Investigating Pretreatment Methods for Struvite Precipitation in Liquid Dairy Manure

Yanwen Shen

Thesis submitted to the faculty of the

Virginia Polytechnic Institute and State University

in partial fulfillment of the requirements for the degree of

Master of Science

In

Biological Systems Engineering

Jactone Arogo Ogejo, Chair

Katharine F. Knowlton, Committee member

Zhiyou Wen, Committee member

June 17, 2010

Blacksburg, VA

Investigating Pretreatment Methods for Struvite Precipitation in Liquid Dairy Manure

Yanwen Shen

Abstract

Phosphorus (P) recovery and re-use is very important today for sustainable nutrient cycling and water quality protection due to the declining global P reserves and increasingly stringent wastewater treatment regulations. P recovery as struvite ($MgNH_4PO_4 \cdot 6H_2O$) is a promising technology because it can be used as a slow-release fertilizer. The objective of this study was to investigate different pretreatment methods to enhance struvite precipitation in dairy manure.

Generally there are two challenges that need to be overcome to precipitate struvite in liquid dairy manure. The first is the relatively high calcium (Ca) concentration. The present study investigated the effectiveness of two calcium binding reagents to reduce the calcium inhibitory effects to enhance the struvite precipitation. A chemical equilibrium model (Visual MINTEQ 2.60) was used to determine the pH to acidify manure and to precipitate struvite. Then, bench-scale experiments were conducted to validate the model results using synthetic and untreated manure. First, the manure was acidified (pH 4.5) to liberate the particulate-bounded Mg^{2+}, Ca^{2+} and inorganic P. Second, EDTA and/or oxalate compounds were added to the manure. Third, pH was increased to 7.5 for struvite precipitation from the liquid filtrate. Results showed that struvite-containing crystals were obtained from the samples treated with calcium removal compounds, with a total suspended solids (TSS) concentration less than 4,000 mg/L

The second challenge is the low dissolved reactive P (DRP, i.e. PO_4-P) to total P (TP) ratio. This study investigated different pretreatment methods for P release to enhance struvite precipitation in liquid dairy manure: enhanced biological phosphorus removal (EBPR), microwave heating (MW) and anaerobic digestion (AD). All of the pretreatment methods resulted in P release but struvite crystals were observed only in precipitates obtained in manure pretreated with MW+H_2SO_4 acidification. Without oxalic acid to reduce the Ca^{2+} effects, all the other pretreatment methods were not effective in enhancing struvite precipitation in liquid dairy manure. Hardly any struvite or crystalline-like solids were found in the non-centrifuged samples, regardless of any pretreatment, indicating the effects of suspended solids and organic matter on struvite precipitation.

A partial economic analysis was conducted to assess the chemical costs of P recovery from liquid dairy manure with different pretreatment methods; P recovery amounts as struvite were modeled by Visual Minteq 2.61.Three pretreatment conditions (untreated manure + oxalic acid, MW + H_2SO_4 acidification, and AD) were selected based on the precipitation results. MW + H_2SO_4 acidification produced the highest struvite quantities among the pretreatment methods to enhance struvite recovery, also with the lowest chemical addition costs.

Acknowledgement

TABLE OF CONTENTS

List of Figures

List of Tables

1. INTRODUCTION

1.1 PROBLEM DEFINITION

Phosphorus (P) is an essential element needed by all living matters for growth and development, as its availability controls many biological productivities. The major source of P is in the form of mined phosphate (PO_4-P) rock and about 90 % of the phosphate rock extracted globally is used as mineral fertilizer for productions of crops, industrial products (e.g. detergents), human food, animal feed additives and other (Smil, 2000; Jasinski, 2008). The global phosphorus fates were analyzed key phosphorus flows were illustrated in Figure 1 (Cordell et al., 2009). Unlike fossil fuels which have the potential to be substituted by renewable energy (e.g. wind, biomass, or thermal energy), phosphorus is a non-renewable resource with no substitute and cannot be manufactured or synthesized. It has been estimated that mined phosphate rock reserves could be exhausted within 50 ~ 100 years if used at the current rate (Cordell et al., 2009). Furthermore, the fertilizer industries recognize that the quality of phosphate rock is declining, thus forcing the cost of extraction, processing and shipping to increase (Driver, 1998; Steen, 1998; Smil, 2000; EcoSanRez, 2003). Additional demands on P are being experienced from the population growth, which requires commensurate increase in food production and the current interest in expanding the production of biofuels derived from crops (Cordell et al., 2009).

Before 1945, organic waste such as animal manure and human excreta was recycled in agriculture as the main P fertilizer for agricultural production (Cordell et al., 2009). Thus, locally produced food was consumed locally, and nutrients from different waste streams would be applied back to the local agricultural land. However, this P

recycle loop was broken because of the explosion in human population growth and associated increasing food demand and urbanization. Thus after 1945, phosphate rock was exploited in large quantities and became the dominant P fertilizer source. The unit price of phosphate rock has increased constantly since early 1970's (Jasinski, 2009). The price increased more than 700 % in a 14-month period between 2007 and 2009 due the pressure of global food crisis and the prediction that phosphate rock is in short supply (Cordell et al., 2009). Based on the consumer behavior and the availability of P, the global P production is estimated to reach the peak point in the next 20 to 30 years (Cordell et al., 2009). The "peak phosphorus" prediction was derived from Hubbert theory (Hubbert, 1949) for oil crisis.

On the other hand, eutrophication of water bodies caused by P enrichment from point and/or non-point sources (e.g. agricultural runoff, municipal sewage and industrial wastewater) has been the focus of water quality protection for a long time. For example, agricultural sources were reported to account for approximately 48 % of the impaired lakes, rivers and streams in United States (USEPA, 2002). Therefore, recovering P released from sources like wastewater and livestock manure has important implications in controlling water pollution and making the use of P sustainable.
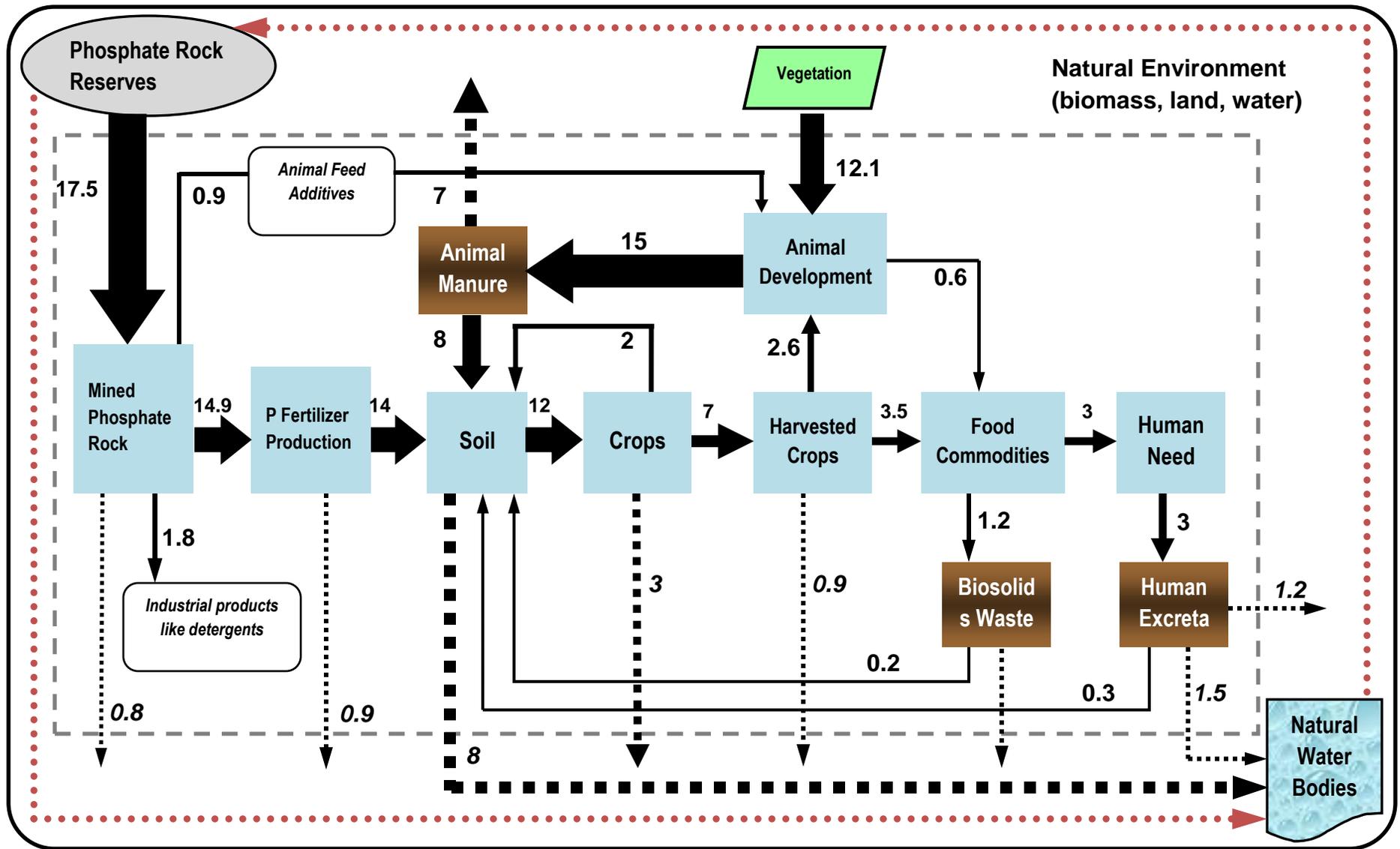
Figure 1. Global key phosphorus flows, where units are in million tons per year (adapted from Cordell et al., 2009)

Today, the upgrades of existing and planning of new wastewater treatment plants are based on improving their performance in nutrient reduction as well as recovery of resources such as phosphorus and energy from biogas production (Giesen, 1999). Recovery of P through precipitation as magnesium ammonium phosphate (struvite) has gained interest in the past decade. The recovery of struvite from municipal wastewater (Ohlinger et al, 2000; Adnan et al., 2003a; Adnan et al, 2003b; Bhuiyan et al., 2008; Forrest et al., 2008), swine wastewater (Burns et al., 2001; Nelson et al., 2003; Suzuki et al., 2005), and industrial wastewater (El Diwani et al., 2007; Kim et al., 2009; Warmadewanthi and Liu, 2009) recovery has been successfully demonstrated. In fact, there are several full scale struvite recovery systems in operation in wastewater treatment plants around the world (Williams, 1999; Ueno and Fujii, 2001; Battistoni et al., 2004; Battistoni et al, 2006). The constituents of struvite i.e., ammonium (NH_4^+), PO_4^{3-}, and magnesium (Mg^{2+}) ions in equal molar concentrations makes it a good fertilizer compared to other phosphate containing fertilizers (Gaterell et al., 2000; Li and Zhao, 2003; Johnson and Richards, 2003; de-Bashan and Bashan 2004; Ponce and De Sa MEGL, 2007).

Animal manure is rich in phosphorus and other nutrients (ASABE, 2005) and has been identified as a potential resource for P recovery and reuse (Greaves et al., 1999; Barnard 2009). However, limited information is available on struvite recovery from liquid dairy manure and some of the challenges associated with struvite recovery have been reported to be (i) the high suspended solids concentration (Schuiling and Andrade, 1999), (ii) low dissolved reactive phosphorus to total phosphorus (DRP/TP) ratio (Barnett, 1994; Harris et al., 2008) and (iii) high Ca^{2+} concentration (Gungor and Karthikeyan,

2005). It has been observed that most of inorganic fraction of total P in dairy manure is predominantly in a particulate-bound form and associated with Ca and Mg (Gungor and Karthikeyan, 2005), leaving very little soluble PO_4^{3-} to precipitate struvite. Furthermore, calcium ions (Ca^{2+}) have been noted to interfere with or inhibit struvite precipitation through reacting with PO_4^{3-} to form calcium phosphates (Le Corre et al., 2005; Wang et al., 2005). Attempts to enhance struvite precipitation from dairy manure included anaerobic digestion, Mg augmentation (Zeng and Li, 2006) and microwave heating assisted with inorganic acid addition and hydrogen peroxide (Pan et al, 2006; Qureshi et al., 2008). These pretreatment methods were employed to increase DRP/TP ratios and/or Mg^{2+} availability. However, very few studies were carried out to study the effects of reducing Ca^{2+} on struvite precipitation from dairy manure.

1.2 RESEARCH OBJECTIVES

The major goal of this study was to investigate the pretreatment methods for struvite precipitation in liquid dairy manure. The specific objectives were to:

- Investigate the effectiveness of ethylenediaminetetraacetic acid (EDTA) and oxalic acid in reducing the effects of calcium to enhance struvite precipitation in liquid dairy manure.

- Evaluate the potential of struvite precipitation in liquid dairy manure pretreated by EBPR (enhanced biological phosphorus removal) treatment.

- Evaluate the struvite precipitation potential in liquid dairy manure treated with thermal and biological-based methods (EBPR, microwave heating and anaerobic digestion).

- Make a comparative chemical costs analysis of struvite precipitation in liquid dairy manure subjected to different pretreatments: (1) untreated manure + oxalic acid; (2) MW + H_2SO_4 acidification; (3) AD + oxalic acid.

REFERENCES

Adnan, A., D. S. Mavinic, and F. A. Koch. 2003a. Pilot-scale study of phosphorus recovery through struvite crystallization - I. Examining the feasibility of applying the process technology. Journal of Environmental Engineering and Science 2(5): 315-324.

Adnan, A., D. S. Mavinic, and F. A. Koch. 2003b. Pilot-scale study of phosphorus recovery through struvite crystallization - II. Applying in-reactor supersaturation ratio as a process control parameter. Journal of Environmental Engineering and Science 2(6): 473-483.

Adnan, A., M. Dastur, D. S. Mavinic, and F. A. Koch. 2004. Preliminary investigation into factors affecting controlled struvite crystallization at the bench scale. Journal of Environmental Engineering and Science 3(3): 195-202.

ASABE. 2005. Manure characteristics. American Society of Agricultural and Biological Engineers (ASABE) Standard D384.2. St. Joseph, Mich.

Barnard, J. 2009. Elimination of eutrophication through resource recovery. International conference on nutrient recovery from wastewater streams. Eds K. Ashley, D. Mavinic, and F. Koch. IWA Publishing, pp 45-54.

Barnett, G. M. 1994. Phosphorus forms in animal manure. Bioresource Technology 49(2): 139-147.

Battistoni, P. 2004. Phosphorus recovery trials in Treviso, Italy – theory modeling and application. Phosphorus in environmental technologies: Principles and applications. London: IWA Publishing, pp. 428-469.

Battistoni, P., B. Paci, F. Fatone, and P. Pavan. 2006. Phosphorus removal from

    anaerobic supernatants: start-up and steady-state conditions of a fluidized bed

    reactor full-scale plant. Industrial & Engineering Chemistry Research 45(2): 663-

    669

Bhuiyan, M. I. H., D. S. Mavinic, and F. A. Koch. 2008. Phosphorus recovery from

    wastewater through struvite formation in fluidized bed reactors: a sustainable

    approach. Water Science and Technology 57(2):175-181.

Burns, R. T., L. B. Moody, F. R. Walker, and D. R. Raman. 2001. Laboratory and in-situ

    reductions of soluble phosphorus in swine waste slurries. Environmental

    Technology 22(11): 1273-1278.

Cordell, D., Drangert, J-O., White, S., 2009. The story of phosphorus: Global food

    security and food for thought. Global Environmental Change 19, 292-305.

de-Bashan, L. E., and Y. Bashan. 2004. Recent advances in removing phosphorus from

    wastewater and its future use as fertilizer (1997-2003). Water Research 38(19):

    4222-4246.

Driver, J., 1998. Phosphates recovery for recycling from sewage and animal waste.

    Phosphorus and Potassium 216, 17-21.

EcoSanRes, 2003. Closing the loop on phorsphorus: Stockholm Environment Institute

    (SEI) funded by SIDA Stockholm.

El Diwani, G., S. El Rafie, N. N. El Ibiari, and H. I. El-Aila. 2007. Recovery of ammonia

    nitrogen from industrial wastewater treatment as struvite slow releasing fertilizer.

    Desalination 214(1-3): 200-214.

Forrest, A. L., K. P. Fattah, D. S. Mavinic, and F. A. Koch. 2008. Optimizing struvite production for phosphate recovery in WWTP. Journal of Environmental Engineering-ASCE 134(5): 395-402.

Gaterell, M. R., R. Gay, R. Wilson, R. J. Gochin, and J. N. Lester. 2000. An economic and environmental evaluation of the opportunities for substituting phosphorus recovered from wastewater treatment works in existing UK fertilizer markets. Environmental Technology 21(9): 1067-1084.

Giesen, A. 1999. Crystallization process enables environmental friendly phosphate removal at low costs. Environmental Technology 20(7): 769-775.

Greaves, J., P. Hobbs, D. Chadwick, and P. Haygarth. 1999. Prospects for the recovery of phosphorus from animal manures: a review. Environmental Technology 20(7): 697-708.

Gungor, K., and K. G. Karthikeyan. 2005. Influence of anaerobic digestion on dairy manure phosphorus extractability. Transactions of the ASAE 48(4): 1497-1507.

Harris, W. G., A. C. Wilkie, X. Cao and R. Sirengo. 2008. Bench-scale recovery of phosphorus from flushed dairy manure wastewater. Bioresource Technology 99(8): 3036-3043.

Hubbert, M. K. 1949. Energy from fossil fuels. Science 109(2823): 103-109.

Jasinski, S. M., 2008. Phosphate Rock, Mineral Commodity Summaries, U. S. Geological Survey.

Jasinski, S. M., 2009. Phosphate Rock, Mineral Commodity Summaries, U. S. Geological Survey.

Johnston, A. E. and Richards, I. R. 2003. Effectiveness of different precipitated phosphates as phosphorus sources for plants. Soil Use and Management 19(1): 45-49.

Kim, D., J. Kim, H-D. Ryu, and S. Lee. 2009. Effect of mixing on spontaneous struvite precipitation from semiconductor wastewater. Bioresource Technology 100(1): 74-78.

Le Corre, K. S., E. Valsami-Jones, P. Hobbs, and S. A. Parsons. 2005. Impact of calcium on struvite crystal size, shape and purity. Journal of Crystal Growth 283(3-4): 514-552.

Li, X. Z. and Q. L. Zhao. 2003. Recovery of ammonium-nitrogen from landfill leachate as a multi-nutrient fertilizer. Ecological Engineering 20(2): 171-181.

Nelson, N.O., R. L. Mikkelsen, and D. L. Hesterberg. 2003. Struvite precipitation in anaerobic swine lagoon liquid: effect of pH and Mg:P ratio and determination of rate constant. Bioresource Technology 89(3): 229-236.

Ohlinger, K. N., T. M. Young, and E. D. Schoeder. 2000. Postdigestion struvite precipitation using a fluidized bed reactor. Journal of Environmental Engineering-ASCE 126(4): 361-368.

Pan, S. H., K. V. Lo, P. H. Liao, and H. Schreier. 2006. Microwave pretreatment for enhancement of phosphorus release from dairy manure. Journal of Environmental Science and Health Part B – Pesticides Food Contaminants and Agricultural Wastes 41(4): 451-458.

Ponce, R. G. and De Sa MEGL. 2007. Evaluation of struvite as a fertilizer: a comparison with traditional P sources. Agrochimica 51(6): 301-308.

Qureshi, A., K. V. Lo and P. H. Liao. 2008. Microwave treatment and struvite recovery potential of dairy manure. Journal of Environmental Science and Health Part B – Pesticides Food Contaminants and Agricultural Wastes 43(4): 350-357.

Schuiling, R. D and A. Andrade. 1999. Recovery of struvite from calf manure. Environmental Technology 20(7): 765-768.

Smil, V. 2000. Phosphorus in the environment: natural flows and human interferences. Annual Review of Energy and the Environment 25: 53-88.

Steen, I. 1998. Phosphorus availability in the 21st century: management of a non-renewable resource, Phosphors and potassium 217: 25-31.

Suzuki, K., Y. Tanaka, K. Kuroda, D. Hanajima, and Y. Fukumoto. 2005. Recovery of phosphorus from swine wastewater through crystallization. Bioresource Technology 96(14): 1544-1550.

Ueno, Y. and M. Fujii. 2001. Three years experience of operating and selling recovered struvite from full-scale plant. Environmental Technology 22(11): 1373-1381.

U.S. Environmental Protection Agency. 2002. 2000 National Water Quality Inventory, EPA 841-R-02-001, Office of Water, U.S. EPA: Washington DC. (http://www.epa.gov/OWOW/305b/).

Wang, L. and G. H. Nancollas. 2008. Calcium orthophosphates: crystallization and dissolution. Chemical Reviews 108(11): 4628-4669.

Warmadewanthi and J. C. Liu. 2009. Recovery of phosphate and ammonium as struvite from semiconductor wastewater. Separation and Purification Technology 64(3): 368-373.

Williams, S. 1999. Struvite precipitation in the sludge treatment stream at slough

    wastewater treatment plant and opportunities for phosphorus recovery.

    Environmental Technology 20(7): 743-747.

Zeng, L. and X. Li. 2006. Nutrient removal from anaerobically digested cattle manure by

    struvite precipitation. Journal of Environmental Engineering and Science 5(4):

    285-294.

2. BACKGROUND

2.1 DAIRY MANURE NUTRIENTS AND FORMS OF PHOSPHORUS

Dairy manure has been used a fertilizer for crops for many years because it is a good source of nutrients (nitrogen, phosphorus, and potassium).However, some nutrients contained in animal diets are not completely utilized by animals. These nutrients include calcium (Ca), magnesium (Mg), sodium (Na), sulfur (S), chloride (Cl), iron (Fe), aluminum (Al), copper (Cu), zinc (Zn) and manganese (Mn) (National Research Council, 2001). On average a mature dairy cow produces 68 kg (or 68 L) manure daily containing 0.45 kg N, 0.078 kg P and 0.103 kg K (ASABE, 2005).

However, if quantity of land-applied manure contains P in excess of crop nutrient requirements, P losses from agricultural land to natural water bodies through runoff and erosion may occur (Weld et al., 2001; Maguire and Sims, 2002) causing deterioration of water quality e.g. eutrophication. With the shift from N-based to P-based nutrient management plans, land may be limiting to dairy farms for manure application. Therefore, P removal and/or recovery treatment may be required on dairy farms to manage the manure N to P ratio.

Total P (TP) concentration in dairy manure varies considerably from farm to farm, depending on dietary P levels, feed source and many other digestive capabilities of the cow (Barnett, 1994). P is present in dairy manure in several forms, varying widely in their stability and bioavailability. Basically, TP is grouped into inorganic P (P_i) and organic P (P_o) (Ormaza-Gonzalez and Statham, 1996). Inorganic P includes dissolved reactive P (DRP) and acid-soluble reactive P (ASRP), taking up to 63.2 % of the TP in animal manure (Barnett, 1994). There are various forms of organic P, including phytate

(i.e. inositol hexaphosphates (IHP)), phospholipids and nucleic acid-type P (e.g. DNA and RNA). Phytate is also called acid-soluble organic P because it could interact with many metal ions to form insoluble or less soluble metal species (Dao, 2003; He et al., 2009). The composition of organic P in manure has been characterized by solution-based techniques such as sequential fractionation (Dou et al., 2002) and enzymatic hydrolysis (He and Honeycutt, 2001) and by solid state ^{31}P nuclear magnetic resonance (NMR) spectroscopy (He et al., 2009), with an emphasis on understanding the metal complexation of organic P. The P forms in manure are illustrated in Figure 2.
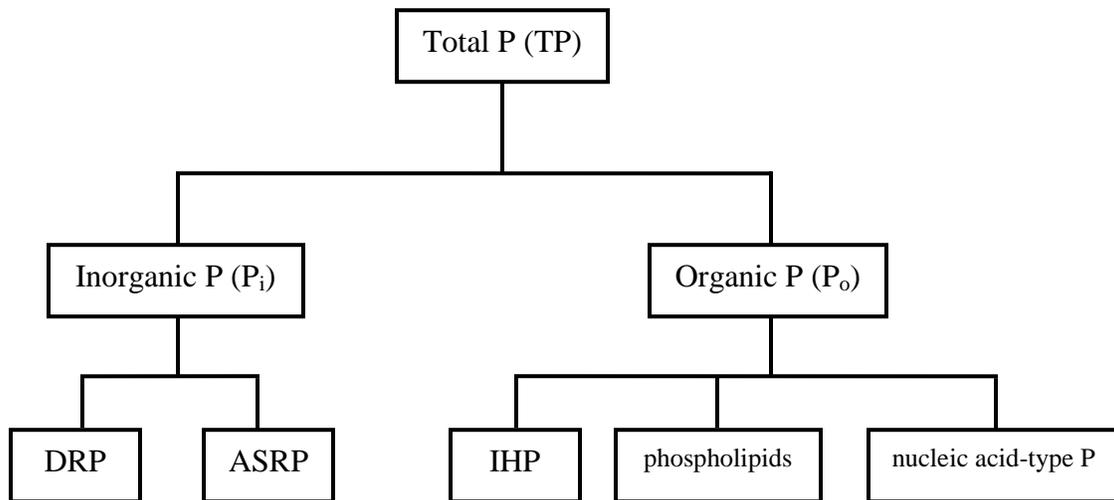
Figure 2. P forms in dairy manure

2.2 PHOSPHORUS RECOVERY

2.2.1 Calcium phosphate

There are several forms of calcium phosphate that can precipitate in solution, depending on pH, reaction time, Ca^{2+} to PO_4-P ratio and concentrations of other ions. Generally, hydroxyapatite (HAP, $Ca_5(PO_4)_3OH$) is the least soluble and the most thermodynamically stable calcium phosphate formed under neutral to basic conditions. In acidic solution, other forms like brushite (DCPD, $CaHPO_4$ $2H_2O$), mononite (DCPA, $CaHPO_4$), octacalcium phosphate (OCP, $Ca_8(HPO_4)_2(PO_4)_4$ $5H_2O$), and amorphous calcium phosphate (ACP, $Ca_xH_y(PO_4)_z$ nH_2O, n=3~4.5) may also form (Musvoto et al., 2000). Furthermore, it is has been observed that the crystallization of HAP involves the formation of metastable precursor phases such as ACP and OCP (Wang and Nancollas, 2008).

Theoretically, calcium phosphate should be useful to the phosphate industry for re-use and recycling, because it is similar in chemical composition as mined phosphate rock used in industry. However, it has not been widely adopted to realize P recovery from wastewater as calcium phosphate in full scale industries. By adding lime, many wastewater treatment plants produced calcium phosphates in the form of slime, contained in huge amounts of sludge with high water content (65 % to 85 %) (Giesen, 1999), which cannot be accepted by industries. Their main objective was P removal, rather than P recovery. Two full-scale P recovery trials (Angel, 1999; Giesen, 1999) used the DHV Crystalactor to facilitate P recovery as calcium phosphate pellets with up to 11 % P content, containing only 5 % to 10 % water. One of the key challenges to operate this technology successfully was to control the bicarbonate/carbonate (HCO_3^-/CO_3^{2-})

concentration of the influent at low levels, otherwise they would precipitate calcium

carbonate ($CaCO_3$). This was overcome by reducing the pH of the influent to 3 to release

CO_2 and then raising it to 9 to induce calcium phosphate precipitation (Giesen, 1999);

this increases the cost of P recovery processes. Furthermore, seed materials addition like

calcite (Song et al., 2006) and silica sand (Giesen, 1999) is required for P recovery as

calcium phosphates, which would add to the process complexity and costs.

Besides bicarbonate/carbonate (HCO_3^-/CO_3^{2-}) alkalinity, calcium phosphate

precipitation is also interfered by other compounds. For example, organic ligands like

citrate inhibit the precipitation by binding to active growth sites of the nuclei (Van Der

Houwen and Valsami-Jones, 2001). Also, high Mg^{2+} concentration in solution with the

presence of sufficient ammonium ions (NH_4^+) has the potential to alter the precipitation

pathway from calcium phosphate to struvite ($MgNH_4PO_4 \cdot 6H_2O$) (Cao and Harris, 2008).

There are questions about the use of calcium phosphate as a fertilizer because of its low

solubility (Wang and Nancollas, 2008), indicating inadequate phosphate release for crops

nutrition requirements. A summary of the advantages and disadvantages of P recovery as

calcium phosphate are listed in Table 1.

Table 1. P recovery as calcium phosphate: advantages and disadvantages

Advantages	Disadvantages
- similar to mined phosphate rock used in industry - can be readily accepted by industries if recovered in a suitable physical form (like pellets)	- usually in the form of slime with high water content, which is useless to industries - hard to recover: need to add external seed materials to facilitate crystallization process - hard to recover: need to reduce CO_3 as pretreatment before inducing calcium phosphate precipitation - hard to recover: be easily interfered by other ions

2.2.2 Magnesium ammonium phosphate (struvite)

One of the most promising wastewater phosphate recovery techniques is its co-precipitation with Mg^{2+} and NH_4^+ as magnesium ammonium phosphate hexahydrate $(MgNH_4PO_4 \cdot 6H_2O)$, commonly known as struvite (de-Bashan and Bashan, 2004). This technique is beneficial for several reasons. First, struvite has the potential to be used as a slow-release fertilizer (Bridger et al., 1962; Parsons et al., 1999). Li and Zhao (2003) showed that it provides easy-taking sources of nutrients (N, P and Mg) for plants. Also, nutrient taking responses of some plants to struvite application were found to be similar or even superior to those obtained with conventional P fertilizers (phosphate rock, monoammonium phosphate and monocalcium phosphates) (Johnson and Richards, 2003; Ponce and De Sa MEGL, 2007). Especially, its low solubility in water (about 0.02 g/100 mL H_2O, at 25 ℃ and 1 atm) ensures nutrient release over a longer period of time and decreases the danger of burning roots of crops struvite is applied (Gaterell et al., 2000). Second, struvite crystallization allows the recovery of both phosphorus and nitrogen simultaneously. Third, struvite crystals are regarded as being more easily recovered than calcium phosphates. It was recently found that struvite is as effective as conventional phosphate rock when being used as fertilizer in agriculture (Ponce and De Sa MEGL, 2007), in agreement with earlier research conclusion (Gaterell et al., 2000). Full-scale struvite recovery industry was reported in Japan and fertilizer companies bought struvite recovered from wastewater treatment plants (WWTPs), using it to adjust the nitrogen/phosphorus/potassium ratio of the fertilizer mixture; the final product has been widely used for paddy rice and other agricultural plants (Ueno and Fujii, 2001).

