

2020-01-08

# Phosphorus Recovery from Synthetic Municipal Wastewater through Lignin-induced Struvite Precipitation

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Li, M. (2020). Phosphorus Recovery from Synthetic Municipal Wastewater through Lignin-induced Struvite Precipitation (Master's thesis, University of Calgary, Calgary, Canada).

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Phosphorus Recovery from Synthetic Municipal Wastewater through  
Lignin-induced Struvite Precipitation

by

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE

DEGREE OF MASTER OF SCIENCE

GRADUATE PROGRAM IN CHEMICAL AND PETROLEUM ENGINEERING

CALGARY, ALBERTA

JANUARY, 2020

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## Abstract

Phosphorus recovery from wastewaters is essential to resolve the problems of the fast depletion of phosphate rocks due to the increasing demand for phosphorus fertilizer, and eutrophication due to excessive phosphorus discharging from wastewater.

In this study, the feasibility of adding alkaline lignin as seed materials to promote phosphorus recovery through fertilizer struvite ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ) crystallization from synthetic municipal wastewater was evaluated via batch experiments. Influencing factors tested included lignin dosage, Mg/P molar ratio, and pH. Lignin addition enhanced phosphorus recovery by 44.6% at a relatively low pH of 7.9 with Mg/P molar ratio of 1.5 and lignin dosage of 6 g/L, resulting in the reduced potential of co-precipitation and the cost-saving on alkali addition. As pH increases, however, this effect becomes less noticeable because of the higher solubility of lignin in wastewater. The characterizations by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy and zeta potential analysis, combined with precipitation modeling by a thermodynamic model software (Visual MINTEQ) were done to understand the process. Struvite-lignin clusters were identified, likely due to the in-situ-pH-favorable nucleation sites on lignin enhanced struvite crystallization.

As for the application in wastewater with different characteristics, the effect of lignin on enhancing phosphorus recovery efficiency is still significant under different  $\text{PO}_4\text{-P}$  and  $\text{NH}_4\text{-N}$  concentrations, indicating the effect-stability and availability of lignin in promoting struvite crystallization. As for the total suspended solids (TSS), the results

show that the effect of TSS on phosphorus recovery efficiency is not significant ( $p > 0.05$ ). Moreover, lignin is more efficient in increasing phosphorus recovery under relatively lower alkalinity while could reduce the co-precipitates potential under higher alkalinity.

Overall, this study provides a new possibility of the use of lignin from paper mill black liquor as seed material to enhance phosphorus recovery from wastewater, making the struvite production more efficient and cost-effective.

## **Preface**

This thesis is original, unpublished, independent work by the author, Mozhu Li, with the contribution of the individuals listed below.

The research shown in this thesis was conducted under the supervision of Dr. Qingye (Gemma) Lu and Dr. Yang Liu, both of which have made significant contributions to all areas of this project.

Huijuan Sun (Department of Civil and Environmental Engineering, University of Alberta) contributed to the X-ray diffraction (XRD) analysis used in Chapter 4 and 5.

## **Acknowledgement**

First and foremost, I would like to thank my supervisors Dr. Qingye (Gemma) Lu and Dr. Yang Liu for their supervision, advice and guidance from the early stages of research to putting this thesis together. I am grateful for the opportunity to work on such an integrated project and for the skills they have allowed me to develop as a part of their groups.

A big thanks to all past and present group members in the Dr. Lu and Dr. Liu group for the support throughout my time in the lab. I feel fortunate to have had the opportunity to work with members of both groups who diversified my knowledge. Special thanks to Huijuan Sun and Huixin Zhang for all the technical and writing support. I would also like to thank Abdul Mohammed from EPCOR for his helpful industrial suggestion.

I would like to acknowledge the University of Calgary and University of Alberta service labs that assisted with several sample analyses and the funding sources (Alberta Innovates-Alberta Bio Future Lignin Challenge 1.0 Program and Alberta Bio Future Lignin Pursuit Program, Canada Research Chair (CRC) in Future Community Water Services (Liu, Y.), NSERC Discovery Grant (Lu, Q.) and the Start-up Fund from the University of Calgary (Lu, Q.)).

Finally, I must thank my parents since I would not be here without my parents' love, support and encouragement. They have supported me through everything I have pursued. I would also like to thank my friends for their support and comfort on the rough days.

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## **List of Symbols, Abbreviations, & Nomenclature**

$K_{sp}$  – Solubility product

EDS – Energy dispersive X-ray spectroscopy

FBC - Fluidized-bed crystallizer

IAP – Ion activity product

ICP-OES – Induced coupled plasma optical emission spectrometry

ICSD – Inorganic crystal structure database

MAP - Magnesium ammonium phosphate

SEM – Scanning electron microscope

SI – Supersaturation index

TSS – Total suspended solids

XRD – X-ray diffraction

# **Chapter 1 Introduction**

## **1.1 Overview of Phosphorus Crisis**

Phosphorus is an essential nutrient to sustain life and also the main part of fertilizers. Currently, the main source of commercial phosphorus fertilizer is natural phosphate rocks, which distribute unevenly and are depleting fast (Su, Abarca, de Luna, & Lu, 2014). It is predicted that current phosphorus reserves will be exhausted as early as in 100 to 130 years (Li, Yin, Wang, Li, & Zhang, 2014). On the other hand, the high concentration of phosphorus in water bodies is an important inducement for eutrophication. A potential solution to address these issues is to recover phosphorus from wastewater for reuse as fertilizer rather than directly discharging phosphorus-containing wastewater.

## **1.2 Overview of Struvite in Phosphorus Recovery**

Recovering phosphorus through fertilizer struvite ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ) production is efficient and commonly applied due to its high phosphorus and nitrogen contents and high accessibility to plants under soil environment (Lee, Kumar, & Jeon, 2016).

To enhance the phosphorus and nitrogen recovery efficiency from wastewater simultaneously, efforts have been made on the optimization of the struvite formation conditions including pH, the molar ratio of Mg/P, influences of competing ions and their concentrations, mixing speed, and temperature (Hermassi, Valderrama, Dosta, Cortina, & Batis, 2015; Shih, Abarca, de Luna, Huang, & Lu, 2017; X. Ye et al., 2016;

Yigit & Mazlum, 2007). Additionally, seed crystal addition has also been applied to promote the struvite nucleation and crystallization process by providing deposit area, thereby reducing the induction period of crystal growth.

Currently the most commonly used seed material is struvite crystal. Compared to unseeded condition, the addition of struvite seeds increases the phosphorus recovery by 5%, the crystallization rate by 21%, (Yu et al. 2013). Some alternative seeds which have been used to facilitate the struvite crystallization are sand, stainless steel mesh, pumice stone, and borosilicate glass (Ali & Schneider, 2006; Le Corre, Valsami-Jones, Hobbs, Jefferson, & Parsons, 2007; Pakdil & Filibeli, 2008; Regy, Mangin, Klein, & Lieto, 2002). However, non-struvite seeds did not bring about significant increase in phosphorus recovery. Therefore, more suitable and efficient seed materials for struvite crystallization are required, to enhance phosphorus recovery efficiency and reduce chemicals costs.

### **1.3 Overview of Lignin as a Seed Material**

Lignin, as the second most abundant biomass present after cellulose, is a kind of natural, amorphous, inhomogeneous, nonlinear three-dimensional polymer with large surface area (Demirbas, 2004; Lalvani, Wiltowski, Murphy, & Lalvani, 1997). Compared to other natural materials, lignin materials are biodegradable and environmental friendly, and are ideal soil amendment for enhanced plant growth (Calvo-Flores, Dobado, Isac-García, & Martín-Martínez, 2015). Due to the alkaline pH of Kraft lignin solution (pH = 10.4), it is hypothesized that Kraft lignin may be used as the seeding materials for

struvite recovery, where lignin serves as the crystal nuclei and provide in-situ-pH-favorable nucleation sites for the crystal growth.

## **1.4 Overall Objectives and Thesis Outline**

The overall objective of this study is to evaluate a possible application of lignin from paper mill black liquor to promote phosphorus recovery from wastewater in both technological and economical aspects. For this purpose, the specific objectives are developed as follows:

1. Evaluate the feasibility of using lignin as seed material to enhance  $\text{PO}_4\text{-P}$  recovery by promoting struvite precipitation and the possibility to reduce the co-precipitates.
2. Optimize lignin-induced struvite precipitation parameters (lignin dosage, Mg/P molar ratio, and pH) from synthetic municipal wastewater based on  $\text{PO}_4\text{-P}$  recovery efficiency.
3. Investigate the stability of lignin effect under different  $\text{PO}_4\text{-P}$  and  $\text{NH}_4\text{-N}$  concentration, total suspended solids (TSS) and alkalinity at relatively low pH.
4. Explore the mechanism associated with the lignin-induced struvite precipitation process.

In this thesis, Chapter 1 provides an overview of information related to the study and describes the recent problems, objectives and outline of the thesis. Chapter 2 is a literature review of phosphorus removal and recovery methods from wastewater,



reported struvite recovery under different conditions and lignin characteristics and its application. Then Chapter 3 introduces the detailed analysis methods used in this study.

Afterwards, Chapter 4 and 5 are the main parts to address the above objectives. Chapter 4 evaluates the feasibility of lignin-induced struvite precipitation to recover phosphorous from synthetic biosolid digestate supernatant and also optimizes the operating conditions (lignin dosage, pH and Mg/P molar ratio) for this process. Chapter 5 investigates whether the effect of lignin is still significant at relatively lower pH in the synthetic wastewater with different characteristics (such as  $\text{PO}_4\text{-P}$  and  $\text{NH}_4\text{-N}$  concentration, total suspended solids (TSS) and alkalinity). Both Chapter 4 and 5 are also prepared as technical papers, which will be submitted for publication.

Finally, Chapter 6 summarizes the conclusions of this study and some recommendations for future work.

## **Chapter 2 Literature Review**

### **2.1 Phosphorus**

As an essential element to all life, phosphorus plays a key role in energy metabolism, genetic components, structural strength and photosynthesis process (Ruttenberg, 2013).

From an agricultural perspective, phosphorus is the main element of fertilizer as the range of phosphorus concentration is vital to sustain soil fertility and food crops production (Cordell, Rosemarin, Schröder, & Smit, 2011).

As for the global phosphorus cycle with human impact, the phosphorus cycle begins with the release of phosphate minerals by weathering. Then the inorganic soluble phosphorus is available for plants to be adsorbed. By the plant uptake, phosphorus ends in the food chain and is finally returned to environment via animal manure and human excreta (Ruttenberg, 2013).

Currently the non-renewable phosphate rocks is the main source for phosphorus fertilizer production. The natural deposits of phosphorus are not evenly distributed throughout the Earth. Main phosphate rock reserves are in China, USA, Morocco and Russia, which are contributing around 75% of world total phosphorus production (Heckenmüller, Narita, & Klepper, 2014). Moreover, The demand for food increases as the population grows, resulting in rapidly growing consumption of phosphorus. The International Water Management Association predicts that by 2050, phosphorus production will increase by 70% overall and even reach up to 100% in developing countries to meet the rapidly growing demand for phosphorus (Cieślik & Konieczka,

2017). Currently the non-renewable phosphate rocks is the main source for phosphorus fertilizer production. Therefore, many scientists claim that the phosphate reserves will be exhausted as early as in 100-130 years (Li et al., 2014).

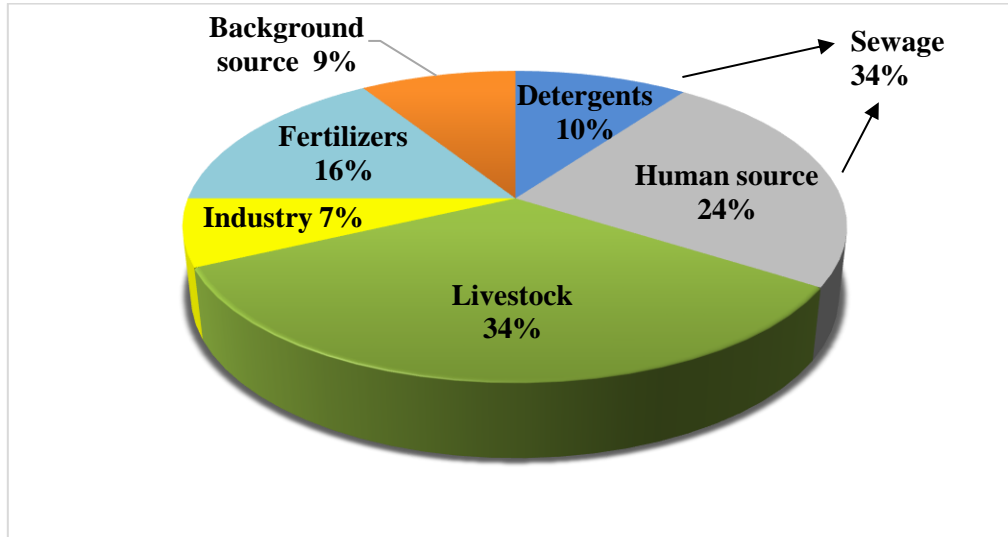
Eutrophication is the crisis caused by the excessive amount of phosphorus release into the environment. High turbidity caused by the overgrowth of aquatic plants decreases the dissolved oxygen and inhibits the penetration of light into lower depths of water bodies which results in reduced growth of submerged aquatic vegetation and benthic organisms (Md Mukhlesur Rahman et al., 2014). In the last half century, phosphorus concentrations in freshwater and terrestrial systems have increased by at least 75% while the estimated Phosphorus flow into the oceans from the total land areas has risen to 22 million tons per year (Syers, Bekunda, & Cordell, 2011).

Therefore, in order to meet the future demand for phosphate fertilizer and alleviate the shortage of existing resources, further solutions such as phosphorus recovery from wastewater are highly required.

## **2.2 Phosphorus Recovery Methods**

Phosphorus in wastewater originates from anthropogenic, livestock, natural or industrial sources. Municipal wastewater or sewage contains a significant amount of N and P along with organic and inorganic substances (De-Bashan, Hernandez, Morey, & Bashan, 2004), while industrial wastewaters are also an important source of phosphorus. Figure 2.1 shows the sources of P in the wastewaters (Md Mukhlesur Rahman et al.,

2014). In order to avoid unfavorable environmental impacts, phosphorus removal and recovery measurements must be implemented.



**Figure 2. 1** Sources of P in the wastewaters  
(Adapted from Md Mukhlesur Rahman et al., 2014)

Several phosphorus-recovery methods have been applied, the process summary of common phosphorus removal and recovery technologies is shown in Table 2.1 (Morse et al. 1998). Chemical precipitation is an early applied physicochemical process, which involves the addition of divalent or trivalent metal salts to wastewater. The insoluble metal phosphates will be precipitated then removed by gravity sedimentation or filtration (Bunce et al. 2018). The most suitable metals are iron and aluminum, added as chlorides or sulfates. Lime may also be used to precipitate calcium phosphate. This technology is easy to install and operate with a high P removal efficiency. However, the disadvantages of this method are the significant increase in sludge production and cost of chemical reagents (Morse, Brett, Guy, & Lester, 1998). As for phosphorus recovery, phosphorus bound to aluminum or iron in sludge is not particularly attractive,

as the plants have relatively low utilization of phosphorus in sludge and it is difficult to apply the sludge to agriculture as a fertilizer (Kyle & McClintock, 1995).

As for the biological process, the development of biological phosphorus removal method was based on the research in the late 1950s. It was found that activated sludge could absorb the phosphorus far more than the amount needed for normal biomass growth under certain conditions (Morse et al., 1998). This technology has the advantage of avoiding the use of chemicals and excess sludge production. However, more complex plant configurations and operating regimes are required, resulting in the difficulty to retrofit unless existing capacity is available or redistributed (Morse et al., 1998).

