Judul : Crystallization of struvite in a hydrothermal solution with and without calcium and carbonate ions

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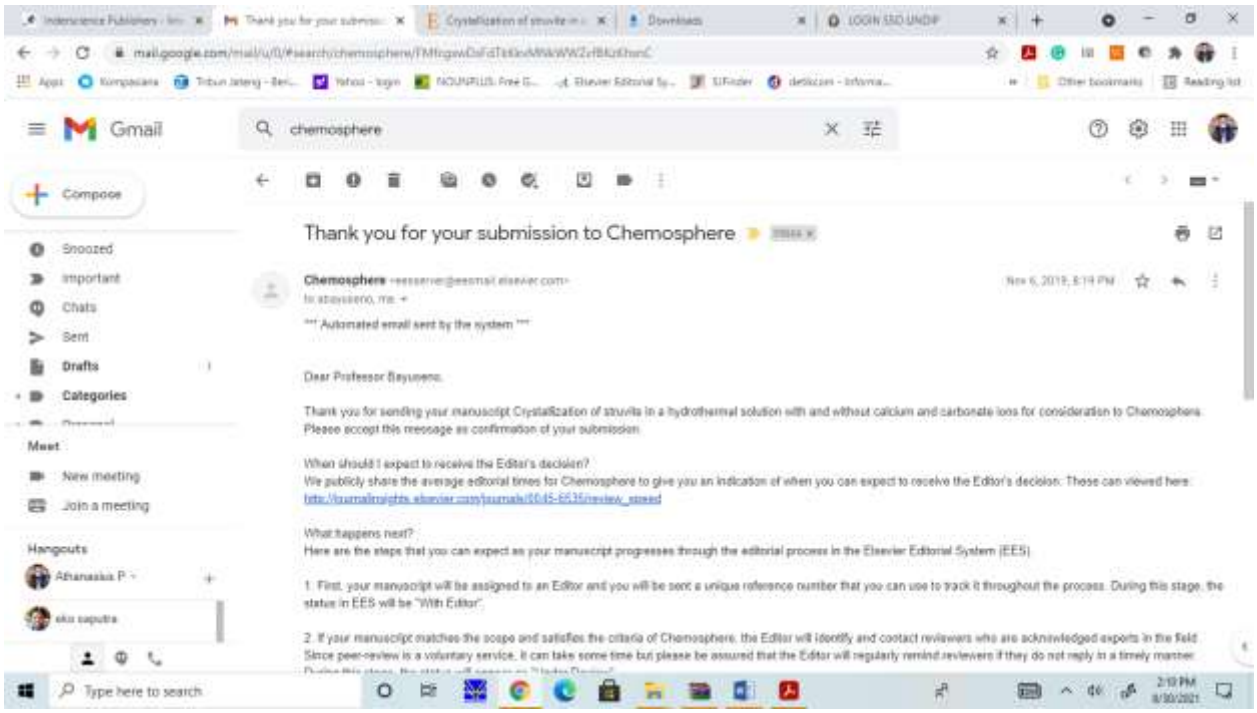
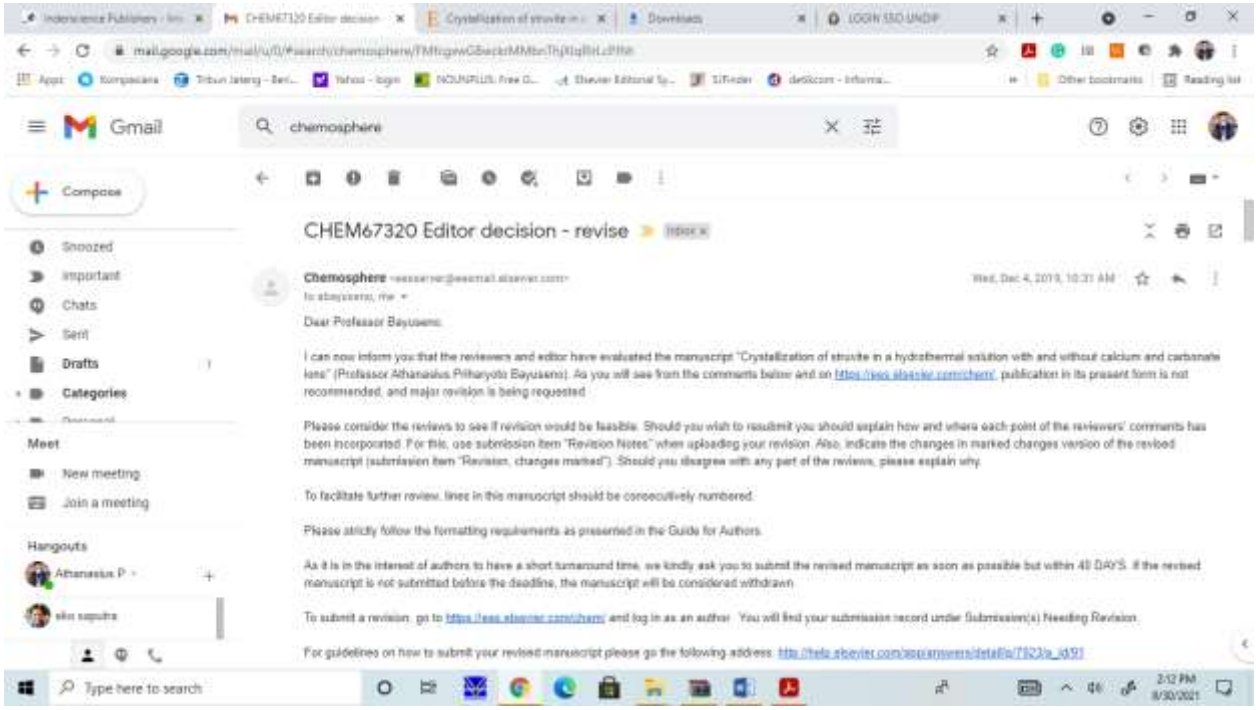




