

Original Research Paper

# Calcium-sorbitol Chelating Technology and Application in Potatoes

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**Abstract:** Researches on low-molecular organic compounds are concentrated in amino acid and Humic acid chelating fertilizer, but few in sorbitol chelated calcium. In this study, selecting sorbitol as chelating agent, the technological conditions of chelating sorbitol with calcium and the effect of sorbitol chelated calcium on potato were studied. The impact factors on the stability of the fertilizer were investigated, including sorbitol dosage, pH value, chelating time and temperature. Then a field experiment was conducted on potato. Three treatments included water sprayed as a control, calcium nitrate and sorbitol chelated calcium sprayed. Each treatment had three replicates. The results showed that by orthogonal experiments, the sorbitol dosage has the greatest influence on the stability of the chelating system. The optimum conditions for the synthesis were determined as follows: The sorbitol dosage of 12 g, the chelating temperature of 50°C, the pH of 4 and the chelating time of 45 min. Compared with those of potatoes fertilized with inorganic calcium nitrate, the yield of potatoes sprayed with sorbitol chelated calcium increased by 14.23% and their marketable tuber percentage increased by 3.58%; the nitrate nitrogen content in potatoes decreased by 11.89%; the accumulation of phosphorus and potassium in potato tubers increased. Generally, the application effect of our prepared sorbitol chelated calcium on potato was remarkable.

**Keywords:** Sorbitol Chelated Calcium, Chelating Condition, Potato, Yield, Quality

## Introduction

It was reported that some organic substances (Tegeger, 2012) are often used as chelating agents in the development of medium and trace elements fertilizer, which can significantly promote plant growth and improve crop quality (Wu *et al.*, 2013). This kind of fertilizer, called chelating fertilizer, can be applied in combination with other solid or liquid fertilizers without chemical reaction and has obvious advantages over mineral fertilizers. EDTA (Doolette *et al.*, 2018), citric acid, tartaric acid and amino acids were used as chelating agents earlier (Trostle *et al.*, 2001; Alvarezfernandez *et al.*, 2005; Ziaulhasan *et al.*, 2010) and then humic acid (Parvan *et al.*, 2012). However, there may be ecological risks due to the source of raw materials (Shao *et al.*, 2001) or their degradation products (Anjos *et al.*, 2013), the application of above-mentioned chelating agents was restricted. Sorbitol, a natural substance extracted from phloem

juice of plants (Yaseen *et al.*, 2009) can be combined with mineral nutrient to produce stable low-molecular complexes. Researches showed that spraying sorbitol chelated calcium had better effect than spraying inorganic calcium nitrate (Ding *et al.*, 2015). When sorbitol chelated calcium was sprayed on the leaves, the speed of passing through the cuticle was faster than spraying inorganic calcium ions and sorbitol chelated calcium was more easily absorbed by leaves (Sawan *et al.*, 2001).

However, China has not yet issued national and industrial standards for the production and detection methods taking sorbitol as chelating agent. The domestic market of sorbitol chelating fertilizer is rather chaotic. The sorbitol chelated calcium fertilizers on the international market only focus on the concentration of total calcium, without specifying the proportion of chelated calcium. The chelating mechanism of sorbitol chelated calcium on crops is unclear.

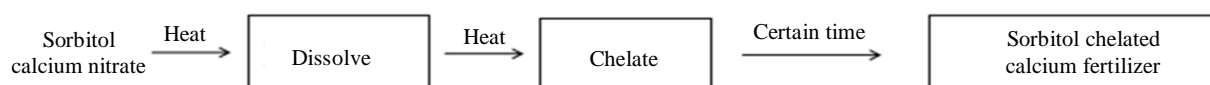


Fig. 1: Flow chart of chelation experiment

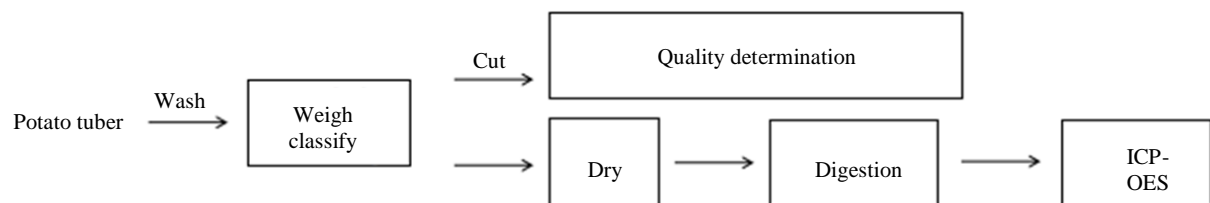


Fig. 2: Flow chart of potato experiment

Potato is an important crop, which has similar yield with corn, rice and wheat (Mlaviwa and Missanjo, 2019). Due to short maturity, potato can be produced almost all year round in some countries (Assa, 2012). There are many researches on the effect of exogenous calcium on potato yield and quality, but most of calcium are inorganic calcium salts (Li *et al.*, 2015; Xin *et al.*, 2008) and few studies follow the effect of sorbitol chelated calcium on potato.