However, up to now the commercial profit of struvite used as fertilizer is still not clear (Massey et al., 2010). Compared with calcium phosphate, many problems are encountered by current phosphate industry in producing struvite (Schipper et al., 2001), including Mg interference during P purification in the "wet" process and NH_3 emissions during heating in the "dry" P manufacturing process. Shu et al. (2006) pointed out that the reasons why struvite is not widely used as fertilizer lie in two primary reasons: its limited availability to farmers and lack of information on its land-applicability and economic benefits.

2.3 STRUVITE PRECIPITATION CHEMISTRY

Struvite is a white orthorhombic crystalline consisting of magnesium, ammonium and orthophosphate in equal molar ratio. It precipitates by the chemical reaction of Mg^{2+}, NH_4^+ and $H_nPO_4^{3-n}$ (with n = 0, 1 or 2), following the general equation (1).

$$Mg^{2+} + NH_4^+ + H_nPO_4^{3-n} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O + nH^+ \qquad (1)$$
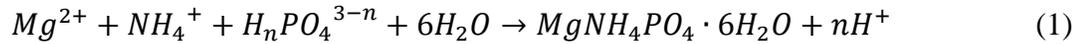
Generally, the formation of a mineral precipitates is controlled by its solubility (Aage et al., 1997; Bhuiyan et al., 2007; Webb and Ho, 1992). The solubility product of struvite can be expressed by equation (2) and (3).

$$MgNH_4PO_4 \cdot 6H_2O \leftrightarrow Mg^{2+} + NH_4^+ + PO_4^{3-} \qquad (2)$$
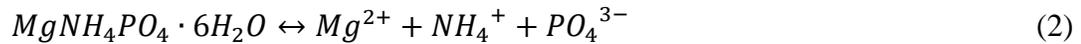
$$K_{sp} = [Mg^{2+}] \cdot [NH_4^+] \cdot [PO_4^{3-}] \qquad (3)$$

As shown in equation (3), the solution will be supersaturated and struvite precipitation will occur when the product of Mg^{2+}, NH_4^+, and PO_4^{3-} concentrations exceeds the value of K_{sp}. Yet the solubility product can also be calculated in terms of conditional solubility product (K_{so}) (Doyle and Parsons, 2002; Le Corre et al., 2009). Its value is only accurate under a given specific conditions because its calculation takes into

account the ionic strength and activity of the ionic species, which are highly pH dependent. The conditional solubility product (K_{so}) is expressed in equation (4), where γ is the activity coefficient (Ohlinger et al., 1998).

$$K_{so} = \left([Mg^{2+}] \cdot \gamma_{Mg}\right) \cdot \left([NH_4^{+}] \cdot \gamma_{NH_4}\right) \cdot \left([PO_4^{3-}] \cdot \gamma_{PO_4}\right) \tag{4}$$

Solution consisting of magnesium, ammonium and phosphate forms ions and complexes including Mg^{2+}, $MgOH^+$, $MgH_2PO_4^+$, $MgHPO_4$ (aq), $MgPO_4^-$, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, NH_3 and NH_4^+ (Ohlinger et al., 1998). The total constituent concentration for Mg, NH_4 and PO_4, denoting $C_{T,Mg}$, C_{T,NH_4}, C_{T,PO_4}, are the sum of measured ionic concentration of their complexes and free ions, illustrated in equation (5)~(7) as follows.

$$C_{T,Mg} = [Mg^{2+}] + [MgOH^+] + [MgH_2PO_4^+] + [MgHPO_4(aq)] + [MgPO_4^-] \tag{5}$$

$$C_{T,NH_4} = [NH_3] + [NH_4^+] \tag{6}$$

$$C_{T,PO_4} =$$

$$[H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] + [MgH_2PO_4^+] + [MgHPO_4(aq)] +$$

$$[MgPO_4^-] \tag{7}$$

One of the key thermodynamic parameters describing struvite saturation degree is the supersaturation ratio (SSR), relating to the ion activity product (IAP) and the conditional solubility product (K_{so}) , as shown in equation (8) (Snoeyink and Jenkins, 1980; Ohlinger, 1999).

$$SSR = \sqrt[3]{\frac{IAP}{K_{so}}} = \sqrt[3]{\frac{(C_{T,Mg}) \cdot (C_{T,NH_4}) \cdot (C_{T,PO_4})}{K_{so}}} \tag{8}$$

The saturation degree of struvite in solution are influenced by many factors, such as pH, its component ions concentrations (Mg^{2+}, NH_4^+, and PO_4^{3-}) and presence of other ionic species (e.g. Ca^{2+}, CO_3^{2-}, K^+). Therefore it is difficult to predict or control struvite precipitation in media like animal manure and municipal wastewater, due to the complexity of the solution.

2.4 FACTORS AFFECTING STRUVITE PRECIPITATION PROCESS

2.4.1 pH

The pH is one of the most important factors affecting the struvite precipitation process, because the struvite solubility and solution supersaturation are directly influenced by it. Firstly, according to equation (1), the pH of solution will be decreased due to the released protons during the precipitation of struvite (Kofina and Koutsoukos, 2005). Thus the rate of pH drop can be used as an indicator of struvite formation (Le Corre et al., 2005). Secondly, the concentration of ammonium ions (NH_4^+) is sensitive to solution pH value, because ammonium will transfer into ammonia gas (NH_3) when pH is raised above 9 (Booker et al., 1999), as shown in equation (9) (Snoeyink and Jenkins, 1980). The decrease of ammonium ions in solution will increase the struvite solubility, thus decrease the solution supersaturation degree with respect to struvite precipitation.

$$NH_4^+(aq) \leftrightarrow NH_3(g) + H^+, \quad pK_a = 9.3 \tag{9}$$

Many researchers investigated the effects of pH on struvite precipitation and reported optimum value between7.5 and 10.7 (Bouropoulos and Koutsoukos, 2000; Ohlinger et al., 1998; Stratful et al., 2001). Adnan et al (2003) found that it was possible to achieve over 90% P removal as struvite at pH 7.3, indicating that very alkaline pH was not necessary to trigger precipitation of struvite.

However, many previous studies pointed out that pH > 8 is needed to precipitate struvite in animal manure wastewater. Burns et al (2001, 2003) enhanced struvite precipitation in swine slurries supernatants by increasing pH value to 8.6 and over 90 % P removal rate was observed in both the bench- and field-scale experiments. This supports the results found by Wrigley et al (1992) when treating the supernatants from anaerobically digested swine waste. Nelson et al (2003) quantified the crossed effects of pH and Mg/P ratio and pointed out that pH for the minimum struvite solubility (ranging from 8.90 to 9.25) was not significantly affected by the Mg to ortho-P ratio.

2.4.2 Mg^{2+}/NH_4-N/PO_4-P ratio

Magnesium (Mg) addition can be used to enhance struvite precipitation in waste streams where Mg^{2+} is a limiting factor (Stratful et al., 2001). Basically, Mg^{2+} to PO_4-P molar ratio above 1:1 is recommended in practice. Beal et al. (1999) induced struvite precipitation from swine waste by increasing the Mg^{2+}/PO_4-P molar ratio from 0.25 to 1 using MgO to supply Mg and increase the pH. Maekawa et al. (1995) obtained maximum PO_4-P removal using Mg/PO_4-P ratio of 1.5. Likewise, Nelson et al. (2003) investigated the interactive effects of pH and Mg/PO_4 ratio and found that increasing Mg to P ratio resulted in P removal at any given pH, indicating the importance of Mg concentration adjustment from practical standpoint because PO_4-P reduction could be achieved with a smaller increase in pH. For example, adequate P removal can be obtained at a pH (8.2) with a correspondingly high Mg/PO_4-P ratio (1.6), rather than at pH 9.0 with a Mg/PO_4 ratio of 1:1. Lower level of alkaline pH not only means less cost of NaOH addition but also avoids potentially negative effects such as NH_3 volatilization resulted from high pH (>9.0). One hypothesis about the benefits of higher Mg/PO_4 ratio was raised by Schulze-

Rettmer (1991), saying that high Mg concentrations promote struvite precipitation by overcoming the effects of complex agents binding to magnesium. Tong and Chen (2007) supported this hypothesis, suggesting that organic matter (soluble COD) would co-precipitate with Mg^{2+}, resulting in decreased PO_4-P removal efficiency. However, Bowers and Westerman (2005) found that excessively high Mg concentrations relative to P suppressed struvite precipitation. They reported that an Mg/TP ratio greater than 1 may decrease P removal rate. It was possible that high concentrations of Mg inhibited struvite precipitation, likely from the formation of other mineral solids (e.g. $MgCO_3$ and $MgHPO_4$).

Besides Mg^{2+}/PO_4-P ratio, ammonium (NH_4^+) concentration is also a very important factor for struvite precipitation. Stratful et al. (2001) investigated the effects of excess ammonium concentration on struvite precipitation and found that higher residual NH_4^+ concentration could limit the further precipitation of excess Mg^{2+} and phosphate and thus increase the yield of pure struvite in the final precipitates. Another possible explanation for beneficial effects of excess ammonium could be that ammonium could provide buffering solution. As shown in equation (1), in an unbuffered system, the pH falls as struvite forms. Experiments carried on the influence of ammonium concentration on calcium phosphate precipitation supported this hypothesis, because no significant drop in pH was observed when amorphous calcium phosphate (ACP) formed as a result of the buffering effects of ammonium (Lopez-Valero et al., 1992). On the other hand, the presence of ammonium in solution with high calcium ions (Ca^{2+}) concentration has the potential to alter the pathway from calcium phosphate to struvite precipitation (Cao and Harris, 2008).

2.4.3 Presence of other ions

Theoretically, any impurities in solution can affect the formation of crystalline compounds through changing the ionic activity and/or suppressing the increase of crystal size due to blocking of growth sites (Jones, 2002). It is known that numerous ions have negative effects on struvite precipitation process by either retarding induction time preceding the first occurrence of crystals or competing PO_4^{3-} with Mg^{2+} to form phosphate minerals (Kofina and Koustsoukos, 2004).

Ca^{2+} received much attention in terms of interfering struvite precipitation. They compete with Mg^{2+} to interact with PO_4^{3-} to form ACP, tricalcium phosphate (TCP), and/or hydroxyapatite (HAP), according to equation (10)~(12) below (Wang and Nancollas, 2008).

$$xCa^{2+} + H_mPO_4^{3-m} + nH_2O \leftrightarrow Ca_xH_y(PO_4)_z \cdot nH_2O, n = 3{\sim}4.5 \qquad (10)$$

$$3Ca^{2+} + 2PO_4^{3-} \leftrightarrow Ca_3(PO_4)_2 \qquad (11)$$

$$5Ca^{2+} + 3PO_4^{3-} + H_2O \leftrightarrow Ca_5(PO_4)_3OH + H^+ \qquad (12)$$
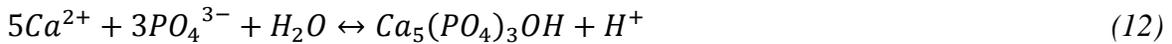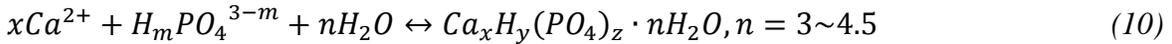
Le Corre et al. (2005) conducted experiments with synthetic solution and reported the significant negative impacts of Ca^{2+} on struvite crystallization with respect to size, shape and purity. Hardly any struvite crystals form when Ca^{2+} to Mg^{2+} molar ratio if greater than 1. Similar observations were found by Wang et al. (2005) that Ca is the major interfering ion in struvite formation from animal manure/wastewater. They employed NH_4/PO_4 ratio in the precipitates as the indicator to estimate the struvite purity and observed a clear trend where struvite purity decreased with Ca^{2+} concentration increased. Harris et al. (2008) investigated the forms of P recovery from flushed dairy

manure and found that poorly crystalline calcium phosphate (ACP and HAP) formed fast enough to be recovered as dominant P minerals in precipitates, which indicated that the greater solubility of struvite ($pK_{sp} = 13.26$, Ohlinger et al., 1998) compared to HAP ($pK_{sp} = 116.8$, Wang and Nancollas, 2008) thermodynamically favors the latter to precipitate, especially in the media with high Ca^{2+} concentration such as liquid dairy manure. Other studies (Bowers and Westerman, 2005; Massey, 2008) also reported the inhibitory effects of Ca^{2+} on struvite precipitation in liquid dairy manure. The P removal efficiencies by struvite precipitation from swine or dairy manure are summarized in Table 2. In manure wastewater where Ca/PO_4-P molar ratio less than 1 coupled with high NH_4-N/PO_4-P ratio, struvite could form as the dominant solid phase in the precipitates. As reported by Nelson et al. (2003), in swine lagoon liquid with Ca/PO_4-P molar ratio of 2.13, struvite crystals were still observed among the precipitates. These findings partially confirmed the benefits brought by excess ammonium on struvite formation (Stratful et al., 2001). However, in flushed dairy manure with Ca/PO_4-P molar ratio > 5, no struvite was found there, indicating that the suppression from high Ca^{2+} concentration overweighed the effects of excess ammonium (Harris et al., 2008). Pastor et al. (2008) observed the negative effects of Ca^{2+} treating EBPR anaerobic digestion sludge liquors with Ca/Mg molar ratios of 0.4 and 1.6 respectively. Only 35.4 % of the removed P precipitated as struvite in high Ca/Mg molar ratio, while 72.6 % in low Ca/Mg molar ratio. However, high P removal efficiencies (91.1 % and 83.1 %) were achieved in both liquors, indicating that P removal was mainly attributed to calcium phosphate precipitation in the former liquor. They also pointed out the importance of management of the sludge treatment line to recover P as struvite precipitates.

Besides Ca^{2+}, other ions such as carbonate/bicarbonate (CO_3^{2-}/HCO_3^-), sodium (Na^+) and sulfate (SO_4^{2-}) also have impacts on either induction time or struvite crystal morphology and sizes (Kabdaşli et al., 2006). In a solution system containing Mg^{2+}, NH_4^+, Ca^{2+}, CO_3^{2-} and PO_4^{3-}, the precipitation conditions are very complex because any form of ions would have inhibitory effects on other precipitates. For example, either Mg^{2+} or CO_3^{2-} ions suppress the formation of calcium phosphates (Ferguson and McCarty, 1971), separately. Coexistence of Mg^{2+} and CO_3^{2-} showed a synergistic inhibitory effect on this suppression and the likely reason for this mitigated inhibition involves the formation of $MgCO_3$ (Cao and Harris, 2008).

2.4.4 Suspended solids and organic matter content

Interference may be caused by suspended solids (TSS) and/or organic compounds and dairy manure typically contains high concentration of these matters. In the efforts to recover struvite from calf manure slurries in pilot-scale system, Schuiling and Andrade (1999) reported that the TSS concentration greater than 1000 mg/L (or 0.1 %) inhibited precipitation of struvite. Schulze-Rettmer (1991) also reported that organic compounds could potentially co-precipitate with Mg^{2+}, resulting in the increase in the equilibrium phosphate concentration. Kofina et al. (2007) investigated the effects of citrate and phosphocitrate on both the kinetics and the morphology of the spontaneous precipitation of struvite in synthetic wastewater supersaturated solutions and demonstrated that these ions can inhibit struvite precipitation by retarding the induction time and increasing the supersaturation level required for precipitation.

Table 2. The P removal by struvite precipitation from swine or dairy manure in published studies

Material	Before treatment				Treatment	Precipitated ratio (%)			Precipitates	Reference
	Mg/PO_4-P	Ca/PO_4-P	Ca/Mg	NH_4-N/PO_4-P		PO_4-P	Mg	Ca		
swine wastewater	0.90	0.80	0.89	6.98	increase pH to 8.1~8.7 by aeration	81.2	71.7	55.7	MAP + HAP	Suzuki et al., 2002
swine wastewater	0.91	0.95	1.04	-	increase pH to 7.3~8.1 by aeration	50.0	37.5	20.5	MAP (95 %)	Suzuki et al., 2005
swine wastewater	0.83	0.86	1.04	16.36	increase pH to 8.0 by aeration	51.4	-	-	MAP (95 %)	Suzuki et al., 2007
					$MgCl_2$ addition + increase pH to 8.0	78.6	-	-	MAP (97 %)	
swine waste slurry	-	-	-	-	$MgCl_2$ addition to Mg/TP 1.6 + increase pH to 9.0	91.0	-	-	MAP (51 %)	Burns et al., 2001
swine waste slurry	0.26	-	-	18	$MgCl_2$ addition to Mg/TP 1.6~3.5 + increase pH to 8.5	98.0	-	-	MAP + brushite	Burns et al., 2003
	0.58	-	-	12		90.4	-	-		
swine wastewater	0.3~0.6	-	-	91.3~124.5	$MgCl_2$ addition to Mg/PO_4-P 2.0 + increase pH to 9.0~9.5	99.2	-	-	MAP	Kim et al., 2004
swine wastewater	0.73	0.74	0.61	19.88	$MgCl_2$ addition to Mg/PO_4-P 1.1~1.4 + increase pH to 8.5	98	-	-	MAP	Laridi et al., 2005
swine lagoon liquid	1.13	2.13	1.88	21.31	$MgCl_2$ addition to Mg/PO_4-P 1.0~1.6 + increase pH to 8.3~9	85	-	-	MAP (91 %)	Nelson et al., 2003
swine manure	0.43	0.39	0.91	14.50	increase pH to 8.5 by NaOH addition	55	36	56	MAP + monetite + brushite	Celen et al., 2007
					$MgCl_2$ addition to Mg/PO_4-P 2.0 + pH increase to 8.5	98	40	0	MAP	
swine manure	0.74	0.48	0.65	13.49	$MgCl_2$ addition to Mg/PO_4-P 1.0 + pH increase to 8.5	94	88	0	MAP	Celen et al., 2007
					$MgCl_2$ addition to Mg/PO_4-P 1.5 + pH increase to 8.5	97	50	0	MAP	
anaerobically digested swine manure	0.78	-	-	7.83	MgO addition to Mg/PO_4-P 2.0 + pH increase to 9	98	-	-	N/A	Moody et al., 2009
liquid swine manure	1.90	3.22	2.49	-	Mg smelting by-products addition to Mg/PO_4-P 3.1 or higher + pH increase to 8.6 or higher	> 96	-	-	no struvite	Parent et al., 2007

Material	Before treatment				Treatment	Precipitated ratio (%)			Precipitates	Reference
	$Mg/PO_4\text{-}P$	$Ca/PO_4\text{-}P$	Ca/Mg	$NH_4\text{-}N/PO_4\text{-}P$		$PO_4\text{-}P$	Mg	Ca		
flushed dairy manure	2.99	5.59	1.29	9.19	increase pH to 8.75	80.4	-	-	amorphous calcium phosphate (ACP)	Harris et al., 2008
untreated dairy manure	3.04	4.44	1.46	10.27	increase pH to 8.5	99.4	-	-	ACP	present study
					add oxalate to decrease Ca/Mg to 0.02 + pH increase to 7.0	94.4	-	-	MAP	
					add EDTA to decrease Ca/Mg to 0.18 + pH increase to 7.0	95.2	-		MAP	
					$MgCl_2$ addition to Ca/Mg 0.25 + pH increase to 7.0	99.6	-	-	N/A	

2.5 PRETREATMENT TO ENHANCE STRUVITE PRECIPITATION IN DAIRY MANURE

Phosphorus recovery via struvite precipitation is limited to available soluble orthophosphate (i.e. dissolved reactive phosphorus, DRP). However, nearly 50% of the TP in dairy manure is in organic form (Wilkie et al., 2004) and most of the inorganic phosphate in dairy manure exists in the insoluble forms of particulate Ca- and $Mg-PO_4$ minerals (Van Rensburg et al., 2003, Gungor and Karthekiyan 2005, 2008). Massey (2008) attempted to recover struvite from liquid dairy manure and obtained low recovery efficiency and suspected that struvite might have been precipitated and present in fine suspended form mixed with other metal-phosphate solids. However, many successful cases about high P removal in untreated animal manure, but few of them were removed by struvite precipitation (Harris et al., 2008). Bowers et al (2007) achieved TP removal rates of 80 % in swine lagoon wastewater but only as high as 49 % in dairy wastewater. Massey (2008) failed to capture struvite from dairy lagoon liquid with only 14% P removal efficiency using a fluidized bed crytallizer similar to what Bowers et al. (2007) used. Therefore, the main obstacles to precipitate struvite in dairy manure can be summarized as (1) low orthophosphate to TP ratio and (2) high Ca concentrations. Five pretreatments that can be used to increase orthophosphate to TP ratio and abate the effects of Ca on struvite precipitation were described below.

2.5.1 Anaerobic digestion

Anaerobic digestion (AD) is a commonly used treatment practice in animal manure management due to the potential benefits like biogas production, COD reduction, volatile solids (VS) destruction, odor mitigation and pathogen reduction. Several recent

researches investigated the effects of AD of animal manure prior to the struvite precipitation in quality and quantity. Moody et al (2009) observed that AD simultaneously increased the concentration of soluble ortho-P (PO_4-P) by 26 % and the amount of available magnesium (Mg^{2+}) by 254 %, and assumed that this would enhance P removal through struvite precipitation in swine waste slurries. A similar conclusion was made by Marti et al (2008) that Mg would be released from organic compounds by their degradation during the AD process in WWTP sludge management line optimization (e.g. configuration modification). These findings offered a strong support for earlier findings by Wrigley et al (1992) and Buchanan (1993).

The influence of AD on forced struvite precipitation might be explained by the following conditions. Volatile fatty acids (VFAs) have been reported to form complexes with Ca and Mg, thus it is expected that high VFA concentrations would inhibit P precipitation (Van Rensburg et al., 2003), but under AD, VFAs are usually consumed thus reducing their concentrations. Gungor and Karthikeyan (2005) evaluated different ratios of inoculum (anaerobically digested dairy manure) to substrate (undigested dairy manure) to test the hypothesis that VS destruction could release Ca and Mg from organo-metal complexes in manure. The molar ratio of Ca^{2+}/DRP after AD treatment was increased in low inoculum to substrate ratios (from 2.66 to 3.15), while the converse was found for high ratios of inoculum to substrate.

2.5.2 Enhanced biological phosphorus removal (EBPR)

More attention is being paid to EBPR municipal wastewater treatment plants due to the potential of increasing soluble P by the release of phosphates taken up by phosphorus accumulating organisms (PAOs, Mino et al., 1998). EBPR occurs through an

anaerobic-aerobic sequence configuration (Mino et al., 1998). In the anaerobic phase, PAOs take up the carbon sources such as volatile fatty acids, degrading the poly-P with the consequent release of DRP. In the aerobic phase, PAOs take up the DRP to recover the poly-P inside and re-build the cell. The high phosphate-containing sludge is a good media for struvite crystallization. Pastor et al. (2008) performed struvite recovery from EBPR sludge in WWTP and observed that P recovery as struvite requires not only the optimization of the crystallization process, but also the efficient management strategy of the sludge treatment configuration line.

2.5.3 Microwave digestion

As a new digestion technology in wastewater treatment, microwave heating exhibits various advantages like precise control of temperature and shorter period of digestion time, compared with conventional conduction digestion. After the successful application to municipal sewage sludges (Liao et al., 2005), Qureshi et al (2008) extended this technique to dairy manure. Microwave digestion of liquid dairy manure was investigated for the release of PO_4-P, NH_4-N, Mg^{2+}, Ca^{2+} and K^+, with and without the addition of oxidizing agent. After 5 min microwave pretreatment, ortho-P to TP ratio was increased from 21 % to 80 %. In addition, more than 36 % of total COD was reduced by microwave digestion assisted with oxidizing agent and the distribution of VFAs shifted to acetic acid dominance by increasing the operating temperature. In spite of a non-consistent trendency, free magnesium (Mg^{2+}), calcium (Ca^{2+}) and potassium (K^+) ions release was also observed by different amounts. The results of second part of the experiment indicated the potential of microwave digestion to enhance the struvite precipitation process. Jin et al (2009) investigated the dairy manure solubilization using

microwave heating technology with different pretreatment conditions and reported struvite recovery potentials.

2.5.4 Ethylenediaminetetraacetic acid (EDTA) or oxalate addition

EDTA is a chelating agent that widely used in industry. Doyle et al., 2003 used it to control unexpected struvite in wastewater treatment to mitigate the pipe blocking problems. Experimental results showed that an EDTA : struvite molar ratio of 2 : 1 dissolved over 90 % of struvite precipitation back into the solution even at above 7.5 pH values, indicating two facts of EDTA: (1) it can dissolve the metal-phosphate precipitation, releasing the free ortho-phosphate ions into the solution; (2) it is more favorable to form metal-EDTA chelate than metal-phosphate compounds. In this respect, it is feasible to mitigate the negative impacts of calcium on struvite precipitation process by adding any agent having stronger binding-strength to capture calcium ions (Ca^{2+}) than soluble ortho-phosphate, such as EDTA and oxalic acid. By removing the Ca-EDTA or Ca-oxalate compounds before struvite precipitation, is more favorable for efficeint struvite recovery with optimal operation control. For full-scale or in-situ application, oxalic acid might be a feasible substitute for EDTA because it is commercially affordable. This concept has been applied to a pilot-scale crystallizer treating effluents from a mixed waste (dairy manure and food processing waste) digester with good struvite harvesting performance (Bowers et al., 2007). On the other hand, simultaneous formation of Mg-EDTA or Mg-oxalate should be noted because the decrease of available Mg would inhibit struvite precipitation. Future efforts should be made to improve this technology.

2.5.5 Bio-Catalytic Calcification (BCC)

Although not considered in this study, biological mineral precipitation represents an interesting breakthrough for wastewater treatmentBio-catalytic calcification (BCC) reactors have been developed as an alternative to chemical precipitation methods for the removal of soluble calcium from industrial wastewater (Hammes et al., 2003a, 2003b), based on ureolytic microbial calcium carbonate ($CaCO_3$) precipitation, facilitating urea hydrolysis, as shown in the equations 13 and 14. In their research, Hammes et al., (2003c) characterized the microbial ecology inside the BCC reactor and observed no significant decrease in soluble magnesium (Mg^{2+}) during the Ca removal process. This observation suggested that struvite crystalline is more favorable to form in BCC effluents. The concept of this novel Ca-removal approach was recently applied to industrial wastewater P removal treatment by Carballa et al (2009), who compared ureolytic induced struvite crystallization with air-stripping strategy and suggested that this novel approach is a feasible alternative to conventional methods technically and economically. They also noted that the N removal should be evaluated in combination with the advantages of sustainable P removal due to the high ammonium concentration contained in BCC effluents.

$$CO(NH_2)_2 + 2H_2O \rightarrow 2NH_4{}^+ + CO_3{}^{2-} \tag{13}$$

$$Ca^{2+} + CO_3{}^{2-} \rightarrow CaCO_3 \tag{14}$$

Dairy manure have relatively high concentrations of urea and calcium. Therefore, there is a great potential for future research on P recovery configuration line improvement by placing a BCC reactor preceding the struvite crystallizer.

REFERENCES

Aage, H. K., B. L. Andersen, A. Blom, and I. Jensen. 1997. The solubility of struvite. Journal of Radioanalytical and Nuclear Chemistry 223(1-2): 213-215.

Adnan, A., D. S. Mavinic, and F. A. Koch. 2003. Pilot-scale study of phosphorus recovery through struvite crystallization - II. Applying in-reactor supersaturation ratio as a process control parameter. Journal of Environmental Engineering and Science 2(6): 473-483.

Angel, R. 1999. Removal of phosphate from sewage as amorphous calcium phosphate. Environmental Technology 20(7): 709-720.

ASABE. 2005. Manure characteristics. American Society of Agricultural and Biological Engineers (ASABE) Standard D384.2. St. Joseph, Mich.

Barnett, G. M. 1994. Phosphorus forms in animal manure. Bioresource Technology 49(2): 139-147.

Beal, L. J., R. T. Burns and K. J. Stalder. 1999. Effect of anaerobic digestion on struvite production for nutrient removal from swine waste prior to land application. Presented at the 1999 ASAE International Meeting in Toronto, Canada. Paper No. 994042. ASAE St. Joseph, MI.

Bhuiyan, M. I. H., D. S. Mavinic, and R. D. Beckie. 2007. A solubility and thermodynamic of struvite. Environmental Technology 28(9): 1015-1026.

Booker, N. A., A. J. Priestley and I. H. Fraser. 1999. Struvite formation in wastewater treatment plants: Opportunities for nutrient recovery. Environmental Technology 20(7): 777-782.

Bouropoulos, N. C. and P. G. Koutsoukos. 2000. Spontaneous precipitation of struvite
from aqueous solutions. Journal of Crystal Growth 213(3-4): 381-388.

Bowers, K. E. and P. W. Westerman. 2005. Performance of cone-shaped fluidized bed
struvite crystallizers in removing phosphorus from wastewater. Transactions of
the ASAE 48(3): 1227-1234.

Bowers, K. E., T. Zhang and J. H. Harrison. 2007. Phosphorus removal by struvite
crystallization in various livestock wastewaters. Presented in Proc. International
Symposium on Air Quality and Waste Management for Agriculture. ASABE
Paper No. 701P0907cd. St. Joseph, MI.

Bridger, G. L., M. L. Salutsky, and R. W. Starostka. 1962. Metal ammonium phosphates
as fertilizers. Journal of Agricultural and Food Chemistry 10(3): 181-188.

Buchanan, J. 1993. Struvite control in flush water recycle components of livestock waste
management systems. M.S. thesis. University of Tennessee, Knoxville, TN.

Burns, R. T., L. B. Moody, F. R. Walker and D. R. Raman. 2001. Laboratory and in-situ
reductions of soluble phosphorus in swine waste slurries. Environmental
Technology 22(11): 1273-1278.

Burns, R. T., L. B. Moody, I. Celen and J. R. Buchanan. 2003. Optimization of
phosphorus precipitation from swine manure slurries to enhance recovery. Water
Science and Technology 48(1): 139-146.

Cao, X. and W. Harris. 2008. Carbonate and magnesium interactive effect on calcium
phosphate precipitation. Environmental Science & Technology 42(2): 436-442.

Carballa, M., W. Moerman, W. De Windt, H. Grootaerd and W. Verstraete. Strategies to
optimize phosphate removal from industrial anaerobic effluents by magnesium

ammonium phosphate (MAP) production. Journal of Chemical Technology and Biotechnology 84(1): 63-68.

Celen, I., J. R. Buchanan, R. T. Burns, R. B. Robinson, and D. R. Raman. 2007. Using a chemical equilibrium model to predict amendments required to precipitate phosphorus as struvite in liquid swine manure. Water Research 41(8): 1689-1696.

Dao, T. H. 2003. Polyvalent cation effects on *myo*-inositol hexa*kis*dihydrogenphosphate enzymatic dephosphorylation in dairy wastewater. Journal of Environmental Quality 32(2): 694-701.

de-Bashan, L. E., and Y. Bashan. 2004. Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997-2003). Water Research 38(19): 4222-4246.

