Enhancement of Struvite Precipitation from Leachate by Coagulation

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Abstract. Nutrient removal from the waste stream discharge is an increasing challenge for the water authorities. Significant capitals are required for the installation of extra treatment process to meet the discharge standards. The alternative of these conventional treatment process is struvite precipitation which bring advantages in nutrient recovery as a commercial fertilizers by production of struvite. Such recovery technology is regarded as a sustainable process as it is able to precipitate out the useful contents in the waste stream and finally collect it as slow-release fertilizers. In struvite precipitation, there will normally be a significant amount of fines formation of the struvite precipitate in the solution, which do not settle. The ability of coagulation process in enhancing struvite precipitate was studied. The optimum conditions for the coagulation to occur, which are alum dosage and pH values were evaluated. Optimization of the alum dosage and pH values were conducted by using the Jar-test apparatus. Results from the experiments show that the additional process of coagulation help to increase the struvite precipitate and yet do not affect their purity. Struvite precipitation with the optimize coagulation discovered 91% of the ammonia nitrogen removal as it indicate that more nitrogen are consumed and precipitate as struvite. The x-ray fluorescence analysis (XRF) is used to test the purity of the struvite sludge, the results showed that the impurities compound such as calcium oxide and potassium oxide presents in struvite precipitation with and without coagulation are basically the same and this proved that the purity of struvite sludge is not affected with additional process of coagulation.

Introduction

Landfill leachate is defined as liquid that passes through a landfill and it extracted dissolved and suspended matter from the landfill. Leachate may consist of large amount of organic matter, ammonia-nitrogen, heavy metals, chlorinated organic and inorganic salts. If not properly treated, leachate will cause significant destruction to human health.

Struvite precipitation has been widely used as a nutrients removal process from the leachate. It is recognized as a highly effective treatment process as it not only purify the waste stream but able to turn the precipitates as useful fertilizer. The process involve magnesium, ammonia and phosphorus ions and finally precipitate out once the three ions are combined. However, the fines precipitant may not settle well due to their size. It is therefore important to study if coagulation, a process normally used in water treatment can enhance the quantity and quality of the struvite precipitants.

This study is therefore conducted with three objectives, which are to determine the effect of coagulation process on settle ability of struvite precipitates and hence examine the optimum condition for the coagulation process. Besides, it evaluates and compare the purity of struvite formed with and without coagulation. The study comprised of laboratory experimental work using the municipal landfill leachate as sample. Alum ($AlSO_4$) was used as the coagulant.

Literature Review

Struvite precipitation has been recognized as an important discovery in the field of wastewater treatment. Struvite precipitation used in the wastewater treatment not only treats the wastewater but also recovers the nutrients which make the process environmentally friendly [1]. Struvite, is a naturally occurring crystal, when combination of Mg^{2+}, $NH4^{+}$ and $PO4^{3-}$ exceed its solubility limit

[2]. Struvite precipitates in crystallize condition with equimolar ratio of magnesium, ammonium, and phosphate ions as MgNH4PO4.6H2O according to the Eq. (1) [3].

$$Mg^{2+} + NH_4 + + PO_4^{3-} + 6\ H_2O \dashrightarrow MgNH_4PO_4.6H_2O \quad (1)$$

Factors Affecting Struvite Precipitation

The factors that affect struvite precipitation are pH, impurities such as calcium, temperature, and the molar ratio of magnesium, ammonia, and phosphorus (M:A:P). Struvite precipitation is highly pH dependent because the activities of both $NH4^+$ and $PO4^{3-}$ are pH dependent. Struvite can precipitate in a wide range of pH between 7.0 and 11.5. However, the most suitable pH ranges are 7.5 to 9.0 [1]. Besides, for a smoother operation of struvite precipitation, higher pH value is preferable. The relationship between pH and nutrients removal ability as directly proportional but to a certain limiting value [1].

Impurities in solution are also known to affect the growth rates of crystalline compounds due to blocking of sites where crystals are formed [4]. The impurities ions such as Ca^{2+} or $CO3^{2-}$ would affect negatively on the growth rate and lengthen the induction time preceding the first occurrence of crystals [4].