Thus, in this study, the preparation technology of sorbitol chelated calcium was studied. Four main factors affecting fertilizer stability were investigated. Subsequently, potato plants were sprayed with the sorbitol chelated calcium and inorganic calcium nitrate on the leaf and their yield and quality were analyzed. It would provide theoretical basis for the synthesis and application of sorbitol chelated calcium.

## The Plan of the Experiment

### Chelation Experiment

The water system synthesis method was adopted (Predieri *et al.*, 2003). First, a certain amount of distilled water was heated to the reaction temperature. Then sorbitol and calcium salts were added into the aqueous solution in turn. Through single factor test, the optimum three levels of each factor were determined from pH (4.0, 7.0, 10.0, 13.0), chelating temperature (55°C, 60°C, 65°C, 70°C, 75°C, 80°C) and chelating time (15 min, 30 min, 45 min, 60 min). Then orthogonal test of four factors and three levels was designed and the optimum synthetic conditions were determined. The experimental flow chart are shown in Figure 1.

### Potato Experiment

In order to verify the application effect of sorbitol chelated calcium, a comparative experiment was set up: Treatment 1 (T1) potatoes were sprayed with water as control, treatment 2 potatoes (T2) and 3 potatoes (T3)

were sprayed with the equal amount of calcium nitrate and sorbitol chelated calcium, respectively. Three spays were applied by 4500 g/hm<sup>2</sup> Ca<sup>2+</sup> in the tuber formation stage, the peak tuber formation stage and the end tuber formation stage of potato plants. All the treatments were triplicated. The experimental flow chart are shown in Fig. 2.

The potato tubers were washed with distilled water to remove extraneous matter and weighed to record yield. Then tubers were dried to a constant weight at 110°C. The dried plant material was ground to pass through 0.5-mm sieve. One g of the ground material was dispelled. After digestion, 15 mL distilled water was added and the content filtered. Concentrations of nitrogen, phosphorus and potassium were determined using ICP-OES.

## Results and Discussion

### Chelation Experiment

#### Effect of Sorbitol Addition on Stabilization

From Fig. 3, the addition of sorbitol has a great influence on the stability of chelating fertilizer under the same conditions. When the amount of solvent was constant and the amount of sorbitol was 12 g or 16 g, chelating fertilizer had the best stability. Mass ratio of chelating agent to calcium ion is (1.45-1.94): 1. With the increase of sorbitol content, the stable period of chelating fertilizer was shortened. The amount of solvent also affected the stabilization time. When the amount of solvent was excessive, the concentration of sorbitol decreased, which reduced the contact probability between chelating agent and calcium ion. When the amount of solvent was too small, the reaction medium was insufficient and the chelating agent and calcium ion could not chelate adequately.

#### Effect of Chelating Temperature on Stabilization

When the amount of sorbitol was 16.0 g, the effect of chelating temperature on the stability of chelating

fertilizer is shown in Fig. 4. The stabilization time of sorbitol chelated calcium fertilizer did not change much when the system temperature rose from 55°C to 70°C. The stability of chelating fertilizer had reached a high level at 55°C. Further study is needed to determine the optimum temperature below 55°C. The stabilization time of sorbitol chelated calcium fertilizer showed a downward trend with the increase of temperature when the reaction temperature exceeded 70°C. And a small

amount of flocculent substance was observed at the bottom of the reactor. The reasons may be as follows: First, the structure of chelates was destroyed by excessive temperature; second, the equilibrium of chelates was affected by excessive temperature, which made the chelate dissociate. Therefore, excessively high temperature would have a negative effect on the stability of the chelating system (Sun *et al.*, 2017; Zhang *et al.*, 2010).

