Assessment of Chemical Speciation and Condition for Magnesium Ammonium Phosphate Precipitation from Swine Effluent by Computer Program

Sutha Khaodhiar, Kannika Saeng-Aroon, and Ramnaree Netvichien

***Abstract*—**Large quantities of nutrient especially nitrogen and phosphorus in swine farm effluent can be precipitated in form of struvite (MAP). MAP can be used as a slow release fertilizers for agriculture purpose and reduced pollutant for eutrofication in water stream. The optimum condition of MAP precipitation was investigated using the Visual MINTEQ software program. Results indicated the highest amount of MAP precipitated at pH 9 condition with a molar ratio of Mg^{2+}:NH_4^+:PO_4^{3-} of 1.2:1. In addition to the MAP precipitation, other solids phases such as brucite, $Mg_3(PO_4)_2$, hydroxyapatite and $MgHPO_4$•$3H_2O$ were determined from the calculation. Furthermore, the amount of total phosphorus, total nitrogen and heavy metals were reduced from swine farm effluents by all solids. The Visual MINTEQ shows similar results to experimental analysis for removal efficiencies of total phosphorus and total nitrogen from swine farm effluent were considered.

***Keywords*—**Swine Effluent, Chemical Precipitation, Struvite, Visual MINTEQ.

I. Introduction

SWINE farm effluent contains nutrients and impurities in large quantities especially nitrogen and phosphorus which is the main reason of eutrofication in receiving water stream. Struvite or magnesium ammonium phosphate (MAP:Struvite) is formed by chemical precipitation of solutions containing ammonia and phosphate in high concentration, and in neutral or alkaline conditions. MAP can be used as a slow-release fertilizers for agriculture purpose. MAP also reduces the concentration of nutrients as nitrogen and phosphorus in swine farm effluents. It is necessary to control factors and conditions in the chemical precipitation. Other precipitates such as calcium hydroxyapatite and other crystals can also co-precipitated during the process. So it is necessary to find the optimum conditions for an occurrence of MAP precipitation.

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The MAP precipitation can be described through the following equation:

$$Mg^{2+}(aq) + NH_4^{\ +}(aq) + PO_4^{\ 3-}(aq) + 6H_2O \leftrightarrow MgNH_4PO_4 \bullet 6H_2O(s) \qquad (1)$$

MAP precipitation occurs when concentrations of these ions exceed their solubility product [1]. Factors for MAP solubility such as pH value, ionic strength and temperature are very important parameters to determine the oversaturation ratio [2]. The oversaturation of the solution in the main parameter tend to solid precipitates [3], therefore using a computer program to calculate and predict the optimum conditions and the appropriate parameters for MAP precipitation is important. Chemical equilibrium model Visual MINTEQ can be used to pre-decide the concentration of involved reagent to MAP recovery in maximum value and reduce nitrogen and phosphorus concentration [4]. In addition, chemical equilibrium model can explain thermodynamic crystal structure and stabilization on chemical phase [5].

II. Materials And Methods

A.Materials

The Carlo Erba ammonium dihydrogen phosphate (Code NO.419787) was used for NH_4^+ source in synthetic swine wastewater. The phosphorus source in synthetic swine wastewater and swine farm effluent was sodium dihydrogen phosphate anhydrous, A.R. Grade (NaH_2PO_4, MW = 120) purchased from QReC. The magnesium source in all experiments was magnesium chloride ($MgCl_2$•$6H_2O$, MW = 203.30) purchased from Ajax Finechem Pty Ltd (B/NO.1103053). Sodium hydroxide ; pellets (NaOH, MW = 40, Ajax Finechem Pty Ltd UN NO.1823) and hydrochloric acid 36% (HCl, MW = 36.46, Ajax Finechem Pty Ltd UN NO. 1789) were used as pH adjuster for alkalinity for acidity, respectively. The LABINCO magnetic stirrers purchased from Science Engineer International (Model LD-716, CAT.NO.71600) and the Avanta FLAA were used in the study. The UV-visible Spectrophotometer analysis were performed using Heios Alpha UV-visible Spectrophotometer. pH of solutions were measured by DENVER Instrument (UB-10, pH/mV Meter). Filter paper 110 mm(Cat.NO. 1004 110) and glass microfiber filter (GF/C) 55 mm (Cat.NO. 1822 055) were products of Whatman.

1.Synthetic swine wastewater precipitation

Synthetic swine wastewaters were prepared in 1,000 mL of distilled water using $MgCl_2•6H_2O$, $NH_4H_2PO_4$ and NaH_2PO_4 for [Mg^{2+}] 68.73 mg/L, [NH_4^+] 286.30 mg/L and [PO_4^{3-}] 74.25 mg/L, respectively for basis data to MAP precipitation.

