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EFFECT OF CALCIUM ADDITIVE ON THE CRYSTALLIZATION OF STRUVITE

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ABSTRACT

Crystallization of struvite [$MgNH_4PO_4.6H_2O$] may lead to the deposition of scale which may create significant problems in the process pipes, pumps and other industrial equipment. However, struvite precipitation can be beneficial for phosphate recovery for use of fertilizer. The aim at the present work was to investigate calcium additive on struvite precipitation. The experiment was carried out in a batch mode using a 1-liter Pyrex glass vessel mechanically agitated for 200 rpm. The scale-forming solution was prepared for mixing solutions to $MgCl_2$ and $NH_4H_2PO_4$ with Mg^{2+}, NH_4^+ and PO_4^{3-} in a molar ratio of 1: 1:1. The crystallization temperature of 30 and 40 °C was selected. Ca was added into the crystallizing solution to chloride dihydrate 0.4M ($CaCl_2{\cdot}2H_2O$). Then each solution was pH adjusted to 9 by addition of KOH. The crystals obtained were characterized using SEM for morphology, EDS for elemental analysis as well as XRPD Rietveld analysis for crystalline phases. The induction periods varied from 10 to 90 min, which means that the struvite crystals began forming 10 to 90 min after mixing of the solution. It was observed that the Ca additive may inhibit the struvite crystallization. SEM analysis revealed that the struvite crystals obtained were predominantly of irregular prismatic morphology. Furthermore, the EDS pattern revealed that the elemental composition of the crystals consisted of Ca, Cl, S, Mg, N, and P, providing that many crystalline phase found in the crystals such as Gypsum, $CaCl_2$, struvite, struvite-(K) and sylvite. It was observed that the Ca additive appeared to inhibit the struvite crystallization.

Keywords: Ca-additives, SEM-EDS analysis, struvite and XRPD Rietveld analysis

INTRODUCTION

Struvite precipitation is now considered as a prospective technology for phosphate recovery from waste solutions, municipal sewage, industrial wastewater, liquid manure (Doyle et al., 2003; Doyle and Parsons, 2002). Recently, the struvite precipitation is becoming interesting (Doyle et al., 2003), because the final product has a potential market for fertilizer industries. This can be only achieved by controlling the properties of product, which reflect to its composition [nitrogen (N), phosphorus (P) and magnesium (Mg) ions in equal molar concentrations (Booker et al., 1999). While the chemical purity and crystal size distribution of the crystal product can be obtained from the precipitation process by controlling values of process parameters and also designing of equipment and apparatus (Rawn et al., 1937; Sarepyiak and Jenkins, 1980). Indeed for the struvite precipitation, the properties and quantity of the final product formed has become a considerable concern in order to be successful and economically valuable at full scale. Consequently, the purity and size of crystal recovered has to be handled for a reuse as fertilizer, whereas the granule formed has to be strong enough for practical reason (collection, transport and land filling). The purity is sometimes controlled for environmental reasons.

Furthermore, the significant factor influencing the process and eventually the crystal quality is the presence of contaminant in the solution such as calcium, chloride, carbonates, sulphates, nitrates, fluorides, fluorosilicates (Doyle and Parsons, 2002; Mehoje et al., 1999). These impurities may inhibit or promote the precipitation reaction and influence the rate of crystal nucleation and growth and finally control the crystal shape and possible particle agglomeration (Booker et al., 1999; Ohlinger et al., 1999). In an alkaline solution and the presence of calcium ions, calcium phosphates (in wastewater systems commonly a poorly crystallized hydroxylapatite) or calcium carbonate, which can react effectively with phosphate or carbonate ions according to the following equations.

$$5Ca^{2+}+3PO_4^{3-}+H_2O \rightarrow Ca_5(PO_4)_3OH+H^+$$

$$Ca^{2+}+CO_3^{2-} \rightarrow CaCO_3$$

The occurrence of phosphates or carbonate mineral may worsen the chemical composition of the product and limits the possibilities of its further use (Stratful et al., 2001; Kofina and Koutsoukos, 2003). Furthermore, the Ca ions present in the solution may control in the struvite formation, in which it will either compete for phosphate ions or interfere with the crystallization of struvite. As a consequence of obstruction for crystallization of struvite, the change in the characteristics of struvite crystals may occur, however this area of research has not been examined in detail in terms of qualitative and quantitative. Thus only limited study has been conducted in this area of research (Le Corre et al., 2005). Here, an improved understanding on struvite precipitation out a solution due to the presence of ion additives is required.