Crystallization is considered a useful and efficient method to recover phosphorus from aqueous phases. By adding the soluble metal salt (Mg or Ca salt), the liquid phosphorus (usually present as the phosphate anion) will be converted into the solid crystal (Hiroyuki & Katsutoshi, 2018). It has been reported that crystallization technology can achieve phosphorus removal efficiency of 80% or higher and the products also have high industrial and agriculture value (Ghosh, Lobanov, & Lo, 2019a). A few full-scale installations have been implemented around the world, such as Ostara, DHV Crystalactor or AirPrex. Nevertheless, this process also requires chemical addition, relatively complex design and operation.

Absorption and ion-exchange process can also be applied to recover phosphorus (Zhao & Sengupta, 1998). For the absorption process, phosphorus is removed by filter media,

which involves the movement of inorganic phosphorus from the wastewater to the surface or body of reactive components (e.g., calcium or iron) contained in the media (Brix, Arias, & Del Bubba, 2001). However, it was reported that P-removal was significantly reduced in the latter portion of a 10-year study (Shilton et al., 2006). Therefore, the stable performance of such materials over longer periods requires more research and investigation. In ion-exchange process, phosphate ions are interchanged between liquid wastewater and solid ion exchanger reversibly, which provide simultaneous phosphorus removal and recovery (Martin, Parsons, & Jefferson, 2009). The polymeric ligand exchanger is typically formed by immobilized particles of a metal cation, and P-selective nanoparticles (such as ferric oxide) are placed on its surface (Zhao & Sengupta, 1998). Much more work is still required to prove the possibility of this technology at full-scale, especially under the variable flow regime.

**Table 2. 1** Main phosphorus removal and recovery technologies---process summary (Morse et al. 1998)

Technology	Process summary	Main input	Auxiliary inputs	Main output	P form/content
Chemical precipitation	Addition of metal salt to precipitate metal phosphate removed in sludge	Wastewater (primary, secondary, tertiary effluent or side-stream)	Fe, Al, Ca May require anionic polymer	Chemical sludge	Mainly chemically bound as metal phosphate
Biological phosphorous removal	Luxury uptake of P by bacteria in aerobic stage following anaerobic stage	Wastewater (primary influent)	May require external carbon source (e.g. methanol)	Biological sludge	Phosphorous biologically bound
Crystallization	Crystallization as different kinds of phosphate using seed materials	Wastewater (secondary effluent or side-stream)	Salt reagent (such as MgCl <sub>2</sub> , CaCl <sub>2</sub> ·2H <sub>2</sub> O), NaOH, seed materials (such as struvite fines, sand)	Calcium phosphate (CP), Magnesium phosphate (MP), Magnesium ammonium phosphate (Struvite or MAP), Potassium magnesium phosphate (KMP)	Phosphate precipitates
Advanced Chemical Precipitation (HYPO)	Crystallisation of Phosphorous/organic matter and hydrolysis to give carbon source for N removal	Wastewater (primary influent)	Polyaluminium chloride (PAC)	Chemical sludge	Chemical sludge

Ion exchange (RIM-NUT)	Ion exchange removes ammonium and phosphate which are precipitated	Wastewater (secondary effluent)	H <sub>3</sub> PO <sub>4</sub> , MgCl <sub>2</sub> , NaCl, NaCO <sub>3</sub> , NaOH	Magnesium ammonium phosphate (Struvite or MAP)	Phosphate slurry
Phosphorous adsorbents	Adsorption and separation	Wastewater	N/A	No information	Calcium phosphate

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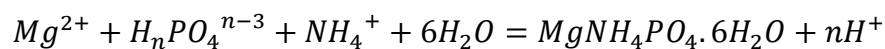


## 2.3 Struvite

### 2.3.1 Struvite Properties

Crystallization processes stand out because they not only achieve high phosphorus removal, but also recover phosphorus from wastewater as useful products eco-friendly. Struvite crystallization is an efficient and commonly applied method that uses magnesium salts to recover and reuse phosphate and ammonium simultaneously as slow-release fertilizers (Lee et al., 2016). Due to the low solubility of struvite, plants can take nutrients for a relatively long period and therefore require less application (Ghosh, Lobanov, & Lo, 2019b). The cheaper source of N and P in wastewater makes it a potential feedstock for the fertilizer industry, provided that the quality of its nucleation and recovery crystals can be controlled effectively (Md Mukhlesur Rahman et al., 2014).

Struvite ( $MgNH_4PO_4 \cdot 6H_2O$ , MAP) formation can be described by the following chemical reaction:

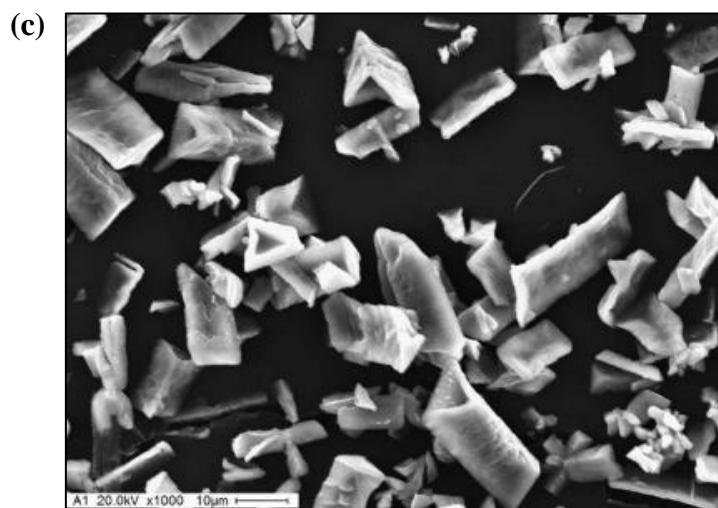
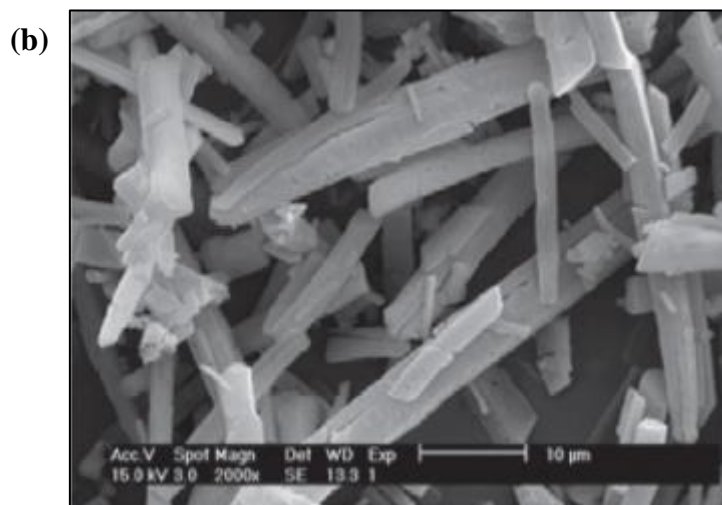
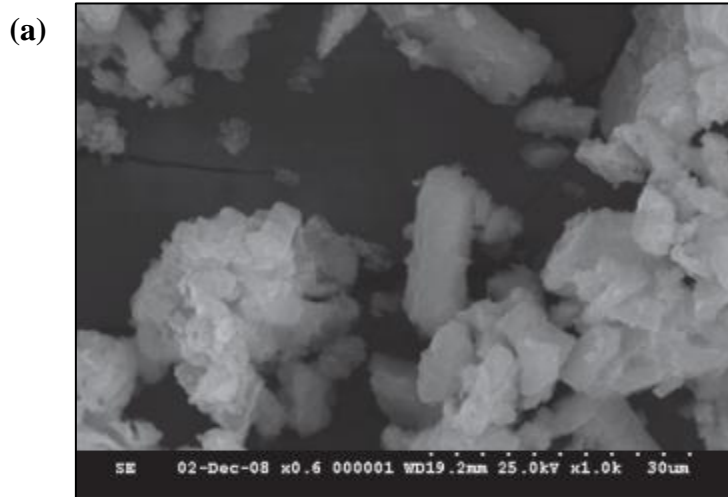


where  $n = 0, 1, 2$  as a function of solution pH. According to the above equation, a suitable molar ratio of magnesium (Mg), phosphorus (P) and ammonium ( $NH_4^+$ ), alkaline pH and proper mixing are necessary for the precipitation of struvite (Rahaman, Ellis, & Mavinic, 2008). Pure struvite is more likely fine white crystalline powder, which is sparingly soluble under neutral and alkaline conditions but readily soluble in

acid. Yellowish or brownish-white, orthorhombic or pyramidal crystals or in platy mica-like structures of struvite may also appear sometimes (Ehrlich, 2010).

The morphology of the struvite crystals have been described from various types of waste streams and processes (shown in Figure 2.2, please see Appendix of the copyright permissions ), which could appear as typical orthorhombic crystals (Huchzermeier & Tao, 2012), irregular-shaped coarse crystals (Md M. Rahman, Liu, Kwag, & Ra, 2011; T. Zhang, Ding, & Ren, 2009), and elongated needle-like structures (Le Corre et al., 2007; Matynia et al., 2013).

Several factors, such as the ion interactions, pH, temperature and reaction time will affect the struvite morphology (Tansel, Lunn, & Monje, 2018). Some compounds similar to struvite may be precipitated under given conditions. Irregular-shaped crystals may be observed as the co-precipitation of other ions will precipitated simultaneously.



**Figure 2. 2** SEM of different struvite crystals.

- (a) Irregular crystal (Md M. Rahman, Liu, Kwag, & Ra,2011)
- (b) Rod-like irregular crystal (Le Corre et al., 2007)
- (c) Orthorhombic crystal (Huchzermeier & Tao, 2012)

### ***2.3.2 Struvite Nucleation and Crystallization***

The primary particle formation processes occurring during crystallization are based on nucleation or crystal birth following by crystal growth until equilibrium. Both stages of crystallization depend on the degree of supersaturation. Supersaturation is the state of a solution where the solute concentration is greater than its value at equilibrium. As struvite contains three specific ions ( $Mg^{2+}$ ,  $NH_4^+$  and  $PO_4^{3-}$ ), and its solute concentration can be defined by the ion activity product (IAP). When the IAP is greater than the solubility product ( $K_{sp}$ ) the system is supersaturated and struvite may nucleate and grow, returning the system to equilibrium (Md Mukhlesur Rahman et al., 2014).

Nucleation can be either primary or secondary. Primary nucleation occurs at higher supersaturation and can be homogeneous and heterogeneous. Homogeneous nucleation takes place in absence of foreign particles in clear solution while heterogeneous is induced by impurities in the solution. Secondary nucleation occurs at lower supersaturation and in presence of existing crystals (Md Mukhlesur Rahman et al., 2014). Crystal growth is a diffusion and integration process, modified by the effect of solid surface on which it occurs.

The parameters that affect struvite crystallization include pH, Mg/P molar ratio, supersaturation, mixing and temperature. With these parameters, the kinetics of struvite formation can be altered and compared. It has also been shown that pH, temperature and other ions can control the supersaturation ratio (Jones, 2002).

### ***2.3.3 Struvite Recovery from Wastewater***

Struvite precipitation prevents the common scaling problem of the pipes and treatment facilities in wastewater treatment plants. On the other hand, struvite contain high concentration of phosphorus and can be used as slow release fertilizer in agriculture and also provide other necessary nutrients for plants such as magnesium and nitrogen (Munch & Barr, 2001). In addition, recovery of phosphorus via struvite formation would decrease the use of limited phosphate reserves to produce fertilizer.

Commercial struvite recovery facilities are currently in operation in countries such as USA, Canada, England, Japan, Germany, Australia, Italy and The Netherlands. Table 2.2 highlights the performance of some technologies occurring worldwide.

**Table 2. 2** Summary of performances of available technologies

Technology (Company)	Operation Location	Process Summary	P recovery efficiency(%)	References
Pearl® process (Ostara Nutrient Recovery Technologies Inc.)	Worldwide	Fluidized bed reactor with magnesium addition following Wasstrip® process	85	(Desmidt et al., 2015; Egle, Rechberger, Krampe, & Zessner, 2016)
AirPrex® process (Berliner Wasserbetriebe)	Germany and the Netherlands	Aeration with CO <sub>2</sub> stripping and MgCl <sub>2</sub> addition	80-90	(Desmidt et al., 2015; Egle, Rechberger, Krampe, & Zessner, 2016)
Crystalactor® (DHV)	China	Fluidized bed crystallizer that is cylindrical with Mg(OH) <sub>2</sub> addition	70-80	(Evelyn Desmidt et al., 2015)
PHOSPAQ™ (Paques®)	Netherlands	Aerated reactor with MgO addition	80	(Evelyn Desmidt et al., 2015)
Multiform (Multiform Harvest Inc.)	United States	Fluidized bed crystallizer that is conical with NaOH and MgCl <sub>2</sub> addition	80-90	(Ghosh et al., 2019a)

### ***2.3.4 Effects of Operating Conditions***

As one of the most influential parameters, the pH is related to the solubility of the product and the degree of solution supersaturation. The struvite precipitation should be carried out at an alkaline pH ranging from 7.0 to 11.0, but the optimal pH range is between 7.5 and 9.0 (Hao, Wang, Lan, & Van Loosdrecht, 2008; Hermassi et al., 2015). Shih et al. (2017) also demonstrated that the optimal pH condition is 9.5 to treat synthetic wastewaters in fluidized-bed crystallizer (FBC). As reported by Rahman et al. (2014), higher pH induced the high nuclear population density, which resulted in the appearance of smaller crystals and larger size diversity. Moreover, for high pH (>10) condition, the precipitations are not pure struvite and some impurities, such as  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}_3\text{PO}_4$  and  $\text{CaHPO}_4$ , may appear (Yigit & Mazlum, 2007).

Generally, for nearly all the waste streams,  $\text{Mg}^{2+}$  addition has been a necessary supplement to optimize the struvite crystallization process (Yee et al., 2019). From previous studies, a wide range of  $\text{PO}_4$  and Mg molar ratio was applied for struvite precipitation process. As for landfill leachate, the optimum  $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$  molar ratio to recover phosphorus was proposed as 1.15:1:1 (T. Zhang, Ding, & Ren, 2009). The struvite was crystallized using an inlet Mg / N / P molar ratio of 1.3 / 4 / 1 by Shih et al. (2017), with the obtained  $\text{PO}_4^{3-}$  recovery efficiency of 95.8%. Also, a significant promotion in removal efficiency was observed when the Mg/P molar ratio is more than 1.8 by (X. Ye et al., 2016). Moreover, increasing concentration of  $\text{Mg}^{2+}$  will increase

the crystal size and  $\text{PO}_4^{3-}$  removal efficiency meanwhile (Korchef, Saidou, & Amor, 2011).

In crystallization, the seed material can serve as a template, on which the crystalline material further accumulates. Seeds control the nucleation by providing surface area, thereby reducing the induction period of crystal development. Several characteristics are desired for the seed materials: large surface area, inertness to crystallizing liquor and isomorphism with precipitating crystal (Ali, 2005). Table 2.3 shows an overview of the struvite crystallization experiments.

Compared to unseeded condition, the addition of struvite seeds increases the phosphorus recovery by 5%, and the crystallization rate to 21% (Yu et al., 2013; T. Zhang, Ding, Ren, et al., 2009). When applying struvite seed to fertilizer wastewater, the induction time was also reduced up to 75 min, which depends on the supersaturation (Y. H. Liu, Rahman, Kwag, Kim, & Ra, 2011). Some alternative seeds used to promote struvite recovery are sand, stainless steel mesh, pumice stone and borosilicate glass with the high surface area (Ali, 2005; Le Corre et al., 2007; Pakdil & Filibeli, 2008; Regy et al., 2002). However, non-struvite seeds had no significant increase in phosphorus recovery, for example, the  $\text{PO}_4\text{-P}$  removals were 79% and 80% without and with stainless steel mesh at a lower Mg dosage, respectively (Le Corre et al., 2007). Non-struvite seeds also led to lower crystallization rate and longer induction time than struvite seeds (Le Corre et al., 2007). Table 2.4 is the summary of different seed material used in struvite precipitation and their effects on phosphorus recovery.



