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Radiation Degradation of Xanthan Gum for Use as Bioadhensive to Improve the Efficiency of Foliar Fertilizer

Nguyen Van Binh, Hoang Dang Sang, Tran Xuan An, Nguyen Thi Thơm, Tran Bang Diep, and Tran Minh Quynh
Hanoi Irradiation Center, Vietnam Atomic Energy Institute, Vietnam

Abstract: In this study, xanthan powder were irradiated at dose of 0-1000 kGy, and 2% xanthan solutions were irradiated at doses of 0-150 kGy under gamma ray to prepare low molecular weight (Mw) xanthan for further application. Apparent viscosity and average viscosity molecular weight of irradiated xanthan much decreased by gamma irradiation as the functions of radiation doses. In solid state, the dose higher than 500 kGy required to obtain the radiation-degraded xanthan with Mw below 0.1×10^6 g/mol, but it was about 50 kGy for the xanthan in aqueous solution. Wettability of some irradiated xanthan were observed to utilize them as adjuvants in foliar fertilizer. The results suggested that irradiated xanthan XT2 with relative low Mw and high wettability can be use as a good adjuvant to improve the efficacy of super NPK 3-18-19 fertilizer in cabbage production in the field tests.

Key words: xanthan, gamma irradiation, viscosity, adjuvant, foliar fertilizer

1. Introduction

Xanthan is a natural polysaccharide produced by *Xanthomonas campestris*, a plant pathogenic bacterium that causes black rot disease of cruciferous plants such as broccoli, cabbage, cauliflower, and other leaf vegetables. To be a hydrophilic and water soluble polysaccharide with a specific solution and rheological properties, xanthan has been widely used as a food additive or rheology modifier in the food industry and other industries (textile, ceramics, paint, petroleum, cosmetic...) [1].

In agriculture, xanthan can act as a binder and/or an adhesive agent to prolong contact of agrochemicals with crops, control the drift of fungicide, herbicide, pesticide and fertilizers after spraying [2]. However, its large molecular size with weak intermolecular forces produces very high viscous solutions even at a low concentration, somewhat limited the application of xanthan in practice. Therefore, some methods have been studied to prepare low molecular weight (Mw) xanthan for further application. It found that xanthan is not easy to be decomposed by enzymatically [3] and chemical hydrolyses [4], but low Mw xanthan can be prepared by irradiation degradation [5].

Xanthan contains a β-glucan backbone with acidic saccharide residues, which are similar to some known elicitor active oligosaccharides [6, 7]. Polysaccharide based elicitors can induce phytoalexin production and some radiation degraded polysaccharides [8] or oligosaccharides [9] stimulate the defence response in plants even at very low concentration. Therefore, it can be predicted that the low Mw degraded xanthan not only can be used as a bio-adhesive agent, but also can act as an elicitor for plants.

Recently, gamma irradiation has been proved as a useful tool to degrade marine polysaccharides such as chitosan, alginate… into smaller molecules, which can be used as bioactive substances [10-12]. Their studies

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Corresponding author: Tran Minh Quynh, Ph.D.; research areas/interests: radiation technology, applied polymer science; environmental biology. E-mail: tmqthuquynh@gmail.com

revealed that the bioactivities of radiation degraded polysaccharides were higher than those of initial ones, then the irradiated chitosan can be used as plant growth promotor (PGP) [11], plant immuno-stimulants [12]. Similar to marine polysaccharides, xanthan and other biopolymers can be degraded by gamma irradiation for further applications. By irradiation of xanthan under gamma rays at a dose of 40 kGy, Li Yanjie et al., found that the resulting degraded xanthan exhibited a higher biocompatibility, which can be used as a stabilizer in food processing. Their results also indicated that the properties of xanthan irradiated with a dose range of 0-500 kGy in solid-state varied greatly, and its molecular weight of xanthan irradiated at 10 kGy much decreased from about $1.71\text{-}2.23\times10^6$ to 1.59×10^4 $g.mol^{-1}$ by irradiation at 500 kGy [13]. Thus, the low molecular weight xanthan can be prepared from commercial xanthan by radiation treatment.