Dear Editor,

Thank you for your letter on our manuscript. We would like to thank the editor and reviewers for their constructive remarks. The manuscript has been improved accordingly. In the text we used track changes for the addition/revision of the manuscript. Following, we wrote in the font style of yellow for the answer of the reviewer.

Reviewer #1: The paper presented the influence of calcium and carbonate on struvite crystallization in solution at pH 9.0 and 10.0. The experiment is well and adequate analysis & discussion was given. In a whole, this paper seems to be relevant enough for the readership and scope of Chemosphere. However, some problems should be taken into account before final acceptance.

Response:

Thank you again for this constructive suggestion.

General comments

1. Line 117 Why was the heating of the reactor set at 120 °C for 24 h? It is known that struvite crystals are not stable at high temperature, and NH_4^+ might be lost. Authors should give out the explanation.

Response:

This is true that the struvite may not stable at high temperature and NH_4^+ might be lost. However, the hydrothermal method in a closed reactor may avoid NH_4^+ volatilization, while the struvite may stay in the precipitate according to previous literature. The statement has been amended accordingly

Revised version:

In this study, the experimental work was designed on a direct alkaline hydrothermal activation, in which KOH was added in the prepared hydrothermal solution in a closed autoclave reactor and heated at fixed temperature and time. Alkali metal hydroxide solutions were employed to activate the hydrothermal reactions because it has been shown to be effective in the struvite crystallization (Bayuseno and Schmahl, 2018). At the temperature of 120 ^{O}C, heating of the mixtures undertaken in the sealed conditions may yield most of the ammonia, if not all, was transformed into NH_3 species resulting from dissolution. However, the closed system of hydrothermal reactor can avoid NH_4^+ volatilization. Further hydrothermal condition at 120 ^{O}C provided the orthophosphate activity increasing in the excess water, implying that minerals other than struvite may be developed (Stumm and Morgan, 1970).

References:

Bayuseno, A.P., Schmahl, W.W., 2018. Hydrothermal synthesis of struvite and its phase transition: Impacts of pH, heating and subsequent cooling methods. J. Cryst. Growth 498, 336-345.

Stum, W., Morgan, J.J., 1970. Aquatic chemistry. Wiley-Intersecience, New York, NY 583.

2. Line 150 What is the basis of pH value and temperatures in this study? There is common view that P recovery from high pH wastewater is cost, resulting in low purity of crystals.

Response: It was a good question and the statement in line 150 has been revised accordingly

Revised version:

In general, struvite can favourably precipitate from high pH values (basic) and temperatures in various mother solutions (artificial urine or in artificial wastewater) (Bouropoulos and Koutsoukos, 2000; Doyle and Parsons, 2002). In particular, hydrothermal treatment of wastewater can effectively transport nutrient components in sewage sludge into the liquid product. Thus the hydrothermal method was adopted in this experimental study because of having great potential in the development of morphology-controlled nanomaterials for P recovery from the solution. Also, the method operates at low temperatures in the one-step process thereby consuming the low energy. Practically, the advantages of the method can reduce environmental impact, produce versatility of many new minerals in any shape and size (Reißmann et al., 2018). Here, the choice of parameter ranges

(pH value and temperature) was guided by the outcome of the previous hydrothermal experiments (Bayuseno and Schmahl, 2018) and this condition was considered still realistic for an economically feasible process of wastewater in struvite.

References:

Doyle, J. D., Parsons, S.A., 2002. Struvite formation, control and recovery. Water Res. 36, 3925–3940.

Bayuseno, A.P., Schmahl, W.W., 2018. Hydrothermal synthesis of struvite and its phase transition: Impacts of pH, heating and subsequent cooling methods. J. Cryst. Growth 498, 336-345.

Bouropoulos, N.C., Koutsoukos, P.G., 2000. Spontaneous precipitation of struvite from aqueous solutions. J. Cryst. Growth 213, 381–388.

Reißmann, D., Thrän, D., Bezama, A., 2018. How to identify suitable ways for the hydrothermal treatment of wet bio-waste? A critical review and methods proposal, Waste Manag. Res. 36, 912–923.

