

The effect of organic matter on the removal of phosphorus through precipitation as struvite and calcium phosphate in synthetic dairy wastewater

Prince Aleta¹, Sanjai J. Parikh², Amy P. Silchuk², Kate M. Scow², Minseung Park¹ and Sungpyo Kim*¹

¹Department of Environmental Systems Engineering, Korea University, Sejong-ro, Sejong City 339-770 Republic of Korea

²Department of Land, Air and Water Resources, University of California, Davis, Ca 95616, United States

(Received October 12, 2017, Revised April 25, 2018, Accepted April 26, 2018)

Abstract. This study investigated the effect of organic matter on the precipitation of struvite and calcium phosphate for phosphorus recovery from synthetic dairy wastewater. Batch precipitation experiments were performed to precipitate phosphorus from solutions containing PO_4^{3-} and NH_4^+ by the addition of Mg^{2+} and Ca^{2+} , separately, at varying pH, Mg/P and Ca/P molar ratios, and organic matter concentrations. Soluble total organic solids exhibited more inhibition to precipitation due to potential interaction with other dissolved ionic species involved in phosphorus precipitation. Xylan with low total acidity only exhibited significant inhibition at very high concentrations in synthetic wastewater (at up to 100 g/L). No significant inhibition was observed for Mg and Ca precipitation at relatively lower concentrations (at up to 1.2 g/L). MINTEQ simulations show that dissolved organic matter (DOM) as humic substances (HS) can cause significant inhibition even at relatively low concentrations of 0.165 g/L fulvic acid. However, scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis suggested that xylan altered the crystal structure of both precipitates and had caused the formation of smaller sized struvite crystals with slightly rougher surfaces. This could be due to xylan molecules adhering on the surface of the crystal potentially blocking active sites and limit further crystal growth. Smaller particle sizes will have negative practical impact because of poorer settleability.

Keywords: phosphorus recovery; struvite; calcium phosphate

1. Introduction

Phosphorus, apart from being an element essential to all life, is also a valuable element in the chemical industry as it is used, in one form or another, for the manufacture of a wide range of products essential to modern society. Most of the phosphorus supply, however, comes from rock phosphate, which is a limited resource that is predicted to deplete within the next century (Cordell *et al.* 2009, Oelkers and Valsami-Jones 2008). The most important use of phosphorus is the production of fertilizers. About 90% of mineral phosphorus is used in agriculture, but only about 20% of it reaches the food consumed globally, while most of it is wasted and end up in rivers and oceans (Childers *et al.* 2011). This further adds to the problem because excessive phosphorus is a serious pollutant in surface waters due to its role in causing eutrophication (Smith and Schindler 2009).

The two most promising alternative sources of phosphorus are municipal wastewater treatment plant and livestock farm effluents (Naidu *et al.* 2012). Approximately 40% of rock phosphorus ends up in animal wastes (Cordell *et al.* 2009, Rittmann *et al.* 2011). Several studies have been devoted to developing processes for recovering the phosphorus from these waste sources. The most well-studied method is through chemical precipitation by the

addition of metal salts, most notably Mg and Ca because of the applicability of their precipitates directly as fertilizers (Rittmann *et al.* 2011). Precipitation of phosphorus with Mg as magnesium ammonium phosphate hexahydrate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) or struvite is most preferred because it recovers two important nutrients (P and N), simultaneously, and is known to have ideal fertilizer properties. The study of struvite precipitation first gained attention when it was found to cause scaling in pipes thus necessitating its removal (Petzet and Cornel 2012, Sharp *et al.* 2013). Alternatively, precipitation with calcium as hydroxyapatite (HAP) ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) is also common due its similarity to rock phosphate in form thus making it a viable replacement for it as raw material in the chemical industry (Cornel and Schaum 2009).

Dairy industry waste is the most abundant nutrient source in the agricultural sector (Hung *et al.* 2005, Karunanithi *et al.* 2016) and thus is one of the most promising alternative sources for recovered phosphorus. The challenge, however, is that these wastes can contain high amounts of metal ions and suspended solids (SS) that can potentially inhibit phosphorus precipitation (Huchzermeier and Tao 2012, Acelas *et al.* 2014, Tao *et al.* 2016). For struvite precipitation, one of the major inhibitors is the calcium ion (Acelas *et al.* 2014, Ye *et al.* 2011), which is present in dairy wastewaters at high concentrations (Kataki *et al.* 2016). A few studies have found that organic matter can also potentially inhibit phosphorus precipitation. However, most of the already limited existing studies have focused on natural organic matter particularly HS (Zhou *et al.* 2015, Song *et al.* 2006, Zhang *et al.* 2015).

*Corresponding author, Professor
E-mail: ub1905ub@korea.ac.kr

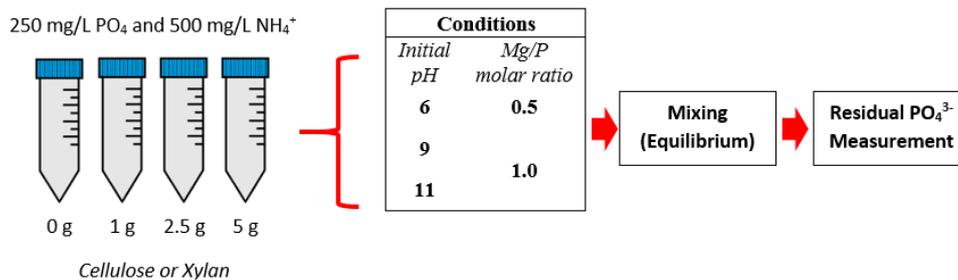


Fig. 1 Schematic diagram for cellulose and xylan experiment

In practice, post-anaerobic digestion streams are the prime targets for phosphorus recovery due to high nutrient concentrations and relatively stable flow rates (Egle *et al.* 2015). However, for dairy manure and wastewater, other organic substances such as fiber, in the form of cellulose, hemicellulose and lignin can be present in high amounts (Burke *et al.* 2005, MacConnell and Collins 2007). Although these volatile organic matters are expected to degrade after anaerobic digestion, studies have found that a significant amount remains undigested (Pelaez-Samaniego *et al.* 2017, Tambone *et al.* 2009).

At present, little information is known about the effect of these organic matter on phosphorus precipitation. The aim of this study was to understand and compare the effect of and hemicellulose on phosphorus precipitation as struvite and calcium phosphate with respect to the quantity of phosphorus removed and quality of the precipitates. The effect on precipitate quality was studied by analyzing the changes in structure and morphology using XRD and SEM analysis, respectively.

2. Material and methods

2.1 Chemicals

Potassium phosphate tribasic (K₃PO₄, ≥ 98.0%) was purchased from Junsei Chemical Co., Ltd., Japan. Ammonium chloride (NH₄Cl, ≥ 98.5%) and magnesium chloride hexahydrate (MgCl₂·6H₂O, ≥ 98.5%) were purchased from Samchun Pure Chemical Co., Ltd., South Korea. Calcium chloride (CaCl₂, ≥ 93.0%) was purchased from Daejung Chemicals and Metals Co., Ltd., South Korea. Cellulose (≥ 98%) was purchased from Sigma-Aldrich Co., Ltd., USA. Xylan from corn core (≥ 75% xylose residue) was purchased from Tokyo Chemical Industry Co., Ltd., Japan.