The aim of the present research was to examine how Ca-ion may affect struvite crystals nucleation and growth, and discuss the impact of this ion on the quality of the crystals. In the present study, struvite crystals were grown by the prepared solution containing MAP composition and then characterized by X-ray powder diffraction (XRPD) for mineralogical phase composition and SEM analysis with EDS for elemental analysis and morphology.

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METHODOLOGY

Materials and crystallization experiments

A batch of crystallization experiments was conducted to examine the effect of Ca ions on struvite crystal growth. Here struvite crystallization was developed from mixed solutions of magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) and ammonium phosphate ($NH_4H_2PO_4$), which were supplied with analytical grade of chemical product by Merck, Germany. The solution was prepared in a 1-L beaker from equal volumes (400 mL) of $MgCl_2 \cdot 6H_2O$ and $NH_4H_2PO_4$ so that the Mg concentration in the final solution was that the ratio of Mg:N:P was 1:1:1. Then each solution was pH adjusted to 9 by addition of KOH. Ratios Mg:Ca:Cl calculated were 2:1:1. Each stock solution was then filtered through a 0.22 µm paper filter to eliminate the presence of impurities, and dried in a desiccator at room temperature. In the present study, all experiments were conducted at room temperature.

Analytical methods

The dried sample of crystals was then characterized by X-ray powder diffraction (XRPD) (Philips 1830/40) for mineralogical phase composition, while elemental composition and morphology of the precipitates were examined by scanning electron microscopy (SEM; JEOL JSM 5200) equipped by EDS.

Thermodynamic chemical modeling

The Visual MINTEQ software program version 3.0 was employed in the study to estimate the solution equilibrium using input of the activities of the various ions present in the solution. This program provided the calculation results on the solubility of solids, simulating equilibrium and speciation of inorganic solutes in the laboratory solution. The Visual MINTEQ can also estimate every precipitated solid phases in oversaturated condition equilibrium. Type of calculation selected for Visual MINTEQ evaluation in this study was the possible solids. The species used in the model were calculated by MINTEQ program by entering input parameters at fixed pH value of 9 and temperatures of 30 and 40 °C. By using these values, the program calculated Mg^{+2}, NH_3, NH_4^+, H_3PO_4, $H_2PO_4^-$, HPO_4^{-2}, $PO4^{-3}$, and $MgNH_4PO_4$. Moreover estimated outputs of minerals were compared to the analysis of XRPD results. The chemical composition of the synthetic waste water for the input of the Program is given in Table-1.

Table-1. The approximate composition of the synthetic wastewater

No	Parameter	Concentration (molal)
1.	Mg	0.20403
2.	NH_4	0.34182
3.	PO_4	0.18297
4.	K	0.21158
5.	Ca	0.22520
6.	Cl	0.12555

RESULTS

Table-2. Model prediction of species for chemical composition of the synthetic waste water.

	pH 9 and temperature of 30 °C		pH 9 and temperature of 40 °C	
Component	% of total concentration	Species name	% of total concentration	Species name
Mg^{+2}	67.366	Mg^{+2}	67.331	Mg^{+2}
	0.194	$MgOH^+$	0.433	MgOH+
	7.293	$MgCl^+$	7.496	MgCl+
	1.119	$Mg(NH_3)_2^{+2}$	2.486	$Mg(NH_3)_2^{+2}$
	1.39	$MgPO_4^-$	1.55	$MgPO_4^-$
	22.639	$MgHPO_4$ (aq)	20.703	$MgHPO_4$ (aq)
$NH4^{+1}$	70.526	NH_4^{+1}	55.938	NH_4^{+1}
	1.336	$Mg(NH_3)_2^{+2}$	2.968	$Mg(NH_3)_2^{+2}$
	25.278	NH_3 (aq)	38.913	NH3 (aq)
	2.665	$CaNH_3^{+2}$	2.061	$CaNH_3^{+2}$
	0.195	$Ca(NH_3)_2^{+2}$	0.119	$Ca(NH_3)2^{+2}$
PO_4^{-3}	0.022	$PO4^{-3}$	0.022	$PO4^{-3}$
	5.429	HPO_4^{-2}	4.409	$HPO4^{-2}$
	0.022	$H2PO_4^-$	0.017	H2PO4-
	1.55	$MgPO_4^-$	1.729	MgPO4-
	25.244	$MgHPO_4$ (aq)	23.086	$MgHPO_4$ (aq)
	10.292	$CaHPO_4$ (aq)	9.082	$CaHPO_4$ (aq)
	55.794	$CaPO_4^-$	60.06	CaPO4-
	0.014	$CaH2PO_4^+$	0.012	CaH2PO4+
	1.456	$KHPO_4^-$	1.411	KHPO4-
	0.167	K_2HPO_4 (aq)	0.162	K_2HPO4 (aq)