Dou, Z., K. F. Knowlton, R. A. Kohn, Z. Wu, L. D. Satter, G. Zhang, J. D. Toth, and J. D. Ferguson. 2002. Phosphorus characteristics of dairy feces affected by diets. Journal of Environmental Quality 31(6): 2058-2065.

Doyle, J. D. and S. A. Parsons. 2002. Struvite formation, control and recovery. Water Research 36(16): 3925-3940.

Ferguson, J. F. and P. L. McCarty. 1971. Effects of carbonate and magnesium on calcium phosphate precipitation. Environmental Science & Technology 5(6): 534-540.

Gaterell, M. R., R. Gay, R. Wilson, R. J. Gochin, and J. N. Lester. 2000. An economic and environmental evaluation of the opportunities for substituting phosphorus recovered from wastewater treatment works in existing UK fertilizer markets. Environmental Technology 21(9): 1067-1084.

Giesen, A. 1999. Crystallisation process enables environmental friendly phosphate

    removal at low costs. Environmental Technology 20(7): 769-775.

Greaves, J., P. Hobbs, D. Chadwick, and P. Haygarth. 1999. Prospects for the recovery of

    phosphorus from animal manures: a review. Environmental Technology 20(7):

    697-708.

Gungor, K. and K. G. Kathikeyan. 2005. Influence of anaerobic digestion on dairy

    manure phosphorus extractability. Transactions of the ASAE 48(4): 1497-1507.

Gungor, K. and K. G. Kathikeyan. 2008. Phosphorus forms and extractability in dairy

    manure: A case study for Wisconsin on-farm anaerobic digesters. Bioresource

    Technology 99(2): 425-436.

Hammers, F., A. Seka, K. van Hege, T. van de Wiele, J. Vanderdeelen, S. D Siciliano and

    W. Verstraete. 2003b. Calcium removal from industrial wastewater by bio-

    catalytic $CaCO_3$ precipitation. Journal of Chemical Technology and

    Biotechnology 78(6): 670-677.

Hammers, F., A. Seka, S. De Knijf, and W. Verstraete. 2003a. A novel approach to

    calcium removal from calcium-rich industrial wastewater. Water Research 37(3):

    699-704.

Hammers, F., Boon, N.; Clement, G.; De Villiers, J.; Siciliano, S. D.; Verstraete, W.,

    2003c. Molecular, biochemical and ecological characterization of a bio-catalytic

    calcification reactor. Applied Microbiology and Biotechnology 62(2-3): 191-201.

Harris, W. G., A. C. Wilkie, X. Cao and R. Sirengo. 2008. Bench-scale recovery of

    phosphorus from flushed dairy manure wastewater. Bioresource Technology

    99(8): 3036-3043.

He, Z. and C. W. Honeycutt. 2001. Enzymatic characterization of organic phosphorus in animal manure. Journal of Environmental Quality 30(5): 1685-1692.

He, Z., C. W. Honeycutt, T. S. Griffn, B. J. Cade-Menun, P. J. Pellechia, and Z. Dou. 2009. Phosphorus forms in conventional and organic dairy manure identified by solution and solid state P-31 NMR spectroscopy. Journal of Environmental Quality 38(5): 1909-1918.

Jin, Y., Z. Hu, and Z. Wen. 2009. Enhancing anaerobic digestibility and phosphorus recovery of dairy manure through microwave-based thermochemical pretreatment. Water Research 43(14): 3493-3502.

Johnson, A. E. and I. R. Richards. 2003. Effectiveness of different precipitated phosphates as phosphorus sources for plants. Soil Use and Management 19(1): 45-49.

Jones, A. G. 2002. Crystallization process system. Oxford, Great Britain: Butterworth/Heinemann.

Kabdasli, I., S. A. Parsons, and O. Tunay. 2006. Effect of major ions on induction time of struvite precipitation. Croatica Chemica Acta 79(2): 243-251.

Kim, B. U., W. H. Lee, H. J. Lee and J. M. Rim. 2004. Ammonium nitrogen removal from slurry type swine wastewater by pretreatment using struvite crystallization for nitrogen control of anaerobic digestion. Water Science and Technology 49(5-6): 215-222.

Kofina, A. N. and P. G. Koutsoukos. 2004. Nucleation and growth of struvite from synthetic wastewater. International Conference on Struvite: Its Role in Phosphorus Recovery and Reuse, Cranfield, UK.

Kofina, A. N. and P. G. Koutsoukos. 2005. Spontaneous precipitation of struvite from synthetic wastewater solutions. Crystal Growth and Design 5(2): 489-496.

Kofina, A. N., K. D. Demadis, and P. G. Koutsoukos. 2007. The effect of citrate and phosphocitrate on struvite spontaneous precipitation. Crystal Growth and Design 7(12): 2705-2712.

Laridi, R. J. C. Auclair and H. Benmoussa. 2005. Laboratory and pilot-scale phosphate and ammonium removal by controlled struvite precipitation following coagulation and flocculation of swine wastewater. Environmental Technology 26(5): 525-536.

Le Corre, K. S., E. Valsami-Jones, P. Hobbs, and S. A. Parsons. 2009. Phosphorus recovery from wastewater by struvite crystallization: A review. Critical Reviews in Environmental Science and Technology 39(6): 433-477.

Le Corre, K. S., E. Valsami-Jones, P. Hobbs, and S. A. Parsons. 2005. Impact of calcium on struvite crystal size, shape and purity. Journal of Crystal Growth 283(3-4): 514-552.

Li, X. Z. and Q. L. Zhao. 2003. Recovery of ammonium-nitrogen from landfill leachate as a multi-nutrient fertilizer. Ecological Engineering 20(2): 171-181.

Liao, P. H., W. T. Wong and K. V. Lo. 2005. Release of phosphorus from sewage sludge using microwave technology. Journal of Environmental Engineering and Science 4(1): 77-81.

Lopez-Valero, I., C. Gomez-Lorente and R. Boistelle. 1992. Effects of sodium and ammonium ions on occurrence, evolution and crystallinity of calcium phosphates. Journal of Crystal Growth 121(3): 297-304.

Maekawa, T., C. M. Laio, and X. D. Feng. 1995. Nitrogen and phosphorus removal for swine wastewater using intermittent aeration hatch reactor followed by ammonium crystallization process. Water Research 29(12): 2643-2650.

Maguire, R.O. and J. T. Sims. 2002. Soil testing to predict phosphorus leaching. Journal of Environmental Quality 31(5): 1601-1609.

Marti, N., J. Ferrer, A. Seco, and A. Bouzas. 2008. Optimization of sludge line management to enhance phosphorus recovery in WWTP. Water Research 42(18): 4609-4618.

Massey, M. S. 2008. Dairy Farm Phosphorus Recovery and Re-use to Reduce Water Quality Risk and Improve Phosphorus Cycling in Agriculture. M. S. Thesis. Colorado State University, Fort Collins, CO.

Massey, M. S., J. A. Ippolito, J. G. Davis, and R. E. Sheffield. 2010. Macroscopic and microscopic variation in recovered magnesium phosphate materials: implication for phosphorus removal processes and product re-use. Bioresource Technology 101(3): 877-885.

Moody, L. B., R. T. Burns and K. J. Stalder. 2009. Effect of anaerobic digestion on manure characteristics for phosphorus precipitation from swine waste. Applied Engineering in Agriculture 25(1): 97-102.

Moriyama, K., T. Kojima, Y. Minawa, S. Matsumoto, and K. Nakamachi. 2001. Development of artificial seed crystal for crystallization of calcium phosphate. Environmental Technology 22(11): 1245-1252.

Murphy, J. and J. P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta 27: 31-36.

Musvoto, E. V., M. C. Wentzel, R. E. Loewenthal, and G. A. Ekama. 2000. Integrated
   chemical-physical processes modeling - II. Simulating aeration treatment of
   anaerobic digester supernatants. Water Research 34(6): 1868-1880.

Nelson, N.O., R. L. Mikkelsen, and D. L. Hesterberg. 2003. Struvite precipitation in
   anaerobic swine lagoon liquid: effect of pH and Mg:P ratio and determination of
   rate constant. Bioresource Technology 89(3): 229-236.

Ohlinger, K. N., T. M. Young, and E. D. Schoeder. 1998. Predicting struvite formation in
   digestion. Water Research 32(12): 3607-3614.

Ohlinger, K. N., T. M. Young, and E. D. Schoeder. 1999. Kinetics effects on preferential
   struvite accumulation in wastewater. Journal of Environmental Engineerin-ASCE
   125(8): 730-737.

Ormaza-Gonzalez, F. I. and P. J. Statham. 1996. A comparison of methods for the
   determination of dissolved and particulate phosphorus in natural waters. Water
   Research 30(11): 2739-2747.

Parent, G., G. Belanger, N. Ziadi, J-P. Deland and J. Laperriere. 2007. Precipitation of
   liquid swine manure phosphates using magnesium smelting by-products. Journal
   of Environmental Quality 36(2): 557-567.

Parsons, S. A., F. Wall, J. Doyle, K. Oldring, and J. Churchley. 1999. Assessing the
   potential for struvite recovery at sewage treatment works. Environmental
   Technology 22(11): 1279-1286.

Pastor, L., N. Marti, A. Bouzas, and A. Seco, 2008. Sewage sludge management for
   phosphorus recovery as struvite in EBPR wastewater treatment plants.
   Bioresource Technology 99(11): 4817-4824.

Ponce, R. G. and De Sa MEGL. 2007. Evaluation of struvite as a fertilizer: a comparison with traditional P sources. Agrochimica 51(6): 301-308.

Qureshi, A., K. V. Lo, and P. Liao. 2008. Microwave treatment and struvite recovery potential of dairy manure. Journal of Environmental Science and Health Part B - Pesticides Food Contaminants and Agricultural Wastes 43(4): 350-357.

Rowland, A. P. and P. M. Haygarth. 1997. Determination of total dissolved phosphorus in soil solutions. Journal of Environmental Quality 26(2): 410-415.

Schipper, W. J., A. Klapwjik, B. Potjer, W. H. Rulkens, B. G. Temmink, F. D. G. Kiestra, and A. C. M. Ljimbach. 2001. Phosphate recycling in the phosphorus industry. Environmental Technology 22(11): 1337-1345.

Schuiling, R. D. and A. Andrade. 1999. Recovery of struvite from calf manure. Environmental Technology 20(7): 765-768.

Schulze-Rettmer, R. 1991. The simultaneous chemical precipitation of ammonium and phosphate in the form of magnesium-ammonium-phosphate. Water Science and Technology 23(4-6): 659-667.

Shu, L., P. Schneider, V. Jegatheesan, and J. Johnson. 2006. An economic evaluation of phosphorus recovery as struvite from digester supernatant. Bioresource Technology 97(17): 2211-2216.

Snoeyink, V. L. and D. Jenkins. 1980. Water Chemistry. New York: John Wiley and Sons.

Song, Y., P. G. Weidler, U. Berg, R. Nuesch, and D. Donnert. 2006. Calcite-seeded crystallization of calcium phosphate for phosphorus recovery. Chemosphere 63(2): 236-243.

Stratful, I., M. D. Scrimshaw, and J. N. Lester. 2001. Conditions influencing the precipitation of magnesium ammonium phosphate. Water Research 35(17): 4191-4199.

Suzuki, K., Y. Tanaka, K. Kuroda, D. Hanajima and Y. Fukumoto. 2005. Recovery of phosphorus from swine wastewater through crystallization. Bioresource Technology 96(14): 1544-1550.

Suzuki, K., Y. Tanaka, K. Kuroda, D. Hanajima, Y. Fukumoto, T. Yasuda and M. Waki. 2007. Removal and recovery of phosphorus from swine wastewater by demonstration crystallization reactor and struvite accumulation device. Bioresource Technology 98(8): 1573-1578.

Suzuki, K., Y. Tanaka, T. Osada and M. Waki. 2002. Removal of phosphate, magnesium and calcium from swine wastewater through crystallization enhanced by aeration. Water Research 36(12): 2991-2998.

Tong, J. and Y. Chen. 2007. Enhanced biological phosphorus removal driven by short-chain fatty acids produced from waste activated sludge alkaline fermentation. Environmental Science & Technology 41: 7126-7130.

Ueno, Y. and M. Fujii. 2001. Three years experience of operating and selling recovered struvite from full-scale plant. Environmental Technology 22(11): 1373-1381.

Van Der Houwen, J.A.M. and E. Valsami-Jones. 2001. The application of calcium phosphate precipitation chemistry to phosphorus recovery: The influence of organic ligands. Environmental Technology 22(11): 1325-1335.

Van Rensburg, P., E. V. Musvoto, M. C. Wentzel and G. A. Ekama. 2003. Modeling
multiple mineral precipitation in anaerobic digester liquor. Water Research 37(13):
3087-3097.

Wang, L. and G. H. Nancollas. 2008. Calcium orthophosphates: crystallization and
dissolution. Chemical Reviews 108(11): 4628-4669.

Webb, K. M. and G. E. Ho. 1992. Struvite ($MgNH_4PO_4$ $6H_2O$) solubility and its
application to a piggery effluent problem. Water Science and Technology 26(9-
11): 2229-2232.

Weld, J. L., A. N., Sharpley, D. B. Beegle and W. J. Gburek. 2001. Identifying critical
sources of phosphorus export from agricultural watersheds. Nutrient Cycling in
Agroecysystems 59(1): 29-38.

Wilkie, A. C., H. F. Castro, K. R. Cubinski, J. M. Owens and S. C. Yan. 2004. Fixed-film
anaerobic digestion of flushed dairy manure after primary treatment: wastewater
production and characterization. Biosystems Engineering 89(4): 457-471.

Wrigley, T., K. Webb and H. Venkitachalam. 1992. A laboratory study of struvite
precipitation after anaerobic digestion of piggery wastes. Bioresource Technology
41(2): 117-121.

3. ABATING THE EFFECTS OF CALCIUM ON STRUVITE PRECIPITATION IN LIQUID DAIRY MANURE

3.1 INTRODUCTION

Published literatures have demonstrated the negative impacts of calcium (Ca) on struvite preciptation (Le Corre et al., 2005; Wang et al., 2005), but limited information is available on enhancing struvite precipitation by reducing the effects of Ca in liquid dairy manure. The Ca concentration of dairy manure is significantly high, and strongly correlated to the diet and bedding management (Clanton et al., 2005). However, standard estimates (ASABE, 2005) showed that typical dairy manure slurry contains 0.4 % Ca, 0.13 % P and 1535 ppm Na (total weight basis), indicating a quite high Ca/TP molar ratio (2.4), which could further suppress the struvite formation. According to the survey of 2006~2009 Rockingham County (VA) farms (Figure 3), the dairy manure Ca ranged from 95 to 11,055 mg/L with an average of 1537 mg/L and a standard deviation of 1245 mg/L. It was found that the average Ca/TP molar ratio (5.9) of the dairy manure in this area of interest exceeded the value of typical manure (ASABE, 2005). Therefore, Ca removal is an essential pretreatment to facilitate struvite precipitation in liquid dairy manure, based on the scope of average level in United States.
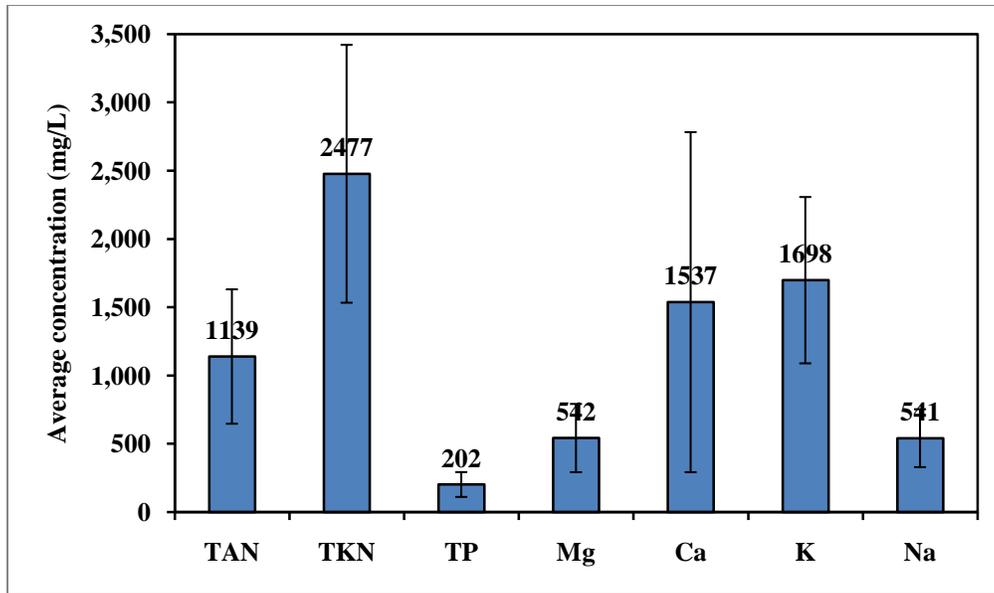
Figure 3. Average characteristics ($n = 107$) of dairy manure in Rockingham County (VA). Error bars show standard deviations.

The bio-catalytic calcification mechanism was used to achieve Ca removal from calcium-rich industrial wastewater based on ureolytic microbiological carbonate precipitation (Hammes et al., 2003) and this technology was further employed to induce struvite production (Carballa et al., 2009). However, such reactors are complex to run and sometimes hard to be stable to provide high removal efficiencies when applied to practical works. In fact, Ca removal can also be accomplished simply by adding Ca-binding reagents such as ethylenediaminetetraacetic acid (EDTA) and oxalic acid ($H_2C_2O_4$), according to equation (15) and (16).

$$Ca^{2+} + [EDTA]^{4-} \rightarrow [EDTA - Ca]^{2-} \qquad (15)$$

$$Ca^{2+} + H_2C_2O_4 \rightarrow CaC_2O_{4(s)} + 2H^+ \qquad (16)$$

On the other hand, since Mg^{2+} availability is the limiting factor in many wastewater management systems for struvite preceptiation, Mg amendment was a general method applied by many investigators to maximate P removal and to recover struvite from animal manure/wastewater (Burns et al., 2001; Burns et al., 2003; Suzuki et al., 2005; Celen et al., 2007). One issue in terms of Ca inhibition and Mg augmentation is the Ca/Mg molar ratio. Diverse findings were reported on the effects of this parameter. Le Corre et al (2005) and Wang et al (2005) found that a Ca/Mg molar ratio greater than 1 in wastewater would significantly suppress struvite formation, while anaerobic supernatants with Ca/Mg ratios of up to 6 were still conductive to recover P precipitates containing highly pure struvite (Huang et al., 2006). These conflicting observations might possibly be explained by the initial absolute Ca^{2+} concentration, not the Ca/Mg molar ratio,

because the Ca/Mg molar ratio can be suppressed by directly reducing the Ca concentration and/or adding external Mg (e.g. $MgCl_6$, MgO). Since the initial Ca/Mg molar ratio is directly attributed to the Ca^{2+}/DRP molar ratio, the latter might be a key factor for struvite production.

This chapter focused on calcium removal in liquid dairy manure to facilitate struvite precipitation. Two compounds, EDTA and oxalic acid that have been used to reduce the potential of forming Ca precipitates in solution were used in this study (Doyle et al., 2003, Doherty, 2006; Cao et al., 2007). The specific objectives are two-folded: (1) to investigate the effectiveness of EDTA and oxalate in enhancing struvite precipitation in liquid dairy manure with high Ca^{2+} concentration; and (2) to compare the two strategies (reducing absolute Ca^{2+} and increasing Mg^{2+}) of struvite precipitation in liquid dairy manure.

3.2 MATERIALS AND METHODS

A series of experiments were conducted to assess how to reduce the effects of Ca^{2+} on struvite precipitation in liquid dairy manure. First, a chemical equilibrium model, Visual MINTEQ 2.60 (Gustafsson, 2008), was used to determine the appropriate conditions required to minimize the Ca^{2+} effects and to enhance struvite precipitation. Then, the chemical modeling results were validated using synthetic liquid dairy manure. The results from the model validation were applied to liquid dairy manure to test struvite precipitation.

3.2.1 Chemical Modeling

Two tests were conducted in the chemical modeling phase: (1) determination of the solution pH at which the bound inorganic phosphate ions are released into solution, and

thus when to add EDTA or oxalic acid; and (2) evaluate struvite precipitation potential

from liquid dairy manure with different Ca^{2+} concentrations.

Visual MINTEQ 2.60 uses saturation index (SI) as a key parameter to evaluate the

saturation states of thermodynamically probable precipitates that could form in solution,

as described in equation (17).

$$SI = log\left(\frac{IAP}{K_{so}}\right) \hspace{4cm} (17)$$

where IAP is the ionic activity product for a specific precipitate, and K_{SO} is the

solubility product. Theoretically, when SI > 0, the solution is supersaturated and

precipitation occurs spontaneously; when SI < 0, the solution is undersaturated and no

precipitation occurs; and SI = 0 implies equilibrium state.

Since Visual MINTEQ 2.60 does not have the characteristics of struvite in its

database, the first step before running the model was to manually load its solubility

product (pK_{SO} = 13.26) and enthalpy of reaction, ΔH = 22.6 kJ/mol (Ohlinger et al., 1998;

Ronteltap et al., 2007). The model was set to calculate the ionic strength of the solution

using Debye-Huckel method for activity correction at room temperature (22 ℃).

3.2.1.1 Test 1: Determining the required pH for manure acidification pretreatment

and constituent ions distribution after adding EDTA or oxalic acid

Five phosphate minerals (struvite, newberyite, monenite, brushite, beta-tricalcium

phosphate) were selected as the solid phases that potentially control availability of

orthophosphate in solution (Gungor and Karthikeyan, 2005b).The pH range considered

for the release of orthophosphate from the solid phases for manure by acidification was

4.0 to 6.5. The composition and concentration of the constituent ions used as inputs in

Visual MINTEQ are presented in Table 3.

Table 3. Average composition of liquid dairy manure

Parameter (unit)	Mean (± SD)
TS (%)	4.61 ($\pm$0.01)
TSS (%)	2.36 ($\pm$0.05)
pH	7.04 ($\pm$0.01)
Total VFA (as acetate, mg/L)	2070 ($\pm$246)
Alkalinity (as $CaCO_3$, mg/L)	9300 ($\pm$676)
Total P (TP, mg/L)	460 ($\pm$14)
dissolved reactive P (DRP, mg/L)	19 ($\pm$1)
DRP of acidified manure (pH 4.5, mg/L)	303 ($\pm$15)
Total Kjeldahl N (TKN, mg/L)	2845 ($\pm$40)
Total NH_4-N (TAN, mg/L)	1405 ($\pm$18)
Mg (mg/L)	712 ($\pm$25)
Ca (mg/L)	1735 ($\pm$55)
Na (mg/L)	908 ($\pm$74)
K (mg/L)	1198 ($\pm$158)
Cu (mg/L)	12.3 ($\pm$6.8)
Zn (mg/L)	15.3 ($\pm$0.8)
Mn (mg/L)	11.3 ($\pm$1.3)
Fe (mg/L)	45 ($\pm$2.5)
Al (mg/L)	27.9 ($\pm$1.8)
S (mg/L)	261 ($\pm$41)

The quantities of EDTA and oxalic acid used as model inputs were set equal to the Ca^{2+} concentration (1735 mg/L = 43.375 mmol/L), based on the stoichiometry of the reaction between oxalate and EDTA with Ca shown in equations (15) and (16) as described in introduction part.

At each pH, the model was set to output the dissolved orthophosphate in solution, equilibrium concentrations of free ions in solution, and amounts of precipitated minerals and/or Ca- and Mg-EDTA chelates formed at the end of the reactions after adding oxalic acid or EDTA to sequester Ca^{2+}. The SI values and the precipitated minerals calculated by the model were plotted against the pH to determine the required pH to release DRP into solution.

3.2.1.2 Test 2: Evaluating struvite precipitation potential

To evaluate the struvite precipitation potential, the model was run under five conditions: positive control (PC), negative control (NC), EDTA treatment (ED), oxalate treatment (OX) and Mg amendment (Mg) described in Table 4. The purpose of including Mg amendment was to compare the effects of Ca/Mg ratio decrease on struvite production resulted from directly reducing the absolute Ca^{2+} concentration through Ca-binding reagents addition and from increasing the Mg^{2+} availability in solution by external Mg amendment. The model inputs of test 2 (Table 5) were derived from manure analysis presented in table 3. The Ca^{2+} and Mg^{2+} inputs for ED and OX were adjusted using removal efficiencies from Test 1. For the Mg amendment test, Mg^{2+} was input as the value to make Ca/Mg ratio at 0.25. The potential minerals that can precipitate based on thermodynamics and kinetics of reactions and used in the model included struvite ($MgNH_4PO_4 \cdot 6H_2O$), newberyite ($MgHPO_4 \cdot 3H_2O$), mononite ($CaHPO_4$), brushite

(CaHPO$_4$·2H$_2$O), magnesite (MgCO$_3$), nesquehonite (MgCO$_3$·3H$_2$O), brucite (Mg(OH)$_2$), and beta-tricalcium phosphate (β-Ca$_3$(PO$_4$)$_2$) (Celen et al., 2007; Gungor and Karthikeyan, 2005a). The precipitation reactions for these minerals are listed in Table 6. The quantities of mineral precipitated was calculated by the model and plotted against pH ranging from 6 to 11.

3.2.2 Testing Model Results With Synthetic Liquid Dairy Manure

3.2.2.1 Preparation of synthetic liquid dairy manure

The composition and concentration of the constituents of the synthetic liquid dairy manure were prepared based on the values presented in Table 3. Stock synthetic solutions were prepared by dissolving laboratory grade MgCl$_2$·6H$_2$O, NH$_4$Cl, KH$_2$PO$_4$, CaCl$_2$·6H$_2$O, NaHCO$_3$, FeCl$_3$·6H$_2$O, AlCl$_3$·6H$_2$O, CuSO$_4$ 5H$_2$O and CH$_3$COONa in deionized water. EDTA and oxalate were added later in the forms of Na$_2$-EDTA·2H$_2$O and H$_2$C$_2$O$_4$·2H$_2$O, respectively. The suspended solids in dairy manure were not accounted for in the synthetic liquid simulate.

Table 4. Table Experimental treatments

Condition	Description
Positive control (PC)	synthetic solution (initial Mg/Ca/PO_4-P molar ratio = 1.6:0.4:1); NaOH addition to raise pH
Negative control (NC)	Liquid dairy manure (initial Ca/Mg molar ratio = 1.46); NaOH addition to raise pH
EDTA treatment (ED)	Disodium-EDTA added to reduce the effects of calcium; NaOH addition to raise pH
Oxalate treatment (OX)	Oxalic acid added to reduce the effects of calcium; NaOH addition to raise pH
Mg amendment (Mg)	$MgCl_2$ $6H_2O$ added to bring Ca/Mg molar ratio to 0.25; NaOH addition to raise pH

Table 5. Visual MINTEQ model inputs

Input	Concentration				
	PC (mmol/L)	NC (mg/L)	ED [a] (mg/L)	OX [b] (mg/L)	Mg (mg/L)
PO_4^{3-}	10 [c]	303	303	303	303
NH_4^+	100	1405	1405	1405	1405
Mg^{2+}	16	712	638.6	712	4164
Ca^{2+}	4	1735	189.3	28.87	1735
Na^+	80	908	908	908	908
K^+	36	1198	1198	1198	1198
HCO_3^-	45	2700	2700	2700	2700
acetate⁻	35	2070	2070	2070	2070
Fe^{3+}	1	53.6	8.4	47.7	53.6
Al^{3+}	1.2	33.7	14.5	18.3	33.7
Cu^{2+}	0.07	4.8	0	1.2	4.8
SO_4^{2-}	8	183.3	183.3	183.3	183.3
Cl⁻	140	1284	1284	1284	1284

[a] The composition and concentrations of the stock synthetic solution for EDTA treatment were similar to negative control, plus addition of 43.4 mM $EDTA^{4-}$.

[b] The composition and concentrations of the stock synthetic solution for oxalate treatment were similar to negative control, plus addition of 43.4 mM $oxalate^{2-}$.

Table 6. Precipitation equations for the possible minerals that can formed during struvite precipitation

Mineral	Reaction	pK$_{sp}$ (25 °C)	Reference
struvite	$MgNH_4PO_4 \cdot 6H_2O \leftrightarrow Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O$	13.26	Ohlinger et al., 1998
newberyite	$MgHPO_4 \cdot 3H_2O \leftrightarrow Mg^{2+} + HPO_4^{2-} + 3H_2O$	5.8	Taylor et al., 1963
monenite	$CaHPO_4 \leftrightarrow Ca^{2+} + HPO_4^{2-}$	6.9	Wang and Nancollas, 2008
brushite	$CaHPO_4 \cdot 2H_2O \leftrightarrow Ca^{2+} + HPO_4^{2-} + 2H_2O$	6.59	Stumm and Morgan, 1981
magnesite	$MgCO_3 \leftrightarrow Mg^{2+} + CO_3^{2-}$	7.46; 8.2	Stumm and Morgan, 1981
nesquehonite	$MgCO_3 \cdot 3H_2O \leftrightarrow Mg^{2+} + CO_3^{2-} + 3H_2O$	5.19	Stumm and Morgan, 1981
β-TCP	$Ca_3(PO_4)_2 \leftrightarrow 3Ca^{2+} + 2PO_4^{3-}$	28.9	Wang and Nancollas, 2008
brucite	$Mg(OH)_2 \leftrightarrow Mg^{2+} + 2OH^-$	11.16	Stumm and Morgan, 1981

3.2.2.2. Struvite precipitation in synthetic liquid dairy manure

The experiments were conducted in batch using a six-station 2 L jar test apparatus (PB700 Phipps & BirdTM, Richmond, VA). 1000 mL of synthetic solution was placed in the jars and mixed at 100 rpm. The initial pH of the solution was measured and adjusted to 4.5 by adding 5 N HCl, if necessary, Then EDTA and oxalic acid was added to their respective treatments and mixed for 30 min. The mixed solution was transferred into 1000 mL Imhoff cones and settled for 60 min. After settling, 200 mL supernatant was placed in a 250 mL beaker for struvite precipitation. Struvite was precipitated by raising the pH of the supernatant to appropriate value, based on the model results for different precipitation conditions (discussed later) while mixing slowly with a magnetic stirrer. After attaining the desired pH, the mixing was continued for about 10 min. and the precipitation test stopped. The resulting solution was filtered with 0.22 µm filter (Millipore, Billerica, MA, USA). The filtrate was analyzed for DRP. The precipitates on the filter paper were dried at 40 °C to prevent the struvite crystals from losing crystallization water (Ohlinger et al., 1998). The dried precipitated materials were analyzed for morphology and structure using scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. Each test was conducted in triplicate.

