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InnoSoilPhos

Brandenburg University of Technology Cottbus - Senftenberg

Mobilization of P from crystalline and amorphous Fe- and Al-hydroxides

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Introduction

In neutral to acidic soils, the availability of phosphorus (P) is affected by its strong affinity for mineral surfaces. Especially the interaction between P and iron- and aluminum-(oxy)hydroxides (Fe- and Al-hydroxides) plays a crucial role in the immobilization and hence, availability of P for plants. In this context, the fixation of P is mainly determined by processes of adsorption, desorption, and precipitation. In that sense, the kinetics and mechanisms of P desorption from synthetic well **crystalline goethite** (α-FeO(OH)) and **gibbsite** (γ-$Al(OH)_3$) as well as from **amorphous ferrihydrite** ($Fe_2O_3 \cdot H_2O$) and **Al-hydroxide** ($Al(OH)_3$) were characterized. The desorption solutions **$CaCl_2$**, and **$CaSO_4$** were chosen as main components of the soil solution, while **humic and citric acid** were selected as organic ligands following humification or produced by plants in the rhizosphere.

Methods

P Adsorption[1,2]

- Batch setup at pH 6
- 16 weeks reaction time
- 2-5 mmol l^{-1} KH_2PO_4
- 10 mmol l^{-1} $CaCl_2$

Crystalline

Goethite *α-FeO(OH)*

Gibbsite *γ-$Al(OH)_3$*

Amorphous

Ferrihydrite *$Fe_2O_3 \cdot H_2O$*

Al-Hydroxide *$Al(OH)_3$*

P Desorption[3]

- Batch setup at pH 6
- 8 weeks reaction time
- 10 mmol l^{-1} desorption solution

$CaCl_2$

$CaSO_4$

Humic Acid

Citric Acid

Results

Fourier-transform-infrared spectroscopy of P adsorption

Identification of P binding motifs

Crystalline

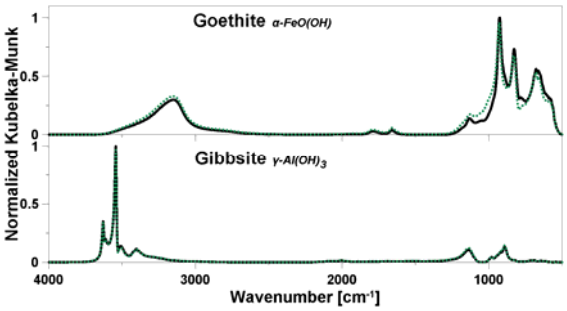

Fig. 1. FT-IR spectra of crystalline goethite and gibbsite before and after P adsorption.

Goethite

- Dominant bidentate mono-protonated
- Minor monodentate mono-protonated
- Mainly P surface complexes

Gibbsite

- Mono-protonated monodentate and bidentate
- Mainly P surface complexes

Amorphous

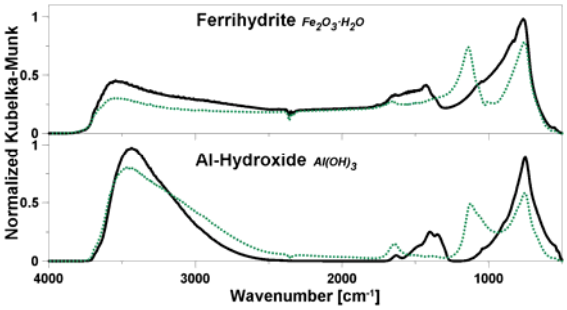

Fig. 2. FT-IR spectra of amorphous ferrihydrite and Al-hydroxide before and after P adsorption.

Ferrihydrite

- Mainly $FePO_4$ precipitation
- Migration into mineral particles

Al-Hydroxide

- Di-protonated monodentate
- Mainly P surface complexes

Efficiency and kinetics of P desorption

Characterization of P mobilization

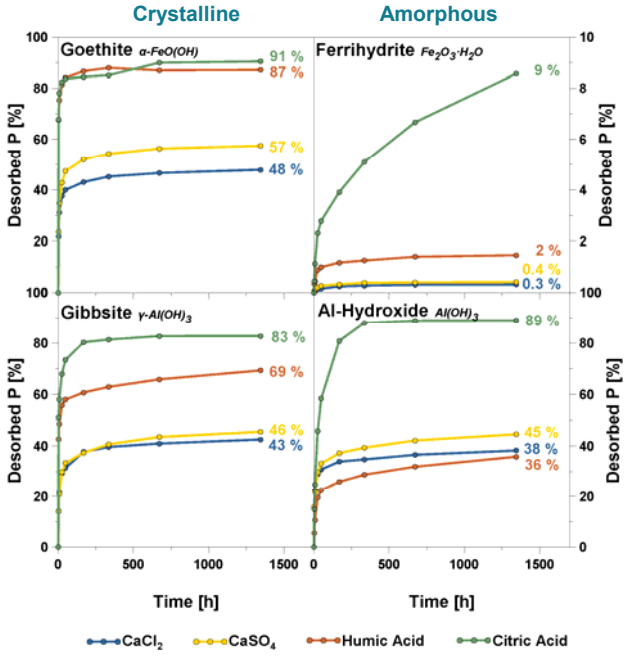

Fig. 3. P desorption kinetics of goethite, gibbsite, ferrihydrite, and Al-hydroxide at pH 6.

Desorption efficiency: $CaCl_2$ < $CaSO_4$ < Humic acid < Citric acid

Inorganic compounds

- Anion exchange
- Affect easily available bound P on hydroxide surface (surface complexes)

Organic compounds

- Citric acid - Dissolution
- Humic acid - Metal-organic complexes
- Affect also stronger bound P within mineral structure or precipitated

With the aim to enhance the mobility of fertilized or naturally bound P in order to optimize the soil P fertility, the great influence of the crystallinity grade of **especially Fe-hydroxides** should be taken into account. In particular, the **high efficiency of citric acid** shows that the mobilization and thus plant-availability of P can be underestimated. The **very low P release by using $CaCl_2$** underlines once again the importance of the accessibility of fertilized or naturally bound P for plant roots, to benefit from the **excretion of organic acids** as a strategy to enhance the P uptake.

References

[1] S. Gypser, F. Hirsch, A. Schleicher, D. Freese (2018): Impact of crystalline and amorphous iron- and aluminum hydroxides on mechanisms of phosphate adsorption and desorption. J. Environ. Sci. 70, 175-189.

[2] A. Ahmed, S. Gypser, P. Leinweber, D. Freese, O. Kühn (2019): Infrared spectroscopic characterization of phosphate binding at the goethite-water interface. PCCP 21, 4421-4434.

[3] S. Gypser, E. Schütze, D. Freese (2019): Crystallization of single and binary iron- and aluminum hydroxides affect phosphorus desorption. J. Plant Nutr. Soil Sci. 182, 741-750.

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