The present study aims to investigate the gamma radiation effects on xanthan in both solid and solution states in order to prepare low Mw radiation degrade xanthan. The effects of various concentrations of low Mw xanthan on the efficiency of foliar fertilizer were also investigated with cabbage production.

2. Material and Methods

A commercial grade xanthan was purchased from Deosen Biochemical Ltd., China. Super NPK 3-18-18 is popular foliar fertilizer for vegetables. NaCl, KCl and other chemicals were bought from Merck and Wako Pure Chemical Ind. Ltd., Japan.

Xanthan in powder and 1% solution were packed in plastic bottles and irradiated under gamma ^{60}Co source at Hanoi Irradiation Center with dose ranges of 0-1000 and 0-200 kGy, respectively.

2.1 Measurements

The 0.5% xanthan solutions were prepared from irradiated xanthan samples, and their apparent viscosities were measured at 25±1°C by using a Brookfield DV-II viscometer with a spindle LV2.

Intrinsic viscosity of xanthan denoted by [η] is a useful experimental parameter in the dilute solutions, where polymer chains are separate, and the [η] of a polymer in solution only depends on the dimensions of the polymer chains. Viscosity data of dilute solution can be used to determine the [η] by extrapolating the specific viscosity (η_{sp}) divided by concentration (c) to zero concentration as the following equation:

$$[\eta] = \lim_{c\to0}\frac{\eta_{sp}}{C} \qquad (1)$$

Viscosity average molecular weight (Mν) of xanthan were determined from intrinsic viscosity using the Mark-Houwink-Sakurada equation:

$$[\eta] = K \times (M\nu)^a \qquad (2)$$

where Mark-Houwink parameters are $K = 2.79\times10^{-5}$ dL/g, and a = 1.2754 for xanthan in NaCl 0.01M, measured at 25°C [14].

Wetting of hydrophobic leaf surface is commonly improved by adding non-ionic surfactants or other adjuvants, which can act as adhesive or moisturizer. Water retention or wettability of the xanthan and irradiated xanthan solutions were measured by contact angle between an aqueous droplet and model surface using image J software [15].

In this experiment, the low Mν xanthan with relative low viscosity and high wettability, obtained by gamma irradiation was chosen as an adjuvant for Super NPK 3-18-18 fertilizer to improve the viscosity and adhesion of foliar fertilizer to the leaf surface. The 10 days old cabbage seedlings were transplanted at 40×60 cm in separate experiment plots of 8.4 m^2 for each treatment. The spraying solutions composed of 0.5% foliar fertilizer and 0 (Control), 25 (T1), 50(T2), 75(T3), 100 ppm (T4) irradiated xanthan were applied to cabbage leaves on 15, 30 and 45 days after planting at the level of 200 litters per ha. Yield of cabbage heads was recorded by harvesting the whole plot, and the effect of xanthan on the efficacy of foliar fertilizer was estimated.

3. Results and Discussion

3.1 Viscosity and Molecular Weight of the Xanthan Irradiated in Solid State

Xanthan is a high viscous polysaccharide with a large molecular size. In dilute salt solution, the viscosity of xanthan increases as a function of salt concentration, but this value decrease with salt content in concentrated solutions [16]. As mentioned in the previous study, the viscosity of xanthan solutions increased with polymer concentration, but it significantly reduced by radiation degradation [5]. In this study, apparent viscosities of 0.5% solutions of initial and irradiated xanthan were plotted as a function of radiation dose (Fig. 1). It was found that the viscosity of irradiated xanthan much decreased by gamma irradiation. This reduction was dose dependent. It was rapidly at a dose lower than 200 kGy and seemed to level off at a dose higher than 400 kGy. Similar results also reported by Murat Sen et al. when they study on the effects of gamma radiation on xanthan powder at room temperature [17].