3. Line 219 I think the citation is not accurate. The experiment design is not adequate to obtain that conclusion. In addition, it seems that only one temperature was set in this study.

Response: this is good suggestion that the quotation is not exact. The statement has been amended accordingly.

Original: Here, struvite and dittmarite crystals were still observed, while pH and temperature are not significant parameters controlling quality of the hydrothermal product (Musvoto et al. 2000b).

Revised version

Struvite and dittmarite crystals were still observed, while pH and temperature are not significant parameters controlling the quality of the hydrothermal product (Bhuiyan et al. 2008; Musvoto et al. 2000b). The previous study identified the mechanisms via supersaturation and ammonia activity in the solution, which struvite precipitated and subsequent partially transformed into dittmarite after heating the hydrothermal reactor containing solution with pH 9 and 10 at 120 ^{O}C (Bayuseno and Schmahl, 2018).

References:

Bayuseno, A.P., Schmahl, W.W., 2018. Hydrothermal synthesis of struvite and its phase transition: Impacts of pH, heating and subsequent cooling methods. J. Cryst. Growth 498, 336-345.

Bhuiyan, M.I.H., Mavinic, D.S., Koch, F.A., 2008. Thermal decomposition of struvite and its phase transition. Chemosphere 70, 1347-1356.

Musvoto, E.V., Wentzel, M.C.M., Ekama, G.A.M., 2000b. Integrated chemical—physical processes modelling II. Simulating aeration treatment of anaerobic digester Supernatants. Water Res. 34, 1868-1880.

3 line 332 "relate to" should be "related to"

Response: The statements in line 332 have been amended accordingly

4 line 332-345. It is better to add related reference in some sentences of this paragraph.

Response: we had added some references on the statement accordingly

Li, X., Ito, A., Sogo, Y., Wang, X., Le Geros, R.Z., 2009. Solubility of Mg-containing β-tricalcium phosphate at 25 °C. Acta Biomater., 5, 508–517.

Lagier, R., Baud, C.-A., 2003. Magnesium Whitlockite, a Calcium Phosphate Crystal of Special Interest in Pathology. Pathol. Res. Pract. 199, 329–335.

Li, G-C., Wang, P., Liu, C-B., 2017. Hydrothermal Synthesis of Whitlockite. J. Inorg. Mater. 32, 1128-1132.

5. line 355 It is not accurate using "at any pH values".

Response: we have revised the statement accordingly

6. In Abstract and Conclusion Part, it is a little general for the main results points in this study. Authors should present more specific results or conclusions.

Response: we had revised the abstract and conclusion part accordingly

Original:

Hydrothermal experiments of struvite crystallization were conducted in an autoclave bomb-reactor that contains the MAP (magnesium, ammonium, and phosphate) solution with or without calcium and carbonate ions. Batch mode of experiments, of which the temperature at the 120 ^{O}C for 24 h, varying $Mg^{2+}/Ca^{2+}/HCO^{-}_{3}$ ratios, and pH (9.0 and 10.0) was selected. XRPD Rietveld method confirmed that struvite and dittmarite could be grown at both pH solutions (9 and 10) in the absence of Ca^{2+} and HCO^{-}_{3} ions. However, depending on $Mg^{2+}/Ca^{2+}/HCO^{-}_{3}$ ratios, minerals including calcite, dolomite, hydroxyapatite, sylvite, struvite, and Mg-whitlockite could be developed at pH 9 and 10. Moreover, the SEM images of the resulting crystal solids can show different morphologies of nanosized particles. These hydrothermal experiments demonstrated the biomineralization process of producing struvite and Ca-phosphate minerals and the significant outcome of controlling $Ca^{2+/}HCO^{-}_{3}$ ions present in the solution.

Revised version

Hydrothermal experiments with magnesium, ammonium, and phosphate (MAP) solution at a temperature of 120 ^{O}C for 24 h and pH (9 and 10), whilst effects of varying $Mg^{2+}/Ca^{2+}/HCO^{-}_{3}$ ratios on struvite crystallization were examined. The study was performed to investigate their effects on the quality and quantity of crystals using the XRPD Rietveld refinement and SEM method. Obviously, the struvite crystallization was inhibited through the forming of calcite, dolomite, hydroxyapatite, sylvite, and Mg-whitlockite under different pH conditions. In the absence of Ca^{2+} and HCO^{-}_{3} ions, struvite and dittmarite were formed at pH solutions (9 and 10). Struvite proportion reduced with pH (9 and 10) under $Mg^{2+}/Ca^{2+}/HCO^{-}_{3}$ ratios (1:1:1 and 2:1:1), and depleted under the $Mg^{2+}/Ca^{2+}/HCO^{-}_{3}$ ratio of 1:2:2. An obvious change in the morphologies of crystals into nanosized particles was observed. Results of the low proportion of struvite for experiments with $Mg^{2+/}Ca^{2+/}HCO^{-}_{3}$ molar ratios may be a drawback for phosphate recovery.

Reviewer #2: This study investigated struvite crystallization with and without calcium and carbonate ions, which was operated under the temperature at the 120°C. The following is my comments.

