Effects of Polyamino Acids on Iron Oxide Speciation in Northern Paddy Soils: Postprint

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Abstract

To understand the characteristics of iron oxide content in different types of paddy soils and to clarify the effects of exogenous polyamino acid addition on the transformation of iron oxide forms in paddy soils, this study selected different types of paddy soils in northern China (brown earth type, meadow soil type, and coastal saline type) as research objects. Treatments with the addition of -polyglutamic acid and polyaspartic acid at 0.05% of the tested soil dry weight were established, with no amino acid addition as a control. After 30 days of constant temperature anaerobic incubation in the laboratory, the contents of total iron, free iron oxide, amorphous iron oxide, and complexed iron, as well as the degree of activation and complexation of iron oxides, were determined for each paddy soil. The results showed that: among the three typical northern paddy soils tested, the free iron oxide content was coastal saline type > meadow soil type brown earth type, the complexed iron content was brown earth type > coastal saline type meadow soil type, while the amorphous iron oxide content was brown earth type > coastal saline type > meadow soil type. The two exogenous polyamino acids had different effects on the transformation capacity of iron oxide forms in different types of paddy soils. Compared with the control without amino acid addition, the amorphous iron oxide and complexed iron contents in brown earth type paddy soil treated with -polyglutamic acid increased by 27.72% and 32.25%, respectively, while polyaspartic acid had no significant promoting effect on amorphous iron oxide and complexed iron contents; in meadow soil type paddy soil, both -polyglutamic acid and polyaspartic acid could significantly increase amorphous iron oxide content, and compared with the control, the complexed iron content increased by 136.24% and 12.00%, respectively; -polyglutamic acid could effectively promote the formation of amorphous iron oxide and complexed iron in coastal saline type paddy soil. In summary, the addition of -polyglutamic acid and polyaspartic acid had no significant effect on the free iron oxide content in paddy soils; whereas the addition of -polyglutamic acid could effectively increase the contents of amorphous iron oxide and complexed iron, decrease the crystallinity ratio, facilitate the increase of available iron content in soil, significantly activate iron oxides, and inhibit the crystallization and aging of iron in various types of paddy soils; while polyaspartic acid had no obvious stimulating effect on amorphous iron oxide and complexed iron in paddy soils.

Full Text

Effect of Polymeric Amino Acids on Iron Oxide Forms in Northern Paddy Soils

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Abstract

To characterize iron oxide content in different paddy soil types and investigate the effects of exogenous polymeric amino acids on iron oxide transformation, three typical northern paddy soils (brown soil type, meadow soil type, and littoral saline soil type) were selected for this study. Treatments included addition of -polyglutamic acid and polyaspartic acid at 0.05% of soil dry weight, with a no-amino-acid control. After 30 days of constant-temperature anaerobic incubation, total iron, free iron oxide, amorphous iron oxide, and complexed iron oxide contents were measured, along with iron oxide activation and complexation degrees. Results showed that among the three tested northern paddy soils, free iron oxide content followed the order: littoral saline soil > meadow soil brown soil; complexed iron oxide content was brown soil > littoral saline soil meadow soil; and amorphous iron oxide content was brown soil > littoral saline soil > meadow soil. The two polymeric amino acids differentially affected iron oxide transformation across soil types. Compared with the control, -polyglutamic acid addition increased amorphous and complexed iron oxide contents by 27.72% and 32.25%, respectively, in brown soil-derived paddy soil, while polyaspartic acid showed no significant promotion effect. In meadow soil-derived paddy soil, both -polyglutamic acid and polyaspartic acid significantly increased amorphous iron oxide content, with complexed iron oxide increasing by 136.24% and 12.00% compared to the control, respectively. -polyglutamic acid also effectively promoted amorphous and complexed iron oxide formation in littoral saline soil-derived paddy soil.

In conclusion, addition of -polyglutamic acid and polyaspartic acid did not significantly affect free iron oxide content. However, -polyglutamic acid effectively increased amorphous and complexed iron oxide contents, decreased the crystallinity ratio, enhanced available iron content, significantly activated iron oxides, and inhibited iron crystallization and aging across all paddy soil types. Polyaspartic acid showed no obvious stimulating effect on amorphous and complexed iron oxides.

