Pretreatment of Methane Fermentation Effluent by Physico-chemical Processes before applied to Soil Trench System

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ABSTRACT

In this study, ammonia stripping and magnesium ammonium phosphate hexahydrate MgNH₄PO₄·6H₂O method (MAP) were evaluated for pretreating methane fermentation effluent before applied to soil trench system. For ammonia stripping, the optimal calcium hydroxide dosage was searched systematically. The results shown that the overdosing of calcium hydroxide, 27.5/l wastewater, achieved not only higher ammonia but higher phosphorus, COD, SS and Turbidity removal efficiency. In addition, the volume and settling rate of precipitation was also relative optimal. As expected, ammonia stripping performance was highly dependent on air/water ratio; however, from the point of view of engineering application, air flow rate as 5 l/min for 1 l wastewater should be optimal. For MAP, the optimal pH was about 9 based on $NH_4^+ - N$, $PO_4^{3-} - P$ and COD removal efficiency. Although $NH_4^+ - N$ and $PO_4^{3-} - P$ removal reached almost maximum at $Mg^{2+}: NH_4^+: PO_4^{3-}$ mole ratio 1:1:1, additional Mg^{2+} dosage, such 1.5:1:1, is preferred for thoroughly $PO_4^{3-} - P$ removal. In conclusion, compared with MAP precipitation, ammonia stripping is much more suitable for pretreating methane fermentation effluent in engineering application.

Keywords: Ammonia stripping, MAP, struvite, physico-chemical pretreatments, methane fermentation effluent

1. INTRODUCTION

The high strength of ammonium, phosphate and suspended solid (SS), 1000 to 3000 mg/l of ammonium nitrogen ($NH_4^+ - N$), 100 to 500 mg/l of total phosphorus (TP), and 15000 to 25000 mg/l of SS, is a common feature of methane fermentation effluent. Such high ammonia, phosphate and SS content are generally difficult of access to

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conventional biological treatment processes. Li and Zhao (1999) confirmed that the performance of a conventional activated sludge process could be significantly affected by a high concentration of ammonia. On the other hand, although today several biological nutrient removal plants exist throughout the world, phosphorus removal may prove more difficult because of its release during either sludge handling or anaerobic digestion(Battistoni, Fava, Pavan, Musacco and Cecchi 1997). In addition, methane fermentation effluent will cause clogging in soil trench system by trapping of suspended and colloidal material in the pores of it (Bouwer and Chaney 1974). So physico-chemical pretreatments such as ammonia stripping, ion exchange, membrane processes or chemical precipitation are required to lower the concentration of ammonia, phosphate and SS prior to application to soil trench system.

1.1 Ammonia Stripping

It is often easier and less expensive to remove nitrogen from wastewater in the form of ammonia than to convert it to nitrate-nitrogen before removing it (Culp, Wesner and Culp 1978). Nowadays, the most common method for eliminating a high concentration of $NH_4^+ - N$ (>1000 mg/l) involved in waste-water treatment technologies is the ammonia stripping process. However a major concern about ammonia air stripping is the release of NH_3 into the atmosphere so as to cause severe air pollution if ammonia can not be properly absorbed with either H_2SO_4 or HCl. Moreover, a large stripping tower will be needed due to foaming when $NH_4^+ - N$ in methane fermentation effluent is stripped out (Culp, Wesner et al. 1978).

For ammonia stripping by adding calcium hydroxide $(Ca(OH)_2)$ to increase pH of wastewater, the phosphorus will also be removed. Calcium–phosphorus precipitation is a common method of phosphorus removal, mainly because of low cost and ease of handling. Removal is achieved by direct precipitation of calcium phosphate (HAP, hydroxyapatite, $Ca_5(PO_4)_3OH$)(Yi and Lo 2003). The formation of HAP can be expressed in the following reaction:

$$5Ca(OH)_2 + 3HPO_4^{2-} \Leftrightarrow Ca_5(PO_4)_3OH \downarrow + 3H_2O + 6OH^-$$
 (2)

In addition, SS can also be removed by adding calcium hydroxide, because of the fact that the CaCO₃ precipitation, due to the reaction between lime and CO₂ absorbing from the ambient air, induces a sweep coagulation process and the larger particles can be entrapped (Elmaleh, Yahi and Coma 1996).