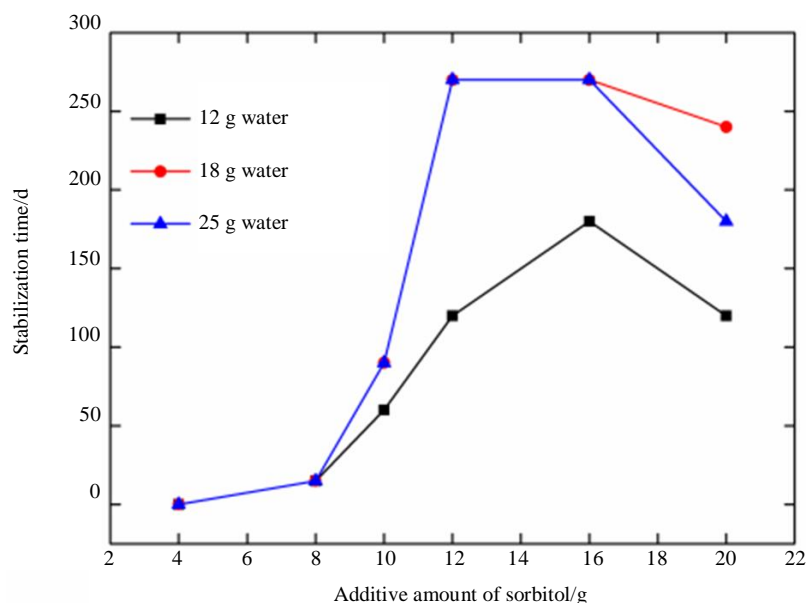


Fig. 3: Effect of addition of sorbitol on stabilization

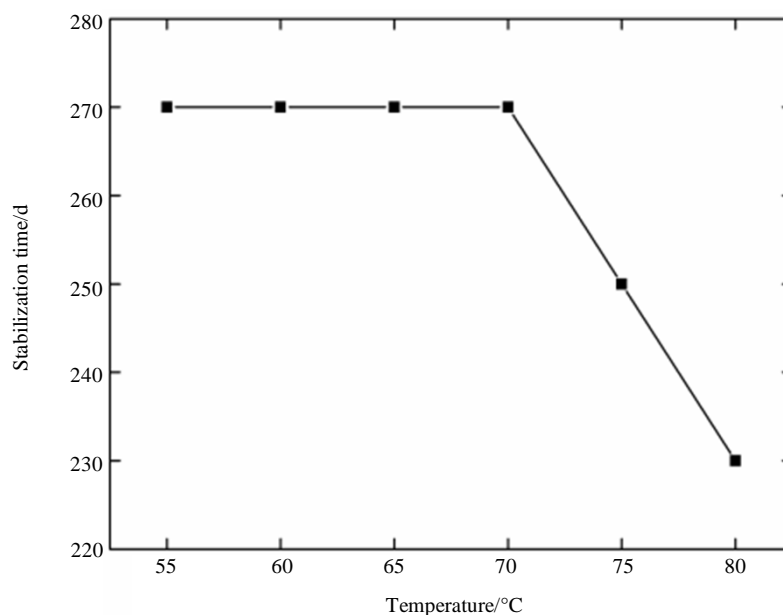


Fig. 4: Effect of chelating temperature on stabilization

### *Effect of pH on Stabilization*

Table 1 show that the stability of sorbitol chelated calcium decreased with the increasing pH. When the pH value was 4.0, the stability of sorbitol chelated calcium was better, because the compounds containing metal ions have higher solubility in acidic conditions and do not form hydroxides with OH<sup>-</sup>. When the pH value was 13.0, the stability of sorbitol chelated calcium became worse. There are two reasons: First, higher alkalinity destroyed the equilibrium of the reaction system; second, OH<sup>-</sup> and Ca<sup>2+</sup> formed calcium hydroxide precipitation in alkaline conditions, resulting in the emergence of solid substances in the solution. Therefore, under the relatively neutral conditions, ligands were less affected by H<sup>+</sup> and OH<sup>-</sup>, which were favourable to the stability of the system.

### *Effect of Chelating Time on Stabilization*

The experimental results are shown in Table 2. When the chelating time was only 15 min, solids were precipitated from chelating solution in a relatively short period of time. The reason is that the reaction between sorbitol and calcium is insufficient due to the short chelating time. When the chelating time was 30 min, the stabilization period of chelating fertilizer reached the maximum. With the extending chelating time, the stabilization mechanism of chelating fertilizer needs to be explained by further studies. Therefore, it is necessary to have a reasonable chelating time. The results from single factor test showed that the chelating time of 30 min was more suitable. From Table 1 and 2, the stabilization period was obviously increased when the amount of sorbitol was increased from 8 g to 16 g, which also proved that the addition of sorbitol has a great influence on the stabilization.

### *Optimization of Sorbitol Chelating Process*

On the basis of single factor experiment, the dosage of sorbitol was controlled to be 8 g, 12 g and 16 g, the chelating temperature was 50°C, 60°C and 70°C, the pH value was 4.0, 7.0 and 10.0 and the chelating time was 15 min, 30 min and 45 min. Orthogonal L9 (3)<sup>4</sup> test design was used to optimize the chelating conditions. The results of orthogonal test and extreme difference analysis are presented in Table 3.