**Table 2. 3** An overview of struvite crystallization experiments

Source of wastewater	Additional chemicals	Mg/P molar ratio	pH range	Reactor type	P recovery efficiency (%)	References
Swine wastewater	MgCl <sub>2</sub>	1.2/1	8.0-9.0	Continuous flow reactor (CFR)	93	(Md M. Rahman et al., 2011)
Swine wastewater	MgCl <sub>2</sub>	0.8/1	7.82–8.92	Batch test in CFR	67	(Y. H. Liu et al., 2011)
Anaerobic digester side-stream	Mg(OH) <sub>2</sub> slurry	1.3/1	8.0-9.0	Pilot-scale MAP reactor	94	(Tünay, Kabdasli, Orhon, & Kolçak, 1997)
Sewage wastewater	By-product of magnesium oxide production (BMP)	1/1.6	8.28–8.41	Full scale sewage treatment plant	90	(Quintana et al., 2008)
Landfill leachate	MgCl <sub>2</sub> , MgO, Na <sub>2</sub> HPO <sub>4</sub>	1.1/1	8.4-9.0	Batch reactor	85.5	(T. Zhang, Ding, & Ren, 2009)
Poultry manure wastewater	MgCl <sub>2</sub> , MgSO <sub>4</sub> , MgO, KH <sub>2</sub> PO <sub>4</sub>	1/1	9.0	Batch reactor	85.4	(Yetilmezsoy & Sapci-Zengin, 2009)
Synthetic wastewater	NaCl <sub>2</sub> , (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> , NH <sub>4</sub> Cl	1.2/1–2.4/1	7.5–8.7	Bench-scale reactor	90	(Adnan, Koch, & Mavinic, 2003a)

**Table 2. 4** Different seed materials used in struvite precipitation and their effects on recovery

Seed used	Source of struvite	Seed size ( $\mu\text{m}$ )	Effects on struvite production	References
Struvite	Synthetic liquor and Sludge from wastewater plant	45–63	Crystals have similar shape with seed (no phase transformation during growth)	Ali (2005)
	Synthetic wastewater	Not Reported	Enhancement of crystallization by 19% at low P concentration; Increased crystal size, settle ability	Liu et al. (2008)
	Coking wastewater	Not Reported	Increase in recovery by approximately 5% (pH 9.5); No effect of overdosing of seed on recovery (pH 9.5)	Zhang et al. (2009)
	Synthetic wastewater	Not Reported	Reduction in induction time up to 75 min depending upon supersaturation	Liu et al. (2011)
Borosilicate glass	Synthetic wastewater	45-63	Slower reaction rate compared to struvite seed	Ali (2005)
Sand grain/quartz particle	Sludge liquor in wastewater plant	210-350	Recovery of 80% of P onto seed bed	Battistoni et al. (2000)
Stainless steel mesh	Synthetic wastewater	1000 $\mu\text{m}$ hole	No significant increase in crystallization; Reduction in struvite fine particle	Le Corre et al. (2007)
Pumice stone	Synthetic wastewater	Not Reported	No effect of seed dosing on recovery; Co-precipitation of Ca & silica on seed	Filibeli (2008)

Recently, there has been a growing interest in the technical and economic aspects of the nutrient recovery process to optimize operating conditions, increase process efficiency and reduce overall costs. Therefore, more suitable and efficient seed materials for struvite crystallization are required, to enhance recovery efficiency and reduce the complex pretreatment steps (e.g. pH adjustment) and the associated high cost of the chemicals.

## **2.4 Lignin**

### ***2.4.1 Lignin Characteristics***

As the second most abundant biomass present after cellulose, lignin covers about 20%-35% in the cell walls of most terrestrial plants. It is usually distributed around the cellulose strands and binds to the hemicellulose (Naseer et al., 2019). As a kind of natural, amorphous, inhomogeneous, nonlinear three-dimensional polymer, lignin acts as a binding agent for various fibrous materials. Based on its structural analysis, lignin has high molecular weight (typically yields between 1000 and 20,000 g/mol) and surface area of 180 m<sup>2</sup>/g (Demirbas, 2004; Lalvani et al., 1997).

Lignin consists of three basic phenylpropanol monomers known as monolignols: p-coumaryl, coniferyl and sinapyl alcohols (Naseer et al., 2019). When incorporated into a lignin polymer, the units that derived from the monolignols are called p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, respectively. The bonds between the three subunits are carbon-carbon bonds, ether bonds (mostly  $\beta$ -O-4 ether bonds) (Figueiredo, Lintinen, Hirvonen, Kostianen, & Santos, 2018).

It is reported that with every passing year 50 million tons of lignin produced annually by paper industries (Hatakeyama & Hatakeyama, 2010). Compared to other natural materials, lignin materials have a wide range of advantages, such as biodegradable properties, availability in various industrial wastes, carbon dioxide neutrality, environmental friendliness, cost-effectiveness and properties as antibacterial agents, stabilizers and antioxidants.

#### ***2.4.2 Lignin Extraction Methods***

Natural lignin is almost colorless, but shows brown or dark brown after treatment with acid or alkali (Agrawal, Kaushik, & Biswas, 2014a; Wang et al., 2016). In addition, the content of phenol, hydroxyl, carboxyl, and sulfonate functional groups is affected by the extraction method (Norgren & Edlund, 2014). The method used to extract lignin from lignocellulosic biomass is by gradually decomposing lignin into lower molecular weight (MW) products (Bruijninx & Weckhuysen, 2014). The extraction methods and sources of lignin can affect the physicochemical properties of the isolated products (Bruijninx & Weckhuysen, 2014). The present main processes for lignin extraction and extracted lignin properties are summarized and shown in Table 2.5.

Kraft lignin is the lignin used in this study, which is produced by the conventional process--Kraft process, which is the principal method used to process lignocellulose, and it accounts for approximately 85% of the whole lignin production (Tejado, Peña, Labidi, Echeverria, & Mondragon, 2007). In the Kraft process, the delignification process is carried out at high temperatures and high pH values, during which lignin is

dissolved in sodium hydroxide and sodium sulfide (white liquor) (Figueiredo et al., 2018). In this process, the initial pH is between 13 and 14 and temperature is around 170 °C, lignin dissolution occurs due to the reaction between hydroxide and hydrosulfide anions, thus resulting in the formation of alkali-soluble fragments. (Azadi, Inderwildi, Farnood, & King, 2013). Then the lignin can be separated from the remaining alkaline solution by an acid (e.g., sulfuric acid) mediated precipitation at the pH range 5 - 7.5 (Tejado et al., 2007).

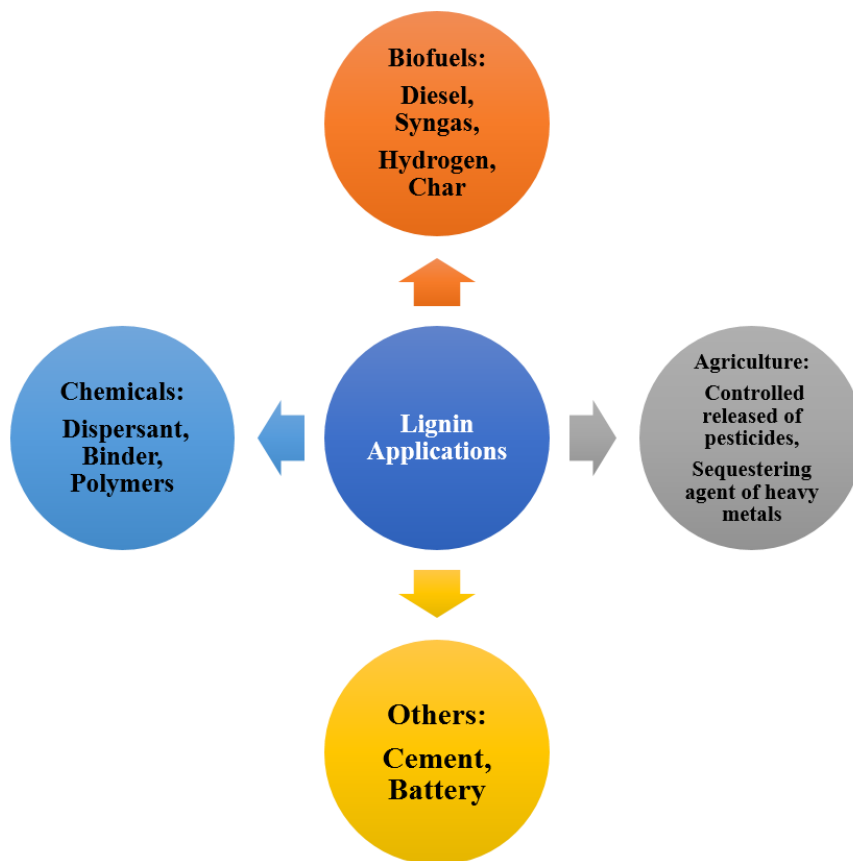
### ***2.4.3 Lignin Applications***

For many decades, lignin was just treated as a kind of waste material or as a very low-grade by-product from the pulping process. Nevertheless, its aromatic structure and specificity have received increasing attention in new applications in different fields today. Generally, lignin-based materials can be used primarily as fuels, chemicals, and polymers. For example, lignin can be used to alter and control the release of fertilizers and herbicides in agriculture, as dispersants and sizing agents in the paper industry, and as adsorbents for the removal of heavy metals from wastewater (Agrawal, Kaushik, & Biswas, 2014b; Azadi et al., 2013; Norgren & Edlund, 2014). The industrial application of lignin and its derivatives is shown in Figure 2.3

**Table 2. 5** Methodologies for lignin extraction and properties of extracted lignin

Extraction process	Treatment conditions	Solubility	Lignin MW (Da)	Functional groups (%)		
				COOH	OH phenolic	Methoxy
Kraft	1st: Sodium hydroxide and/or sodium sulfide (pH = 13–14 and T = 170°C) 2nd: Sulfuric acid (pH = 5–7.5)	Alkali; Organic solvents	1000–15,000	4.1*	2.6*	14*
Sulfite	Metal sulfite + Sulfur dioxide (Ca <sup>2+</sup> , Mg <sup>2+</sup> or Na <sup>+</sup> ) (pH = 2–12 and T = 120–180 °C, for 1–5 h)	Water	1000–50,000	No Data	No Data	No Data
Soda	13–16 wt% of Sodium hydroxide (T = 140–170 °C) + Anthraquinone (catalyzer)	Alkali	1000–3000	7.2–13.6	2.6–5.1	10–16
Organosolv	Organic solvents (ethanol, methanol, acetic and formic acid), usually mixed with water (T=170-190 °C)	Wide range of organic solvents	500–5000	3.6–7.7	3.4–3.7	15.1–19

\*Values referred to softwood.



**Figure 2. 3** Main industrial applications of lignin and its derivatives

(Adapted from Figueiredo et al., 2018)

Kraft lignin has a solution pH of 10.4, which falls within the range of pH required for struvite precipitation to happen. As such, it is hypothesized that adding an appropriate amount of Kraft lignin could induce the struvite precipitation in such ways the lignin could serve as the crystal nuclei and provide in-situ-pH-favorable nucleation sites for the crystal growth.

Additionally, as a natural and eco-friendly material, lignin and some modified lignin have beneficial effect on soil ecosystem. Lignin usually acts as a soil quality controller by retaining nutrients and water, promoting soil stabilization, suppressing disease and preserving soil. Moreover, for environmental safety, lignin plays a role in the reduction

of greenhouse gas emissions and biodegradation of organic pollutants (Calvo-Flores et al., 2015). Therefore, lignin has great potential to promote struvite crystallization and enhance phosphorus recovery efficiency meanwhile help improve the soil quality.



## **Chapter 3 Experimental Analysis Methods**

Several analysis methods are applied in this study to measure the phosphate concentration and characterize the precipitates. The introduction and the details of each method are discussed as follows.

### **3.1 Measurement of Phosphorus in Wastewater**

Colorimetric analysis and inductively coupled plasma optical emission spectroscopy (ICP-OES) are the two main methods for phosphorus determination and measurement in wastewater. Phosphorus concentration is usually measured colorimetrically, most commonly by the molybdate blue–ascorbic acid colorimetric method of Murphy and Riley (1962). As for the principle of this method, ammonium molybdate and antimony potassium tartrate react in an acidic medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration. The phosphorus concentration can be quantified by measuring the absorbance of the colored solution at 880 nm wavelength using a spectrophotometer. Only orthophosphate forms a blue color in this test. Polyphosphates and some organic phosphorus compounds may be converted to the orthophosphate form by sulfuric acid hydrolysis.

With the ICP-OES, the process is based on the ionization of a sample by an extremely hot plasma, usually made from argon gas for elemental detection and measurement analysis (Adesanwo, Ige, Thibault, Flaten, & Akinremi, 2013). A major advantage of

ICP-OES is its ability to determine several elements simultaneously in a wide range of concentrations.

The variations in P determination by the two analytical methods were mostly due to the differences in their ability to determine varying forms of phosphorus in wastewater. The differences between phosphorus determinations by the two analytical methods in the extractants were probably due to the presence of organic phosphorus, which was included in ICP determination but not in colorimetric determination (Adesanwo et al., 2013). In this study, the phosphorus concentration is measured by the two methods and their results are statistically similar probably because of the lack of organic phosphorus in the synthetic water. Also in real wastewater, other factors such as the presence of colloidal particles may also influence the measurement result of the two methods (Adesanwo et al., 2013).

According to the previous study, there were significant correlations between the two methods of phosphorus determination in the various waters and wastewaters with linear correlation coefficients ranging between 0.94 and 1.00, therefore it is possible to convert the result of one method to the other (Adesanwo et al., 2013).

### **3.2 X-ray Diffraction (XRD)**

X-ray diffraction (XRD) techniques are usually used for the identification of crystalline phases of various materials and the quantitative phase analysis subsequent to the identification. As a non-destructive technique, XRD requires minimal sample preparation to minimize errors in analysis (Idris & El-Zahhar, 2019).

The Bragg equation,  $n\lambda = 2d\sin\theta$  is one of the main principles of XRD analysis. In this equation,  $n$  is an integer,  $\lambda$  is the characteristic wavelength of the X-rays incident on the crystallize sample,  $d$  is the interplanar spacing between rows of atoms, and  $\theta$  is the angle of the X-ray beam relative to the planes. Based on this equation, X-rays scattered by the atoms in the plane of the periodic structure are in phase and diffracted in the direction defined by the angle  $\theta$  (Sima et al., 2016). The X-ray diffraction result consists of several sets of diffraction intensities and corresponding observation angles. The diffraction pattern can be considered as a chemical fingerprint and can be chemically identified by comparing the diffraction pattern to a database of known patterns, thus the material composition of the sample can be identified.

XRD technology has an advantage in elucidating the three-dimensional atomic structure of crystalline solids. The properties and functions of the material depend to a large extent on the crystal structure. Therefore, XRD has been widely used as an indispensable analysis method in materials research, development and production.

In this study, XRD (Rigaku Ultimate IV, Japan) was conducted with a  $\text{CuK}\alpha 1$  radiation ( $\lambda = 1.541 \text{ \AA}$ ), a scanning rate of  $0.06^\circ \text{ s}^{-1}$ , and incidence angles of  $5\text{-}90^\circ$  ( $2\theta$ ).

### **3.3 Scanning Electron Microscope (SEM)**

A scanning electron microscope (SEM) is a kind of electron microscope to analyze the that surface features, shape and size of the sampled particles (Idris & El-Zahhar, 2019).