Keywords: Paddy soil; Iron oxide forms; -Polyglutamic acid; Polyaspartic acid

Introduction

Iron oxides are important components of soil colloids that play crucial roles in soil structure formation in neutral and acidic paddy soils. They also influence chemical equilibria including adsorption-desorption, precipitation-dissolution of heavy metal pollutants and nutrient ions such as oxyanions, thereby affecting nutrient availability and the biological toxicity of heavy metal contaminants. Consequently, iron oxides have received widespread attention in soil chemistry, environmental chemistry, and biogeochemistry.

In agricultural practice, -polyglutamic acid and polyaspartic acid have been widely applied as crop nutrient synergists and water-retaining agents. As organic acids and soil organic nitrogen sources, both -polyglutamic acid and polyaspartic acid are biodegradable, non-toxic, highly water-soluble, and have strong water-retention capacity. Their abundant -carboxyl groups can chelate numerous base cations, thereby improving fertilizer utilization efficiency and soil nutrient availability. Research by Yao and Zhu Zhiliang et al. has demonstrated that -polyglutamic acid and polyaspartic acid can effectively chelate and activate heavy metal ions, showing great potential for remediating heavy metal contaminated soils.

The structure, morphology, and properties of iron oxides are often influenced by other soil components such as clay minerals and organic matter. As macromolecular organic compounds, amino acids frequently interact and coagulate with iron oxides, exerting certain controls over the physical, chemical, and biological properties of soil environmental systems. Studying the effects of exogenous amino acid addition on iron oxide transformation and activation is valuable not only for promoting the agricultural application of polymeric amino acids and understanding iron oxide transformation processes, but also for artificially regulating iron oxide activation in paddy soils and ensuring the safe use of polymeric amino acids in paddy fields. However, relevant research remains scarce.

Paddy soils in Liaoning Province represent major agricultural soils in Northeast China, with brown soil type, meadow soil type, and littoral saline soil type being typical examples. Previous studies on iron oxide forms in different paddy soil types have focused primarily on wetting-drying and freezing-thawing cycles, or compared iron form differences through factors such as pH, temperature, and illumination. While soil iron oxides respond sensitively to exogenous organic acid addition, research on the effects of polymeric amino acids on soil iron forms remains limited. This study employed laboratory anaerobic incubation experiments using two polymeric amino acids— -polyglutamic acid and polyaspartic acid—as exogenous materials. By measuring amorphous iron oxide, free iron oxide, and complexed iron oxide contents in different paddy soil types, we aimed to elucidate iron form transformation characteristics under amino acid addition and explore amino acid effects on clay mineral degradation through changes in iron free and activation degrees. The results have important practical significance for understanding substance migration and transformation in Northeast paddy soils and for environmental protection.

1.1 Materials

The tested paddy soils were collected from Shenyang and Panjin cities in Liaoning Province, with rice cultivation histories exceeding 40 years. Based on their origin, they were classified as brown soil type paddy soil, meadow soil type paddy soil, and littoral saline soil type paddy soil. Samples were collected in April 2015 before cultivation from 0–20 cm depth. Soil samples were air-dried, debris-removed, and passed through a 1 mm sieve for later use. The two tested polymeric amino acids were -polyglutamic acid (-PGA) and polyaspartic acid (PASP), both analytical grade, produced by Nanjing Xuankai Biotechnology Co., Ltd. -PGA is a polypeptide molecule polymerized from -amino and -carboxyl groups through deep fermentation, with a polymerization degree of 200–700 and relative molecular mass of 100–1,000 kD, featuring numerous highly active free side-chain carboxyl groups. PASP is a polymer formed by condensation of aspartic acid monomers through amino and carboxyl groups, with a smaller relative molecular mass of 4,300 D.

Basic chemical properties of the tested soils are shown in Table 1 , and contents of various iron oxide forms are presented in Table 2 .

Table 1 Basic properties of different paddy soil types tested in the experiment

Paddy soil type	Location	Organic matter (g · kg 1)	Available N (mg · kg 1)	Available P (mg · kg 1)	Total N (g · kg 1)	Total P (g · kg 1)	EC (dS · m 1)
Brown soil	Shenyang	5.59					
Meadow soil	Shenyang	7.33					
Littoral saline soil	Panjin						

Table 2 Contents of different forms of iron oxide in three types of tested paddy soils

Paddy soil type	Total Fe (g · kg 1)	Free iron oxide (g · kg 1)	Amorphous iron oxide (g · kg 1)	Complex iron oxide (g · kg 1)
Brown soil	41.8±0.88Bb	15.18±0.196Cc	3.52±0.05Aa	0.56±0.06Aa
Meadow soil	36.5±0.71Cc	15.76±0.168Bb	2.96±0.05Cc	0.12±0.03Bb
Littoral saline soil	57.1±0.55Aa	23.73±0.364Aa	3.26±0.04Bb	0.14±0.22Bb

Different capital and lowercase letters in the same column indicate significant differences among different paddy soil types at 0.01 and 0.05 levels, respectively.