In the process of struvite precipitation, the temperature of effluent may affect the struvite solubility and crystal morphology [4]. The solubility product is related to the super saturation state of the solution for the crystallization of struvite. The precipitation of struvite is more difficult to obtain at high temperature [4]. Study has also shown that temperature has a negligible influence on struvite precipitation between the temperature range of $25^\circ C$ to $40^\circ C$ [3].

Based on the Eq. (1), there is a need of equimolar quantity of magnesium, ammonium, and phosphate in order to form struvite. However, the experimentally obtained ratio may differ for optimum ammonia removal as struvite due to the presence of some other species in the effluent that would form byproducts [3]. The study reported also showed that a slight excess of magnesium and phosphorus resulted in better removal of ammonia [3].

An external sources of these elements are needed for fulfilling the struvite precipitation requirement. Three types of magnesium, namely $MgSO_4$, $MgCl_2$, and MgO, are generally used in struvite precipitation. As compared to MgO, $MgSO_4$ and $MgCl_2$ are more widely used because of their lower cost, faster dissociation and shorter reaction time [6]. For the phosphorus source, H_3PO_4 is used because of its lower cost as compared to other phosphorus salts such as Na_2HPO_4 and $Ca(H_2PO_4)_2$ [5].

Application of Struvite Precipitation in Water and Wastewater Treatment Plant

The discharges of nitrogen and phosphorus to the environment are undesirable and it may accelerate eutrophication. Furthermore, certain forms of nitrogen are toxic to aquatic life and cause disease to the human who consume the contaminated water. Struvite precipitation has the potential for removing the nutrients such as ammonia and phosphorus from the wastewater streams. It is essential process in the water treatment plant for getting rid the nutrients from the waste streams.

Application of Struvite Precipitation as Fertilizers

The fertilizing property of struvite has been demonstrated in the 1960s in Germany and the United States [6]. Struvite is an effective fertilizer as its nutrients releasing rate is very slow. The slow-release struvite has been recognized as a highly effective source of phosphorus, nitrogen and magnesium for plants. The advantages of using struvite is that it is slightly soluble in water and soil and therefore, the nutrients will be released at a slower rate throughout the season and the plants can take up most of the nutrients without wasted by leaching. This slow-release behavior is ideal for coastal agriculture. Besides, struvite needed to apply less frequent as compare to conventional fertilizers. Rothbaum and Rohde [7] found that struvite showed higher growth of grass, fruit and various crops, compare with conventional fertilizers. It is well suited for fertilizing turf grass not only providing the nitrogen and phosphorus, but also for the presence of the magnesium, because it is the vital element of chlorophyll, which is responsible for the green coloration of the plants [7].

Coagulation Process

One of the problems faced in struvite precipitation is the residuals of fines particles of struvite precipitate that is difficult to settle [4]. Therefore, coagulation process plays an important role to enhance the formation of struvite crystal. By adding the coagulant into the solution, it will help to increase the size of the particles, and enhance the particles settling characteristics.

The agglomeration of particles of various sizes and characteristics found in water and wastewater is typically achieved by addition of coagulant [8]. Their role is to bring particles in suspension in contact by limiting the forces which naturally keep them apart from one another. As particles in water invariably possess a negative surface charge, their stability in water is principally the result of electrostatic repulsions. The role of coagulants, which are generally positively charged is to favor the aggregation through physical collision and particle bridging and thus stabilize the particles [8].

Methodology

The Jar Test experiments were performed to determine the optimum dosing for the struvite coagulation and the optimum pH values for the struvite coagulation. Analysis of the wastewater parameters, which include turbidity, ammonia content and chemical oxygen demand (COD) were conducted. Besides, analysis for struvite was performed by the x-ray fluorescence analysis (XRF) to determine the purity of the struvite precipitate with and without coagulation.

Sample Collection

The samples in this study was the municipal landfill leachate collected from Tanjung Langsat landfill site. About 20L of sample was collected in sealed bottles under minimized exposure to oxygen. Sampling of leachate was carried out during dry season to prevent dilution. It was transported to the laboratory and stored at temperature less than $4^{\circ}C$.

