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by Luluk Edahwati

Formation and controlling of struvite crystals using a novel-vertical reactor: study on purity and morphology variation

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Abstract

Struvite ($MgNH_4PO_4 6H_2O$) is a mineral deposit which is commonly found in the industrial waste-water treatment. The aim of present study was to investigate on the struvite formation using a design of vertical reactor where air was used for a media of agitation. The crystal forming solution was prepared using a mixture of equimolar (MAP) solution for each (0.6313 mol) NH_4OH, $MgCl_2$ dan H_3PO_4 which were placed in separately intake. Crystallisation process was monitored by controlling a flow rate from each inlet. Subsequently the solution was mixed and agitated in the inside of reactor. The continous process was ended up at 60 minutes. Here pH solution of 8, 9 and 10 and a temperature of 30 °C were selected in the study. The materials characteristion of crystals was conducted using SEM/EDX for morphology and elemental analysis; and XRD Rietveld method for mineralogical phase composition. The results showed that mass of crystals at rate of 27.51 mg/h was produced during this experiment and a irregular platy shape crystals was observed under SEM imaging. The elemental analysis of the sample was composed of Mg, P, N and O belonging to struvite. The XRD Rietveld method confirmed that the struvite family-crystals were formed in the precipitate. Obviously the reactor can be potentially used for producing struvite at a high rate.

Keywords: A novel continous reactor, struvite, SEM EDX and XRD Rietveld Method.

Introduction

Phosphorus (P) is one of the main sources of nutrients that can produce eutrophication in aquatic systems (Abdelrazig and Sharp, 1988). Although phosphorus is commonly considered as pollutants in natural water, its recovery has become an interesting area of research in providing a valuable resource of phosphorus in agricultural fertilizers, food supplies, and as a raw material in a fertilizer industry (Sarkar, 1991). On the other hand, the phosphorus mineral resources are economically viable for only 50 years (Frost et al., 2004), Thus the phosphorus recovery from the wastewater collection provides great benefits in

addition to preventing water contamination and devastation mineral resources (Musvoto et al., 2000). Today, various wastewater such as swine waste, agro-industrial effluents, landfill leachate, calf manure, coke manufacturing and leather tanning, contain rich in nitrogen ions (N), phosphorus ions (P) and magnesium ions (Mg) (Loewenthal et al, 1994). The importance of these ions in the wastewater, which can be the main source of the nutrient removal, specifically biological nutrient removal (BNP) processes, can be precipitated as a mineral struvite ($MgNH_4PO_4 \cdot 6H_2O$). Here the struvite precipitation method has become played an important role in nutrient recovery of wastewater.

Further, the mineral are frequently deposited on the surface of the inside diameter of pipe and pump, hence leading to the reduction of performance and increasing the maintenance cost of the equipment (Whitaker Dan Jeffery, 1970). Moreover, the different strategy on preventing struvite formation is adopted by using chemical additives inhibitor (Suzuki et al, 2005; 2007); (Mehta and Batstone, 2013) (Stratful et.al. 2001; Kofina dan Koutsoukos, 2005). Consequently, the formation of "uncontrolled" struvite is one of the main research commonly conducted on the environmental engineering, particularly in the waste-treatment systems (Gaterell et al., 2000), On the other hand, at that time, struvite has a commercial trade and so research on struvite formation and prevention has no longer become a decisive topic. Thus, research on struvite is more oriented product towards controlling the formation and nutrient recovery for the needs of the fertilizer industry.

Struvite formation and growth rate are mainly controlled by pH (Ohlinger et al, 1999; Matynia et al., 2006), super saturation ratio (SSR) (Kofina and Koutsoukos, 2005), temperature (Boistelle et al., 1983), intensity mixing /concentration mixing (Ohlinger et al., 1999) and the presence of foreign ions in solution (Le Corre et al., 2005). The Struvite crystal growth rate will increase with increasing pH in the range of pH 8.5 - 9.5 (Bouropoulos and Koutsoukos, 2000). Stuvite crystal growth rate can be also controlled by the type of reactor used. It was reported that a mixing intensity using a fluid bed reactor yielded the relatively lower rate of struvite growth than that using a stirred tank reactor (Myerson and Ginde, 2002). Since struvite precipitation is known as an effective method to remove and recover phosphorus as a marketable fertilizer, the use of a designed reactor for struvite crystallization has become a global concern.

