Phosphate Recovery from Wastewater of Fertiliser Industries by Using Gypsum Waste

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One of the fertiliser industries in Indonesia produces wastewater from the production process of phosphoric acid, which has a pH of 1.6 to 3, and phosphate concentration of 1,000 - 6,000 mg/L. This waste has been processed by the neutralisation system for phosphate precipitation with the addition of lime (CaO). The effluent from this treatment process still contain high concentrations of phosphate, further process is required to reduce it. The production processes in this fertiliser industry generates solid waste gypsum from the production process. Currently, this solid waste is dried out and has never been harnessed. The calcium (Ca) contained in the gypsum can be utilised to eliminate the phosphate by chemical precipitation. This study was conducted to identify the use of gypsum waste from the waste of fertiliser industry as a phosphate precipitation agent. Effect of molar ratio and pH to reduce phosphate are the main factors that were analysed in this study. The samples were taken from the effluent basin of the sewage treatment process for phosphoric acid production. At this stage the waste still contains 3,826 mg/L of PO_4^{3-}. The gypsum waste was taken from the waste drying facility. It was analysed by using SEM-EDS method to determine the percentage of Ca and other elements in the waste. The variables in this study were the molar ratio of $[Ca^{2+}]$: $[PO_4^{3-}]$, pH and settling time. The study was conducted on a laboratory scale using mechanical stirring (*jar test*) with the addition of gypsum waste at a speed of 200 rpm for ± 60 min. The precipitation was then carried out, and subsequently the supernatant was taken and the residual phosphate was analysed. The software PHREEQC v 2.8 was applied to predict the precipitation process and the mineral generated from the process. This software works with thermodynamic principles, and is an open-source software that can be downloaded and modified for additional database. The result of this study shows that the gypsum waste contains 29.1 % of Ca. These results were used to determine the amount of gypsum to be added for a variety of molar ratios. Based on the modelling by using PHREEQC software, the dominant precipitate was hydroxyapatite. The optimum reduction of phosphate occurred in the molar ratio $[Ca^{2+}]$: $[PO_4^{3-}]$ of 2 : 1. The percentage of phosphate removal was 99 %, obtained at pH 8.5. The precipitation was going well with the settling time of 60 min. The main mineral generated from this process was hydroxyapatite. This parameter can be used to design further treatment for phosphate reduction, which requires the addition of precipitation and sedimentation unit, in addition to the neutralisation process that have been available in this factory.

1. Introduction

One of the biggest petrochemical industries in Indonesia has three production units, namely nitrogen fertiliser production unit, phosphate fertiliser production unit and phosphate acid production units. Wastewater produced from these three production units are mixed into one treatment process and being treated in wastewater treatment unit. Total wastewater that has been produced is 362.4 m^3/h with its main characteristic being the high concentration of ammonium, phosphate, fluoride and sulfate (Gresik Petrochemical Company, 2015). The treatments that have been applied for this wastewater are physical and chemical treatments. Chemical substance added to the treatment process is CaO, with an adjustment of pH by adding NaOH. The effluent from this treatment is discharged directly into the sea.

However, the concentration of phosphate in the effluent is still high, exceeding the quality standard threshold. Based on the effluent standard, the concentration of phosphate should not exceed 50 mg/L as PO_4^{3-}. The problem with high concentration of phosphate in effluent of wastewater is eutrophication. The main commercial method to remove phosphorus from wastewater is by chemical precipitation (Grzmil and Wronkowski, 2006). The most suitable metal salts for chemical precipitation of phosphorus are calcium, iron and aluminum (de-Bashan and Bashan, 2004).