Analytical Methods

The raw and treated samples was collected and analyzed. In this study, the samples were analyzed for turbidity, COD, and ammonia.

Turbidity. Turbidity is a measure of cloudiness or haziness of a fluid caused by suspended solids that are usually invisible to the naked eye. It is one of the test used to indicate the quality of waste discharges and natural waters. Its main concern is about colloidal and residual suspended matter. The turbidity test was conducted with a Turbidity Meter (HACH 21000) as shown in Figure 1. 10 mL of sample water are filled in the bottle provide for turbidity test. The turbidity meter gave the reading of the sample water in NTU. A plot of turbidity versus coagulant dose was used to determine for the optimum conditions.

Figure 1: Turbidity meter

Chemical Oxygen Demand. COD test is commonly used to indirectly measure the amount of organic compounds in water. COD is a useful measure of water quality as it can determine the amount of organic pollutants found in surface water such as lakes and rivers. It is expressed in milligrams per liter (mg/L), which indicates the mass of oxygen consumed per liter of solution. COD test was performed with Reactor Digestion Method (Method 8000). The samples was stirred with magnetic stir plate to obtain homogenized sample. The sample was pipette into the vial and heated for 2 hours in COD reactor, HACH DRB200 (Figure 2). A blank sample consisting of deionized water was prepared in the same procedure. Both the sample and blank were cool to room temperature. Then, the sample and the blank were inserted into the cell holder and the reading of COD content was obtained in milligram per liter (mg/L).

Figure 2: COD Reactor HACH DRB200

Ammonia. The concentration of ammonia-nitrogen was determined by using HACH DR6000 Spectrometer (Figure 3). The sample was prepared by mixing well the 25 mL of sample, 3 drops of mineral stabilizer, and 3 drops of polyvinyl alcohol dispersing agent. Meanwhile, the blank sample was prepared by using deionized water. Finally, 1 mL of Nessler Reagent was added to the mixing cylinder. After 1 minute of reaction time. 10 mL of the sample was poured into a sample cell inserted it into the cell holder. Finally, the reading of the ammonia content was recorded.

Figure 3: HACH DR6000 Spectrophotometer

Experimental Procedures

The collected samples were treated using controlled struvite precipitation. Similar conditions were applied to the samples, such as source of magnesium and phosphorus, pH, and molar ratio of the magnesium, ammonia and phosphorus. To optimize the coagulation conditions, the struvite precipitation was performed in a jar-test apparatus, equipped with six beakers with a working volume of 500 mL. The Mg and P were first added into the leachate samples and stirred until they were dissolved and do not remains in the bottom of the beaker. The initial pH of the samples were maintained at pH 9.0 by appropriate addition of NaOH solutions. The mixtures were then mixed at 50 rpm for 20 minutes. Alum was added at different dosage into each of the beaker, the alum dosage ranges from 10 mg/L to 125 mg/L. Slow mixture was performed for 15 minutes at 30 rpm and finally settling for 30 minutes without mixing. After the settling period of 30 minutes, the supernatant was withdrawn from each beaker and was analyzed for turbidity, COD and ammonia. The withdrawal of sample was taken place by using the plastic syringe from a point located about 2cm below the top liquid level at the beaker, whereas the produced wet sludge volume was estimated from the sludge level on the bottom of the glass beakers. This testing was expected to obtain the optimum dosage of alum for the coagulation process of struvite to occur.

To study the effect of pH in the coagulation, similar procedure of conventional jar-test was conducting by varying the pH of the samples. The pH was varying between 6.5 to 8.5 with constant dosage of the coagulant, alum. The dosage of the alum was the optimum dosage studied in the previous runs. By this, pH was adjusted before adding alum. The optimum pH for the coagulation process was then determined in this testing.

To determine the purity of the struvite precipitates, the struvite precipitation was carried out on the leachate sample under two experimental conditions, namely with coagulation (optimized condition) and without coagulation. The sludge from each experimental conditions were collected and sent for the XRF analysis.

Controlled Struvite Precipitation

Based on the methodology of the study described from previous Section, the controlled struvite precipitation mentioned before was set as in Table 1.

