Control of Struvite (MgNH4 PO4.6H2O) Scale Deposit in an Industrial Process

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Conference Paper

Control of Struvite (MgNH$_4$ PO$_4$ .6H$_2$O) Scale Deposit in an Industrial Process

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ABSTRACT

Struvite or Magnesium Ammonium Phosphate Hexahydrate (MgNH$_4$ PO$_4$.6H$_2$O) is one of the precipitates generally formed in the piping system. The formation of struvite in the piping system is one of the serious problems that can cause blockages, reduced flow volume, and pipe diameter to increase maintenance and production costs. This formation of struvite scale in the industrial instrument is detrimental; however, struvite can be used as raw material for slow-release fertilizers. This study will observe the effect of pH in the range of 8, 8.5, 9, 9.5, and 10 on the formation of struvite compositions, consisting of Mg, NH$_4$, PO$_4$, Ca, and K in the surrounding temperature of 35°C. The results of this study will be observed using visual MINTEQ software. The result shows that the most suitable pH for struvite formation is 9.5.

Keywords: Precipitation, wastewater, struvite

Introduction

Generally, wastewater is considered as one of the major polluting agents (Rahman et al., 2014), since for the most part, it contains a high measure of natural matter, nitrogen, phosphorus, a lot of magnesium, diverse full-scale miniature components, and weighty metals. Degradation of the tools in the industry is often caused by sediment or scale that appears on the surface or inside the construction of the tool. These degradations will cause blockage on the pipes, damage to important utilities such as rotators, siphons, heat exchangers, and gear in touch with effluents (Le Corre et al., 2005). However, several components in wastewater can be transformed into struvite minerals that have various benefits in agriculture. For instance, the observation of struvite precipitation as a method to recover important minerals for fertilizer such as phosphorus and ammonium has increased for the past decades (Doyle & Parsons, 2002).

Table1. Struvite properties

Properties	Value
Formula	MgNH$_4$PO$_4$.6H$_2$O
Molecular weight	245.43 gmol/L
Solubility	Slightly soluble
Specific gravity	1.7
Crystal type	Orthorhombic

Struvite is a material produced from the crystallization of some molecules in wastewater, which are magnesium, ammonium, phosphate, and water ($MgNH_4PO_4.6H_2O$). It hardly dissolves in neutral and basic solution but effortlessly dissolves in acids. Struvite is considered a material that can be easily modified in high and fluctuating temperatures or default temperatures, as shown by low specific graffiti (1.7). Due to this reason, struvite is suitable as fertilizer in the area, which is easily flooded (Rahman et al., 2014). As stated before, struvite consists of 4 essential mains molecules of Mg^{2+}, NH^{4+}, PO_4^{3-}, and H_2O in equimolar concentration, which soluble in base liquid, as shown on the reaction (Jimenez et al., 2016):

$$Mg^{2+} + NH^{4+} + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O \qquad (1)$$

Primarily there are two stages of struvite formation, which are crystalization and steady phase. In the crystalization phase, the reaction occurred as nucleation started and finally grew to become aggregate. The following step is the steady phase, where the dimension is not deformed and is in a constant state. There are some factors, which affect the development of struvite crystallization. First is the beginning state of the molecules, kinetic reaction, mass transfer between phases, and thermodynamics (Rahman et al., 2014).

Moreover, two other main factors influence the formation of struvite, first is the effect of pH or acidity. The activity of struvite components is highly dependent on pH. It affected the IAP (Ion Activity Product) of struvite compounds, such as Magnesium and Ammonium. pH and IAP have a comparable value. The increment of pH will increase IAP too. To develop struvite formation, the IAP value needs to be higher than the Ksp value or the product solubility (Ariyanto et al., 2015). Moreover, pH also affected struvite thermodynamic properties and solubility (Fitriana,2016). The optimum pH for struvite formation is in the range of 7 to 11, as it relates to the struvite component activation. The second main factor is the effect of the molar ratio. As mentioned before, the equimolar ratio for the development of struvite sediment needs to be $[Mg^{2+}]$: $[NH^{4+}]$: $[PO_4^{3-}]$ as 1: 1: 1. The right amount of magnesium affects the reaction process and saturation level of the struvite as well as PO_4^{2-} (Edahwati et al. 2020). Attempts to control the development of struvite sediments have been completed by (Suzuki et al., 2005) through a weakening of struvite with wastewater; preventive measures with substance augmentations of iron salts that have been done or the expansion of substance inhibitors observed by (Stratful et al. 2001; Kofina and Koutsoukos, 2005; Edahwati et al. 2015). The mineral struvite can be applied in agriculture as a raw material for plants fertilizer because the mineral struvite is very beneficial for plant growth and development. Thus, in this study, the effect of pH variations from 8 to 9.5 on the struvite components consisting of Mg, NH4, PO4, Ca, K will be observed at the specific temperature of 35°. The result will also be observed using XRF and SEM analysis.

Materials and Method

The beginning of the experiments starts by creating the solution. Synthetic wastewater was prepared as the mixing solutions, consisting of NH_4OH, $MgCl_2$, and H_3PO_4 with a molar ratio of 1: 1: 1 in 500 mL. The experimental set-up for this observation consists of a cylinder reactor, as shown in Figure 1. The temperature of the batch stirred crystallizer is set at 35°C.