2.Swine farm effluent precipitation

Swine farm effluents were collected after anaerobic digester with biogas production by grab method (Pracha Farm in Nakhornpathom, Thailand) for a period of 10 days. The swine farm effluents were analyzed for COD, SS, total phosphorus, total nitrogen, Mg^{2+} and Ca^{2+} were 476 mg/L, 125.53 mg/L, 254.5 mg/L, 31.01 mg/L, 55.47 mg/L and 68.76 mg/L, respectively. The total nitrogen, total phosphorus, Mg^{2+} and Ca^{2+} were used as basis data to MAP precipitation.

3.Computer modeling

The Visual MINTEQ software program version 3.0 is a geochemical modeling developed from DOS program (MINTEQA2) by U.S. EPA. The program use to calculate the solubility of solids, simulate equilibrium and speciation of inorganic solutes in natural and laboratory solutions [6]. The Visual MINTEQ predicts every solid phases that precipitate in oversaturated condition equilibrium [7]. Type of calculation chosen for Visual MINTEQ assessment in this study was the possible solids since the results indicates amount of solids precipitated at equilibrium without considering the results at starting point.

Anticipation of using chemical equilibrium model was to approximate amount of required reagents and optimum condition for MAP precipitation in swine farm effluent [8]. Input mass data for magnesium and chloride ion and pH of solutions were varied for the Visual MINTEQ calculation of MAP precipitation. In synthetic swine wastewater calculation, input mass data of [Mg^{2+}] were 0.0204 M, 0.0224 M and 0.0245 M and of [Cl^-] were 0.0408 M, 0.0448 M and 0.0490 M. pH of the solutions were 7, 7.5, 8, 8.5, 9, 9.5 and 10. The input mass data of swine farm effluent were 0.0292 M, 0.0328 M, 0.0364 M, 0.0400 M and 0.0436 M for [Mg^{2+}] and 0.0584 M, 0.0656 M, 0.0728 M, 0.0800 M and 0.0872 M for [Cl^-] at pH values of 7, 8, 9 and 10.

B.Experimental method

MAP precipitation from synthetic swine wastewater and swine farm effluent were performed in batch experiment at room temperature (25±3ºc). Molar ratio of Mg^{2+}:NH_4^+:PO_4^{3-} were varied from 1:1:1, 1.1:1:1 and 1.2:1:1 by adding 4.15 g, 4.55 g and 4.98 g of $MgCl_2•6H_2O$, respectively in 1,000 mL of distilled water for synthetic swine wastewaters. The swine farm effluents were precipitated in 500 mL of distilled water by adding reagents to collect all concentrations of ionic species. The molar ratio of Mg^{2+}:NH_4^+:PO_4^{3-} were varied from 0.8:1:1, 0.9:1:1, 1:1:1, 1.1:1:1 and 1.2:1:1, by adding 1.25 g, 1.44 g, 1.62 g, 1.80 g and 1.99 g of $MgCl_2•6H_2O$, respectively and 1.03 g of NaH_2PO_4. Every solutions of synthetic swine wastewaters and swine farm effluents were stirred by magnetic stirrer with 240 rpm for 10 minutes and 120 rpm for 15 minutes. pH values of synthetic swine wastewaters were adjusted pH value to 7, 7.5, 8, 8.5, 9, 9.5 and 10, while pH values of swine farm effluents were adjusted to 7, 8, 9 and 10 using NaOH and HCl. All samples were settled for 30 minutes for chemical precipitation. The solid phases were filtered out, dried at room temperature for 48 hours and weighed. All involved parameters of remaining solutions from swine farm effluents were analyzed.

C.Analytical method

pH of solutions were measured by pH meter (DENVAR INSTRUMENT). Total solid phases were weighed for four decimal places using scales (DRAGON 204, METTLER TOLEDO). Suspended solids were separated by filtration through GF/C (55mm Ø, Whatman). COD were analyzed by titration method (Closed reflux). All metal ions were determined by Standard method (METHOD 3005A). Total phosphorus was measured by Colorimetrical method with UV-visible spectrophotometer. Nesslerization method was used to measure number of total nitrogen.

III. RESULTS AD DISCUSSIONS

A.Chemical precipitations : effect of pH and Mg:P molar ratio

Chemical precipitation from synthetic swine wastewaters depended on pH and Mg:P molar ratio of solutions. Amount of precipitates increased when pH and concentration of solutions increased. The total precipitates formed in the great value at equilibrium with condition of pH equal to 9 and 1.2:1 molar ratio for synthetic swine wastewaters in Fig.1.

