

# Study of $\text{Cd}^{2+}$ , $\text{Al}^{3+}$ , and $\text{SO}_4^{2-}$ Ions Influence on Struvite Precipitation from Synthetic Water by Dissolved $\text{CO}_2$ Degasification Technique

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## Abstract

The effect of cadmium, aluminum, and sulphate ions on struvite precipitation kinetics and morphology of solids obtained was investigated in this study. Thus, these ions were introduced as additives in solution where struvite precipitation was achieved. The main results obtained showed that the  $\text{Cd}^{2+}$  ions cause the probable co-formation, with struvite, of an amorphous phase observed from  $\text{Cd}^{2+}$  concentration of 10 mg/L; the addition of aluminum ions in the solution does not affect the nature of the crystalline phase, identified as struvite. However, these ions cause the formation of agglomerates of larger and larger as the concentration rises. Moreover, their increasing improved significantly the yield of phosphates removal; although the sulfate ions have no effect on the nature of the precipitated phase identified as struvite, independently of molar ratio studied, they affect the thermal decomposition of struvite. This latter is done in a single step by increasing the concentration of these ions for the  $\text{SO}_4^{2-}/\text{PO}_4^{3-}$  molar ratio of 8.

## Keywords

$\text{CO}_2$  Degasification Technique, Struvite Precipitation,  $\text{Cd}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{SO}_4^{2-}$

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## 1. Introduction

Struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) is a sparingly soluble salt which can be used as a valuable fertilizer in agriculture [1]. It can also contribute to scaling phenomenon as it can precipitate with other hard salts in wastewater treatment equipments plants [2]-[4]. Many parameters are susceptible to control the precipitation of this salt: supersaturation ratio [4], concentration of major ions [5], temperature [6], pH [7], nature of materials [4], airflow rate [7] and foreign ions [8] [9]. Several techniques have been used to precipitate struvite: stirring [9], aeration [10]-[12], seeding [13],  $\text{CO}_2$  degasification technique [4] [7]. During struvite precipitation, a relatively important ratio of phosphate can be recovered according to conditions and technique used. Indeed, Suzuki *et al.*, (2005) [12] have obtained 65%; Ali and Schneider, (2006): 70% [14], Battistoni *et al.*, (2002): 80% [10], Saidou *et al.*, (2009a): 92% [7], Jaffer *et al.*, (2002): 97% [11], and Guadie *et al.*, (2014): 98% [15]. The study aims to investigate the effect of some foreign ions on struvite precipitation. Thus,  $\text{Cd}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{SO}_4^{2-}$  were added, separately, in solution where struvite might precipitate, and the effect of each ion on kinetics and morphology of struvite was studied using  $\text{CO}_2$  degasification technique reported previously [4] [7].

## 2. Materials and Methods

### 2.1. Synthetic Water Preparation

Synthetic water used in all experiments in this work was prepared by mixing the respective aqueous solutions of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  in desired proportions in a calcium carbonate solution. This solution was previously prepared by dissolving calcium carbonate solids in a flow of  $\text{CO}_2$ . Reagents  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (purity > 99%),  $\text{NH}_4\text{H}_2\text{PO}_4$  (purity > 99%) and  $\text{CaCO}_3$  (purity: 99%) were respectively supplied by Fluka, Sigma Aldrich and Merck.

The study of the effect of cadmium, aluminum and sulfate ions was carried out using solutions prepared from  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{Na}_2\text{SO}_4$  solids. Cadmium ions were adding in synthetic solution at a concentration varying from 0 to 100 mg/L; aluminum from 0 to 6 mg/L. Sulfate ions were introduced at  $\text{SO}_4^{2-}/\text{PO}_4^{3-}$  molar ratio between 0 and 8. It should be noted that all these experiments are conducted at  $25^\circ\text{C}$ , an airflow rate of  $40 \text{ L} \cdot \text{min}^{-1}$ , an initial solution pH of 6.5 in a PVC cell by the  $\text{CO}_2$  degasification technique [7].

### 2.2. Analyzes

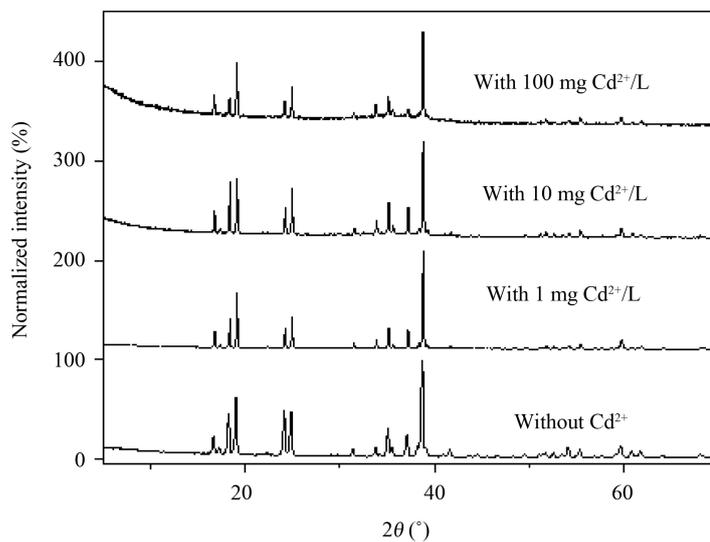
The phosphate concentration in the solution was determined by the colorimetric method using the reagent vanadomolybdic UV-visible spectrophotometer (model: HACH DR/4000). The solids obtained were analyzed using different physicochemical techniques: X-rays diffraction (XRD: X-PERT PRO model), scanning electron microscopy (SEM: Phillips model), infrared (IR: PerkinElmer model), laser particle size (model: Malvern Mastersizer 2000), differential scanning calorimetry (DSC: Mettler Toledo model).

