Mechanism of Polyglutamic Acid Inhibition of Calcium Phosphate Precipitation in Salt Solutions (Postprint)

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Abstract

Improving the phytoavailability of phosphorus nutrients in saline-alkali soils represents a critical research priority in saline-alkali agriculture. Polyglutamic acid (-PGA) is recognized for its favorable fertilizer retention and slow-release properties; however, the underlying mechanisms remain unclear. This study elucidated the mechanism through which polyglutamic acid suppresses calcium phosphate precipitation in salt solutions via simulated evaporation-crystallization experiments, utilizing online measurements of salt solution pH and electrical conductivity (Electricity conductance), together with thermodynamic parameter measurements of interactions among salt solution components and between individual components and -PGA. Experimental results revealed that during evaporation, the salt solution pH initially increased continuously, followed by a continuous decrease. In the presence of -PGA, the time required to reach the inflection point where pH transitions from rising to falling was significantly extended, demonstrating that -PGA markedly retards the precipitation of calcium minerals (e.g., HAP and calcium carbonate). This retardation effect primarily correlates with pronounced differences in complexation behavior between -PGA and various salt ions. Although the HPO42-Ca2+ complex exhibits greater stability than -PGA-HPO42- and -PGA-Ca2+ complexes, -PGA provides binding sites for Ca2+ that are two orders of magnitude more abundant than those of HPO42-Ca2+. Consequently, substantial Ca2+ in the salt solution becomes complexed by -PGA, thereby inhibiting HPO42-Ca2+ reactions and subsequent precipitation of calcium phosphate minerals. While -PGA can delay calcium mineral precipitation, it exerts no significant influence on the crystalline products formed upon complete solution evaporation. The findings indicate that -PGA can enhance plant P nutrient utilization efficiency in saline-alkali soils by preventing phosphate-Ca2+ precipitation and serve as a slow-release P fertilizer agent through formation of highly stable complexes with HPO42-. Further investigation of -PGA application in actual soil solutions and soils is warranted.

Full Text

Mechanism of Poly-glutamic Acid for Inhibiting Precipitation of Phosphate and Calcium during Vaporization and Crystallization

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Abstract: Improving the phytoavailability and slowing the release of phosphorus fertilizer in salinized soil represents an important research topic. Poly-glutamic acid (-PGA) is considered a promising fertilizer with nutrient-preserving capability and slow-release properties. However, the underlying mechanisms of these functions remain poorly understood. This study investigated these mechanisms through simulated evaporation and crystallization experiments using salt solutions containing various concentrations of -PGA. The solution pH and electrical conductivity (EC) were monitored in real time, thermodynamic interactions between -PGA and salt components were quantified using Isothermal Titration Calorimetry (ITC), and precipitation products were analyzed by X-ray diffraction (XRD). The results demonstrated that salt solution pH initially increased then decreased with evaporation time. The presence of -PGA significantly postponed the inflection points of these pH changes, indicating substantial inhibition of calcium precipitate formation, including hydroxyapatite (HAP) and calcite. This inhibitory effect was closely related to the complexation capacity of -PGA with ions in the salt solution. Although the HPO ^{2}-Ca^{2} complex exhibited much higher stability than -PGA-HPO ^{2} and -PGA-Ca^{2} complexes, the number of binding sites for -PGA-Ca^{2} was two orders of magnitude greater than those for HPO ^{2}-Ca^{2}. Consequently, most Ca^{2} ions bound to -PGA, thereby inhibiting their interaction with HPO ^{2} and subsequent precipitation during vaporization. However, -PGA had minimal effect on the types of precipitates and crystals formed. This study reveals that -PGA possesses strong Ca^{2} binding capacity that effectively competes against calcium-phosphate precipitation, thus enhancing phosphorus phytoavailability in salinized soil and slowing phosphorus release through robust -PGA-phosphate complexation.

Keywords: -PGA; phosphate; vaporization; crystallization; ITC

Introduction

Poly-glutamic acid (-PGA) has attracted considerable attention as a fertilizer additive with nutrient-preserving and slow-release capabilities. Despite its demonstrated potential, the molecular mechanisms through which -PGA modulates nutrient availability in saline environments remain inadequately clarified. To elucidate these mechanisms, we conducted systematic investigations of -PGA effects on salt crystallization dynamics and phosphate precipitation behavior under controlled evaporation conditions.

Materials and Methods

Simulated evaporation and crystallization experiments were performed using salt solutions containing varying concentrations of -PGA (2.5, 5, 10, and 20 mg·L^{1}). Solution pH and electrical conductivity were recorded continuously throughout the evaporation process. Thermodynamic interactions between -PGA and ionic components were characterized using Isothermal Titration Calorimetry (ITC) at 40°C, enabling quantification of binding constants (Ka), dissociation constants (Kd), and free energy changes (ΔG). Precipitated solids were collected and analyzed using X-ray diffraction to identify crystalline phases.

Results and Discussion

pH and EC Dynamics During Evaporation

The pH of salt solutions typically exhibited an initial increase followed by a progressive decrease as evaporation proceeded. -PGA significantly delayed the inflection points of both pH rise and fall (Fig. 1). At a concentration of 20 mg·L^{1} -PGA, the pH stabilization period extended to 75,000 seconds, while at 2.5 mg·L^{1}, the effect persisted for 92,520 seconds. This postponement indicates that -PGA substantially inhibits the precipitation of calcium-containing minerals. The presence of -PGA also moderated EC changes, reflecting its interference with ion crystallization processes.

[Figure 1: see original paper]

XRD Analysis of Precipitation Products

XRD analysis revealed that control solutions without -PGA produced characteristic peaks for sodium chloride at 27° (111), 32° (200), 45° (220), 56.5° (222), 66° (400), 75.3° (420), and 83.9° (422) diffraction angles, along with calcium carbonate (calcite) reflections. In contrast, solutions containing -PGA showed reduced intensity of calcium precipitate peaks, including hydroxyapatite (HAP) at 31.78° (211), 45.3° (302), and 66.4° (422), confirming the inhibitory effect on calcium phosphate formation (Fig. 2). Notably, -PGA did not alter the fundamental crystal structures of the precipitates but rather modulated their precipitation kinetics.

[Figure 2: see original paper]

Thermodynamic Interactions via ITC

Isothermal titration calorimetry demonstrated that -PGA forms stable complexes with both Ca^{2} and phosphate ions. Although the HPO^{2}-Ca^{2} complex possesses higher intrinsic stability than -PGA-ion complexes, -PGA exhibited approximately 100-fold more binding sites for Ca^{2} compared to phosphate. This stoichiometric advantage means that -PGA effectively sequesters the majority of free Ca^{2} ions, preventing their interaction with phosphate and subsequent precipitation. The thermodynamic parameters (ΔG, ΔH, and binding entropy) confirmed that -PGA-Ca^{2} complexation is spontaneous and thermodynamically favorable under experimental conditions.

Conclusion

This study demonstrates that -PGA inhibits calcium-phosphate precipitation primarily through competitive binding of Ca^{2} ions, thereby enhancing phosphorus bioavailability in saline soils. The strong complexation capacity of -PGA, combined with its minimal impact on final precipitate composition, makes it an effective agent for controlled nutrient release. These findings provide mechanistic insights into the fertilizer-preserving properties of -PGA and support its application in saline-alkali soil management.

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