3.2.3 Struvite Precipitation in Liquid Dairy Manure

Struvite precipitation from liquid dairy manure was also conducted in batch following the same procedures as synthetic solutions. The first set of tests was done using raw manure with no amendment (control), raw manure + EDTA, raw manure + oxalic acid and raw manure + $MgCl_2$ $6H_2O$The second set of tests was performed using the centrate from centrifuged acidified manure with no amendments (control) and amended

with EDTA, oxalic acid and $MgCl_2$ $6H_2O$, respectively.. The purpose of employing the second set was to assess the effects of suspended solids on struvite precipitation. The pH of manure was decreased from 7.0 to 4.5 by adding 5 N HCl and then the treatment (control, EDTA, oxalic acid and $MgCl_2$ $6H_2O$) administrated. The manure was then centrifuged using an Eppendorf centrifuge (model 5804, Hamburg, Germany) at 10,000 rpm for 15 min. The centrate was transferred to a 250 mL beaker and then struvite precipitation conducted following the same procedures as described in 3.2.2. All the tests were done in triplicate.

3.2.4 Sampling and Analysis

Samples were collected during parts of the study dealing with testing model results with synthetic liquid dairy manure and struvite precipitation from liquid dairy manure. Samples were taken before and after the required treatment were administered. The pH in this study was measured using a handheld meter (Multi 340i, WTW Inc., West Wareham, Mass.). The liquid samples were analyzed for ortho-phosphate to assess removal of reactive phosphate from solution. The ortho-phosphate was analyzed using HACH kit with DR/2800 spectrophotometer (HACH, USA). The solid or particulate fractions were subjected to SEM and XRD analysis for identification and determination of the presence of struvite crystals. X-ray Diffraction (XRD) data were collected with the Scintag PAD V via Omni-Scientific automation using Tasker (TXRD) software interface at the department of Geology and Geophysics, Yale University. The morphology of the precipitated material was examined using scanning electron microscopy (SEM, Zeiss EVO 40XVP, Germany) at the Morphology laboratory at Virginia Tech, Veterinary School.

3.3 RESULTS AND DISCUSSIONS

3.3.1 Chemical Equilibrium Modeling

3.3.1.1 Manure acidification pretreatment and EDTA/oxalate treatment

Saturation indices for the phosphate minerals considered in this study were presented in Fig 4 (a). At pH 4.5 or below, the SI values for all the phosphate minerals are negative, indicating that all the inorganic phosphate is in dissolved phase. The SI values of monenite ($CaHPO_4$) and brushite ($CaHPO_4\ 2H_2O$) turn positive at pH 4.6 or higher, implying potential for their formations occurring in solution. The model also predicted the amounts of precipitates formed (mM) and dissolved proportion (%) of total DRP at each pH level respectively, as shown in Fig 4 (b). For example, it was noted that the proportion of ortho-P in dissolved phase increased from 43 % to 100 % when pH dropped from 5.0 to 4.5. Hence, the pH of liquid dairy manure should be decreased to below 4.5 to release most of the DRP back into the solution as dissolved reactive phosphate, based on the model results. This required acidification pH (4.5) was lower than the frequent value (pH 5.0) used in research literature for calcium phosphate dissolution (Wang and Nancollas, 2008). But it was not unexpected because monenite and/or brushite precipitate at pH < 7.0 (Musvoto et al., 2000) and an even stronger acidification level (pH 3.8) was adopted by Zhang et al (2010) to release P from calcium phosphate for struvite fertilizer production. Furthermore, according to modeling results, it was apparent that nearly all (99.2 %) of the DRP was precipitated by Ca and/or Mg at pH 6.5, forming several solids phases, but it might not be the case in the real condition because the detected DRP concentration of the raw liquid dairy manure (pH 7.04) accounts for 6.27 % of its total ortho-P (based on Table 3).
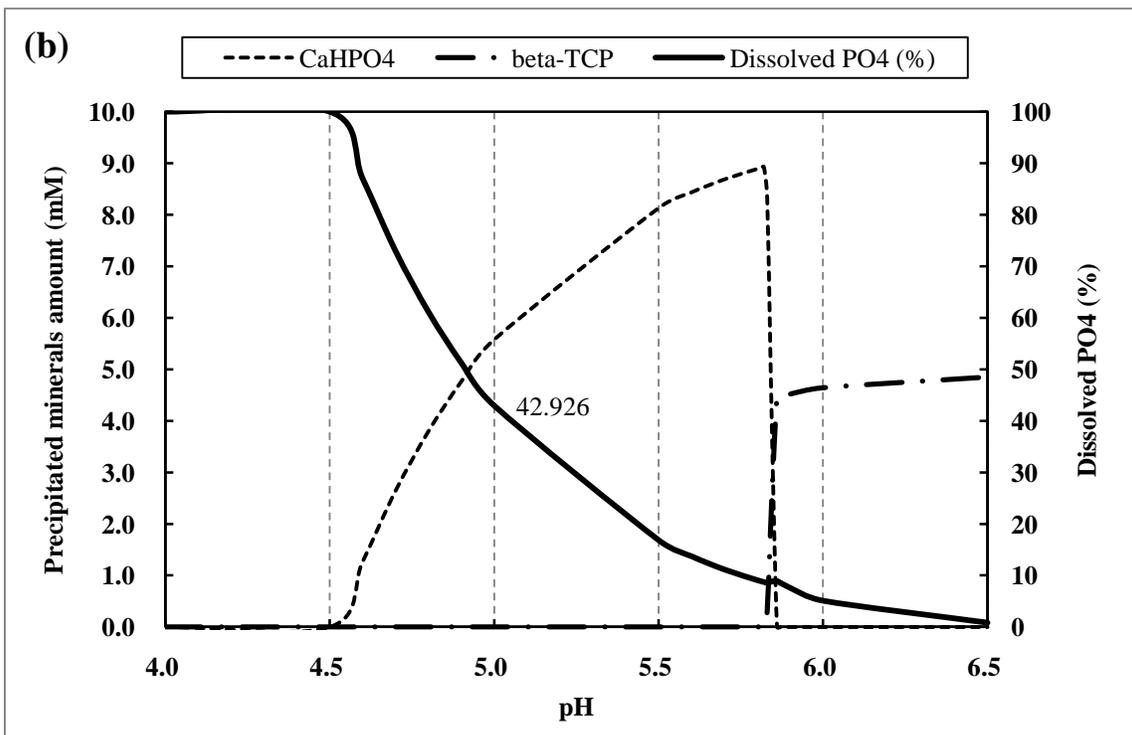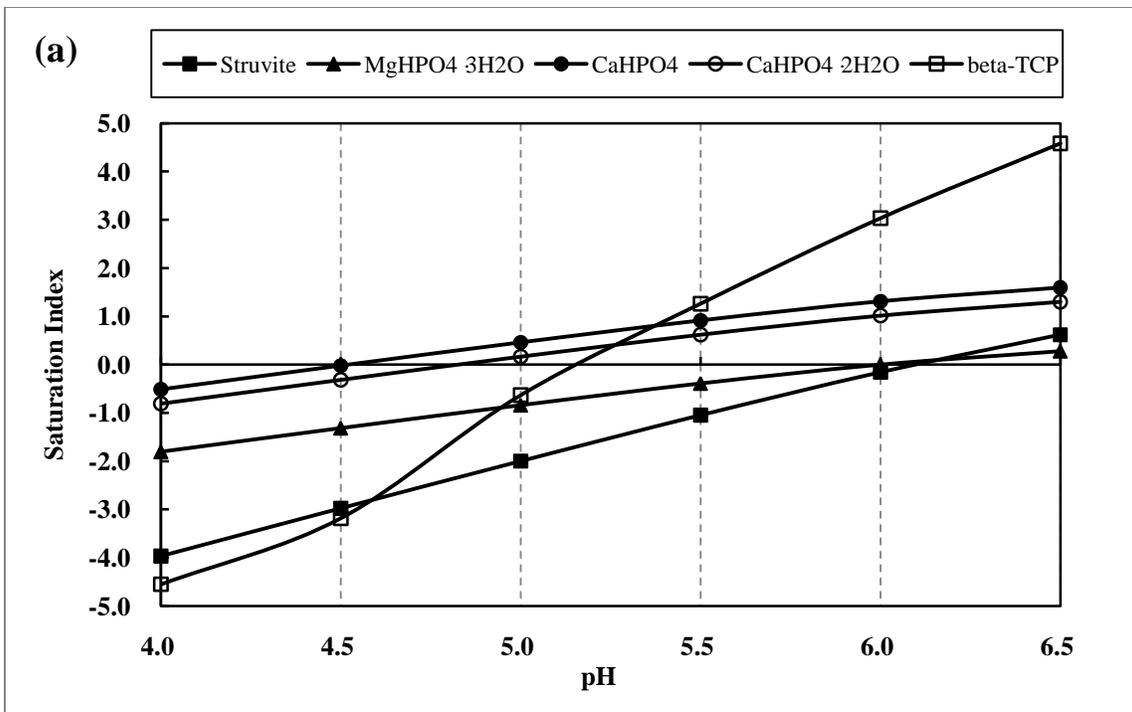
Figure 4. Model predictions of the (a) saturation index of minerals at pH 4.0 to 6.5 and (b) quantities of minerals precipitated dissolved DRP fraction

EDTA does not form mineral precipitates but metal-EDTA chelates with Ca^{2+}, Mg^{2+} and the other metal cations in solution. Thus, instead of saturation index, the distributions of species in the dissolved phases were used in the analysis (data not shown). The model outputs showed that 89.1% Ca^{2+} and 10.3 % Mg^{2+} was captured by EDTA to form Ca-EDTA and Mg-EDTA chelates, respectively, indicating that only 10.9 % Ca^{2+} (187.2 mg/L) remained in solution compared to 89.7 % Mg^{2+} (638.55 mg/L). Thus, it was predicted that Ca/Mg molar ratio was decreased to 0.18 from 1.46.

3.3.1.2 Struvite precipitation

The SI values and the corresponding amounts of minerals precipitated at pH 6 to 11 under the five conditions tested were shown in Figure 5 to 9. For the positive control, struvite precipitation occurs at pH as low as 6.1 and struvite was predicted to be a dominant solid phase of the precipitates with pH 6.5 or higher (Figure 5). This was expectable because the Mg//Ca/DRP ratio adopted in positive control was 1.6/0.4/1, which was suggested as an optimal condition for struvite production (Munch and Barr, 2001; Nelson et al., 2003; Wang et al., 2005). The amounts of struvite precipitates approximately reach its maximum value at pH 7.2 and this value keeps stable at higher pH. When the pH was above 7.0, large amounts of magnesite ($MgCO_3$) were estimated to form simultaneously with struvite precipitation, due to the high Mg^{2+} concentration and high alkalinity. So the optimum pH was estimated to be 7.0~7.2 to precipitate struvite as the main solid phase in positive control solution. For the negative control, no struvite was predicted to be present in the precipitated minerals (Figure 6) regardless of pH and the model output the main solid phases as β-$Ca_3(PO_4)_2$, $MgCO_3$ and/or $Mg(OH)_2$, which was pH specific. One obvious issue was the high Ca/Mg molar ratio (1.46) in negative control.

The SI values and the solid phase distributions under the EDTA and oxalic acid

treatment were presented in Figure 7 and 8. For EDTA treatment, struvite and $CaHPO_4$

were predicted as the main solid phases at pH 6.5 or below, but $CaHPO_4$ phase

disappeared when pH was above 6.5. Like the positive control modeling results, struvite

and $MgCO_3$ were predicted to be the dominant precipitates with pH increased to 7.0 or

higher, due to the high alkalinity and low Ca^{2+} concentration after EDTA addition. For

oxalic acid treatment, the modeling results were quite similar to those of EDTA set

except for the solid phase at pH 6.0~6.5 ($MgHPO_4 \ 3H_2O$ instead of $CaHPO_4$ was

present), resulting from the even lower Ca^{2+} concentration and comparatively higher

Mg^{2+} concentration in solution treated by oxalate, compared with solution treated by

EDTA. For Mg amendment treatment (Figure 9), there was no struvite forming in

mineral precipitates and the dominant solid phases were $MgCO_3$ and β-$Ca_3(PO_4)_2$ with

pH below 9.5, because of the excessively high Mg^{2+} concentration and high Ca^{2+}

concentration.
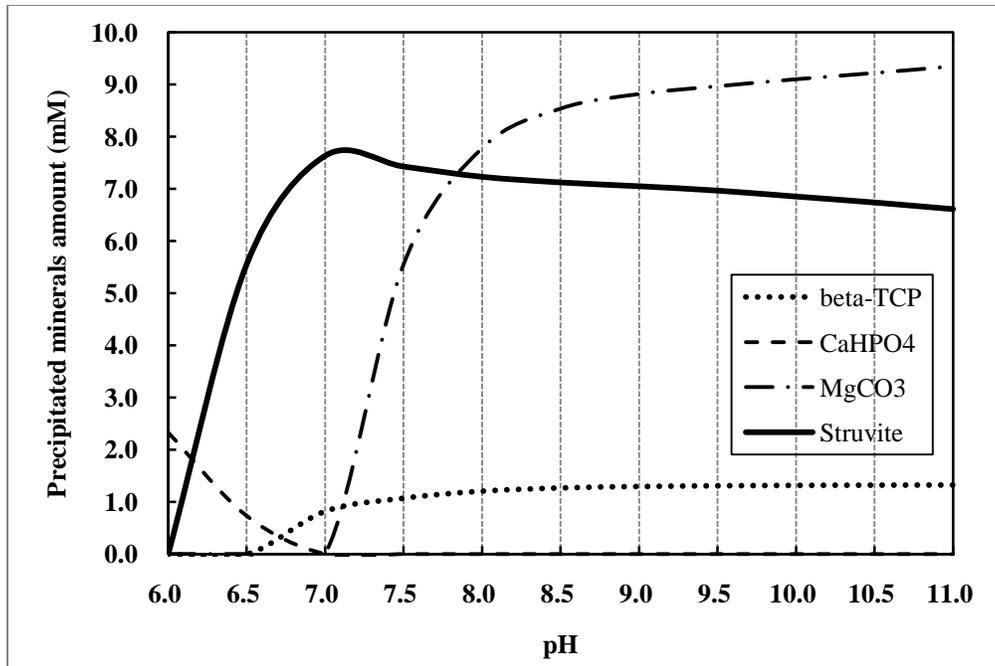
Figure 5. Model predictions for struvite precipitation in the positive control with Mg/Ca/PO$_4$-P molar ratio of 1.6/0.4/1
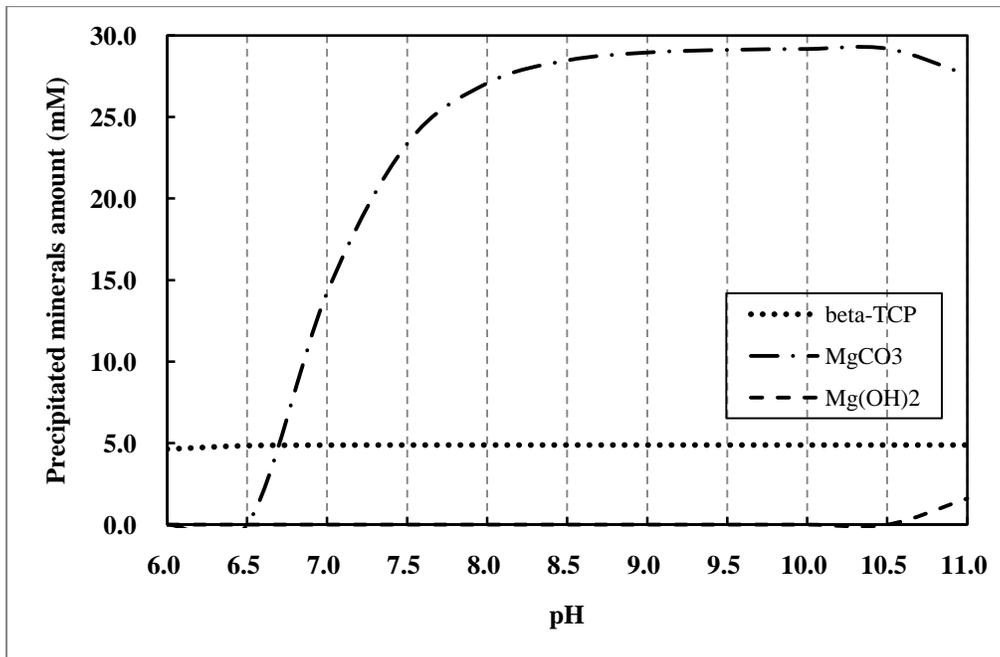

Figure 6. Model predictions for struvite precipitation in the negative control with Ca/Mg/PO$_4$-P molar ratio of 4.43/3.04/1
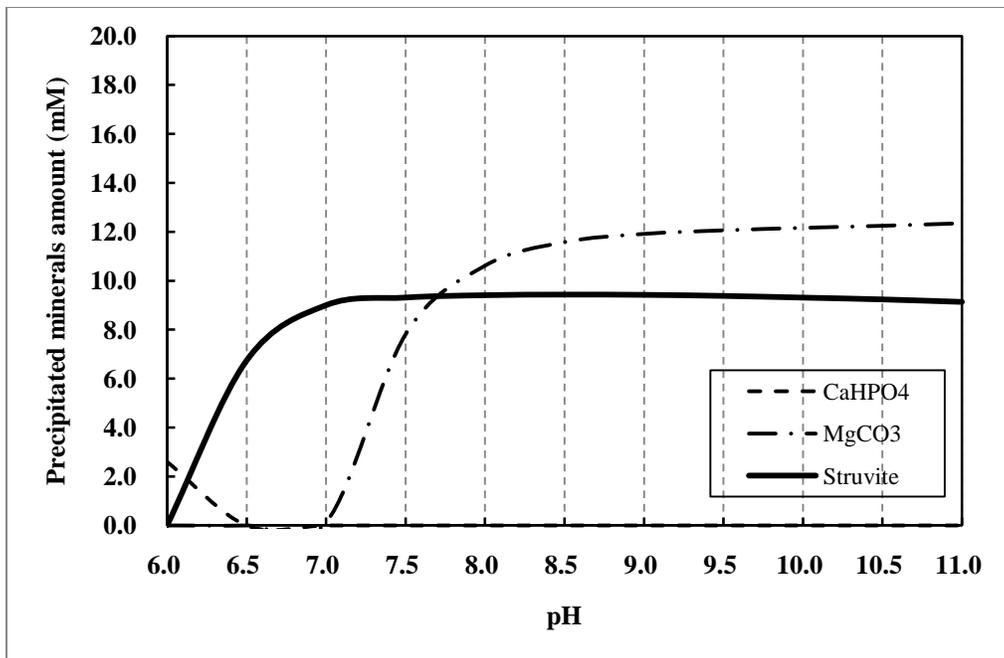
Figure 7. Model predictions for struvite precipitation in the EDTA treated dairy manure
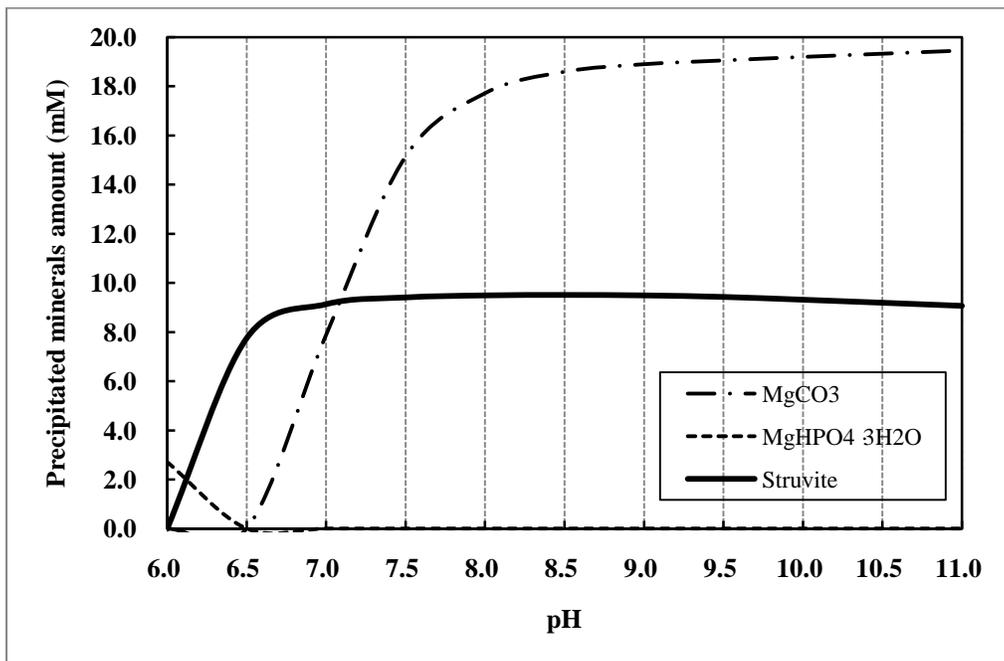
Figure 8. Model predictions for struvite precipitation in the oxalic acid treated dairy manure
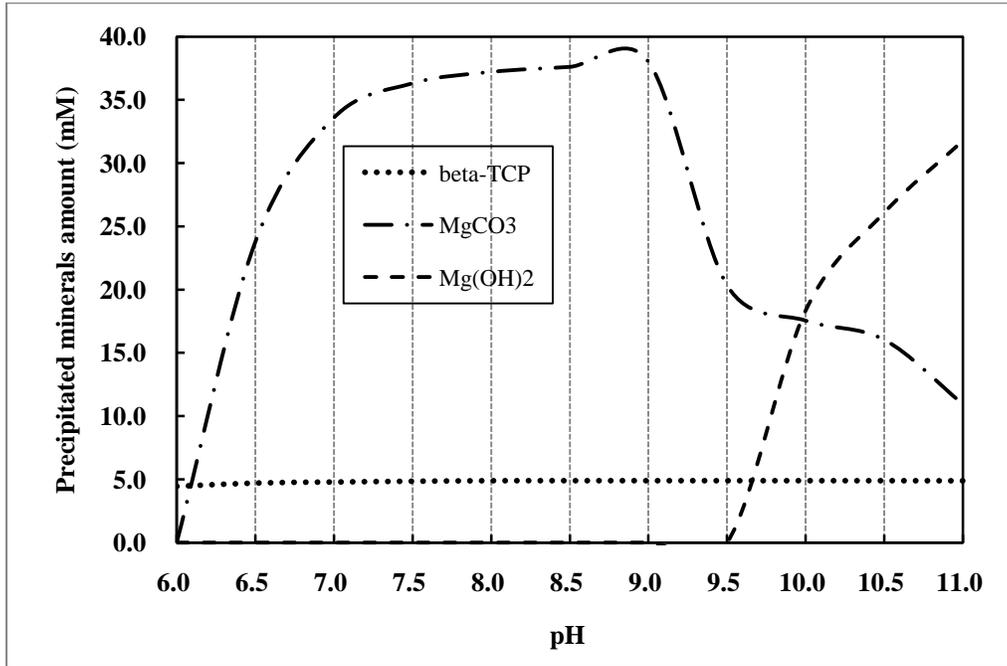
Figure 9. Model predictions for struvite precipitation in the Mg amended (Ca/Mg 0.25) dairy manure

3.3.2 Synthetic Liquid Dairy Manure Experiments

All treatments with synthetic liquid dairy manure removed up to 99.6 % soluble phosphate (Table 7), resulting from Mg- and Ca-phosphate formation. The SEM and XRD analyses performed to determine the morphology and structure of the precipitates are presented in Figure 10 (a), (b), (c), (d) and (e) for the positive control, negative control, EDTA treatment, oxalic acid treatment and Mg amendment respectively. The XRD patterns of the positive control, in which the Mg/Ca/DRP ratio was 1.6/0.4/1, matched the database reference pattern for struvite, confirming a dominant presence of struvite in the precipitates. In contrast, no definite peaks were observed in the XRD patterns of the negative control (Figure 10 b), in which the Ca/Mg/DRP ratio was 4.44/3.04/1. The morphology of the precipitates observed under SEM for the positive control showed well defined crystals (Figure 10 a) while the images for the negative control had plenty of a powdery amorphous compound indicating no crystalline structure, thus no struvite present. The observation of struvite in the positive and no struvite in the negative control was consistent with the observations by Le Corre et al (2005) at ratios in similar ranges. The SEM pictures confirmed the XRD results, where orthorhombic struvite crystals were clearly visible with small amounts of amorphous material on the surface in the positive control and no discernible struvite in the negative control sample.

Table 7. DRP removal from synthetic liquid dairy manure

| Condition	Final DRP (mg/L)	Removal efficiency (%)
positive control	28.8 ($\pm$1.8)	95.8 ($\pm$0.3)
negative control	4.2 ($\pm$1.5)	99.4 ($\pm$0.2)
EDTA treatment	32.3 ($\pm$1.0)	95.2 ($\pm$0.2)
oxalate treatment	37.8 ($\pm$0.8)	94.4 ($\pm$0.1)
Mg amendment	1.2 ($\pm$0.3)	99.6 ($\pm$0.0)

(a) Positive control: Ca/Mg/DRP = 0.4/1.6/1
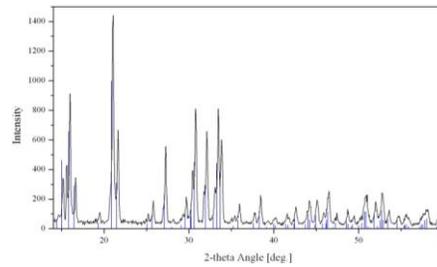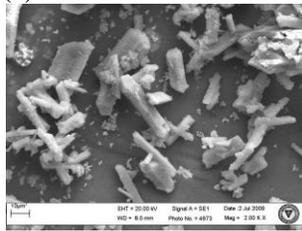
(b) Negative control: Ca/Mg/DRP = 4.44/3.04/1
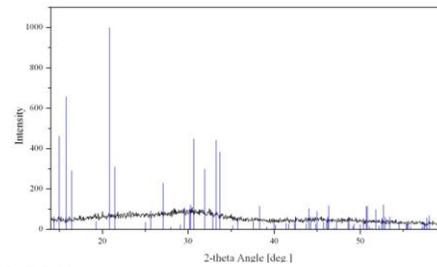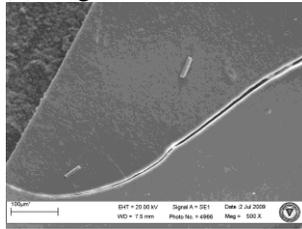
(c) EDTA treatment: Ca/Mg/DRP = 0.48/2.72/1
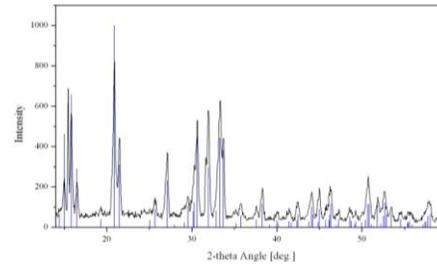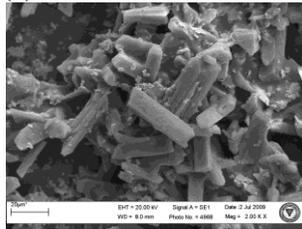
(d) Oxalate treatment: Ca/Mg/DRP = 0.07/3.04/1
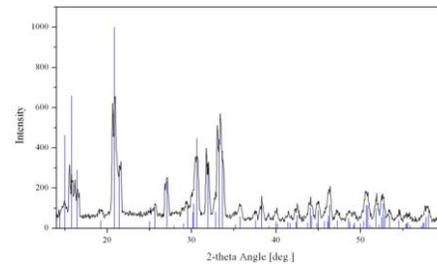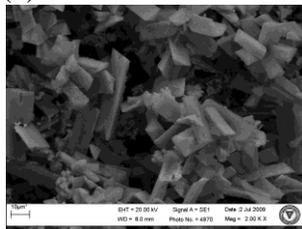
(e) Mg amendment: Ca/Mg/DRP = 4.44/17.75/1
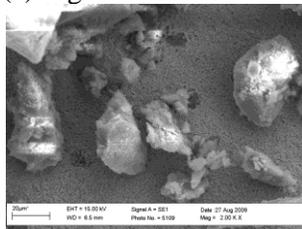
Figure 10. SEM and XRD results of recovered precipitates from synthetic liquid dairy manure for (a) positive control, (b) negative control, (c) EDTA treatment, (d) oxalate treatment and (e) Mg amendment. The blue vertical lines are the XRD patterns from the reference (struvite) in the database.

The XRD patterns generated for the precipitates recovered from EDTA and oxalic acid treated synthetic solution showed dominant presence of struvite (Figure 10 c and d). The corresponding SEM pictures clearly show agglomerates of orthorhombic crystalline. Thus the XRD and SEM images verified the Minteq model results, that struvite precipitates as a dominant solid phase in EDTA and/or oxalic acid treated solution. Large amounts of white precipitates were observed to form rapidly when treating the synthetic liquid with oxalic acid. These were assumed to be Ca-oxalate precipitates based on observations reported by Cao et al. (2007) that kinetically favored Ca-oxalate forms preemptively, which inhibits calcium phosphate precipitation. For Mg amendment, hardly any crystal-like solids were found in the SEM image, indicating no struvite formation, which was in accordance with the Minteq model result (Figure 10 e). The clear difference in the potential to precipitate struvite in two different solutions tested could probably explained by the varying Ca/DRP ratios (positive control = 0.4, Mg amendment = 4.44), implying that not only the Ca/Mg molar ratio affects struvite precipitation, but also the absolute Ca/DRP ratio. Since the Ca/Mg molar ratio is directly derived by Ca/DRP ratio, the latter might be used as a determinative parameter for struvite production in the wastewater management systems. Though successful struvite recovery was reported through Mg amendment (Nelson et al., 2003; Suzuki et al., 2005; Celen et al., 2007) in swine wastewater, no struvite crystals were observed in this negative control test, indicating that the high P removal was mainly attributed to amorphous calcium phosphates (ACP) formation. It was also noted that Mg amendment does not work effectively to enhance struvite precipitation from solutions where Ca/DRP ratio is greater

than 1. Alternatively, Ca^{2+} reduction pretreatment should be carried out firstly to produce struvite crystals.

