3. EFFECTS OF THE OPTIMISED pH AND MOLAR RATIO ON STRUVITE PRECIPITATION IN AQUEOUS SYSTEM

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EFFECTS OF THE OPTIMISED pH AND MOLAR RATIO ON STRUVITE PRECIPITATION IN AQUEOUS SYSTEM

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ABSTRACT

Struvite ($MgNH_4PO_4.6H_2O$) is one of phosphate minerals, commonly forms into aqueous solutions. It can be precipitated as mineral deposits for optimization of phosphate recovery based on the pH optimum, molar ratio and temperature levels. This paper presents results of a study on the struvite precipitation under the influence of pH variation, at optimized molar ratio and temperature, which were calculated from an experimental design methodology. Based on the methodology, a laboratory prepared struvite, made by mixing solutions to NH_4OH, $MgCl_2$ and H_3PO_4 for a molar ratio of 1: 2: 1 in a 500 mL volume of batch stirred crystalliser at room temperature. The crystallization was done at 200 rpm and the pH variation was adjusted to 8, 9 and 10 with KOH for a time of 70 minutes. The resulting crystals were filtered and dried at room temperature for 48 h and subsequently stored for further analysis. Material characterisation of the crystals was conducted using XRPD Rietveld method of mineralogical composition. SEM equipped by EDX was employed for investigation of morphology and elemental composition of the crystals obtained. During the experiment, struvite crystals were firstly nucleated and subsequently developed at major value. The increase in pH is assumed to convert some of the struvite phase into struvite (K) and minor sylvite (KCl). It demonstrates that Visual MINTEQ can be employed to estimate the mineral formation out the synthetic solutions.

Keywords : Crystallisation, pH optimum, Struvite, Struvite (K) and XRPD Rietveld method

INTRODUCTION

Formation of struvite ($MgNH_4PO_4.6H_2O$) scale deposits are one of the key issues in the wastewater treatment plants [Giesseli et al., 2000; Priestley et al., 1997], because it can be precipitated out the solution and eventually block in the pipes, and thus influencing the efficiency of treatment processes and causing maintenance problems [Whitaker and Jeffery, 1976; Battistoni et al., 1997; 2000]. Efforts to control of struvite scale formation have been made through the dilution of struvite crystals with water effluents [Suzuki et al. 2005; 2007]; preventive action by chemical additives of iron salts, [Mehta and Barysone, 2012] or addition of chemical inhibitors [StruEa] et al. 2001; Kofina and Koutsoukos, 2005]. In contrast, struvite precipitation has gained interest as a route to phosphorus and ammonium recovery from wastewaters [Doyle and Parsons, 2002].

Basically, the wastewaters contain rich source of nitrogen (N), phosphorus (P) and magnesium (Mg) ions, which provides it a potentially marketable product for the fertiliser industry, while the properties of the final product should be controlled [Tünay et al., 1997; Shin and Lee, 1997; Schulze-Rettmer, 1991; Snoeyink and Jenkins, 1980; Loewenthal et al., 1994]

Further, phosphorus (P) is one of the main sources of nutrients yielding eutrophication in aquatic systems [Abdelrazig and Sharp, 1988]. This can only be prevented by treatment of municipal or agricultural wastewaters for reducing the phosphorus concentrations in the wastewater reaching surface water streams. Although P is considered as a pollutant in a water body, phosphorous is a valuable resource in agricultural fertilizers, food supply, and industrial raw materials [Sarkar, 1991]. However, the phosphorous resources are likely to be limited to the recent enormous utilization. It has been reported previously that [Frost et al., 2004], phosphorous mineral resources are economically feasible for only 50 years. Thus, P recovery from wastewater provides benefits to prevent water pollution, remove scales of the inner surface of panels and pipes, facilitate successive treatment steps, and prevent the devastation of mineral resources [Muryoto et al., 2008].

Here a strategic way for P recovery from the waste water is to develop an effective nucleation and growth of struvite crystals. Struvite nucleation and growth rate are mainly controlled by pH, mixing energy and starting molar ratios [Koralewska et al., 2009; Nelson et al., 2003; Kofina & Koutsoukos,

2005; Ohlinger et al., 1999; Bouropoulos and Koutsoukos, 2000).