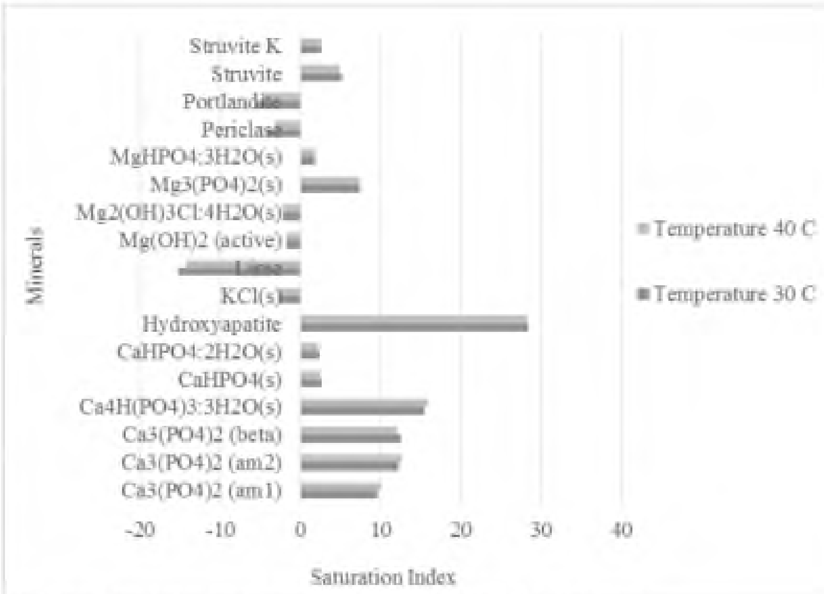

Figure-1. Mineral speciation results predicted by Visual MINTEQ calculation.

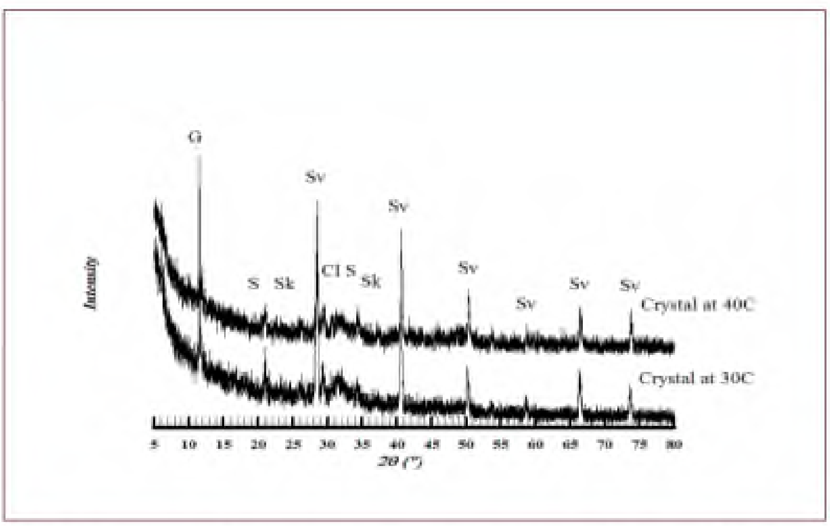

Figure-2. XRPD patterns of the precipitates obtained at temperature of 30 and 40 ^{O}C and pH 9. The principal diffraction peaks of the predominant minerals are shown for reference purposes. The peaks are labelled Cl ($CaCl_2$), G (gypsum), S (struvite), SK (struvite-K) and Sv (sylvite).