3.3.3 Liquid Dairy Manure Experiments

The phosphate removals from the liquid dairy manure were presented in Table 8. The removal efficiencies were greater than 90 % for both the non- and centrifuged manure, suggesting no influence of suspended solids on phosphate removal. The SEM and XRD analysis performed on the material recovered from the non-centrifuged and the centrifuged dairy manure are presented in Figure 11 and 12, respectively. No distinct crystals were observed in the non-centrifuged manure imaged by SEM, regardless of any treatments. The XRD patterns of the material precipitated from EDTA treatment was primarily amorphous with 3 peaks at $2\theta = 21°$, $31°$ and $34.5°$. Compared with the reference struvite pattern, there may be some presence of struvite crystals. Material recovered from oxalate treated manure appeared crystalline but no match existed between the peaks in the sample's XRD pattern and reference pattern for struvite, implying no formation of struvite. No XRD analyses were conducted for the control and Mg amendment tests in non-centrifuged set due to the absence of crystals observed in SEM images (Fig 11 a and 11 d).

Table 8. DRP removal from liquid dairy manure

	Condition	Final DRP (mg/L)	Removal efficiency (%)
Centrifuged	control	18.6 ($\pm$1.6)	93.9 ($\pm$0.1)
	EDTA treatment	29.9 ($\pm$10.9)	90.2 ($\pm$3.6)
	oxalate treatment	24.6 ($\pm$0.2)	91.9 ($\pm$0.1)
	Mg amendment	5.7 ($\pm$0.8)	98.1 ($\pm$0.0)
Non-centrifuged	control	17.4 ($\pm$1.8)	94.3 ($\pm$0.6)
	EDTA treatment	25.1 ($\pm$7.1)	91.7 ($\pm$2.3)
	oxalate treatment	23.9 ($\pm$0.3)	92.1 ($\pm$0.1)
	Mg amendment	3.3 ($\pm$0.2)	98.9 ($\pm$0.0)

(a) NC-control
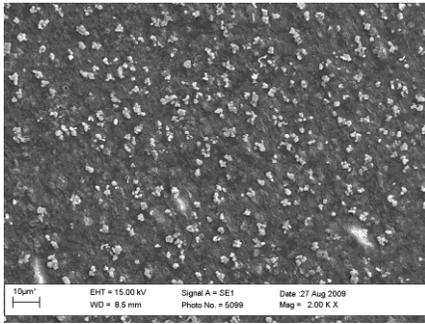
(b) NC-EDTA treatment
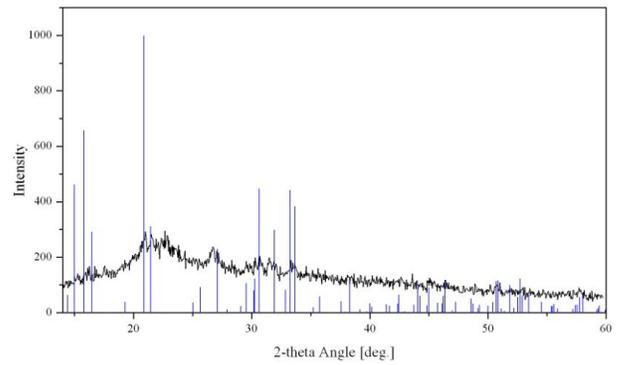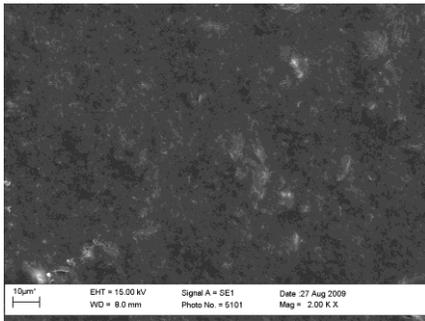
(c) NC-oxalate treatment
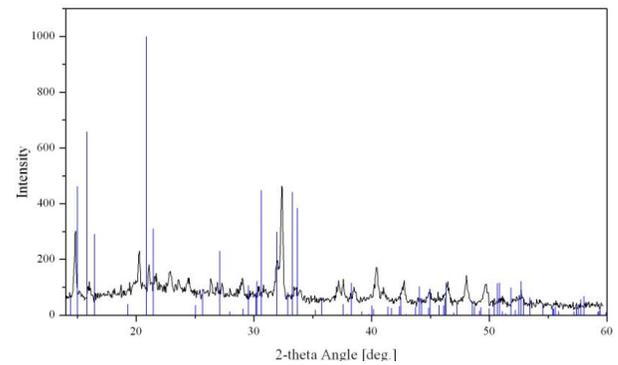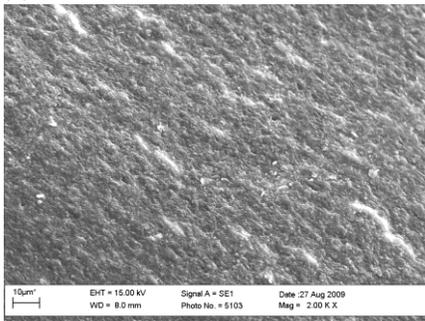
(d) NC-Mg amendment
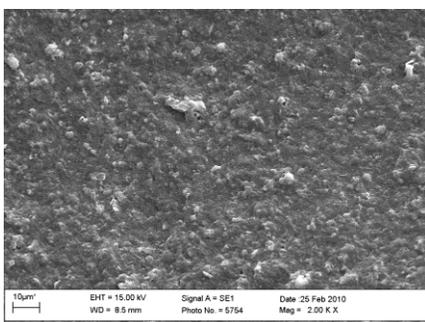
Figure 11. SEM and XRD results of recovered precipitates from non centrifuged (raw) liquid dairy manure for the untreated and the EDTA and oxalic acid treatments. The blue vertical lines are the XRD patterns from the reference (struvite) in the database.

(a) Control
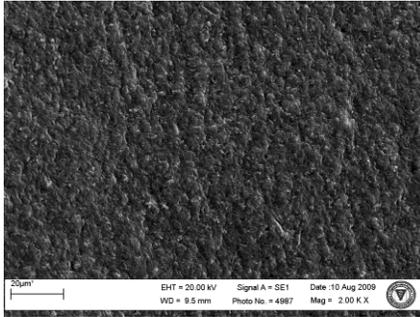
(b) EDTA treatment
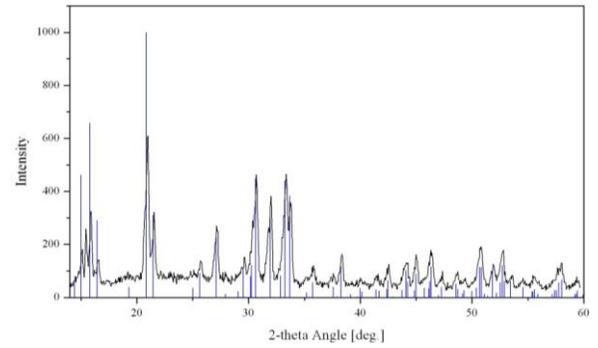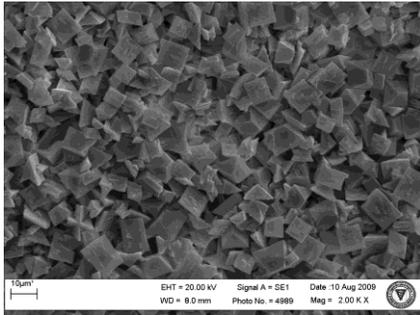
(c) Oxalate treatment
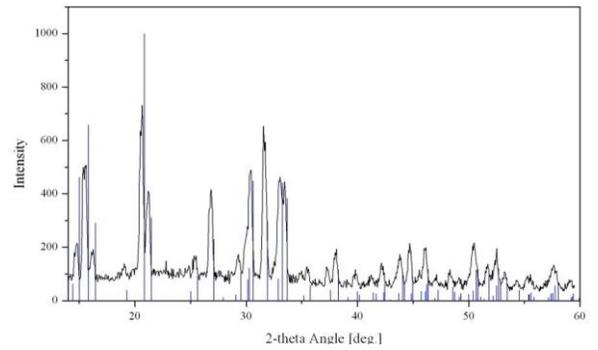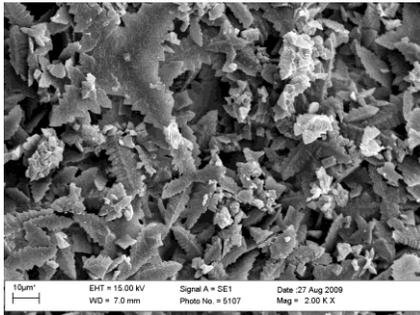
(d) Mg amendment
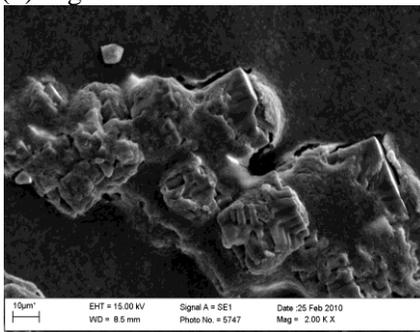
Figure 12. SEM and XRD results of recovered precipitates from centrifuged liquid dairy manure for the (a) untreated (control), (b) EDTA treatment, (c) oxalic acid treatment and (d) Mg amendment. The blue vertical lines are the XRD patterns from the reference (struvite) in the database.

For the centrifuged manure the EDTA treatment produced short prism-shaped crystals (Figure 12 b), while the oxalic acid treatment produced leaf-like crystals (Figure 12 c). The XRD patterns confirmed the dominance of struvite crystals in both EDTA and oxalate treated samples, although the morphology of the crystals looked quite different from the long, orthorhombic-shaped struvite previously observed in synthetic solution and also by Le Corre et al. (2005). The diverse morphology (blocky and dendritic shape) of the struvite obtained in the experiment is not unusual, and might be caused by differences in physical properties of the crystals formed (Adnan et al., 2004). Furthermore, pH and crystal growing time also affect the morphology of final struvite crystals. Many twin and dendritic struvite crystals were observed at pH>8 (crystal growing time > 24 hours), while struvite crystals take blocky and hemimorphic morphology at pH 7.5 (crystal growing time 3~8 hours) (Prywer and Torzewska, 2009). No crystalline materials were observed in the control (Figure 12 a). Some mineral-precipitates-like solids were found in SEM image of Mg amendment test (Fig 12 d) but the morphology is not crystalline. Therefore, EDTA and/or oxalate addition could reduce the calcium effects in order to facilitate struvite precipitation in liquid dairy manure, which was consistent with the results obtained in Minteq model synthetic solutions.

The TSS concentrations used in this study were 0.44 % and 2.15 %, for the centrifuged and the non centrifuged dairy manure, respectively. These TSS values are much higher than the 0.1% Schuling and Andrade (1999) reported interferes with struvite precipitation. As has been noted, there was better struvite precipitation in the centrifuged manure (Figure 12) compared to the non centrifuged manure (Figure 11), directly

attributed to the varying TSS, the non centrifuged manure had almost four times TSS compared to the centrifuged manure.

3.4 CONCLUSIONS

Recovery of P through precipitation as magnesium ammonium phosphate (struvite) from animal manure including dairy cattle will be the key to finding ways to recover and reuse phosphorus as the phosphate rock reserve diminishes in quantity and quality, for the use of phosphorus to be sustainable. To recover struvite from dairy manure, the first step is to precipitation. Precipitation of struvite in a medium like dairy manure is a challenge because of the interference of high calcium concentration. This study has shown that:

- Acidifying the manure to pH 4.5, followed by addition of EDTA or oxalic acid will reduce the inhibitory effects of calcium and enhance struvite precipitation.

- Struvite can be precipitated at pH 7.0 in dairy manure, thus it is not necessary to raise the pH to values > 8.0 as presented in some literature.

- Ca/DRP molar ratio should be employed as the determinative parameter instead of the Ca/Mg molar ratio to evaluate the potential of struvite precipitation in wastewater management systems.

- Mg amendment works ineffectively to enhance struvite precipitation for solutions with Ca/DRP molar ratios higher than 1.

- Precipitation of struvite can be achieved in the medium with 4,400 mg/L total suspended solids concentrations.

REFERENCES

Adnan, A., Dastur, M., Mavinic, D.S., Koch, F.A., 2004. Preliminary investigation into factors affecting controlled struvite crystallization at the bench scale. Journal of Environmental Engineering and Science 3(3), 195-202.

ASABE. 2005. Manure characteristics. American Society of Agricultural and Biological Engineers (ASABE) Standard D384.2. St. Joseph, Mich.

Burns, R. T., L. B. Moody, F. R. Walker, and D. R. Raman. 2001. Laboratory and in-situ reductions of soluble phosphorus in swine waste slurries. Environmental Technology 22(11): 1273-1278.

Burns, R. T., L. B. Moody, I. Celen and J. R. Buchanan. 2003. Optimization of phosphorus precipitation from swine manure slurries to enhance recovery. Water Science and Technology 48(1): 139-146.

Cao, X., W. G. Harris, M. S. Josan, and V. D. Nair. 2007. Inhibition of calcium phosphate precipitation under environmentally relevant conditions. Science of the Total Environmment 383(1-3): 205-215.

Carballa, M., W. Moerman, W. de Windt, H. Grootaerd and W. Verstraete. 2009. Strategies to optimize phosphate removal from industrial anaerobic effluents by magnesium ammonium phosphate (MAP) production. Journal of Chemical Technology and Biotechnology 84(1): 63-68.

Celen, I., J. R. Buchanan, R. T. Burns, R. B. Robinson, and D. R. Raman. 2007. Using a chemical equilibrium model to predict amendments required to precipitate phosphorus as struvite in liquid swine manure. Water Research 41(8): 1689-1696.

Clanton, C. J., D. R. Schmidt, K. A. Janni, M. I. Endres. 2005. Dolomitic limestone bedding effects on dairy manure characteristics. Applied Engineering in Agriculture 21(4): 697-706.

Doherty, W. O. S. 2006. Effect of calcium and magnesium ions on calcium oxalate formation in sugar solutions. Industrial & Engineering Chemistry Research 45(2): 642-647

Doyle, J. D., K. Oldring, J. Churchley, C. Price, and S. A. Parsons. 2003. Chemical control of struvite precipitation. Journal of Environmental Engineering 129(5): 419-426.

Gungor, K., and K. G. Karthikeyan. 2005a. Influence of anaerobic digestion on dairy manure phosphorus extractability. Transactions of the ASAE 48(4): 1497-1507.

Gungor, K., and K. G. Karthikeyan. 2005b. Probable phosphorus solid phases and their stability in anaerobically digested dairy manure. Transactions of the ASAE 48(4): 1509-1520.

Gustafsson, J. P. 2008. Visual MINTEQ, ver 2.60. Department of Land and Water Resources Engineering, Royal Institute of Technology, Stockholm, Sweden.

Hammes, F., A. Seka, S. de Knijf, and W. Verstraete. 2003. A novel approach to calcium removal from calcium-rich industrial wastewater. Water Research 37(3): 699-704.

Huang, H., D. S. Mavinic, K. V. Lo, and F. A. Koch. 2006. Production and basic morphology of struvite crystals from a pilot-scale crystallization process. Environmental Technology 27(3): 233-245.

Le Corre, K. S., E. Valsami-Jones, P. Hobbs, and S. A. Parsons. 2005. Impact of calcium on struvite crystal size, shape and purity. Journal of Crystal Growth 283(3-4): 514-552.

Munch, E. V. and K. Barr. 2001. Controlled struvite crystallization for removing phosphorus from anaerobic digester sidestreams. Water Research 35(1): 151-159.

Musvoto, E. V., M. C. Wentzel, R. E. Loewenthal, and G. A. Ekama. 2000. Integrated chemical-physical processes modeling - II. Simulating aeration treatment of anaerobic digester supernatants. Water Research 34(6): 1868-1880.

Nelson, N.O., R. L. Mikkelsen, and D. L. Hesterberg. 2003. Struvite precipitation in anaerobic swine lagoon liquid: effect of pH and Mg:P ratio and determination of rate constant. Bioresource Technology 89(3): 229-236.

Ohlinger, K. N., T. M. Young, and E. D. Schoeder. 1998. Predicting struvite formation in digestion. Water Research 32(12): 3607-3614.

Prywer, J. and A. Torzewska. 2009. Bacterially induced struvite growth from synthetic urine: experimental and theoretical characterization of crystal morphology. Crystal Growth & Design 9(8): 3538-3543

Ronteltap, M., M. Maurer, and W. Gujer. 2007. Struvite precipitation thermodynamics in source-separated urine. Water Research 41(5): 977-984.

Schuiling, R. D and A. Andrade. 1999. Recovery of struvite from calf manure. Environmental Technology 20(7): 765-768.

Stumm, W. and J. J. Morgan. 1981. Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters. Wiley-Interscience, New York.

Suzuki, K., Y. Tanaka, K. Kuroda, D. Hanajima, and Y. Fukumoto. 2005. Recovery of phosphorus from swine wastewater through crystallization. Bioresource Technology 96(14): 1544-1550.

Taylor, A. W., A. W. Frazier and E. L. Gurney. 1963. Solubility products of magnesium ammonium and magnesium potassium phosphates. Transactions of the Faraday Society 59: 1580-1584.

Wang, J., J. G. Burken, X. Zhang, and R. Surampalli. 2005. Engineered struvite precipitation: impacts of component-ion molar ratios and pH. Journal of Environmental Engineering 131(10): 1433-1440.

Wang, L. and G. H. Nancollas. 2008. Calcium DRPs: crystallization and dissolution. Chemical Reviews 108(11): 4628-4669.

Zhang, T., K. E. Bowers, J. H. Harrison and S. Chen. 2010. Releasing phosphorus from calcium for struvite fertilizer production from anaerobically digested dairy effluent. Water Environment Research 82(1): 34-42.

4. THERMAL AND BIOLOGICAL-BASED PRETREATMENT METHODS FOR PHOSPHORUS RELEASE TO ENHANCE STRUVITE PRECIPITATION

4.1 INTRODUCTION

One of the challenges to overcome to precipitate struvite in liquid dairy manure is the low DRP to TP ratio. This chapter focused on DRP release to facilitate struvite precipitation in dairy manure using thermal and biological-based pretreatment methods. The thermal method was based on microwave-assisted heating and the biological-based methods included EBPR and AD.

4.2 OBJECTIVES

The objective of this study was to evaluate the struvite precipitation potential in liquid dairy manure treated with thermal and biological-based methods (EBPR, microwave heating and AD).

4.3 MATERIALS AND METHODS

4.3.1 EBPR pretreatment

4.3.1.1 Source and characteristics of EBPR aerated mixed liquor (AML)

The manure used in the EBPR study was collected from the floor of the free stall barn by scraping, diluted with tap water at a 1:2 ratio (one part manure and one part water) and ran through a mechanical separator with 3.18 mm screen size openings to remove solids (Knowlton et al., 2005). The separated liquid manure was further diluted using tap water before being feed to the reactor. The overall dilution of the manure fed to the EBPR systems was 1:10.

The EBPR was obtained from a pilot-scale EBPR system which has been operational for three years (Gungor et al., 2009; Hong, 2009). Briefly, two parallel EBPR systems consisting separate feed tanks, separate fermenters, separate SBRs, and a common effluent storage tank were used. Manure was fermented in a mixed, semi continuous-flow mode (Gungor et al 2009) before feeding to the downstream SBR for EBPR wasting into the effluent storage tanks at the end of the process. The SBR was operated on an 8-h cycle consisting of four sub cycles. Each sub-cycle had a 2 min feeding, 40 min anaerobic, and 70 min aerobic phases. The last sub cycle had a 40 min settling phase in addition to the feed, anaerobic, and aerobic phases in the first three sub-cycles. At the beginning of each sub-cycle 1.2 L of fermented liquid dairy manure was fed into SBR. Five minutes before the end of the aeration phase during the fourth sub-cycle, 1.2 L of the AML in the SBR was pumped from the system (wasted) into the effluent storage tank. The AML left in the SBR was then allowed to settle for a period of 40 min (aerators and mixers were turned off), before pumping out 3.6 L of the SBR supernatant (low P content effluent stream) into the effluent storage tank (Hong, 2009).

The AML from the two parallel EBPR systems was collected struvite precipitation experiments. The chemical characteristics of the AML are presented in Table 9.

Table 9. Characteristics of EBPR AML in this study

Parameter (unit)	EBPR effluent
pH	7.92
Total P (mg/L)	137.1
DRP (mg/L)	25.2
TKN (mg/L)	635.1
TAN (mg/L)	110.2
Mg (mg/L)	113.8
Ca (mg/L)	406.8
Na	36.6
K (mg/L)	66.9
S (mg/L)	56.3
Fe (ppm)	17.6
Al (ppm)	15.1
Zn (ppm)	4.2
Cu (ppm)	1.2
Mn (ppm)	4.2
Cl (ppm)	225.0

4.3.1.2 EBPR AML preparation

For EBPR to be used as a treatment, it is necessary to release the DRP inside the PAO back into solution for struvite recovery. This requires the EBPR AML to undergo an anaerobic storage prior to struvite precipitation. Two experiments were conducted to investigate the release of DRP from PAO based on (1) time of storage under anaerobic storage and (2) addition of external carbon source (sodium acetate)

Sodium acetate (NaAc) was used as the external carbon source. Dosages of NaAc ranging from 0 to 20 mg/mL were applied to AML and allowed to sit anaerobically for 24 hours before measurement of DRP released back in solution. Another test was conducted to determine the release of DRP over time (storage period of 48 h) under anaerobic conditions using the optimum NaAc dosage and a control. At the end of each experiment setting, samples were collected and centrifuged at 10,000 for 15 min, filtered through 0.45 μm filter paper and then analyzed for DRP concentration.

4.3.2 Microwave heating

Microwave heating was conducted in a CEM MARSXpress microwave digestion system (CEM Corporation, Matthews, NC, USA), delivering approximately 1600 W IEC of microwave energy at a frequency of 2450 MHz, equipped with a real-time temperature and pressure control. The system can accommodate up to 40 vessels simultaneously. The vessel was a CEM Teflon closed vessel with pressure relief device. Each vessel has a capacity of 75 mL, with the working volume of 30 mL.

Liquid dairy manure (Table 3) was acidified to pH 4 by adding 5 N HCl or 5 N H_2SO_4. Raw manure without inorganic acid addition served as control. Thirty (30) mL of each of the acidified manure and the control was transferred to microwave vessels and

then subjected to microwave digestion. The microwave was operated at 100% power of 1200 W under ramp-to-temperature working mode (15 min ramp time, five minute hold at the designed temperature, and then cooled to room temperature). Microwave heating at temperatures 60, 90, 120, 150, 170, 200 and 220 ℃ were tested to investigate the effects of temperature on microwave-based P solubilization, similar to the series selected by Pan et al. (2006) and Qureshi et al. (2008). Each run was conducted in triplicate. After each heating treatment, the vessels were cooled to room temperature and the pH and the DRP concentration of the digested manure were determined.

4.3.3 Anaerobic digestion

4.3.3.1 Feed characteristics

The anaerobic digester was started up using a mixture of separated flushed dairy manure and sedimentation tank effluent from the Virginia Tech Dairy Complex with volume ratio of 1 : 1 (day 1 ~ 3) and 3 : 1 (day 4 ~ 6) and the digester was fed using 100 % flushed manure from day 7 to day 16. From day 17, feed was the liquid dairy manure collected from a dairy farm located in Rockingham County, VA and flushed manure as described earlier. The amount of flush manure in the manure was decreased by 25 % every 3 days. After 25 days, the feed was 100% dairy manure from the Rockingham dairy. The characteristics of the dairy manure used in this study are presented in Table 10.

Table 10. Anaerobic digestion feed characteristics

Parameter (unit)	Substrate
TS (%)	4.09
VS (%)	1.29
pH	7.38
Total P (mg/L)	364.15
DRP (mg/L)	30.67
TKN (mg/L)	2740.51
TAN (mg/L)	1515.12
Mg (mg/L)	639.89
Ca (mg/L)	1461.93
K (mg/L)	1794.71
Na (ppm)	919.56
Total COD (mg/L)	63160
Soluble COD (mg/L)	22787

4.3.3.2 Reactor design and setup

A single-stage complete mix reactor (Figure 13) was used in this study. The
digester was 0.25 m in diameter, 0.40 m tall with a 12 L working volume and a 3 L head
space. The digester was made from a schedule 40 PVC pipe capped off the 0.95 cm thick
PVC plates. Two Cole-Parmer pumps (Masterflex, Model 77200-62, Cole Parmer
Instrument Co., Chicago, IL) were used to feed, mix and discharge the reactor contents.
The digester was heated a heating coil (Chromalox company, Richmond, VA) mounted to
the side of the reactor. The digester temperature was controlled at 38 ± 1 ℃ by a
temperature controller (Model 11-463-47A, Fisher Scientific, Waltham, MA). The
sequence of the operation of the pumps and mixers was controlled by Chrontrol time
controllers (Chrontrol Co., San Diego, CA). The HRT was kept at 20 days and the reactor
was fed and discharged 4 times per day (every 6 hours).

4.3.4 Struvite precipitation

Struvite precipitation from pretreated liquid dairy manure was conducted in batch
following the same procedures as described in 3.2.3. The first set of tests was done using
EBPR sludge + NaAc, EBPR influent, microwave digested manure (MW) + H_2SO_4, MW
+ HCl, MW without acidification, MW + H_2SO_4 + oxalic acid, MW + HCl + oxalic acid,
MW + oxalic acid, anaerobic digested manure (AD), AD + oxalic acid. The second set of
tests was performed using the centrate of acidified manure according to the first set. The
purpose of employing the second set was conducted to investigate the effects of
suspended solids on struvite precipitation.
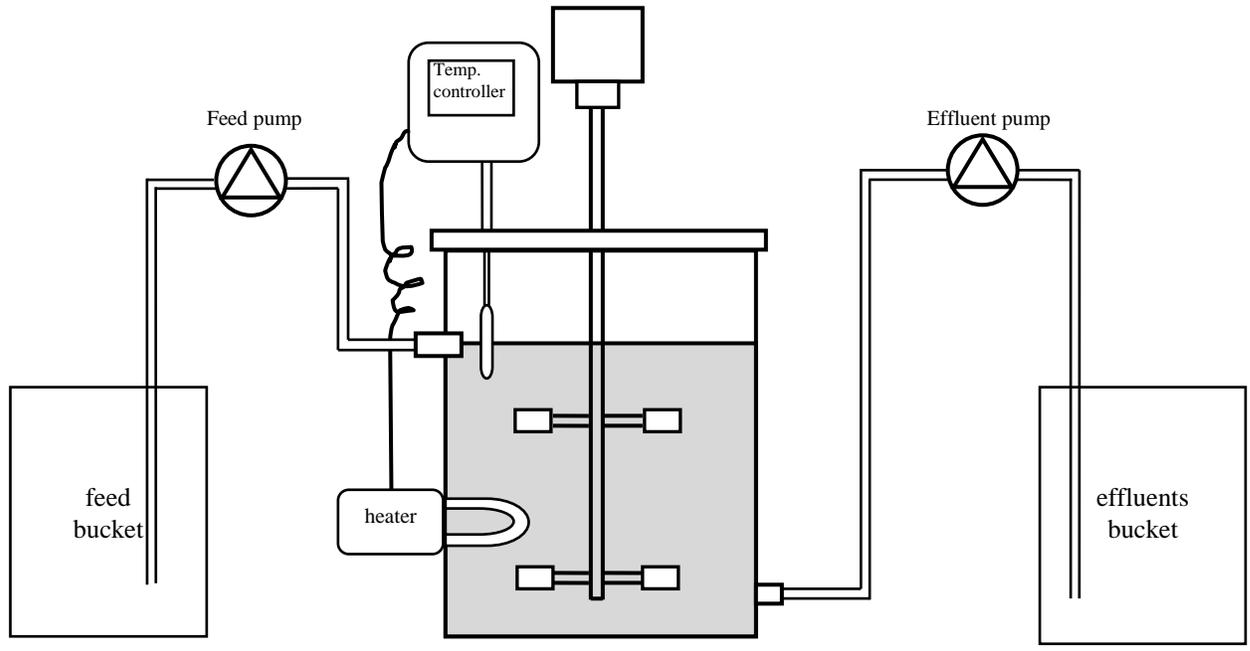
Figure 13. Flow diagram of single-stage complete mix digester

The pH of the pretreated manure was decreased to 4.5 by adding 5 N HCl, if necessary and then the appropriate treatment administrated. The manure was then centrifuged using an Eppendorf centrifuge (model 5804, Hamburg, Germany) at 10,000 for 15 min. The centrate was transferred to a 250 mL beaker and then struvite precipitation conducted following the same procedures as described in 3.2.2. All the tests were done in triplicate.

4.3.5 Sampling and Analytical Methods

Anaerobic digester feed and effluents were sampled twice a week and analyzed for pH, TS, VS, total COD and soluble COD. The pH was measured using a handheld meter (Multi 340i, WTW Inc., West Wareham, MA); TS and VS were determined according to standard methods (APHA, 1995); total COD and soluble COD (filtered through 0.45 μm filter paper) were analyzed using HACH high range COD digestion vials (HACH Company, Loveland, CO). The composition of biogas produced was measured by SRI gas chromatograph (model 8610C) with molecular sieve packed column and HayeSep D packed column (SRI Company, Torrance, CA, USA) every other week.

The precipitates were analyzed using SEM at an accelerating voltage of 5 kV using FEI Quanta 600 FEG environmental scanning electron microscope (FEI Company, Hillsboro, OR). Simultaneously, solid phase element composition was identified using Bruker QUANTAX 400 Energy Dispersive X-ray Spectrometer (EDS, Bruker AXS Inc., Madison, WI), equipped with a high speed silicon drift detector. EDS was performed at voltage of 15 kV and a working distance of 11.8 ~ 12.5 mm. XRD analysis was

conducted at Crop and Soil Environmental Science Department, Virginia Polytechnic Institute and State University following the same procedures as described in section 3.2.4.