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1.2 MAP Precipitation

An alternative promising method of $NH_4^+ - N$ and P removal from methane fermentation effluent is through the precipitation of MAP (magnesium ammonium phosphate hexahydrate $MgNH_4PO_4 \cdot 6H_2O$) commonly known as struvite. The formation of MAP can be expressed in the following reaction:

$$Mg^{2+} + PO_4^{3-} + NH_4^+ + 6H_2O \Leftrightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow$$
 (1)

This method has been studied and practiced for different types of wastewater, such as tannery effluent in leather industries (Tunay, Kabdasli, Orhon and Kolcak 1997), digester supernatant (Siegrist 1996) in wastewater treatment plants and also landfill leachate(Li, Zhao and Hao 1999). Compared with these studies, there is an advantage for applying struvite precipitation process to methane fermentation effluent, because struvite constituent ions, $NH_4^+ - N$ and PO_4^{3-} , are among the predominant ions present in methane fermentation effluent, thereby minimizing the need to add chemicals. Several potential markets that could utilize struvite have been identified. They are, as a slow release fertilizer, as a raw material to the phosphate industry, for use in making fire resistant panels and as a binding material in cements (Sarkar 1990; Schuiling and Andrade 1999).

Although many researches confirmed the efficiency of ammonia and phosphorus removal by MAP precipitation, the SS removal efficiency of MAP precipitation still need to be evaluated.

In this study, ammonia stripping and MAP were evaluated for pretreating methane fermentation effluent before applied to soil trench system. For ammonia stripping, although there are many researches used calcium hydroxide to increase pH, however almost no papers systematically searched optimal dosage of calcium hydroxide based on $NH_4^+ - N$, $PO_4^{3-} - P$, COD and SS removal efficiency that was accomplished in a bath experiment. And effect of aeration rate on $NH_4^+ - N$ removal was also studied. For MAP precipitation most papers focused on either $NH_4^+ - N$ or $PO_4^{3-} - P$ removal, the effects of pH and $Mg^{2+}: NH_4^+ - N: PO_4^{3-} - P$ mole ratio on $NH_4^+ - N, PO_4^{3-} - P$, COD and SS removal need to be quantified in this study. Finally these two methods were compared based on engineer application.

2. METHODS

The temperature effect of all reactions were not taken into account, the temperature was about $15\,^{\circ}\text{C}$.

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2.1 Characteristics of Methane Fermentation Effluent

Methane fermentation effluent obtained from an anaerobic digestion energy plant, Sanwa city, Japan, was stored under 4 °C until experiments. Characteristics of methane fermentation effluent, such as pH, temperature and concentrations of TN, ammonia, nitrate, TP, orthophosphate and COD, were analyzed before experiments, and results were shown in Table 1.

Parameters	Sample 1	Sample 2
Sample date	2005.12.14	2005.12.20
pН	7.50	7.55
Temperature (°C)	15	16
Total Suspended Solid (mg/l)	20000	18000
Turbidity (FAU)	51700	52300
COD (mg/l)	2290	1720
TN (mg/l)	1770	1410
$NH_4^+ - N$ (mg/l)	1510	1160
$NO_3^ N $ (mg/l)	34	27
TP (mg/l)	279	159
Ortho-P (mg/l)	74	84

Table 1. Characteristics of methane fermentation effluent

2.2 Ammonia Stripping

2.2.1 pH Adjustment and Removal of Phosphorus and SS

Different dosages of calcium hydroxide, 3, 5, 7, 9, 11, 13 and 15 g, were added to 400 ml methane fermentation effluent in 500 ml beakers, and the mixtures were stirred for 30 minutes for the dissolve of calcium hydroxide and the reaction between calcium and phosphate. Then the result mixtures were allowed to precipitate, and pH, $NH_4^+ - N$, $PO_4^{3-} - P$ and COD were measured three times in two days.