The results showed that according to the R values, the primary and secondary order of factors affecting the stability of the system is A > D > C > B, namely, sorbitol additive dosage > chelating time > pH value > chelating temperature. Therefore, the best chelating condition was A2-B1-C1-D3, namely, the sorbitol additive amount was 12 g, the chelating temperature was 50°C, the pH value was 4.0 and the chelating time was 45 min. Under these conditions, the stabilization time of sorbitol chelated calcium fertilizer could be up to one year.

### *Potato Experiment*

#### *Effects on Yield and Commodity of Potatoes*

Table 4 shows yield factors of potato tubers under different fertilizer treatments. Compared with the blank control treatment, the total tuber yield of potatoes sprayed with sorbitol chelated calcium increased by 3.1%, while it decreased by 9.78% when being sprayed with calcium nitrate. High concentration of exogenous free calcium can reduce the yield of potato (Li *et al.*, 2015) and the absorption of chelated calcium by crops can effectively avoid the yield reduction. In addition, the large and medium tuber rate of potatoes increased with the two calcium fertilizers treatments, while the small tuber rate decreased. There was significant difference in large tuber rate between the two calcium fertilizers. The large tuber rate of potato sprayed with sorbitol chelated calcium was significantly higher than that treated with calcium nitrate. For the marketable tuber percentage, there was no difference between potatoes treated with calcium nitrate and the blank. The marketable tuber percentage of potatoes treated with sorbitol chelated calcium was 3.58% higher than that treated with calcium nitrate. Generally, the application effect of sorbitol chelated calcium on potato was better than that of calcium nitrate.

#### *Effects of Different Treatments on Quality and N/P/K Accumulations of Potatoes*

Table 5 shows that the content of soluble sugar in potato tubers increased and the content of nitrate nitrogen decreased with calcium fertilizer treatments. Compared with spraying calcium nitrate, the soluble sugar content of potatoes sprayed with sorbitol chelated calcium increased by 8.8% and the nitrate nitrogen content decreased by 11.89%. In addition, the application of calcium fertilizers could improve the absorption of phosphorus and potassium in potato tubers. The accumulation of phosphorus in potato tubers treated with calcium nitrate and sorbitol chelated calcium increased by 1.7% and 10.9% respectively and the accumulation of potassium increased by 6.4% and 11.7% respectively. Furthermore, the increase of phosphorus and potassium accumulation in potatoes sprayed with sorbitol chelated calcium was greater than that of calcium nitrate treatment. Therefore, the application of sorbitol chelated calcium could promote the absorption of phosphorus and potassium more effectively.

#### *Correlations Analysis*

Table 6 shows that sorbitol chelated calcium was positively correlated with yield, phosphorus accumulation and potassium accumulation, which indicates that chelating fertilizer had a significant impact on the three indicators. Sorbitol chelated calcium was negatively correlated with nitrate nitrogen content ( $r =$

-0.956). Spraying chelating fertilizer can effectively reduce nitrate nitrogen content in plants. The significant relationships between yield and quality indexes were as

follows: Yield and nitrate nitrogen content ( $r = -0.889$ ), yield and phosphorus accumulation ( $r = 0.846$ ), yield and potassium accumulation ( $r = 0.915$ ).

**Table 1:** Effect of pH on stabilization

pH Stabilization time(d)	8	12	16
pH Stabilization time/dsorbitol (g)			
4.0	21	270	270
7.0	21	270	270
10.0	21	250	250
13.0	16	200	200

**Table 2:** Effect of chelating time on stabilization

Chelatingtime/min	8	12	16
Stabilization time (d) sorbitol (g)			
15	10	150	150
30	21	270	270
45	21	270	270
60	21	270	270

**Table 3:** Analysis of L9 (3)4 test results

	A Additive amount of sorbitol (g)	B Chelating temperature (°C)	C pH value	D Chelating time (min)	Stabilization time (d)
1	8.000	50.0	4.0	15.0	015
2	8.000	60.0	7.0	30.0	021
3	8.000	70.0	10.0	45.0	021
4	12.00	50.0	7.0	45.0	270
5	12.00	60.0	10.0	15.0	150
6	12.00	70.0	4.0	30.0	270
7	16.00	50.0	10.0	30.0	250
8	16.00	60.0	4.0	45.0	270
9	16.00	70.0	7.0	15.0	150
k1	19.00	178.3	185.0	105.0	
k2	230.0	147.0	107.0	140.3	
k3	223.3	147.0	147.0	187.0	
R	211.0	31.3	78.0	82.0	