4.4 RESULTS AND DISCUSSIONS

4.4.1 EBPR P release and struvite precipitation

The DRP release in EBPR AML was shown in Figure 14. With the same storage time (24 hours), the DRP concentration increased with the increase of NaAc dosage up to 10 mg/mL AML. Beyond 10 mg/mL AML dosage amount, there was minimal increase in DRP concentration (Figure 14 (a)). Thus, 10 mg NaAc / mL AML was selected as the dosage for external carbon source amendment. Figure 14 (b) showed the DRP release with different anaerobic storage time and it was found that "AML only" curve and "AML + NaAc" curve had the same increasing tendency: DRP kept increasing from 0 to 24 hours and beyond 24 hours, no significant ($P > 0.1$) DRP increases were observed. For "AML only", the DRP concentration increased 172.8 %, from 13.79 mg/L at 0 hours to 37.61 mg/L at 24 hours; for "AML + NaAc", the DRP concentration increased 252.1 %, from 13.79 mg/L at 0 hours to 48.54 mg/L at 24 hours. Additionally, the DRP release was significantly different ($P < 0.05$) between "AML only" and "AML + NaAc", indicating the positive effects of external carbon resource on DRP release in EBPR AML.
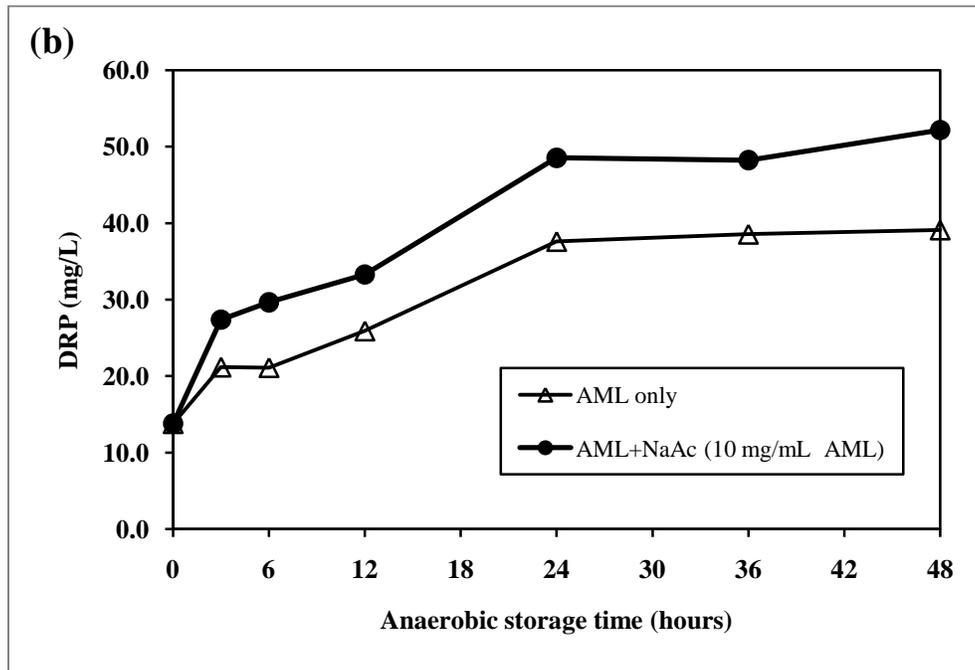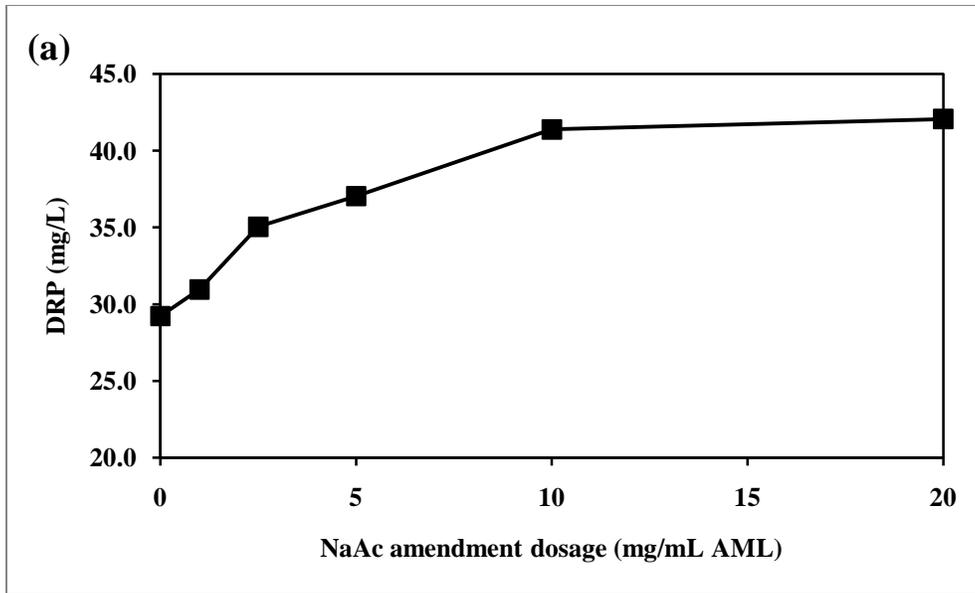
Figure 14. The effects of (a) NaAc amendment dosage and (b) anaerobic storage time on P release in EBPR AML

As shown in Table 11, DRP reductions (43.8 ~ 69.4 %) were achieved in all the treatments after precipitation process, although removal efficiencies varied in different manure medium. It was apparent that Ca^{2+} availability was increased by about 50 % while Mg^{2+} concentration only 11 % in EBPR AML, based on values measured in EBPR feed. Moreover, NH_4-N removals were observed in all the treatments, which could be attributed to struvite precipitation and/or volatilization losses. Mg^{2+} reductions were relatively low (<10 %) in the solutions compared to Ca^{2+} reductions, indicating that at least magnesium phosphate (including struvite) was not the dominant solid phase of the precipitates in EBPR AML.

4.4.2 Precipitates characteristics from EBPR treated manure

Energy dispersive X-ray spectroscopic analyses of solids precipitated from different EBPR mediums were listed in Table 12 and Figure 15. As indicated in chemical analysis (section 4.4.1), Mg phosphate did not appear in any precipitation medium as the dominant solid phase. Instead, calcium was detected as the major elemental composition consisting of almost all the precipitates except for non-centrifuged influents sample. Phosphorus (P), oxygen (O) and calcium (Ca) appeared to be the main elemental presence in the solids precipitated from centrifuged set and P to O molar ratios (>4) implied that other solid phases existed in the precipitates besides calcium phosphate.

Table 11. Compositions of EBPR feed and AML before and after struvite precipitation (C-AML, centrifuged AML; NC-AML, non-centrifuged AML; C-Feed, centrifuged feed; NC-Feed, centrifuged feed)

Parameters	C-AML (before) (mg/L)	C-AML (after) (mg/L)	NC-AML (before) (mg/L)	NC-AML (after) (mg/L)
DRP	58.72	17.97	59.52	28.76
TAN	131.59	113.83	140.20	119.83
Mg^{2+}	111.44	105.45	112.64	109.05
Ca^{2+}	375.07	268.42	389.45	294.78
K^+	131.25	136.22	132.24	150.14
pH	4.0	8.0	4.0	8.0

Parameters	C-Feed (before) (mg/L)	C-Feed (after) (mg/L)	NC-Feed (before) (mg/L)	NC-Feed (after) (mg/L)
DRP	37.15	13.18	38.35	21.57
TAN	134.35	86.05	131.42	109.86
Mg^{2+}	99.46	89.87	101.86	97.06
Ca^{2+}	244.45	204.91	263.63	232.47
K^+	109.37	129.26	115.34	133.24
pH	4.0	8.0	4.0	8.0

Table 12. Energy dispersive X-ray spectra analysis results of precipitated solids from different EBPR mediums

| EBPR manure	Point	P (mass %)	O (mass %)	Mg (mass %)	Ca (mass %)
C - AML	1	11.21	38.82	1.59	18.05
	2	11.69	34.74	1.30	19.35
	3	10.96	31.60	1.04	20.38
	4	11.38	47.44	2.04	17.34
NC - AML	1	0	41.07	0	0.78
	2	0	34.79	0.69	1.40
	3	1.92	43.56	0.53	1.21
	4	0	51.97	1.10	21.95
Feed - C	1	24.13	56.18	18.77	0.59
	2	12.41	42.42	2.44	17.63
	3	12.36	45.18	3.03	19.02
	4	13.30	34.08	2.16	20.79
Feed - NC	1	0	25.95	0.90	1.52
	2	3.20	47.48	3.12	5.05
	3	2.21	46.03	1.33	2.09
	4	0	7.63	0.10	1.01
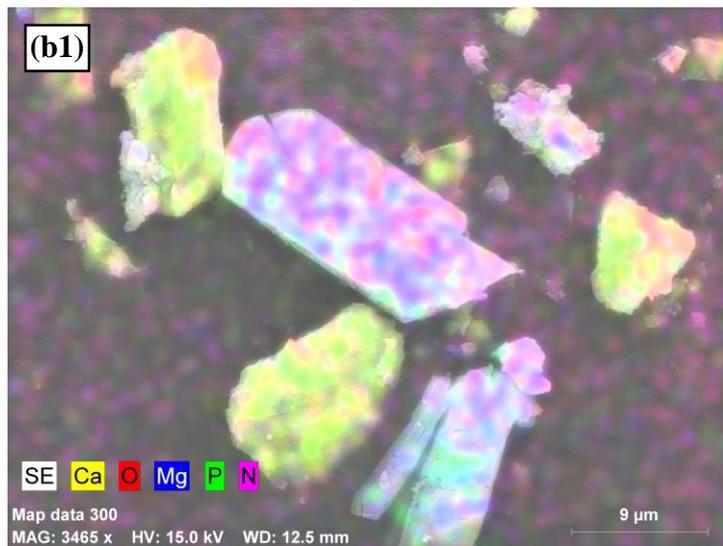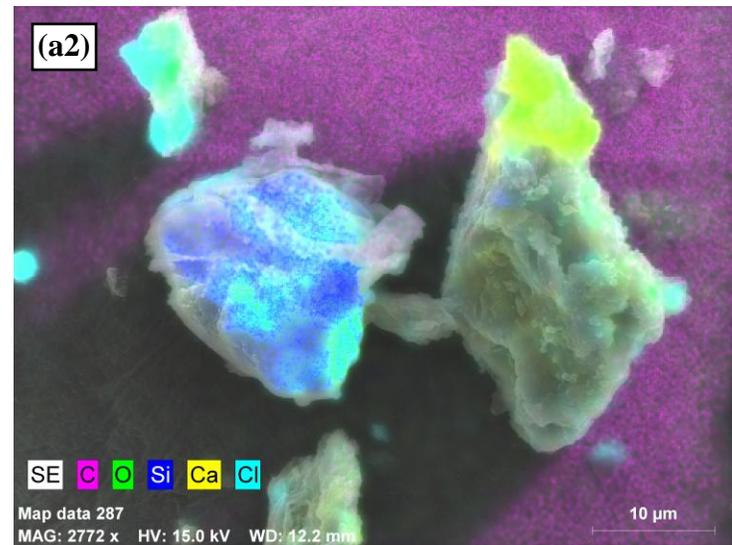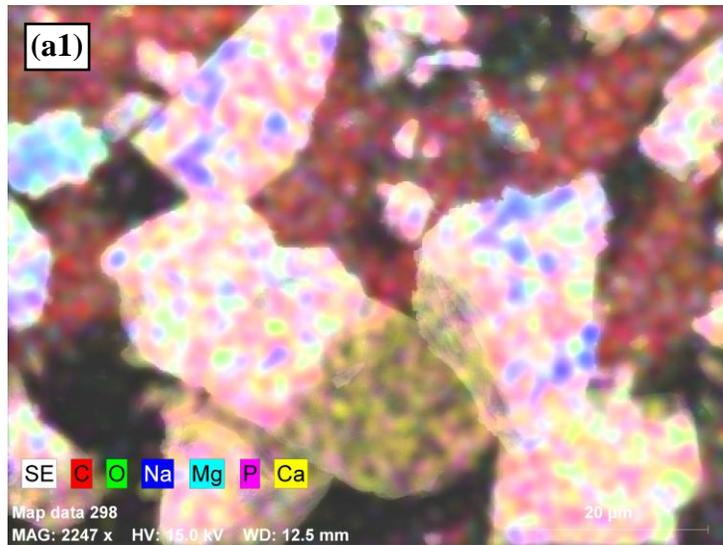
Figure 15. Energy dispersive X-ray mapping analysis of precipitated solids from different EBPR mediums: (a1) C - AML; (a2) NC - AML; (b1) C - Feed; (b2) NC - Feed.

The SEM images and XRD patterns results are shown in Figure 16 ~ 18. Hardly any crystals were observed in SEM image of centrifuged EBPR AML (Figure 16 (a)) and the corresponding XRD diffractograms (Figure 16 (b)) did not match with standard struvite diffraction patterns. The precipitates were heterogeneous, consisting of various solid phase including calcite ($CaCO_3$), huntite ($CaMg_3(CO_3)_4$), quartz (SiO_2), brushite ($CaHPO_4 \cdot 2H_2O$) and newberyite ($MgHPO_4 \cdot 3H_2O$), compared with JCPDF library database (ICDD, International Center for Diffraction Data). In contrast, orthorhombic Mg phosphate crystalline (Figure 17) was found in SEM image although it was surrounded by amorphous precipitates and EDS analysis showed an approximate 1:1:4.5 molar ratio of Mg:P:O, with a mass composition of 24.13 % P, 18.77 % Mg, 56.18 % O and 0.59 % Ca. This difference in the potential to produce Mg phosphate from EBPR AML and feed can be probably explained by the varying Ca^{2+}/DRP and/or Ca^{2+}/Mg^{2+} molar ratios (Table 11); the Ca^{2+}/Mg^{2+} molar ratio of EBPR AML (2.02) was higher than that of EBPR feed (1.47) and therefore Mg phosphate formation was more suppressed by high Ca^{2+} in the solution. The SEM images for non-centrifuged (NC) set (Figure 18 (a); (c)) exhibited amorphous structure, coupled with EDS results showing elemental compositions were 17.97 % C, 43.56 % O and 30.84 % Si and small amounts of Ca, Na and Cl, indicating high strengths of organic matters and suspended solids like quartz in the precipitation system.
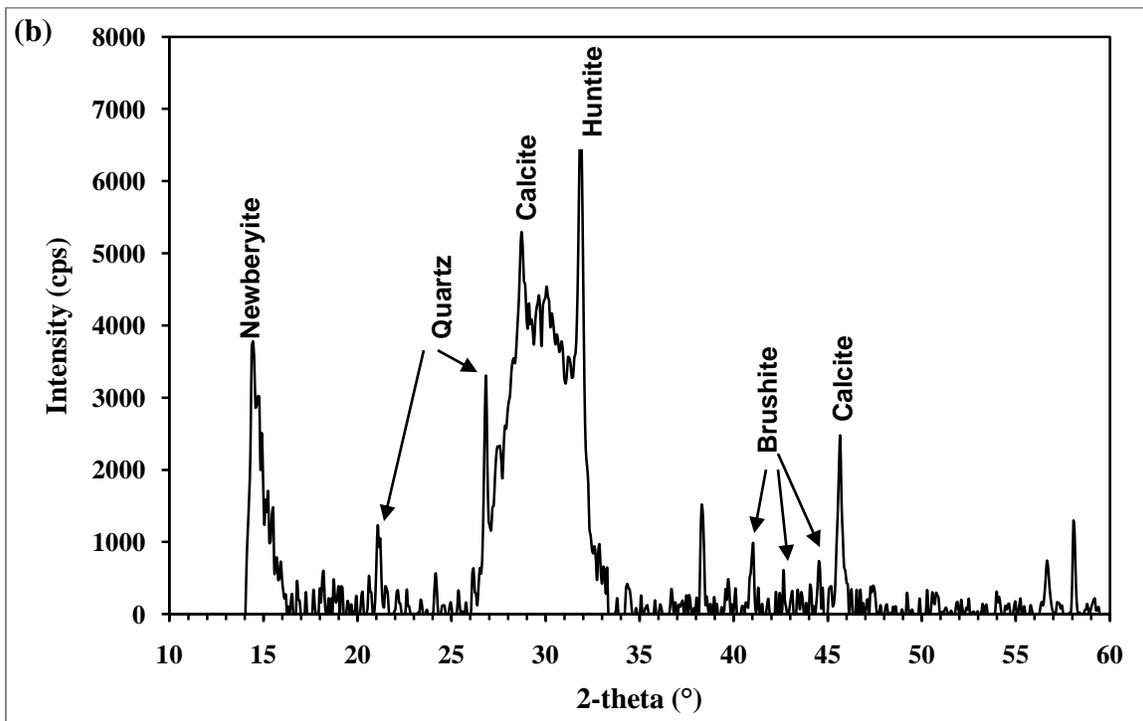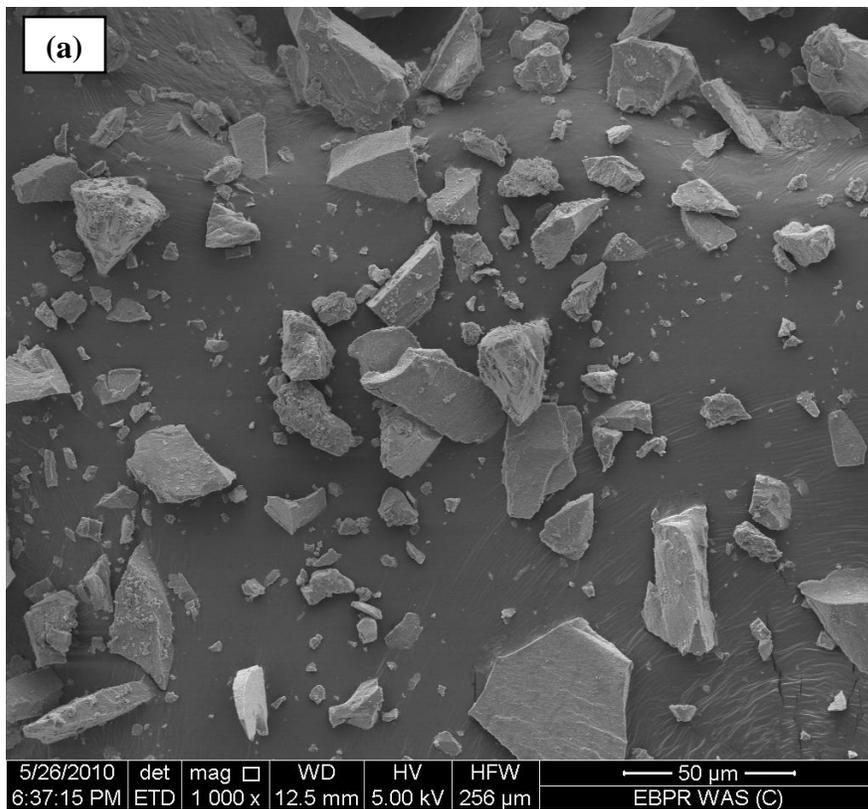
Figure 16. SEM image and (b) XRD patterns of precipitated solids from centrifuged EBPR AML
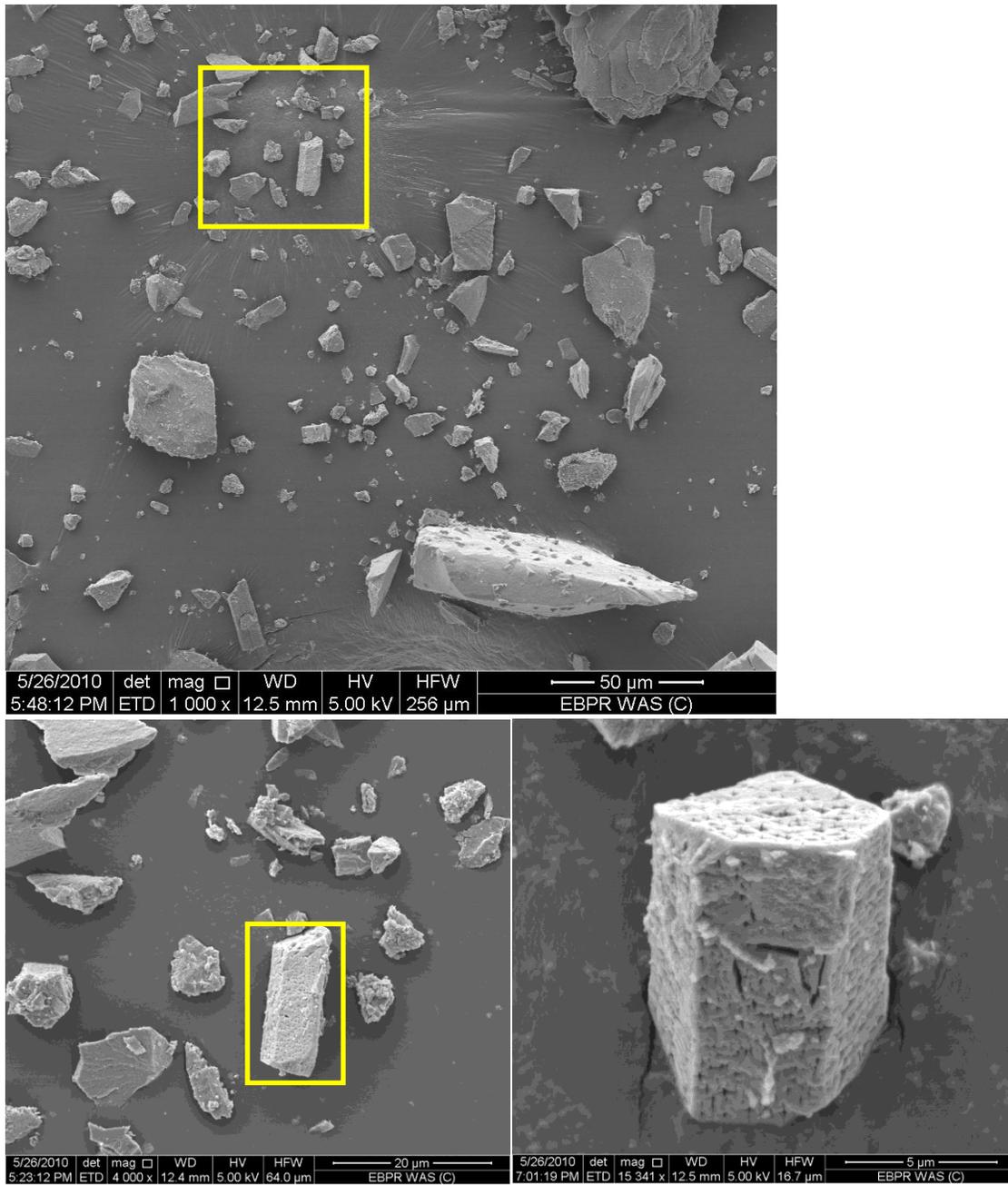
Figure 17. SEM images of precipitated solids from centrifuged EBPR feed; the EDS analysis output an approximate 1:1:4.5 molar ratio of Mg:P:O for focused orthorhombic crystal , with a mass composition of 24.13 % P, 18.77 % Mg, 56.18 % O and 0.59 % Ca
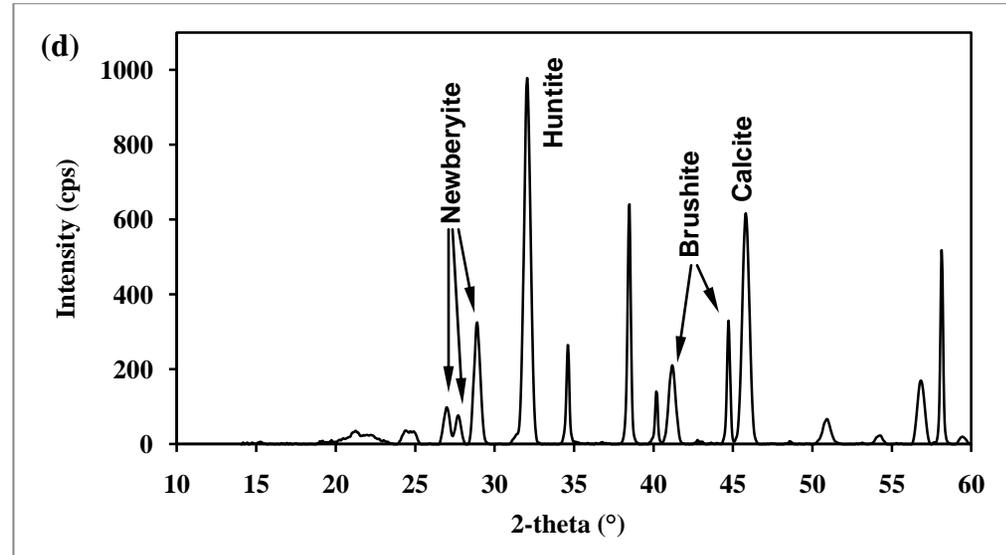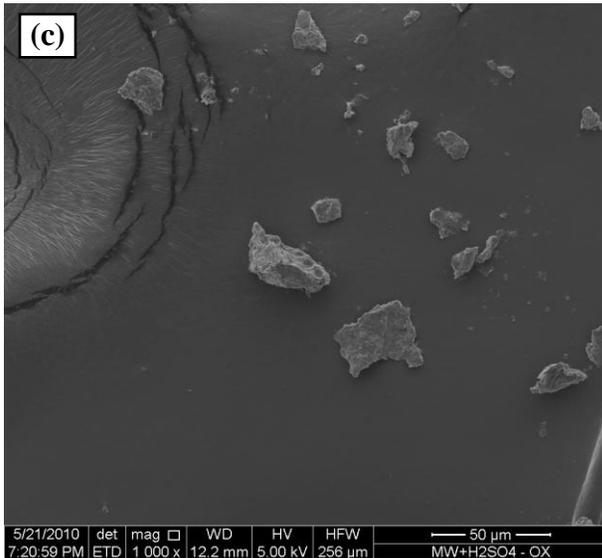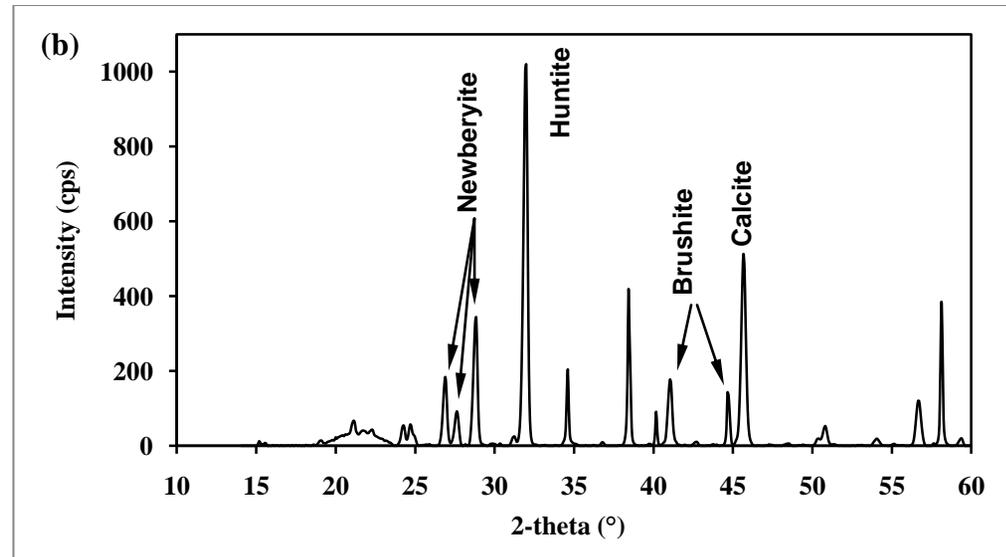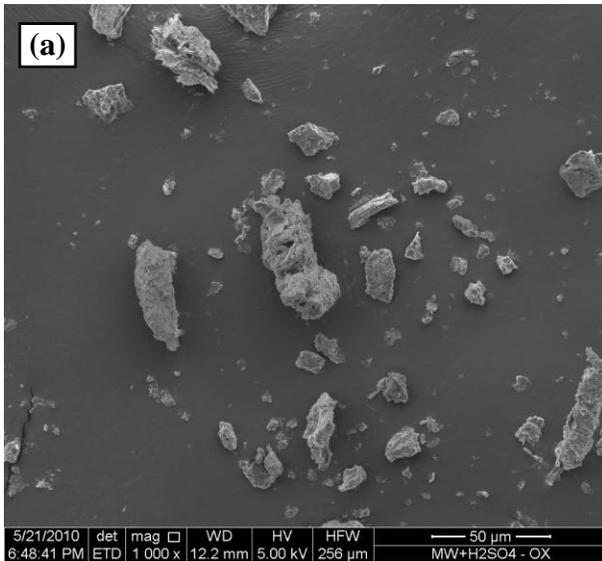
Figure 18. SEM image and (b) XRD patterns of non-centrifuged EBPR AML; (c) SEM image and (d) XRD patterns of non-centrifuged EBPR feed

4.4.3 Microwave P solubilization and struvite precipitation

Figure 19 (a) showed the DRP concentrations of microwave-digested dairy manure at varying heating temperatures and the first data point of each curve (at 25 ℃) was the DRP concentration of manure pretreated with administrated acidification treatment (using HCl or H_2SO_4 to pH, and the control) prior to microwave heating. Acidification pretreatment facilitated P solubilization in liquid dairy manure but the results were different for HCl and H_2SO_4. For HCl acidification, the DRP concentration kept a slight increasing trend with heating temperature raised from 60 ℃ to 150 ℃; however, it plunged to 175.56 ($\pm$5.18) mg/L at 170 ℃ from peak value 297.60 ($\pm$2.35) mg/L obtained at 150 ℃ and DRP concentration remained constant at temperature higher than 170 ℃. For manure acidified with H_2SO_4, its DRP concentration decreased from 60 ℃ to 120 ℃ but increased to a large extent as the heating temperature increased from 120 ℃ to 170 ℃. There was not significant DRP increase at temperature higher than 170 ℃. In contrast, there was apparent DRP decrease occurred instead of increase in manure without acidification treatment. This was consistent with what was observed by Pan et al (2006); however, it could not be demonstrated that there was no P solubilization occurring in the manure treated with only microwave radiation. The pH of manure in "microwave only" series was measured (Figure 19 (b)) and it showed that pH increased with the increase of microwave heating temperature. Hence, it was probable that DRO was released from manure without acidification pretreatment after being microwave digested but precipitated as Ca- and/or Mg-bounded phosphate solids immediately; since Ca^{2+} and/or Mg^{2+} was sufficient in manure solution, Mg- or Ca-phosphate precipitation occurs easily at pH higher than 8.
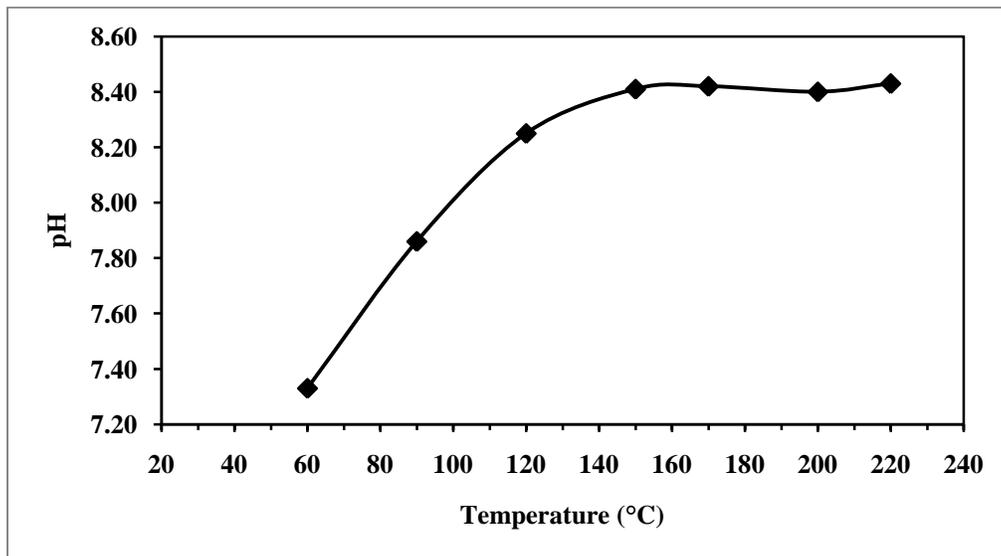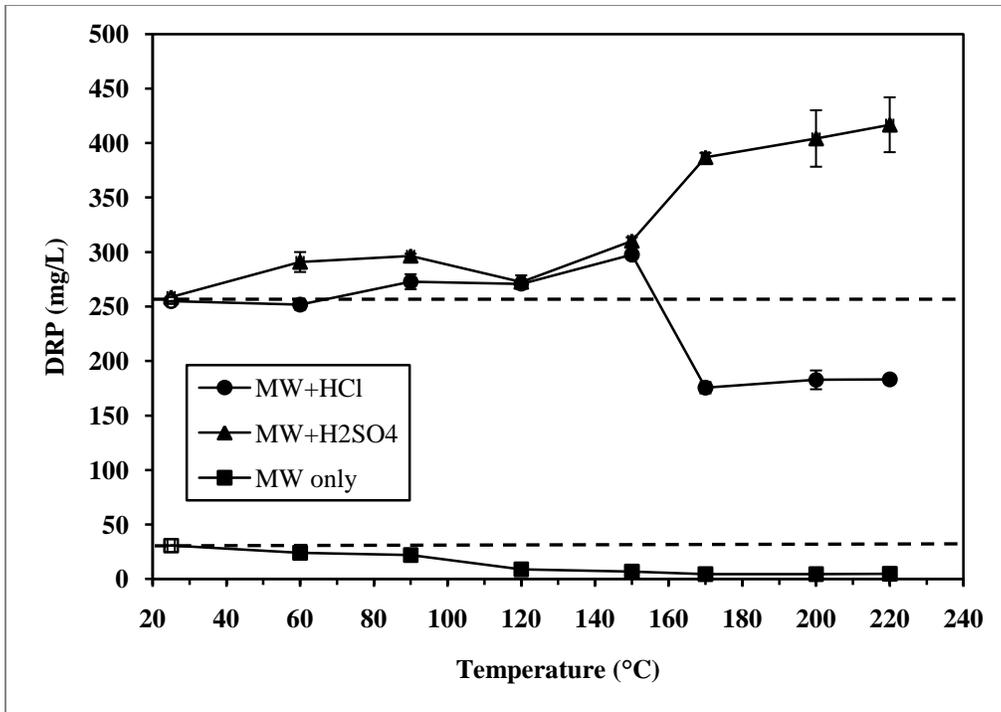
Figure 19. (a) DRP concentrations digested using microwave radiation with different acidification pretreatment methods versus heating temperatures (data were means of 3 replicates and error bars showed standard deviations); (b) pH value of microwave digested manure without acidification pretreatment versus heating temperatures. The dash lines in Figure 19 (a) represented the DRP concentration of acidified manure (254.96 mg/L) and untreated manure (30.67 mg/L), respectively.