2.2.2 Air Stripping

After adding optimal dosage of calcium hydroxide to methane fermentation effluent, precipitation was allowed to settle for 8 hours. The supernatants were used in air stripping.

Air stripping was conducted in 500 ml beakers. Supernatants of 200 ml were added to the beakers, and ammonia stripping was started by aeration using diffusers at different rate, 0, 0.6, 1, 2 l/min. Ammonium nitrogen in the supernatant was analyzed during

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one day.

2.3 MAP Precipitation

It can be found that although concentration of $PO_4^{3-} - P$ is very high, the mole ratio of $NH_4^+ - N:PO_4^{3-} - P$ is about 20.4 or 13.8 for wastewater sample 1 or sample 2 respectively (Table 1). So beside Mg, additional phosphorate should also be added to maximize MAP precipitation.

MAP precipitation experiments were carried out using 400 ml methane fermentation effluent in 500 ml closed flasks using magnesium chloride (MgCl $_2 \cdot 6H_2O$) as the magnesium source and sodium hydrogen phosphate (NaH $_2PO_4 \cdot 2H_2O$) as the phosphate source. After mixing the flasks for 15 min until a stable pH is reached (equilibrium state), samples were precipitated for 30 min in order to separate the crystallized precipitate from bulk liquid. After precipitation, supernatants were analyzed. 10 M NaOH and 10 M HCl were used to adjust pH for the minimum of MAP solubility.

2.4 Analytical Procedures

Analytical procedures for the determination of pH, $NH_4^+ - N$, $PO_4^{3-} - P$, COD and SS of wastewater were conducted according to Standard Methods (APHA 1998). Turbidity was measured by using Hach DR4000.

3. RESULTS AND DISCUSSION

3.1 Ammonia Stripping

Wastewater sample 1 was used in the experiments of ammonia stripping.

3.1.1 pH Adjustment and Removal of Phosphorus and SS

After the dissolve of calcium hydroxide (30 min), pH was measured, and the effect of different dosages to pH was depicted in Figure 1. It can be found that pH increased over 12 when 5 g calcium hydroxide was added, and no increases were found for additional increase of dosages. To evaluate the settling rate of precipitations, the precipitation volume after 24 hours was measured, and the result was also shown in Figure 1. The settlements of precipitations for dosages of 9 and 15 g were very slowly, however those for dosages of 3 and 11 g were very quickly, and the precipitation volumes were almost stable in 1 hour. And the precipitation for dosages of 3, 5, 7 and 9 g were almost black, however those for the over-dosages of 11, 13 and 15 g were light black, many white precipitations could also be found.

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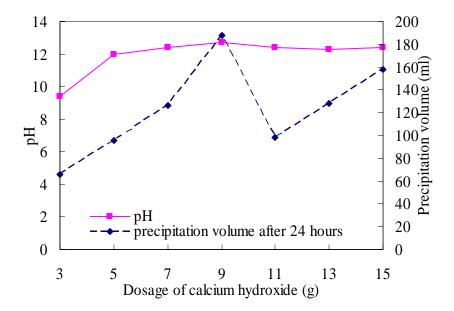


Figure 1 Effect of calcium hydroxide dosages on pH of supernatant and precipitation volume after 24 hours settlement

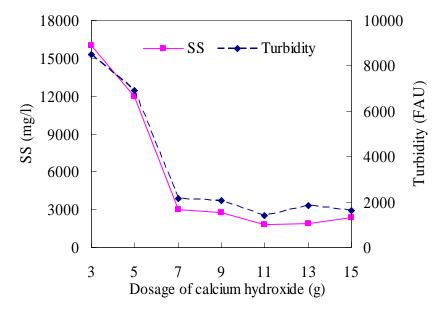


Figure 2 Effect of calcium hydroxide dosages on SS and turbidity in supernatant after 24 hours settlement

