Preparation of Oligoalginate Immobilized Hydrogel by Radiation and Its Application for Hydroponic Culture

Le Quang Luan† and Duong Hoa Xo

Biotechnology Center of Ho Chi Minh City
2374 Highway 1, Trung My Tay Ward, District 12, Ho Chi Minh City
†lequangluan@gmail.com

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The nutrient immobilized hydrogel was prepared by γ-irradiation of carboxylmethyl cellulose (CMC) and polyacrylamide (PAM) supplemented with nutrient and oligoalginate. The gel fraction of prepared hydrogel was increased with increase of irradiation dose, while the swelling degree was decreased. The hydrogel prepared with 20% CMC, 20% PAM, 1% oligoalginate and nutrient at 15kGy irradiation was the best for the growth of plant. The oligoalginate immobilized hydrogel promoted the germination of seeds and growth of seedling plants. In hydroponic cultivation, the growth and development of plants on oligoalginate immobilized hydrogel were much better than that of plants growing on coir dust. The nutrient and oligoalginate immobilized hydrogel showed a promising application for hydroponics as a new technique for production of safety vegetables with high yield and quality.

Key Words: oligoalginate, carboxylmethyl cellulose, hydroponics, γ-ray irradiation, nutrient immobilized hydrogel

1. Introduction

Carboxylmethyl cellulose (CMC), which is the most popular and the cheapest cellulose ether, is an anionic linear polymer. This polymer was widely used for preparation of hydrogels by crosslinking using chemical agents such as AlCl₃, methylenebisacrylamide, divinylsulphone, or using radiation techniques with a special condition in paste. However, only some of CMC hydrogels have been used in agriculture for water control purpose, because the swelling of homopolymer hydrogel prepared from CMC is not so high. While, copolymer hydrogels prepared by grafting of functional monomers such as acrylic acid onto CMC and grafted hydrogels prepared by cross-linked polyacrylamide (PAM) chains onto CMC via a free radical polymerization method using irradiation were found to have many potentials for agricultural application such as: high swelling capacity; agrochemical absorbent and slow control release; ease of biodegradation.

In agriculture, the supplementation of agrochemicals is necessary for improving production of crop. Conventional application can result in excess amount of active substance causing the environmental pollution. Biodegradable polymer immobilized nutrient is proposed as a good materials for controlled-release nutrient. In addition, oligoalginate can be used as a growth promoter for plants. The present paper reports a study on preparation of an oligoalginate immobilized hydrogel by grafting of cross-linked PAM chains onto CMC using γ-irradiation as a novel material for agriculture and hydroponic.
2. Experimental

2·1 Materials

The polymers used in this study were sodium salt of carboxymethyl cellulose (CMC) with DS ∼0.91 and molecular weight (Mw) ∼5×10^5 supplied by Daicel Co. Ltd., Japan and cationic polyacrylamide (PAM) with Mw ∼6.5×10^6, charge density 150 C/g and cationicity of 19% provided by Cytec Industries Inc., West Paterson, NJ. Tested vegetables are Chinese mustard (Brassica juncea Var rugosa) and lettuce (Lactuca sativa). The hyponex nutrient with the content of 251.86 ppm N; 59.85 ppm P; 300.99 ppm K; 244.99 ppm Ca; 50.59 ppm Mg; 7.9 ppm Fe; 0.3 ppm B and 1.5 ppm Mn was supplied by Saigon Thuy Canh Corp. Oligoalginate with molecular weight ca. 14 kDa was prepared by radiation degradation of alginate described previously. The hydroponics system using deep flow technique was supplied by Saigon Thuy Canh Corp. Other chemicals were reagent grade and used without further purification.

2·2 Preparation of hydrogels

For preparing hydrogel, the nutrient was dissolved in water before adding CMC and/or polyacrylamide (PAM). The prepared mixture was kept overnight to complete the swelling and irradiated by γ-rays from a Co-60 source.

2·3 Determination of gel fraction and swelling

For determination of gel fraction and swelling, hydrogel samples were accurately weighted (W_o) and then extracted with distilled water using Soxhlet system for 6h. After extraction, the samples were dried in a vacuum oven at 80°C to a constant weight (W_1). The gel fraction was calculated according to the following equation:

\[
\text{Gel fraction (\%) } = \left( \frac{W_o}{W_1} \right) \times 100
\]

After the insoluble hydrogel (W_i) was immersed in distilled water for 48 h at room temperature, sample was weighted (W_2). The swelling was calculated according to the following equation:

\[
\text{Swelling (g/g) } = \left( \frac{W_2 - W_i}{W_i} \right)
\]

2·4 Germination ratio and growth of plants

The germination ratio and the growth and development of seedling plants on hydrogels were determined as follow: 30 g swollen hydrogel was put in a plastic pot, then placed the seeds on the surface of the gel. The germination ratio was recorded after 4 days and the root length, plant height, fresh biomass were determined after 14 days. Coir dust supplied with nutrient solution was used as the control.

