THERMODYNAMIC CONTROL OF VIVIANITE FORMATION IN WASTEWATER

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INTRODUCTION & AIM

Phosphorus is recognized as a critical raw material, while global phosphate reserves are limited and subject to geopolitical risks. Wastewater treatment plants represent an important secondary phosphorus source and provide opportunities for nutrient recovery. Among available strategies, precipitation of vivianite $(Fe_3(PO_4)_2 \cdot 8H_2O)_s$ is particularly attractive due to its high selectivity for phosphate, low sludge volume, magnetic separability, and compatibility with circular economy reuse. However, most recovery processes are still optimized empirically and lack rigorous thermodynamic control.

This work develops a comprehensive thermodynamic modeling framework aimed at predicting and controlling vivianite crystallization. The goals are to determine stability domains, minimize competing mineral formation, optimize pH and Fe:P ratios, and quantitatively estimate residual dissolved phosphorus after treatment.

METHOD

A heterogeneous chemical equilibrium model was constructed by integrating hydrolysis reactions, metal–ligand complex formation, ligand protonation equilibria, mineral precipitation and dissolution processes, and full mass- and charge-balance constraints. Species distribution diagrams and mineral stability fields were calculated for synthetic and real wastewater compositions across the pH range 7–11.

MODELED SYSTEM

The aqueous phase includes Fe^{2+}, phosphate species (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}), Ca^{2+}, hydroxide ions, and background ligands. Potential competing solids include vivianite, hydroxyapatite, calcium phosphates, and iron hydroxides.

THERMODYNAMIC BASIS

Vivianite precipitation is described by:

$$3Fe^{2+} + 2PO_4^{3-} + 8H_2O = Fe_3(PO_4)_2 \cdot 8H_2O_{(S)}$$
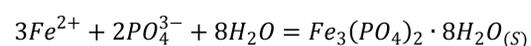
The overall Gibbs free energy ΔG_{total} of the crystallization–dissolution process is calculated as, taking into account all the secondary reactions in saturated solutions,

$$\Delta G_{total} = -RTlnK_{S(vivianite)}\alpha_{Fe^{3+}}^3\alpha_{PO_4^{3-}}^2 + RTln\left(C_{Fe^{3+}}^0\right)^3\left(C_{PO_4^{3-}}^0\right)^2,$$

where $K_{S(vivianite)}$ is the solubility product of vivianite, C_i^0 is the analytical/total concentration of the component "i" in heterogeneous mixture.

To take into account the metal ion hydrolysis and complexation and phosphate protonation, the α coefficients are used. By the sign and value of ΔG_{total} the possibility of the formation of sparingly soluble salt and the precipitation completeness under specified conditions can be determined. Thus, for $\Delta G_{total} > 0$ the spontaneous crystallization takes place, otherwise, if $\Delta G_{total} < 0$, then the solid phase is not formed. Equality $\Delta G_{total} = 0$ reflects the beginning of precipitation-dissolution of the sparingly soluble salt. Thus, negative values of ΔG_{total} indicate and define the stability region of vivianite.

RESULTS & DISCUSSION

Thermodynamic simulations showed that vivianite is the dominant phosphate phase over a wide pH range (approximately 5–10), which is fully compatible with anaerobic sludge digestion. Optimal crystallization occurs at pH 7.0–7.5 with Fe:P molar ratios between 1.5 and 1.8, when ΔG_{total} takes maximum values. Within this range, vivianite selectivity is maximized and co-precipitation of calcium phosphates and iron hydroxides is minimized. Carbonate ions did not significantly inhibit vivianite formation. Sulfide ions may compete with phosphate for Fe^{2+}, but their influence becomes significant only at high sulfide concentrations.

The effect of temperature was minor, indicating that the choice between mesophilic and thermophilic digestion has little impact on vivianite crystallization.

Efficient crystallization occurs when saturation index SI > 4. Very high SI values led to rapid precipitation and formation of small, poorly crystalline particles. The dominant factor controlling SI was the sharp increase in the concentration of PO_4^{3-} species at higher pH.

The optimal pH is around 7, where controlled nucleation and crystal growth produce high-quality vivianite. Increasing pH promotes formation of competing phases, while excess iron leads to additional sludge generation. Controlled iron dosing significantly improves phosphorus recovery efficiency.

Compared to struvite or hydroxyapatite recovery, the vivianite pathway requires minimal pH adjustment, offering a major economic advantage.

CONCLUSION

The framework provides species distribution diagrams, saturation indices, and ΔG_{total} stability maps. These outputs allow quantitative prediction of residual dissolved phosphate and iron concentrations and enable rational adjustment of process parameters before implementation.

The proposed approach improves phosphorus recovery efficiency, reduces chemical consumption, decreases sludge production, and enhances selectivity. The model is adaptable to different wastewater matrices and supports the design of sustainable and low-impact nutrient recovery technologies aligned with circular economy principles.

Vivianite formation in wastewater is thermodynamically controllable rather than empirical. Near-neutral pH and moderate *Fe* dosing maximize selective phosphorus recovery. Gibbs free energy–based modeling provides a predictive tool for efficient and sustainable wastewater treatment design.

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