Further, the use of fluidized bed reactors for obtaining good quality products is regarded an important scheme for controlling precipitate specific properties of the product such as purity, crystal size distribution, shape, filterability, and sedimentation rate. In this case, a reactor has been recognized to provide the production of chemicals in well crystalline form and with

controlled particle size distribution. It was likewise reported that the gel production and very small particles due to the formation of agglomerates can be solved using the reactor. The fluidized beds can be taken as the best equipment for precipitating compounds from diluted solutions [Plasari and Muhr (2009)]. This group of precipitating reactor can categorized as the effective reactor of providing the treatment capacity per unit volume is tenths times higher than the capacity of classical reactors, no matter the compound concentration. In particular, a batch reactor operates mechanically stirrer yielding the inhomogeneous crystalline form, because of the shape of the crystal is destroyed by facing movement stirrer. Using a flow reactor pipe with insulated oblique operation may continuously result in better crystals, because the crystals formed may be not hit by the stirrer. Nevertheless, only limited study for struvite precipitation has been performed on the use of the flow reactor pipe with air agitation.

This study was undertaken to investigate the struvite formation potential at an artificial wastewater using the novel-vertical flow reactor. In the present work, an air-agitated and insulated skewed reactor was designed for mixing the crystal forming solution within the inside reactor. This vertical reactor was selected because the pattern of flow in the reactor may control the continuous reaction of the solution. The crystals precipitated from the reactor was subsequently characterized using X-ray powder diffraction (XRPD) method for phase composition analysis and SEM/EDX (scanning electron microscopy/energy dispersive spectroscopy) for morphology and elemental analysis.

METHODOLOGY

Materials and crystallization experiment

The experiments were conducted in the vertical reactor with a working volume of 500 ml. The reactor scheme of the pilot plant for struvite crystallization is given in Figure 1. The working principle of this oblique sectional reactor is similar to the stirred tank reactor, as a function of the canted bulkhead which is designed to solve the air bubbles entering into the reactor. With the bulkhead jagged and inflows in the opposite way, there is eddy inside the reactor and then that the contiguity between the reagent granulated and incoming air can take place properly. To observe the dynamics of the mixing process and the quality of liquid-solid separation in the thickener used the glass tube reactor. It was mentioned in the literature that the mixing of the reacting fluids in the inside reactor requires stirrers (Sellami et al., 2005). Thus, the reactor used in this present study was equipped with air bubbles stirrer in order to ensure

the accurate mixing in all precipitation zones. The air flowing speed is set to a value of 240 mililiter per minute.

The reactor is composed of two zones, the reacting zone with a cylinder of 50 cm in height and 5 cm in outside diameter; 2,5 cm inside diameter and the liquid-solid separation zone on the bottom of the reactor. In the conical part, the supernatant liquid leaves the reactor owing to an overflow system (Outlet 1). The solid accumulated in the reaction zone leaves the reactor through an outlet at the bottom of the reactor (Outlet 2). The first solution (solution A) was composed of NH_4OH (the ammonium source), solution B of HPO_4 (the phosphorus source) and solution C of $MgCl_2 \cdot 6H2O$ (the magnesium source) with analytical grade (Merck, Germany). pH-adjusted to 8, 9 and 10 with KOH. Equimolar (0,03 M) of each A, B and C solution was initially prepared in 500 ml-glass beaker at room temperature and then was placed on the top of the reactor. These solution flowed naturally. Subsequently the solution of KOH for pH maintenance was injected from the bottom together with air. The reaction process was set to 60 minutes, while every 5 minute intervals were determined to pH monitoring. After the process was completed, the precipitate was then filtered and dried at room temperature for 48 hours. The dried product were subsequently analyzed by XRD Rietveld analysis for mineralogical characterization of the crystal, while the elemental composition and morphology of the crystals was performed using SEM equipped by EDX.
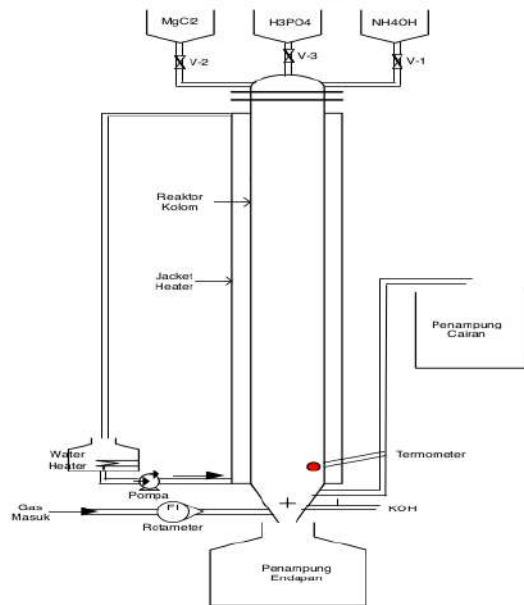