2.2 Batch tests

Phosphorus precipitation was achieved through batch tests using synthetic wastewater solutions (SWS). The solutions were to contain 250 mg/L of PO₄³⁻, 500 mg/L NH₄⁺, and varying concentrations of Mg²⁺ or Ca²⁺ based on selected Mg/P and Ca/P molar ratio. The three selected molar ratios were based on stoichiometric equivalent, 50% and 100% excess of the metal ion concentration based on struvite and HAP precipitation with magnesium and

calcium, respectively. For example, since 1 mol of PO₄³⁻ stoichiometrically requires 1.67 mol of Ca²⁺ to form 1 mol of HAP (or 1.0 Ca:P molar ratio), therefore 50% excess of Ca²⁺ is equivalent to 2.5 mol Ca²⁺ for 1 mol of PO₄³⁻ (or 2.5 Ca:P molar ratio). Stock solutions were made by dissolving potassium phosphate tribasic (K₃PO₄), ammonium chloride (NH₄Cl), magnesium chloride hexahydrate (MgCl₂·6H₂O), and calcium chloride (CaCl₂) in ultrapure water to produce the SWS for PO₄³⁻, NH₄⁺, Mg²⁺ and Ca²⁺, respectively. Initial solution pH was also varied by the addition of appropriate amounts of 1.0 M and 2.0 M NaOH or 2.0 M HCl solutions.

2.2.1 Struvite precipitation test in the presence of cellulose and hemicellulose

Two major components of organic matter (OM) present in dairy manure, cellulose and hemicellulose, were selected to understand the effect of OM on struvite precipitation. Varying amounts of cellulose and hemicellulose (as xylan) were added to SWS containing PO₄³⁻ and NH₄⁺ in 50 mL conical tubes. Each SWS were then spiked with appropriate volumes of Mg²⁺ stock solution corresponding to the Mg/P molar ratio being tested. The solutions were then allowed to reach equilibrium by continuous mixing using a tube rotator. The equilibrium concentration of free reactive PO₄³⁻ was then measured to quantify phosphorus removal. Fig. 1 shows a schematic diagram of this experimental procedure. All experiments were done in triplicates.

2.2.2 Struvite and hydroxyapatite precipitation in the presence of low soluble xylan concentration

After investigating struvite formation in the presence of two different types of OM, the effect of relatively low xylan concentration on phosphorus removal by struvite and hydroxyapatite precipitation was studied. Variable concentrations of xylan (0, 0.6 and 1.2 g/L) based on typical hemicellulose concentrations in anaerobically digested dairy manure filtrate (Tambone *et al.* 2009, Huchzermeier and Tao 2012, Tao *et al.* 2016) was tested. Batch precipitation tests were conducted using a jar tester at ambient temperatures. Immediately before the start of the reaction, one set of SWS was spiked with Mg stock solution, and the other with Ca stock solution. Upon the addition of Mg and Ca, the solutions were stirred at 260 rpm for 120 min. The pH was measured using Thermo Scientific Orion 4-Star pH meter after 60 min and appropriate amounts of 2.0 M NaOH or 2.0 M HCl solution was added to maintain the designated pH.

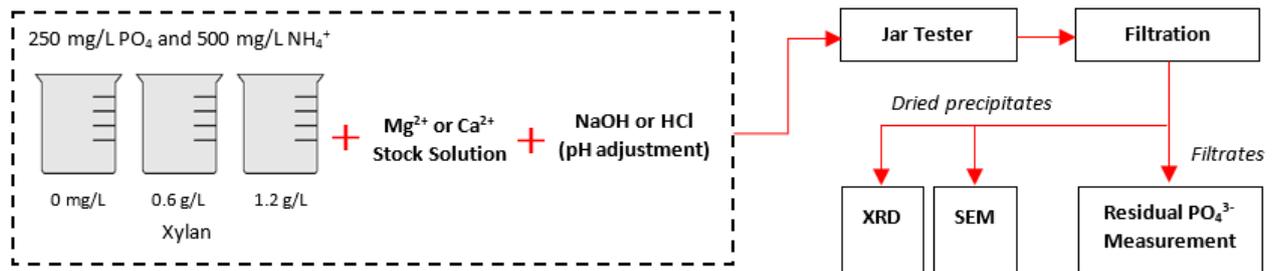


Fig. 2 Schematic diagram for xylan experiment on struvite and hydroxyapatite precipitation

Table 1 Parameters set for the experiments performed

pH	Xylan (g/L)	Molar ratio	
		Mg/P	Ca/P
<i>Variable pH</i>			
6	0		
9	0.6	1.5	2.5
11	1.2		
<i>Variable molar ratio</i>			
	0	1	1.67
9	0.6	1.5	2.5
	1.2	2	3.33

Two sets of experiments were performed. In the first experiment, the solution pH was varied while maintaining constant Mg/P and Ca/P molar ratios. The two sets of synthetic solutions were spiked with Mg and Ca stock solutions to attain 1.5 and 2.5 Mg/P and Ca/P molar ratios, respectively. In the second experiment, the Mg/P and Ca/P molar ratios were varied while maintaining constant solution pH. For the Mg precipitation, each solution was spiked with Mg stock solution corresponding to 1, 1.5 and 2 Mg/P molar ratio. For the Ca precipitation, they were spiked with Ca stock solution corresponding to 1.67, 2.5 and 3.33 Ca/P molar ratio. Table 1 summarizes the parameters for this experiment. All experiments were done in triplicates.

After 120 min, the final solutions were then filtered using a vacuum filtration system and GF/C grade glass microfiber filters (Whatman, UK). The residues collected were dried in a desiccator cabinet at ambient conditions for 24 hours. The filtrates were collected for compositional analysis. Fig. 2 shows the schematic diagram for the entire experimental procedure.

2.3 Chemical and instrumental analyses

Phosphorus removal efficiency (PRE) was quantified based on the concentration of residual PO_4^{3-} which was measured using molybdovanadate methods (HACH, USA) with a DR6000 UV/VIS spectrophotometer (HACH, USA). The precipitates were characterized by SmartLab X-ray diffractometer (Rigaku, Japan). The morphology of the collected precipitates was analyzed using JSM-6500 scanning electron microscope (Jeol, Japan).

2.4 Visual MINTEQ

Visual MINTEQ 3.1 was used to simulate the effect of

dissolved organic matter (DOM) on phosphorus precipitation with Mg^{2+} and Ca^{2+} . The Stockholm Humic Model (SHM) was used to simulate effects of humic substances as fulvic acid. Initial conditions were set to be the same as in the batch experiments for low xylan concentrations. Fixed pH and molar ratio of Mg/P and Ca/P were varied. DOM concentration was set at 0, 50, 100, 600, 1200 and 2000 mg/L. Equilibrium concentration data particularly that of PO_4^{3-} was then analyzed.

3. Results

3.1 Effect of cellulose and hemicellulose on struvite precipitation

First, the effect of insoluble cellulose and soluble xylan on phosphorus removal by struvite precipitation was studied. Residual PO_4^{3-} was measured after precipitation in the presence of varying amounts of cellulose and xylan to measure their influence on phosphorus removal efficiency (PRE). Fig. 3 shows the PRE after struvite precipitation at varying pH, Mg/P molar ratio, and cellulose and xylan concentration. From Figs. 3(a) and 3(b), varying the amount of cellulose from 0 to 100 g/L did not significantly affect residual PO_4^{3-} concentrations regardless of Mg/P ratio and pH. On the other hand, Figs. 3(c) and 3(d) shows that 100 g/L of xylan in solution resulted in reduced PRE, except at Mg/P molar ratio of 0.5 at pH 9.