1. in ABSTRACT section, the authors described the process and impact factors. Unfortunately, I did not read substantial conclusions. Also, important data should be added.
Response: Thank you for suggestion, we added some data in revised version

Revised version

Hydrothermal experiments with magnesium, ammonium, and phosphate (MAP) solution at a temperature of 120 ^{O}C for 24 h and pH (9 and 10), whilst effects of varying $Mg^{2+}/Ca^{2+}/HCO^{-}_{3}$ ratios on struvite crystallization were examined. The study was performed to investigate their effects on the quality and quantity of crystals using the XRPD Rietveld refinement and SEM method. Obviously, the struvite crystallization was inhibited through the forming of calcite, dolomite, hydroxyapatite, sylvite, and Mg-whitlockite under different pH conditions. In the absence of Ca^{2+} and HCO^{-}_{3} ions, struvite and dittmarite were formed at pH solutions (9 and 10). Struvite proportion reduced with pH

(9 and 10) under $Mg^{2+}/Ca^{2+}/HCO^{-}_{3}$ ratios (1:1:1 and 2:1:1), and depleted under the $Mg^{2+}/Ca^{2+}/HCO^{-}_{3}$ ratio of 1:2:2. An obvious change in the morphologies of crystals into nanosized particles was observed. Results of the low proportion of struvite for experiments with $Mg^{2+/}Ca^{2+/}HCO^{-}_{3}$ molar ratios may be a drawback for phosphate recovery.

2. Line 27-28. Considering that hydrothermal treatment will cost a lot of energy, I don't think this method is practical for struvite recovery. Why the authors thought "simple to use" of hydrothermal method to struvite precipitation. Reasons?

Response: this is a good suggestion that the use of hydrothermal methods may cost a lot of energy. However, the method is considered as simple, cost-effective and easy to set up, then it has become a realistic option for ammonium and phosphorus recoveries in struvite according to previous literature (Xue et al., 2015). The statement has been amended accordingly.

Revised version

Recently, the hydrothermal system is widely known to be simple, cost-effective and easy to set up (Jesse and Davidson, 2019; Xue et al., 2015). Moreover, the system is suitable for use of wastewater treatment because of their low energy consumption (low temperatures in the single-step process), reduction of environmental impact, prod Recently, the hydrothermal system is widely known to be simple, cost-effective and easy to set up (Jesse and Davidson, 2019; Xue et al., 2015). Moreover, the system is suitable for use of wastewater treatment because of their low energy consumption (low temperatures in the single-step process), reduction of environmental impact, production with the versatility of struvite in any form and size. Correspondingly the hydrothermal method is a realistic option for ammonium and phosphorus recoveries from wastewater in struvite. However, the treatment stage benefit of wastewater by the hydrothermal method is slightly offset by generating a new waste residue containing chlorides, water-soluble sulfate and alkali ions (Jesse and Davidson, 2019). Hence, a degree of compromise may be required in the selection of hydrothermal treatment due to the competition between the quality benefits of struvite for a slow-release fertilizer and producing other pollutants (Li et al. 2019). Nevertheless, it is envisaged that the large good-quality crystals and quantity of struvite can be achieved by the hydrothermal treatment (Zhu et al., 2019).

References:

Jesse, S.D., Davidson P C., 2019. Treatment of post-hydrothermal liquefaction wastewater (PHWW) for heavy metals, nutrients, and indicator pathogens, Water 11, 854.

Zhu,Y., Wei, J., Liu, Y., Liu,X., Li, J., Zhang, J., 2019. Assessing the effect on the generation of environmentally persistent free radicals in hydrothermal carbonization of sewage sludge. Scientific Reports 9, 17092.

Xue, X., Chen, D., Song, X., Dai, X., 2015. Hydrothermal and pyrolysis treatment for sewage sludge: Choice from product and from energy benefit. Energy Procedia 66, 301-304.

3. Line 31, "Accordingly hydrothermal synthesis of struvite has become a promising technology",What about economic calculation? The authors should clear the audience's doubts.

Response: this is a good suggestion. The statement has been amended accordingly.

Revised version

Furthermore the hydrothermal synthesis of struvite can be adopted in wastewater treatment for recovering phosphorus in a relatively pure, publicly acceptable and potentially commercial form (de-Bashan and Bashan, 2004). As compared to other methods of crystallization and synthesis, hydrothermal synthesis methodology can produce safely crystalline phases, which may become unstable at a higher temperature, provide benefits for dewatering and avoiding water evaporation occurring in the single hydrothermal process with high energy-efficiency. The method is also desirable for the carbonization of sewage sludge leading to the stabilized solid product and can recreate a role as a final treatment step for sewage sludge disposal (Reißmann et al., 2018). Additionally, the potential untapped market for struvite as a slow fertilizer make this option feasible in parallel with the nutrient reduction achieved in the wastewater (Williams, 1998; Durrant et al., 1999).