Calcium precipitation is a common method of phosphorus removal, mainly because of its low cost and simple handling (Yi and Lo, 2003). Removal is achieved by direct precipitation of calcium phosphate known as hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$). This mineral is the most stable form of calcium phosphorus precipitate (Jiang and Graham, 1998). Phosphorus removal efficiency in this process ranges from 75 % to 85 % (Moriyama et al., 2001). Excess of calcium salt, pH, and initial concentration of phosphate affect precipitation process (House, 1999). Molar ratio between calcium and phosphate influence the type of precipitate formed in the solution, for instance hydroxypatite is found at the molar ratio ([Ca]:[P]) of 1.67 (Hosni et al., 2007). The optimum pH for precipitation of calcium phosphate is alkaline, from 8.0 to 10 (House, 1999). Different methods to supply calcium in treatment process were found, such as by adding calcite ($CaCO_3$) (Gunawan et al., 2011), gas concrete (Oguz et al., 2003) and coal fly ash (Chen et al., 2007).

In this case, the petrochemical industry produces gypsum waste from the manufacturer unit that produces Cement Retarder. Gypsum ($CaSO_4 \cdot 2H_2O$) can be used as chemical substance to precipitate phosphate because of the presence of calcium ions. Currently, many of gypsum wastes from this company have been sold as a recycle material for other industries. The quantity of gypsum waste in the manufacturer dumping site is still a lot, since they produce more than 100 t/d of gypsum waste. This research aims to utilise the gypsum waste to treat wastewater containing phosphate in petrochemical industry. Several laboratory experiments were conducted to analyse the optimum condition for reusing the gypsum waste as a precipitation agent for the treatment of wastewater containing phosphate.

2. Materials and Method

The sample of wastewater was collected from effluent pond of the wastewater treatment process in a petrochemical industry. Major chemical composition of the wastewater includes 3,826 mg/L of PO_4^{3-}, 1,724 mg/L of NH_4^+-N, 20 mg/L of F^-, and 53 mg/L of Mg^{2+}. The pH value of wastewater was under the range of 1.72 to 2.5 and the TSS was 155 mg/L. Gypsum waste was taken from dumping site area and the composition was analyzed by using SEM-EDS (Carl Zeiss EVO MA 10).

Approximately 500 mL of wastewater was used in the precipitation experiments with the addition of certain amount of gypsum waste in few different molar ratio of [Ca]:[PO_4^{3-}]. Sodium hydroxide (10 M) and nitric acid (10 M) were used for pH adjustment. Batch experiment was conducted using jar test at 200 rpm for 60 min, subsequently the samples were taken at a certain time of interval. Precipitate was allowed to settle for 30 min before it was separated from solution. The samples were then measured by spectrophotometer (Genesys 20) for its residual phosphate. The turbidity was measured by a turbidity meter (Orbeco-Hellige 956-10).

For characterisation, the precipitate was separated from the solution by filtration and by drying it in room temperature at least for 48 h. A small piece of the dried filter paper with calcium phosphate precipitate cake on its surface was carefully cut and sputtered for SEM-EDS analysis (Carl Zeiss EVO MA 10). Crystal structure of precipitate was analyzed by X-ray diffraction (XRD) after precipitate was dried and was crushed to powder form.

PHREEQC was used for modelling of calcium phosphate species that might be formed in precipitate. This model was developed by US Geology Survey to predict the equilibrium concentration and speciation of selected ions in solution (Parkhurst et al., 1999). This model allows user to create personal thermodynamic database in which the possible solid phases are inserted with their characteristic values of solubility product (K_{sp}) and stoichiometric coefficient. The equilibrium concentrations of dissolved and precipitated ionic species can be calculated based on the input of concentration, pH, temperature, and ionic strength. The thermodynamic database that is considered in PHREEQC modelling includes all of the possibility calcium phosphate precipitation, such as monetite, brushite (DCPD), octacalcium phosphate (OCP), hyproxyapatite (HAP), and tricalcium phosphate (OCP).