SEM produces micro-images by scanning the sample surface with a focused beam

of electrons. Electrons interact with atoms in the sample and produce various signals containing information about the surface topography and composition of the sample. The electron beam is scanned in a raster scan pattern, and the image is produced by combining the position of the electron beam and the intensity of the detected signal.

Some special preparations for the SEM samples may be required to increase their electrical conductivity and stabilize them, otherwise they cannot withstand the high vacuum conditions and the high energy beam of electrons. For conventional SEM imaging, the sample must be electrically conductive at least on the surface and must be grounded to prevent static charge buildup. Non-conductive materials are usually coated with an ultra-thin conductive material (such as carbon or gold) which can be deposited on the sample by low vacuum sputtering or high vacuum evaporation (Abd Mutalib, Rahman, Othman, Ismail, & Jaafar, 2017). In this study, struvite samples were coated with carbon powder and mounted rigidly on a specimen holder using a conductive adhesive.

### **3.4 Energy Dispersive X-Ray Spectroscopy (EDS)**

Energy dispersive X-ray energy spectroscopy (EDS) is a type of chemical microanalysis technique used in conjunction with the SEM. The EDS detects the X-rays emitted from a sample during electron beam bombardment to characterize the elemental composition of the analytical volume.

When the sample is bombarded by the electron beam of the SEM, electrons are emitted from the atoms consisting of the sample surface. The resulting electron vacancies are

filled with higher state electrons and emit X-rays to balance the energy difference between the two electronic states. Then by evaluating the relationship between X-ray energy spectrum and count, the elemental composition of the sample volume can be determined (Abd Mutalib et al., 2017).

## **Chapter 4 Feasibility Evaluation and Optimization of Lignin-induced Struvite Precipitation**

### **Phosphorus Recovery from Synthetic Municipal Wastewater through Lignin-induced Struvite Precipitation**

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#### **4.1 Abstract**

Phosphorus recovery from water bodies is essential to resolve the problems of the fast depletion of phosphate rocks due to the increasing demand of phosphorous fertilizer and eutrophication due to excessive phosphorus discharging from municipal wastewater. In this study, the feasibility of adding alkaline lignin as seed materials to promote phosphorus recovery through fertilizer struvite ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ) crystallization from synthetic municipal wastewater was evaluated via batch experiments. Influencing factors tested included lignin dosage, Mg/P molar ratio, and pH. Lignin addition enhanced phosphorus recovery by 44.6% at a relatively low pH of 7.9 with Mg/P molar ratio of 1.5 and lignin dosage of 6 g/L, resulting in the reduced potential of co-precipitation and the cost saving on alkali addition. As pH increases, however, this effect becomes less noticeable because of the higher solubility of lignin in wastewater. The characterizations by X-ray diffraction, scanning electron

microscopy, energy dispersive X-ray spectroscopy and zeta potential analysis, combined with precipitation modeling by a thermodynamic model software (Visual MINTEQ) were done to understand the process. Struvite-lignin clusters were identified, likely due to the in-situ-pH-favorable nucleation sites on lignin enhanced struvite crystallization. This study provides a new possibility of the use of lignin from paper mill black liquor as seed material for phosphorus recovery from wastewater, making the struvite production more efficient and cost-effective.

## **4.2 Introduction**

Currently, the main source of commercial phosphorus fertilizer is natural phosphate rocks, which distribute unevenly and are depleting fast (Su et al., 2014). On the other hand, the high concentration of phosphorus in water bodies is an important inducement for eutrophication. A potential solution to address these issues is to recover phosphorus from wastewater for reuse as fertilizer rather than directly discharging phosphorus-containing wastewater. Recovering phosphorus through fertilizer struvite ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ) production is efficient and commonly applied due to its high phosphorus and nitrogen contents and high accessibility to plants under soil environment (Lee et al., 2016).

To enhance the phosphorus and nitrogen recovery efficiency from wastewater simultaneously, efforts have been made on the optimization of the struvite formation conditions including pH, the molar ratio of Mg/P, influences of competing ions and their concentrations, mixing speed, and temperature (Hermassi et al., 2015; Shih et al.,

2017; X. Ye et al., 2016; Yigit & Mazlum, 2007). Additionally, seed crystal addition has also been applied to promote the struvite nucleation and crystallization process by providing deposit area, thereby reducing the induction period of crystal growth. A desirable seed material requires a large surface area, inertness to crystallizing liquor, and isomorphism with precipitating crystal (Adnan, Dastur, Mavinic, & Koch, 2004). Currently the most commonly used seed material is struvite crystal. Compared to unseeded condition, the addition of struvite seeds increases the phosphorus recovery by 5%, the crystallization rate by 21%, (Yu et al. 2013).

Some alternative seeds which have been used to facilitate the struvite crystallization are sand, stainless steel mesh, pumice stone, and borosilicate glass (Ali & Schneider, 2006; Le Corre et al., 2007; Pakdil & Filibeli, 2008; Regy et al., 2002). However, non-struvite seeds did not bring about significant increase in phosphorus recovery, for example, the PO<sub>4</sub>-P removals were 79% and 80% without and with stainless steel mesh at a lower Mg dosage at pH 9, respectively (Le Corre et al., 2007). Non-struvite seeds also led to lower crystallization rate and longer induction time than struvite seeds (Ali & Schneider, 2006). Therefore, more suitable and efficient seed materials for struvite crystallization are required to enhance phosphorus recovery efficiency and reduce chemicals costs.

Lignin, as the second most abundant biomass present after cellulose, is a kind of natural, amorphous, inhomogeneous, nonlinear three-dimensional polymer with large surface area (Demirbas, 2004; Lalvani et al., 1997). It is estimated that over 30 million tons of lignin produced annually by paper industries (Hatakeyama & Hatakeyama, 2010). Compared to other natural materials, lignin materials are biodegradable and



environment-friendly, and are ideal soil amendment for enhanced plant growth (Calvo-Flores et al., 2015). Due to the alkaline pH of Kraft lignin (pH= 10.4), it is hypothesized that Kraft lignin may be used as the seeding materials for struvite recovery, where lignin serves as the crystal nuclei and provide in-situ-pH-favorable nucleation sites for the crystal growth.

The objective of this study is to examine the feasibility of using lignin as seed to promote struvite precipitation and explore the mechanism associated with this process. The optimal operating conditions including lignin dosage, Mg/P molar ratio, and pH will be obtained, and the co-precipitates with struvite will be predicated by Visual MINTEQ software and identified by characterization analysis. Overall, this study demonstrates a possible application of lignin from paper mill black liquor to promote phosphorus recovery from wastewater in both technological and economical aspects.

## **4.3 Experimental Materials and Methods**

### ***4.3.1 Materials***

This study was carried out using synthetic biosolid digestate supernatant for all batch experiments, following the real biosolid digestate supernatant wastewater composition (Yang et al., 2019). The main components of the synthetic wastewater and their concentrations are shown in Table 4.1. The reagent salts used for preparing the synthetic wastewater, sodium dihydrogen phosphate [ $\text{NaH}_2\text{PO}_4$ ] and ammonium chloride [ $\text{NH}_4\text{Cl}$ ] were purchased from Sigma Aldrich (analytical grade). To examine the impacts of magnesium on struvite recovery, chloride hexahydrate ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) of

various Mg/P molar ratios was added and results were compared.

The Kraft lignin used in this study was obtained from West Fraser Hinton Pulp (Alberta, Canada). This kind of lignin has faint woody odor and light to dark brown color. It has low solubility in water but is soluble in alkali solutions. The lignin contains low ash and low sulfur (0 to 3% by wt.%) content, with a specific gravity of 1.02-1.60.

**Table 4. 1** Composition of synthetic pre-Ostara<sup>®</sup> supernatant

Parameters	Mean $\pm$ SD
PO <sub>4</sub> -P (mg/L)	250.0 $\pm$ 10.2
NH <sub>4</sub> -N (mg/L)	1000.0 $\pm$ 20.5
Temperature (°C)	21.0 $\pm$ 1.5
pH <sub>initial</sub>	5.65 $\pm$ 0.60

\*SD: Standard deviation

### ***4.3.2 Struvite Precipitation Experiments***

Struvite precipitation experiments were conducted using magnetic stirrer with each experiment conducted in triplicates. To facilitate struvite precipitation, rapid-mixing at 200 rpm for 1 min was conducted, followed by slow-mixing at 60 rpm for 45 mins. The mixture in the beaker was then allowed to settle for 1 h. The supernatant was taken and filtered through a 0.45  $\mu$ m glass fiber filter for the residual PO<sub>4</sub>-P concentration measurement. After that, the precipitate was separated by centrifuging samples at 5000 rpm for 10 mins, washed three times with distilled water, and finally dried at 40°C overnight to obtain the dry precipitate for further characterizations.

The influencing factors including lignin dosage, reaction pH, and Mg/P molar ratio were studied to examine their impacts on phosphorus recovery. 1 M MgCl<sub>2</sub> was added to

adjust the Mg/P molar ratio and 1 M NaOH was used to adjust the pH to the desired value.

### ***4.3.3 Chemical Analysis and Calculation***

The PO<sub>4</sub>-P concentration in the solution was measured by Hach methods (TNT844, Hach, USA) before and after the reaction. The composition of the precipitate was analyzed via X-ray diffraction (XRD; Rigaku Ultimate IV, Japan) with copper radiation and peak comparison to the Inorganic Crystal Structure Database (ICSD). The morphology and elemental composition of the precipitates were determined via scanning electron microscopy (SEM; Zeiss Sigma 300 VP-FESEM, USA) and energy dispersive X-ray spectroscopy (EDS; Bruker EDS System, USA). The recovery efficiency of PO<sub>4</sub>-P was calculated by Eq. (1):

$$\text{Recovery efficiency} = \left( \frac{C_I - C_R}{C_I} \right) \times 100\% \quad (1)$$

where  $C_I$  is the initial concentration of PO<sub>4</sub>-P (mg/L) in the aqueous phase and  $C_R$  is the concentration of residual PO<sub>4</sub>-P (mg/L) after reaction.

The lignin precipitates were also characterized by XRD, SEM and EDS. The zeta potential of lignin was measured in folded capillary zeta cells on a zeta potential analyzer (Zetasizer nano series, Malvern, UK).

### ***4.3.4 Mineral Precipitation Modelling***

Supersaturation is the thermodynamic force driving crystallization and precipitation.

The supersaturation index (SI) of struvite can well reflect the thermodynamic and

crystallization behavior of struvite (Yanyang Zhang, Zhang, & Pan, 2015). As the phosphorus recovery efficiency and the crystal growth are affected greatly by on the chemical nature of the solution, the calculation of the supersaturation index (SI) is necessary to quantify these processes. The supersaturation index (SI) was calculated using Eq. (2) and (3), respectively:

$$SI = \lg \frac{IAP}{K_{SP}} \quad (2)$$

$$IAP_{struvite} = \{Mg^{2+}\}\{NH_4^+\}\{PO_4^{3-}\} \quad (3)$$

where IAP is the ion activity product,  $\{Mg^{2+}\}\{NH_4^+\}\{PO_4^{3-}\}$  indicate the ion activity of each component and  $K_{sp}$  is the solubility product of the precipitation phase, which is fixed at the given temperature and pressure (Mehta & Batstone, 2013).

The saturation index is the quantity used to determine the potential for a certain mineral to precipitate under the given conditions. When  $SI = 0$ , the solution is in equilibrium; when  $SI < 0$ , the solution is undersaturated and precipitation does not occur; and when  $SI > 0$ , the solution is supersaturated so precipitation can occur (E. Desmidt, Ghyselbrecht, Monballiu, Verstraete, & Meesschaert, 2012). A thermodynamic model software (Visual MINTEQ, ver.3.0) was used to calculate the supersaturation index (SI) and predict the potential precipitates in solution under different conditions.

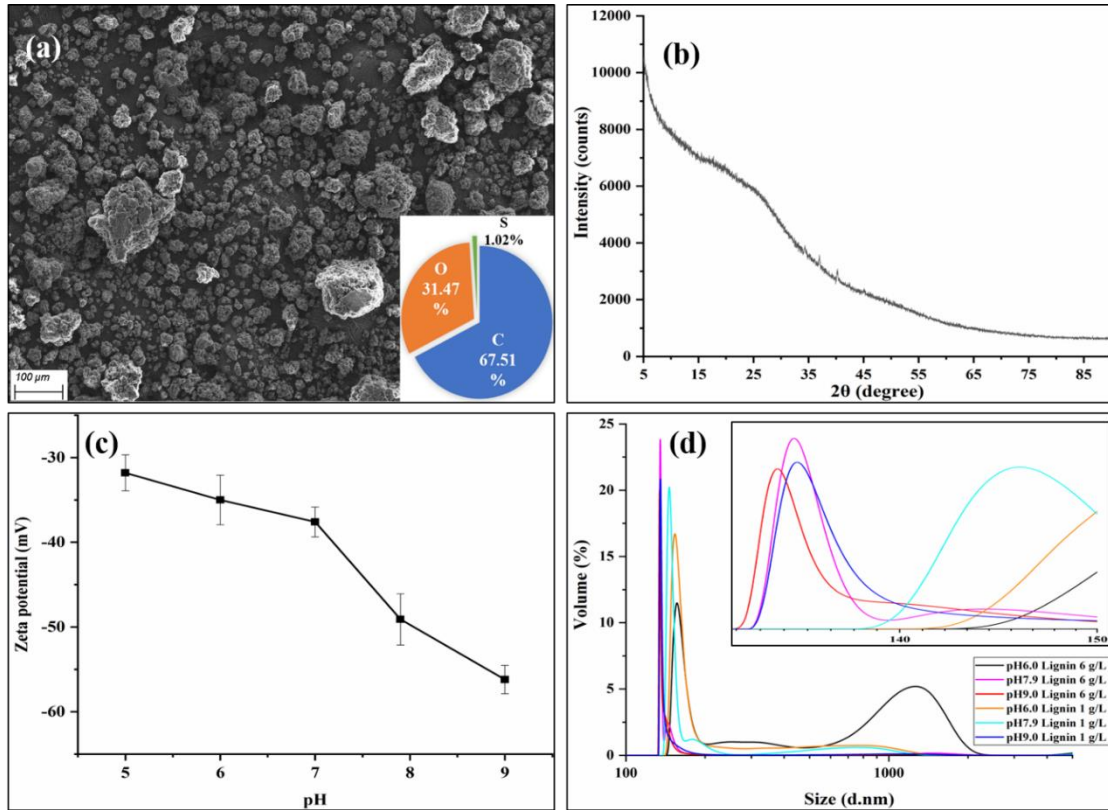
## 4.4 Results and Discussion

### 4.4.1 Characterization of Lignin

Figure 4.1 shows the various characterization results of Kraft lignin used in this study. The SEM imaging (Figure 4.1(a)) shows that lignin particles are amorphous with a rough surface, and size of larger particles is around 100  $\mu\text{m}$  due to aggregation, while the XRD analysis (Figure 4.1(b)) also illustrates that the structure of lignin is amorphous. As EDS result (Figure 4.1(a)) shows, the atom concentrations of carbon and oxygen are 67.51% and 31.47%, respectively, and the sulfur concentration is as low as 1.02%. Under room temperature, the zeta potentials of 20 mg/L lignin aqueous solution at pH of 7.9 and 9 are -49.1 mV and -56.8 mV, respectively (Figure 4.1(c)). As pH increases, the zeta potential remains negative and the absolute value increases as well, which indicates that the lignin suspension has relatively better stability at higher pH. The changing trend of lignin zeta potential at different pH is consistent with that obtained from the previous study (Klapiszewski, Królak, & Jesionowski, 2014).

