

MODELLING OF MAGNESIUM OXIDE APPLICATION FOR STRUVITE PRECIPITATION

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ABSTRACT

The kinetics of struvite precipitation in digestion sludge supernatant was described. The effect of aeration and the magnesium compound solubility was investigated. The kinetic equation was proposed and constant rate values were calculated. The removing CO₂ from digestion sludge supernatant and solubility of Mg compound have main effect on kinetics process.

KEYWORDS

struvite, reaction kinetics, precipitation.

INTRODUCTION

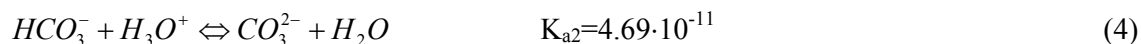
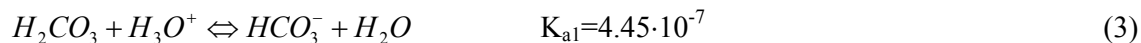
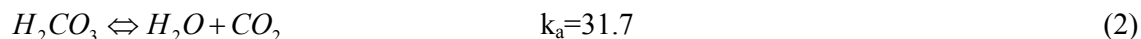
It is well known that activated sludge bacteria accumulate phosphate ions in aerobic conditions. In the sludge anaerobic digestion process previously formed poly-phosphate hydrolyze to phosphate, and the high amount of ammonium and carbon dioxide were formed too as a final product. The extremely high ammonia and phosphate concentrations are present in digested sludge supernatant. In the atmospheric pressure the carbon dioxide solubility decrease and in the presence of small amounts magnesium ions caused the struvite crystals are formed:



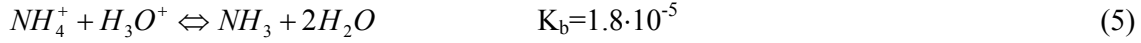
Struvite formation highly depend on substrates concentrations and pH value.

In digested sludge supernatant the following ions equilibriums can be written as follow:

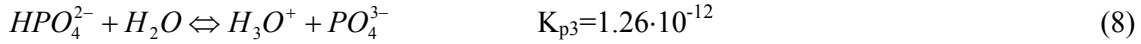
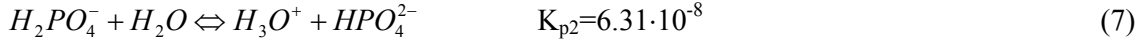
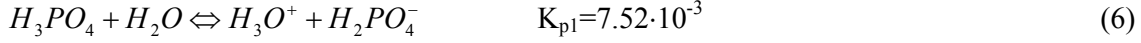
- carbon dioxide equilibrium:



- ammonia equilibrium:



- phosphate equilibrium:



On the basis above equilibrium the concentrations of weak acid and bases for the row digested sludge supernatant may be calculated from the equations:

$$[H_2CO_3] = \frac{[H_3O^+]^2}{K_{a1}K_{a2} + [H_3O^+]^2 + [H_3O^+]^2} C_{CO_2} \quad (9)$$

$$[HCO_3^-] = \frac{K_{a1}[H_3O^+]}{K_{a1}K_{a2} + K_{a1}[H_3O^+] + [H_3O^+]^2} C_{CO_2} \quad (10)$$

$$[CO_3^{2-}] = \frac{K_{a1}K_{a2}}{K_{a1}K_{a2} + K_{a1}[H_3O^+] + [H_3O^+]^2} C_{CO_2} \quad (11)$$

$$[H_3PO_4] = \frac{[H_3O^+]^3}{K_{p1}K_{p2}K_{p3} + K_{p1}K_{p2}[H_3O^+] + K_{p1}[H_3O^+]^2 + [H_3O^+]^3} C_{PO_4} \quad (12)$$

$$[H_2PO_4^-] = \frac{K_{p1}[H_3O^+]^2}{K_{p1}K_{p2}K_{p3} + K_{p1}K_{p2}[H_3O^+] + K_{p1}[H_3O^+]^2 + [H_3O^+]^3} C_{PO_4} \quad (13)$$

