



# Starch-based hydrogel loading with carbendazim for controlled-release and water absorption



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## ABSTRACT

Starch, with properties of eco-friendliness and abundance, is one of the most important natural polymers. Starch-based hydrogels were investigated as carriers of carbendazim to combine controlled-release and water absorption (WA). Three carbendazim-loaded hydrogels (CLHs) with different WA capacities were prepared by solution polymerization. The CLHs were characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and liquid-chromatography mass-spectrometry (LC-MS/MS). Release kinetics of CLHs was investigated using  $^{14}\text{C}$ -labeling method. The diffusion parameters of CLHs were 0.47, 0.57 and 0.81 in deionized  $\text{H}_2\text{O}$  ( $\text{ddH}_2\text{O}$ ). WA affected release profile significantly, the release longevity reaching 240 h when WA was 800 g/g in  $\text{ddH}_2\text{O}$ . Solution pH influenced release profiles and the lowest release rate occurred in the lowest pH. Addition of CLH (1.3 g/kg soil) markedly increased water-holding capacity (WHC) of soil by 8.2%. The study indicated that starch-based CLH was a good controlled-release agent for carbendazim and water absorbent for soil.

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## 1. Introduction

Fungicides are essential to disease control and maintenance of agricultural production (Singh, Sharma, & Gupta, 2009). Carbendazim, a widely used fungicide, is used to control and prevent a wide range of fungal diseases of crops (Anastassiades & Schwack, 1998; Itak, Selisker, Jourdan, Fleeker, & Herzog, 1993; Wang et al., 2009; Yu, Chu, Pang, Xiang, & Fang, 2009). When applied by conventional methods, carbendazim is invariably subject to wastages like photo-degradation, leaching, etc. (Sun et al., 2014), thus, frequent application is needed. However, excessive use of carbendazim can cause undesirable effects on humans. Its detection in tomatoes and wastewater has caused public concerns (Bollmann et al., 2014; Liu et al., 2014). Therefore, there is an urgent need to develop a new method for carbendazim application. The use of various delivery systems, including microcapsules, microspheres, and beads is

effective at decreasing wastage of agrochemicals (Freiberg & Zhu, 2004; Jarosiewicz & Tomaszewska, 2003; Taki, Badens, & Charbit, 2001). The fungicides thiram and tebuconazole have been loaded into polymers for slow-release (Asrar, Ding, La Monica, & Ness, 2004; Singh et al., 2009).

Large parts of the world, especially in China, are arid and semi-arid regions. Soil in these areas has weak WHC and does not efficiently retain rain water. Hydrogels are polymeric network structures that can absorb large amounts of water and retain water for specific periods (Liu, Miao, Wang, & Yin, 2009; Tong & Zhang, 2005). Recently, there has been an increased interest in the use of natural polysaccharides based hydrogels in the fields of agriculture (Thakur & Thakur, 2014a) due to their enormous advantages such as economic/low cost, biodegradability, acceptable specific strength, low density, good thermal properties, recyclability, no health risk, bounty and enhanced energy (Thakur, Thakur, & Gupta, 2013a; Thakur, Thakur, & Gupta, 2013b; Thakur, Gupta, & Thakur, 2014a; Thakur, Thakur, & Gupta, 2014b; Thakur, Thakur, Raghavan, & Kessler, 2014c). Natural polysaccharides such as starch, cellulose (Thakur et al., 2014a,b,c), chitosan (Thakur & Thakur, 2014b), lignin (Thakur & Thakur, 2015; Thakur et al., 2014a,b,c), alginate and psyllium polysaccharide (Thakur & Thakur, 2014a) are well-known examples of bio-renewable resource for environmentally friendly hydrogels. Among various types of natural polymers, starch

**Abbreviations:** CLH, carbendazim-loaded hydrogel; WA, water absorption;  $\text{ddH}_2\text{O}$ , deionized  $\text{H}_2\text{O}$ ; LC-MS/MS, liquid-chromatography mass-spectrometry; WHC, water-holding capacity; PBS, phosphate buffer solution; AA, acrylic acid; MMA, methyl methacrylate; AM, acrylamide.

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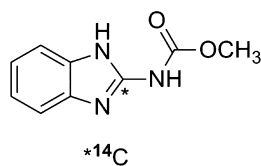


Fig. 1. Chemical structure of  $^{14}\text{C}$ -labeled carbendazim.

based hydrogels have attracted great attention all over the world because of economical effectiveness, environmental friendliness and easy modification with vinyl monomers onto it. The  $-\text{OH}$  on the anhydroglucose unit of starch has the potential to form complex copolymer networks, which often has the property of absorbing large amounts of water (Zhang et al., 2013).

Replacement of conventional application of agrochemicals by a combination of controlled-release and water absorption systems has received much attention. Fertilizers, pesticides cypermethrin and micronutrients copper sulfate have been successfully incorporated into hydrogels (Liang & Liu, 2006; Rudzinski, Chipuk, Dave, Kumbar, & Aminabhavi, 2003; Yang, Tong, Geng, Li, & Zhang, 2013). However, there are few reports on hydrogels loading carbendazim.

In this work, CLH with specific WHC and slow-release properties were prepared in two steps. The release behaviors of CLH in  $\text{ddH}_2\text{O}$  and phosphate buffer solution (PBS) were learnt. The effects of WA on release profiles and kinetics were investigated. What's more, the influences of pH and salt ion on the release rate were also determined.

