within one day. However, when the SA content is 7% and 9%, the release rate of nitrogen decreases dramatically: the release percentage is only 9.4% and 6.1% within one day, 89.2% and 79.4% within 10 days, respectively. This is because the diffusion of water through the film is slowed down and the diffusion pathway for urea molecules is increased with the increase of the film coating thickness.

Plasticizers play an important role in film coating. Plasticizers are commonly incorporated with the polymeric films to change flexibility, fragility, and tensile strength of the resulting films^{34, 35}. Many compounds can be used as plasticizer and perform different outcomes due to their intrinsic properties and interaction with polymers. In this study, triacetin was used as a hydrophobic plasticizer to enhance the flexibility of SA film in terms of controlling nutrient release from coated fertilizers. Figure 5C shows the nitrogen release behaviour from the SA and CMS/XG double coated fertilizers containing different amount of triacetin (0-20%, $W_{\text{triacetin}}/W_{\text{SA}}$). The content of SA and CMS/XG is fixed at 9% and 11.3%, respectively. It can be seen that the release rate of nitrogen in the coated fertilizers decreases with the increase of triacetin in SA. When triacetin is absent in the SA film, the release rate is fast, more than 35% released with 24 h. However, when the triacetin content is 20%, the nitrogen release rate decreases dramatically, indicating that the SA film with the plasticizer triacetin could control the release of fertilizer nutrient effectively.

It is important to note that the nitrogen release behaviors are predicted to be different when the double coated fertilizers are applied to different soils under different environmental

conditions. More extensive experiments on this topic should be carried out in further studies for the practical application.

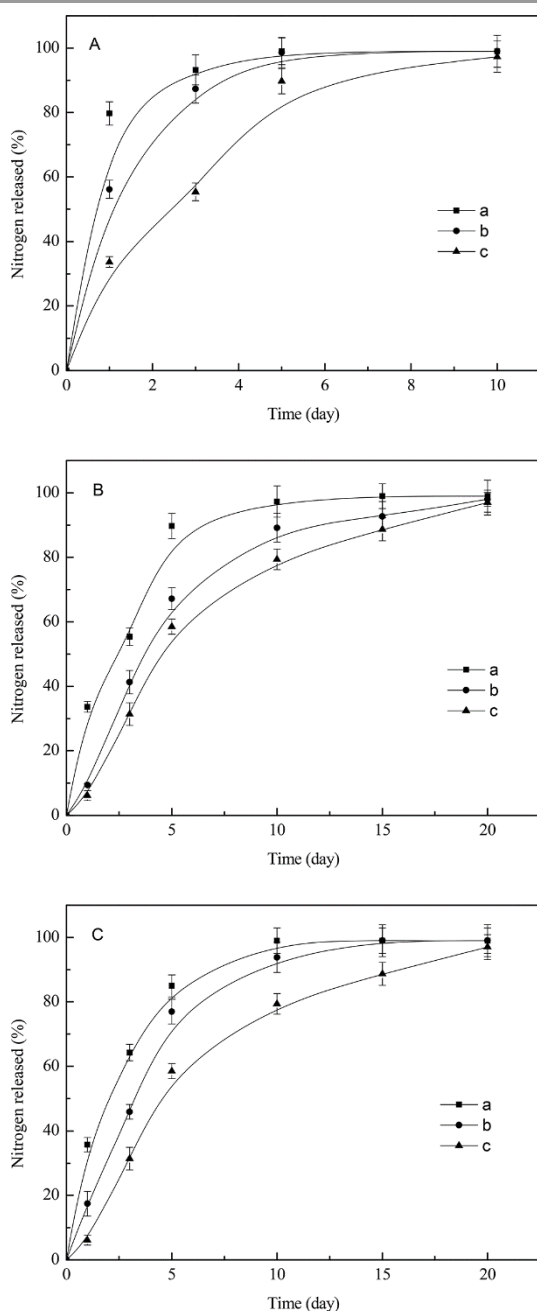


Figure 5. (A) Release profiles of nitrogen from fertilizer cores (a), fertilizer coated with SA single coating (5% SA, 20% triacetin) (b), and fertilizer coated with SA and CMS/XG double coatings (5% SA, 20% triacetin, and 11.3% CMS/XG) (c); (B) Effect of SA coating film content on nitrogen release behaviour: SA 5% (a), SA 7% (a), and SA 9% (c). All samples contain plasticizer triacetin 20 %, outer coating CMS/XG 11.3 %; (C) Effect of plasticizer triacetin content on nitrogen release behaviour: without triacetin (a), triacetin 10% (b), and triacetin 20% (c). All samples contain SA 9%, CMS/XG 11.3 %.

Effect of the coated fertilizers on water-holding capacity of soil

Water is a renewable resource, but its availability is variable and limited. Rising water scarcity is partially a consequence of

the increasing demand for food. Agricultural production accounted for about 90% of global fresh water consumption during the last century³⁶. To ensure food security, it is important to promote water-saving agriculture by means of an integrated management that includes water-efficient irrigation, agronomic water-saving techniques, and appropriate agriculture management³⁷. Nowadays, research on the technology of chemical-saving water have been drawing extensive attention. Superabsorbent polymers, a group of water saving materials, have been used for soil conditioning from 1950s³⁸. A considerable drawback for traditional superabsorbents, which are usually cross-linked polyacrylates, is their environmental impact. In this study, a new kind of polysaccharide based polymer CMS/XG with a weakly cross-linked network structure has been successfully prepared as a fertilizer coating and soil conditioner. The influence of the double coated fertilizers on water-holding capacity of soil was determined from the swelling property of the soil/coated fertilizer mixture after saturation. The water-holding capacity of soil is 41.1, 43.5, and 46.6% for the coated fertilizers when the application rates were 0, 1, and 2%, respectively.

It is noted that soil/coated fertilizer mixtures retain more water than the control soil, and the water content increases with increasing amount of the coated fertilizers in the soil. With irrigation, the problem always exists that too much water may be applied and lost to the aquifer or through evaporation. Therefore, the coated fertilizers will be useful for improving utilization efficiency of water and prolonging irrigation cycles in drought prone environments.

Conclusions

A slow release system of urea fertilizer has been obtained by coating the fertilizer cores with environmentally friendly SA and CMS/XG double coatings. The double coated fertilizer had preferable slow-release properties: nutrient nitrogen reached a steady state of releasing equilibrium within 20 days. Kinetics of release in soil showed that the process of nitrogen release can be controlled by changing the thickness of coating and the content of plasticizer. Moreover, the polysaccharide based absorbent material CMS/XG used as a novel coating played an important role in retarding nutrient release, as well as in holding water in soil. All of the results of the present work indicated that the environmentally friendly coated urea fertilizer can effectively reduce nutrient loss and improve use efficiency of water.

Acknowledgements

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