$$[HPO_4^{2-}] = \frac{K_{p1}K_{p2}[H_3O^+]}{K_{p1}K_{p2}K_{p3} + K_{p1}K_{p2}[H_3O^+] + K_{p1}[H_3O^+]^2 + [H_3O^+]^3} C_{PO_4} \quad (14)$$

$$[PO_4^{3-}] = \frac{K_{p1}K_{p2}K_{p3}}{K_{p1}K_{p2}K_{p3} + K_{p1}K_{p2}[H_3O^+] + K_{p1}[H_3O^+]^2 + [H_3O^+]^3} C_{PO_4} \quad (15)$$

Digested sludge supernatant pH value is controlled by the carbonaceous system, and its decreasing is necessary to phosphate $[PO_4^{3-}]$ ion concentration increasing. It may be done by the supernatant aeration or by base addition.

The magnesium ions deficit can be eliminated by soluble or insoluble magnesium compounds addition.

The effect of the alkalization method, the kind and dose of magnesium compound and the stirring intensity on the struvite precipitation kinetics was the aim of our investigation.

METHODS

The investigation on struvite precipitation were carried out in the 1000 ml reactors. The magnesium oxide or magnesium chloride solution were used. as the source of magnesium ions. The reaction mixture was stirred and aerated or 0,1 M sodium hydroxide solution was added to decrease pH value.

The pH value and ammonia concentration were measured electrochemically by glass and ion selective electrode. The phosphate concentration was determined colorimetrically by vanadomolybdo phosphoric acid method.

The kinetics of mineral precipitation for many soluble salts type was described by Koutsoukos as follow:

$$\frac{dM_{v^+} A_{v^-}}{dt} = -k_s \left[\left([M^{m+}]^{v^+} [A^{a-}]^{v^-} \right)^{1/v} - \left([M^{m+}]_{\infty}^{v^+} [A^{a-}]_{\infty}^{v^-} \right)^{1/v} \right]^n \quad (16)$$

where:

$[M^{m+}]$, $[A^{a-}]$, $[M^{m+}]_{\infty}$, $[A^{a-}]_{\infty}$ are the concentrations of crystal lattice ions in the solution and at equilibrium respectively

k – precipitation rate constant

s – factor proportional to the total number of growth sites on the added seed material

n – factor determined experimentally

In our experiments following simplifying assumptions were done:

- the ammonia to phosphate molar ratio is high and the ammonia concentration has no effect to precipitation kinetics
- similarly the magnesium compounds were added in excess and the effect of magnesium concentration can be negligible.

Finally the following kinetic equation describing phosphate concentration is follow:

$$\frac{dc}{dt} = -k'(c - c_{\infty}) \quad (17)$$

where:

c- phosphate concentration

c_{∞} - equivalent phosphate concentration

The constant rate k' may be determined from the following integrated form:

$$\ln \left(\frac{c_0 - c_{\infty}}{c - c_{\infty}} \right) = k' t \quad (18)$$

The phosphate concentration can be calculated on the basis of equation:

$$c = (c_0 - c_{\infty}) e^{-k' t} + c_{\infty} \quad (19)$$

RESULTS AND DISCUSSION

In the first experiment series stirring and aeration was used to repelling carbon dioxide and to pH increasing.

The result showed aeration and stirring intensity increasing had the positive effect on phosphate precipitation. It was observed both MgO or MgCl₂ was used as magnesium ions source, although application of soluble magnesium compound were favorable.