For manure pretreated with H_2SO_4, microwave digestion at 170 ℃ resulted in highest P solubilization; for HCl acidification pretreatment, highest P release yield occurred at 150 ℃. Therefore, the manure treated with the two pretreatment methods was selected for further struvite precipitation.

The DRP/TP ratio was increased from 6.7 % to 55.4 % by acidification only in room temperature and further increased to 84.1 % (MW+H_2SO_4, 170 ℃) and 67.4 % (MW+HCl, 150 ℃) respectively. Therefore, acidification contributed to the major part of DRP increase in dairy manure. Microwave digestion only made contribution to DRP increase at 150 ℃ (HCl) or 170 ℃ (H_2SO_4). This increase might be partly attributed to microwave converting part of organic P to DRP.

In addition, there was significant difference ($P < 0.05$) between the DRP concentration of MW+H_2SO_4 and that of MW+HCl at 150 ℃ or higher temperatures. This could possibly attribute to the interactions occurring between the ions (SO_4^{2-} and Cl^-) and organic P forms of the liquid dairy manure. The presence of SO_4^{2-} might facilitate the P solubilization. The polar substances in the dairy manure were heated more rapidly than non-polar substances (de la Hoz et al., 2005), resulting in "explosion" effect, which accelerated the disruption of organic P complexes (i.e. soluble organic P, lipid-P, nucleic acid-type-P). Hence, presence of SO_4^{2-} might have positive impact on the degraded P substances, improving their conversion to DRP. Also, the acid loading might impose effects on the DRP release process, depending on the type of inorganic acid used in the acidification pretreatment prior to the microwave heating. Since the normality was identical for both H_2SO_4 and HCl (5 N) to reach the goal of pH 4, the acid loading was

supposed to be the same. However, such loading rate might be optimal for H_2SO_4 at 170 ℃, while not the best for HCl.

4.4.4 Precipitates characteristics (microwave treatment)

SEM-EDS analyses of solids precipitated from microwave digested manure with different acidification pretreatments were presented in Table 13, Figure 20 and Figure 21. Among the centrifuged set, Ca, P and O were the major elements found in microwave digested (MW) manure with HCl acidification pretreatment and control, probably resulting from the high Ca^{2+} availability caused by microwave digestion (Qureshi et al., 2008); Mg presented only as one of the minor composition in the precipitates. In contrast, Mg phosphate solid phase was found as the dominant solid phase in MW manure pretreated with H_2SO_4 acidification, where the randomly selected 3 points element analysis results showed an average Mg : P : O molar ratio of 1 : 1.2 : 4.5 (Table 13; Figure 20 (a1)). These Mg phosphates may be struvite based on their dendritic and rod-like (Figure 21 (a1)) morphology (Babic-Ivanic et al., 2002), even though this was not confirmed by the EDS examination. Additionally, heterogeneous poorly-crystalline materials were found in the precipitates as the minor solid phase, with a mass composition of 8.70 % Ca, 14.75 % Na, 15.01 % S and 46.95 %. Hence, H_2SO_4 addition was demonstrated to suppress the negative effects of Ca^{2+} on struvite formation, although we could not determine whether it was the individual SO_4^{2-} effect or the interactive effects of SO_4^{2-} and other components (e.g. organic ligands and macroelements like Na^+ and K^+) due to the complex composition of dairy manure, since the microwave digestion was found to facilitate nutrients (N and P) release (Qureshi et al., 2008) and COD solubilization (Jin et al., 2009) in dairy manure. However, such Ca^{2+} mitigation effect

was not observed in either MW manure or MW+HCl manure (Figure 20 (b1), (c1);

Figure 21 (b1), (c1)). Similar to many experimental runs, no struvite-like crystals were

found among the non-centrifuged MW manure, regardless of acidification pretreatment

(Figure 20 (a2), (b2), (c2)). EDS results showed that C, O and Si were the general

element compositions in the solids precipitated in non-centrifuged manure, in spite of the

TSS reduction resulted from the microwave digestion. For example, TSS concentration of

H_2SO_4 acidified manure was decreased from 2.15 % to 1.01 % after being subjected to

microwave digestion at 170 ℃ for 5 min, but complex TSS compositions like organic

ligands and quartz still interfered with struvite formation in manure. As for the MW

manure treated with oxalic acid to minimize the Ca^{2+} inhibition prior to struvite

precipitation, the element compositions were Mg, P and O, with traces of Ca, Na and K,

where the Mg : P : O molar ratios indicated Mg phosphate as the dominant solid phase. It

was noticed that dendritic and leaf-like Mg phosphate crystalline partially covered with

small rhombohedral crystal consisting of Ca and O (shown in yellow spots in Figure 20

(a3), (b3) and (c3)) were the main structural characteristics of the precipitates. Specially,

crystals precipitated from MW+H_2SO_4 manure pretreated with oxalic acid had a

crystalline, large and homogeneous nature (Figure 21 (b1)), different from those from

MW+HCl or MW control, which were generally very small in nature (Figure 21 (b2),

(b3)).

Table 13. EDS analysis results of precipitated solids from microwave digested (MW) manure

| MW manure	Point	P (mass %)	O (mass %)	Mg (mass %)	Ca (mass %)
H_2SO_4 - C	1	22.85	49.43	16.49	0.12
	2	26.00	52.72	16.54	0.11
	3	27.56	51.34	17.76	0.13
	4	2.97	46.95	2.67	8.70
H_2SO_4 - NC	1	1.05	28.58	0.01	2.00
	2	1.52	51.60	0.92	3.28
	3	1.58	55.67	0.69	1.93
	4	1.28	33.50	0.23	3.79
H_2SO_4 - C+OX	1	22.46	44.16	14.29	0
	2	22.00	44.95	13.49	0
	3	22.78	52.87	15.66	0
	4	15.50	55.33	11.53	10.48
HCl - C	1	12.44	44.77	2.94	19.63
	2	6.71	35.55	1.59	15.77
	3	20.88	53.75	15.61	1.37
	4	11.31	23.87	1.54	19.82
HCl - NC	1	2.95	33.20	0.02	6.63
	2	2.46	43.36	0.17	3.40
	3	2.10	36.04	1.02	5.67
	4	1.99	47.57	1.23	2.76
HCl – C+OX	1	23.54	55.26	18.42	0
	2	19.86	50.85	15.28	0
	3	20.26	44.74	13.62	0
	4	21.45	61.01	18.00	0
control - C	1	12.55	31.90	1.77	23.50
	2	8.66	22.48	0.09	21.62
	3	9.84	7.11	0	28.80
	4	11.15	46.11	3.59	20.90
control - NC	1	3.14	48.62	0.72	8.88
	2	1.35	44.32	2.85	3.86
	3	6.91	43.67	3.75	13.73
	4	3.71	50.48	1.62	7.95
control – C+OX	1	23.71	54.77	17.80	0.34
	2	22.66	49.11	15.36	0.32
	3	5.62	60.22	4.72	23.16
	4	25.19	52.31	18.77	0.61
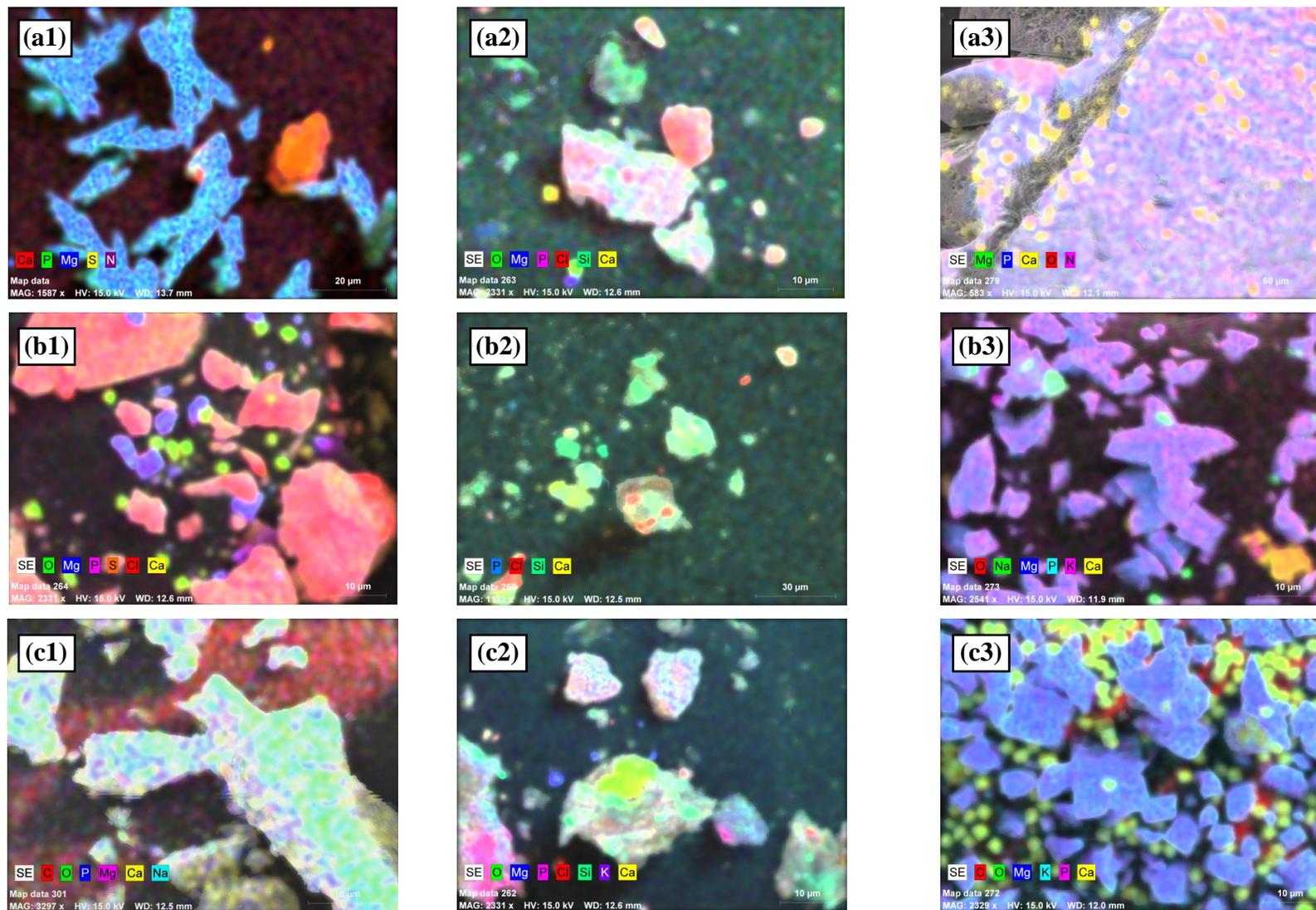
Figure 20. Energy dispersive X-ray mapping analysis output of microwave digested manure with varying acidification pretreatments: (a1) H₂SO₄ (centrifuged); (a2) H₂SO₄ (non-centrifuged); (a3) H₂SO₄+oxalic acid (centrifuged); (b1) HCl (centrifuged); (b2) HCl (non-centrifuged); (b3) HCl+oxalic acid (centrifuged); (c1) control (centrifuged); (c2) control (non-centrifuged); (c3) control+oxalic acid (centrifuged)
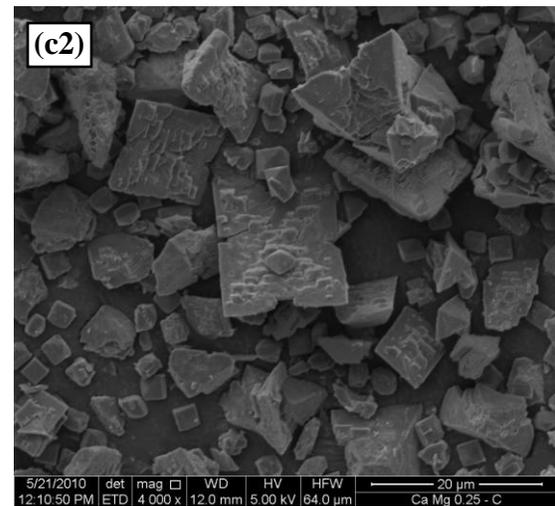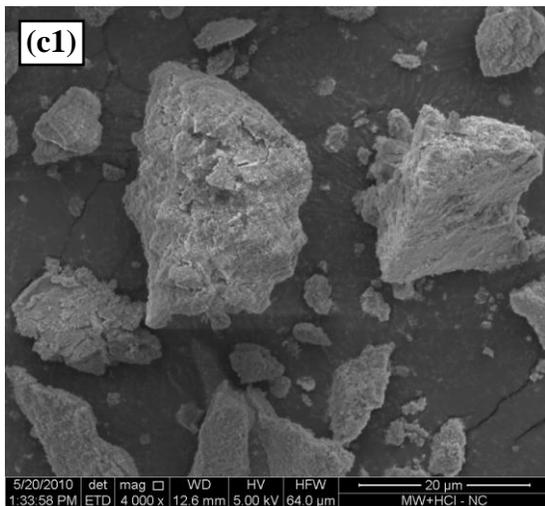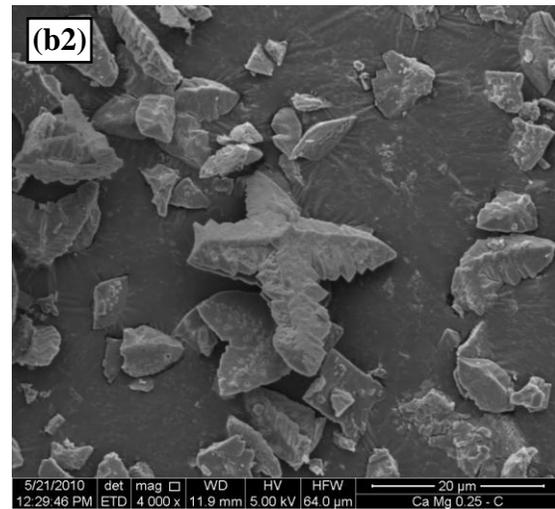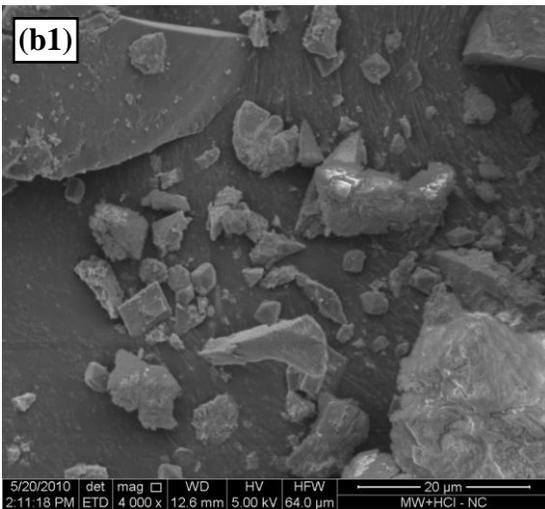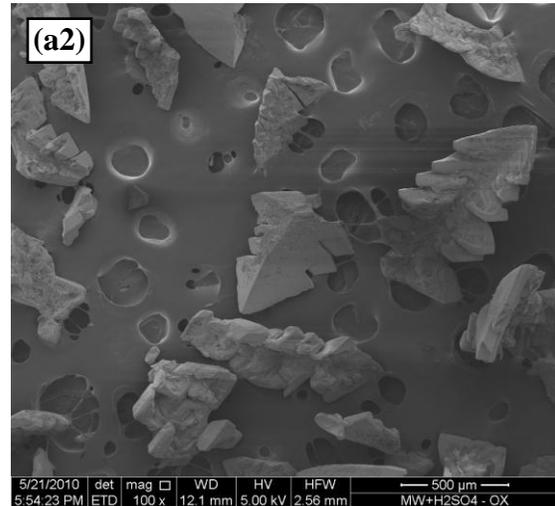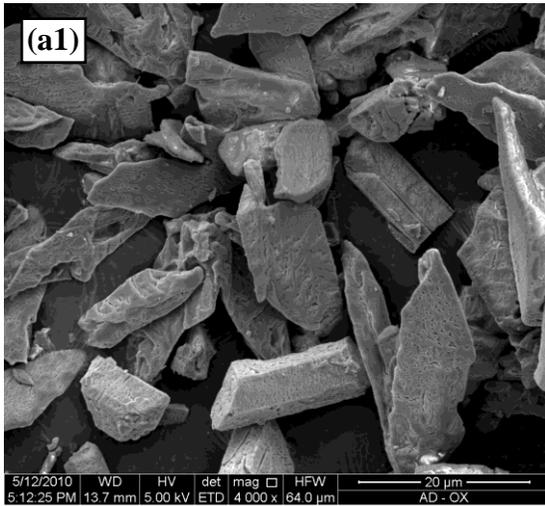
Figure 21. Scanning electron micrographs of solids precipitated from MW manure with pretreatment of (a1) H_2SO_4 (centrifuged); (a2) H_2SO_4+oxalic acid (centrifuged); (b1) HCl (centrifuged); (b2) HCl+oxalic acid (centrifuged); (c1) control (centrifuged); (c2) control+oxalic acid (centrifuged)

XRD analyses were conducted to further identify the structural characteristics of these materials precipitated from MW manure, shown in Figure 22 to 24. The diffractogram of the materials precipitated from MW manure with H_2SO_4 pretreatment matched well with standard struvite (Figure 22 (a)), confirming the presence of struvite crystalline as the dominant solid phase (Figure 20 (a1)). This indicated that the presence of SO_4^{2-} might mitigate the inhibition of Ca^{2+} on struvite formation, possibly resulting from the Ca^{2+} capture by SO_4^{2-}. However, precipitates obtained from $MW+H_2SO_4$ manure with oxalic acid pretreatment were heterogeneous, a mixture of struvite, newberyite and magnesite (Figure 22 (b)). This discrepancy is attributed to (1) the possible suppression from SO_4^{2-} to inhibit struvite formation; (2) the probable ammonia losses due to volatilization and (3) the high alkalinity inducing the co-precipitation of $MgCO_3$.

No struvite crystals were observed in MW+HCl or MW without acidification manure (Figure 23 (a) and Figure 24 (a)). With the oxalic acid amendment, the diffractograms of the materials from MW+HCl and MW without acidification manure match perfectly with the struvite standard (Figure 23 (b) and Figure 24 (b)). Therefore, although microwave digestion plus HCl acidification contributed to the DRP release in dairy manure (Figure 19 (a)), this pretreatment could not effectively enhance struvite precipitation in dairy manure with high Ca concentration.
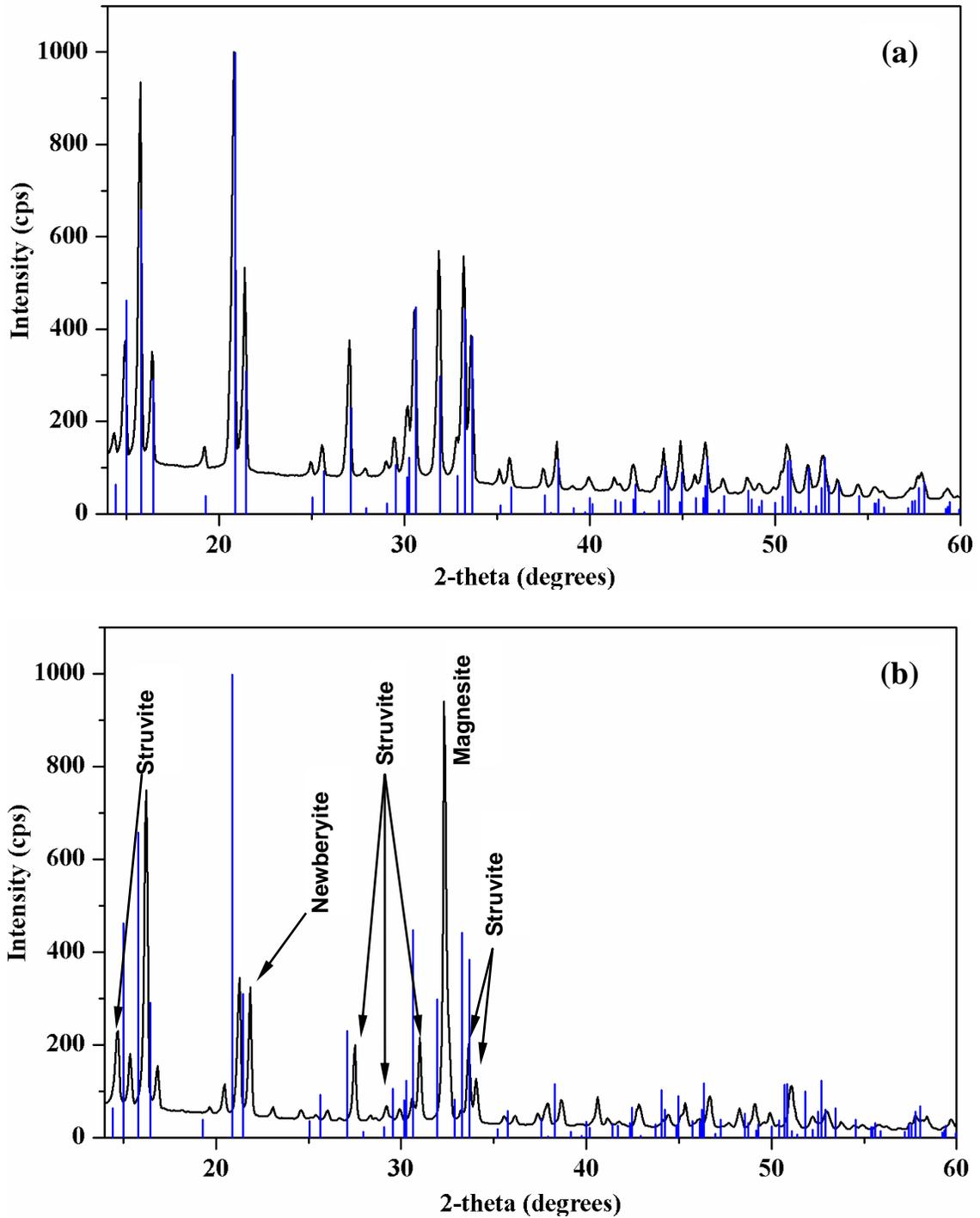
Figure 22. X-ray diffractograms of materials precipitated from MW manure pretreated with (a) H_2SO_4 (centrifuged); (b) H_2SO_4+oxalic acid (centrifuged). Blue lines represented standard struvite crystals (JCPDF-2 # 71-2089)
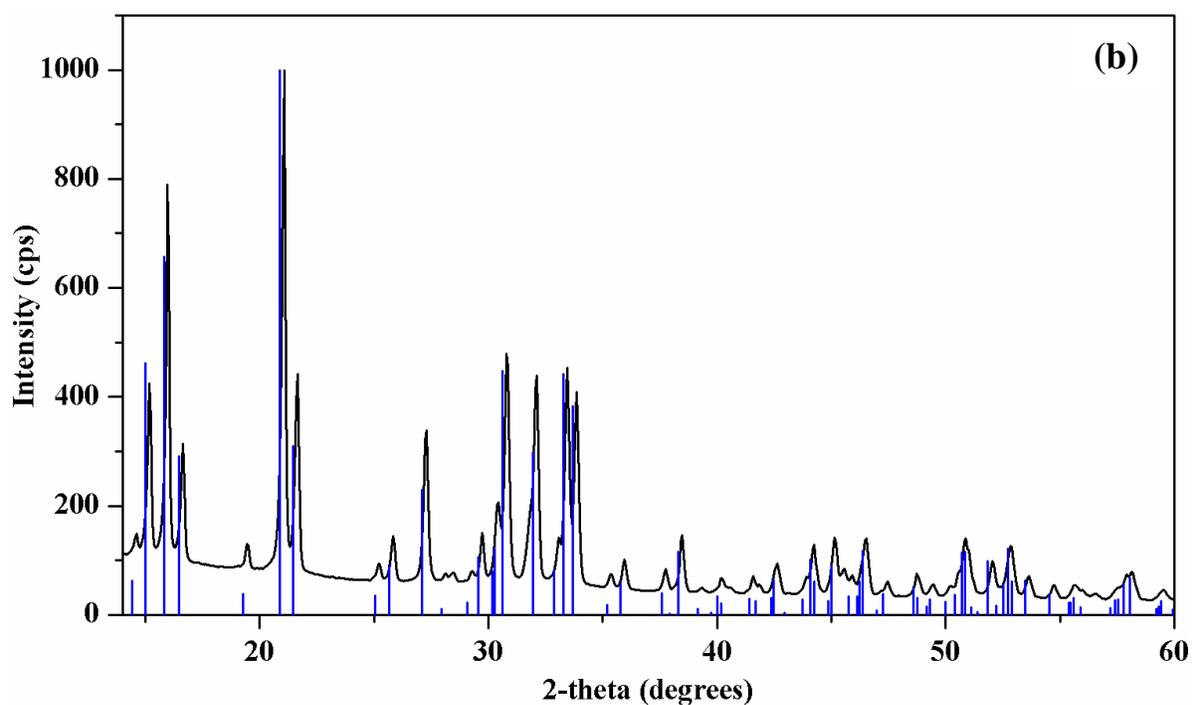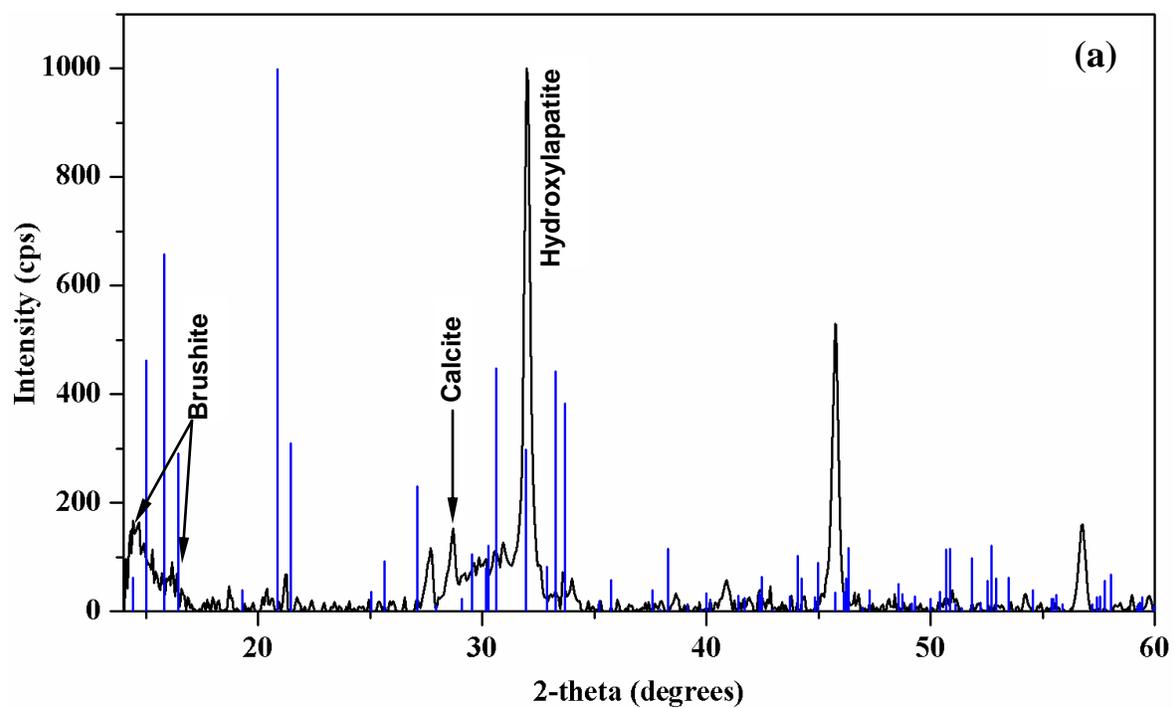
Figure 23. X-ray diffractograms of materials precipitated from MW manure pretreated with (a) HCl (centrifuged); (b) HCl+oxalic acid (centrifuged). Blue line represented standard struvite crystals (JCPDF-2 # 71-2089)
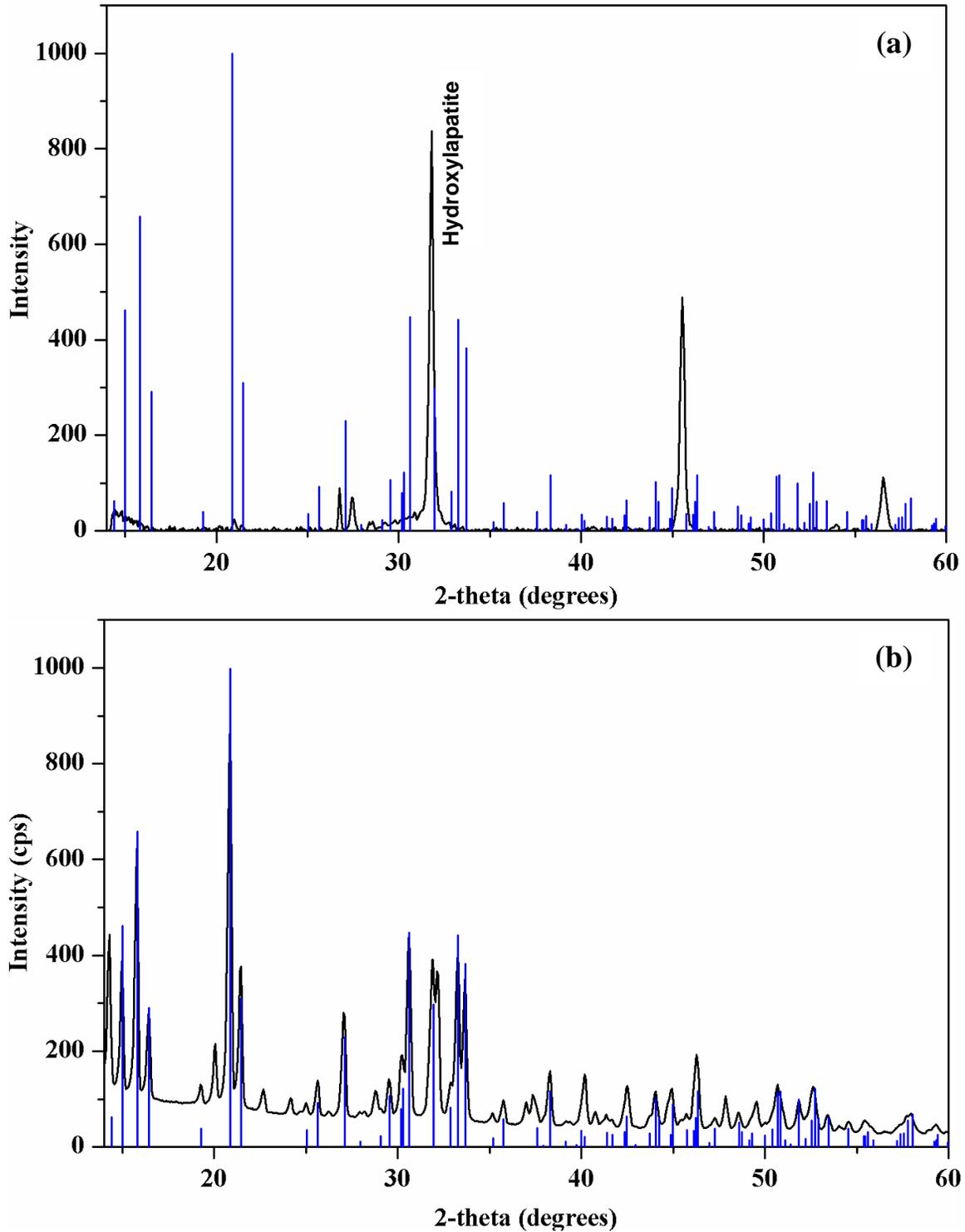
Figure 24. X-ray diffractograms of materials precipitated from MW manure (a) without acidification pretreatment; (b) with oxalic acid pretreatment. Blue line represented standard struvite crystals (JCPDF-2 # 71-2089)