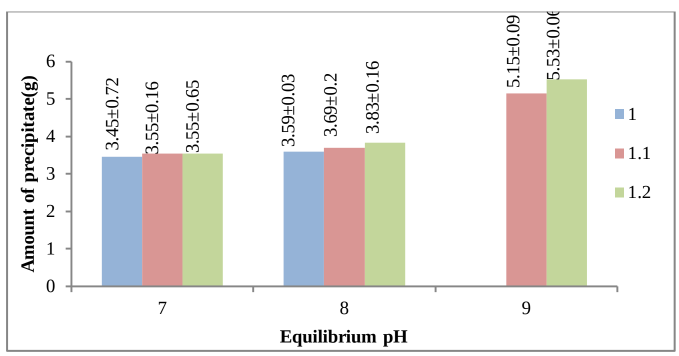

Fig.1 Amount of total precipitates at equilibrium from synthetic swine wastewater at various pH values and Mg:P molar ratios of the solution

TABLE I
THE COMPARISON OF SWINE FARM EFFLUENT CHARACTERISTIC BEFORE AND AFTER CHEMICAL PRECIPITATION

Parameter	Concentration (mg/L)	
	Before precipitated	After precipitated
COD	476.00 ± 29	48±0
SS	125.53 ± 15	7±3
TKN	254.50 ± 9	25
TP	31.01 ± 6	6
Mg2+	55.47 ± 3	0
Ca2+	68.76 ± 2	0.44
K+	225.32 ± 19	31

Amount of SS and COD, TKN, TP, Mg^{2+}, Ca^{2+} and K^+ after chemical precipitation decreased when the pH and Mg:P molar ratio increased because organic and inorganic solubles settled from solution in precipitates form. The optimum condition to remove SS, COD, TKN, TP, Mg^{2+}, Ca^{2+} and K^+ are equilibrium pH at 9 and 1.2:1 molar ratio for swine farm effluent.

Precipitates phase from chemical precipitation were characterized by XRD (2 theta 10-70 degree, Increment 0.02 degree, Scan speed 1 sec per step) and SEM. The precipitates phase of synthetic swine wastewater shows in Fig.2 at pH 9, 1:1 molar ratio and swine farm effluent precipitates phase shows in Fig.3 when the solution pH equal to 9 and 1.2:1 molar ratio. The characterization indicated these precipitates were MAP.

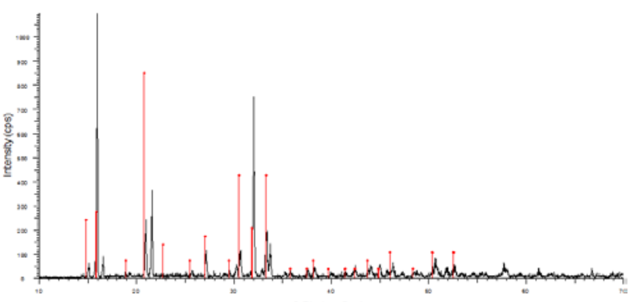

Fig.2 Precipitates phase of synthetic swine wastewater at equilibrium pH 9, 1:1 molar ratio compared with standard MAP pattern by XRD

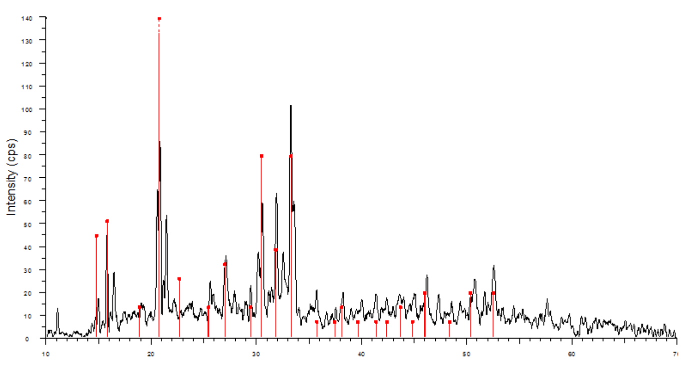

Fig.3 Precipitates phase of swine farm effluent at equilibrium pH 9, 1.2:1 molar ratio compared with standard MAP pattern by XRD

Compositions of precipitates form from synthetic swine wastewater show in Table II and from swine farm effluent show in Table III.

TABLE II
THE COMPOSITION OF PRECIPITATES FORM FROM SYNTHETIC SWINE WASTEWATER

Element	Weight(%)
Oxygen	49
Magnesium	21
Phosphorus	30

TABLE III
THE COMPOSITION OF PRECIPITATES FORM FROM SWINE FARM EFFLUENT

Element	Weight(%)
Oxygen	54
Magnesium	19
Phosphorus	26
Potassium	0.7
Calcium	0.3

B.Computer modeling assessment

1.Optimum condition for MAP precipitation

Result from Visual MINTEQ predicted for MAP precipitation in swine farm effluent are shown in Fig.4.