For the size distribution of lignin in aqueous solution (Figure 4.1(d)), as pH decreases under the same lignin dosage, both of the size range and average size increase gradually, which is consistent with the previous study that the size of the lignin particles increased with decreasing pH, confirming that more and more lignin precipitated as the pH was subsequently decreased (Moreva, Alekseeva, & Chernoberezhskii, 2010). As lignin dosage increases, the average size increases as well and bimodal distribution occurs at lower pH, which is likely due to the aggregation, while no significant differences at

higher pH because of the higher solubility of lignin.



**Figure 4. 1** The characterization of lignin used in this study : (a) SEM image (x100 magnification) and EDS analysis (Atom %), (b) XRD analysis, (c) Zeta potential of 20 mg/L lignin at different pH and (d) Size distribution at different pH and dosage.

#### ***4.4.2 Impact of Lignin Concentration on Struvite Crystallization***

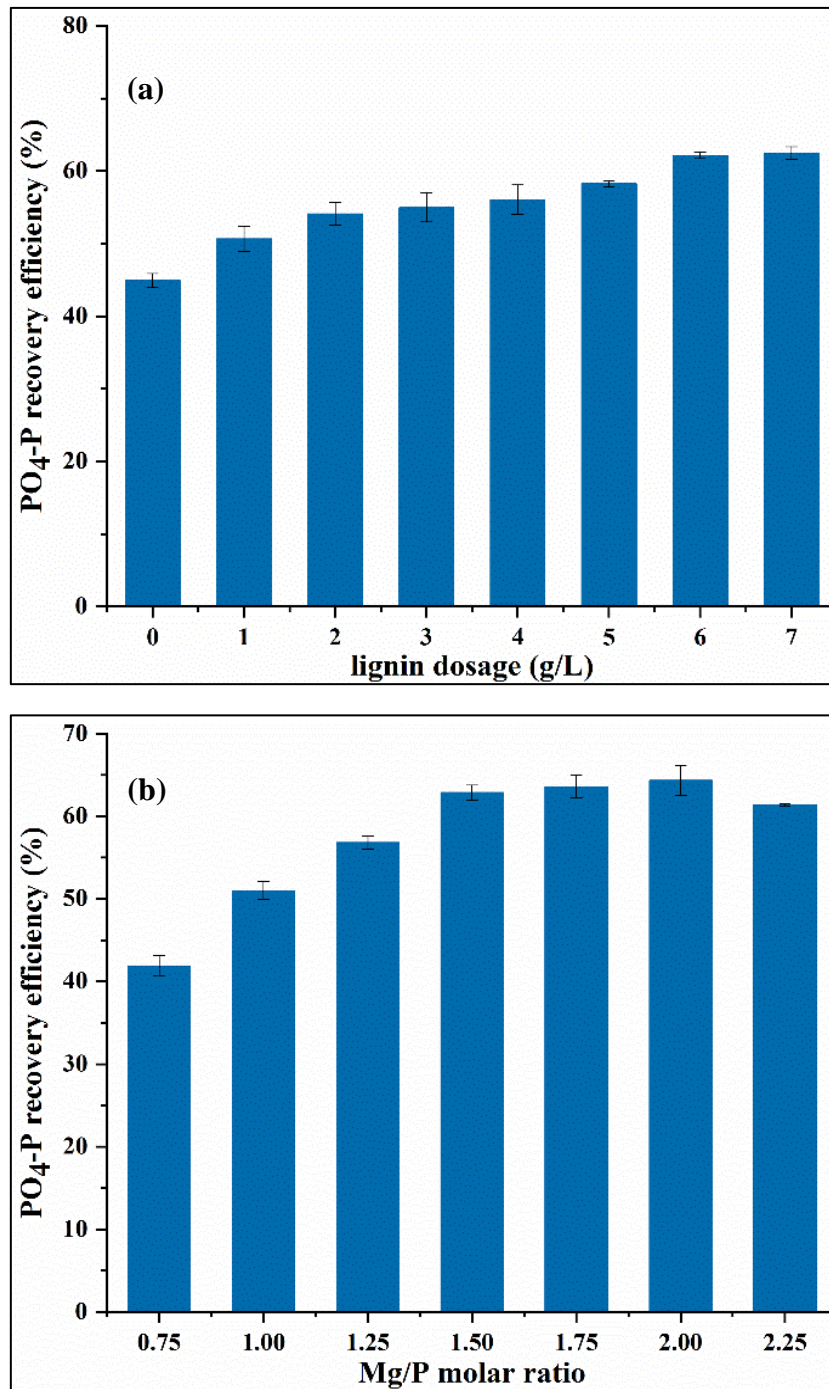
Based on the assumption that lignin could improve the recovery efficiency of PO<sub>4</sub>-P, different doses of lignin were added to the synthetic wastewater at the beginning of rapid mixing. Figure 4.2(a) shows the influence of lignin dosage on PO<sub>4</sub>-P recovery efficiency with a Mg/P molar ratio of 1.5. In the series of experiments, the initial pH was adjusted to 7.9 to mimic the pH of the raw biosolid digester supernatant.

The results indicate that the use of lignin contributes to an obvious enhancement on the phosphorus recovery. In comparison to no lignin addition without any seeding, addition of 6 g/L lignin improves the PO<sub>4</sub>-P recovery efficiency by 44.6% ( $p < 0.05$ ). For other non-struvite seed materials used in previous work, stainless steel mesh helped increase the PO<sub>4</sub>-P recovery efficiency only by 5.0% at a higher Mg dosage (Kataki, West, Clarke, & Baruah, 2016; Le Corre et al., 2007). As such, lignin is more efficient to enhance PO<sub>4</sub>-P recovery efficiency in comparison to other non-struvite seed materials. As lignin dosage increases, the recovery efficiency of PO<sub>4</sub>-P increases gradually, while it is not significantly improved by increasing the lignin dosage from 6 to 7 g/L. Therefore, 6 g/L lignin dosage is considered to be the optimal lignin usage to improve the PO<sub>4</sub>-P recovery under relatively low pH such as 7.9.

It was also observed in our study that due to the alkaline nature of the lignin used, solution pH slightly increased. For instance, with an initial synthetic wastewater pH of 7.9, after 6 g/L lignin addition, solution pH rose to 8.02. To examine the impact of pH on phosphorus recovery, we conducted one control experiment where pH was adjusted

to 8.02 (by adding 1M NaOH solution) but with no lignin addition. It was observed that pH adjustment only had minor effects on enhancing PO<sub>4</sub>-P recovery efficiency (increases from 44.94% ± 0.94% [pH=7.9] to 48.09% ± 1.30% [pH=8.02]; much lower than 62.17% ± 1.47% with no pH adjustment but 6g/L lignin addition). Therefore, it can be concluded that the impact of solution pH change by lignin addition was insignificant. Lignin can be used as seed materials for enhanced phosphorus recovery through promoting a localized pH change and phosphorus crystallization.





**Figure 4. 2** Effect of lignin dosage and Mg/P molar ratio on PO<sub>4</sub>-P recovery: (a) lignin dosage at Mg/P molar ratio =1.5, and (b) Mg/P molar ratio at lignin dosage = 6 g/L (initial pH = 7.9, [PO<sub>4</sub>-P] = 250 mg/L, [NH<sub>4</sub>-N] = 1000 mg/L).

#### ***4.4.3 Impact of Mg/P Molar Ratio on Struvite Crystallization***

As Figure 4.2(b) shows, under pH of 7.9 and 6 g/L lignin addition, when increasing the Mg/P molar ratio from 1.0 to 1.5, the PO<sub>4</sub>-P recovery efficiency increases from 51% to 62.86% ( $p < 0.05$ ). At a given pH, the increase in the Mg/P ratio would increase the degree of saturation with respect to struvite formation, which, in turn, would enhance the PO<sub>4</sub>-P recovery (Ali & Schneider, 2006). Further increases in Mg/P molar ratio to 2.0 does not improve the PO<sub>4</sub>-P recovery significantly, which is consistent with previous studies (Kim, Min, Lee, Yu, & Park, 2017; Yee et al., 2019).

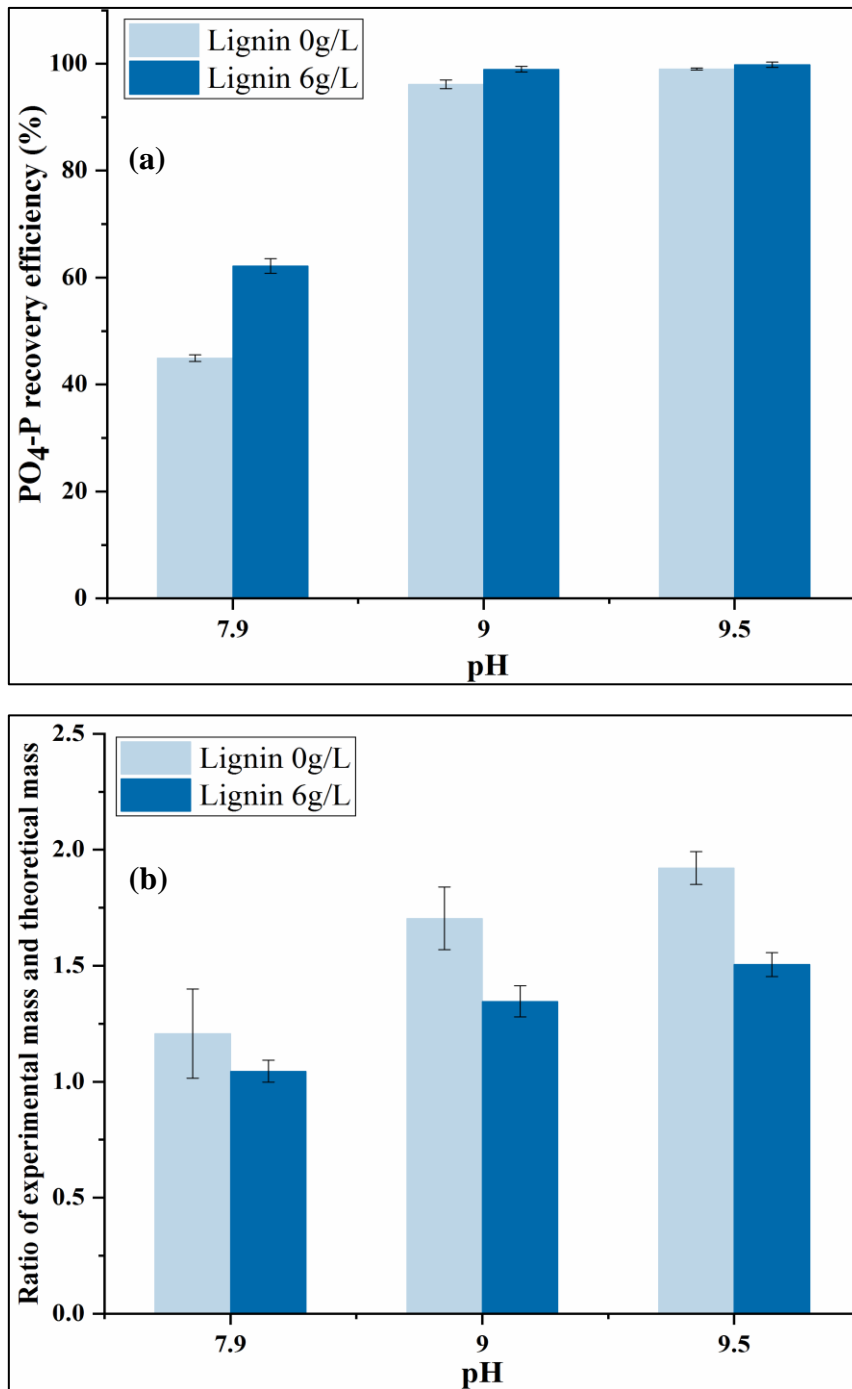
However, when the Mg/P molar ratio is higher than 2.0, the PO<sub>4</sub>-P recovery efficiency starts to decrease. The possible reason could be that excessive magnesium will induce the formation of other co-precipitates. Consequently, considering both the PO<sub>4</sub>-P recovery efficiency and the operating cost, the Mg/P molar ratio of 1.5 is preferred in this study.

#### ***4.4.4 Impact of pH on Struvite Crystallization***

Based on the above experimental results, the optimal lignin dosage is 6 g/L and the optimal Mg/P molar ratio is 1.5. Under these optimal conditions, the influences of pH on PO<sub>4</sub>-P recovery efficiency were studied and the results are shown in Figure 4.3(a).

As pH increases from 7.9 to 9.5, the PO<sub>4</sub>-P recovery increased significantly due to the increased supersaturation ( $p < 0.05$ ). In comparison to no lignin addition without seeding, the addition of 6 g/L lignin increases PO<sub>4</sub>-P recovery efficiency by 44.6% at

pH of 7.9, the increment is 2.8% at pH of 9.0, and the increment is only 0.1% at pH of 9.5. The PO<sub>4</sub>-P recovery is already very high (>95%) under pH 9.0 and 9.5, as a result, the addition of lignin does not make a considerable contribution. Thus, the effect of lignin on enhancing PO<sub>4</sub>-P recovery is significant for lower pH conditions, which will meanwhile save the operation cost by reducing the demand for alkali addition. Struvite crystallization process require the consumption of large amounts of alkali, which increasing the economic cost and limit the practical application of the phosphorus recovery technology (Yusheng Zhang, Li, & Lin, 2012). Therefore, lignin could be considered as a cost-efficient phosphorus recovery additive material.



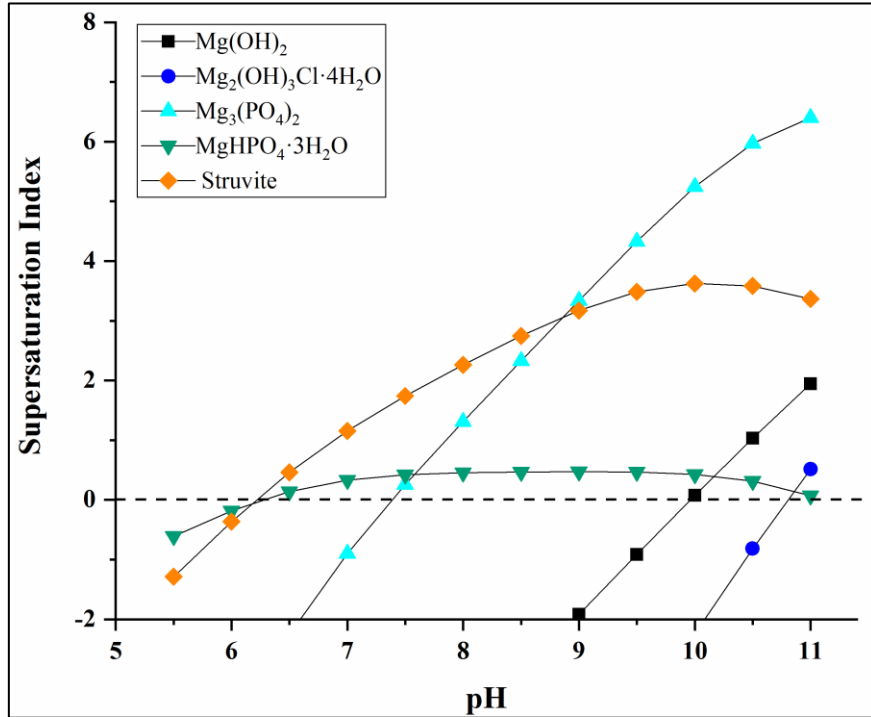
**Figure 4. 3** (a) PO<sub>4</sub>-P recovery efficiency and (b) Ratio of experimental mass recovered to theoretical struvite recovered as a function of pH (Mg/P molar ratio = 1.5, [PO<sub>4</sub>-P] = 250 mg/L, [NH<sub>4</sub>-N] = 1000 mg/L, [Mg] = 290 mg/L, lignin dosage = 6 g/L).

