Citric Acid Enhances Phosphate Release from Humic Acid-Iron Hydroxide Coprecipitates

The presence of citric acids could mildly obstruct the structural development of the Fe domain in humic acid–iron hydroxide coprecipitates, as shown by X-ray absorption spectroscopy techniques.

Recent research led by Yu-Min Tzou (National Chung Hsing University) and his team has demonstrated the sorption of citric acid onto two humic acid–iron hydroxide coprecipitates (HAFHCPs), as well as the mutual effects of citric acid and phosphate (P) sorption on these HAFHCPs at different C/Fe ratios. Their findings show that as the C/Fe ratio increases to 0.5, the maximum sorption capacity (MSC) of citric acid on HAFHCP-Y50 and HAFHCP-A50 decreases by 9.1–16.7% (**Fig. 1**). In addition, the citric acid sorption capacity of HAFHCP containing humic acid was extracted from volcanic soil of Yangmingshan (HAFHCP-YHA) is approximately 92% of that of HAFHCP containing the Sigma-Aldrich humic acid (HAFHCP-AHA). This trend is likely due to competition for sorption sites on iron hydroxide (FH) surfaces between YHA and citric acid, which is driven in part by the electrostatic repulsion between negatively charged HA and citric acid at pH 5.5.

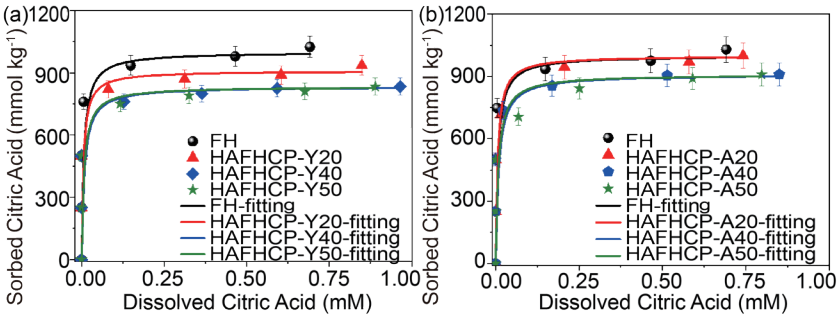

Fig. 1: Citric acid sorption isotherms for iron hydroxide (FH) and HAFHCP containing (a) YHA and (b) AHA with initial C/Fe ratios of 0.2, 0.4, and 0.5 (HAFHCP-Y20, Y40, Y50, A20, A40, and A50) fitted with the Langmuir isotherm model (solid lines). [Reproduced from Ref. 1]

Using X-ray absorption spectroscopy (XAS) at **TLS 16A1**, Tzou and coworkers observed through Fe K-edge X-ray absorption fine structure (EXAFS) analysis that the k^3-weighted $\chi(k)$ data for iron hydroxide (FH) and FH with sorbed citric acid were largely similar. However, slight differences emerged at $k \approx 5.0$, 7.5, and 8.5 $Å^{-1}$ between free HAFHCP-Y50/A50 and HAFHCP-Y50/A50 with sorbed citric acid. These findings suggest that citric acid impedes the structural development of Fe domains in HAFHCP, increasing dissolved Fe content and reducing the sorption capacity for citric acid (**Fig. 1**). A previous study by Tzou and his colleagues showed that HAFHCP-Y50 likely contains a relatively homogeneous distribution of C and Fe domains. In contrast, HAFHCP-A50 appears to have a ferrihydrite core with humic acid growing on its surface and possesses fewer polar functional groups. This arrangement results in greater Fe dissolution when citric acid is sorbed.

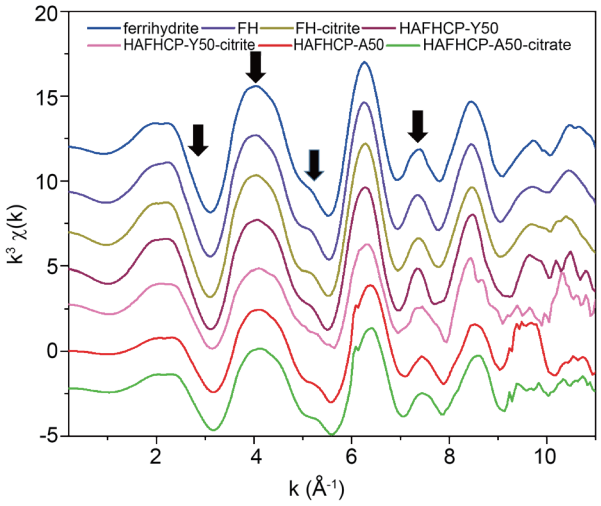

Fig. 2: Fe K-edge EXAFS spectra after sorption of citric acid on FH, HAFHCP-Y50, and HAFHCP-A50. Initial amounts of added citric acid were 0 and 2500 mmol kg^{-1}. [Reproduced from Ref. 1]