Table 1: Controlled Struvite Precipitation

Source of Magnesium	Magnesium Chloride (MgCl)
Source of Phosphorus	DiSodium Hydrogen Phosphate Dihydrate ($Na_2HPO_4.2H_20$)
pH	9
Molar ratio of Magnesium: Ammonia: Phosphorus	1.5:1:1.5
Temperature	Room temperature

Results and Discussions

This chapter discusses about the result from the experiments. The data of this study obtained from the data collections stage were studied and analyzed. Graphs and tables are used to describe the data taken from the experiments for purpose of easier comparison.

Leachate Sample

There are two leachate samples taken from Tanjung Langsat Municipal Landfill Sites, but at different time which are 14 January 2016 and 25 February 2016. The characteristic of the raw samples are tested and recorded as show in Table 2. Even they are from the same municipal landfill sites, but the characteristic of the leachate samples were different.

Table 2: Characteristics of the leachate samples

Parameters	**Sample 1**	**Sample 2**
Ammonia-nitrogen content (mg/L)	1700	2725
Turbidity (NTU)	538	638
Chemical Oxygen Content (mg/L)	5750	39250

Optimum Alum Dosage

The experiments were done for both samples in order to investigate the optimum alum dosage for the coagulation process, which is after struvite precipitation. The alum dosages varied from 10 mg/L to 125 mg/L. There were three parameters of concern which are ammonia nitrogen content, turbidity and the COD of the supernatants.

Ammonia-nitrogen contents in the leachate samples can act as indicator showing the performances of the alum in the coagulation process which to precipitate the fines of particles of struvite. Theoretically, the ammonia nitrogen content decrease in the struvite precipitation as the reaction consume nitrogen with the present of phosphorus and magnesium to form the precipitate, struvite. With appropriate dosage of alum, the fines particles will further settled and precipitated in the bottom of the beaker as sludge.

Based on Figure 4, it can be concluded that the optimum alum dosage is 25 mg/L for both sample 1 and sample 2. It is because it give the highest percentage of the removal of the ammonia nitrogen content for the leachate samples. After the optimum dosage of alum, increasing alum dosage is not helping in increasing the precipitation of the fines precipitates, it do not increase the removal of ammonia nitrogen in the supernatants.

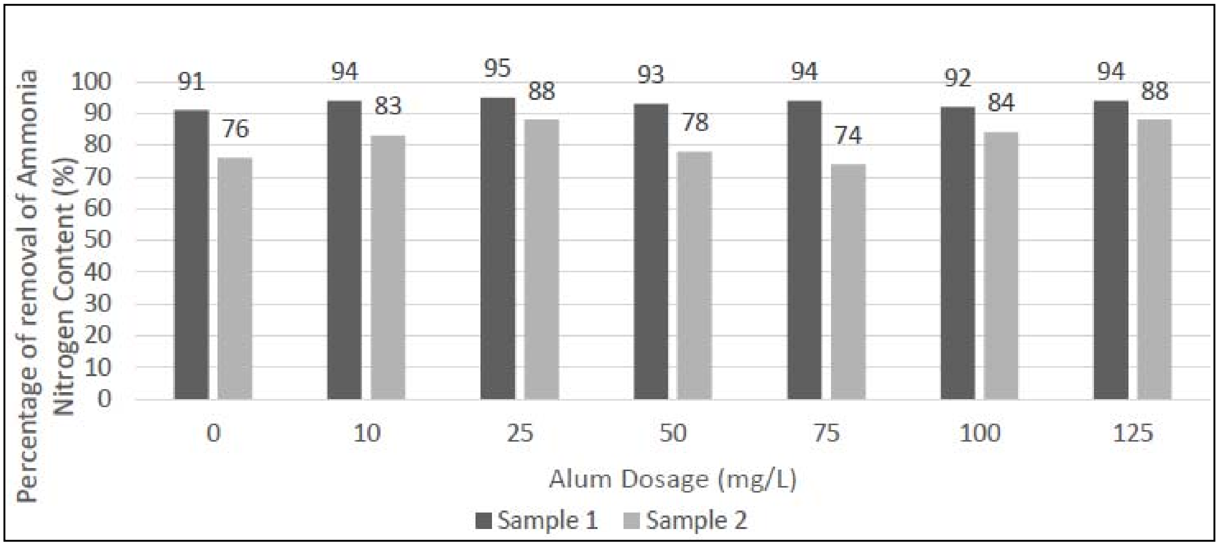

Figure 4: Optimization of alum dosage using jar test with respect to ammonia-nitrogen content