References:

Durrant, A. E., Scrimshaw, M. D., Stratful, I., Lester, J. N., 1999, Review of the feasability of recovering phosphate from wastewater for use as a raw material by the phosphate industry. Environ Technol, 20, 749-758.

de-Bashan, L.E., Bashan, Y., 2004. Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003). Water Res. 38, 4222–4246.

Reißmann, D., Thrän, D., Bezama, A., 2018. How to identify suitable ways for the hydrothermal treatment of wet bio-waste? A critical review and methods proposal, Waste Manag. Res. 36, 912–923.

Williams, S., 1998, Struvite precipitation in the sludge treatment stream at Slough wastewater treatment plant and opportunities for phosphorus recovery. Environ Technol. 20 (7), 743-747.

4. Line 39-40, "intensive research" of hydrothermal method for struvite? I doubt this comment.

Response: this is a good suggestion. The statement has been amended accordingly.

Revised version

The hydrothermal method has attracted more attention recently, as the appropriate method of struvite crystallization by generating large good-quality crystals and nanoparticles with control over their content and composition (McMillen and Kolis, 2016). It was suggested previously that 100 m^3 wastewater could be converted into 1 kg of struvite (Shu et al., 2006). If the wastewater in the world can be treated by struvite crystallization, 63000 tons of P_2O_5 can be recovered. This value is equal to 16 % of world phosphate rock consumption for mineral fertilizers, whereas phosphate rock is a non-renewable resource that would be depleted within the century. Moreover, 171 g struvite with the purity at least 95 % can be produced from livestock wastewater per square meter without washing. Thus phosphate recovery from wastewater through the hydrothermal synthesis of struvite could be potential options (de-Bashan and Bashan, 2004).

References:

de-Bashan, L.E., Bashan, Y., 2004. Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003). Water Res. 38, 4222–4246.

McMillen, C.D., Kolis, J.W., 2016. Hydrothermal synthesis as a route to mineralogically-inspired structures. Dalton Trans., 45, 2772–2784.

Shu, L., Schneider, P., Jegatheesan, V., Johnson, J., 2006. An economic evaluation of phosphorus recovery as struvite from digester supernatant. Bioresour. Technol. 97, 2211-2216.

5. Line 64, I don't think calcium carbonate is easily to be formed. What about the solubility product constants of these three minerals?

Response: Calcium carbonate ($CaCO_3$) has a very low solubility in pure water (15 mg/L at 25°C), therefore in supersaturated solution, calcium carbonate may be formed according to chemical reaction of Ca and CO_3. As one of the most abundant biominerals, $CaCO_3$ exists as three polymorphs (calcite, aragonite, and vaterite) and an unstable amorphous form (ACC).

Revised version

It has been demonstrated previously that interaction of calcium, phosphate, or carbonate ions in the solutions may produce calcium phosphate hydrate (hydroxylapatite) and calcium carbonate as follows (Le Corre et al. 2005):

$$5\,Ca^{2+} + 3\,PO_4^{3-} + H_2O \rightarrow Ca_5(PO_4)_3OH + H^+ \quad pKsp = 54.45 \qquad (1)$$

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+ \quad pKsp = 6.40 \qquad (2)$$

where pKsp is solubility product constants in form of - log10 Ksp at 25°C. Hydroxyapatite has a higher solubility product constant than that of calcium carbonate indicating the more soluble compound in hydrothermal solution, and it may be precipitated depending on the alkalinity and supersaturation (Ajikumar et al., 2005). However, calcium carbonate ($CaCO_3$) has a lower solubility product constant, it may be easily precipitated in forms of either calcite (pKsp= 8.48), aragonite (pKsp = 8.34) or vaterite (pKsp = 7.91).

References:

Ajikumar, P.K., Wong, L.G., Subramanyam, G., Lakshminarayanan, R., Valiyaveettil, S., 2005. Synthesis and characterization of mono dispersed spheres of amorphous calcium carbonate and calcite spherules. Cryst.Growth Des.5, 1129-1134.

6. MAP, struvite, mixed use throughout the text? Line 116, "by 80 vol. % with the ...", means what? Section 2.2, XRD is normal use for mineral analysis. No need to waste much text for XRD description.

Response: We use MAP (Mg^{2+}, $NH_4^+$and PO^{3-}_4) ions, which are components of struvite, while struvite is magnesium ammonium phosphate hexahydrate. We used the maximum 80 % volume of the total volume of the autoclave with the precursor suspension. We used a common XRPD (x-ray powder diffraction), on which powder was used for measurement analysis. It is a good suggestion and we have amended the statement accordingly.

Revised version

Moreover, a Teflon lined hydrothermal synthesis reactor with 50 ml capacity was filled by 80 % of the total volume of the reactor with the precursor suspension.

Revised version

For the XRPD measurement, a sample holder with capillary glass tube (diameter = 0.5 mm) was filled-up by the dried powder and then exposed to an x-ray beam on an STOE-diffractometer (Germany) in transmission (Debye-Scherrer) geometry. The XRPD data were analyzed for phase identification by a search-match program using the MATCH software. Furthermore, the phase compositions of the hydrothermal product was determined by the Rietveld method with the Program Fullprof-2k, version 3.30 (Rodriguez-Carvajal, 2005). The Rietveld refinement program used the crystal structure model obtaining from the referenced crystal structure model (American mineralogist of crystal structure database -AMCSD) (Downs and Hall-Wallace, 2003).