Understanding how HAFHCPs influence P availability is critical, particularly when organic acids and P coexist. To explore this, three experimental systems were developed to assess the cross-competitive sorption of P and citric acid on FH and HAFHCPs. Across all three systems, P sorption onto FH, HAFHCP-YHA, and HAFHCP-AHA followed the same order: P–C > S > C–P (**Fig. 3**, see next page). In the P–C, S, and C–P systems, P sorption on FH, HAFHCP-Y50, and HAFHCP-A50 differed significantly, having a decreasing trend of 1669–1780, 1245–1365, and 1018–1132 mmol kg^{-1}, respectively (**Fig. 3**). Notably, in the C–P system, pre-sorbed citric acid reduced P sorption by 50% compared with the MSC of P on FH (2250 mmol kg^{-1}) likely because of citric acid acting as a diffusion barrier for P. In

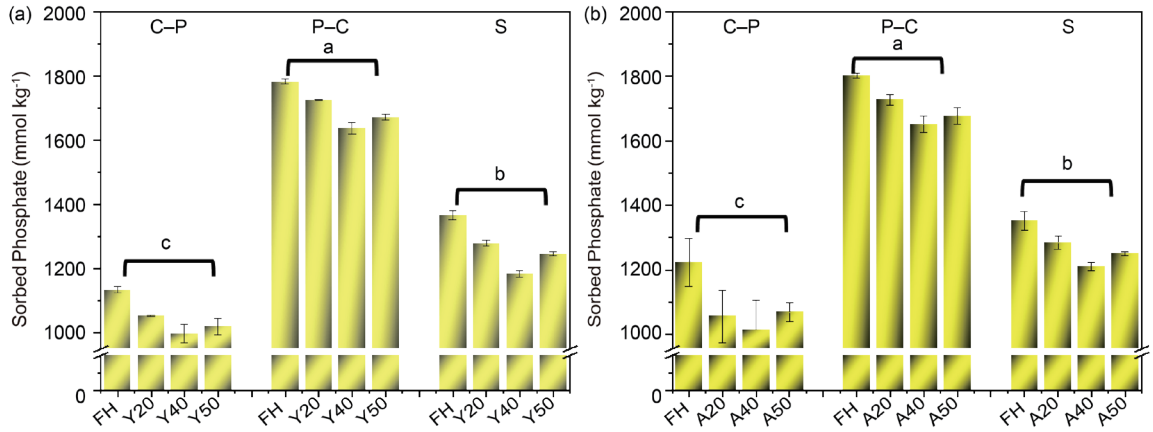

Fig. 3: The P sorption capacity for FH and HAFHCP containing (a) YHA and (b) AHA with initial C/Fe ratios of 0.2, 0.4, and 0.5 (HAFHCP-Y20, Y40, Y50, A20, A40, and A50) on cross-competitive sorption systems of C–P, P–C, and S. The order of addition for the different sorption systems are as follows: (1) For the C–P system, 1000 mmol kg^{-1} of citric acid was first added into FH/HAFHCP suspensions for 42 h, and then 2250 mmol kg^{-1} of P was added and allowed to react for another 42 h. (2) For the P–C system, 2250 mmol kg^{-1} of P was added and allowed to react with FH/HAFHCP for 42 h prior to the addition of 1000 mmol kg^{-1} of citric acid. The mixtures were then allowed to react for another 42 h. (3) In the S system, both P and citric acid were added simultaneously and allowed to react for 42 h. Statistical analysis was performed using one-way analysis of variance followed by Fisher's least-significant-difference (LSD) multiple-comparisons test at a significance level of $P < 0.05$. Significant differences between groups are denoted by different letters (a, b, c), as determined by Fisher's protected LSD test at a significance level of $P = 0.05$. [Reproduced from Ref. 1]

contrast, in the P–C system (where P was pre-sorbed), the presence of citric acid reduced P sorption by approximately 20%. Such effects may result from dissolved Fe functioning as a bridging agent between citric acid and P. Overall, these results indicate that citric acid strongly enhances P release in the C–P system.

In summary, this study emphasizes the role of HAFHCPs in the cross-competitive sorption of citric acid and P. The findings show that factors such as C/Fe ratios, the organic composition of humic acids, and the presence of citric acids (as observed through XAS) are key to understanding P availability. Consequently, the implementation of soil management strategies that foster favorable conditions for P availability is crucial for the sustainable utilization of P resources. (Reported by Kai-Yue Chen, National Chiayi University)

This report features the work of Yu-Min Tzou and his collaborators published in Environ. Res. ***240****, 117517 (2024).*

TLS 16A1 Tender X-ray Absorption, Diffraction

- EXAFS
- Environmental and Earth Sciences, Chemistry

Reference

1. M. M. M. Ahmed, K.-Y. Chen, F.-Y. Tsao, Y.-C. Hsieh, Y.-T. Liu, Y.-M. Tzou, Environ. Res. **240**, 117517 (2024).