3.2 Effect of low soluble xylan concentrations on struvite and hydroxyapatite precipitation

3.2.1 Variable pH

To study the potential inhibitory effects of relatively low soluble fiber xylan on the precipitation of phosphorus using Mg^{2+} and also its alternative Ca^{2+} , the amount of phosphate removed from the solutions were measured and the phosphorus recovery efficiency (PRE) was computed. The concentrations used were based on typical hemicellulose concentrations in anaerobically digested dairy manure filtrate (Tambone *et al.* 2009, Huchzermeier and Tao 2012, Tao *et al.* 2016). PRE was computed based on the measured residual reactive phosphate in the collected filtrates. Fig. 4 shows the measured PREs at different pH and xylan concentrations after Mg and Ca precipitation at 1.50 and 2.50 Mg/P and Ca/P molar ratio, respectively, at pH 9 and 11.

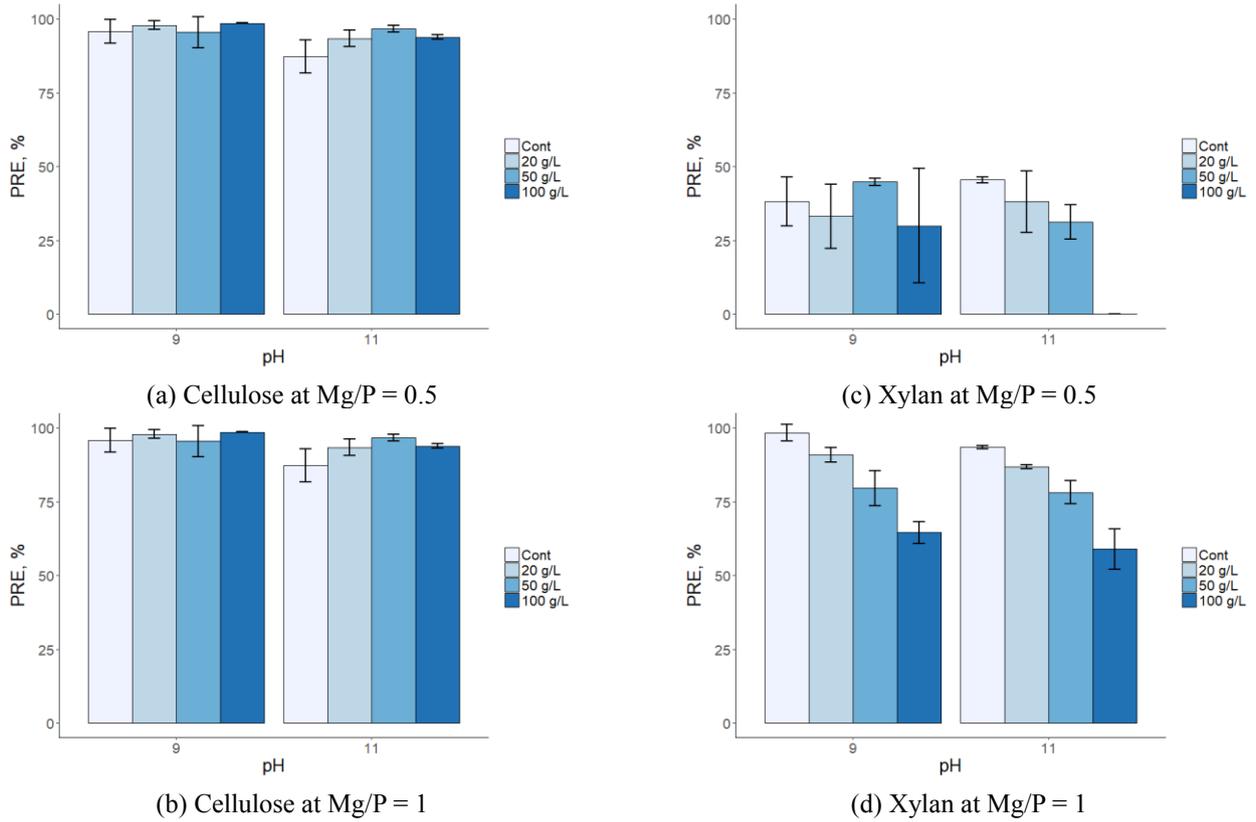


Fig. 3 Effect of different amounts of cellulose and xylan on phosphorus removal at varying Mg/P molar ratios

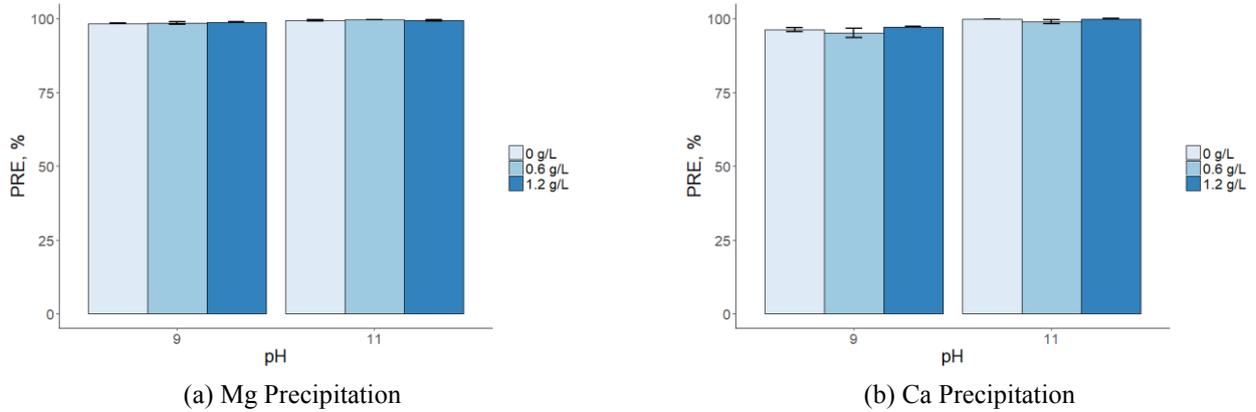


Fig. 4 Phosphorus removal rates for Mg and Ca precipitation at varying xylan concentration, and pH at 1.5 Mg/P and 2.5 Ca/P molar ratios

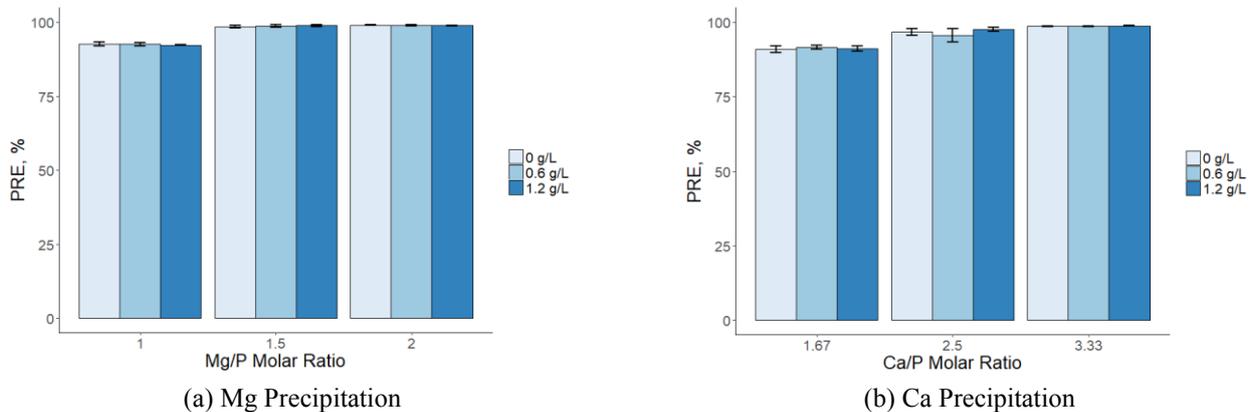


Fig. 5 Phosphorus removal rates for Mg and Ca precipitation at varying xylan concentration and molar ratios at pH 9