2·5 Hydroponic cultural test

The hydrogels were tested in hydroponic system as follow: The seedling plants after 2 weeks were planted in a plastic pot containing 50 g swollen hydrogel, then applied into a hydroponic system using deep flow technique for cultivation. The control was carried out with coir dust instead of hydrogel and the nutrient solution was supplied in the same amount as the nutrient in the group using hydrogels. The root length, plant height, fresh biomass and dried matter content were determined after 28 days of cultivation. To determine the collapse of hydrogel, 50 g swollen gel was put into a pot and then applied in a hydroponic system, then the remaining gel was determined every week.

3. Results and discussion

Qiu et al. reported that 20% of CMC can be cross-linked to form hydrogel by irradiation of 10–40 kGy and the gel strength improved obviously with addition of activated carbon (5–10%). In this study, the effect of additives for the hydrogel preparation by radiation was investigated using 20% of CMC.
and 10–20% PAM. The hydrogel was prepared by irradiation of polymers after mixed with nutrient solution and analyzed the gel fraction at the dose of 10–30 kGy (Fig. 1). CMC in 20% solution can be crosslinked by irradiation and the gel fraction was 33–65% at 10–30 kGy (data not showed). The gel fractions of 20% CMC by irradiation were increased with the concentration of PAM. The gel fractions of irradiated samples were found at 49.2–76.2% by the addition with 10% PAM and 58.2–91.4% by the addition with 20% PAM, respectively. On the other hand, the gel fractions were decreased in addition with nutrient and the values were about 31.1–55.6% with 10% PAM and 36.7–72.8% with 20% PAM, respectively. The addition of oligoalginate is effective to recover the gel fractions with nutrient and the values were 39.2–66.8% with 10% PAM and 46.7–82.6% with 20% PAM, respectively.

These results showed that the supplementation of 1% oligoalginate in the sample contained 20% CMC, 20% PAM and nutrient, the gel fraction increased in 10% compared to that of the sample without supplemented of oligoalginate. Thus the supplementation of nutrient inhibited the gel formation, while the addition of oligoalginate increased the gel fraction of CMC and PAM by irradiation.

The swelling of the hydrogel prepared in Fig. 1 was analyzed and shown in Fig. 2. The swelling of hydrogels prepared with 20% CMC, 20% PAM, nutrient and oligoalginate were decreased with the increase of the irradiation dose. The reason is due to the increase of crosslinking point in hydrogels when the dose was increased. The swelling degree was dramatically reduced at dose range of 10–15 kGy and then it was gradually reduced at 20–30 kGy. The addition of nutrient in the mixture reduced the swelling degree of the hydrogels from 24.6 to 50.8 g/g compared to those of the non-addition ones, while the supplementation of oligoalginate enhanced the swelling degree of the hydrogels irradiated at 10–30 kGy from 8.4 to 18.9 compared to those of without supplemented samples. The reason may due to the cross-link of oligoalginate with PAM in the hydrogel network which lead to the increase of gel fraction after irradiation. Thus, the hydrogels prepared with the mixture of 20% CMC, 20% PAM, nutrient and oligoalginate were found to have gel fraction more than 36.7% (10 kGy) and swelling degree from 110 (30 kGy) to 351 (10 kGy) g/g.

Hu et al. informed that oligoalginate induced ger-
In this study, the effect of hydrogels entrapped with nutrient and oligoalginate for plant germination and growth of Chinese mustard was tested. Fig. 3 shows the effect of oligoalginate for the germination ratio of Chinese mustard seeds on hydrogels with 20% CMC, 20% PAM and nutrient. The germination ratio on hydrogels prepared by irradiation of 10 to 30 kGy was higher than that on coir dust supplemented with nutrient. The oligoalginate entrapped in hydrogel enhanced the germination and the best germination rate was found on hydrogels irradiated at 10 and 15 kGy. The research on the influence of hydrogel namely Agrisorb on the germination of lettuce and onion seeds reported by Pazderů and Koudela also pointed out that the moisture control by hydrogel is an important reason for enhancement of germination rate of the seeds. Therefore, the reasons for enhancing the germination rate of Chinese mustard seeds in this study may due to the suitable moisture level and the present of oligoalginate in the irradiated hydrogels.