1.2 Experimental Design and Methods

The experiment began in July 2015, with three treatments: -polyglutamic acid (-PGA), polyaspartic acid (PASP), and deionized water (CK). Three paddy soil types (1 kg each) were placed in incubation cups. Based on common agricultural application rates (450 kg · hm 2), equivalent to 0.05% of dry soil weight, the two polymeric amino acids were added and thoroughly mixed. Each treatment had three replicates. Distilled water was added to maintain a 2 cm water layer above the soil surface. Nitrogen gas was purged for 5 minutes to remove oxygen, followed by sealing with rubber stoppers and aluminum caps. Soils were incubated at 30 °C under flooded conditions for 30 days.

1.3 Testing Methods

After incubation, soil samples were removed, air-dried in a ventilated area, passed through a 60-mesh sieve, and analyzed for various iron oxide forms. Free iron oxide was extracted using the dithionite-citrate-bicarbonate (DCB) method proposed by Mehra and Jackson. Amorphous iron oxide was extracted using the oxalate-oxalic acid method (pH 3.2) (Tamms method). Complexed iron was extracted using sodium pyrophosphate. Total iron was determined by HF-HClO4-HNO3 tri-acid digestion. Iron in solutions was measured by atomic absorption spectrophotometry.

1.4 Calculation Methods

Free degree = DFe/TFe (1)
Activation degree = OFe/DFe [20] (2)
Complexing degree = CFe/DFe (3)
Crystal gel ratio = (DFe OFe)/OFe (4)

Where: TFe = total iron content, DFe = free iron oxide content, OFe = amorphous iron oxide content, CFe = complexed iron content.

1.5 Data Processing

Data were processed using Microsoft Excel 2010, and statistical analysis was performed using SPSS 20.0 software.

2.1 Effects of Exogenous Polymeric Amino Acids on Free Iron Oxide in Paddy Soils

Changes in free iron oxide content in different paddy soils after -polyglutamic acid (-PGA) and polyaspartic acid (PASP) treatments are shown in Figure 1 [Figure 1: see original paper]. After PASP treatment and anaerobic incubation, free iron oxide contents in all paddy soils decreased to varying degrees compared with initial values (Table 2). Brown soil-derived paddy soil showed the highest free iron oxide content under PASP treatment. After -PGA and PASP treatments, meadow soil-derived paddy soil had free iron oxide contents of 11.27 g · kg 1 and 10.44 g · kg 1, respectively, with PASP treatment being significantly lower than CK, indicating that PASP could effectively reduce free iron oxide content in meadow soil-derived paddy soil. In littoral saline soil-derived paddy soil, free iron oxide contents under all treatments were higher than those in brown and meadow soil types, with no significant differences among treatments.

2.2 Effects of Exogenous Polymeric Amino Acids on Amorphous Iron Oxide in Paddy Soils

As shown in Figure 2 [Figure 2: see original paper], amorphous iron oxide contents in all three paddy soils increased after a period of anaerobic incubation. Brown soil-derived paddy soil had the highest amorphous iron oxide content, which significantly increased to 6.25 g · kg 1 after -PGA treatment, while no significant difference was observed after PASP treatment compared with CK. In meadow soil-derived paddy soil, both amino acid treatments significantly increased amorphous iron oxide content compared with CK, but the total amount was lower than that in brown soil-derived paddy soil. This is because the meadow soil-derived paddy soil in the Liaozhong area had relatively low organic matter content, which could not continuously provide energy and electron donors for iron oxide dissolution. In littoral saline soil-derived paddy soil, -PGA treatment caused significant differences in amorphous iron oxide content compared with the other two treatments. After PASP addition, amorphous iron oxide content increases were less pronounced than with -PGA treatment, showing no significant difference from CK, indicating that PASP could not effectively promote iron oxide activation. In contrast, -PGA treatment promoted amorphous iron oxide accumulation in all three paddy soils, suggesting that -PGA is readily absorbed and utilized by microorganisms, thereby promoting iron oxide activation in paddy soils. Although littoral saline soil-derived paddy soil had higher organic matter content than brown soil-derived paddy soil, the generated amorphous iron oxide content after incubation was lower, possibly because the abundant base cations (e.g., Mn2+, Na+, Mg2+, Ca2+) in littoral saline soil competed with iron ions for electrons during iron reduction, inhibiting iron oxide activation.