Figure 1: A vertical pipe reactor scheme for the experiment

Materials characterization by XRPD and SEM

XRPD data was collected using Cu-Kα radiation, a graphite diffracted beam monochromator, and scintillation detector on a Bragg-Brentano focusing diffractometer (D5005 SHIMATZU). The scan parameters (5-90 $2\theta^O$, 0.020 steps, 15 seconds/step) and the diffracted beam slits of 0.2^O were selected. The finding of possible crystalline phases in the precipitates was performed by a PC-based search-match program (the X'Pert plus Philips software). The x-ray source was generated from x-ray tube operated at 50 kV and 40 mA. The identified crystalline phase was subsequently verified by the XRD Rietveld method (Rietveld, 1969). This was performed by the Rietveld program available in the X'Pert plus Philips software. The diffraction line widths (FW) as a function of tan (θ) used the u-v-w formula of Caglioti et al, (1958), and u, v and w were refined to calculate the crystallite size. The refinement strategy of the XRPD data could be found in detailed discussion elsewhere (Bayuseno and Schmahl, 2015).

Further, scanning electron microscopy (SEM) on a JEOL DSM apparatus equipped with an EDX was to characterize the microstructure and morphology. For the examination, the powder sample of the precipitate were initially mounted on a circular metallic sample holder and subsequently sputtered with carbon.

RESULTS AND DISCUSSION

Examination on crystallization time of struvite

The pH variation observed for struvite crystallization during the experimental study was given for pH 8, 9 and 10. This pH change was demonstrated as a function of crystallization time given in Figure 2. In the run of pH 8, the initial pH of 8 underwent the sharp reduction until the crystallization time increased to 40 minutes and then remained unchanged for a period of 20 minutes. In contrast, the pH change in run of pH 9 varied between 0.006 and 0.080, which could be observed at the first minute and then remained constant for about 2 minutes. As the crystallization time reached to almost 10 minutes, the pH dropped dramatically. Subsequently the pH decreased gradually until the struvite crystallization was possibly ended in 60 minutes. Moreover, the experimental run of pH 10, the induction period occurred for about 5 minutes. In the pH range of 9.95 and 10, the pH remained unchanged for 10 minutes, and then dropped again as pH reached at 9.90. In the last 20 minutes, pH was obviously constant and decreased abruptly to last at 60 minutes.

Further the system consisted of basically a complex mixture of ions. Precipitation reaction involved the change of system composition through abstraction of ions and release of hydrogen ion as well as alteration of the buffer capacity of the system and ionic strength of the solution. An increase in the change in pH and a reduction in induction time may be the characteristic of the speed for formation of first crystals of struvite which control the quality of the crystals product. Here crystals at rate of 27.51 mg/h can be obtained during the study.
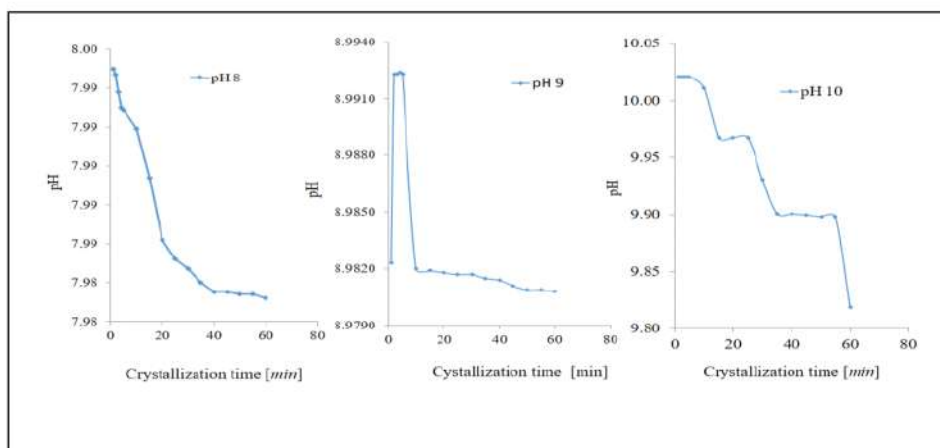
Figure 2 pH changes for various pH experiments

Mineralogical analysis of precipitate

Search-match analysis of the XRPD patterns of the precipitating solid was based on PDF (powder diffraction file) database providing that the crystal product was composed of struvite (PDF#71-2089) and sylvite (KCl) (PDF#76-3368). Subsequently, this identified crystalline mineral was refined by the Rietveld Method using the ICSD (Inorganic Crystal Structure Database). The ICSD were obtained in the literature described by Witacher (1977). XRPD patterns of the crystal product were observed in Figure 3 with three different results of Rietveld refinement methods for sample with various pH noted.
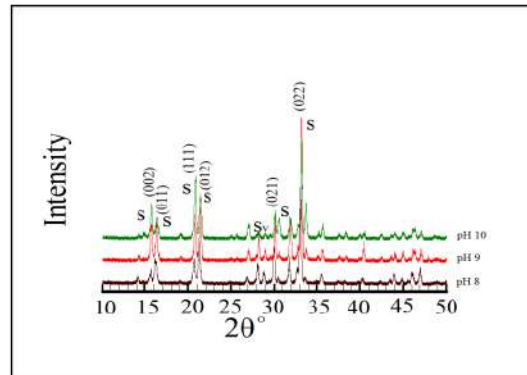
Figure 3 pattern of XRPD analysis of crystals obtained from various pH experiments; Noted S = struvite and Sv = sylvite