## 3. Results and Discussion

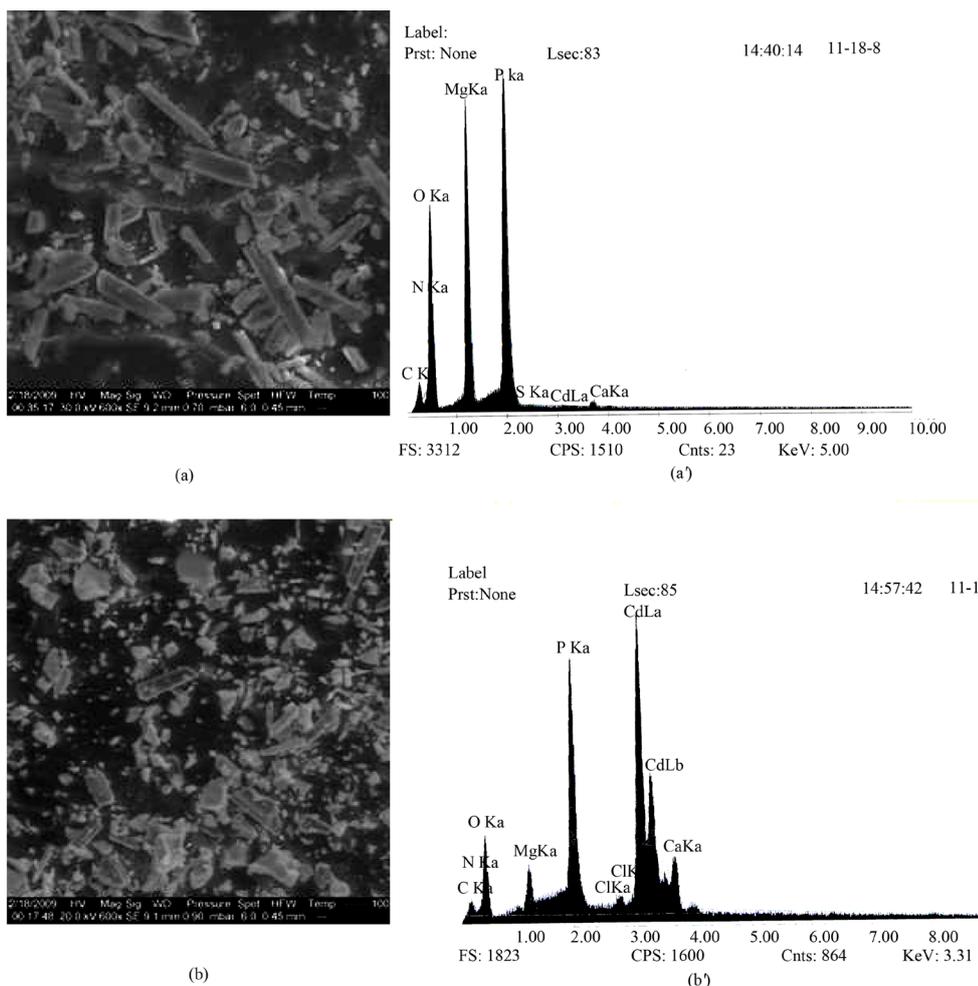
### 3.1. Effect of $\text{Cd}^{2+}$

X-rays diffractograms of solids obtained after addition of  $\text{Cd}^{2+}$ , with concentrations ranging from 0 to  $100 \text{ mg} \cdot \text{L}^{-1}$ , showed, in addition to precipitation of struvite, probable occurrence of an amorphous phase affecting the resolution peaks of struvite from a cadmium concentration of  $10 \text{ mg} \cdot \text{L}^{-1}$  (Figure 1). This phase is more pronounced when the concentration of  $\text{Cd}^{2+}$  increased. This finding is also supported by the decrease of the characteristics of struvite needles (Figure 2(a) & Figure 2(b)). It is unidentified, but it is probably consisting of Cd, Ca and P as shown elemental analysis (EDAX) of the sample (Figure 2(a') & Figure 2(b')). This result is in agreement with the study of Ronteltap *et al.*, (2007) [16].