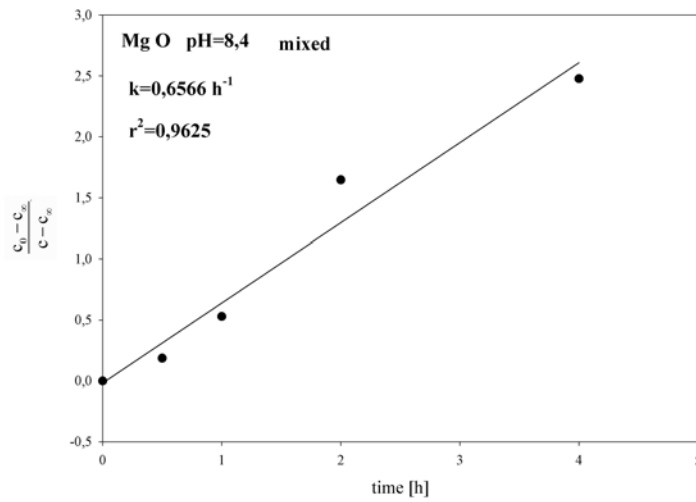


Figure 1a. The phosphate precipitation kinetics in stirred sample (100 min^{-1}), MgO dose 100 mg/l.

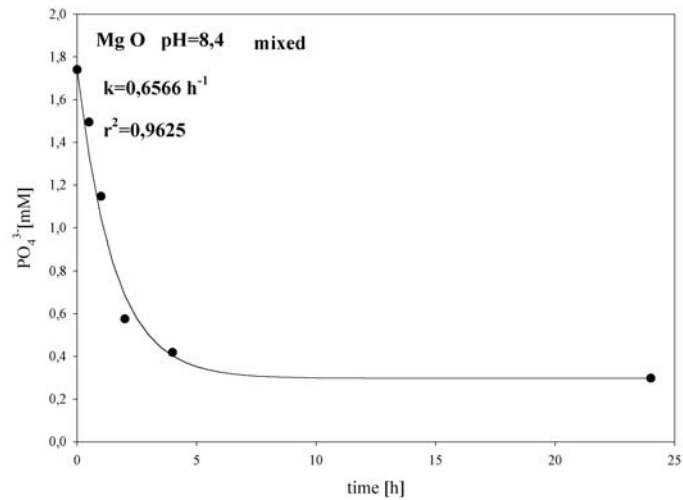


Figure 1b. The phosphate precipitation kinetics in stirred sample (100 min^{-1}), MgO dose 100 mg/l.

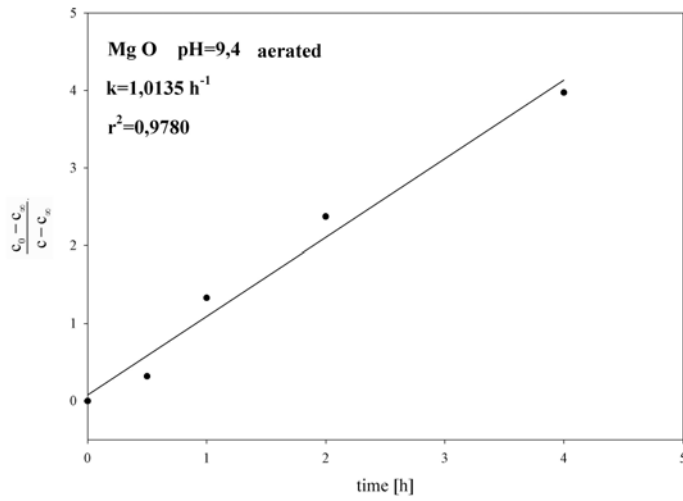


Figure 2a. The phosphate precipitation kinetics in aerated sample, MgO dose 86 mg/l.