Fig. 3 Germination of Chinese mustard seeds on hydrogels after 4 days. The seeds were immersed into the hydrogels and kept in dark condition and the germination rate were determined after 4 days. The coir dust containing nutrient solution was used as a control.

Fig. 4 Growth of 14 days seedling on hydrogel; (a): Plant height, (b): Root length, (c): Fresh biomass. The seedling plants after germination were kept in a greenhouse condition for 14 days and then the seedling plants were removed to determine growth and development indexes. The coir dust containing nutrient solution was used as a control.
On the other hand, oligoalginate has been proven to stimulate growth of rice and peanut plants cultivated hydroponically, root development of lettuce, elongation of carrot and rice roots. Recently, oligoalginate reported to increase shoot, root length, shoot dry weight, content of total chlorophylls and carotenoids and nitrate reductase activity involved in nitrogen assimilation, and alkaloid contents, mainly morphine and codeine, in opium poppy plants (*Papaver somniferum*). Furthermore Sarfaraz et al. also informed this component strongly increased shoot and root length of fennel plants (*Foeniculum vulgare*), the weight of fennel tubers, seed yield, content of total chlorophylls, carotenoids, and proline, nitrate reductase activity, and the level of essential oil. The growth of seedling of Chinese mustard on hydrogels with 20% CMC, 20% PAM and nutrient was analyzed after 14 days cultivation (Fig. 4). The plant height, root length and fresh biomass of seedlings grown on irradiated hydrogels were much better than that of seedling grown on coir dust. In addition, the hydrogel supplemented with oligoalginate enhanced the growth and development of seedling. The highest effect on growth and development of Chinese mustard seedling was obtained by the hydrogels prepared from the irradiation dose of 10 and 15 kGy. Thus, the hydrogels prepared at the doses of 10 and 15 kGy showed an optimum effect on the germination ratio and growth of Chinese mustard seedlings.

In the test of growth and development of vegetables on hydrogels in hydroponic cultivation, hydrogels of 20% CMC, 20% PAM, nutrient and oligoalginate were applied as substrates for growing of lettuce and Chinese mustard and the coir dust.
supplemented with nutrient was used as the control. The hydroponic system consists plastic pipes connected based on circulating method and deep flow technique as shown in Fig. 5 was applied for testing in this study. Fig. 6 and Fig. 7 show the growth of Chinese mustard and lettuce cultivated on hydrogels in hydroponic system, respectively. The parameters such as shoot height, root length and fresh biomass of Chinese mustard and lettuce grown on hydrogels were much better than that of plants grown on coir dust. The growth of plants on hydrogel irradiated at 15 kGy was better than that of plants grown on hydrogel irradiated at 10 kGy. In particularly, compared to the growth on coir dust, the shoot height, root length, fresh biomass and dried matter content of Chinese mustard grown on hydrogel were increased 34, 48, 62 and 14% respectively, while that of lettuce were increased 34, 333, 265 and 19%, respectively. The results show that the supplementation of oligoalginate significantly promotes the growth and development of tested vegetables in hydroponic system. These result indicated the potential application of this hydrogel for agriculture and horticulture as well.

Fig. 8 showed that the degree of collapse for the hydrogels of 20% CMC, 20% PAM and nutrients irradiated at 15kGy was almost the same with and without oligoalginate during 5 weeks applying in hydroponics culture. This result indicated that oligoalginate may not crosslinked with CMC and PAM. On the other hand, the remaining contents of oligoalginate immobilized hydrogel were 72.8% after 1 week and 44.7% after 2 weeks in hydroponics system. In
hydroponics culture, beside supply the nutrient, the hydrogel is also used as a matrix for keeping the vegetables standing in system. The remaining hydrogel was enough for vegetables standing in the culture system for 2 weeks (Fig. 9). The hydrogel was collapsed 84.2% after 3 weeks, 93.8% after 4 weeks and the gel was completely collapsed after 5 weeks application in hydroponics system. The results also showed a suitable application that the harvested product after five weeks cultivation will not contain the matrix that may caused some drawback in collected product and environmental pollution.

4. Conclusions
The nutrient and oligoalginate immobilized hydrogel prepared by γ-irradiation was effective for the germination of seeds and the growth of lettuce and Chinese mustard in hydroponic cultivation. The optimum condition for plant growth was the hydrogel...
of 20% CMC, 20% CMC, nutrient and oligoalginate irradiated at 15 kGy resulting of 62% gel fraction and 187 g/g swelling. The hydrogel was completely collapsed after 5 weeks used in a hydroponic system. The nutrient and oligoalginate immobilized hydrogel showed a promising effect for application in hydroponics culture, a new technique for production of high yield and high quality vegetables, and environmental protection as well.

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