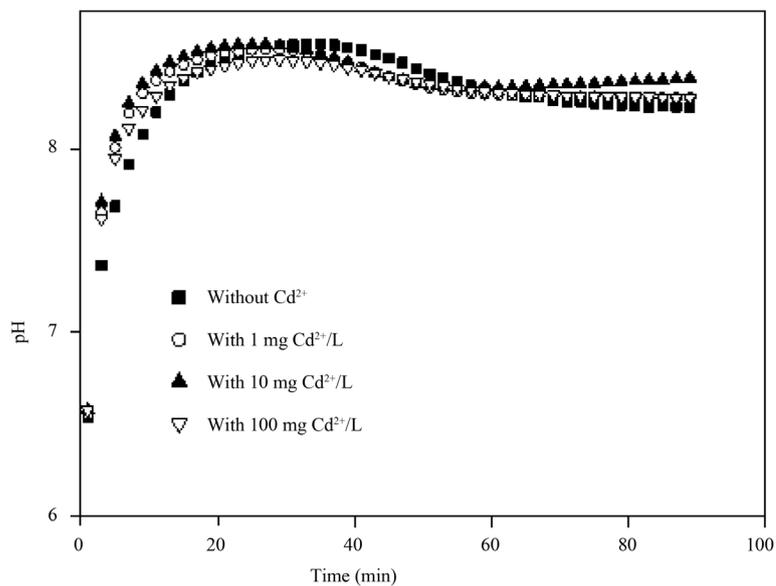
The temporal evolution of the pH of the solution, the time course of  $\text{PO}_4^{3-}$  concentration in the solution for different  $\text{Cd}^{2+}$  concentration are shown in Figure 3 and Figure 4. The precipitation pH and induction times are practically constant. Thus, we deduced that the addition of  $\text{Cd}^{2+}$  did not affect these two parameters. Furthermore, the yield of 35.5% phosphates removal for  $\text{Cd}^{2+}$  concentration equal to  $10 \text{ mg} \cdot \text{L}^{-1}$  (Table 1) was obtained. Beyond this concentration, the yield decreases. This result is probably related to the formation of the amorphous phase. Indeed, Figure 2(b') showed that the solid phase obtained contains less magnesium than that of Figure 2(a'). Consequently, given struvite equimolarity, the compound obtained in the presence of  $100 \text{ mg} \cdot \text{L}^{-1}$  of  $\text{Cd}^{2+}$



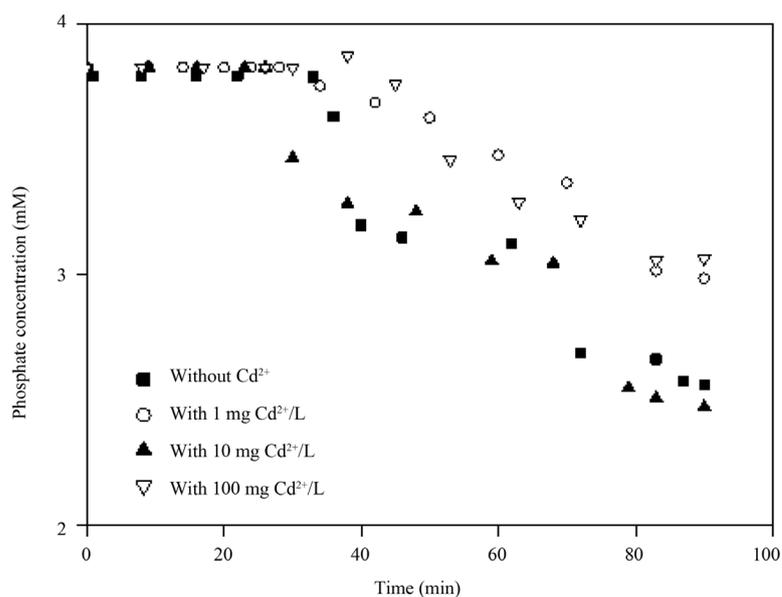
**Figure 1.** Superposition of X-rays diffractograms of precipitates obtained for different  $\text{Cd}^{2+}$  concentration.



**Figure 2.** SEM pictures (a) (b) and EDAX spectra ((a') (b')) of solids obtained for different  $\text{Cd}^{2+}$  concentration: ((a) (a')): 1 mg  $\text{Cd}^{2+}$ /L; ((b) (b')): 100 mg  $\text{Cd}^{2+}$ /L.



**Figure 3.** Temporal evolution of solution pH for different Cd<sup>2+</sup> concentration.



**Figure 4.** Temporal evolution of solution phosphate concentration for different Cd<sup>2+</sup> concentration.

**Table 1.** Induction time, Precipitation pH, and Phosphate removal ratio for different Cd<sup>2+</sup> concentration.

Cd <sup>2+</sup> concentration (mg/L)	Induction time $t_i$ (min)	Precipitation pH	Phosphate removal (%)
0	35	8.57	32.55
1	29	8.54	21.97
10	27	8.57	35.33
100	30	8.48	19.9

contains less phosphate than that obtained in the presence of 1 mg/L of Cd<sup>2+</sup>. These remarks may explain the decrease in phosphate removal ratio observed when the Cd<sup>2+</sup> concentration increased.

### 3.2. Effect of $\text{Al}^{3+}$

The addition of aluminum ions in the solution did not affect the nature of the crystalline phase, identified to struvite. However, influence on peak intensities was observed (Figure 5).