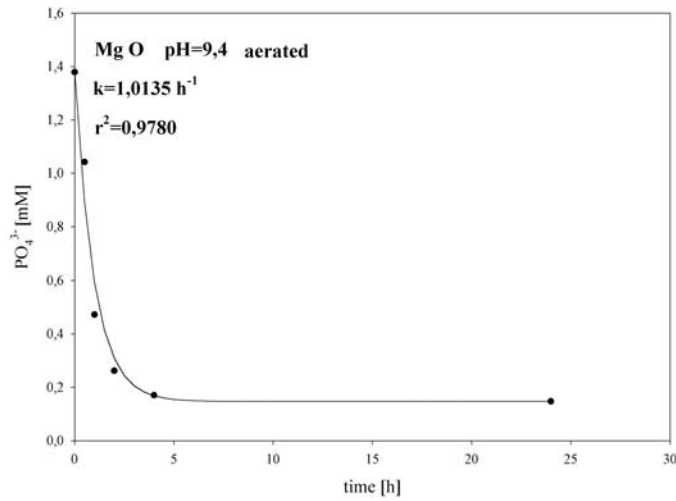


Figure 2b. The phosphate precipitation kinetics in aerated sample, MgO dose 86 mg/l.

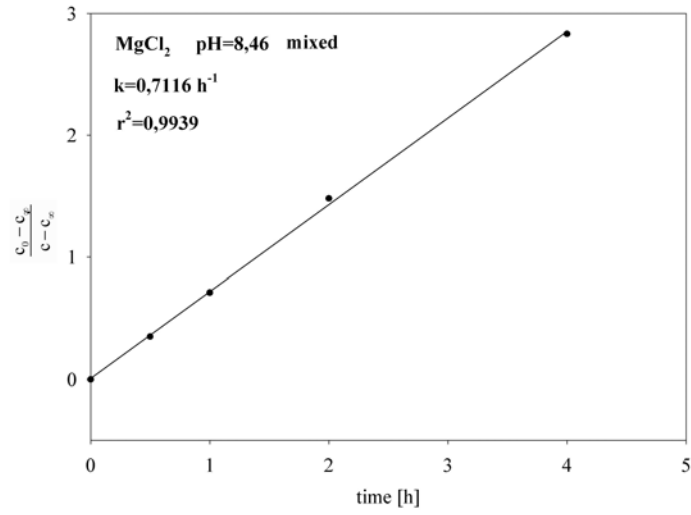


Figure 3a. The phosphate precipitation kinetics in stirred sample (100 min^{-1}), MgCl_2 dose 463 mg/l.

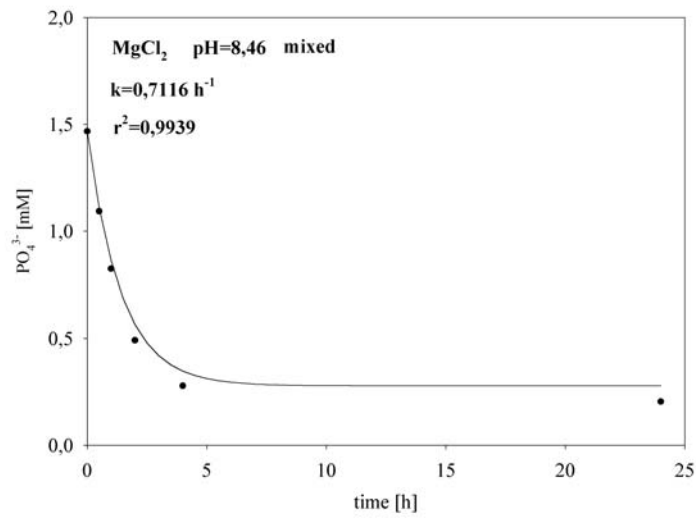


Figure 3b. The phosphate precipitation kinetics in stirred sample (100 min^{-1}), MgCl_2 dose 463 mg/l.