Therefore, the effective technique for optimizing the precipitation process of struvite is to select the optimized parameters which can be adapted to the experimentation work. The purpose of the present study was to examine the effectiveness of struvite crystallisation in a stirred batch crystalliser while examining the influence of pH, temperature and supersaturation on struvite formation. The precipitation products were then characterized by XRPD for the mineral phase composition, and SEM/EDX for the morphology and elemental analysis.

METHODOLOGY

Solution preparation

A synthetic wastewater was prepared for the mixing solutions to NH_4OH, $MgCl_2$ and H_3PO_4 for a molar ratio of 1:2:1 in a 500 mL volume of batch stirred crystalliser at room temperature. Double-distilled deionized water was used in all experiments. Analytical grades of ammonium hydroxide, magnesium chloride, and phosphate hydroxides were supplied from Merck (Germany). In this work, struvite solution was prepared for mixing NH_4OH, $MgCl_2$ and H_3PO_4 in the mol ratio of 1:2:1 and then

stirred at 200 rpm for 30 minutes. Temperature of 40 °C and an initial pH of 8, 9 and 10 were adjusted. The precipitated deposit obtained was then dried at room temperature for 48 hours and subsequently analyzed by by powder X-ray diffraction (XRPD) (Philips 1830-40) scanning electron microscopy (SEM, JEOL JSM 5200).

Chemical equilibrium modeling

The Visual MINTEQ software programs version 3.0 was used in the study to predict solution equilibrium based on input of the activities of the various ions present in the solution. The program is able to calculate the solubility of solids, simulate equilibrium and speciation of inorganic solutes in the prepared solutions. The Visual MINTEQ could predict every precipitated solid phase in oversaturated condition equilibrium. The minerals selected in the model were calculated by MINTEQ program by entering total Mg^{2+}, PO_4, NH_4, K, Ca, Cl and hydrogen (H+) values at variation of pH value (8, 9 and 10). By using these values, the program calculated Mg^{2+}, NH_3, NH_4, H_2PO_4, H_3PO_4, HPO_4^{2-}, PO_4^{3-}, and $MgNH_4PO_4$. Moreover model outputs of minerals were compared to the experimental XRDP results. The chemical composition of the synthetic wastewater for the input of the Program is given in Table 1.

Table-1. The approximate composition of the synthetic wastewater

Parameter	Concentration (mol)
Mg	0.005092
NH_4	0.010184
PO_4	0.005092
K	0.21156
Cl	0.010184

X-ray powder diffraction (XRPD) Rietveld analysis

XRPD measurements were conducted on A Philips PW 1710 Diffractometer equipped with a Co-tube and measurement parameters: 40 kV, 40 mA, 0.02° step, 2 s per step, 5 - 90 ° 2θ. Phase identification was made with (Powder Diffraction File)-PDF-2 Philips software. Rietveld refinement of the XRPD data was carried out with Program Fullprof-2k, version 3.30 [Rodriguez-Carvajal, 2005], with the crystal structure database from the published data in Mineralogical Society of America (Table 2). Results presented here was obtained by refining fundamental parameters of (i) the 2 θ° scale zero position, (ii) the polynomial fitting for the background with six coefficients, (iii) the phase scale factors, (iv) the cell parameters, (v) the peak asymmetry, (vi) the peak shape functions, (vii) the atomic coordinates, (viii) anisotropic temperature factors, and (ix) the preferred

orientation with March-model. Site occupation factors were not refined during Rietveld refinement, because of all struvite peaks are overlapped with peaks of other minerals. The error of the Rietveld quantifications can be estimated to about ± wt. % (1ρ) per phase. The final Rietveld scale factors were converted to PCs-by-weight using the "ZMV" expressions below.

$$wt.\% (analyte\ phase) = \frac{[s ZMV]_{analyte\ phase}}{\sum [s(ZMV)]_{all\ phase}}$$

where s, Z, M and V signify the phase scale factors; number of formula units/cell; formula weights and unit cell volumes, respectively.