In addition, these ions led to the formation of agglomerates of larger and larger amounts when its concentration increased (Figure 6). These results are in agreement with those of Le Corre *et al.* (2007) [17] according to which the  $\text{Al}^{3+}$  ions are considered as coagulants.

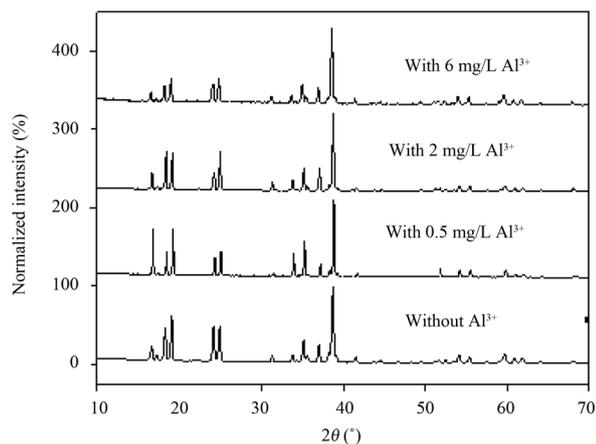
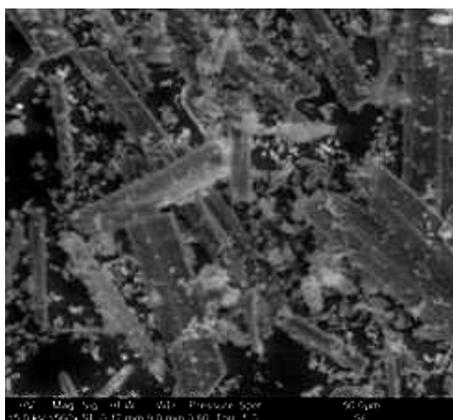
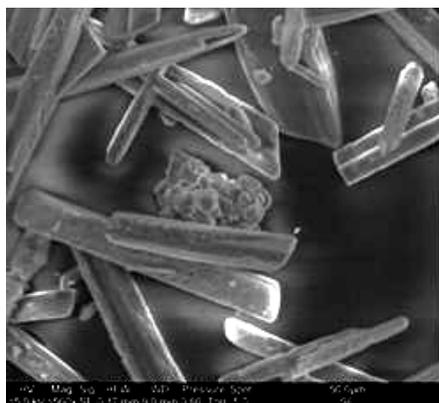


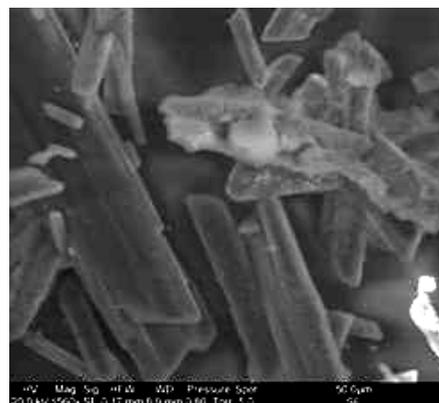
Figure 5. Superposition of X-rays diffractograms of solids obtained for different  $\text{Al}^{3+}$  concentration.



(a)



(b)



(c)

Figure 6. SEM pictures of solids obtained for different  $\text{Al}^{3+}$  concentration: (a) 0.5 mg/L; (b) 2 mg/L; (c) 6 mg/L.

On the other hand, the addition of aluminum ions generally led to a reduction of the induction time which changed from 35 to 21 min, when its concentration varied from 0 to 6 mg/L. The precipitation pH varied between 8.57 and 8.98 in the studied interval of  $\text{Al}^{3+}$  concentration (Figure 7 and Table 2). It is also noted that the phosphate removal yield was, significantly, improved by the addition of these ions, as the latter passed from 32 to 67% when the concentration of  $\text{Al}^{3+}$  ions varied from 0 to 6 mg/L (Figure 8 and Table 2).

