

Evolution of monocalcium phosphate monohydrate in solution containing humic matter

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Abstract

The evolution of monocalcium phosphate monohydrate (MCP) to dicalcium phosphate dihydrate (DCPD) depends particularly on the concentration of compounds in solution (Ca^{2+} , H_2PO_4^- , humic matter) and on pH.

Complexation of calcium by humic matter involves an increase in the concentration of calcium ions in solution and the adsorption of humic matter at the surface grains of the DCPD formed blocks the active growth sites of DCPD. Therefore, an increase in the amount of humic matter in solution is associated with a decrease in the evolution rate and the amount of DCPD formed.

1. Introduction

The behaviour in soil of phosphate fertilizer depends on various factors such as soil pH and temperature, the amount of calcium, the presence of iron and aluminium, the amount of organic matter and especially the amount of humic matter [1–4]. These factors determine the best use of phosphate fertilizers by plants. Calcium phosphate monohydrate $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (MCP) is one of the main constituents of phosphate fertilizers, so it is very important to investigate its evolution.

The purpose of the present investigation was to study the evolution of MCP to dicalcium phosphate dihydrate $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (DCPD) at pH 5.

2. Materials and methods

Humic compounds were extracted from compost with a basic solution (pH 10) of ammonium carbonate and ammonia to obtain ammonium humates [1]. As humic compounds are insoluble in acid solution, calcium was first eliminated with acidic treatment. The extracted solution of ammonium humates was adjusted to pH 8 by elimination at 50 °C of excess ammonia. The main characteristics of the solution of humic matter are given in Table 1.

The dry substance content of the solution of humic matter was determined by dry evaporation at 110 °C of the humic solution. The ash contents was determined by heating at 900 °C during 3 h of the dry residue

obtained. The content of organic matter was determined by oxidation with potassium permanganate in basic solution [1].

The MCP used in this study was a Prolabo product (Rectapur).

For study of the transformation of MCP to DCPD at pH 5, 2.5 g MCP was dissolved in 250 ml H_2O containing various proportions of humic matter. Under these experimental conditions, the MCP was entirely dissolved and the Ca^{2+} and H_2PO_4^- ions were liberated in the solution; we observed a significant decrease in pH until a value of about 3. The pH of the solution was adjusted to 5 using a dilute solution of NH_4OH (0.2 N). The DCPD then begins to precipitate and the pH decreases. The pH value was kept at 5 using the same ammonia solution until the pH stabilized. The evolution is monitored by the volume of ammonia necessary to maintain the pH of the solution at 5. In fact the amount of ammonia added corresponds to the number of OH^- ions necessary to neutralize the H^+ ions liberated during the formation of DCPD, and therefore to the amount of DCPD formed.

The time $t = 0$ is fixed at the moment when the evolution solution reaches pH 5.

TABLE 1. Main characteristics of the solution of humic matter

pH of humic solution	8
Amount of dry matter (g l^{-1})	5.9
Amount of ash (g l^{-1})	0.21
Amount of organic matter (g l^{-1})	2.38

Final solutions containing 0 mg l^{-1} , 40 mg l^{-1} and 80 mg l^{-1} of organic compounds were obtained by the introduction of 0 ml, 17 ml and 34 ml of solution of humic matter.

3. Results and discussion

Analysis of curves (Fig. 1) showing the transformation in solution at pH 5 of MCP to DCPD indicate that the evolution kinetic of MCP to DCPD is slower and the amount of DCPD formed less, when the concentration of humic compounds in the solution is large.

Two mechanisms can explain this result. Firstly dicalcium phosphate has adsorption properties [5, 6]. The adsorption of humic matter is established using calcium

ions of DCPD as a “calcium bridge”. When the first DCPD grains are formed, humic matter is adsorbed on the surface of the grains and blocks the active growth sites, decreasing the rate of growth of DCPD.

Secondly, humic compounds are known to have chelating efficiency for Ca^{2+} ions [1, 4]. Under these conditions of pH and concentration, without humic matter, we are in the stable supersaturation zone of the solubility diagram of DCPD [7], and the precipitation is rapid.

The introduction into the solution of increasing amounts of humic matter is accompanied by a decrease in the amount of calcium in solution due to the formation of calcium–humic matter complexes. The pH value is kept at 5, and the decrease in the amount of calcium ions in the solution brings the reaction system close to