2.3 Effects of Exogenous Polymeric Amino Acids on Complexed Iron in Paddy Soils

As shown in Figure 3 [Figure 3: see original paper], complexed iron contents in different paddy soils increased after polymeric amino acid treatment compared with initial values (Table 2). -PGA treatment produced the highest complexed iron contents across all soil types, with significant increases compared with both CK and PASP treatments. After PASP treatment, the complexation degree of iron oxides varied among soil types: complexed iron content in brown soil-derived paddy soil was significantly lower than CK; in meadow soil-derived paddy soil, no significant difference was observed between PASP and CK treatments, both around 0.2 g · kg 1; and in littoral saline soil-derived paddy soil, PASP treatment significantly increased iron oxide complexation compared with CK.

Figure 1 [Figure 1: see original paper] Effects of exogenous polymerized amino acids on free iron oxide contents in different paddy soil types. -PGA: -polyglutamic acid; PASP: polyaspartic acid. Different lowercase letters indicate significant differences among treatments at the 0.05 level.

Figure 2 [Figure 2: see original paper] Effects of exogenous polymerized amino acids on amorphous iron oxide contents in different paddy soil types. -PGA: -polyglutamic acid; PASP: polyaspartic acid. Different lowercase letters indicate significant differences among treatments at the 0.05 level.

Figure 3 [Figure 3: see original paper] Effects of exogenous polymerized amino acids on complex iron oxide contents in different paddy soil types. -PGA: -polyglutamic acid; PASP: polyaspartic acid. Different lowercase letters indicate significant differences among treatments at the 0.05 level.

2.4 Effects of Exogenous Polymeric Amino Acids on Iron Oxide Characteristic Parameters in Paddy Soils

Free degree, the ratio of free iron oxide (Fed) to total iron (Fet), is an important indicator of soil weathering degree. Free iron oxide formation is closely related to climatic conditions, while its activation degree is associated with pH, Eh, organic matter, and land use patterns. Table 3 shows that without exogenous amino acid addition, meadow soil-derived paddy soil had higher iron free degree, while brown and littoral saline soil-derived paddy soils had lower values. After -PGA and PASP addition, no significant changes in iron oxide free degree were observed across soil types.

Activation degree, the ratio of amorphous iron oxide (Feo) to free iron oxide, is also an indicator of soil weathering degree. Table 3 results indicate that -PGA treatment significantly increased iron oxide activation degree across all soil types, whereas PASP treatment decreased activation degree in brown and saline soil-derived paddy soils, showing no promotional effect on iron oxide activation.

Iron oxide complexing degree represents the proportion of iron oxide complexed with organic matter relative to free iron oxide, and is closely related to soil organic matter content. -PGA treatment increased soil iron complexing degree (Table 3). Brown soil-derived paddy soil had significantly higher iron complexing degree than the other two soil types, which was related to its higher inherent organic matter content, with -PGA addition further promoting iron oxide complexation. After PASP treatment, no significant changes in iron complexing degree were observed in any soil type.

The crystal gel ratio of iron oxides represents the ratio of crystalline iron oxides and their hydrates to amorphous iron oxide, and is closely related to iron oxide morphology, activation, and aging. Table 3 results show that polymeric amino acid treatments caused varying changes in iron oxide crystal gel ratios across soil types. After -PGA treatment, the crystal gel ratio decreased, indicating that -PGA inhibited iron oxide crystallization and effectively prevented iron oxide aging.

Flooded anaerobic conditions are important environmental factors for iron reduction processes in paddy soils. Different paddy soil origins result in varying soil properties due to different pedogenic processes. Brown soil-derived paddy soil in Northeast China developed from residual slope deposits of acidic parent materials, undergoing deposition, weathering, and pedogenesis with obvious eluviation, clayification, and strong biological accumulation. The accumulation of amorphous and complexed iron oxides may result from enhanced clayification increasing colloid content and iron activation, and from significant positive correlation between amorphous/complexed iron oxide formation and organic matter content. During organic matter decomposition, some iron oxides are reduced, with portions becoming water-soluble iron that subsequently hydrolyzes or oxidizes to form amorphous iron hydroxides, while organic matter inhibits iron oxide crystallization. Meadow soil-derived paddy soil mainly originated from sandy alluvium in the Songnen Plain and lower Liao River Plain, with slightly alkaline micro-environment and relatively low total iron and aluminum contents, resulting in lower amorphous and complexed iron oxide contents. Littoral saline soil-derived paddy soil, located in the coastal plain of Northeast China with marine alluvial parent material, has high salinity and strong alkalinity, where iron exists primarily as crystalline iron oxides and their hydrates. Iron availability in salt-affected soils is low due to sensitivity to soil pH, resulting in relatively low complexed iron oxide content.