**Table-2.** Crystal structure models used in Rietveld refinements

Structure models	PDF number	Authors
Struvite [MgNH$_4$PO$_4$•6H$_2$O]	PDF#712089	Whitaker and Jeffery (1970)
Stuvite-(K) [KMgPO4•6H$_2$O]	PDF#35-0812	Graeser et al. (2008)
Newberyite [MgHPO$_4$•3H$_2$O]	PDF# 76-3368	Abbona et al. (1979)
Sylvite [KCl]	PDF#89-6096	Ott (1926)

RESULTS

Visual MINTEQ results

The parameters presented in Table 1 were entered into Visual MINTEQ to determine the saturation indexes (SI) value for estimating the possibility for the formation of struvite and other minerals out from the solution.
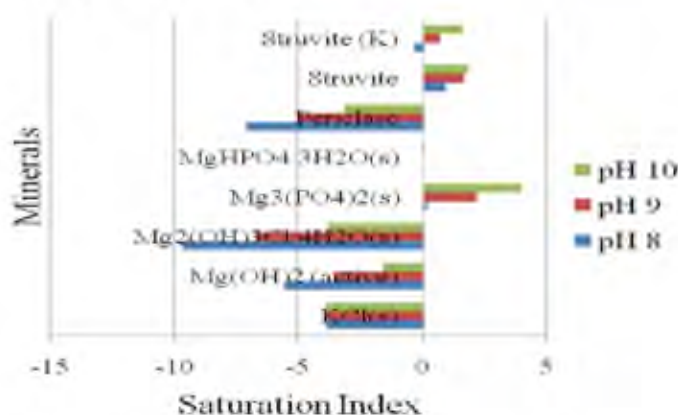
Figure-1. Modeling results of minerals from MINTEQ calculation

Material characterization results

In order to confirm the presence of minerals predicted by Visual MINTEQ, three samples of precipitates obtained at different pH were subjected to X-ray diffraction.
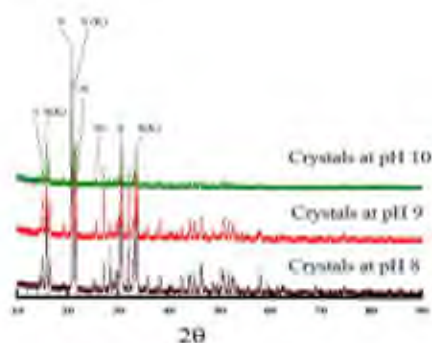
Figure-2. XRPD patterns of the precipitates obtained at temperature of 40 °C and pH variations.

The morphology of the crystals precipitated spontaneously is shown in the scanning electron micrograph in Fig. 3a. The resulting struvite structures may accommodate cation of Mg^{2+}, N^{3+}, O^{2-} and P^{3+}, as shown by the EDX spectrum (Fig. 3b).
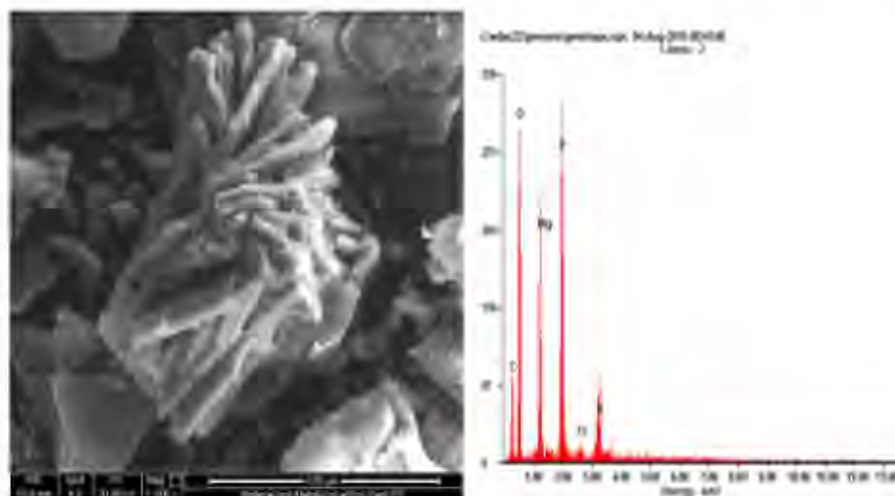

Figure-3. a) Crystal morphology   b) EDX spectrum of precipitates obtained at pH 8 and temperature of 40 °C.

Table-3. XRPD-based mineralogy of the precipitates obtained at pH variation and mixing speed of 200 rpm

pH	8	9	10
Struvite (K)	18.5	32.5	47.3
Struvite	71.8	66.1	51.3
Newberyite	8.9	0	0
KCL	0.8	1.4	1.4

DISCUSSIONS

Figure 1 shows results of the calculated SI as a function of the pH variation. As can be seen, all pH conditions had a positive SI value, which theoretically showed that there was a potential for struvite and other mineral formation. These minerals found in the program were subsequently confirmed in the XRPD data. Thus, calculating the SI on a regular basis can practically forecast possible struvite and other mineral formation.