3. Results and Discussion

3.1 The characteristic of Gypsum Waste

The characteristic of gypsum from the waste of petrochemical industry was analysed by SEM-EDS. The aim of this analysis is to identify the morphology and the chemical content of the gypsum waste. Figure 1 shows the morphology and the percentage of the main elements of this gypsum waste.
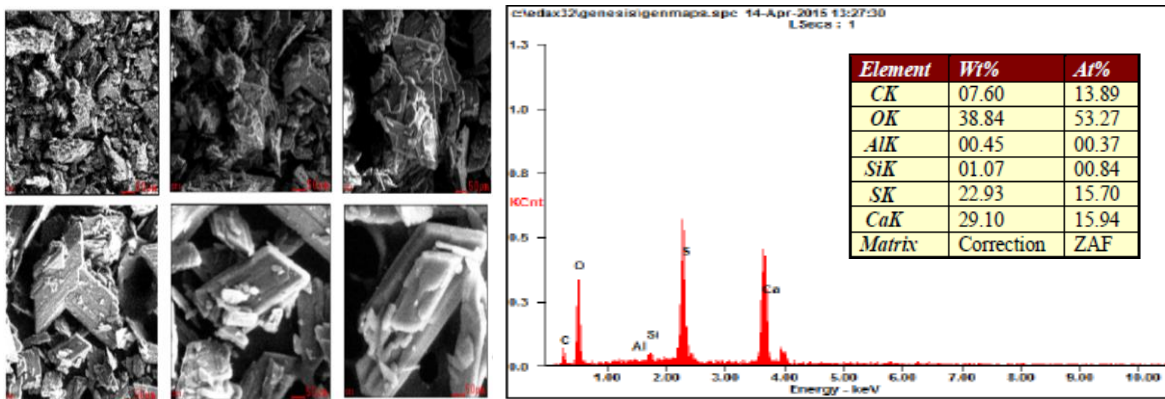
Figure 1: The result of SEM-EDX for gypsum waste

The result of SEM-EDS analysis showed that the gypsum waste content of 29.10 % of Ca, 22.93 % of S, 1.07 % of Si and 0.45 % of Al. This result demonstrates that this waste can be used as precipitation agent since it contains relative high level of Calcium. Based on this analysis, the quantity of calcium concentration that should be added to precipitate the phosphate was identified with the variation on molar ratio ($[Ca^{2+}]$: $[PO_4^{3-}]$) and variation of pH.

3.2 Effect of pH and Molar ratio of [Ca^{2+}]:[PO_4^{3-}]

It has been recognised that the molar ratio ($[Ca^{2+}]$: $[PO_4^{3-}]$) is an important parameter. The effects of molar ratio on residual soluble phosphorus predicted soluble phosphorus and mineral species are depicted in Figure 2.
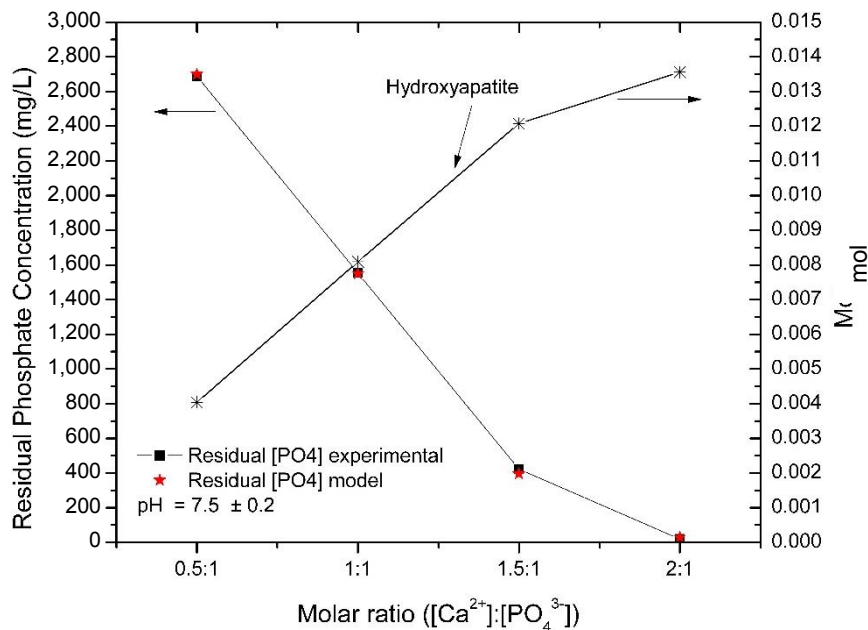