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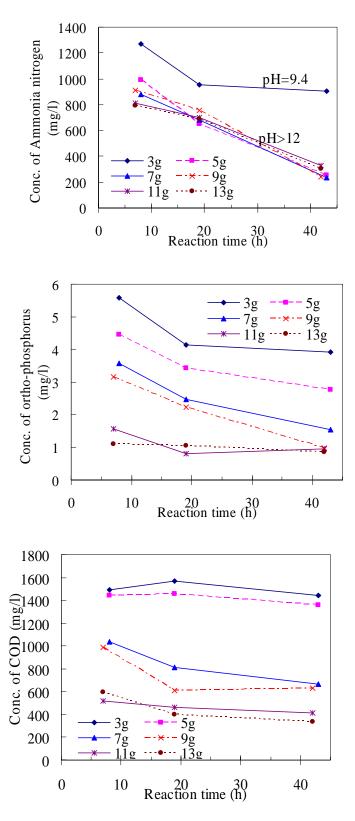


Figure 3 Effect of calcium hydroxide on $NH_4^+ - N$, $PO_4^{3-} - P$ and COD removal The SS and turbidity variations of supernatant were measured and depicted in Figure

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2. It can be found that all dosages had very good turbidity removal efficiency, from the original 51700 FAU to lower than 9000 FAU. And with the increase of dosages from 3 g to 7 g, SS and turbidity decreased sharply and when the dosages were greater than or equal to 11 g, SS and turbidity reached an almost stable value for additional increase of dosages.

And the variations of $NH_4^+ - N$, $PO_4^{3-} - P$ and COD were shown in Figure 3. Ammonium nitrogen removal maintained an almost same level when pH increased to 12, and for dosage of 3 g (pH =9.4), the efficiency of $NH_4^+ - N$ removal is relative low under no aeration condition. Ortho-phosphorus reached a relative low level for all dosages after calcium phosphorate precipitation formed and settled for about 8 hours, with following settlement the concentration of $NH_4^+ - N$ and $PO_4^{3-} - P$ decreased continuously. And the efficiency of COD removal increased with the increase of dosages, and COD maintained an almost stable level in following settlement.

From the result of pH adjustment and removal of phosphorus and SS, it can be found that the limit factors for optimal dosage of calcium hydroxide is not phosphorus, but pH adjustment (higher than 12), COD, SS and turbidity removal and the settlement of HAP and CaCO₃ precipitation. Because phosphorus was removed to a relative low level for all calcium hydroxide dosages.

As expected, ammonia removal was significantly higher at pH 11 than that at lower pH (Figure 3), because the proportion of volatile NH_3 of total ammonia-nitrogen NH_4^+ – N is a function of pH and temperature (Srinath and Loehr 1974). Based on the result, the dosage of calcium hydroxide, 27.5 g/l wastewater, was optimal for NH_4^+ – N, PO_4^{3-} – P, COD, SS and turbidity removal, which is greater than 8 g for landfill leachates gotten by Ozturk, Altinbas et al. (2003). Compared with our result, 8 g calcium hydroxide may unable to raise pH close to 12 and then can not obtain good ammonia stripping efficiency, which may be cause by the higher buffer capacity of methane fermentation effluent than landfill leachates. Moreover even a dosage greater than 8 g just suited for raising pH to 12, a good ammonia removal rate can be obtained, however COD, SS and turbidity removal will remain inferior and the settling rate of precipitation will be slow. The NH_4^+ – N, PO_4^{3-} – P, COD, SS and turbidity removal rate for the optimal dosage of calcium hydroxide after precipitation formed and settlement for 24 hours was 53.4%, 98.7%, 82.8%, 91% and 97.2%.