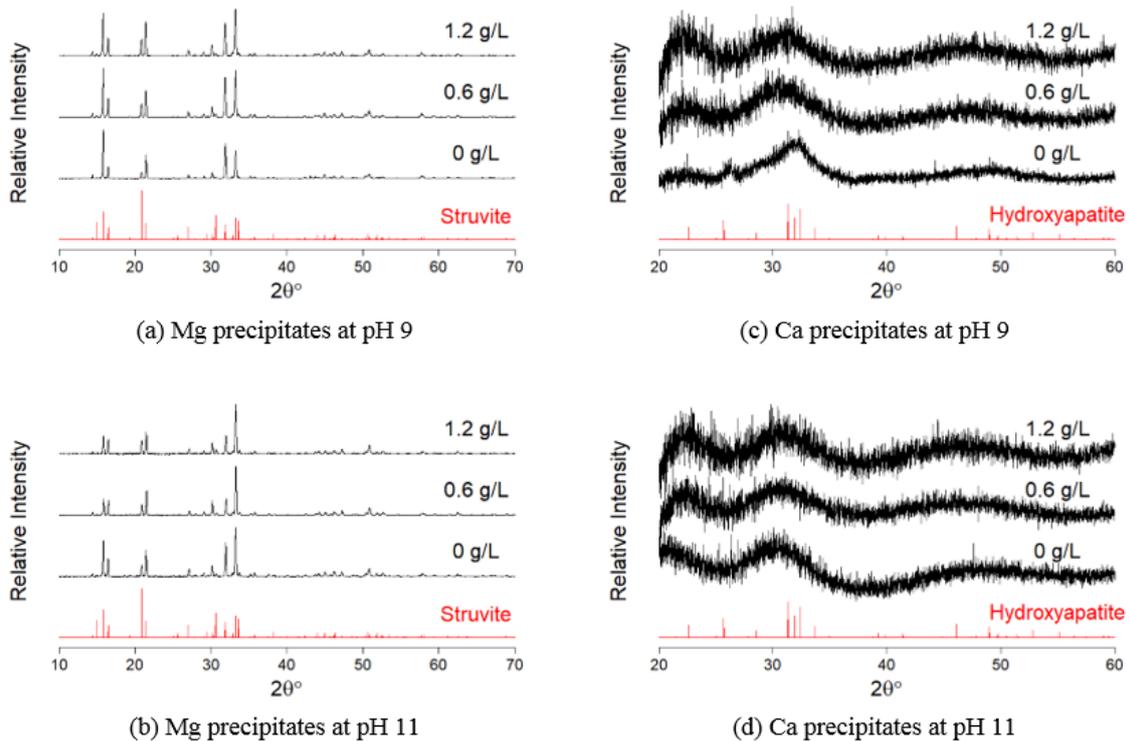


Fig. 6 XRD patterns for Mg and Ca precipitates at varying pH and xylan concentrations along with reference pattern

Based on the results, no significant differences were observed between the PRE in the absence and presence of 0.6 and 1.2 g/L of xylan at both pH. However, PRE improved at higher pH for Ca^{2+} precipitation.

The inhibitory effects of xylan on P precipitation using Mg and Ca was tested on low and high Mg/P and Ca/P molar ratios. Fig. 5 shows the measured PREs for both Mg and Ca precipitation at pH 9 at varying molar ratios. At stoichiometric ratios (1.00 for Mg and 1.67 for Ca), xylan did not significantly affect the removal of P for both Mg and Ca precipitation. At twice the stoichiometric molar ratios (2.00 for Mg and 3.33 for Ca), the same results were found.

3.3 Effect of soluble xylan on precipitate quality

3.3.1 X-ray diffraction analysis

X-ray diffraction (XRD) analysis was performed to identify and analyze the crystal structure of the collected precipitates. Figs. 6(a) and 6(b) shows the results from the XRD analysis of the precipitates for Mg and Figs. 6(c) and 6(d) for the Ca precipitates. The precipitates were identified to be struvite and amorphous hydroxyapatite for the Mg and Ca precipitates, respectively. For both precipitates, alterations in the relative intensities of some peaks were observed as the concentration of xylan increased. The diffraction peaks for the hydroxyapatite precipitates were very broad compared to struvite precipitates with sharp peaks.

3.3.2 Scanning electron microscopy analysis

Scanning electron microscopy (SEM) analysis of the precipitates was done to further understand the effect of xylan on the quality of the precipitates. Fig. 7 shows images of the struvite precipitates at pH 9 with 0 and 1.2 g/L xylan

concentrations. The struvite precipitates for both with and without xylan were observed to be needle-shaped, which is consistent with findings from other studies (Ye *et al.* 2014, Shih and Yan 2016, Li *et al.* 2015). Observation of Figs. 7(a) and 7(b) clearly suggests that the presence of xylan caused a decrease in the average particle size. At higher magnification as shown in Figs. 7(c) and 7(d), it can be observed that the precipitates in the presence of xylan had a slightly rougher surface compared to those precipitated in its absence. For the Ca precipitates, no valuable information could be collected on the effect of xylan on the average particle sizes due to the large variability of the particle sizes. A closer look at the surface of the precipitates shows no significant difference exists between those precipitated in the presence and absence of xylan.

4. Discussion

In the first experiment, a comparison was made on the effect of cellulose and hemicellulose on phosphorus removal by struvite precipitation. Natural cellulose biopolymer is made up of glucose residues and is known to be insoluble in water (Medronho *et al.* 2012). Hemicellulose, specifically xylan from corn core, on the other hand, is comprised of 4-O-methyl-D-glucuronic acid, L-arabinose and D-xylose residues in approximately 2.7:1.9 ratios, respectively (Oliveira *et al.* 2010, Kumar and Negi 2012), and is soluble in water. Residual PO_4^{3-} concentration was used as an indirect measure of phosphorus removal such that lower values meant more phosphorus was precipitated. As shown in Fig. 3, up to 100 g/L of xylan in solution resulted in less phosphorus precipitation, while