The purity of the produced crystals can be seen that there is no much difference observed in the product, which contained major struvite and minor sylvite as confirmed by XRPD Rietveld quantitative analysis. The impurity of sylvite may be resulted from the reaction of potassium and chloride and subsequently precipitated during sample drying. From these experiments, the only little difference in purity of struvite crystals was observed for various pH experiments.

Estimation of crystallite size and morphology of precipitate

Crystallite size of crystal product from the reactor was determined by XRPD method. Here this term used is to refer "grain size" within the particle, because X-Ray diffraction is more sensitive to the crystallite size inside the particles. From the well-known Scherrer formula, the average crystallite size, L (Å) can be determined as follows:

$$FW(S) \times \cos(\theta) = \frac{K \times \lambda}{L} \qquad (1)$$

where λ is the X-ray wavelength in nanometer (nm), FW is the peak width of the diffraction peak profile at half maximum height contributed by small crystallite size in radians and K is a constant related to crystallite shape, normally taken as 0.9. The effect of pH on crystal size is defined in terms of the XRPD peak broadening and the FW from the Rietveld refinement results varying with 2θ as $\cos \theta$ was explored to find the crystallite size. The calculated crystallite size of struvite from the different pH solution is given in Table 1.

Table 1- Calculated crystallite size of precipitate obtained from various pH experiments

2θ	hkl	pH 8 L (Å)	pH 9 L (Å)	pH 10 L (Å)
15.95	[002]	64.94	53.22	38.19
16.50	[011]	20.46	16.65	11.89
20.98	[111]	16.37	13.71	9.71
21.54	[012]	35.15	29.57	20.85
32.13	[021]	9.63	8.56	5.89
33.79	[022]	21.06	18.91	12.96

From this table, it can be first seen that the mean crystallite size of struvite crystals decreases as the solution pH increases. Supersaturation appears to have a greater effect on crystal size at the higher pH values (pH 9 and 10). Here size appears to reduced with supersaturation, whereas this trend is suppressed at the lower pH values. In all experiments, agglomerated and irregular shape crystals of struvite were obtained as illustrated by the SEM photograph (Figure 4). The crystal product has the typical platy shape of struvite and their size is bigger ($^\sim$50 μm).
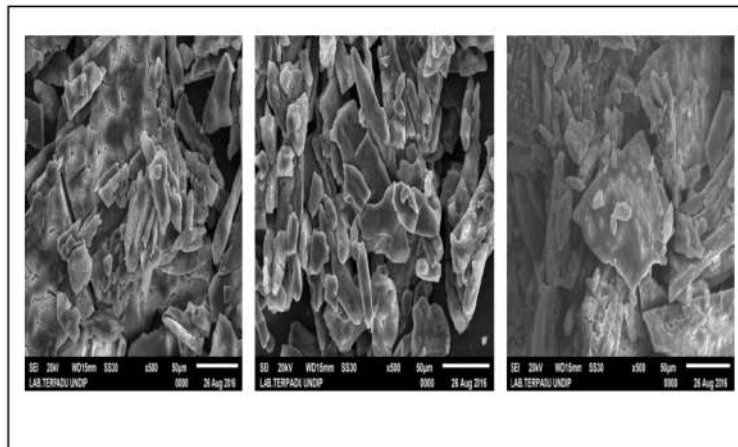

Figure 4 SEM micrograph of struvite crystals obtained from pH solution of 8. 9 and 10

Conclusion

The impact of pH and MAP equimolar concentrations on struvite crystallization has been investigated using the designed vertical reactor and analytical tools of material characterization including XRD and SEM-EDS. It has been shown that the use of air agitated for mixing solution has a significant impact on struvite crystallization in terms of size shape and purity of

the product recovered. In the present study, it has been found that increasing the pH reduces the crystal size and inhibits the struvite growth, or affects struvite crystallization. No more crystalline product of struvite was formed. but a substance identified as impurity of sylvite was also produced. The pH and flow rate impact on struvite crystal morphology will have to be considered in the future in order to improve the recovery and reuse as a fertiliser. Further works need conducting to study struvite nucleation and growth at different flow rate and solution composition.

Acknowledgements

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