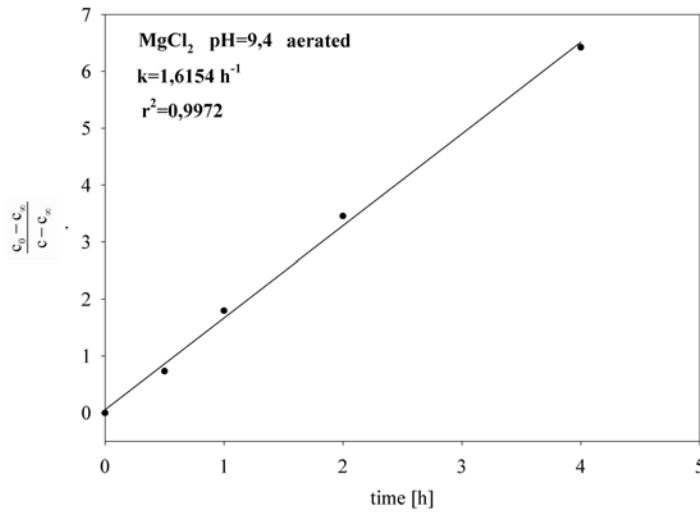


Figure 4a. The phosphate precipitation kinetics in aerated sample, $MgCl_2$ dose 452 mg/l.

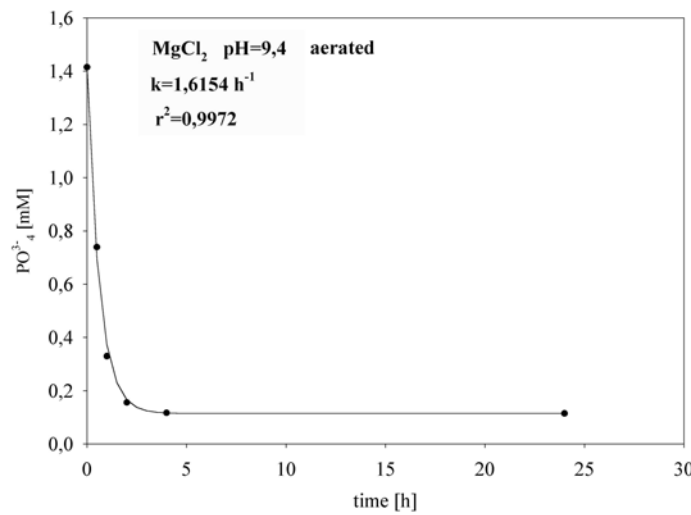


Figure 4b. The phosphate precipitation kinetics in aerated sample, $MgCl_2$ dose 452 mg/l.

In the gently aerated sample the pH value were 9.5 and above units, the mixing of the sample caused increasing pH only to 9.12 units.