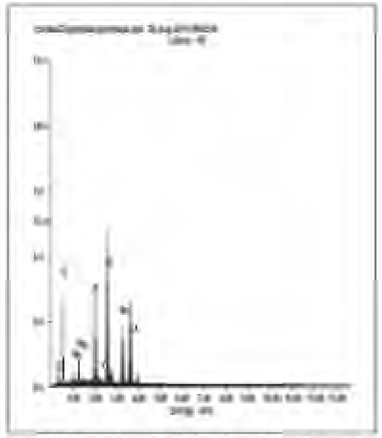

Figure-3. a) Typical SEM morphology for the crystals b) EDS analysis of the deposits formed at pH 9 and temperature of 30 °C.

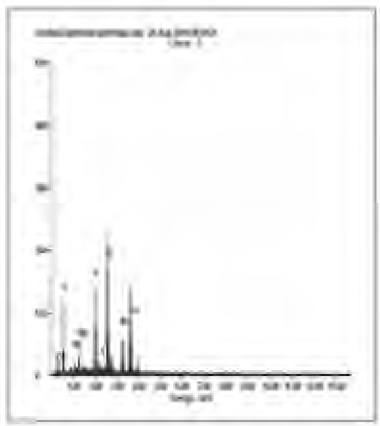

Figure-4. a) Typical SEM morphology for the crystals b) EDS analysis of the deposits formed at pH 9 and temperature of 40 °C.

DISCUSSIONS

Chemical equilibrium model and mineral speciation results

The precipitation potential of minerals was predicted by the Visual MINTEQ using the values in Tables-1. The chemical equilibrium model was calculated in the program provided [redacted] Table-2 . At temperature of 30 °C, when the Mg2: NH_4 :PO_4 molar ratio was 1:1:1 and pH 9, the highest NH_4 removal was obtained [redacted] 0.526%. However, at temperature of 40 °C, when the Mg^{+2} :NH^{+4} :PO_4^{-3} molar ratio was 1:1:1 and pH 9, the lowest NH_3 removal was obtained as 55.938%. At the equilibrium pH 9 and in the presence of Ca ions, the element Mg^{2+}, NH^{4+}, and PO_4^{3-} may form ion complexes, such as MgOH+, MgCl, $Mg(NH_3)_2^{+2}$, $MgPO_4$ [redacted] MgHPO4+, NH_4^{+}, $Mg(NH_3)_3^{+2}$, NH_3, $CaNH_3^{+2}$, $Ca(NH_3)_2^{+2}$, $Ca(NH_3)_3^{+2}$, HPO_4^{-2}, H_2PO_4-, $MgPO_4$-, $MgHPO_4$, $CaHPO_4$, $CaPO_4$-, CaH_2PO_4+, $KHPO_4$-, K_2HPO_4 in the system. These ion complexes agree with the finding results of previous works (Bouropoulos and Koutsoukos, 2000; Ohlinger et al., 2000).

Furthermore the predicted minerals were precipitated out the solution shown in Figure 1. The saturation indexes (SI) value is presented in the study for estimating the possibility for the formation of mineral speciation. A system can be oversaturated when S > 1, in which mineral precipitation potential exists. If S ≤ 1, the system can be at equilibrium or undersaturated for minerals and the precipitation may not occur. Therefore for the mineral growth and accumulation, a positive SI values must be usually required. As can be seen, some minerals at temperature conditions had a positive SI value. In this pH 9, a few crystals can possibly form as hydroxyapatite, newberyite, struvite-(K), struvite, and $Mg_3(PO4)_2$. These crystals formed was influenced by solution pH and concentration of magnesium and phosphate. On the other hand, minerals of sylvite were underestimated. These estimated minerals found in the system were subsequently verified in the analysis of XRPD data.