According to the PO<sub>4</sub>-P recovery shown in Figure 4.3(a), the theoretical amount of struvite in the collected samples could be used as a baseline value to check co-precipitates existing in the product. The measured mass of struvite with lignin addition was obtained by subtracting the mass of the added lignin from the mass of collected precipitates.

As shown in Figure 4.3(b), the ratio of the experimental mass measured to theoretical struvite recovered is calculated. For the condition of non-lignin addition, under higher pH, the ratio of the excess mass is larger, hence a larger amount of the mass collected may not be attributed to struvite. However, when the lignin was added during the reaction, the ratios of the excess mass were lower than the ratios of non-lignin control conditions under all the tested pH, which indicates fewer co-precipitates and higher purity of struvite were achieved.

#### ***4.4.5 Compositions of Precipitate***

Figure 4.4 depicts the calculated supersaturation index using Visual MINTEQ software, which gives a good indication of the compounds which can be potentially precipitated from the synthetic wastewater under different pH values.



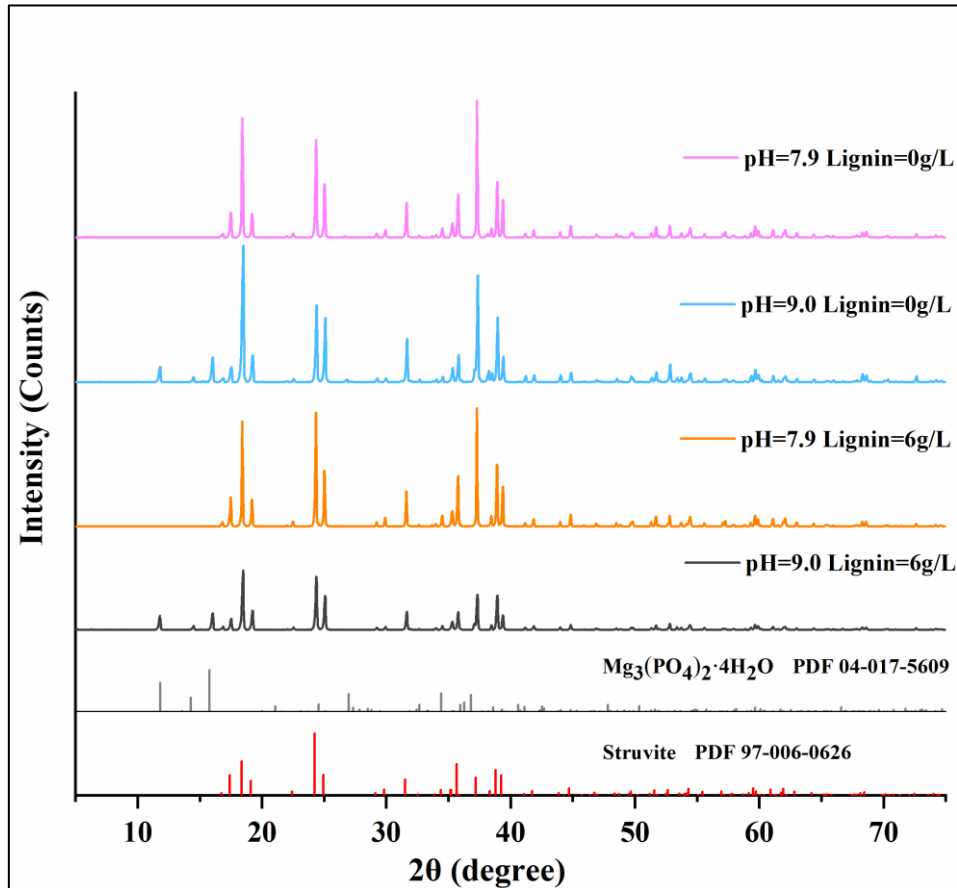
**Figure 4. 4** Saturation index of different compounds that can be formed from ions present in the synthetic supernatant as a function of pH (without lignin addition).

In addition to struvite, some other compounds may precipitate simultaneously. Only if the solution pH is higher than 6.21, struvite will begin to precipitate.  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{Mg}_3(\text{PO}_4)_2$  may form when pH ranges from 6.5 to 10. When pH further increases, the *SI* of struvite decreases and  $\text{Mg}(\text{OH})_2$  and  $\text{Mg}_2(\text{OH})_3\text{Cl} \cdot 4\text{H}_2\text{O}$  will precipitate to compete with struvite. As a result, the phosphorus recovery efficiency will decrease when pH is too high, which is consistent with the previous studies (Yigit & Mazlum, 2007).

The XRD analysis was performed to determine the composition of the precipitate at certain conditions (Mg/P molar ratio = 1.5, pH = 7.9 and 9.0, lignin dosage = 6 g/L and 0 g/L). As shown in Figure 4.5, with the addition of lignin, there was no difference for the observed peak position, but some peak intensity is lower than the non-lignin control

condition. As lignin is an amorphous material that does not show sharp diffraction peaks (as Figure 4.1(d) shows), it can hardly be detected in XRD analysis. When struvite is mixed with lignin, there may be some interference with the peak intensity caused by lignin due to its amorphous nature. Also, the different sample volume used during the analysis will also affect the peak intensity (Jian & Hejing, 2003).

When pH = 7.9, the precipitates with/without lignin addition mostly match with the reference crystalline struvite card (PDF 97-006-0626), indicating a high purity of the precipitation. While for pH 9.0, in addition to struvite,  $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  can also be found in the precipitates since several characteristic peaks are observed when  $2\theta$  is less than 16.8 degree referenced to  $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  card (PDF 04-017-5609). The XRD results are consistent with the prediction of Visual MINTEQ (Figure 4.4).



**Figure 4. 5** XRD analysis of solid precipitate at different pH and lignin dosage

#### ***4.4.6 Morphology and Elemental Analysis***

The morphology characteristics of the precipitate under the different conditions are obtained by SEM. Figure 4.6 shows two magnification views (200x and 1000x) for the samples at different conditions.

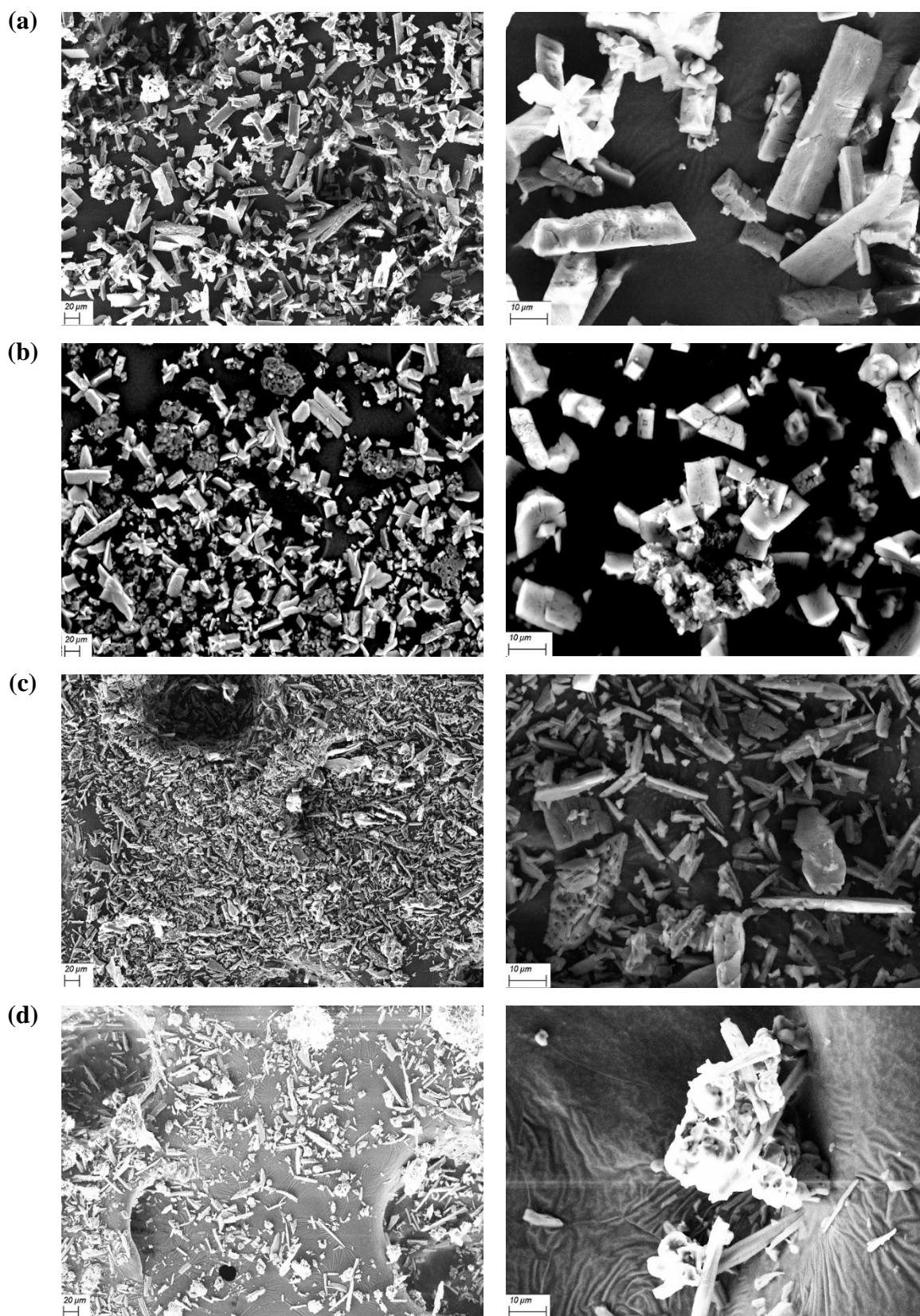
Without the lignin addition, rod-shaped orthorhombic crystals and X-shaped crystals are observed in the precipitate at pH of 7.9 as shown in Figure 4.6(a), which indicates that some crystals grow in multiple directions at the same time. As Figure 4.6(c) shows, at pH of 9, most of the crystals are fine rod-shaped particles and the size of crystals are rather small. According to previous studies (Ghosh et al., 2019b; Xiaoning Liu et al.,



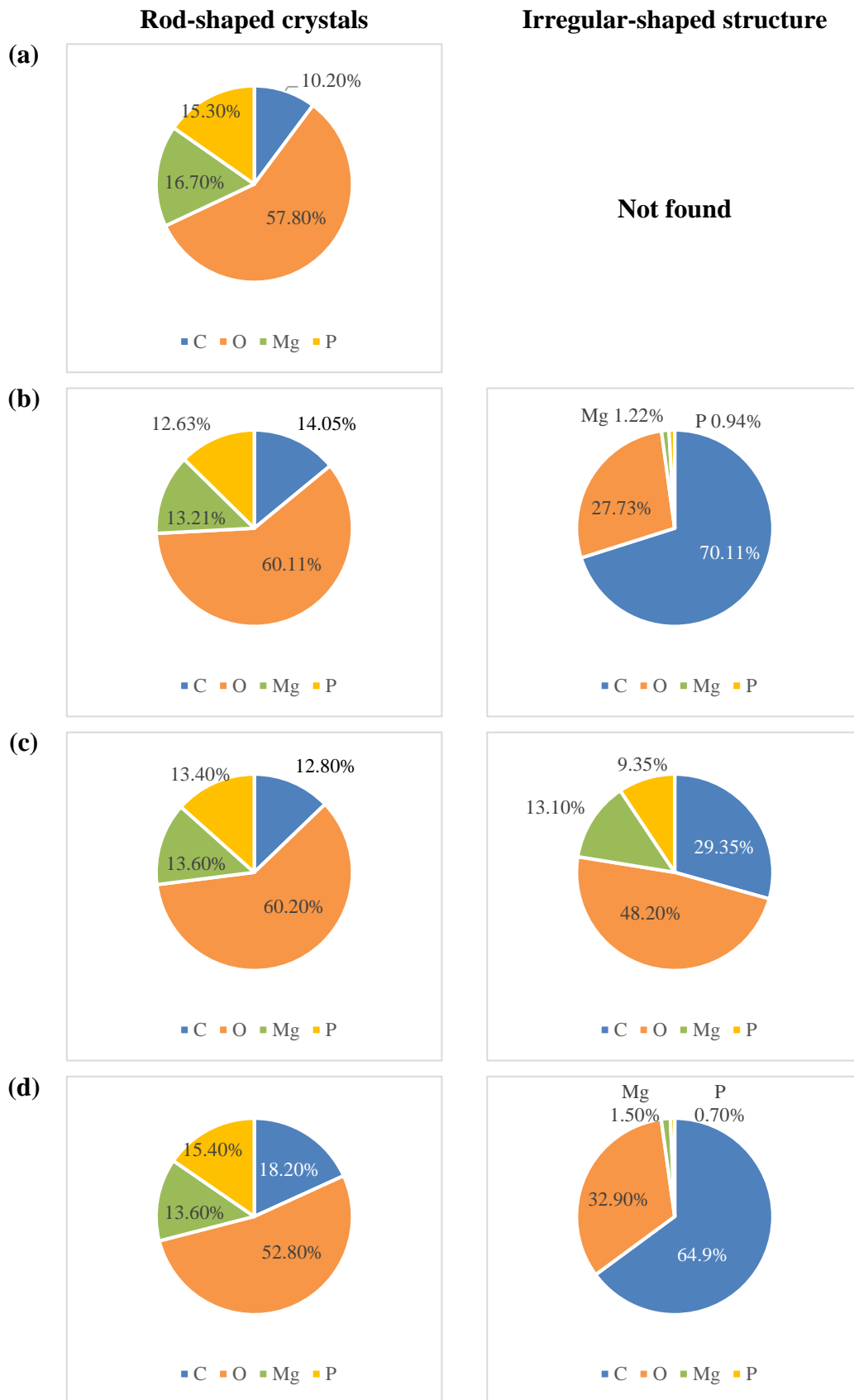
2013), a higher supersaturation leads to a higher nucleation rate compared to the crystal growth rate, resulting in a larger amount of fines. Additionally, some irregular-shaped crystals also appear which might be the co-precipitates.

The morphology of struvite with the lignin addition is shown in Figures 4.6(b) and (d), which is similar to the struvite morphology previously studied by Ali and Schneider (2006) using quartz sand as seed materials. After the addition of lignin, some struvite crystals adhere to and grow on the surface of amorphous and porous lignin, forming a larger cluster of lignin-struvite, while other separated crystals retain their rod or needle shape. Thus, the average particle size is larger and fewer fine particles form, which makes the crystals more likely to settle down after the reaction.

As observed in Figure 4.7, the EDS results also indicate that the rod-shaped crystal is struvite because the results correspond to a theoretical molar ratio of Mg to P of almost 1:1 for all the tested conditions. For the lignin-added conditions, the irregular amorphous are confirmed as lignin as the vast majority of the elements are C and O. Without lignin addition, the irregular particles also appear under pH 9.0. The EDS result shows that the Mg/P molar ratio of the irregular particles is 1.40, which indicates that the particles may contain co-precipitates, most likely  $\text{Mg}_3(\text{PO}_4)_2$ . In addition, magnesium is detected on the surface of lignin due to adsorption. However, since only the limited surface points composition analysis can be provided by EDS, it does not represent all potential co-precipitates.



**Figure 4. 6** SEM images of the precipitate from synthetic wastewater at (a) pH=7.9, lignin = 0 g/L, (b) pH = 7.9, lignin = 6 g/L, (c) pH = 9.0, lignin = 0 g/L, and (d) pH = 9.0, lignin = 6 g/L (left = 200x magnification, right = 1000x magnification).