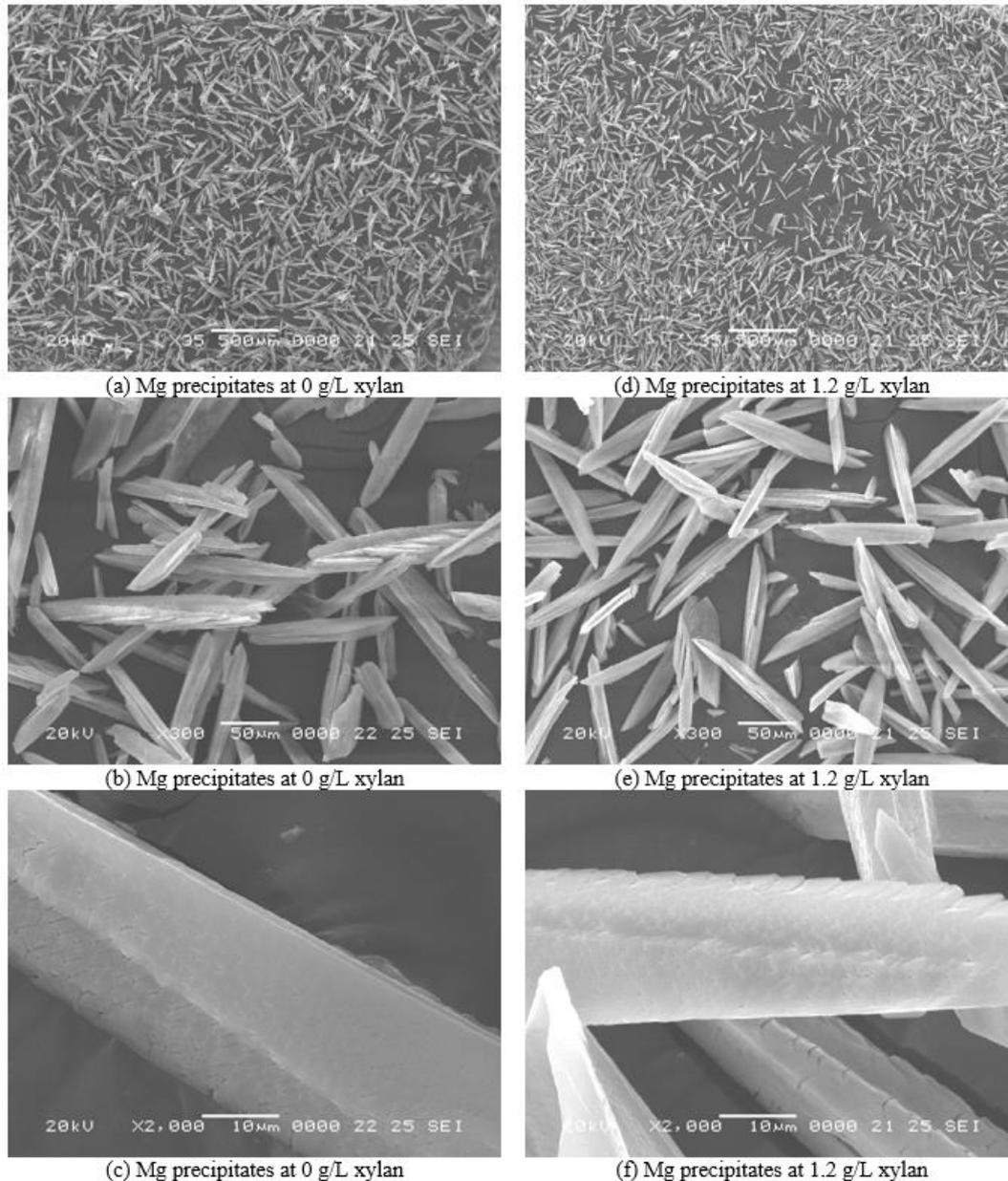


Fig. 7 SEM images of Mg precipitates at (a)-(c) 0 g/L and (d)-(f) 1.2 g/L xylan concentration at different magnifications

increasing the amount of cellulose to the same amount caused no significant effects even at a higher Mg/P molar ratio. This indicates that up to 100 g/L of xylan caused more inhibition compared to cellulose. This could be attributed to intermolecular interactions between the ions involved in phosphorus precipitation, such as PO_4^{3-} , NH_4^+ or Mg^{2+} and the carboxylic acid group in the glucuronic acid residues of the dissolved xylan (Fig. 8).

To further explore the influence of xylan, especially at relatively lower concentrations common in dairy wastewaters, its effect on phosphorus precipitation with Mg^{2+} and additionally the alternative Ca^{2+} was studied. Although calcium phosphate precipitation does not recover nitrogen, it remains an attractive alternative for phosphorus recovery because of lower operational costs (de-Bashan and Bashan 2004), its similarity to rock phosphate, the abundance of Ca^{2+} in dairy wastewaters (Cornel and Shaum

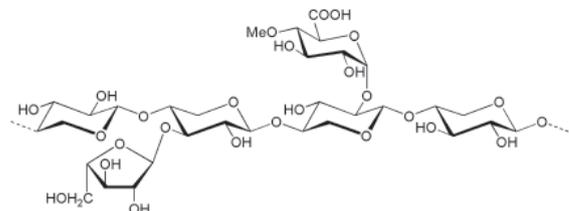


Fig. 8 Structure of (L-arabino)-4-O-methyl-D-glucurono-D-xylan (Heinze and Daus 2011)

2009) and its ability to inhibit struvite precipitation (Yan and Shih 2016). Phosphorus removal was measured at different conditions in the presence of 0, 0.6 and 1.2 g/L xylan, which are values that correspond to typical hemicellulose concentrations in anaerobically digested dairy manure filtrate (Tambone *et al.* 2009, Huchzermeier and Tao 2012, Tao *et al.* 2016). At constant molar ratio and