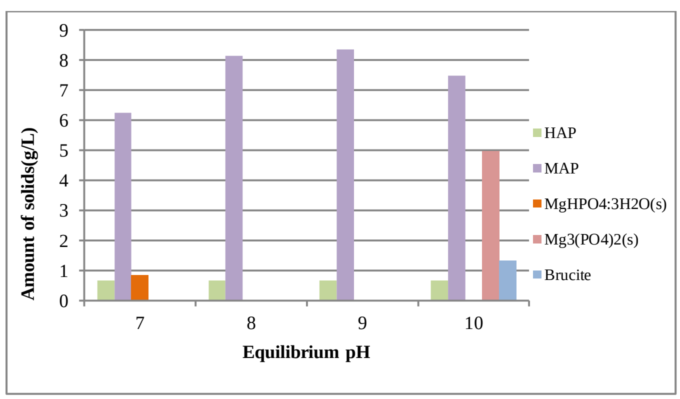

Fig.4 Types and amount of swine farm effluent precipitates by Visual MINTEQ calculation at 1.2:1 molar ratio and various equilibrium pH

The maximum MAP precipitation occured at pH 9 and 1.2:1 molar ratio. Additional to HAP, MAP, $MgHPO_4 \cdot 3H_2O$, $Mg_3(PO_4)_2$ and brucite were precipitated. However MAP was predominant phases precipitated out of the reaction.

2.Comparison of phosphorus and nitrogen removal efficiencies between calculation and chemical precipitation

Phosphorus and nitrogen removal efficiencies predicted from the Visual MINTEQ increased when pH of solution and Mg:P molar ratio increased, especially at equilibrium pH 9 and 1.2:1 molar ratio due to occurrence of MAP, magnesite and $MgHPO_4 \cdot 3H_2O$ at these conditions. Moreover, ammonium ion tends to ammonia gas (NH_3) at high pH [1].The calculation results agreed with result of chemical precipitation of swine farm effluent in Fig.5 and Fig.6.

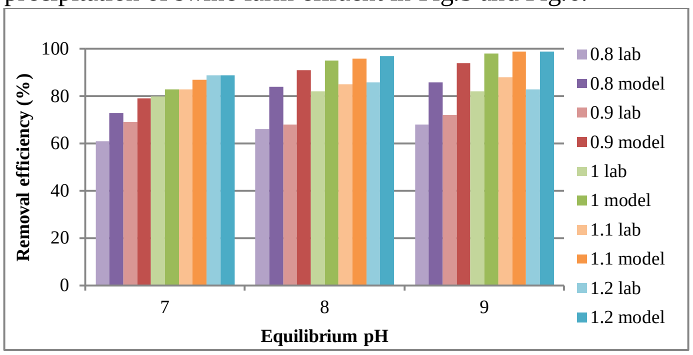

Fig.5 Comparison of phosphorus removal efficiencies between calculation and chemical precipitation of swine farm effluent at various Mg:P molar ratio

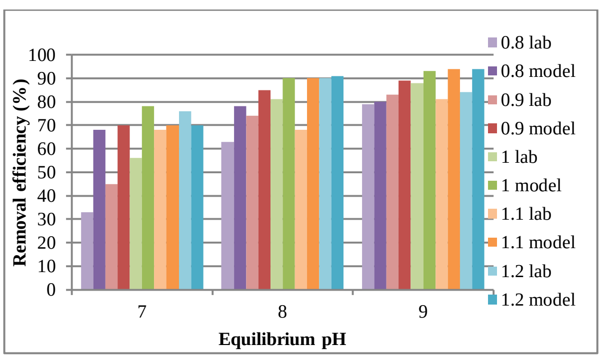

Fig.6 Comparison of total nitrogen removal efficiencies between calculation and chemical precipitation of swine farm effluent at various Mg:P molar ratio

IV. Conclusions

A. Chemical precipitates in synthetic swine wastewater and swine farm effluent depends on pH solution and Mg:P molar ratio.

B. The optimum condition for chemical precipitates and removal of SS, COD, TP, TN and heavy metals of swine farm effluent is at pH 9 and 1.2:1 Mg:P molar ratio.

C. Other wastewaters such as domestic wastewater and urines wastewater should be to MAP precipitates due to compose high nitrogen and phosphorus.

D. The Visual MINTEQ can be indicated optimum conditions for dominant MAP precipitates from swine farm effluent.

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