**Figure 4. 7** EDS analysis of rod-shaped crystal and irregular structure observed in SEM images of precipitate (Atom%) based on point analysis. (a) pH = 7.9, lignin = 0 g/L, (b) pH = 7.9, lignin = 6 g/L, (c) pH = 9.0, lignin = 0 g/L, and (d) pH = 9.0, lignin = 6 g/L.

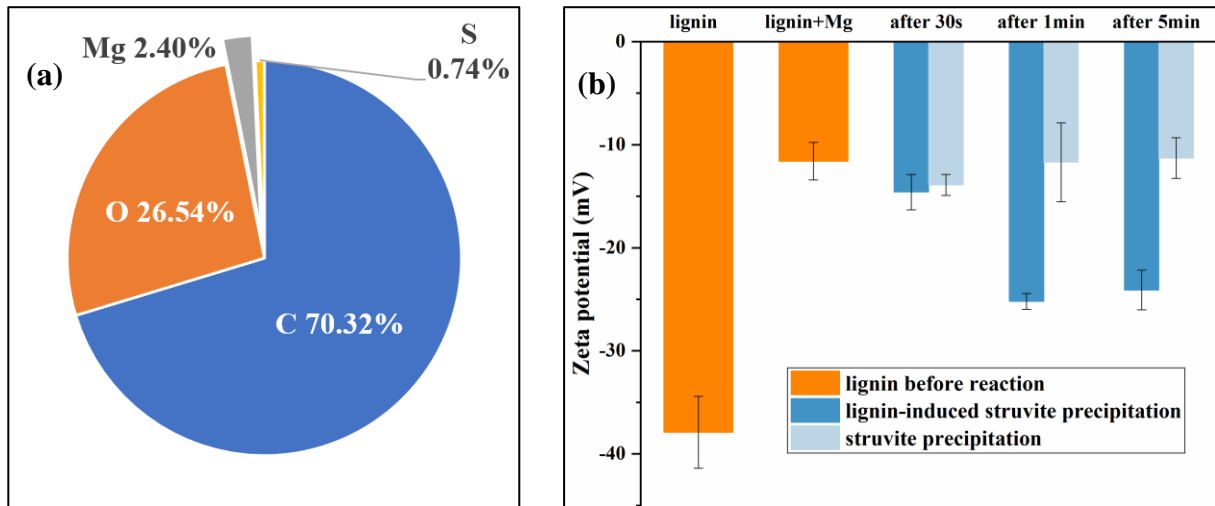
#### ***4.4.7 Mechanism of Lignin-induced Struvite Precipitation***

As shown by the results mentioned above, the lignin could play a role as a kind of seed material to promote struvite formation and aggregation. According to the structure and characteristics of lignin, the possible mechanisms are discussed as follows.

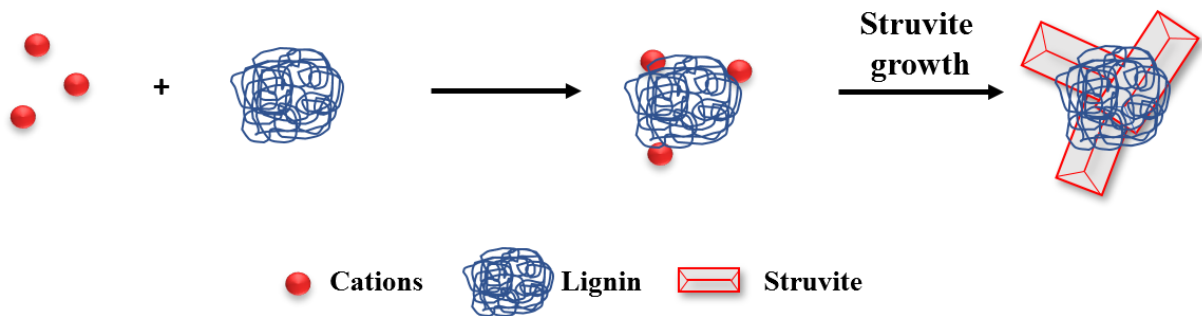
By virtue of the superficial groups with a negative charge (such as de-protonated phenolic, hydroxyl, and carboxyl groups) and impurities (such as salts), Kraft lignin molecules carry negative charges on the surface in the solution and behaves like an alkaline core (Ajao et al., 2018). In order to investigate the adsorption of  $Mg^{2+}$ , 0.3g Kraft lignin powder was mixed with the 50 mL 0.5 M  $MgCl_2$  solution for 5 min (lignin= 6g/L, pH 7.9). Then the lignin was washed three times by distilled water and dried at room temperature to do further analysis. Figure 4.8(a) shows the EDS results of lignin before and after mixing with  $MgCl_2$ , which indicate that some  $Mg^{2+}$  are adsorbed to the lignin surface, which is likely due to electrostatic attraction. Moreover, as Figure 4.8(b) shows, after mixing with the  $MgCl_2$ , the zeta potential of lignin increased from -37.9 to -11.6 mV, which also confirmed the absorption of  $Mg^{2+}$ . When the reaction started, the zeta potential of the lignin decreased in the first 1 min, then became stable. The change of zeta potential indicates that struvite may grow on the lignin surface to form a larger cluster.

As Figure 4.9 shows, the adsorption of cations (mostly  $Mg^{2+}$ ) leads to an increase of the local ion concentration. The supersaturation index at the local sites on the surface of lignin is also increased which thus promotes the struvite growth. Lignin has a large

surface area as a result of the specific amorphous and cross-structure, so it could provide many in-situ-pH-favorable nucleation sites for struvite crystal growth. Larger particles are preferred because they are easier to collect during the operation, reducing the loss of fine particles and increasing the recovery efficiency.



**Figure 4. 8** (a) EDS analysis of lignin after mixing with MgCl<sub>2</sub> (b) Zeta potential changes during the reaction



**Figure 4. 9** Schematic of lignin-induced struvite precipitation

## **4.5 Conclusions**

The feasibility of adding lignin as seeds to enhance the phosphorus recovery from synthetic wastewater has been established. The effect of lignin is significant especially at lower pH (pH = 7.9, Mg/P molar ratio = 1.5:1, lignin dosage = 6 g/L). Compared with other non-struvite seed materials, lignin shows its superiority in eco-friendliness and effectiveness for enhancing phosphorus recovery efficiency. While compared with struvite seed, lignin mitigates the production of co-precipitate and reduces the need to adjust pH thus saves the cost of alkali. The software modeling result predicts the variability of possible co-precipitates under different pH, which is further confirmed by XRD results. The morphology and elemental analysis also indicate that some struvite grows onto lignin to form a larger cluster, which is likely due to the aggregation of lignin and in-situ-pH-favorable nucleation sites provided by lignin with the large surface area. Overall, this study proposes a new possible use of lignin and makes struvite recovery more cost-effective afterward.

## **4.6 Acknowledgement**

The authors acknowledge the funding from Alberta Innovates-Alberta Bio Future Lignin Challenge 1.0 Program and Alberta Bio Future Lignin Pursuit Program, Canada Research Chair (CRC) in Future Community Water Services (Liu, Y.), Natural Sciences and Engineering Research Council of Canada (NSERC) Discovery Grant (Lu, Q.) and the Start-up Fund from the University of Calgary (Lu, Q.).

## **Chapter 5 Performance Evaluation of Lignin-induced Struvite Precipitation from Synthetic Wastewaters with Different Characteristics at Relatively Low pH**

### **Performance Evaluation of Lignin-induced Struvite Precipitation to Recover Phosphorus from Synthetic Wastewaters at Relatively Low pH: Effects of Ammonia and Phosphate Concentrations, Total Suspended Solid and Alkalinity**

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#### **5.1 Abstract**

To solve the problems of eutrophication and resource crisis, the recovery of phosphorus by struvite ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ) precipitation has become a focus of recent research. The feasibility of using Kraft lignin powder as a seed to promote struvite precipitation has been demonstrated in the previous study in Chapter 4. In this study, the effect-stability of lignin at different wastewater characteristics was investigated. Lignin-induced struvite crystallization was tested under various initial concentrations of  $\text{PO}_4\text{-P}$  and  $\text{NH}_4\text{-N}$ , total suspended solids (TSS) and alkalinity. At pH 7.9, the enhancement of  $\text{PO}_4\text{-P}$  recovery remains around 45% under different  $\text{PO}_4\text{-P}$  and  $\text{NH}_4\text{-N}$  concentrations. Moreover, lignin is more effective under relatively lower alkalinity and still workable to reduce co-precipitates potential under higher alkalinity. Also, the effect

of TSS on PO<sub>4</sub>-P recovery is not significant in this study. Overall, the effect of lignin in promoting phosphorus recovery is relatively stable and can be used in synthetic wastewater with different characteristics.

## **5.2 Introduction**

Phosphate rock is the main commercial source of phosphorus commonly used by the fertilizer, detergent and insecticide industries (Cordell et al., 2011). However, the known reserves of high-quality phosphate rock are limited and the exploitation rate is increasing fast (Su et al., 2014). The phosphorous industry is now searching for more sustainable sources to produce high purity material. Meanwhile, significant levels of phosphates are released into the environment with wastewater, which is a very important reason for eutrophication leading to water crisis all over the world (Ryu, Lim, Kang, & Lee, 2012). Therefore, the recovery of phosphates from wastewater is one such potential source that, not only has economic merit, but also makes the wastewater treatment industry more sustainable. Struvite precipitation is an ideal technique for phosphorus recovery because of its good fertilizer efficiency (Ping, Li, Wu, Yang, & Wang, 2016).

As the second most abundant biomass in plants, lignin is widely used in industry and agriculture (Demirbas, 2004; Figueiredo et al., 2018). As for phosphorus recovery process, the feasibility of using Kraft lignin powder as seed to promote struvite precipitation is evaluated in previous study (Chapter 4). The results indicate that the lignin is more effective to promote phosphorus recovery from the specific synthetic



biosolid digestate supernatant at pH 7.9, meanwhile, the potential of co-precipitates and cost of alkali are also reduced.

Phosphorus recovery as struvite was a process of chemical crystallization and precipitation (Z. Ye et al., 2014), therefore wastewater characteristics, such as pH, ammonia concentrations, phosphate concentrations and alkalinity, are thought to be crucial for the nature of phosphate precipitates from various sources, such as domestic, landfill, and aquaculture wastewaters (Huang, Liu, Xu, & Gao, 2016; Kataki et al., 2016; Tao, Fattah, & Huchzermeier, 2016). The characteristics of wastewater vary widely depending on their source and treatment process. For the different water-volume flushed blackwater, the total phosphorus will ranges from 38 mg/L with 9 L flushed to 330 mg/L with 1 L flushed (Gao, Zhang, Florentino, & Liu, 2019). In addition, different dewatering methods and operating procedures may result in changes in concentration of the total suspended solids (TSS) in the wastewater, which may affect the crystallization, struvite purity and morphology of struvite (Barnes, Li, & Chen, 2007; E. Desmidt et al., 2013). Ping et. (2016) found that as the concentration of TSS increases, the  $\text{PO}_4\text{-P}$  recovery efficiency decreases linearly. The possible reason could be the suspended solids can reduce the effective ions collision and hinder the adsorption of ions on crystal nucleus. Moreover, some suspended solids could adhere to struvite crystal surface, which might impact the struvite growth.

Due to the high alkalinity in the anaerobic digester wastewater, the effect of alkalinity has been studied. Previous research showed that alkalinity has a great influence on the struvite crystallization process (Xueyu Liu, Xiang, Song, Qian, & Meng, 2015; Wei et

al., 2019), but the comprehensive study on the effect of alkalinity is limited. For the lignin-induced struvite precipitation, it is not clear whether the effect of lignin in different wastewaters is still significant.

Therefore, the objective of this study is to investigate the impactors and application potentials of lignin-induced struvite precipitation. Considering the effect-stability and availability of lignin, the performance of lignin-induced struvite precipitation at a relatively lower pH under other different wastewater characteristics, such as  $\text{PO}_4\text{-P}$  and  $\text{NH}_4\text{-N}$  concentrations, total suspended solids (TSS) and alkalinity are evaluated in this study.

## **5.3 Materials and Methods**

### **5.3.1 Materials**

The synthetic wastewater with different ammonia and phosphate concentrations were prepared using sodium dihydrogen phosphate [ $\text{NaH}_2\text{PO}_4$ ] and ammonium chloride [ $\text{NH}_4\text{Cl}$ ]. The alkalinity was adjusted by adding sodium bicarbonate [ $\text{NaHCO}_3$ ], which was purchased from Sigma Aldrich (analytical grade). Chloride hexahydrate ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) was added as precipitants. All the reagents used were purchased from Sigma Aldrich (analytical grade).

TSS is defined as solids in wastewater that can be trapped by the filter. In this study, the suspended solid was separated from the real biosolid digestate supernatant wastewater by centrifuge at 5000 rpm for 10 mins, and then added to the synthetic

wastewater to mimic the different TSS concentrations.

The Kraft lignin used in this study was obtained from West Fraser Hinton Pulp (Alberta, Canada). This kind of lignin has more consistent physical-chemical properties, which is different from the conventional lignin materials that are often treated as waste product. It has low solubility in water but is very hydrophilic in alkali solutions. The lignin contains low ash and low sulfur content (0 to 3 wt%), with a specific gravity of 1.02-1.60.

### ***5.3.2 Struvite Precipitation Experiments***

The struvite precipitation was conducted with a magnetic stir bar at 200 rpm for 1 min at room temperature, then decreased to 60 rpm for 45 mins, and settled for 1 h to allow for precipitation. The supernatant was filtered through a 0.45  $\mu\text{m}$  glass fiber filter to measure the residual  $\text{PO}_4\text{-P}$  concentration. After centrifuging the suspension samples at 5000 rpm for 10 mins, the precipitate was collected by decanting the supernatant, Then the precipitate was washed with distilled water by repeated dispersing in water, centrifugation and decanting the supernatant for three times, and finally dried at 40  $^{\circ}\text{C}$  overnight for further characterizations.

Based on the phosphorus recovery increment study in Chapter 4, the optimal conditions of lignin-struvite precipitation are at a relatively low pH of 7.9 with Mg/P molar ratio of 1.5 and lignin dosage of 6 g/L. Therefore, 1 M  $\text{MgCl}_2$  was added to adjust the Mg/P molar ratio to 1.5 and 1 M  $\text{NaOH}$  was used to adjust the pH to 7.9 for this study.

### ***5.3.3 Chemical Analysis and Calculation***

The PO<sub>4</sub>-P concentration in the solution was measured by Hach methods (TNT844, Hach, USA) before and after the reaction. To measure TSS, water samples were filtered through a 0.45 µm pre-weighted filter. The residue remaining on the filter was dried in an oven at 105 °C until the weight of the filter no longer changed. Therefore, the increase in filter weight represents the mass of the TSS, and the TSS concentration can be further calculated (Ismail, Khulbe, & Matsuura, 2019).

Precipitate was analyzed via X-ray diffraction (XRD; Rigaku Ultimate IV, Japan) and scanning electron microscopy (SEM; Zeiss Sigma 300 VP-FESEM, USA) with energy dispersive X-ray spectroscopy (EDS; Bruker EDS System, USA). The peaks of the XRD results were compared to the Inorganic Crystal Structure Database (ICSD) for struvite confirmation using the references card PDF #97-006-0626.