Figure 1. Experimental set-up

In this study, the synthetic wastewater with equimolar solution was then stirred at 200 rpm for 60 minutes. The temperature is set at 35℃ and an initial pH of 8, 8,5, 9, 9,5, and 10 was adjusted. The precipitated deposit was analyzed using XRF (X-Ray Fluorescence) and SEM (Scanning Electron Microscopy).

Results and Discussions

The detailed percentage for each struvite composition in different pH is shown in Table 2. We can see from the table that struvite composition dominantly consists of Mg, NH_4, and PO_4, with a composition of around 21 to 28%. Whereas, Ca gives about 10 to 20 %. The least constituent is K which gives only 4 to 14 % of the composition. The trend of each struvite component with the increment of pH can be well seen in figure 2. First of all, we can see that the Mg, NH_4, PO_4, Ca, and K component, each has non-monotonic behavior with the increasing pH, which showed by the fluctuating condition.

Table 2.   XRF analysis results of the struvite mineral in different pH

Component (%)	pH				
	8	8.5	9	9.5	10
Mg	21,72	23,61	25,12	27,14	20,69
NH_4	22,83	22,78	26,91	24,36	23,05
PO_4	23,57	24,67	28,33	33,21	24
Ca	18,23	19,74	15,17	10,78	18,73
K	14.1	9.2	4.47	4.51	13.53

Mg and PO_4 both have an increasing trend ranging from pH 8 to 9.5 and dramatically decrease at pH 10. NH_4 also shows an increasing trend from pH 8 to pH 9. However, it begins to decrease at pH 9.5 and 10. Moreover, Ca and K show more fluctuating trends. Ca show a short increment from pH 8 to pH 8.5 before decreasing drastically at pH 9 and 9.5 and increasing again at pH 10. Opposite with other components, K shows a decrement from pH 8 to 9 and starts to increase again from pH 9.5 to 10.
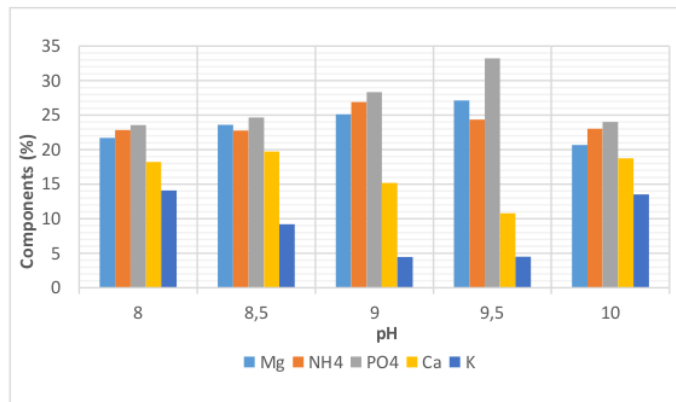

Figure 2. Effect of pH variations on Mg, NH_4, PO_4, Ca, K content (%) at temperature 35°C

From all those fluctuation conditions, we can see that Mg and PO4 composition are the highest at pH 9.5. NH4, Ca, and K is the highest at pH 9, 8.5, and 8, respectively. This behavior shows that the most suitable pH for struvite formation is in between pH 9 to 9.5. This result is inline with a study by (Liu et al., 2018), which result also showed that most struvite produced occurs at pH 9 – 9.5 compared to pH 7 and 8 this is because when struvite crystals are formed, the charged positive ions (H+) will be released into the solution so that it will increase the pH of the solution. Moreover, the composition of fertilizer of pure struvite consists of N, P2O5, K2O, and Mg with 5.7:29: 0: 16.4, respectively. The P content of struvite by and large ranges from 11-26%, relying upon the source and creation process, of which 1–2% is dissolvable in water and the rest of the solvent in a corrosive environment (Sidik, 2013)

Figure 3. SEM analysis of *struvite* precipitation at pH 9.5 at temperature 35℃

At pH 8 to 8.5, the development of struvite is less optimum than pH 9 or 9. and at pH 10 where many impurities formed, thus decreasing the formation of struvite. These results are supported by a study from [Battistoni et al., 2005], which showed that an increase in the pH of the solution from 8 to resulted in a phosphate recovery efficiency of up to 80%, and a decrease occurred when the pH of the solution was above 10. It is because at a pH above 10, the formation of $Mg(OH)_2$ will increase, thereby reducing the availability of ions Mg2+, which can decrease the productivity of crystal struvite formation. Ca in solution affects the rate of growth of crystalline compounds, which causes a blocking in which crystals can form, thereby inhibiting the growth of struvite. Furthermore, The SEM analysis results of struvite at the optimum pH of 9.5 and temperature 35℃ are shown in figure 3. It was clear from figure 3 that the shape of the struvite sediment is mainly like a rod with a sharp end. However, the surface is rough due to the impurities from the sedimentation process.

Conclusions

The conclusion of this study is summarized as follows. Struvite materials are majority dominated by Mg, NH_4, PO_4 components, with each 20 to 25% composition. Whereas the least component is K with 4 to 14 % composition. There is a fluctuating trend of each *struvite* component with the increment of pH. However, the optimum pH for *struvite* formation is at 9.5 due to the ion availability and fewer impurities. The SEM analysis of struvite formation in this study shows a rod shape with a sharp end, with a rough surface due to the impurities.

Acknowledgment

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