The struvite formation potential can also be used as the primary indicator in the precipitation analysis. This is a relative value that depends on the SI value of a particular system. The increase in the concentrations of struvite constituent ions (ammonium, magnesium and phosphate) and

conditions (pH, temperature and conductivity) at the solution may determine the extent of the formation potential. The Visual MINTEQ programs provided that minerals of struvite-(K), struvite, and $Mg_3(PO4)_2$ should be precipitated. On the other hand, minerals of sylvite were undersaturated.

In Fig 2, a typical XRD spectrum of the solid precipitate obtained as a function pH is shown. Initially, the classical (albeit computerized) XRPD search-match method was used to identify the XRPD peaks that all the patterns agree very well with the PDF#71-2089) value of struvite, the PDF#35-0812 value of struvite-(K) [$KMgPO_4 \cdot 6H_2O$], the PDF#70-2345 value of newberyite [$MgHPO_4 \cdot 3H_2O$] and PDF# 76-3368 value of sylvite (KCl). Furthermore, those minerals identified in the search-match

procedure was subsequently judged by the full profile Rietveld refinement, as the peaks of phases which have been overlapped in the search match or mistakenly assigned phases clearly stand out in the difference plot of the calculated and the measured diffraction profile [Prince, 1993; Rietveld, 1969; Winburn et al., 2000].

The reflections characteristic for struvite and other minerals are also shown and they were matched with those of reference materials in Table 1. The exclusive formation of struvite at pH 8 is in agreement with reports in the literature concerning the stability diagrams of struvite and newberyite [Abbona et al., 1979; Mehta and Batstone, 2013]. Reports on the spontaneous formation of struvite in supersaturated solutions suggested that the crystal habit of struvite depends on the solution pH and the solution supersaturation [Doyle and Parsons, 2002].

Further, the mineral species predicted by model and found by experimentation are in agreement except for periclase and $Mg_3(OH)_3CO_3\cdot4H_2O$ and $Mg_3(PO_4)_2$. These minerals may have dissolved to be below the detection of X-ray diffraction. On the other hand, sylvite was found in the sample because it may be precipitated during drying. Quality of struvite crystals formed into the precipitating process as a function of pH at temperature of 40°C was evaluated by the XRPD Rietveld method (Table 2). In the resulting precipitate of pH 8, there is an evidence for the major formation of the struvite (71.78 wt.%) and struvite-(K) (18.52 wt.%), but the minor minerals of newberyite (8.9 wt.%) and sylvite (0.9 wt.%).

A decreased amount of struvite was subsequently observed as a result of the increasing pH 9 and 10, compared to those in the previous precipitating solids. While struvite-(K) was still formed out with increasing pH, newberyite disappeared. This is because newberyite is commonly unstable at pH > 6.5 [Abbona et al., 1979]. The significant reduction of the struvite content for the struvite-(K) formation may be attributed the decreased probability of ammonium concentration. Moreover, the major phase arising out of the solution to pH 9 was found to be struvite (66.1 wt.%) and struvite-(K) (32.5 wt.%), but only minor impurities of sylvite (1.4 wt.%) were unexpectedly produced. Similarly, amounts of the major phases such as struvite (51.3 wt.%) and struvite-(K) (47.3 wt.%) were formed in the precipitating solids with pH 10, while the minor amount of sylvite was still developing.

CONCLUSIONS

The computer model developed using Visual MINTEQ in this investigation accurately predicts equilibrium dissolved mineral constituent concentrations. Accuracy of the tool was examined by comparing the output of calculation using the composition data into synthetic waste water and phase identification with XRPD Rietveld method. The tool should prove useful for in engineering and plant operation practitioners interested in preventing Struvite scale damage to infrastructure and in harvesting the nutrients nitrogen and phosphorus from waste water streams. A mixture of Struvite, Struvite (K) and Newberyite is a major mineral controlling MAP ions recovery out of the solution at the temperature of 40°C and initial pH 8. The significant amounts of Struvite and struvite-(K) were precipitated out the solution with increasing pH at the same temperature. Over the range of pH examined and the temperature of 40°C, the precipitated Struvite and struvite-(K) became major minerals controlling MAP ions recovery. The minor impurity of sylvite was formed into all precipitating solids studied. The Struvite crystals precipitated from the solution to the pH variation showed the same morphology as a function of pH variation.

Acknowledgements

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