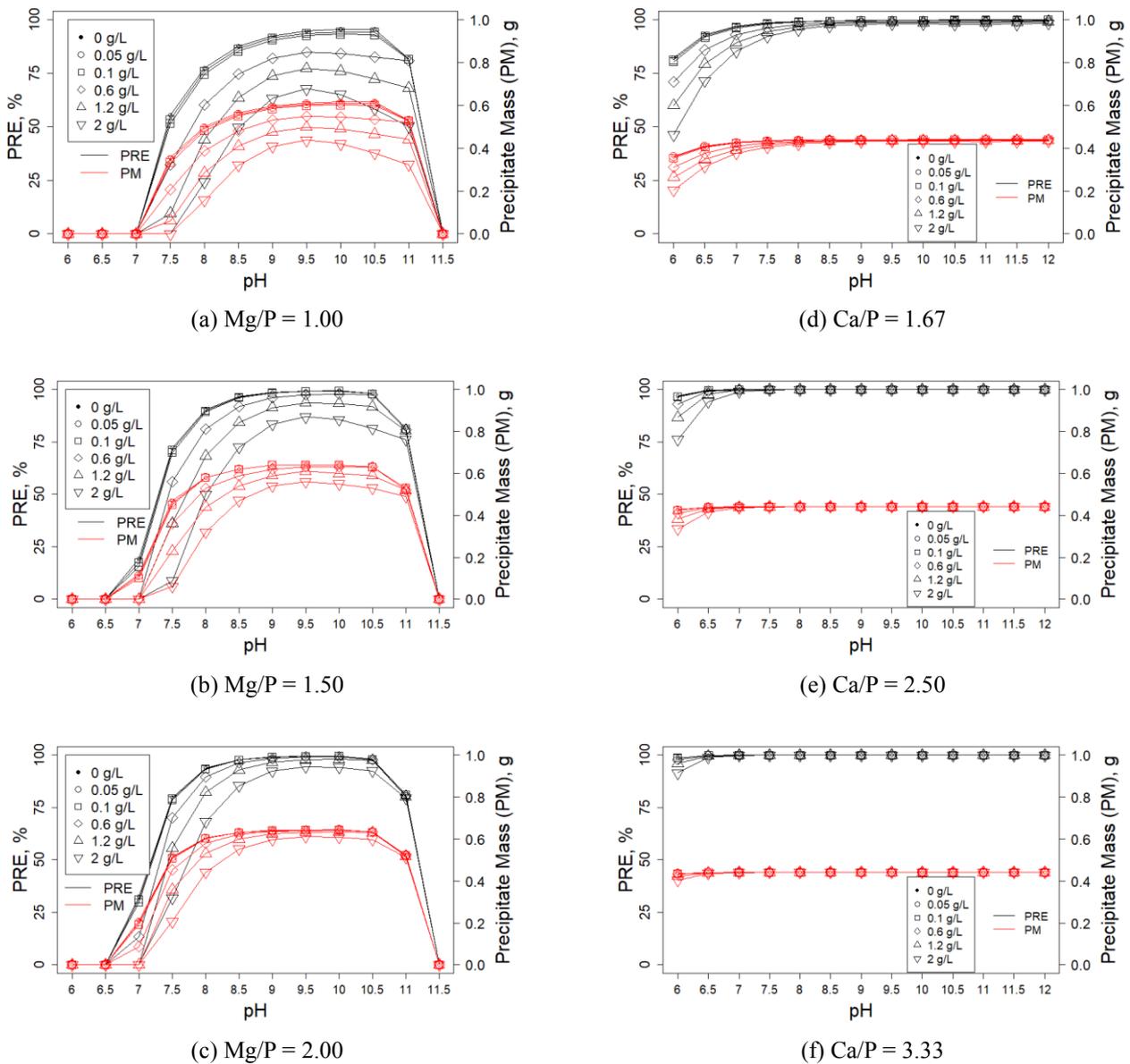


Fig. 9 MINTEQ model of the effect of HS on phosphorus removal by addition of (a)-(c) Mg and (d)-(f) Ca.

variable pH, no significant inhibition was observed at pH 9 and 11 for both Mg^{2+} and Ca^{2+} precipitation in the presence of up to 1.2 g/L of xylan. At constant pH, and variable Mg/P and Ca/P molar ratio, increasing xylan concentration to up to 1.2 g/L also did not cause significant inhibition even at low molar ratios for both Mg^{2+} and Ca^{2+} precipitation. No precipitates were recovered at pH 6 due to increased solubility of precipitates. It was evident, therefore, that at 1.2 g/L of xylan, intermolecular interactions between xylan molecules and relevant ionic species were not sufficient to cause significant inhibition despite having low Mg^{2+} and Ca^{2+} concentrations at low Mg/P and Ca/P molar ratios, respectively.

To better understand how DOM and the functional groups present affect phosphorus precipitation, equilibrium-based computer simulations were conducted using visual MINTEQ. These simulations probed the effect of DOM as

fulvic acid (FA), the more soluble component of HS, on the chemical equilibrium for the precipitation of struvite and hydroxyapatite. Fig. 9 shows how varying DOM concentrations affected phosphate precipitation for both Mg and Ca precipitation.

Based on the simulation results, a decrease in PRE could be observed even at 0.05 g/L concentration of both Mg and Ca precipitation (Fig. 9). Evidently, phosphorus precipitation further decreased at higher HS concentrations. However, higher Mg/P and Ca/P molar ratios decreased the effect of HS on the precipitation due to increased supply of Mg^{2+} and Ca^{2+} ions. This is because HS is well known to have high tendency to complex with metallic ions, such as Mg^{2+} and Ca^{2+} , due to the presence of carboxylic and phenolic acid groups (Janoš *et al.* 2008). The soluble component of HS, fulvic acid, contains several acidic functional groups amounting to 900 to 1400 mmol/100 g

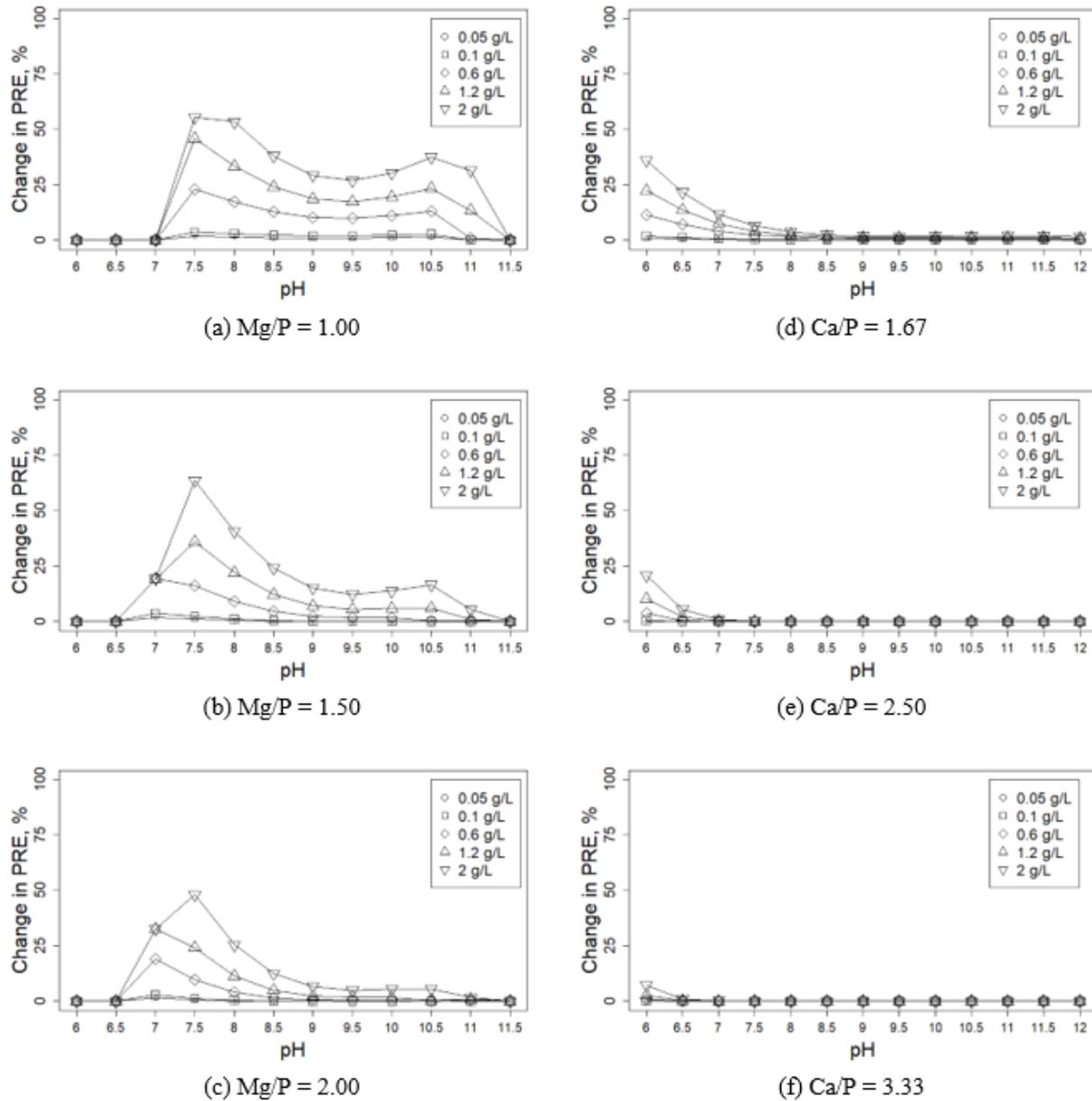


Fig. 10 Change in PRE in the presence of different DOM concentrations

total acidity (Peña-Méndez *et al.* 2005). This has also been observed in other experimental studies. Zhou *et al.* (2015) found that dissolved HS caused significant inhibition by complexing with Mg^{2+} species at weak alkaline pH, lowering the amount available for crystallization. However, inhibition was minimized at higher Mg/P molar ratios and higher pH. Song *et al.* (2006) found the same results with HS in Ca^{2+} precipitation. This tendency for HS to bind with metal ion species is due to the presence of carboxylic and phenolic acid groups (Zhou *et al.* 2005, Janoš *et al.* 2008) because of their high affinity to such ions.