From the previous result, 11 g of calcium hydroxide per 400 ml wastewater, or 27.5 g of calcium hydroxide per 1 l wastewater, was regarded as optimal dosage for pH adjustment, removal of phosphorus, COD and SS, and the settlement of the

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precipitation was relative quick.

3.1.2 Air Stripping

Dosage of 27.5 g calcium hydroxide was added to 1 l methane fermentation effluent for pH adjustment and phosphorus, SS removal before air stripping.

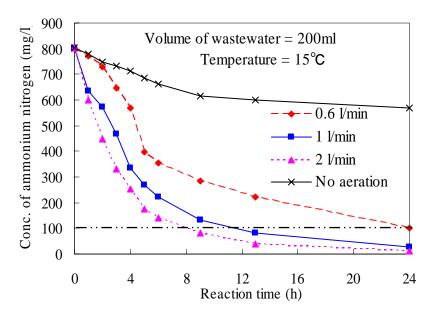


Figure 4 Effect of aeration rate on NH₄⁺ – N removal

During the beginning 30 minutes, a large of foams produced especially for rate of 2 l/min, the foams were destroyed manually, however, after that time, the production of foams decreased very quickly. In addition, only 200 ml supernatants were used in 500 ml beakers, so the loss of solution caused by foam can be omitted. The $NH_4^+ - N$ removals for different aeration rate during 1 day were shown in Figure 4. The ammonium removal rate increased greatly when aeration was applied. And after 12 hours for aeration rate of 1 l/min, 8 hours for 2 l/min, the residual $NH_4^+ - N$ decreased lower than 100 mg/l. However even after 24 hours, that was still over 100 mg/l for aeration rate of 0.6 l/min.

Ammonia stripping performance is as expected highly dependent on air/water ratios. From the result of air stripping, it can be found that for 1 l wastewater, ammonia removal rate almost reached maximum 95.3% after 12 hours at air rate of 10 l/min. And after air stripping for 12 hours at air flow rate of 5 l/min, the ammonia removal rate also reached 89.9%. The result is similar with that obtained by Ozturk, Altinbas et al. (2003). For air flow rate of 3 l/min for 1 l wastewater, even after 24 hours the concentration of $NH_4^+ - N$ was still over 100 mg/l and ammonia removal rate was 72.1%. And for no aeration, the concentration of $NH_4^+ - N$ was still over 600 mg/l

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and ammonia removal rate was only 25.1%. The result is because increase in air flow rate increases the gas–liquid surface area, which in turn controls the amount of NH₃ diffused from water (Srinath and Loehr 1974). However, from the point of view of engineering application, air flow rate as 5 l/min for 1 l wastewater should be optimal, because much more costly method of 10 l/min for 1 l wastewater increased only about 5% ammonia removal efficiency.

And because the temperature of the experiment is about 15 °C, and the fact that higher temperature increases ammonia stripping efficiency (USEPA 1973; Liao, Chen and Lo 1995), it can be expected higher temperature such as 50 °C, 80 °C would shorten the air stripping time greatly.

3.2 MAP Precipitation

Wastewater sample 2 was used in the experiments of MAP precipitation experiment.

3.2.1 Effect of pH

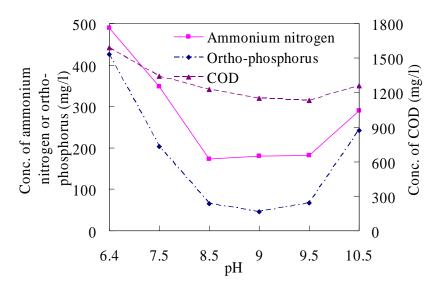


Figure 5 Effect of pH on $NH_4^+ - N$, $PO_4^{3-} - P$ and COD removal

After adding MgCl₂·6H₂O + Na₂HPO₄·12H₂O (final Mg²⁺: NH₄⁺ – N:PO₄³⁻ – P mole ratio of 1:1:1) to the methane fermentation effluent samples, a white-color precipitate rapidly settled as soon as stirring stopped. And pH of the methane fermentation effluent dropped from an initial concentration of 7.5 to 6.4. To identify the effect of pH to residual nitrogen, phosphate and COD in the treated methane fermentation effluent, 10 M NaOH solution was used to raise the pH of it from 6.4 to 10.5 and the experimental results are plotted in Figure 5. The results indicated that NH₄⁺ – N was efficiently decreased from 1507 to 181 mg/l at pH of 9. Ortho-phosphorus and COD also kept almost same tendency as NH₄ – N except the