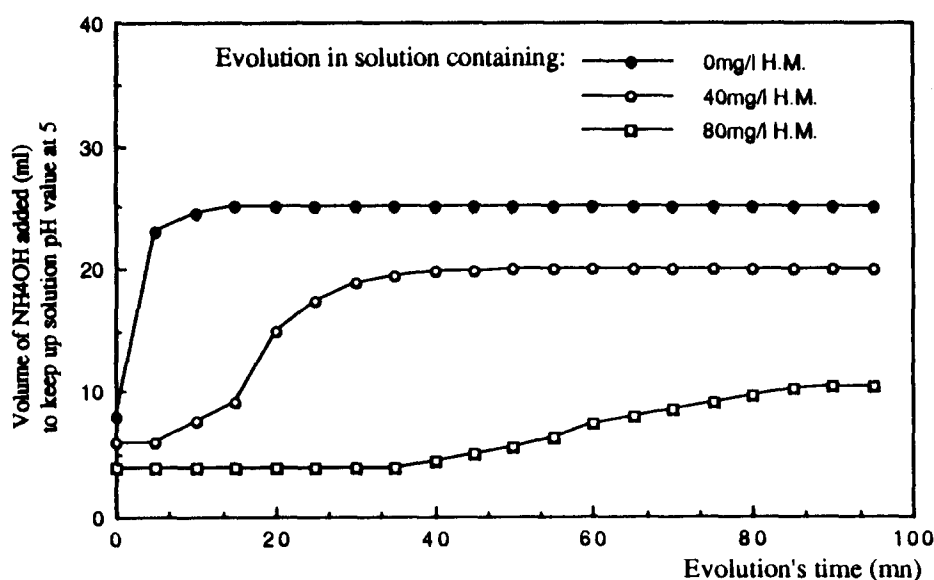


Fig. 1. Effect of the concentration of humic matter in the solution on the transformation kinetic of MCP to DCPD.

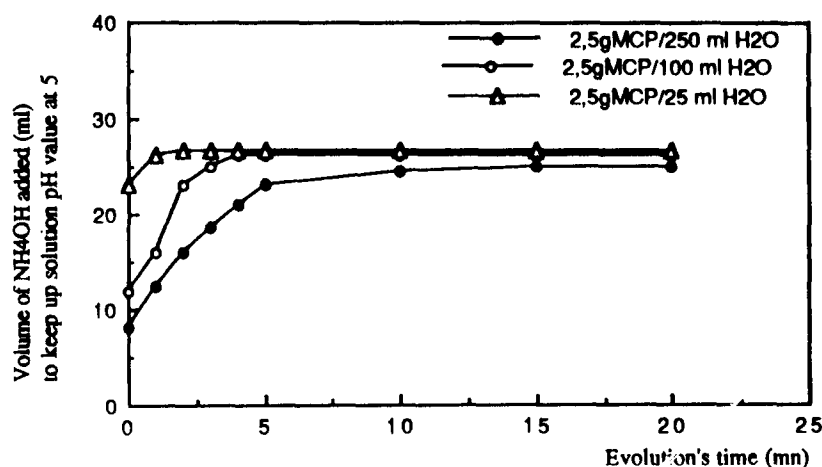


Fig. 2. Effect of the ratio of solid to solution on the evolution kinetic of MCP to DCPD.

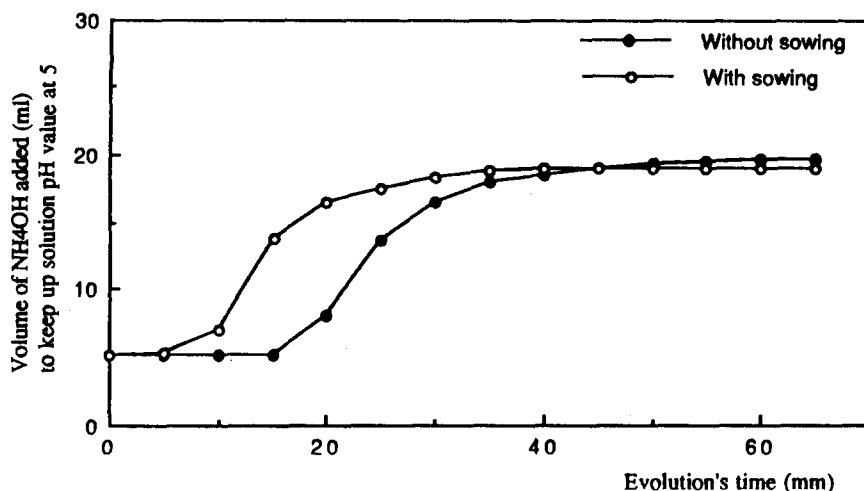


Fig. 3. Effect of the introduction of sowing on the evolution kinetic of MCP to DCPD.

the metastable supersaturation domain, where the growth rate is slow, and therefore causes slower precipitation. In addition, when we vary the concentration of ions in solution, we move away from or approach the solubility curve, and the precipitation rate of DCPD changes. The increase in the ratio of solid to solution (Fig. 2) (from 2.5 g MCP and 250 ml H₂O to 2.5 g MCP and 25 ml H₂O) is equivalent to an increase in the concentration of ions in the solution. At the same pH value (pH 5), the precipitation of DCPD is quicker when the solution is more concentrated in calcium and phosphate.

The fixation of calcium as calcium humates and the adsorption of humic matter on DCPD grains are two phenomena which prevent the formation of DCPD.

Moreover, the introduction of sowing in a supersaturated solution increases the precipitation rate of a solid. The seed introduced acts as a nucleus [5]. This effect was checked by introducing DCPD sowing in a supersaturated solution of pH 5 (Fig. 3). This effect was examined in the presence of humic matter; in this case the formation kinetic of DCPD is slow and the acceleration of growth due to the introduction of sowing can easily be seen.

4. Conclusion

The humic matter protects monocalcium phosphate monohydrate from evolution to dicalcium phosphate dihydrate, which is less soluble, by restricting the rate of formation and the amount of dicalcium phosphate formed.

Moreover, an increase in the ratio of solid to solution and the introduction of sowing favour this evolution.

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