Figure 2: Residual soluble phosphate as affected by molar ratio ($[Ca^{2+}]$:$[PO_4^{3-}]$)

With the molar ratio ($[Ca^{2+}]$: $[PO_4^{3-}]$) of 0.5:1, only 31.79 % of phosphate was removed under pH 7.5. the removal efficiency increased significantly with the increasing of molar ratio, and 98.84 % of phosphate was removed when molar ratio was 2:1. Hao et al. (2008), mentioned that the optimal precipitation process of calcium phosphate was under molar ratio of ($[Ca^{2+}]$: $[PO_4^{3-}]$) of 1.2:1 in which presence of high concentration of ammonium and under alkaline pH. As pointed out, the increase of molar ratio will increase the phosphate removal efficiency (Battistoni et al., 2006). The excess concentration of calcium in the solution induces maximum phosphate precipitation. The characteristics of wastewater from this industry was it contains fluoride

at a concentration of 20 mg/L as F⁻. Gunawan et al. (2011) stated that the F⁻ ions present in the waste that is dominant with PO_4^{3-} can increase the need for calcium as a precipitation agent, since F⁻ will tend to bind to Ca^{2+} apart with PO_4^{3-}. This condition causes the higher demand of calcium when compared with the theoretical chemical reaction.

Solid species that were formed in solution were modelled and the dominant species was hydroxapatite. The increasing of molar ratio will increase precipitation of hydroxapatite, though this mineral is the most stable form of calcium phosphorus precipitate (Jiang and Graham, 1998). The analysed residual phosphorus concentration in the aqueous phase showed a clear equilibrium with this mineral phase. The trend was in line with model prediction.

The pH condition was one of the critical parameter for precipitation because the ion activity of phosphate significantly depends on pH (Nelson et al., 2003). Figure 3 shows experimental results and model prediction of phosphate removal as affected by pH with molar ratio of 2:1, reaction time of 60 min and 200 rpm of mixing process.
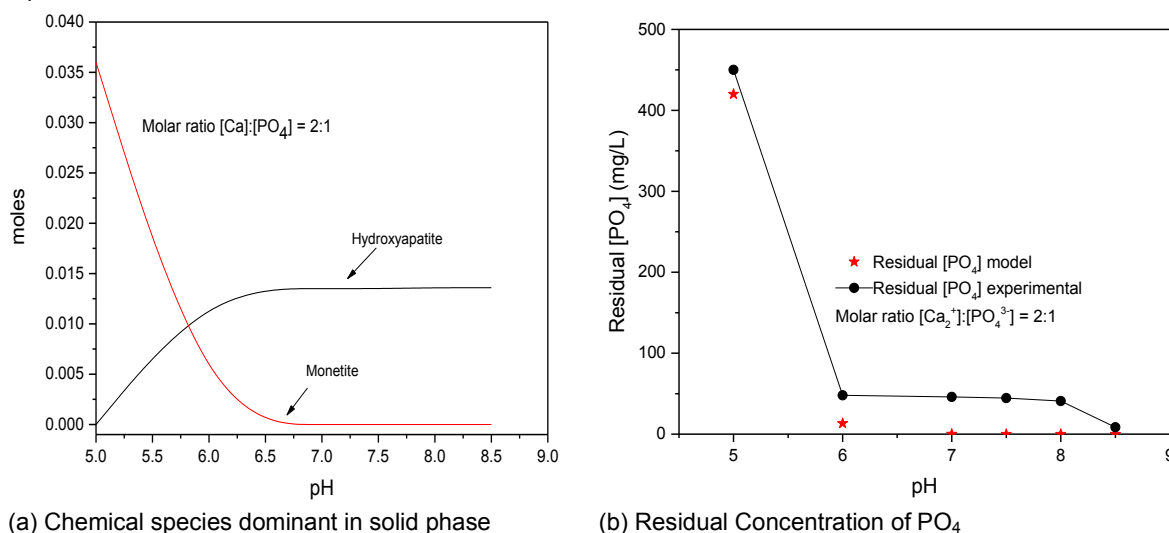