Further dried powder samples were investigated by SEM technique for the crystal morphology identification. In this manner, the samples were placed on the Al-stubs using double-sided conductive tapes, and the powder surface was coated with carbon.

References:

Downs, R.T., Hall-Wallace, M., 2003. The American Mineralogist crystal structure database. American Mineralogist. 88, 247-250.

Rodriguez-Carvajal J. Program Fullprof.2k, version 3.30, Laboratoire Leon Brillouin, France, June 2005.

7. In the Material and Methods, Phosphate (2374 mg/L) and Mg:Ca:HCO3 molar ratio was so high, which was also shown in Table 1? Unbelievable.

Response:

We got this phosphate concentration based on equal molar of 0.025 mol/L of $HH_4H_2PO_4$ which provided 2374 mg/L.

8. Line 105-119, the prepared solution of Mg, P, Ca, and HCO3- could reach 25 mmol/L, and pH was set to 9 and 10, which indicated that without heating, struvite precipitation or calcium phosphate precipitation could occurred spontaneously. In other words, what goals did the authors want to achieve by using heating? Also, the degree of supersaturation should be determined.

Response:

We proposed the hydrothermal method which plays an important role in producing the quality of struvite crystal with control content and composition. A literature review had been conducted to determine the likelihood of formation for new minerals along with struvite in a short period of time and subsequent mineral stabilities achieved after heating and cooling of the reactor (Bhuiyan et al., 2008; Kontrec et al., 2005). The loss of water and ammonium at the increasing temperature in the closed reactor are also important factors for struvite decomposition, while cooling method may be related to the rehydration of struvite structure in the period of time.

A further degree of supersaturation of minerals could be determined using the chemical equilibrium model in the AQION program. This program can be used for predicting mineral formation at varying pH and temperatures, while the precipitation kinetics of all minerals were not counted in the AQION program. Thus, the model simulations provided under prediction for the potential of mineral formed in the closed reactor under hydrothermal condition (see-Chemical equilibrium modelling of minerals).

Revised version

Additionally, the heating rate of the hydrothermal reactor has a substantial role in the performances of struvite production. A literature review on each of the phosphate minerals provided a possibility of minerals formed in the period of time, while subsequent mineral stabilities could be influenced by the rate of heating and cooling of the reactor (Bhuiyan et al., 2008; Kontrec et al., 2005). For instance, struvite and dittmarite can be crystallised in a short period of time, and subsequent decomposition of those minerals may result from the slow hydration in the solution (Montes et al., 2009). Hydroxyapatite might be also formed from a hydrothermal synthesis of transforming slurries, solutions or gels under mild reaction conditions typically below 350 ^{o}C. Correspondingly the thermal stability, phase transition and decomposition of the products from the hydrothermal system would

provide a better knowledge for engineering of struvite crystals and effects of reaction conditions on crystal quality.

References

Bhuiyan, M.I.H., Mavinic, D.S., Koch, F.A., 2008. Thermal decomposition of struvite and its phase transition. Chemosphere 70, 1347-1356.

Montes, F., Rotz, C.A., Chaoui, H., 2009. Process modeling of ammonia volatilization from ammonium solution and manure surfaces: a review with recommended models, Trans. ASABE 52, 1707-1719.

Kontrec J, Babic-Ivancic V, Brecevic, L., 2005. Formation and morphology of struvite and newberyite in aqueous solutions at 25 and 37 °C. Coll. Antropol. 29, 289-294.

9. Line 117, under such high temperature (120 °), will bicarbonate still keep the same concentrations?
Response: So far hydrothermal synthesis of struvite has been implemented in a closed reactor because of an energy-effective method for dewatering and avoiding water evaporation. Moreover, hydrothermal treatment can involve the carbonization of sewage sludge, leaving the stabilized solid product, therefore acting as a final treatment step for sewage sludge disposal. The hydrothermal method uses the closed reactor hereby avoiding water evaporation and bicarbonate still keeps the same concentration in the solution. We had added texts accordingly.

Revised version

In this condition, the generation of autogenous pressure occurred within the autoclave-closed reactor, in which water evaporation could be avoided leading to bicarbonate keep at the same concentration in the solution. Hydrothermal process may also involve the carbonization of the solution, yielding the stabilized solid product, thereby acting as a final treatment step for the slurry disposal.

10. Line 143-148, did the calculation of saturation index include the impacts of temperature? We should know that temperature was 120° in the experiments.

Response: The relative supersaturation was also calculated using the speciation program of AQION. AQION has inbuilt solubility products for various relevant minerals and additional mineral constants (solubility products) used for the equilibrium calculation in Table 2. The solution pH was varied for different simulations at a constant temperature. Chlorine or sodium ion concentration was allowed to vary to balance the charge of the solution. The statement had been amended accordingly.