Our results demonstrate that both -PGA and PASP affected iron oxide transformation, with -PGA significantly increasing amorphous iron oxide content and effectively promoting iron oxide activation and complexation, while PASP showed less pronounced effects. The differential effects of the two amino acids are related to their molecular weights. Research by Li Xueyuan and Stevenson et al. indicates that soil organic matter affects iron oxide dispersion, migration, coagulation, and deposition by altering surface chemical properties. Both -PGA and PASP are highly active organic substances with functional groups including hydroxyl, amino, and carboxyl groups. Iron oxides typically combine with organic acids through hydrogen bonding, electrostatic adsorption, and surface ligand exchange. Iron oxides and their hydrates have large specific surface areas, and negatively charged organic acids can undergo ligand exchange with terminal –OH groups on iron oxide edges, releasing OH . The strongly affine OH can then undergo protonation reactions with H+, while metal ions, after water molecule removal, have surface hydroxyl groups that protonate and more readily coordinate with organic acids. Although -PGA and PASP have similar structures and chemical properties, PASP' s lower molecular weight results in fewer free hydroxyl, amino, and carboxyl groups on side chains, leading to lower probability and capacity for coordination exchange with iron oxides compared with -PGA, and consequently less significant activation and complexation effects.

Both -PGA and PASP influenced iron oxide transformation in soils, with -PGA more effectively reducing free iron oxide content, decreasing crystal gel ratio, and promoting iron oxide activation and complexation in brown soil-derived paddy soil. This suggests that organic acids formed during amino acid decomposition accelerate dissolution of poorly soluble iron oxides, increasing soil soluble iron content. Among the three soil types, both amino acids showed the best activation and complexation effects in brown soil-derived paddy soil, possibly due to soil pH. Research by Xiong Yi et al. demonstrated significant negative correlation between soil pH and activation degree. Acidic soils exhibit increased iron solubility and reduction, with low pH and reducing environments promoting transformation of insoluble Fe(III) to soluble Fe(II). Therefore, acidic brown soil-derived paddy soil is more conducive to iron oxide activation, consistent with conclusions from Xu Zhongjian et al. regarding acid rain leaching experiments on red soils showing that acidic conditions favor increased active iron content and activation degree. Additionally, at pH 5, 80% of Fe3+ can form complex chelates with strongly acidic carboxyl and hydroxyl groups, making acidic conditions more favorable for iron complexation. In littoral saline soil-derived paddy soil, -PGA and PASP showed less pronounced effects on free iron oxide transformation, possibly because abundant base cations (K+, Na+, Mg2+, Ca2+) competed with iron for amino acid adsorption sites, reducing iron adsorption and dissolution. Soil pH is also a direct factor controlling iron compound activity. In meadow soil-derived paddy soil, both amino acids effectively reduced free iron oxide content and promoted activation and complexation, likely due to low inherent organic matter content making it more responsive to exogenous organic materials.

Both -PGA and PASP can promote iron oxide transformation to varying degrees, but the mechanisms underlying their effects on iron oxide activation, complexation, and crystallization remain unclear and require further investigation.

Conclusions

1) The two amino acids differentially affected iron oxide transformation in paddy soils. While -PGA and PASP addition did not significantly affect free iron oxide content, -PGA effectively increased amorphous and complexed iron oxide contents, enhancing available iron content, whereas PASP showed no obvious stimulating effect on amorphous and complexed iron oxides.
2) Different paddy soil types showed varying responses to the two amino acids. -PGA effectively promoted amorphous and complexed iron oxide formation, while the free functional groups on both amino acids strongly adsorbed abundant base cations in littoral saline soil-derived paddy soil, reducing their adsorption capacity for iron oxides.
3) Iron oxide activation and complexation are interrelated: higher activation degree corresponds to lower iron crystallinity, making soluble iron more readily complexed.

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Note: Figure translations are in progress. See original paper for figures.