## 2. Materials and methods

### 2.1. Materials

Cassava starch was from Heyu (China). Acrylamide (AM), potassium peroxydisulfate (KPS),  $N,N'$ -methylenebisacrylamide (MBA), 2,2'-azobis(2-methylpropanimidine)dihydrochloride (AIBA, 99%) were from Sinopharm (China). Acrylic acid (AA) and methyl methacrylate (MMA, 99.0%) were from Aladdin (USA). Non-labeled carbendazim (96%) was obtained from Sigma-Aldrich (Germany).  $^{14}\text{C}$ -carbendazim (>97% radiochemical purity and chemical purity,  $5\ \mu\text{Ci}/\text{mg}$  specific radioactivity) was from Radio-labeled Chemicals (USA). The structure and radioactive marker position for carbendazim were shown in Fig. 1. Scintillation grade reagents 1,4-bis(5-phenyloxazolyl)-benzene (POPOP) and 2,5-diphenyloxazole (PPO) were from Arcos Organics (Geel, Belgium). Scintillation cocktails were used as assistant solvent to quantify radioactivity (Wang et al., 2013). Ingredients of cocktail were as follows: 6.0 g of PPO, 0.4 g of POPOP, 350 mL of glycol ether, and 650 mL of dimethylbenzene.

### 2.2. Preparation of carbendazim-loaded beads

The starch-*g*-(acrylic acid-*co*-methyl methacrylate) ((starch-*g*-(AA-*co*-MMA)) beads were synthesized as follows. A mixture of 1 g of dry starch and 14 mL of  $\text{ddH}_2\text{O}$  was stirred vigorously under a  $\text{N}_2$  atmosphere and reflux condensing condition. The mixture was then heated at  $85\ ^\circ\text{C}$  for 30 min to allow gelatinization of starch. The gelatinized starch was divided into two parts, Part1: 1/3 of starch paste (volume) was directly used in the synthesis of carbendazim-loaded beads; Part 2: 2/3 of starch paste (volume) was used in the synthesis of hydrogel.

A predetermined quantity of carbendazim was dissolved in 1.5 mL of AA, and the resulting solution was introduced into a reaction flask containing 9 mL of  $\text{ddH}_2\text{O}$  and 1.5 mL of MMA. The flask was immersed in a temperature-controlled water bath and stirred mechanically at a speed of 300 rpm. After the mixture was

Table 1  
Water absorption (WA) of H1, H2, and H3.

Hydrogel	Molar ratio (NaOH/AA)	WA in $\text{ddH}_2\text{O}$ (g/g)	WA in tap water (g/g)
H1	0.95	800	160
H2	0.80	500	140
H3	0.60	250	90

gradually heated to  $70\ ^\circ\text{C}$ , 0.05 g of AIBA followed by the addition of 1/3 volume (Part 1) of gelatinized starch to the system to form the beads. Reaction under a  $\text{N}_2$  atmosphere with reflux condensation was proceeded for 5 h. The product (labeled as mixture 1), was directly used for the next step. In mixture 1, active carbendazim was present both in starch-*g*-(AA-*co*-MMA) beads and in the solution in which the beads were dispersed.

### 2.3. Preparation of CLH

AA, which was partially deprotonated by various amount of NaOH (5 mol/L), was mixed with AM, KPS, MBA which had been dissolved in  $\text{ddH}_2\text{O}$ . The resulting solution was then blended with the remaining 2/3 volume of starch paste (Part 2) in flask under vigorous stirring to obtain mixture 2.

Mixture 2 was blended with mixture 1, which had been cooled to room temperature. Blending was continued with increasing temperature (up to  $70\ ^\circ\text{C}$ ) until a rubbery product was obtained. The product was then dried, grounded, and sieved to obtain a uniform powder.

By changing the amount of NaOH in mixture 2, three samples with various NaOH/AA molar ratios (0.95, 0.80 and 0.60) were prepared and named as H1, H2 and H3 shown in Table 1.

### 2.4. Characterization

Samples of carbendazim, CLH, and bead powder were mixed with KBr for FTIR spectroscopy using a Bruker Vector-22 FTIR spectrophotometer (Germany). The morphologies and surfaces of the CLHs and beads were observed by TM-1000 SEM microscope (Japan).

### 2.5. Confirmation of carbendazim in CLH

$^{14}\text{C}$ -labeled carbendazim evenly mixed with nonlabeled carbendazim was used as tracer to confirm the carbendazim in CLH. The synthesis process of hydrogels loading  $^{14}\text{C}$ -labeled carbendazim was the same as the nonlabeled mentioned above, and the properties remained unchanged. A predetermined amount of CLH was immersed in 50 mL of  $\text{ddH}_2\text{O}$  in a conical flask, which was continuously oscillated for 24 h. The solution was then extracted thrice consecutively with dichloromethane. The dichloromethane phases were then combined and dried. The final extract was redissolved in methanol and passed through a  $0.22\ \mu\text{m}$  filter. The sample was analyzed by 6530 Accurate-Mass Q-TOF LC-MS/MS (Agilent, USA) with the ESI source operated in positive-ion mode.

### 2.6. WA test of the CLHs

Accurately weighed amounts of CLH samples were immersed in excess  $\text{ddH}_2\text{O}$  and tap water until swelling equilibrium was reached. Then the swollen CLHs were taken out and the excess water was removed by filtering through 100-mesh sieve. Weights of the swollen CLHs were measured. The WA capacity could be defined as follows:

$$\text{WA} = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

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