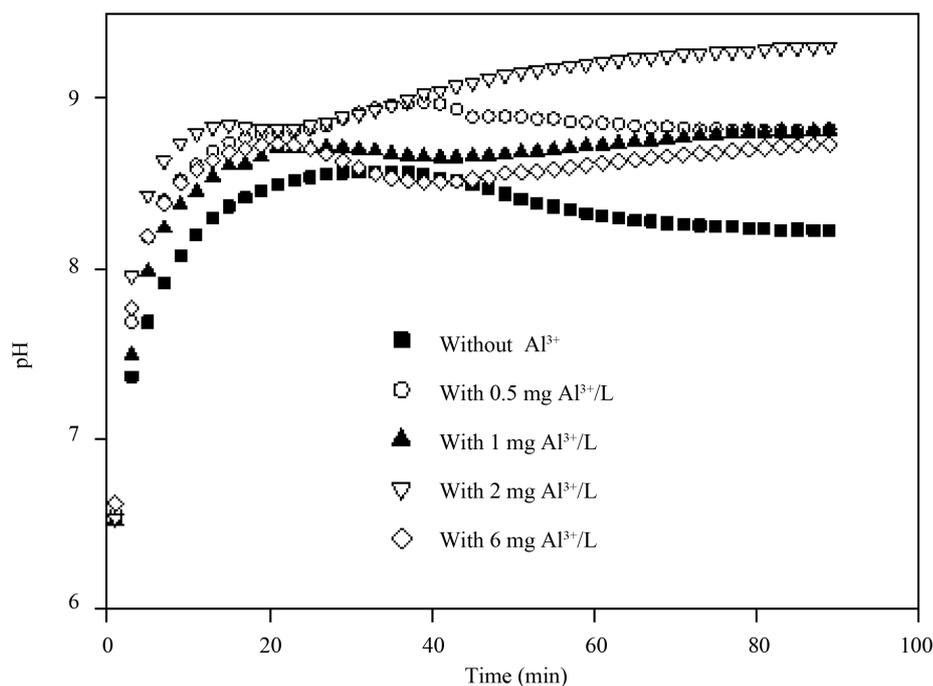


Figure 7. Temporal evolution of solution pH for different  $\text{Al}^{3+}$  concentration.

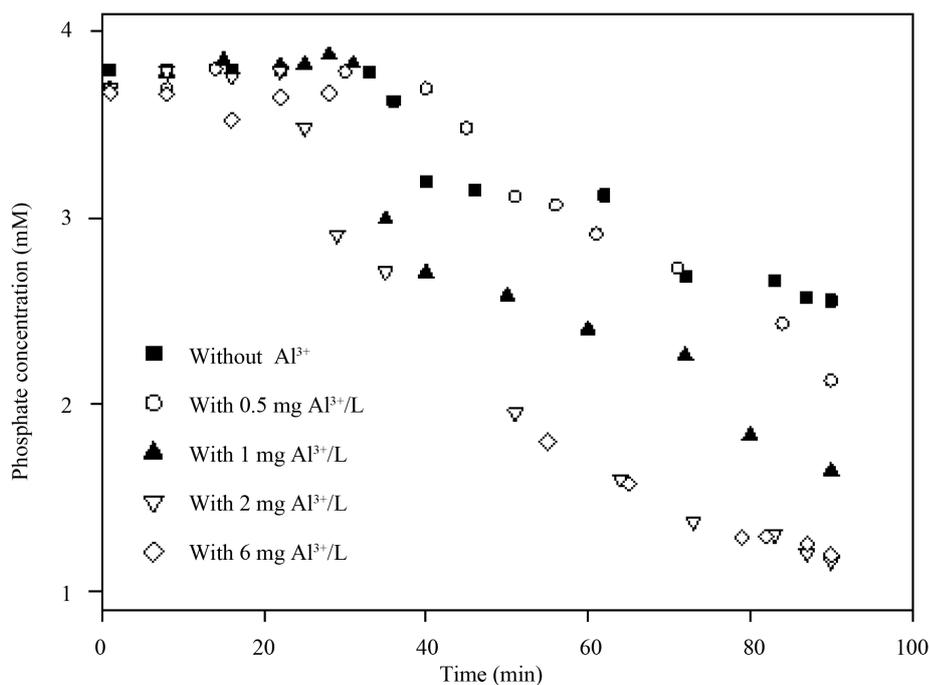


Figure 8. Temporal evolution of solution phosphate concentration for different  $\text{Al}^{3+}$ .

### 3.3. Effect of $\text{SO}_4^{2-}$

To determine the effect of sulfate ions on struvite precipitation, increasing amounts of this ion were added in the solution so that the  $\text{SO}_4^{2-}/\text{PO}_4^{3-}$  molar ratios varied from 0 to 8. The solids obtained, analyzed by X-ray diffraction, for these molar ratios, is identified to struvite (Figure 9). Just, the peak intensities were changed when this molar ratio increased. Moreover, the SEM pictures, and the elemental analysis showed the same grain morphology (Figure 10(b)) and the presence of the same elements of struvite (Figure 10(a') & Figure 10(b')).

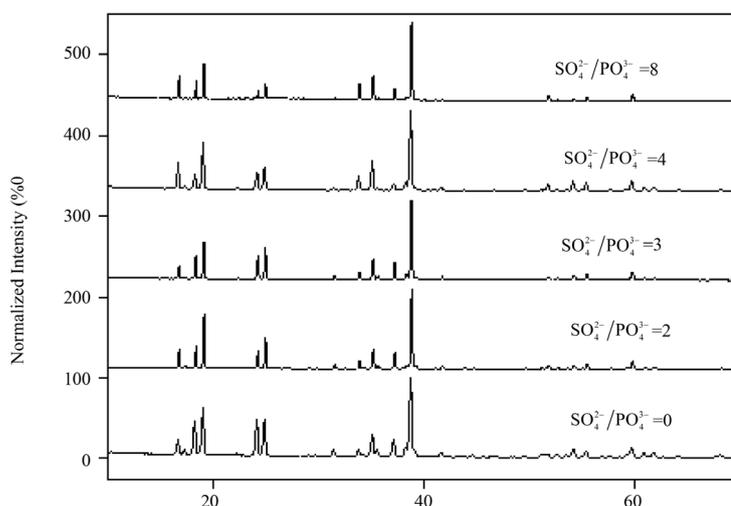
On the other hand, the precipitation pH of the compound ranged from 8.6 to 8.9 in this range of the molar ratio studied (Figure 11 and Table 3). Moreover, the best phosphate recovery efficiency is obtained for  $\text{SO}_4^{2-}/\text{PO}_4^{3-}$  molar ratio = 2 (about 42%) (Figure 12 and Table 3). In addition, the induction time remained almost constant (about 20 min) in the interval [2] [4] molar ratio (Figure 12 and Table 3). This parameter passed to 43 min when the molar ratio became equal to 8. This result is in agreement with the study of Kabdasli *et al.* (2006) [18] who found an increase in the induction time of struvite with the concentration of  $\text{SO}_4^{2-}$ . Increasing the amount of sulfate in the solution affected also the thermal decomposition of struvite. Indeed, figure 13, showed the presence of two types of evolution of the solid obtained. The first is observed at  $\text{SO}_4^{2-}/\text{PO}_4^{3-}$  molar ratio of 2 where it passed from a monotransformation ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} \rightarrow \text{MgHPO}_4 + \text{NH}_3 \uparrow + 6\text{H}_2\text{O} \uparrow$ ) to multitransformation by a gradual elimination of ammonia and water by the following equations:

