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Characterization, swelling and slow-release properties of a new controlled release fertilizer based on wheat straw cellulose hydrogel

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ABSTRACT

A novel wheat straw based semi-interpenetrating polymer networks (semi-IPNs) hydrogel with slow-release fertilizers of nitrogen and phosphorus was prepared by the method of solution polymerization. The influences of particle sizes, salt solutions, ionic strength and pH changes on the swelling and fertilizer releasing properties of the product were investigated. Effect of cations on both swelling and fertilizer release properties were observed in the order of $Na^+ > K^+ > Ca^{2+}$. The product could hold more water in the pH range of 6–9. The swelling behaviors of the product in various salt solutions, ionic strength and pHs conditions were evaluated by Schott's second-order swelling kinetics model. The fertilizers diffusion parameters of the product could be assessed by a cubic form perfectly according to the diffusion coefficients in the kinetic equation.

1. Introduction

Fertilizer and water are two important limiting factors in increasing demands for bioenergy crops. As a result, improving the utilization efficiency of fertilizer nutrients and water resources has become more and more important on driving an ever-increasing demand for global agricultural production. Of all the nutrients required by crops, nitrogen (N) is the one most often deficient in soil. However, due to the high soluble characteristic of nitrogen fertilizer, it has shown the greatest potential for losses. Leaching and flooding were normally considered to be the major N loss pathways. Phosphorus was also an important constituent element of protoplasm and nucleus which can stimulate the growth and development of crops. Generally, only 10–20% of the conventional phosphorus fertilizer applied to soil is absorbed by crops. Furthermore, the loss of nutrients (N and P) could directly cause world-wide eutrophication problems in surface freshwater bodies and coastal ecosystems. The adoption of slow-release fertilizers has been considered as a promising strategy to simultaneously improve the use efficiency of conventional fertilizer and reduce the environmental hazards. Compared to the conventional way, the slow-release fertilizers have many outstanding properties, such as lessening the fertilizer loss rate, reducing the application frequency, providing the sustainable nutrients and lowering the potential negative effects on the overdosage [1,2].

Hydrogel is a kind of hydrophilic polymers with three-dimensionally crosslinked structure. This structure is capable to absorb and hold a large number of water, and the preserved water can be hardly removed even under certain pressure. Hydrogel could reduce the consumption of irrigation water, improve the amount of fertilizer retained in soil and lower the death rate of plants [3]. As a result, it has been extensively applied in agriculture and horticulture due to their excellent properties [4]. Semi-interpenetrating polymer networks (semi-IPNs) are a way to blend two polymers, and the feature of this network is the penetration of some branched or linear macromolecules onto a molecular dimension of networks [5]. The product generated by this blending method usually displays exceptional performances superior to either single polymer [6]. In this study, poly(vinyl alcohol) (PVA) was involved in the semi-IPNs as linear macromolecule. As a water-soluble polymer, PVA has been widely applied in biomedical and pharmaceutical field because of its performance advantages such as non-toxic, non-carcinogenic, chemical resistance and bioadhesive properties [7]. Besides, PVA is used in the hydrogel preparation because that it can greatly enhance the mechanical toughness properties of hydrogel.

Hydrogels, composed of linear and crosslinked polymers, can be utilized to enhance the characteristic of polymer composites owning to the structure of semi-IPNs. However, the application of hydrogels also faced some problems such as poor biodegradability, high

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production cost and weak salt resistance [8,9]. In this work, wheat straw cellulose (WSC) was introduced to alleviate those problems. The cellulose grafted hydrogel has gained increasing attention either in academic or industrial field owning to its eco-friendly property and expected biodegradability [10,11]. Wheat straw (WS), one typical fiber crops containing 40–60% of natural cellulose, hemicelluloses and lignin, has a tremendous amount of readily available hydroxyl groups. These groups can easily trigger a chain of chemical reactions (*e.g.* copolymerization, esterification and etherification), and therefore the natural WS is suitable to be employed for hydrogels preparation.

Currently, the research on methods of combining fertilizers with hydrogels have been reported in other works to obtain composites with slow-release and water-retention properties, including chemically combined fertilizers [12,13], physically mixed fertilizers and coated fertilizers [14–19]. However, some of these sustained release methods only achieve the property of slow releasing fertilizers, but not the function of water-retention, such as hydrogel coated fertilizers [20], polyethylene and paraffin. Therefore, it is important to exploit an economical fertilizer containing both slow-release and water-retention properties. Recently, Ni et al. developed a slow-release nitrogen fertilizer chemically coated by modified cellulose hydrogel, aiming at controlling the release rate of nutrient and improving the water-holding ability of soil. However, its water swelling capacity was obviously limited [21]. Wu et al. prepared a fertilizer by double-coated method, which owned the inner coating (chitosan) and out coating (P(AA-co-AM)) [19]. But there were two major problems for this pathway: (i) the nondegradable coating materials would be left in the soil after the release of fertilizers, thereby resulting in another environmental problem; (ii) this approach was achieved at a high production cost. We should also point out that most of these sustained fertilizers focused only on nitrogen nutrients, and a few reports were concerned about other fertilizers, such as phosphorous fertilizer. To overcome the above disadvantages, a new preparation approach was required urgently.