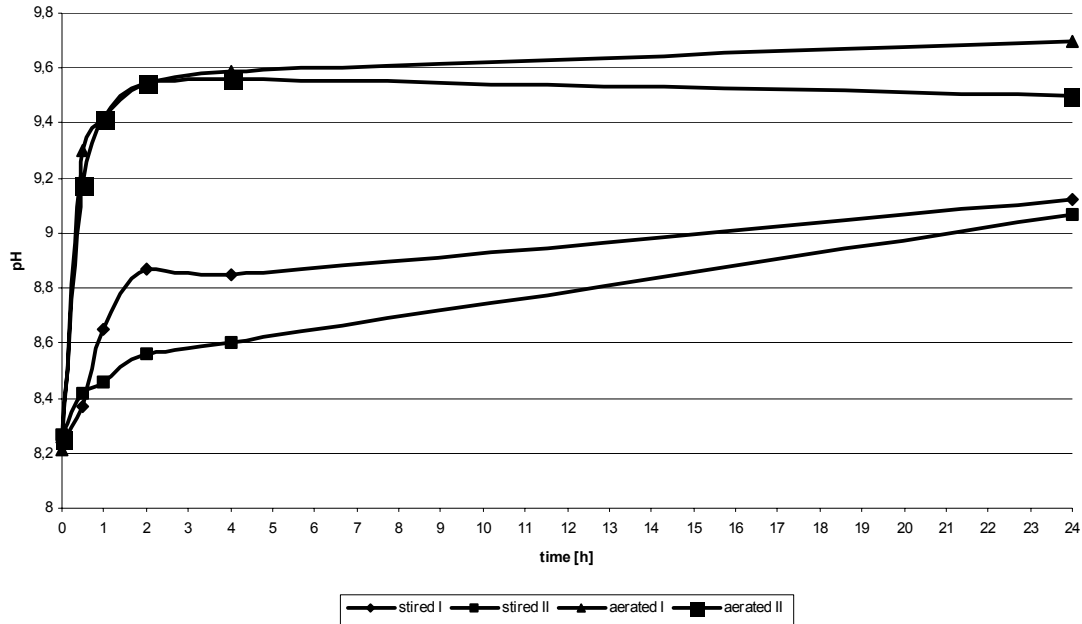


Figure 5. pH value in stirred and aerated samples.

The effect of aeration can be negligible, when the sodium hydroxide solution were used to pH correction. The final pH values were 9,5 units and above. In these cases the effect of the good solubility magnesium compound was clearly observed. The some highest reaction rate were obtained when magnesium chloride were used.

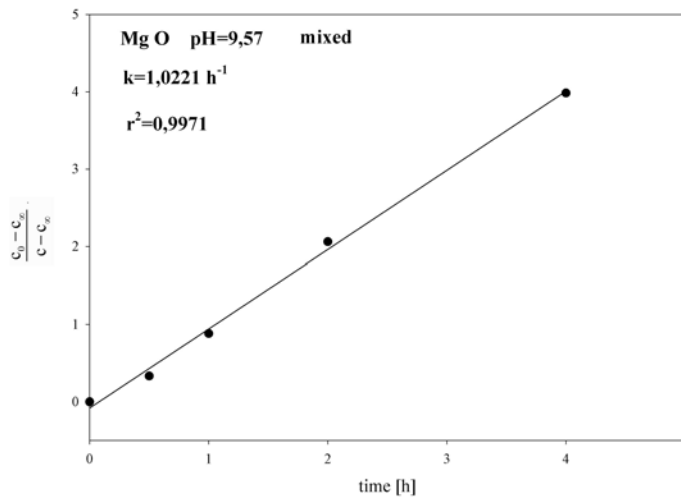


Figure 6a. The phosphate precipitation kinetics in alkalized and stirred sample (100 min^{-1}), MgO dose 80.09 mg/l.

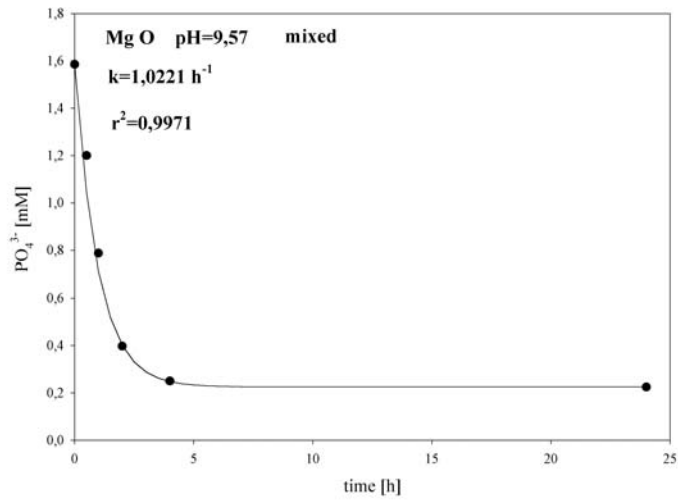


Figure 6b. The phosphate precipitation kinetics in alkalized and stirred sample (100 min^{-1}), MgO dose 80.09 mg/l.