Revised version

Conversely, the spontaneous mineral precipitation would occur if the SI value is more than 0. In this study, the SI calculation for potential minerals precipitated from the hydrothermal solution is listed in Table 1.

Further relative supersaturation was calculated using the speciation program of AQION. The AQION program has inbuilt solubility products for various relevant minerals and additional mineral constants (solubility products) used for the equilibrium calculation (Table 2). The solution pH was varied for different simulations at a constant temperature. Chlorine or sodium ion concentration was also allowed to vary to balance the charge of the solution. Here, pH values (9 and 10) and temperature of 120 ^{O}C were selected as the input parameters.

11. Figure 5a, I did not see any particles are similar to struvite crystals, which were obtained in the absence of Ca and HCO3. However, in Table 3, the author confirmed that this experimental operation would obtained struvite. Confusing.
From morphologies of Figure 5a and 5b, I do not see big difference. How the author made a big different conclusion about crystallite minerals.

Response: Figures 5a and 5 b was not correct for the caption. See Figures 5a-d, the description of this figure had been modified accordingly.

Revised version

Fig. 5 SEM image of morphology crystals precipitated from the hydrothermal solution at **a)** pH of 9 in the absence of Ca and HCO_3-ions; **b)** pH of 9 with the molar Mg: Ca: HCO_3 of 1:1:1; and **c)** pH 10 in the absence of Ca and HCO_3-ions and d) pH 10 with the molar Mg: Ca: HCO_3 of 1:1:1 respectively.

12. Table 3, the solubility products of all minerals should be listed.
How did the authors calculate the contents of various minerals in the final solids? It was a little confused that whitlockite, coupling with hydroxyapatite, could be formed in the same reaction. Also, the authors did not present sufficient evidence about how the minerals were determined. XRD determination is not sufficient.

Response: we had added the solubility products of all minerals accordingly.

Revised version:

The XRPD phase quantification results in the precipitates at varying Mg^{2+}/Ca^{2+}/ HCO^{-}_{3} molar ratios of the hydrothermal solution are presented in Table 3 including the solubility product constants of all minerals. However, the solubility product constant for dittmarite is not available in the literature, however, it was suggested that its value is close to that of struvite (Bhuiyan et al., 2008). According to the constant values, most minerals identified by the XRPD method were proposed to be precipitated by the hydrothermal method observed during the study, instead of sylvite which may be formed after drying the samples.

References:

Bhuiyan, M.I.H., Mavinic, D.S., Koch, F.A., 2008. Thermal decomposition of struvite and its phase transition. Chemosphere 70, 1347-1356.

Response: we had added the texts on material characterisation section

Revised version

So far the use of the conventional XRD method has a restriction in that some X-ray diffraction peaks in the diffractogram of multiple mineral phases having significant overlapped peaks could not be accurately identified. However, the drawbacks of superimposed peaks in traditional XRD analysis could be solved by the application of the Rietveld full profile fitting analysis (Rietveld, 1969; Mahieux et al., 2010; Perwitasari et al., 2017; Winburn et al., 2000). The Rietveld method was chosen in the study because: (i) quantitative data for major-minor phases were required, (ii) significant (sometimes total) overlapping peaks were found in samples, and (iii) best confidence in the reliability of result was needed. Here the Rietveld method relies on well known-crystal structure database for phases of natural and synthetic materials. In particular, high-resolution powder diffraction using a Debye-Scherrer transmission geometry was selected to provide better analytical XRD data for avoiding the generation of preferred orientation on the crystalline samples of the hydrothermal product.

The calculation for the contents of various minerals was performed using the refined scale factor of the Rietveld method using the Full-prof software to provide the relative weighted fractions of each mineral composition. In this method, the amounts of all phases present in the sample could be quantified simultaneously. The phase quantification procedure involved the identification of major and minor phases. Correspondingly, total of (wt.%) the relative weighted fractions of the crystalline phases would be 100 %.

References:

Mahieux, P.-Y., Aubert, J.-E., Cyr, M., Coutand, M.. Husson, B., 2010. Quantitative mineralogical composition of complex mineral wastes–contribution of the Rietveld method. Waste Manage. 30, 378-388.

Perwitasari DS, Edahwati L, Sutiyono S, Muryanto S, Jamari J, Bayuseno AP., 2017. Phosphate recovery through struvite-family crystals precipitated in the presence of citric acid: mineralogical phase and morphology evaluation, Environ. Technol. 38, 2844-2855.

Rietveld, H.M., 1969. A profile refinement method for nuclear and magnetic structures. J. Appl. Crystallogr., 2, 65-71.

Winburn, R.S., Grier, D.G., McCarthy, G.J., Peterson, R. B., 2000. Rietveld quantitative X-ray diffraction analysis of NIST fly ash standard reference materials. Powder Diffr., 15 163-172.

Response: we had added the texts on discussion section.