However, as shown in previous Fig. 8, xylan from corn core roughly has about 200 mmol carboxylic acid per 100 g of monomer based on the approximate 2:7:19 ratio of 4-O-methyl-D-glucuronic acid, L-arabinose and D-xylose, respectively (Oliveira *et al.* 2010, Kumar and Negi 2012). It is therefore predicted that xylan would have lesser

affiliation with cationic species such as Mg and Ca.

PRE for Mg precipitation peaked at pH 10 for all Mg/P molar ratios before plummeting to zero beginning from pH 10.5 to 11.5. This decrease was because $Mg(OH)_2$ (brucite) was predicted to precipitate at higher pH by the simulation. It was also predicted that higher Mg/P molar ratio decreases the pH required to favor brucite precipitation. For Ca precipitation, on the other hand, only hydroxyapatite was predicted to precipitate. Higher Ca/P molar ratio decreases the pH required to reach peak PRE, after which the value remains constant. In comparing the effect of HS between Mg and Ca precipitation, it was clear that Ca precipitation of phosphorus was less affected. This could be due to the higher affinity of fulvic acid, the soluble component of HS, for Mg compared to Ca (Murray and Linder 1984).

In Fig. 10, the difference between the PRE in the presence and absence of HS was plotted. Consistently, the

magnitude of the effect of HS on Ca precipitation was less compared to Mg precipitation. Again, minimum change in PRE for Ca precipitation was reached at lower pH as Ca/P molar ratio was increased. For Mg precipitation, minimum change in PRE was attained at pH 9.5 on all Mg/P molar ratio, which is around the optimum pH for struvite precipitation (Li *et al.* 2012, Kim *et al.* 2017, El Diwani *et al.* 2007).

For the effect of organic matter on precipitate quality, analysis of the XRD patterns for both Mg and Ca precipitates showed that increasing xylan concentration caused changes in the relative intensities of some diffraction peaks. This suggests that the presence of xylan caused changes in the crystal structures of the precipitates. Furthermore, the observed decrease in crystal size based on SEM analysis for Mg precipitates in the presence of xylan supports the idea that it may have blocked active sites on the crystal surface, thus limiting further crystal growth (Zhang *et al.* 2015, Borsos *et al.* 2015).

Therefore, although xylan did not complex with the metal ion species, there is evidence that they may have adhered on the crystal surfaces thereby causing the precipitation of smaller crystals. This has many negative implications, particularly for engineering applications. For example, precipitate collection methods involving gravity could be affected by the smaller particle sizes. Furthermore, the adhesion of foreign matter on the precipitates could yield lower quality products. The mechanism of the adhesion of xylan, considering its chemical structure, on the crystal surfaces, however, is not clearly understood and will be explored in future studies.

5. Conclusions

Experiments have found that soluble total organic solids exhibit more inhibition to precipitation due to potential interaction with other dissolved ionic species involved in phosphorus precipitation. Soluble OM with higher total acidity, however, is more inhibiting than others with lower total acidities. In this case, xylan with low total acidity only exhibited significant inhibition at very high concentrations in synthetic wastewater (at up to 100 g/L). No significant inhibition was observed for Mg and Ca precipitation at relatively lower concentrations (1.2 g/L). Based on simulation results, the presence of acidic functional groups in OM is important for the limitation of phosphorus precipitation. Examination of the quality of the Mg and Ca precipitates formed in the presence of xylan, however, suggested that its presence altered the crystal structure of both precipitates and had caused the formation of smaller sized struvite crystals. Crystal sizes for Mg precipitates were also observed to be smaller when precipitated in the presence of xylan. A slight change in crystal surface was also observed on the surface of struvite crystals. This could have been due to xylan molecules adhering on the surface of the crystal potentially blocking active sites and limit further crystal growth. Smaller particle sizes will have negative practical impact, for instance in the collection of the precipitates by gravity settling because of poorer settleability of the precipitates.

Acknowledgments

This study was supported by the Korean Ministry of Environment (MOE) as “Waste to Energy and Recycling Human Resource Development Project”.

References

- Acelas, N.Y., Flórez, E. and López, D. (2014), “Phosphorus recovery through struvite precipitation from wastewater: effect of the competitive ions”, *Desalination Water Treat.*, **54**(9), 2468-2479.
- Borsos, A., Majumder, A. and Nagy, Z.K. (2015), “Multi-impurity adsorption model for modeling crystal purity and shape evolution during crystallization processes in impure media”, *Cryst. Growth Design*, **16**(2), 555-568.
- Burke, G., Singh, B.R. and Theodore, L. (2005), *Handbook of Environmental Management and Technology*, John Wiley and Sons, Inc., U.S.A.
- Childers, D.L., Corman, J., Edwards, M. and Elser, J.J. (2011), “Sustainability challenges of phosphorus and food: Solutions from closing the human phosphorus cycle”, *BioScience*, **61**(2), 117-124.
- Cordell, D., Jan-Olof, D. and White, S. (2009), “The story of phosphorus: Global food security and food for thought”, *Global Environ. Chang.*, **19**(2), 292-305.
- Cornel, P. and Schaum, C. (2009), “Phosphorus recovery from wastewater: needs, technologies and costs”, *Water Sci. Technol.*, **59**(6), 1069-1076.
- de-Bashan, L.E. and Bashan, Y. (2004), “Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997-2003)”, *Water Res.*, **38**(19), 4222-4246.
- Egle, L., Rechberger, H. and Zessner, M. (2015), “Overview and description of technologies for recovering phosphorus from municipal wastewater”, *Resour. Conserv. Recy.*, **105**, 325-346.
- El Diwani, G., Rafie, S.E., Ibiari, N.N.E and El-Aila, H.I. (2007), “Recovery of ammonia nitrogen from industrial wastewater treatment as struvite slow releasing fertilizer”, *Desalination*, **214**(1-3), 200-214.
- Heinze, T. and Daus, S. (2011), “Chapter 4 xylan and xylan derivatives-Basis of functional polymers for the future”, *Renewable Resources for Functional Polymers and Biomaterials: Polysaccharides, Proteins and Polyesters*, The Royal Society of Chemistry, U.K., 88-129.
- Huchzermeier, M.P. and Tao, W. (2012), “Overcoming challenges to struvite recovery from anaerobically digested dairy manure”, *Water Environ. Res.*, **84**(1), 34-41.
- Hung, Y., Britz, T. and van Schalkwyk, C. (2005), *Treatment of Dairy Processing Wastewaters*, in *Waste Treatment in the Food Processing Industry*, CRC Press, U.S.A., 1-28.
- Janoš, P., Kříženecká, S. and Madronová, L. (2008), “Acid–base titration curves of solid humic acids”, *React. Funct. Polym.*, **68**(1), 242-247.
- Karunanithi, R., Szogi, A., Bolan, N.S., Naidu, R., Ok, Y.S., Krishnamurthy, S. and Seshadri, B. (2016), *Phosphorus Recovery from Wastes*, in *Environmental Materials and Waste*, Elsevier Inc., U.S.A., 687-705.
- Kataki, S., West, H., Clarke, M. and Baruah, D.C. (2016), “Phosphorus recovery as struvite: Recent concerns for use of seed, alternative Mg source, nitrogen conservation and fertilizer potential”, *Resour. Conserv. Recy.*, **107**, 142-156.
- Kim, D., Min, K.J., Lee, K., Yu, M.S. and Park, K.Y. (2017), “Effects of pH, molar ratios and pre-treatment on phosphorus recovery through struvite crystallization from effluent of anaerobically digested swine wastewater”, *Environ. Eng. Res.*,