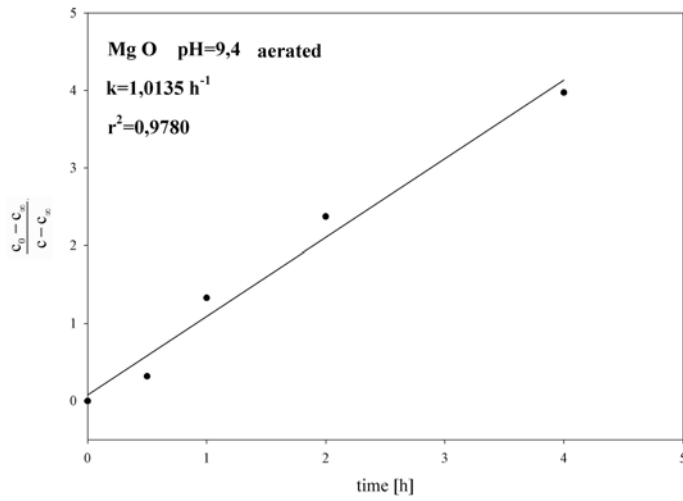


Figure 7a. The phosphate precipitation kinetics in alkalized and aerated sample (100 min^{-1}), MgO dose 99.7 mg/l.

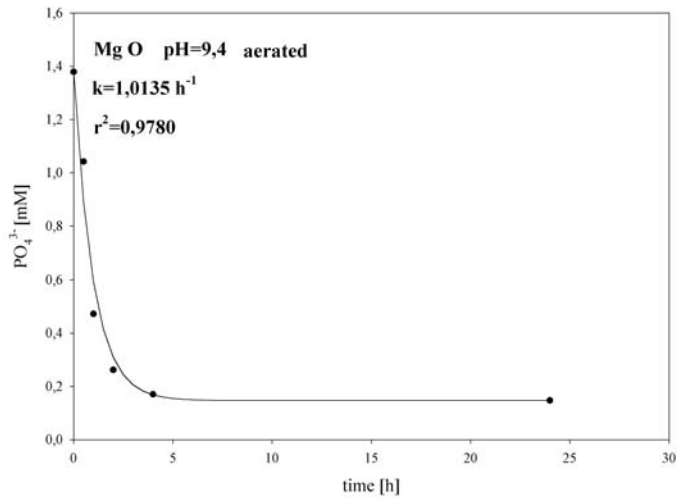


Figure 7b. The phosphate precipitation kinetics in alkalized and aerated sample (100 min^{-1}), MgO dose 99.7 mg/l.

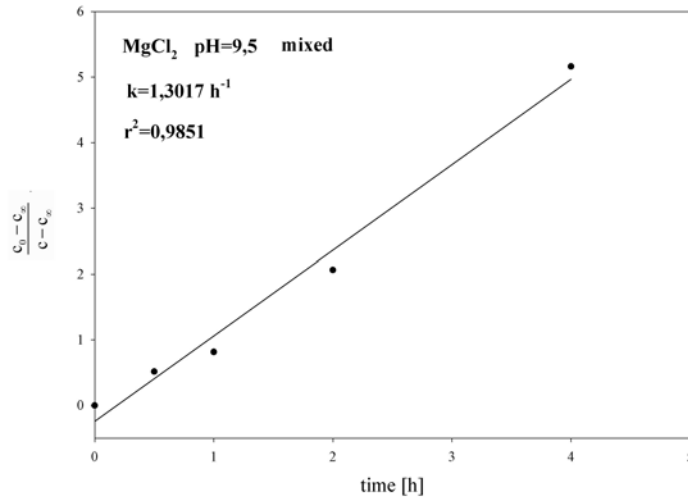


Figure 8a. The phosphate precipitation kinetics in alkalized and stirred sample (100 min^{-1}), MgCl₂ dose 602.1 mg/l.