To determine average viscosity molecular weight (Mv) of xanthan, dilute solutions of xanthan were prepared in NaCl 0.01 M and their relative viscosities were measured using a Ubbelohde 1B viscometer. Intrinsic viscosity and Mv of irradiated xanthan were calculated and presented in Table 1. The molecular weight of initial xanthan was about 2.69×10^6 g/mol, much reduced by radiation scission. The irradiated xanthan with Mv under 0.1×10^6 g/mol can be obtained by gamma irradiation at doses of 500 and 1000 kGy. Radiation degradation of β-(1→4) glycosic bonds in xanthan molecules produced smaller fragments with various sizes, and low molecular weight xanthan can be easily prepared by radiation scission. However, high radiation doses do not expected in practice.

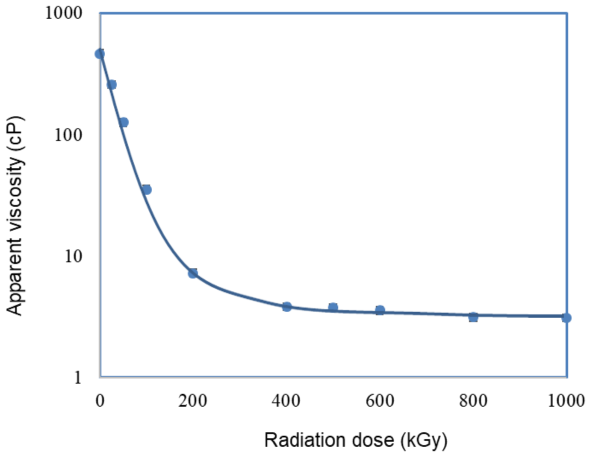

Fig. 1 Apparent viscosity of the xanthan irradiated at solid state as function of radiation dose.

Table 1 Effects of gamma radiation on intrinsic viscosity and molecular weight of xanthan irradiated at solid state.

Radiation dose (kGy)	Intrinsic viscosity (η, dL/g)	Average viscosity molecular weight (Mv, 10^3 g/mol)
0	4418.00	2685.707
25	1711.85	1277.059
50	1170.29	947.770
75	958.66	810.553
100	614.16	571.684
150	309.40	333.953
200	181.24	219.573
500	32.01	56.389
1000	6.61	16.360

3.2 Viscosity and Molecular Weight of the Xanthan Irradiated in Aqueous State

As one can be seen in Fig. 2, apparent viscosity of the xanthan solution irradiated by gamma radiation also much decreased. This may be explained by radiation scission of xanthan produced smaller molecules with improved mobility. Similar to the xanthan irradiated at solid state, the viscosity of xanthan solutions irradiated with gamma ray also reduced as a function of radiation dose. However, the reduction in the viscosity of the xanthan irradiated in aqueous solution was faster than that of the irradiated xanthan powder. These values of the xanthan irradiated at doses higher than 100 kGy were about 3 cP, similar to water. In the case of an aqueous solution, the free radicals produced by water radiolysis such as hydroxyl radical (OH^*), hydrated electron (e^-_{aq}) attacked and further accelerated the radiation scission of polymer in solution [18]. Radiation degradation resulted in a reduction in the average size (Mν) of xanthan as indicated in Table 2.

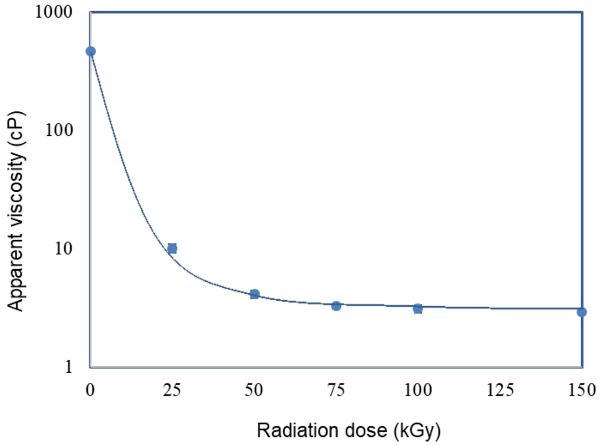

Fig. 2 Apparent viscosity of the xanthan irradiated at aqueous state as function of radiation dose.