**Table 4:** Effects of calcium fertilizer applications on yield and commodity of potato

Index	Treatment		
	T1	T2	T3
Yield (kg/667m <sup>2</sup> )	3877.27±93.32 <sup>a</sup>	3498.19±202.16 <sup>a</sup>	3995.94±370.52 <sup>b</sup>
Large tuber rate (%)	62.50±4.81 <sup>a</sup>	69.59±4.62 <sup>a</sup>	67.51±4.10 <sup>b</sup>
Medium tuber rate (%)	16.67±4.81 <sup>a</sup>	19.30±4.57 <sup>a</sup>	25.22±4.31 <sup>a</sup>
Small tuber rate (%)	20.83±1.25 <sup>a</sup>	14.01±6.08 <sup>ab</sup>	7.26±1.26 <sup>a</sup>
Marketable tuber percentage (%)	70.83±2.41 <sup>a</sup>	79.26±4.67 <sup>a</sup>	82.10±3.27 <sup>b</sup>

**Table 5:** Effects of calcium fertilizer applications on tuber quality and N/P/K accumulation of potato

Content	Treatment		
	T1	T2	T3
Soluble sugar content (mg/g)	1.19±0.06 <sup>a</sup>	1.25±0.10 <sup>a</sup>	1.36±0.11 <sup>a</sup>
Nitrate Nitrogen Content (µg/g)	139.35±3.33 <sup>a</sup>	134.13±12.93 <sup>a</sup>	118.18±7.02 <sup>a</sup>
Soluble Protein Content (mg/g)	7.18±0.14 <sup>a</sup>	5.55±0.49 <sup>b</sup>	7.15±0.38 <sup>a</sup>
Accumulation of nitrogen (g/plant)	2.12±0.57 <sup>a</sup>	1.95±0.18 <sup>a</sup>	2.04±0.22 <sup>a</sup>
Accumulation of phosphorus (g/plant)	0.239±0.023 <sup>a</sup>	0.243±0.024 <sup>a</sup>	0.265±0.02 <sup>a</sup>
Accumulation of potassium (g/plant)	0.94±0.13 <sup>a</sup>	1.00±0.08 <sup>a</sup>	1.05±0.15 <sup>a</sup>

**Table 6:** Correlations analysis of various indicators

	Chelation or not	Yield	Nitrate Nitrogen content	Soluble sugar content	Accumulation of phosphorus	Accumulation of potassium
Chelation or not	1					
Yield	0.971**	1				
Nitrate Nitrogen content	-0.956**	-0.889*	1			
Soluble sugar content	0.703	0.593	-0.876*	1		
Accumulation of phosphorus	0.943**	0.846*	-0.988**	0.865*	1	
Accumulation of potassium	0.889*	0.915*	-0.913**	0.776	0.838*	1

## Conclusion

The influence of preparation technology of sorbitol chelated calcium on its stability was discussed. Stabilized sorbitol chelated calcium fertilizer can be prepared by controlling reaction conditions. According to single factor test and orthogonal test, the factors affecting the stability of sorbitol chelated calcium were determined as follows: Dosage of sorbitol additive amount > chelating time > pH value > chelating temperature. The optimum process parameters were obtained by adjusting the reaction conditions. But there is still a lot of work to be further explored, such as the stability of sorbitol chelated calcium under external forces such as ultrasound, oscillation, high-speed centrifugation and the qualitative analysis of the separated and purified chelated calcium by spectrophotometry and conductivity methods.

The effect of calcium fertilizer on potato has been confirmed by many studies (Liu *et al.*, 2011; Palta, 2010), but the effect of sorbitol chelated calcium on potato growth has not been studied systematically. The plants experiment revealed that sorbitol chelated calcium enhanced yield of potatoes. Compared with inorganic calcium fertilizer, sorbitol chelated calcium can effectively promote the absorption and utilization of main nutrients in soil and improve the quality of potatoes. In future, the following study should focus on the effects of sorbitol chelated calcium fertilizer on soil ecological environment by developing analytical methods.

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## Author's Contributions

**Pengchao Li, Tengsheng Li and Qianqian Wei:** Participated in all experiments, coordinated the data-analysis and contributed to the writing of the manuscript.

**Cunzhen Geng, Lingyu Li and Dongyun Yan:** Designed the reached plan and summarized the experimental data and approved the final manuscript.

## Ethics

The authors declare their responsibility for any ethical issues that may arise after the publication of this manuscript.

## Conflict of Interest

The authors declare that they have no competing interests. The corresponding author affirms that all of the authors have read and approved the manuscript.

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