**Table 2.** Induction time, precipitation pH, and phosphate removal ratio for different  $\text{Al}^{3+}$  concentration.

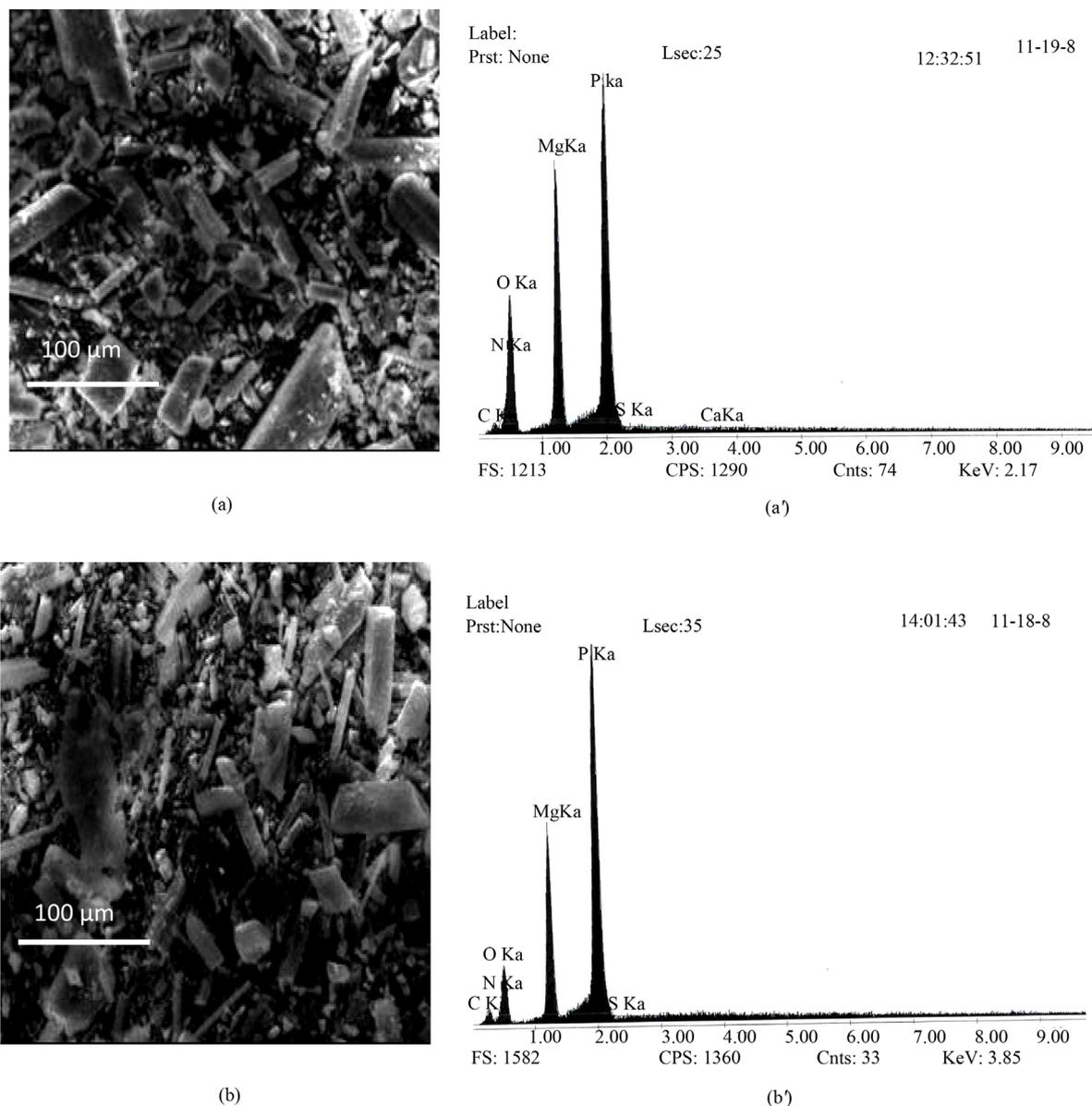
$\text{Al}^{3+}$ concentration (mg/L)	Induction time $t_i$ (min)	Precipitation pH	Phosphate removal (%)
0	35	8.57	32.55
0.5	40	8.98	42.4
1	27	8.71	55.55
2	15	8.84	68.69
6	21	8.73	67.5

**Table 3.** Induction time, precipitation pH, and phosphate removal ratio for different  $\text{SO}_4^{2-}/\text{PO}_4^{3-}$  molar ratios.