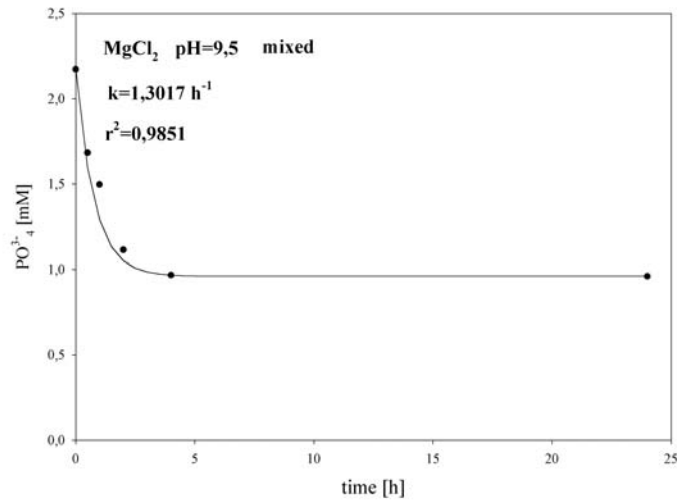


Figure 8b. The phosphate precipitation kinetics in alkalized and stirred sample (100 min^{-1}), MgCl_2 dose 602.1 mg/l.

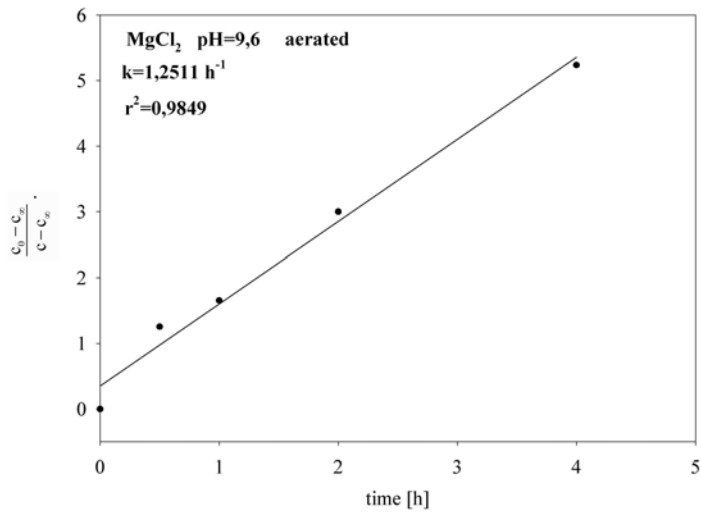


Figure 9a. The phosphate precipitation kinetics in alkalized and aerated sample, MgCl_2 dose 413.3 mg/l.

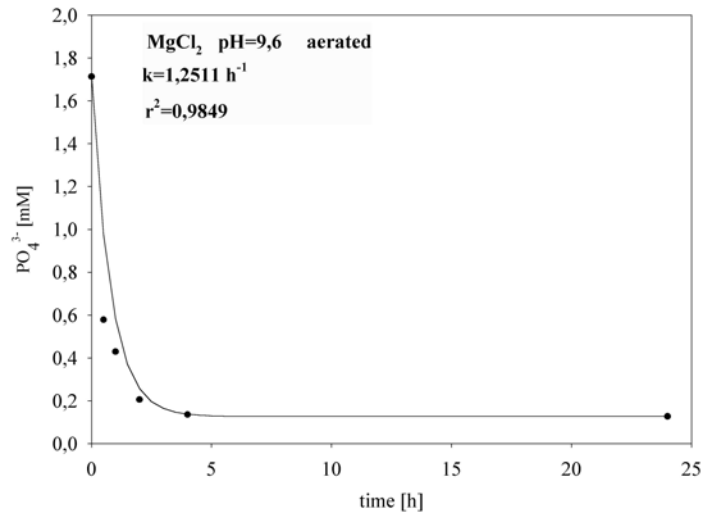


Figure 9b. The phosphate precipitation kinetics in alkalized and aerated sample, MgCl_2 dose 413.3 mg/l.

REFERENCES

Koutsoukos P., Amjad Z., Tomson M.B. and Nancollas G.H. (1980). Crystallization of calcium phosphates: A constant composition study. *J. Am. Chem. Soc.*, **27**, 1553–1557.