Revised version

Regarding whitlockite versus hydroxyapatite, only a few studies can be found in the literature, in that evolution of those minerals could be linked to a living process in biology and pathology (Lagier and Baud, 2003). It was suggested that whitlockite and hydroxyapatite could be formed together in an aqueous system at a temperature compatible with biological conditions. Therefore, they may be formed in the hydrothermal condition (Li et al., 2017). In this study, hydrothermal synthesis of the MAP solution with varying Mg/Ca/HCO3 molar ratios at 120 ^{O}C provided direct experimental evidence of whitlockite and hydroxyapatite formed in the precipitating products, as the finding was confirmed by XRD Rietveld method in agreement with the crystal structure database (Downs and Hall-Wallace, 2003). Still, much work need to be done for finding a crystallization mechanism of those minerals.

References:

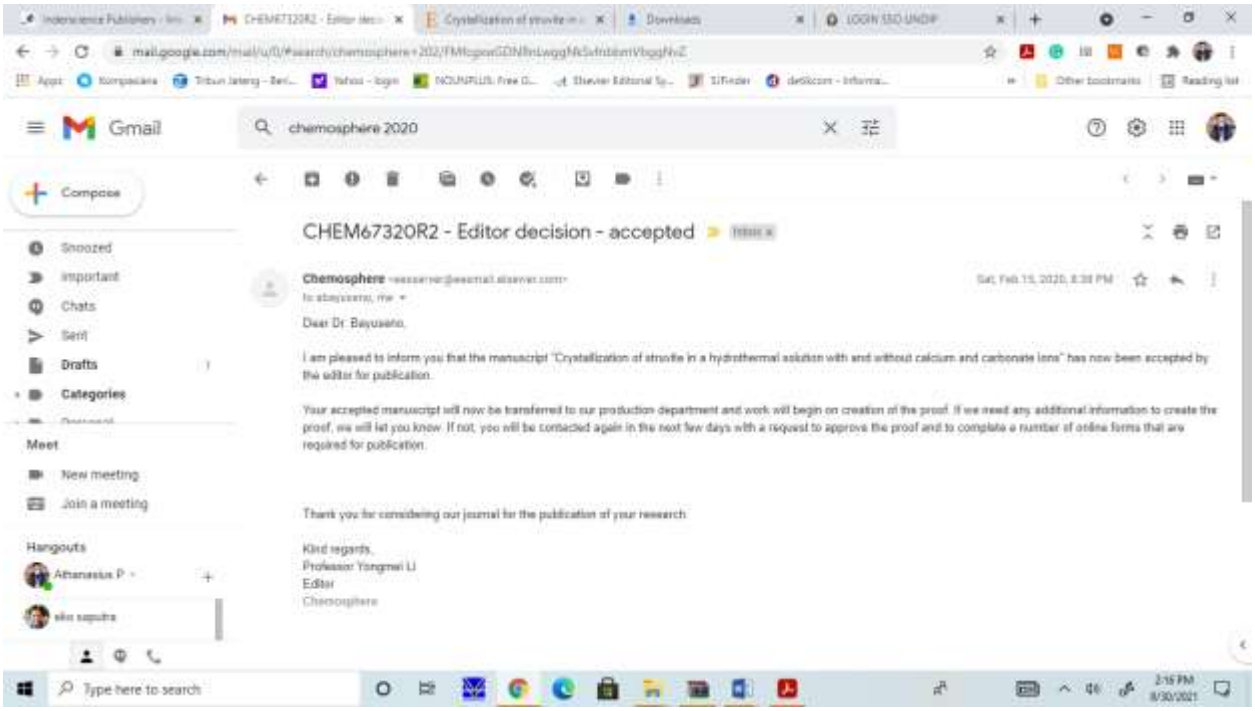
Downs, R.T., Hall-Wallace, M., 2003. The American Mineralogist crystal structure database. American Mineralogist. 88, 247-250.

Lagier, R., Baud, C.-A., 2003. Magnesium whitlockite, a calcium phosphate crystal of Special Interest in Pathology. Pathol. Res. Pract. 199, 329–335.

Li, G-C., Wang, P., Liu, C-B., 2017. Hydrothermal synthesis of whitlockite. J. Inorg. Mater. 32, 1128-1132.

Response: we had added the texts on material characterisation section

The calculation for the contents of various minerals was performed using the refined scale factor of the Rietveld method using the Full-prof software to provide the relative weighted fractions of each mineral composition. In this method, the amounts of all phases present in the sample could be quantified simultaneously. The phase quantification procedure involved the identification of major and minor phases. Correspondingly total of (wt.%) the relative weighted fractions of the crystalline phases would be 100 %.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Athanasius P
CHEM67320R2 - Editor decision - accepted
Chemosphere
Dear Dr Bayuseno,
I am pleased to inform you that the manuscript "Crystallization of struvite in a hydrothermal solution with and without calcium and carbonate ions" has now been accepted by the editor for publication.
Your accepted manuscript will now be transferred to our production department and work will begin on creation of the proof. If we need any additional information to create the proof, we will let you know. If not, you will be contacted again in the next few days with a request to approve the proof and to complete a number of online forms that are required for publication.
Thank you for considering our journal for the publication of your research.
Kind regards,
Professor Yongmei Li
Editor
Chemosphere
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