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variation extent of COD was relative smaller. However $PO_4^{3-} - P$ still maintained the same level as original concentration even at pH of 9, in another word $PO_4^{3-} - P$ was almost not removed by MAP precipitation. And SS and turbidity in supernatant was still 12000 mg/l and 5420 FAU respectively.

From Figure 5, it can be found that $NH_4^+ - N$ and $PO_4^{3-} - P$ removal is highly dependent on pH especially for $PO_4^{3-} - P$, with the pH increased from 6.4 to 9, $NH_4^+ - N$ decreased from 489 to 181 mg/l, however $PO_4^{3-} - P$ decreased from 426 mg/l to 46 mg/l. Because H^+ concentration although does not directly enter the MAP equation, struvite precipitation is highly pH dependent. Because the activities of both NH_4^+ and PO_4^{3-} are pH dependent. As pH increases from 7 to 9, the percent of total $NH_4^+ - N$ present as NH_4^+ decreases from 99% to 64% (Stumm and Morgan 1970). In the same range of pH change, the fraction of total $PO_4^{3-} - P$ present as the PO_4^{3-} anion increases 250 fold (Stumm and Morgan 1970). Because of the overwhelming increase in the proportion of total $PO_4^{3-} - P$ present as PO_4^{3-} within the pH range of 7–9, the pH effect on PO_4^{3-} activity has a greater influence on struvite precipitation than does the pH effect on NH_4^+ activity.

The optimal pH of 9 obtained in our research is close to that gotten by Li, Zhao et al. (1999) for landfill leachate and Nelson, Mikkelsen et al. (2003) for anaerobic swine lagoon liquid.

3.2.2 Effect of
$$Mg^{2+}: NH_4^+ - N: PO_4^{3-} - P$$
 Mole Ratio

Based on the previous result, the pH of 9 was regarded as optimum, and the pH of all mixtures in following experiments were adjusted to 9.

Different $Mg^{2+}: NH_4^+ - N: PO_4^{3-} - P$ mole ratios, with Mg^{2+} or $PO_4^{3-} - P$ overdose and underdose, were tested to find the optimal ammonia and phosphorus removal rate (Figure 6). With the increase of Mg^{2+} dosage, ammonia and phosphorus removal efficiency also increased, however when Mg^{2+} dosage were bigger than 1, the increase of both removals were very little.

The adjustment of $PO_4^{3-}-P$ reached almost same tendency as that for Mg^{2+} . However with the higher $PO_4^{3-}-P$ dosage, bigger than 1, ammonia removal increased a little means much higher residual $PO_4^{3-}-P$ concentration.

The $Mg^{2+}:NH_4^+-N:PO_4^{3-}-P$ mole ratio of 1:1:1 may be enough for NH_4^+-N removal, however the phosphorus concentration was still high (Figure 6). From the result, it can be found with the increase of Mg^{2+} concentration, $PO_4^{3-}-P$ concentration decreased continuously from 51 mg/l for $Mg^{2+}:NH_4^+-N:PO_4^{3-}-P$

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mole ratio of 1:1:1 to 19 mg/l for 1.5:1:1. The result is similar as that obtained by Maekawa, Liao et al. (1995). And this additional Mg²⁺ is necessary, because of the difficulty to treat the higher concentration phosphorus by subsequent biological methods.