$\text{SO}_4^{2-}/\text{PO}_4^{3-}$	$t_i$ (min)	Precipitation pH	Phosphate Removal (%)
0	35	8.57	32.55
2	20	8.6	42.15
3	22	8.8	39.8
4	21	8.6	32.28
8	43	8.9	27.22



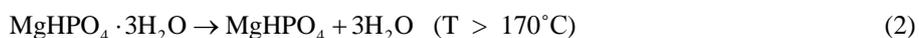
**Figure 9.** Superposition of X-rays diffractograms of solids obtained for different  $\text{SO}_4^{2-}/\text{PO}_4^{3-}$  molar ratios.



**Figure 10.** SEM pictures and EDAX spectra of solids obtained: ((a) (a'))  $\text{SO}_4^{2-}/\text{PO}_4^{3-} = 2$ ; ((b) (b')):  $\text{SO}_4^{2-}/\text{PO}_4^{3-} = 8$ .



Then:



This result is in agreement with the previous studies [19] [20].

By increasing  $\text{SO}_4^{2-}$  concentration, there is a decrease in the temperature of the first step, reaching about  $110^\circ\text{C}$  which became the only decomposition step of struvite by removing simultaneously 6 molecules of water with ammonia when  $\text{SO}_4^{2-}/\text{PO}_4^{3-}$  molar ratio reached 8. These observations showed that the decomposition of struvite, in one step, is facilitated by increasing its amount for  $\text{SO}_4^{2-}/\text{PO}_4^{3-}$  molar ratio of 8.

#### 4. Conclusions

After this study, we can conclude as follow:

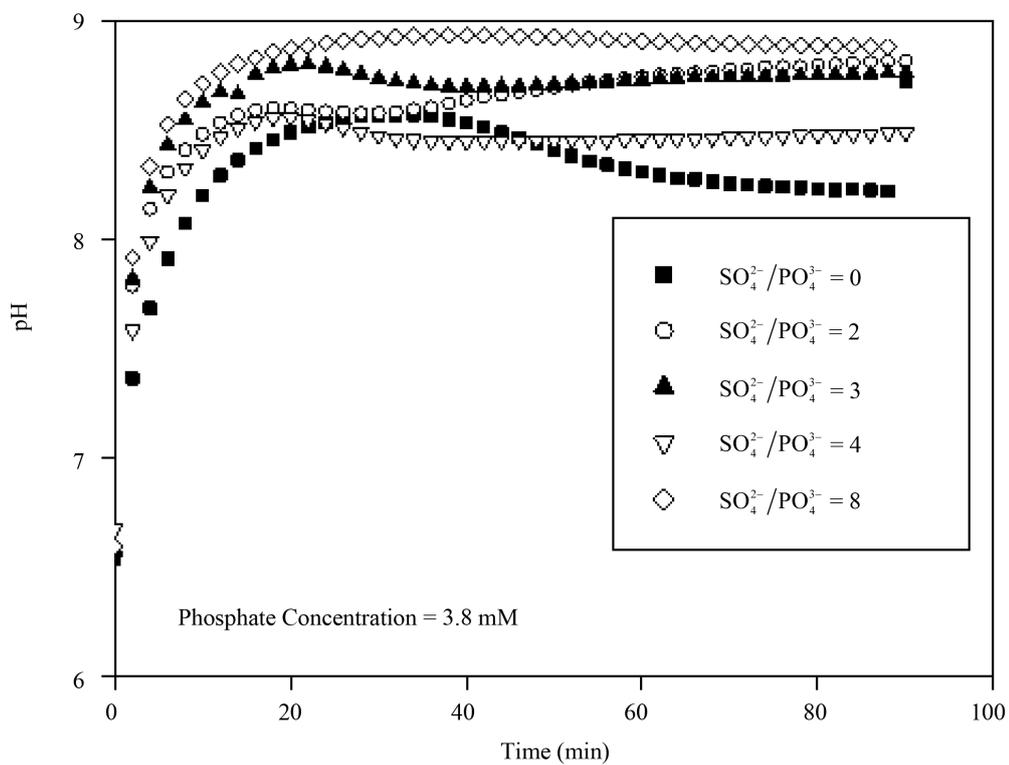


Figure 11. Temporal evolution of solution pH for different  $\text{SO}_4^{2-}/\text{PO}_4^{3-}$  molar ratio.