Figure 2 shows the results of X-ray powder diffraction analysis conducted on the formed precipitates at temperatures of 30 and 40 °C. The presence of minerals was identified by the location of the intensity peaks, corresponding to the standard database lines (PDF-Powder Diffraction File) such as $CaCl_2$ (PDF#740992), gypsum (PDF#761746), struvite (PDF#35-0812), struvite-K (PDF#75-2345). These results also confirm that peaks of Struvite and Struvite K in low intensity were found in the pH 9 and at temperatures of 30 and 40°C . It indicates that those minerals may be formed into the low concentrations. They were further confirmed by comparison between solid analysis of phosphate/magnesium concentrations on the Visual Minteq program (Table 2). It has been shown that the precipitation of Struvite reduces the pH which suggests that $HPO4^{2-}$ would precipitate in the reaction rather than $PO4^{3-}$ according to following reaction:

$$Mg^{2+} + NH4^{+} + HPO4^{2-} + 6H_2O \longrightarrow MgNH_4PO_4.6H_2O + H^{+}$$

It must be yet pointed out that other precipitates may occur for pH values above 9 (Bouropoulos and Koutsoukos, 2000; Ohlinger et al., 2000).

Undesirable amounts of precipitated Struvite may be also contributed to the presence of Ca ions. For example, calcium ions (Ca^{2+}) with the typical concentrations of 10-60 mg/l in municipal wastewater plants has been suggested as representative ions for hampering struvite crystal nucleation and growth. Calcium ions can actively react with phosphate to form calcium phosphates. Previous works on the effects of calcium on struvite crystallization reported that calcium ions with struvite co-precipitation may retard the nucleation induction and inhibit the growth of struvite crystal formation (Le Corre et al., 2005). Moreover, calcium, as an impurity, could be a negative factor of struvite formation. The presence of calcium at high levels in the synthesized wastewater would inhibit struvite formation, because of the possible formation for calcium-phosphorus precipitates. Besides, the presence of impurities in the solution affects the growth rate of crystals by blocking of active growth sites and inhibiting the increase of crystal size (Prywer and Olszynski, 2013).

Solid precipitates were characterized as the field scanning electron microscopes (SEM) coupled with energy dispersive X-ray analysis (SEM-EDS). The SEM investigation into pH 9 is shown in Figure 3. The SEM images reveal that the deposits formed have typical irregular prismatic shaped crystals, while the most common elements identified with EDS are O, Na , Mg , P , S , Cl , N , and Ca . These elemental analyses further confirm that the deposits formed into this condition are gypsum, $CaCl_2$ and Struvite, in agreement with XRPD. In term of literature, the formation of struvite crystals can be found in the pH range of 7-11 (Bouropoulos and Koutsoukos, 2000; Ohlinger et al., 2000). In this range pH, a few crystals may form as trimagnesium phosphate [$Mg_3(PO_4)_2.8H_2O$], magnesium hydrogen phosphate [$MgHPO_4.3H_2O$], and bobierrite [$Mg_3(PO_4)_2.8H_2O$] (Musvoto et al., 2000). However, in this study these three of kind the crystals formed were not identified by the XRPD Rietveld method, because these minerals may be precipitated in the order of days and are influenced by solution pH and concentration of magnesium and phosphate (Musvoto et al., 2000).

The SEM images of the precipitates formed into condition 40 °C and initial pH 9 are shown in Figure 4. The needle-shaped crystals morphology is clearly found. The crystals may be Struvite as indicated elements of Mg, N, P and O in the EDS spectrum . Other minerals of gypsum and $CaCl_2$ are possible and elements of Ca , Cl , S and O are shown in the EDS spectrum . However , minerals of Struvite-(K) and sylvite (KCl) are not shown in the SEM-EDS analysis , though both minerals can be identified by the XRPD method. These minerals may be identified with other spots. Here successful P recovery should need an effective nucleation and growth of Struvite crystals so that desirable amounts of precipitated Struvite can be recovered typically from the gravitational settling process.

CONCLUSIONS

The impact on Mg and Ca solution concentrations on struvite precipitation has been investigated using the analytical tools including XRPD and SEM-EDS. It has been shown that the presence of Ca ions in solution has a significant impact on struvite crystallization in terms of the shape and purity of the product recovered. Gypsum, $CaCl_2$, struvite, struvite-(K) and sylvite can be identified as mineral species developed in the solution. In the present study, it has been found that the calcium concentration present inhibits the struvite growth, or affects struvite crystallization and leads to the formation of many minerals rather than crystalline struvite. Ca impact on struvite crystal morphology will have to be considered in the future in order to improve the recovery and reuse as a fertilizer. Further works needs to be done on the effect of Ca concentration on identification of phases development in the synthetic waste water system.

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