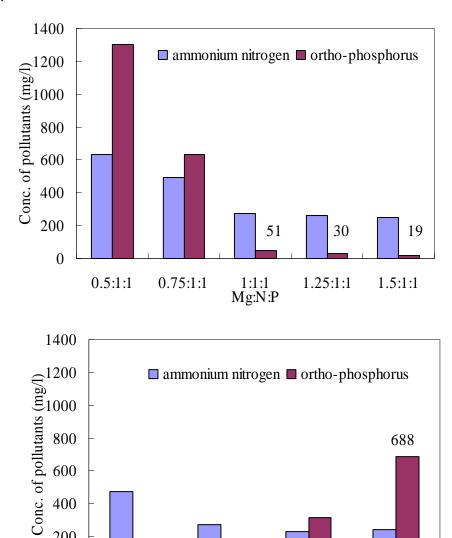


Figure 6 Effects of $Mg^{2+}:NH_4^+-N:PO_4^{3-}-P$ mole ratio on NH_4^+-N , $PO_4^{3-}-P$ removal

1:1:1

Mg:N:P

1:1:1.25

1:1:1.5

200

0

1:1:0.75

On the other hand, even though the increase of $PO_4^{3-}-P$ concentration also increased the ammonia removal rate, the residual $PO_4^{3-}-P$ concentration is relative high, 688 mg/l for $Mg^{2+}: NH_4^+ - N: PO_4^{3-} - P$ mole ratio of 1:1:1.5, which is adverse for wastewater treatment.

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3.3 Comparison between Ammonia Stripping and MAP Precipitation

If optimal $Mg^{2+}: NH_4^+ - N: PO_4^{3-} - P$ mole ratio, such as 1.5:1:1 obtained in our research, is applied in MAP precipitation, $NH_4^+ - N$ and $PO_4^{3-} - P$ can be removed in a very short time, less than 1 hour. However for in ammonia stripping, besides the time consuming of the settlement of HAP, CaCO₃ precipitation, air stripping required for $NH_4^+ - N$ removal also takes a relative long period.

The settlement of MAP precipitation is rather rapid compared with HAP, CaCO₃ precipitation in ammonia stripping, and in which a large of foams are also produced; however the later has also a relative high COD, SS and turbidity removal capacity by adding overdosing of calcium hydroxide.

For pH adjustment, it is rather difficult and expensive for MAP precipitation than that for ammonia stripping. However much more acid is required to neutralize the effluent of ammonia stripping than that of MAP precipitation before applied to soil trench system.

Compared with ammonia stripping that had no requirements for wastewater, MAP precipitation is much more suitable for wastewater with $NH_4^+ - N:PO_4^{3-} - P$ close to 1 and much more Mg^{2+} available that can save the quantity of chemical additions required for maximizing MAP precipitation. And the higher $NH_4^+ - N:PO_4^{3-} - P$ mole ratio of methane fermentation effluent makes beside Mg^{2+} , additional phosphorous should also be added.

In conclusion, although there are some advantages for MAP precipitation, ammonia stripping is much more suitable for pretreating methane fermentation effluent in engineering application.

4. CONCLUSIONS

- 1). By adding overdose of calcium hydroxide, 27.5 g per 1 l wastewater, $NH_4^+ N$, $PO_4^{3-} P$, COD, SS and turbidity can be effectively removed, the treated wastewater can be directly applied to soil trench system, with no further physico-chemical $NH_4^+ N$ or $PO_4^{3-} P$ treatments are required except pH adjustment.
- 2). Although $NH_4^+ N$ and $PO_4^{3-} P$ removal reached almost maximum at $Mg^{2+}: NH_4^+ N: PO_4^{3-} P$ mole ratio 1:1:1, additional Mg^{2+} dosage, such 1.5:1:1, is preferred for thoroughly $PO_4^{3-} P$ removal.
- 3). Compared with MAP precipitation, ammonia stripping is much more suitable for pretreating methane fermentation effluent in engineering application, under the

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condition that ammonia is to be adsorbed with the H_2SO_4 or HCl.

5. ACKNOWLEDGEMENTS

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