Table 2 Effects of gamma radiation on intrinsic viscosity and molecular weight of xanthan irradiated at aqueous state.

Radiation dose (kGy)	Intrinsic viscosity (η, dL/g)	Average viscosity molecular weight (Mν, g/mol)
0	4418.00	2685.707
25	287.29	315.097
50	60.43	92.803
75	26.16	48.141
100	8.20	19.387
150	2.50	7.630

It is obvious that both viscosity and molecular weight of irradiated xanthan decreased with the increase of radiation dose, similar to radiation scission of xanthan in solid state. However, the irradiated xanthan with Mν below 0.1×10^6 g/mol obtained by irradiation at a dose of 50 kGy, much smaller than that for xanthan irradiated in solid state. Yanjie Li et al. also reported that solution of xanthan was a typical radiation degradation material, which can be broken at random under gamma irradiation [13]. The degradation of xanthan in aqueous solution depends on the amount of free radicals formed during radiation processing. Therefore, low Mν xanthan can be obtained by gamma degradation of xanthan solution at lower radiation dose.

3.3 Contact Angle

To utilize low Mw radiation degraded xanthan as an adjuvant to improve leaf wetting, prolong the contact of hydrophilic solutes on the plant leaf, the wettability of the 0.5% solutions of various irradiated xanthan were evaluated by the contact angle. In this experiment, 4 kind of radiation degraded xanthan having Mw within 1.0-2.0 (XT1); 0.6-1.0 (XT2); 0.3-0.6 (XT3) and $0.1\text{-}0.3\times10^6$ g/mol (XT4) were prepared from 2% solution of initial xanthan (XT0) by gamma irradiation. Fig. 3 shows the interactions of the droplets of these irradiated xanthans with a model surface. Adhesion of the droplet on the surface depended on Mw of xanthan. The lower the xanthan Mw, the smaller the contact angle. These results suggested that wettability and adhesion of the xanthan reduced by gamma irradiation. However, the high adhesion capacity of the xanthan may obstruct the penetration of nutrients through the plant tissues. Moreover, it is difficult to prepare the high concentrated solutions of high Mw xanthan. Therefore, the irradiated xanthan XT2 was chosen as an adjuvant to improve the efficacy of foliar fertilizer.

3.4 Effects of the Foliar Fertilizer Supplemented With Irradiated Xanthan on Cabbage Production

Various concentrations of the irradiated xanthan (XT2) was added to the solution of foliar fertilizer before spraying on plant leaf to investigate their effects on cabbage growth and production. As observed in Fig. 4, the cabbages fertilized with the fertilizer containing irradiated xanthan were growing faster, and some treated plants begin to form heads (red arrows). After harvesting, the yield of cabbage head per plot and yield increment were calculated and presented in Table 3. The addition of irradiated xanthan to foliar fertilizer resulted in the bigger cabbage heads. The highest yield was 41.18 kg per plot achieved by applying super NPK 3-18-18 supplementing with 75 ppm irradiated xanthan. This value about 11.48 % higher than that of the control fertilized by super NPK only. It was found that there were insignificant differences in the yield between the plants treated with the fertilizer supplementing with 50, 75, 100 ppm irradiated xanthan. Therefore, the XT2 of 50 ppm was suggested for cabbage production.