In the present work, a novel semi-IPNs hydrogel with slow-release fertilizers of nitrogen and phosphorus (WSC-g-PAA/PVA/NP), on the base of wheat straw cellulose-g-poly (acrylic acid) (WSC-g-PAA) network and linear poly(vinyl alcohol) (PVA), was prepared by the method of solution polymerization. To be specific, this preparation method was developed by transferring nitrogen and phosphorus directly into the mixture during the procedure of synthesizing semi-IPNs hydrogel, which was gained through graft copolymerization between WSC and acyclic acid (AA) and the further interpenetration onto PVA. Fourior-transform infrared (FTIR) and scanning electron microscope (SEM) were carried out to investigate the surface chemical functional groups and external morphologies of the semi-IPNs hydrogel. In order to better understand the product's swelling, fertilizer release properties and evaluate its potential application in soil, the swelling kinetics and fertilizer release behaviors of WSC-g-PAA/PVA/NP in solutions with various pHs, ions and ionic strengths were also determined.

2. Experimental

2.1. Materials

The reagents used in this work including urea, acyclic acid (AA), potassium hydroxide (KOH), dipotassium hydrogen phosphate (K_2HPO_4), poly(vinyl alcohol) (PVA), N,N′-methylene-bis-acrylamide (MBA), sodium sulfite (Na_2SO_3), potassium persulfate ($K_2S_2O_8$), and ammonium cerium nitrate ($(NH4)_2Ce(NO_3)_6$) were of analytical grade (provided by Dengke factory, Tianjin, China). Wheat straw (WS) was gained from Liaocheng, Shandong, China. Distilled water was applied in solution preparation, swelling and fertilizer release experiments.

2.2. Preparation of WSC-g-PAA/PVA/NP

The wheat straw was crushed and sifted through a 100-mesh sieve after being washed and dried. The powder sample was immersed in 10 wt% ammonia for about two days at a weight ratio of 1:12, and then the mixture was filtered and washed several times with distilled water in a vacuum filter. Thereafter, the filtered residue was soaked in nitric acid (1 mol/L) at 100 °C for 45 min, still maintaining a 1:12 mass ratio. After that, the mixture was filtered and washed *via* the same way, and then dried under a temperature of 75 °C to gain wheat straw cellulose (WSC).

The semi-IPNs WSC-g-PAA/PVA/NP hydrogel based on WSC-g-PAA network and linear PVA was prepared by a way of solution polymerization. Approximately 1.0 g WSC was placed in a three-neck flask equipped with a stirrer, and the flask was put in a water bath to make sure that the whole process was carried out under a constant condition of 50 °C. About 10 ml $K_2S_2O_8$ (20 g/L) and 4 ml $(NH4)_2Ce(NO_3)_6$ (10 g/L) were transferred into the flask to trigger the reaction, stirring for 15 min, and then 3.3 ml Na_2SO_3 (20 g/L), 2 g urea and 10.0 g AA with a 75% neutralization degree were added in proper order. After 15 min, during which the graft copolymerization reaction happened between AA and WSC, 2 ml cross-linker MBA (20 g/L) was added. Finally, 1.6 g K_2HPO_4 and 33.3 ml PVA (60 g/L) were put in after 45 minutes. Keeping stirring for additional 4 h, the polymerization reaction was completed and the resulting product could be obtained after drying the mixture to a constant mass. The obtained products need to be milled and sifted through three different screens of 20, 40 and 60 mesh, and then they were stored for further use.

2.3. Characterization

The Fourior-transform infrared (FTIR) of the prepared WSC-g-PAA/PVA/NP was achieved from a NEXUS-470 series FTIR spectrometer (Thermo nicolet, NEXUS). The pellets employed in FTIR analysis were made by mixing powdered samples with KBr. The variation of external morphology of samples was probed using a Hitachi S-520 SEM instrument (Tokyo, Japan), and the particle samples were oiled by gold under vacuum conditions before observing. The fertilizer (N and P) contents of WSC-g-PAA/PVA/NP were examined by an Energy Dispersive Spectrometer instrument (Elementar Vario EL III, Germany).

2.4. Study of water absorption and fertilizer release properties

2.4.1. Measurement of swelling and fertilizer release

The samples of 0.20 g was soaked in adequate distilled water for about 5 h until the gels reached the swelling equilibrium under static state (at room temperature). Then the swollen gels were separated from water using a 100-mesh gauze and weighted. The water absorbency Q_{eq} (g/g) of the samples could be calculated according to the following equation:

$$Q_{eq} = \frac{M - M_0}{M_0} \tag{1}$$

where M(g) and M_0(g) imply the mass of swollen and dried gels, respectively.

To determine the release behavior of nitrogen and phosphorus fertilizers from WSC-g-PAA/PVA/NP in water, the following procedures were conducted: an accurate mass of 1.0 g dried samples were bathed in 1000 ml distilled water bottled in Erlenmeyer flask equipped with a stopper under unstirred condition. Approximately 2 ml of immersion solution was drawn out from the flask at various moment to detect the release quantity of fertilizer (nitrogen and phosphorus) using a UV–visible spectrophotometer. Then, the percentage of fertilizer release can be calculated by:

$$\text{Fertilizer release (\%)} = \frac{0.5 \times C_i}{0.2 \times C} \times 100\% \tag{2}$$