(a) Chemical species dominant in solid phase   (b) Residual Concentration of PO_4

Figure 3: *Residual soluble phosphate as affected by pH*

For the molar ratio of 2:1 and at pH under range 6 to 8.5 indicates that the residual phosphate has already meet the standard of quality (i.e., below 50 mg/L). At pH 7, the phosphate residual was of 48 mg/L and achieved the removal efficiency of 96 %. The removal of phosphate was increased to 99.77 % under pH of 8.5. The residual phosphorus concentrations from experiments were in line with the model. Concerning to the precipitates, the hydroxyapatite was still the dominant solid in pH range of 7 to pH of 8.5. Monetite was appeared under small amount of concentration with pH of 7. van-Kemenade and Bruyen (1987) found that above of pH 6.7 the order of increasing stability of calcium phosphate precipitation is HAP > DCPD > OCP, and the stability sequence changes to HAP > OCP > DCPD at pH 6.7. Again, it is indicated that hydroxyapatite is the most stable form of calcium phosphate precipitation.

3.3 Precipitate Analysis

Solid precipitates were characterised by field emission scanning electron microscope (SEM) with energy dispersive spectrometer (EDS) and X-ray diffraction (XRD). Different compound forms were determined, as well as their size and morphology. Figure 4 shows the SEM-EDS of the solid characteristic under pH 8.5 and molar ratio ($[Ca^{2+}]$: $[PO_4^{3}]$) of 2 : 1. The chemical composition from EDS results showed that the calcium and phosphate were dominant. Based on morphology of the formed precipitate, it is implied that hydroxyapatite was found in the solid phase. The fluoride element was detected in the EDS microanalysis. It could be because the element was trapped in the flocs during filtration process.

Precipitates formed under pH 8.5 with molar ratio ($[Ca^{2+}]$: $[PO_4^{3}]$) of 2 : 1 were analysed by XRD in Figure 5. Some characteristic peaks of hydroxyapatite were found in precipitate, mixed with amorphous precipitate. This result was compared with standard JCPDS of hydroxyapatite file number 9-432.

Cao et al. (2007) mentioned that the presence of several ions, such as Si^{2+}, CO_3^{2-} and Mg^{2+} have some effects on precipitation of hydroxyapatite under range molar ratio ($[Ca^{2+}]$: $[PO_4^{3}]$) of 1.45 to 1.65. However, in this treatment process with excess concentration of calcium, the presence of other ions did not have significant effect on the retarded precipitation of hydroxyapatite.
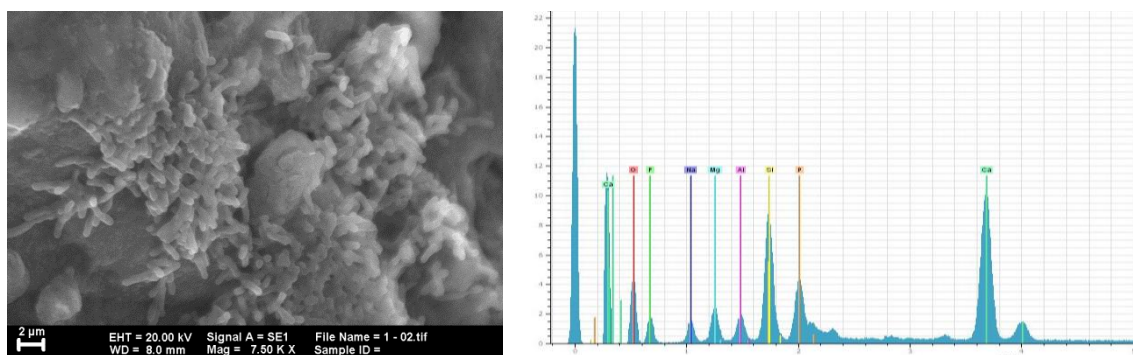
Figure 4: SEM-EDX of Precipitate under pH of 8.5 and molar ratio ($[Ca^{2+}]$: $[PO_4^{3-}]$) of 2:1
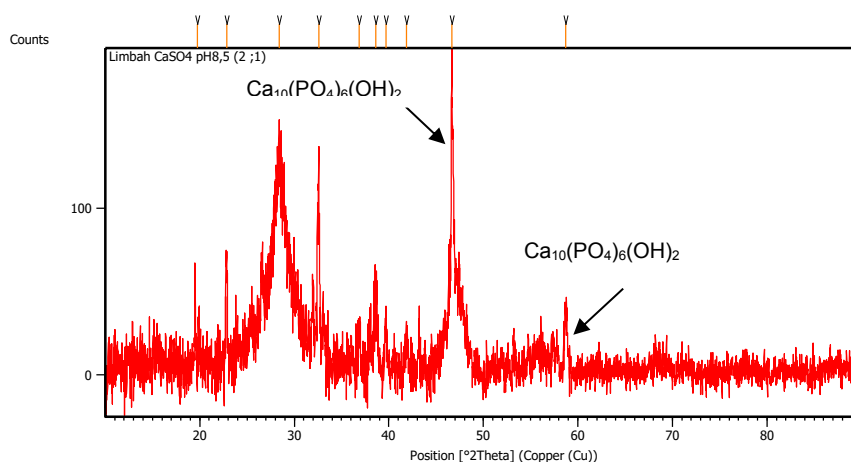