Higher removal of ammonia-nitrogen content in the leachate samples is discovered in the samples with addition of alum compared to the controlled struvite precipitation. These showed that the usage of alum is definitely enhancing the struvite precipitation by increasing the settleability of the fine particles of struvite. Turbidity of the supernatants after the experiment indicated the cloudiness and haziness of the samples. The higher the value of turbidity for the samples, the higher the amount of the fine particles present. The results indicate that the turbidity of the supernatants is decreases from the raw sample to controlled struvite precipitation for both sample 1 and sample 2 with percentage of decrease of 14% and 33% respectively. By this, it clearly showed that the present of struvite precipitation can help to purify the leachate samples and end up with the useful precipitate. The minimum turbidity of the supernatants occur at the alum dosage of 50 mg/L for sample 1 while 25 mg/L for sample 2.

COD is the indication to show the amount of the organic compound in the samples. The lower the COD, the lower the amount of organic compound in the samples. Relatively, the value of COD reduces significantly from the raw samples to the samples comply with struvite precipitation which is 33% for sample 1 and 40% for sample 2. By this, it can be concluded that struvite precipitation is also useful in removing the organic compound in the leachate samples as forming the struvite precipitate. With the increasing alum dosage, the COD remains relatively constant for both sample 1 and sample 2. The amount of alum do not play any significant role in removing the chemical oxygen demand for the leachate samples.

Optimum pH Value

According to the previous discussion, it is deduced that the optimum dosage of alum is 25 mg/L. Hence, the following experiments were done by using constant alum dosage and varying pH values, starting from pH 6 to pH 8.5.

With the same argument mentioned before, the optimum pH for the coagulation to occur can be determined by referring to the minimum ammonia nitrogen content in the samples after experiments. Variations of the pH values should result in different performances in removing ammonia nitrogen content so as to increase the settle ability and precipitation of fines particles of struvite. The optimum pH for coagulation process to occur is pH 6 for sample 1 and pH 8 for sample 2.

Turbidity of the leachate samples after the experiment with varying pH values showed different performances for both samples. For sample 1, controlled struvite precipitation showed a removal of turbidity with 32% as compared to raw sample, while the samples with varying pH of pH 6, pH 6.5, pH 7, pH 7.5 gave an average of removal of 40%. There was pH 6 with optimum removal of turbidity of 55%. However, the turbidity for the leachate samples with pH nearly alkaline condition showed poor performance in removal of turbidity. By this, it can deduced that pH 8 and pH 8.5 are not suitable for the coagulation process to occur for sample 1. The results for sample 2 in turbidity are different from sample 1. It is because the turbidity decreases as the pH value increases. There is the most turbidity remain at sample with pH 6 but relatively lower turbidity at pH around 7.5 to 8.5. As a result, the characteristics of the raw sample 1 and 2 may be different as reacting with different of pH values in the coagulation process. The optimum pH for sample 1 is pH 6 while pH 8 for sample 2.

Performances on removal of COD with varying pH are differ for sample 1 and sample 2. For sample 1, the optimum pH value at pH 6 as it give the most percentage of removal of COD at 30%, however, the average percentage of removal is 25% among all pH value. It indicate that the chemical oxygen demand do not act as a strong supporting parameter to determine the optimum condition for the coagulation process of struvite. In the other hand, COD for the samples with varying pH give greater value than in controlled struvite precipitation for sample 2. It show that the adjusting pH value do not help in enhancing the coagulation process of struvite but even worsen the efficiency in removal of chemical oxygen demand.