- 22(1), 12-18.
- Kumar, Samit and Negi, Y.S. (2012), "Corn cob xylan-based nanoparticles: Ester prodrug of 5-aminosalicylic acid for possible targeted delivery of drug", *J. Pharm. Sci. Res* **4**(12), 1995-2003.
- Li, H., Yao, Q.Z., Wang, Y.Y., Li, Y.L. and Zhou, G.T. (2015), "Biomimetic synthesis of struvite with biogenic morphology and implication for pathological biomineralization", *Sci. Rep.*, **5**, 7718.
- Li, Z., Ren, X., Zuo, J., Liu, Y., Duan, E., Yang, J., Chen, P. and Wang, Y. (2012), "Struvite precipitation for ammonia nitrogen removal in 7-aminocephalosporanic acid wastewater", *Molecules*, **17**(2), 2126-2139.
- MacConnell, C.B. and Collins, H.P. (2007), "Utilization of re-processed anaerobically digested fiber from dairy manure as a container media substrate", *Proceedings of the International Symposium on Growing Media*, Nottingham, U.K., September.
- Medronho, B., Romano, A., Miguel, M.G., Stigsson, L. and Lindman, B. (2012), "Rationalizing cellulose (in)solubility: reviewing basic physicochemical aspects and role of hydrophobic interactions", *Cellulose*, **19**(3), 581-587.
- Murray, K. and P. W. Linder (1984), "Fulvic acids: structure and metal binding", *J. Soil Sci.*, **35**(2), 217-222.
- Naidu, R., Lamb, D.T., Bolan, N.S. and Gawandar, J. (2012), *Recovery and Reuse of Phosphorus from Wastewater Sources*, in *Advanced Nutrient Management: Gains from the Past-Goals for the Future*, Occasional Report No. 25, Fertilizer and Lime Research Centre, Massey University, New Zealand.
- Oelkers, E.H. and Valsami-Jones, E. (2008), "Phosphate mineral reactivity and global sustainability", *Elements*, **4**(2), 83-87.
- Oliveira, E.E., Silva, A.E., Junior, T.N., Gomes, M.C., Aguiar, L.M., Marcelino, H.R., Araujo, I.B., Bayer, M.P., Ricardo, N.M., Oliveira, A.G. and Egito, E.S. (2010), "Xylan from corn cobs, a promising polymer for drug delivery: Production and characterization", *Bioresour. Technol.*, **101**(14), 5402-5406.
- Pelaez-Samaniego, M.R., Hummel, R.L., Jingwei Ma, W.L. Jensen, J., Kruger, C. and Frear, C. (2017), "Approaches for adding value to anaerobically digested dairy fiber", *Renew. Sustain. Energy Reviews*, **72**, 254-268.
- Peña-Méndez, E.M., Havel, J. and Patočka, J. (2005), "Humic substances—compounds of still unknown structure: applications in agriculture, industry, environment and biomedicine", *J. Appl. Biomed.*, **3**(1), 13-24.
- Petzet, Sebastian and Cornet, P. (2012), "Prevention of struvite scaling in digesters combined with phosphorus removal and recovery-The FIX-Phos process", *Water Environ. Res.*, **84**(3), 220-226.
- Rittmann, B.E., Mayer, B., Westerhoff, P. and Edwards, M. (2011), "Capturing the lost phosphorus", *Chemosphere*, **84**(6), 846-853.
- Sharp, R., Vadiveloo, E., Fergen, R., Moncholi, M., Pitt, P., Wankmuller, D. and Latimer, R. (2013), "A theoretical and practical evaluation of struvite control and recovery", *Water Environ. Res.*, **85**(8), 675-686.
- Shih, K. and Yan, K. (2016), *The Crystallization of Struvite and Its Analog (K-Struvite) from Waste Streams for Nutrient Recycling*, *Environmental Materials and Waste*, Elsevier, U.S.A., 665-686.
- Smith, V. H. and Schindler, D.W. (2009), "Eutrophication science: where do we go from here?", *Trends Ecol. Evol.*, **24**(4), 201-207.
- Song, Y., Hahn, H.H., Hoffmann, E. and Weidler, P.G. (2006), "Effect of humic substances on the precipitation of calcium phosphate", *J. Environ. Sci.*, **18**(5), 852-857.
- Tambone, F., Genevini, P., D'Imporzano, G. and Adani, F. (2009), "Assessing amendment properties of digestate by studying the organic matter composition and the degree of biological stability during the anaerobic digestion of the organic fraction of MSW", *Bioresour. Technol.*, **100**(12), 3140-3142.
- Tao, W., Fattah, K.P. and Huchzermeier, M.P. (2016), "Struvite recovery from anaerobically digested dairy manure: A review of application potential and hindrances", *J. Environ. Manage.*, **169**, 46-57.
- Yan, H. and Shih, K. (2016), "Effects of calcium and ferric ions on struvite precipitation: A new assessment based on quantitative X-ray diffraction analysis", *Water Res.*, **95**, 310-318.
- Ye, Z., Chen, S., Lu, M., Shi, J., Lin, L. and Wang, S. (2011), "Recovering phosphorus as struvite from the digested swine wastewater with bittern as a magnesium source", *Water Sci. Technol.*, **64**(2), 334-340.
- Ye, Z., Shen, Y., Ye, X., Zhang, Z., Chen, S. and Shi, J. (2014), "Phosphorus recovery from wastewater by struvite crystallization: Property of aggregates", *J. Environ. Sci.*, **26**(5), 991-1000.
- Zhang, Qi, Zhao, S., Ye, X. and Xiao, W. (2015), "Effects of organic substances on struvite crystallization and recovery", *Desalination Water Treat.*, **57**(23), 10924-10933.
- Zhou, P., Yan, H. and Gu, B. (2005), "Competitive complexation of metal ions with humic substances", *Chemosphere*, **58**(10), 1327-1337.
- Zhou, Z., Hu, D., Ren, W., Zhao, Y., Jiang, L.M. and Wang, L. (2015), "Effect of humic substances on phosphorus removal by struvite precipitation", *Chemosphere*, **141**, 94-99.

CC