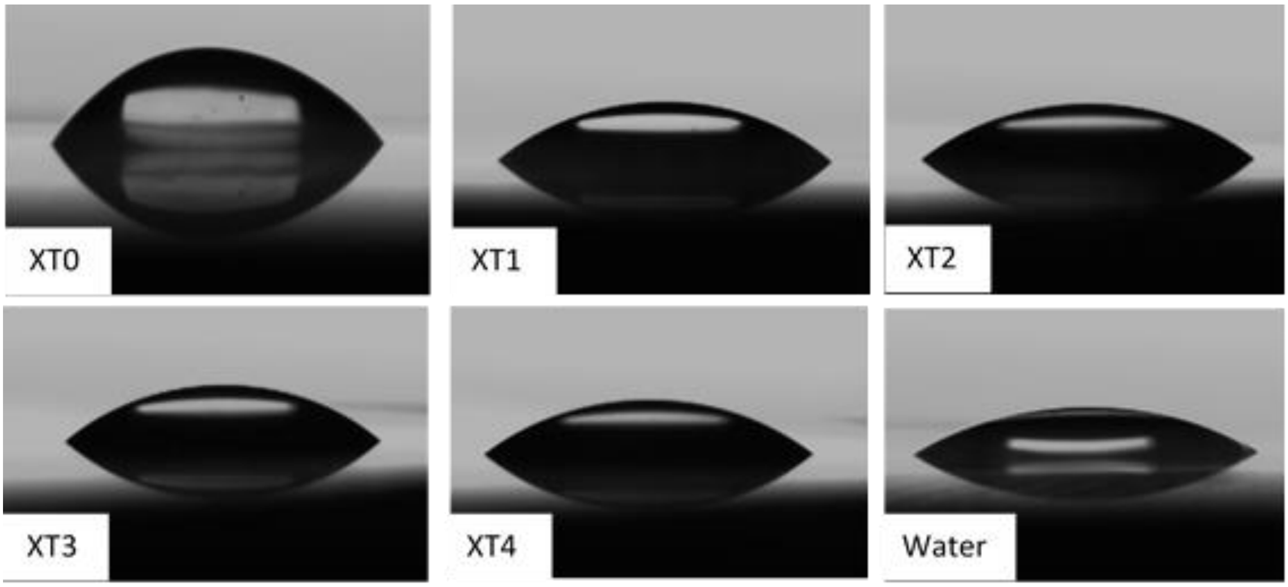

Fig. 3 Silhouette of the droplets of initial xanthan 0.5% (XT0); xanthan 0,5% irradiated at 37.5 (XT1); 55 (XT2); 70 (XT3) and 100 kGy (XT4); and pure water.

Fig. 4 Cultivation of cabbage without (control) and with irradiated xanthan in experimental plots.

Table 3 Effect of irradiated xanthan supplementing to spraying solution of foliar fertilizer on the production of cabbage.

Treatments	Yield per plot (kg)	Yield Increment (%)
Control (Super NPK 3-18-18)	36.94	-
T1 (Super NPK+25 ppm LXT)	38.98	5.52
T2 (Super NPK+50 ppm LXT)	40.99	10.96
T3 (Super NPK+75 ppm LXT)	41.18	11.48
T4 (Super NPK+100 ppm LXT)	40.82	10.50

4. Conclusion

The effects of gamma radiation on xanthan irradiated at both solid and aqueous states were investigated. The results revealed that radiation scission broke xanthan molecules into smaller fragments with lower viscosity and molecular weight. The reductions of apparent viscosity and average viscosity molecular weight of xanthan by gamma irradiation were dose dependent. And radiation degradation of xanthan in aqueous solution was stronger than that in solid state.

Contact angles of some radiation-degraded xanthan on the model surface were observed. The irradiated xanthan with relatively low viscosity and high wettability XT2 were chosen as an adjuvant that supplemented to super NPK 3-18-18 fertilizer for cabbage production. The results indicated that XT2 of 50 ppm is suitable to use as an adjuvant to improve the efficiency of foliar fertilizer for cabbage.

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References

[1] Anil Lackke, Xanthan — A versatile gum, *Resonane* (2004) 25-33.

[2] J. F. Mukerabigwi, Q. Wang, X. Ma, M. Liu, S. Lei, H. Wei, X. Huang and Y. Cao, Urea fertilizer coated with biodegradable polymers and diatomite for slow release and water retention, *J. Coat. Technol. Res.* 12 (2015) (6) 1085-1094.