Purity of Struvite With and Without Coagulation

Another set of experiment was conducted for the struvite precipitation with and without coagulation process. The coagulation process was conducted with the optimum alum dosage and pH values determined in the previous section which is 25 mg/L and pH 8 for the leachate sample 2.

The results in Figure 4 indicate that struvite precipitation with coagulation has better performances in removing the ammonia nitrogen content and turbidity. Even though it possess higher COD, but COD is not an important parameter in struvite precipitation as it can be removed in other subsequent process.

Table 3: Struvite precipitation with and without coagulation

Parameter	**Sample A (Struvite precipitation without coagulation)**	**Sample B (Struvite precipitation with coagulation)**
Ammonia-nitrogen (mg/L)	457	233
Turbidity (NTU)	301	106
Chemical oxygen demand (mg/L)	31250	32850

In order to examine the purity of the sludge collected for both samples, XRF analysis was carried out. Sample A is the results of struvite precipitate without coagulation and vice versa for sample B. Table 4 shows the results obtained for both samples.

In struvite precipitation, magnesium oxide and phosphorus pentoxide are two compounds that indicate the formation of struvite. As shown in Table 4, the amount of magnesium oxide and phosphorus pentoxide in Sample B (with coagulation) is higher than in Sample A. It indicates that there are more magnesium and phosphorus captured in the sludge from struvite precipitation with coagulation. By this, conclusion can be made that as the coagulation improves settle ability of the fines particles, more composition of magnesium and phosphorus are present in the sludge.

Besides, it is also discovered that the impurities compound such as calcium oxide and potassium oxide present in higher concentration with the struvite precipitation with coagulation (Sample B). Coagulant, alum do help in the settlement of the fines particles of struvite precipitate, but at the same time, in help to coagulate more impurities compound in the leachate sample and settled down together with the struvite precipitate. However, the differences between the composition of impurities compound in Sample A and Sample B are not significant and can be neglected as indicating that the purity of the struvite sludge with and without coagulation is basically the same.

Table 4: XRF analysis results

No	Chemical	Formula	Composition (%)	
			Sample A	**Sample B**
	Origin-g		8	8
	Added-g		2	2
1	Calcium oxide	CaO	1.40%	1.53%
2	Potassium oxide	K2O	1.43%	1.90%
3	Sulfur Trioxide	SO3	0.35%	0.29%
4	Ferrum	Fe	0<LLD	0<LLD
5	Carbon	C	-	0.10%
6	Silicon	Si	0<LLD	0<LLD
7	Magnesium oxide	MgO	5.60%	10.70%
8	Aluminum	Al	0<LLD	0<LLD
9	Phosphorus pentoxide	P2O5	20.50%	29.70%
10	Sodium oxide	Na2O	16.40%	3.35%
11	Chlorine	Cl	14.80%	2.4.3,24%
12	Carbon dioxide	CO2	0.10%	-

By this, it can be concluded that the purity of the struvite will not affected by the additional process of coagulation. Moreover, the coagulation process help to settle more of the struvite sludge and as alum helps to increase the settle ability of the fines particles of struvite remain in the supernatants.

Conclusions

The conclusion that can be drawn from this study are as follows:

1. The additional process of coagulation did help to increase the settle ability of the fines particles of struvite precipitate remain in the leachate samples and hence result in more struvite sludge.
2. The optimum dosage of the alum for the coagulation process to perform is 25 mg/L for both sample 1 and sample 2; the optimum pH value for the coagulation process to perform is pH 6 for sample 1 and pH 8 for sample 2.
3. Purity of the struvite precipitate do not affected by the additional process of coagulation as proved by the results from XRF analysis.

Further study should be conducted to explore more on the both elements stated above. Suggestions for the further study are as follow:

1. Different source of leachate samples can be used to assess its influence on the optimum alum dosage and pH value for coagulation process.
2. Vary the coagulant which is cheaper in cost to test their performance in the coagulation process and to examine whether they affect the purity of the struvite sludge or not.
3. Adjust the conditions for the controlled struvite precipitation such as pH value, molar ratio of magnesium, ammonia, and phosphorus, external magnesium sources and phosphorus source to check their influence in the rate of nutrient removal.

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