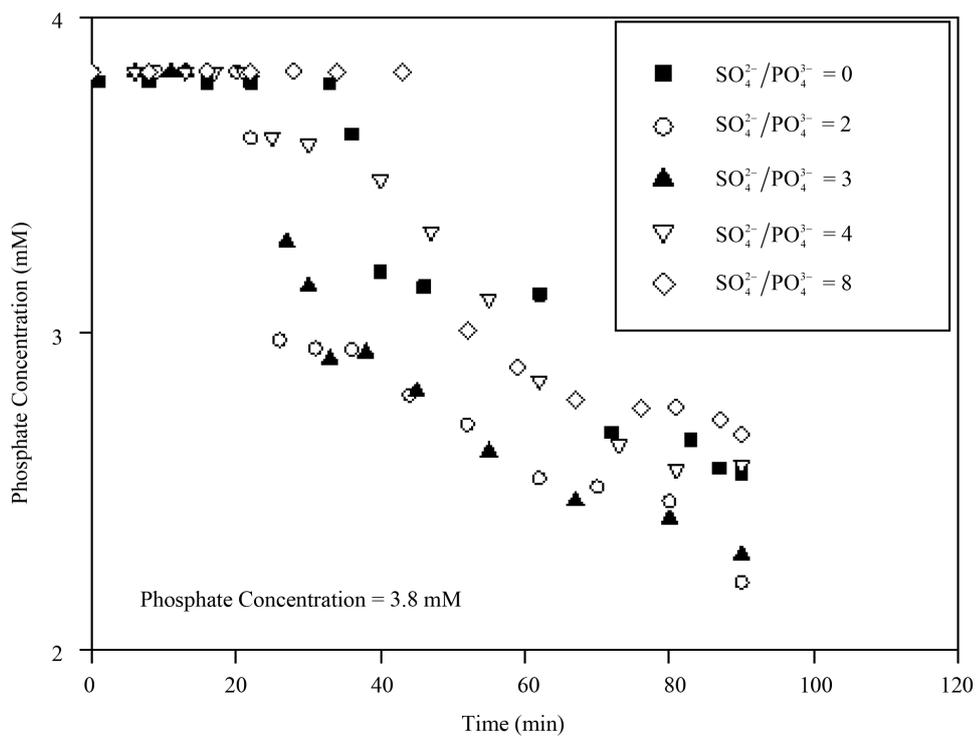
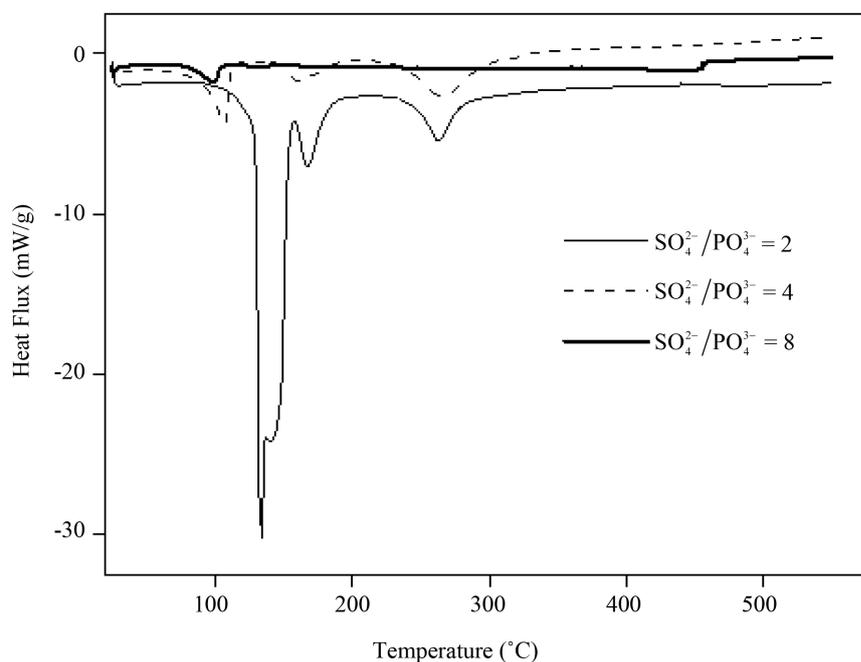


Figure 12. Temporal evolution of solution phosphate concentration for different  $\text{SO}_4^{2-}/\text{PO}_4^{3-}$  molar ratios.



**Figure 13.** Heat flux in function of temperature for different  $\text{SO}_4^{2-}/\text{PO}_4^{3-}$  molar ratios.

- The  $\text{Cd}^{2+}$  ions cause the probable co-formation, with struvite, of an amorphous phase observed from  $\text{Cd}^{2+}$  concentration of 10 mg/L.
  - The addition of aluminum ions ( $\text{Al}^{3+}$ ) in the solution does not affect the nature of the crystalline phase, identified to struvite. However, these ions cause the formation of agglomerates of larger and larger as the aluminum concentration rises. Moreover, their increasing improves significantly the yield of phosphate removal.
- Although the sulfate ions ( $\text{SO}_4^{2-}$ ) have no effect on the nature of the precipitated phase, identified to struvite, irrespective of molar ratio studied, however, they affect the thermal decomposition of struvite. This latter is done, in a single step, by increasing the concentration of these ions for the molar ratio of 8.

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