[3] H. L. Liu, C. D. Huang, W. X. Dong, Y. G. Du, X. F. Bai and X. Z. Li, Biodegradation of xanthan by newly isolated Cellulomonas sp. LX releasing elicitor active xantho-oligosaccharides induced phytoalexin synthesis in soybean cotyledons, *Process Biochemistry* 40 (2005) 3701-3706.

[4] T. Sun, X. Y. Xiong, J. Xie, J. J. Liu and D. X. Zhou, Degradation and oxidation resistance of xanthan gum, *Hunan Agricultureal Science* 1 9(2010) 19-21. (in Chinese).

[5] Tran Minh Quynh, Nguyen Van Binh and Tran Xuan An, Preparation of low molecular weight xanthan by gamma radiation degradation, *Vietnam Science and Technology* 60 (2018) (3) (3) 41-44. (in Vietnamese).

[6] P. E. Jansson, L. Kenne and B. Lindberg, Structure of the extracellular polysaccharide from Xanthamonas capetris, *Cabohydrate Research* 45 (1975) 275-282.

[7] L. Q. Luan and N. H. P. Uyen, Radiation degradation of (1→3)-β-glucan from yeast with a potential application as a plant promoter, *International Journal of Biological Macromolecules* 69 (2014) 165-170.

[8] T. Kume, N. Nagasawa, S. Matsuhashi, N. S. Ishioka, F. Yoshii, L. X. Tham, N. Q. Hien, P. T. L. Ha, N. D. Lam and L. S. Reliev, Radiation degradation of carbohydrates and their biological activities for plants, *JAERI-Conf 2000-001*, 2001, pp. 166-169.

[9] R. A. Dixon, The phytoalexin response: Elicitation, signaling and control of host gene expression, *Biological Review* 61 (1986) 239-291.

[10] F. Yoshii, N. Nagasawa, T. Kume, T. Yagi, K. Ishii, L. S. Relleve, T. Puspitasari, T. M. Quynh, L. Q. Luan and N. Q. Hien, *Proceedings of the FNCA Workshop on Application of Electron Accelerator JAERI-Conf. 2003-016*, 2003, p. 43.

[11] Tran Minh Quynh, Nguyen Duy Lam and Fumio Yoshii, Antibacterial activity of radiation degraded carboxymethyl chitosan, *Nuclear Science and Technology* 2 (2012) 36-42.

[12] L. Q. Luan, N. Nagasawa, M. Tamada and T. M. Nakanishi, Enhancement of plant growth activity of irradiated chitosan by molecular weight fractionation, *Radioisotopes* 55 n(2006) 21-27.

[13] Li Yanjie, Ha Yiming, Wang Feng and Li Yongfu, Effect of irradiation on molecular weight and antioxidant activity

of xanthan gum, *Journal of Nuclear Agricultural Sciences* 24 (2010) (6) 1208-1213.

[14] M. Milas, M. Rinaudo and B. Tinland, The viscosity dependence on concentration, molecular weight and shear rate of xanthan solutions, *Polymer Bull.* 14 (1985) 157-164.

[15] C. D. Holder, Leaf water repellency of species in Guatemala and Colorado (USA) and its significance to forest hydrology studies, *J Hydrol* 336 (2007) 147-154.

[16] E. D. Vega, E. Vasquez, J. R. A. Diaz and M. A Masuelli, Influence of the ionic strength in the intrinsic viscosity of xanthan gum. An experimental review, *Journal of Polymer and Biopolymer Physics Chemistry* 3 (2015) (1) 12-18.

[17] Murat Sen, Hande Hayrabolulu, Pinar Taskin, Murat Torun, Maria Demeter, Mihalis Cutrubinis and Olgun Guven, Radiation induced degradation of xanthan gum in the solid state, *Radiation Physics and Chemistry* 124 (2015) 225-229.

[18] R. J. Woods and Pikaev A. K., *Applied Radiation Chemistry: Radiation Processing*, New York: John Wiley & Sons, Inc., 1994, pp. 352-355.