Figure 5: X-RD of *precipitate under* pH of 8.5 and molar ratio ($[Ca2+]$: $[PO_4^{3}]$) of *2 : 1*

3.4 Conceptual Design of Wastewater Treatment

The main wastewater treatment in petrochemical industry is the neutralisation with the addition of chemicals namely lime (CaO). There are three production units in this industry that produces waste with different characteristics. Wastewater from the production unit 1 contains a high concentration NH_4 with is relatively on base pH, the second production units produce waste with high concentrations of PO_4^{3-} and highly acidic pH, while for the third production unit, the wastewater dominantly contains F^- with an acidic pH. The waste of each unit will be channeled into an equalisation pond. The treatment is continued by adding NaOH to neutralise the pH, afterward it goes to the chemical processing with the addition of CaO. The wastewater then goes into the sedimentation unit and the supernatant will be discharged directly into the sea.

As described earlier that the main problem is the PO_4^{3-} concentration that still exceeds the threshold of quality standards, and based on this study, the chemical processing unit can be added to the treatment process by adding gypsum waste as precipitation agent and continued by sedimentation tank. However, the other major concern is also the presence of high concentrations of NH_4^+-N in the effluent. Based on this experiment, other methoda that can be developed for the treatment of wastewater in this industry is that the gypsum can be added in the effluent of wastewater from unit 2 of the production process, in order to reduce the amount of phosphate that afterward will be mixed with other wastewater from different units of production. Then, phosphate with lower concentration will be mixed with wastewater that contains high concentration of NH_4^+-N can be treated by using other method by precipitation of magnesium ammonium phosphate (MAP) or struvite. This will be very beneficial for the industry because of the wastewater treatment process can produce two products of phosphate recovery items, namely hydroxyapatite and struvite, which are both can be used as a fertilizer.

4. Conclusions

In this study, it can be suggested that gypsum waste can be utilized as precipitation agent for the removal and recovery of phosphate. Molar ratio ($[Ca^{2+}]$: $[PO_4^{3-}]$) and pH give an effect on precipitation treatment process. Excess concentration of calcium is necessary to achieve a high removal efficiency of phosphate.

Total of 99 % phosphate removal or recovery was obtained when molar ratio ($[Ca^{2+}]$: $[PO_4^{3-}]$) was 2 : 1 in reaction time of 60 min. The optimum pH for removal and recovery of phosphate was pH of 8 to 8.5. Based on thermodynamic model by using PHREEQC, the hydroxyapatite was the dominant precipitate in solid phase. SEM-EDS and X-RD analysis also confirmed similar results with the prediction model.

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