4.4.5 Anaerobic digestion performance

The characteristics of AD influents and effluents were shown in Table 14. As expected, TS and VS destructions were observed in anaerobically digested manure. The DRP concentration was increased, indicating some P conversion occurring from poly-P and/or organic P to DRP. The reduction in NH_4-N concentration may be indicative of NH_3 volatilization occurring from the digested manure; this was expected due to the initial high NH_4-N concentration, which would result in high volatilization rates (Brunke et al., 1988). On the other hand, decrease in organic N (29.8 %) indicated the N solubilization achieved by AD treatment. Slight mass losses were observed in total Mg, Ca, Na and K, but the molar ratio of Ca/Mg was the same before and after AD treatment. Although the Mg^{2+} availability was not evaluated in this study, it has been reported that AD treatment contributed to increase in available Mg^{2+} in livestock manure (Buchanan, J., 1993; Moody et al., 2009). However, calcium effects were not taken into accounts in these studies. Since the Ca/Mg of the undigested manure in this case was high to produce negative effects on struvite formation, it was expected at the first place that struvite precipitation would not be enhanced by anaerobic digestion.

Table 14. Characteristics of AD influents and effluents

Parameter (unit)	Influent	Effluent
TS (%)	3.98	2.58
VS (%)	1.21	0.87
pH	7.43	7.25
Total COD (mg/L)	59220	42080
Soluble COD (mg/L)	22437	18453
Total P (mg/L)	364.2	296.1
DRP (mg/L)	30.7	55.0
Organic N (mg/L)	1310.9	920.3
TAN (mg/L)	1429.6	1300.2
Mg (mg/L)	639.9	536.8
Ca (mg/L)	1461.9	1239.0
Na (mg/L)	919.6	769.7
K (mg/L)	1794.7	1737.0

4.4.6 Precipitates characteristics (anaerobic digestion)

SEM-EDS analysis results of the solids precipitated from anaerobically digested and raw manure were shown in Table 15 and Figure 25. No evidence of crystalline materials were found in anaerobically digested manure; in centrifuged sample, irregular-shaped solids and ball-like materials with smooth surface were found to be the dominant compositions (Figure 25 (a1)), while for the non-centrifuged sample, SEM imaging yielded a mixture of organic ligands with C and O as the major elements (non shown) and irregular-shaped solids (Figure 25 (a2)), which were quite similar to what was observed (Figure 25 (b2)) in raw manure (non-centrifuged). In contrast, crystals were observed in the materials precipitated from anaerobically digested manure pretreated with oxalic acid, with blocky crystalline features (Figure 25 (a3)), and other particles had the same rhombohedral crystal as what was observed in microwave set (section 4.4.4), with Ca and O as the major element composition. EDS results showed a Ca : C : O molar ratio of approximate 1.2 : 1 : 5.

XRD analyses were conducted to further confirm whether struvite precipitation was enhanced by anaerobic digestion, shown in Figure 26. Apparently, struvite crystals only precipitated in the anaerobically digested manure pretreated with oxalic acid (Figure 26 (b)), while heterogeneous phased crystalline solids (not struvite) were found (Figure 26 (a)). XRD patterns indicated that the material was a mixture of calcite and hydroxyapatite. Hence, the high Ca/Mg molar ratio (1.38) inhibited the struvite formation in anaerobically digested manure, even though the DRP availability was increased.

Table 15. EDS analysis for precipitated solids from raw and anaerobically digested manure

Manure	Point	P (mass %)	O (mass %)	Mg (mass %)	Ca (mass %)
Digested - C	1	5.49	47.45	3.25	27.24
	2	9.42	47.18	3.14	19.37
	3	9.58	45.61	3.10	15.81
	4	10.52	44.48	4.07	20.40
Digested - NC	1	2.19	43.46	0.90	2.87
	2	1.89	25.68	0.88	33.84
	3	3.10	55.56	3.67	23.08
	4	2.81	39.06	0.05	4.60
Digested - C+OX	1	24.40	52.16	18.08	0.99
	2	22.58	52.62	16.95	0.64
	3	1.58	53.82	0.58	33.28
	4	2.84	51.35	1.19	38.60
Raw - C	1	6.03	10.85	1.02	13.50
	2	2.62	16.81	1.78	2.41
	3	4.63	8.63	0.68	5.66
	4	0	3.49	0	0
Raw - NC	1	2.33	45.99	2.95	3.20
	2	0	45.69	3.23	3.22
	3	4.48	38.81	1.48	4.90
	4	4.04	46.40	2.03	6.82
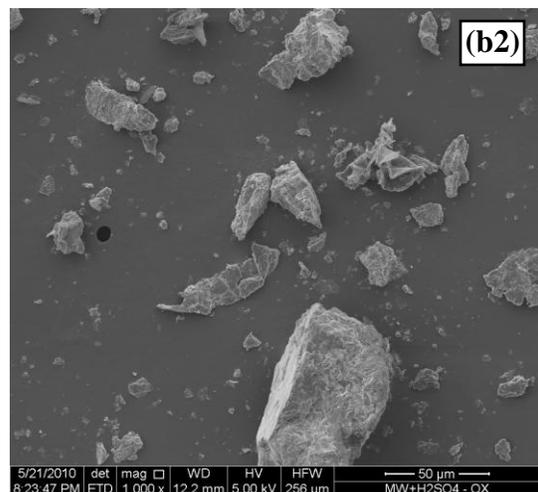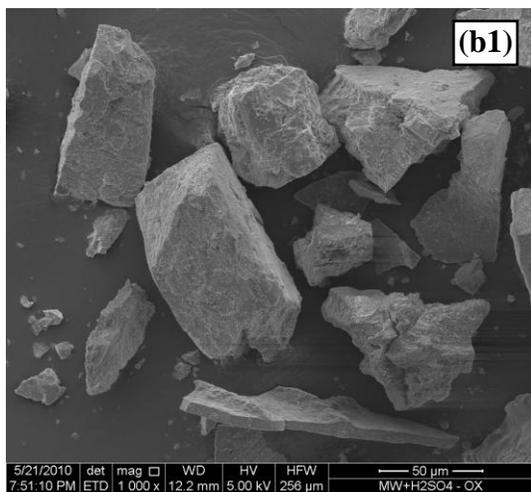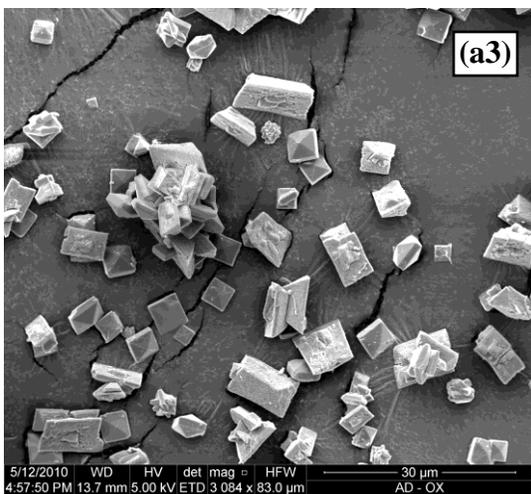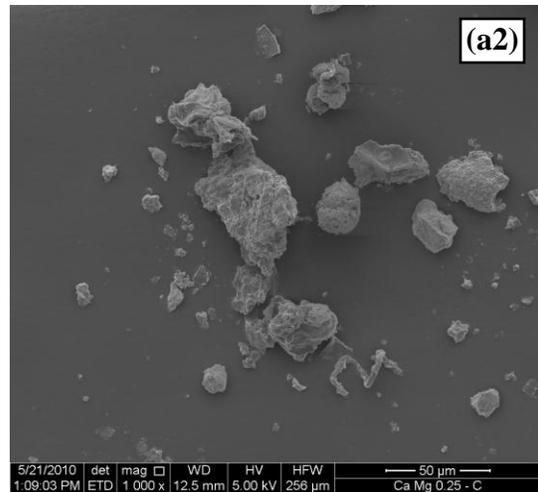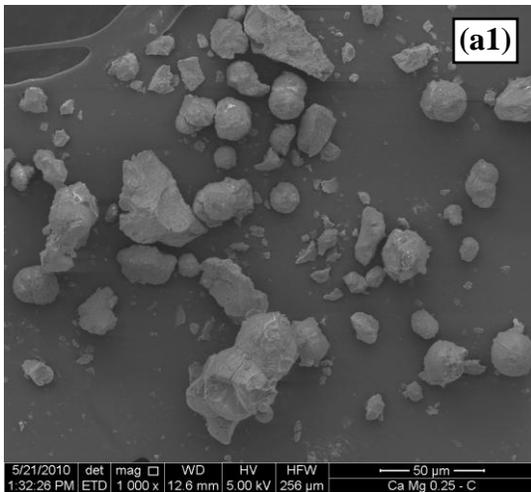
Figure 25. Scanning electron micrographs of solids precipitated from (a1) anaerobically digested manure (centrifuged); (a2) anaerobically digested manure (non-centrifuged); (a3) anaerobically digested manure pretreated with oxalic acid (centrifuged); (b1) raw manure (centrifuged); (b2) raw manure (non-centrifuged)
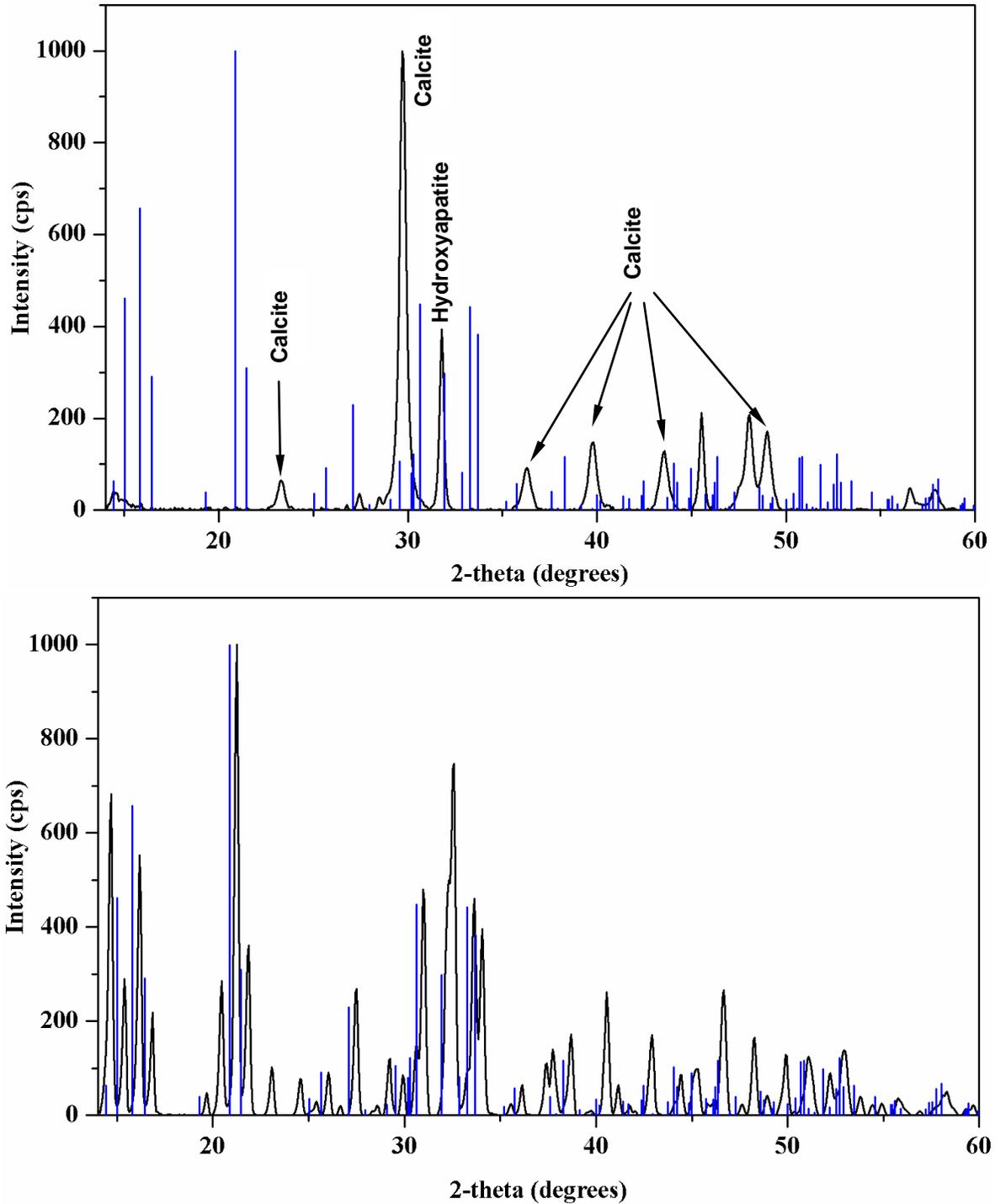
Figure 26. X-ray diffractograms of materials precipitated from (a) anaerobically digested manure; (b) anaerobically digested manure pretreated with oxalic acid. Blue line represented standard struvite crystals (JCPDF-2 # 71-2089)

4.4.7 TSS effects

Table 4.8 showed the TS and TSS concentrations of dairy manure under different pretreatments. The non-centrifuged manure contained significantly higher TS and TSS than those of the centrifuged manure, regardless of pretreatment methods. This provided evidence that suspended solids (including particle fines and organic matter) interfered struvite precipitation, as discussed in 3.3.3, which also explains why no crystal minerals but fibers and irregular-shaped particles (probably the mixture of organic matter and minerals) were found in SEM-EDS imaging results (pictures not included). On the other hand, struvite, magnesium phosphate, and/or other amorphous precipitate (possibly calcium phosphate) were observed in centrifuged sets, where in low calcium manure (those with oxalic acid amendment), pure struvite crystals were found.

Table 16. TS and TSS concentrations of different dairy manure

Acidified dairy manure (pH 4)	TS (unit)	TSS (unit)
Centrifuged untreated	2.3 %	0.4 %
Untreated	4.2 %	2.2 %
Centrifuged EBPR sludge	0.3 %	1580 mg/L
EBPR sludge	3.3 %	2.4 %
Centrifuged microwave digested (MW) +H_2SO_4 manure	392 mg/L	86 mg/L
MW + H_2SO_4 manure	4.2 %	1.2 %
Centrifuged MW + HCl manure	438 mg/L	103 mg/L
MW + HCl manure	4.2 %	1.2 %
Centrifuged MW manure	987 mg/L	374 mg/L
MW manure	4.2 %	1.4 %
Centrifuged anaerobically digested manure	1.5 %	0.2 %
Anaerobically digested manure	3.0 %	1.9 %

4.5 CONCLUSIONS

- No struvite crystals were found in EBPR effluents due to the high Ca^{2+} to Mg^{2+} molar ratio.

- No struvite crystals were found in AD effluents but large amounts of struvite with high purity were observed to precipitate in AD effluents pretreated with oxalic acid to remove the Ca^{2+} interference.

- Acidification pretreatment affected struvite precipitation potential in microwave digested manure: struvite crystals were found as the dominant solid phase in microwave digested manure (MW manure) with H_2SO_4 acidification. However, presence of struvite was not found in MW manure pretreated with HCl acidification or MW manure without acidification.

- TSS has a significant effect on struvite precipitation. No struvite or other types of crystals were found in non centrifuged manure (containing high TS and TSS).

REFERENCES

Babic-Ivancic, V., J. Kontrec, D. Kralj and L. Brecevic. 2002. Precipitation diagrams of struvite and dissolution kinetics of different struvite morphologies. Croatica Chemica ACTA 75(1): 89-106

De la Hoz, A., A. Diaz-Ortiz and A. Moreno. 2005. Microwaves in organic synthesis. Thermal and non-thermal microwave effects. Chemical Society Reviews 34(2): 164-178.

Gungor, K., M. B., Muftugil, J. A. Ogejo, K. F. Knowlton and N. G. Love. 2009. Prefermentation of liquid dairy manure to support biological nutrient removal. Bioresource Technology 100(7): 2124-2129.

Hong, Y. 2009. Enhanced Biological Phosphorus Removal for Liquid Dairy Manure. M. S. Thesis. Virginia Polytechnic Institute and State University, Blacksburg, VA.

Jin, Y., Z. Hu, and Z. Wen. 2009. Enhancing anaerobic digestibility and phosphorus recovery of dairy manure through microwave-based thermochemical pretreatment. Water Research 43(14): 3493-3502.

Knowlton, K. F., N. G. Love and C. M. Parsons. 2005. Dietary phosphorus effects on characteristics of mechanically separated dairy manure. Transactions of the ASAE 48(3): 1253-1258.

Pan, S., K. V. Lo., P. Liao and H. Schreier. 2006. Microwave pretreatment for enhancement of phosphorus release from dairy manure. Journal of Environmental Science and Health Part B 41(4): 451-458.

Qureshi, A., K. V. Lo, and P. Liao. 2008. Microwave treatment and struvite recovery potential of dairy manure. Journal of Environmental Science and Health Part B - Pesticides Food Contaminants and Agricultural Wastes 43(4): 350-357.

Srida, V. 1998. Microwave radiation as a catalyst for chemical reactions. Current Science 74(5):

446-450.

5. ECONOMIC EVALUATION OF DIFFERENT PRETREATMENT METHODS TO ENHANCE STRUVITE PRECIPITATION IN LIQUID DAIRY MANURE

5.1 INTRODUCTION

Different pretreatment methods enhanced struvite precipitation in liquid dairy manure by increasing DRP availability and/or mitigating Ca^{2+} interference. Therefore, it is necessary to conduct pretreatment costs analysis because (1) the amounts of struvite production varied among manure with different pretreatment methods and (2) the chemical cost of each pretreatment was different.

5.2 OBJECTIVE

The objective was to assess the chemical costs of P recovery from liquid dairy manure with different pretreatment methods.

5.3 MATERIALS AND METHODS

Three pretreatment methods, untreated manure + oxalic acid (RM+OX), anaerobically digested manure + oxalic acid (AD+OX), and microwave digested manure pretreated with H_2SO_4 acidification (MW+H_2SO_4), were selected for a partial cost analysis based on chemical dosing and processes shown in Figure 27 Visual Minteq 2.61 modeling was used to estimate the amounts of struvite precipitated pretreated manure and using similar procedure described in section 3.1. Model inputs are listed in Table 17 and pH was fixed at 8 for struvite recovery.
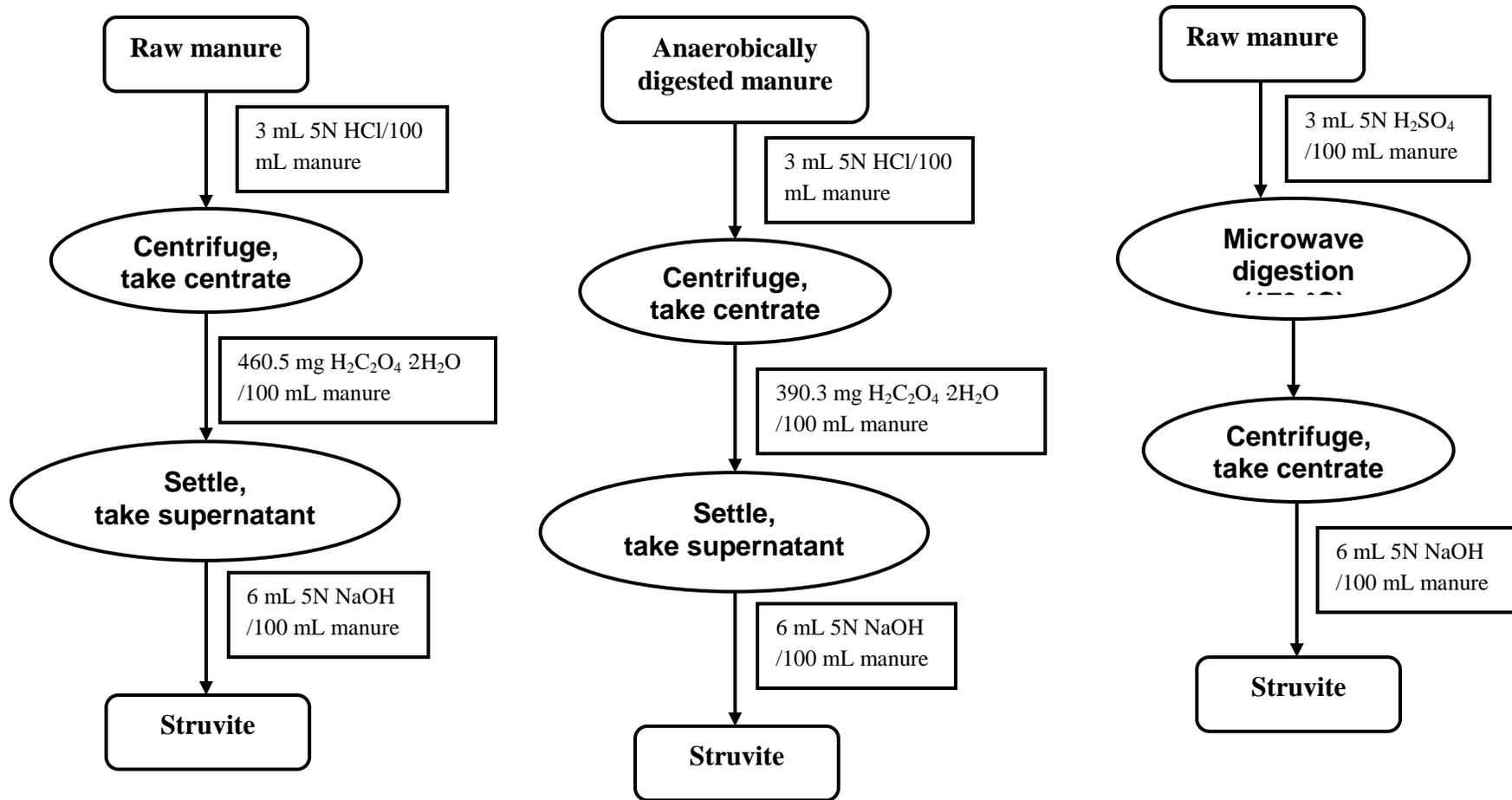
Figure 27. Schematic process of enhanced struvite precipitation with different pretreatment methods

Table 17. Visual Minteq inputs for different pretreated manure

Inputs (mg/L)	RW+OX	AD+OX	MW+H$_2$SO$_4$
PO$_4^{3-}$	781.3	878	1186
NH$_4^+$	1838	1671.6	1838
Mg^{2+}	639.9	536.8	639.9
Ca^{2+}	71.3	68.5	1461.9
K$^+$	1794.7	1737	1794.7
Na$^+$	919.6	769.7	919.6
SO$_4^{2-}$	733.4	596.8	20,000
CO$_3^{2-}$	2200	2800	2200
Cl$^-$	1434	1111	1434

A simple partial economic analysis was conducted based on the current market price of chemicals added to enhance struvite precipitation, while capital costs (e.g. anaerobic digestion building, centrifuge and microwave heater) and other operating costs such as labor, were not included in this study. The chemical costs were presented based on their market prices by Fisher Scientific. The annual dairy manure production calculation was based on a dairy farm with 200 cows, excreting 68 L manure per day per animal (ASABE, 2005).

5.4 RESULTS AND DISCUSSIONS

Table 18 showed the quantities of struvite produced from liquid dairy manure with different pretreatment methods and the recovery efficiencies were calculated according to the equation below. The higher recovery efficiencies achieved in AD+OX and MW+H_2SO_4 runs partially attributed to the initial higher DRP concentrations (Table 17), compared to that of untreated manure.

$$Struvite\ recovery\ efficiency = \frac{mass\ of\ P\ precipitated\ as\ struvite}{mass\ of\ Total\ P\ in\ excreted\ manure} \times 100\ \%$$

Chemical costs analysis and struvite recovery production quantities were summarized in Table 19 and 20 The microwave digested manure with H_2SO_4 acidification pretreatment produced the highest quantities of struvite out of the 3 pretreatments, with the lowest chemical costs. However, since this study only focused on chemical addition costs, we could not conclude that this pretreatment was optimum to recover struvite in field application on full scale, because apparently the capital investment of microwave heating might be higher other pretreatments considered. Additionally, just struvite quantities could not account for the profit that the dairy

farm made from struvite fertilizer production, the transportation fee (0.08 cents/liter per 20 miles) should also be included when applied to practice.

Table 18. Quantities of struvite recovered from manure subjected to different pretreatment methods by Visual Minteq 2.61.

Pretreatment	Struvite amounts (mg/L)	Recovery efficiency (%)
RM+OX	1977.1	68.7
AD+OX	2196.7	76.3
MW+H_2SO_4	2960.1	80.9

Table 19. Chemical costs analysis for struvite recovery from manure with different pretreatments

Pretreatment	Chemical added	Dosage (per liter manure)	Unit cost	Chemical cost ($/L manure)
RW+OX	36.5-38 % HCl (~12 N)	12.5 mL	$ 96.87/2.5 L	0.484
	$H_2C_2O_4$ $2H_2O$ powders	4605 mg	$ 318.4/5 kg	0.293
	NaOH pellets	12 g	$ 277.9/10 kg	0.333
AD+OX	36.5-38 % HCl (~12 N)	12.5 mL	$ 96.87/2.5 L	0.484
	$H_2C_2O_4$ $2H_2O$ powders	3903 mg	$ 318.4/5 kg	0.249
	NaOH pellets	12 g	$ 277.9/10 kg	0.333
MW+H_2SO_4	98 % H_2SO_4 (~ 36 N)	4.17 mL	$ 97.13/2.5 L	0.162
	NaOH pellets	12 g	$ 277.9/10 kg	0.333

Table 20. Annual chemical costs of struvite recovery and corresponding struvite productions for a typical dairy farm (200 cows with 68 L manure/day animal)

Pretreatment	Chemical costs ($/L manure)	Struvite production (kg/year farm)
RW+OX	1.110	9,819
AD+OX	1.066	10.906
MW+H_2SO_4	0.495	14,693

5.5 CONCLUSIONS

- Microwave digested manure pretreated with H_2SO_4 produced the highest struvite quantities among the 3 pretreatment methods to enhance struvite recovery, also with the lowest chemical addition costs.

REFERENCES

ASABE. 2005. Manure characteristics. American Society of Agricultural and Biological Engineers (ASABE) Standard D384.2. St. Joseph, Mich.