### ***5.3.4 Mineral Precipitation Modelling***

Supersaturation index (SI) of various minerals that might be formed together with struvite was performed by the equilibrium speciation model Visual MINTEQ (ver.3.0) to predict the potential co-precipitates. The different ion concentrations of feed synthetic wastewater was utilized as model input. SI was calculated using Eq. (1):

$$SI = \lg \frac{IAP}{K_{SP}} \quad (1)$$

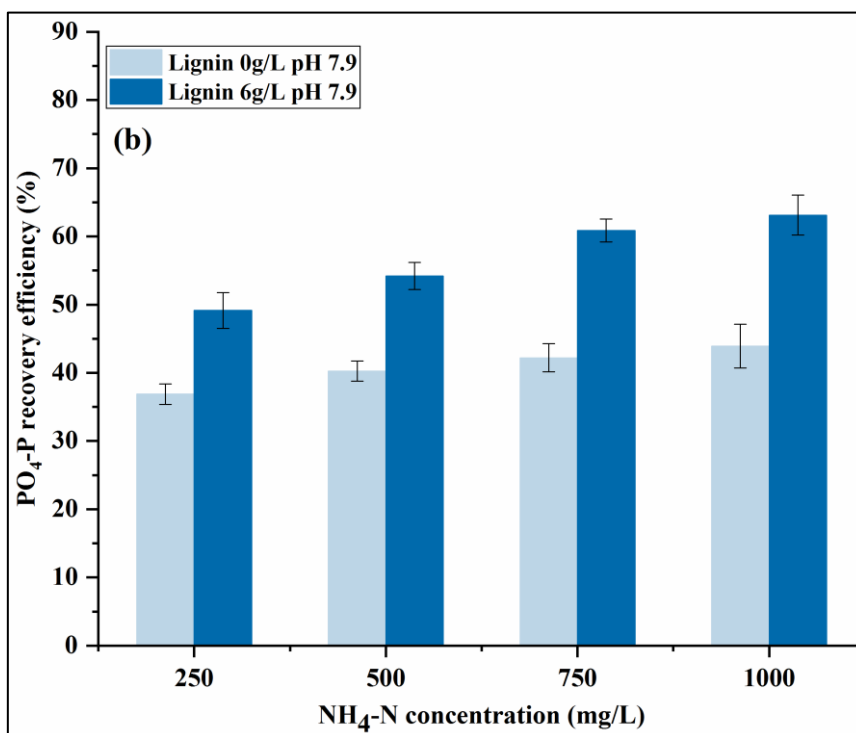
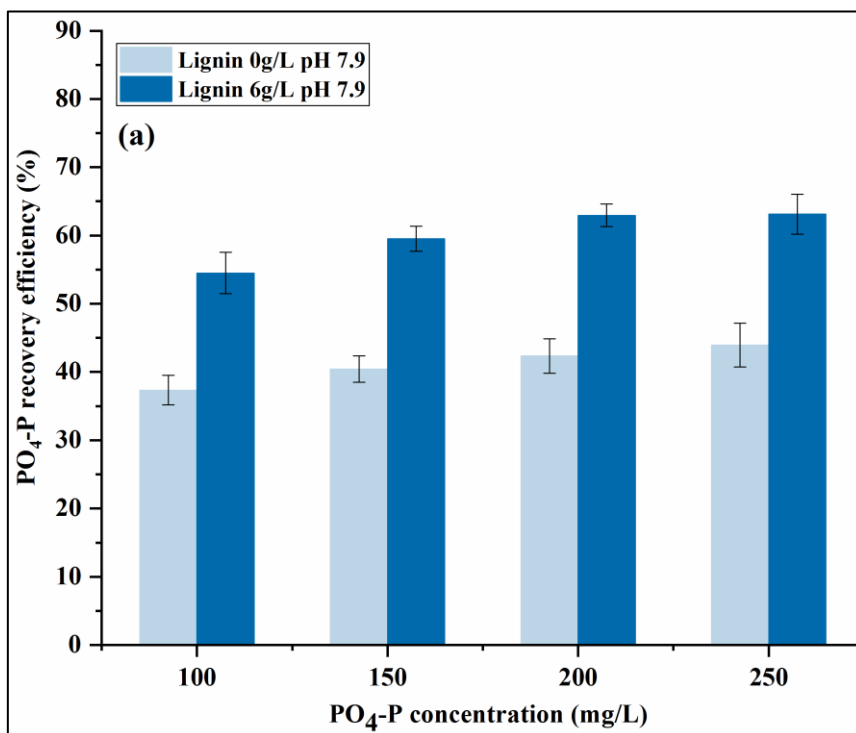
where IAP is the ion activity product and  $K_{sp}$  represents the solubility product of the precipitation phase. The minerals only precipitate when  $SI > 0$  (E. Desmidt et al., 2012).

## 5.4 Results and Discussion

The influencing factors, including concentrations of phosphate  $\text{PO}_4\text{-P}$ , ammonia  $\text{NH}_4\text{-N}$ , TSS and alkalinity were studied to examine their impacts on the performance of lignin-induced struvite precipitation.

### *5.4.1 Impact of $\text{PO}_4\text{-P}$ concentration on Struvite Crystallization*

The  $\text{PO}_4\text{-P}$  recovery efficiencies at different initial  $\text{PO}_4\text{-P}$  concentrations were examined at the lignin dosage of 0 g/L and 6 g/L, respectively. As shown in Figure 5.1(a), when the initial  $\text{PO}_4\text{-P}$  concentration is 100 mg/L, the  $\text{PO}_4\text{-P}$  recovery efficiency is 37.33% at the lignin dosage of 0 g/L, and it reaches 54.51% at the lignin dosage of 6 g/L ( $p < 0.05$ ). At a higher initial  $\text{PO}_4\text{-P}$  concentration of 250 mg/L, the  $\text{PO}_4\text{-P}$  recovery efficiency rises up to 43.93% without the lignin addition and 63.13% at the lignin dosage of 6 g/L ( $p < 0.05$ ), respectively. The  $\text{PO}_4\text{-P}$  recovery increment as a result of lignin addition from 0 g/L to 6 g/L is all around 45% within the range of  $\text{PO}_4\text{-P}$  concentration studied. Therefore, at a lower pH of 7.9, the use of lignin is effective to enhance phosphorus recovery at different  $\text{PO}_4\text{-P}$  concentrations.



**Figure 5. 1** Impact of initial (a) PO<sub>4</sub>-P concentration (Mg/P molar ratio = 1.5, [NH<sub>4</sub>-N] = 1000 mg/L) and (b) NH<sub>4</sub>-N concentration (Mg/P molar ratio = 1.5, [PO<sub>4</sub>-P] = 250 mg/L) on PO<sub>4</sub>-P recovery efficiency at pH 7.9.

The influence of initial PO<sub>4</sub>-P concentration on PO<sub>4</sub>-P recovery efficiency is consistent with previous results that the reduction in available PO<sub>4</sub>-P concentration will decrease the phosphorus removal (Marti, Bouzas, Seco, & Ferrer, 2008; Ping et al., 2016). The struvite crystallization is mainly attributed to the supersaturation index (SI) degree of the initial conditions determined by the concentration of all the three struvite constituent ions (Mg<sup>2+</sup>, PO<sub>4</sub><sup>3-</sup>, NH<sub>4</sub>) (Adnan, Koch, & Mavinic, 2003b). As the concentration of PO<sub>4</sub>-P increases, the degree of supersaturation increases as well, leading to a faster struvite growth rate and consequently, a higher PO<sub>4</sub>-P recovery efficiency.

#### ***5.4.2 Impact of NH<sub>4</sub>-N Concentration on Struvite Crystallization***

As shown in Figure 5.1(b), the PO<sub>4</sub>-P recovery efficiencies at different initial NH<sub>4</sub>-N concentrations were also tested at the lignin dosage of 0 g/L and 6 g/L. The result is similar to that obtained under different initial PO<sub>4</sub>-P concentrations. As the NH<sub>4</sub>-N concentration increases from 250 to 1000 mg/L, the PO<sub>4</sub>-P recovery efficiency increases gradually under both lignin dosages of 0 g/L and 6 g/L ( $p < 0.05$ ). The addition of lignin is still effective at various NH<sub>4</sub>-N concentrations with the maximal increment of PO<sub>4</sub>-P recovery of 44.6%.

It has been found that the higher NH<sub>4</sub>-N concentration not only promotes the PO<sub>4</sub>-P recovery but also increases the purity of the precipitate (Stratful, Scrimshaw, & Lester, 2001; Wu, Qian, & Li, 2017). It is because of that the NH<sub>4</sub>-N concentration could influence the supersaturation of the solution and affect the struvite crystallization. Moreover, except for the effect on increasing ion strength, another possible reason is

that excess  $\text{NH}_4\text{-N}$  is capable of maintaining the pH of the solution because of its buffering capacity, which is conducive to the struvite formation (Wu et al., 2017).

Therefore, at a lower pH of 7.9, the effect of lignin on enhancing  $\text{PO}_4\text{-P}$  recovery efficiency is still significant at different  $\text{PO}_4\text{-P}$  and  $\text{NH}_4\text{-N}$  concentrations, which indicates the effect-stability and availability of lignin in promoting struvite crystallization.

#### ***5.4.3 Impact of TSS on Struvite Crystallization***

After investigating the effect of  $\text{PO}_4\text{-P}$  and  $\text{NH}_4\text{-N}$  concentrations, the real phosphorus-rich biosolid digestate supernatant, which was collected from a digester sludge thickening lagoon in the City of Edmonton, was used to evaluate the performance of phosphorus recovery efficiency. The lagoon supernatant was pretreated on-site in an Ostara® facility for phosphorus removal. The characteristics of this kind of wastewater are shown in Table 5.1 (Yang et al., 2019).

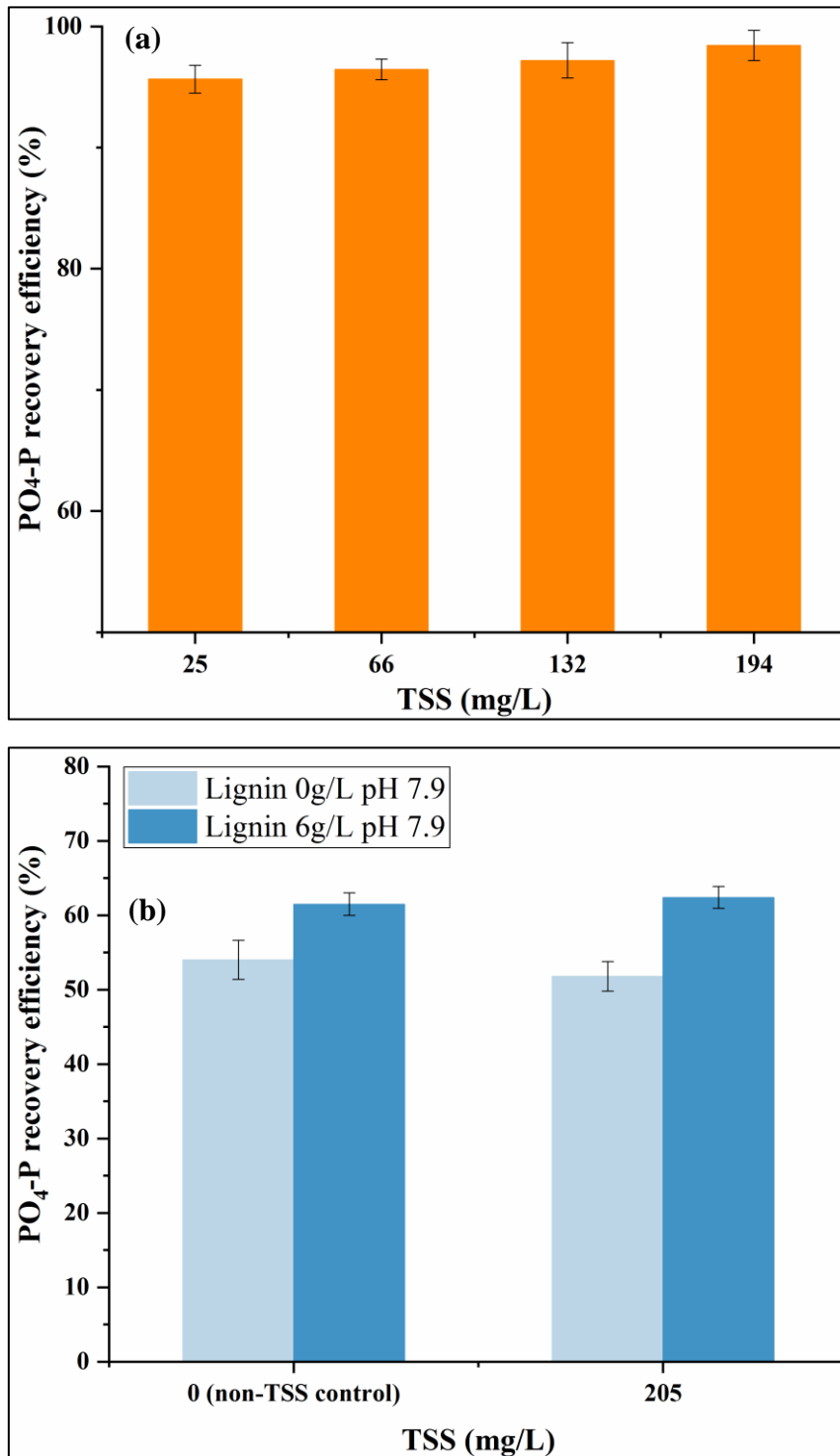
When we use the real biosolid digestate supernatant under its origin pH 7.9, the  $\text{PO}_4\text{-P}$  recovery efficiency with or without lignin addition is  $98.67\% \pm 0.83\%$  and  $95.55\% \pm 1.25\%$ , respectively, which is much higher than the  $\text{PO}_4\text{-P}$  recovery efficiency from synthetic wastewater. The composition of real biosolid digestate supernatant is relatively complex compared to synthetic wastewater. Therefore, the total suspended solids (TSS) and alkalinity are considered as the possible impactors resulting in the higher  $\text{PO}_4\text{-P}$  recovery efficiency.



**Table 5. 1** Composition of the pre-Ostara® biosolid digestate supernatant

Parameters	Unit	Mean $\pm$ S.D.
TSS	g TSS/m <sup>3</sup>	305 $\pm$ 107
NH <sub>4</sub> <sup>+</sup>	mg N/L	891.9 $\pm$ 79
NO <sub>2</sub> <sup>-</sup>	mg N/L	0.4 $\pm$ 0.7
NO <sub>3</sub> <sup>-</sup>	mg N/L	0.2 $\pm$ 0.7
PO <sub>4</sub> <sup>3-</sup>	mg PO <sub>4</sub> -P/L	235 $\pm$ 15.4
Alkalinity	mg CaCO <sub>3</sub> /L	3180 $\pm$ 51.9
pH	-	7.87 $\pm$ 0.15

Firstly, the different concentrations of TSS is tested. Different dewatering methods and operation procedures may cause variable TSS concentrations in municipal wastewater, which could influence the crystallization of struvite (Ping et al., 2016). Figure 5.2(a) shows that under the real biosolid digestate supernatant with different TSS, there are nearly no differences of the PO<sub>4</sub>-P recovery efficiency ( $p > 0.05$ ). Figure 5.2(b) also depicts the relationship between the TSS and phosphorus recovery efficiency with or without the lignin addition at pH 7.9 using the synthetic biosolid digestate supernatant. When the TSS was altered from 0 to 205 mg/L, the change of PO<sub>4</sub>-P recovery efficiency was not significant ( $p > 0.05$ ), which indicates that in this study under the tested pH range, the PO<sub>4</sub>-P recovery efficiency for both lignin- and non-lignin- struvite precipitation is not interfered by the suspended solids. Moreover, TSS is not the related reason for the higher PO<sub>4</sub>-P recovery efficiency of real pre-Ostara® biosolid digestate supernatant.



**Figure 5. 2** Impact of total suspended solids (TSS) on PO<sub>4</sub>-P recovery efficiency  
 (a) real biosolid digestate supernatant (b) synthetic biosolid digestate supernatant  
 (Mg/P molar ratio = 1.5, [PO<sub>4</sub>-P] = 250 mg/L, [NH<sub>4</sub>-N] = 1000 mg/L).

#### ***5.4.4 Impact of Alkalinity on Struvite Crystallization***

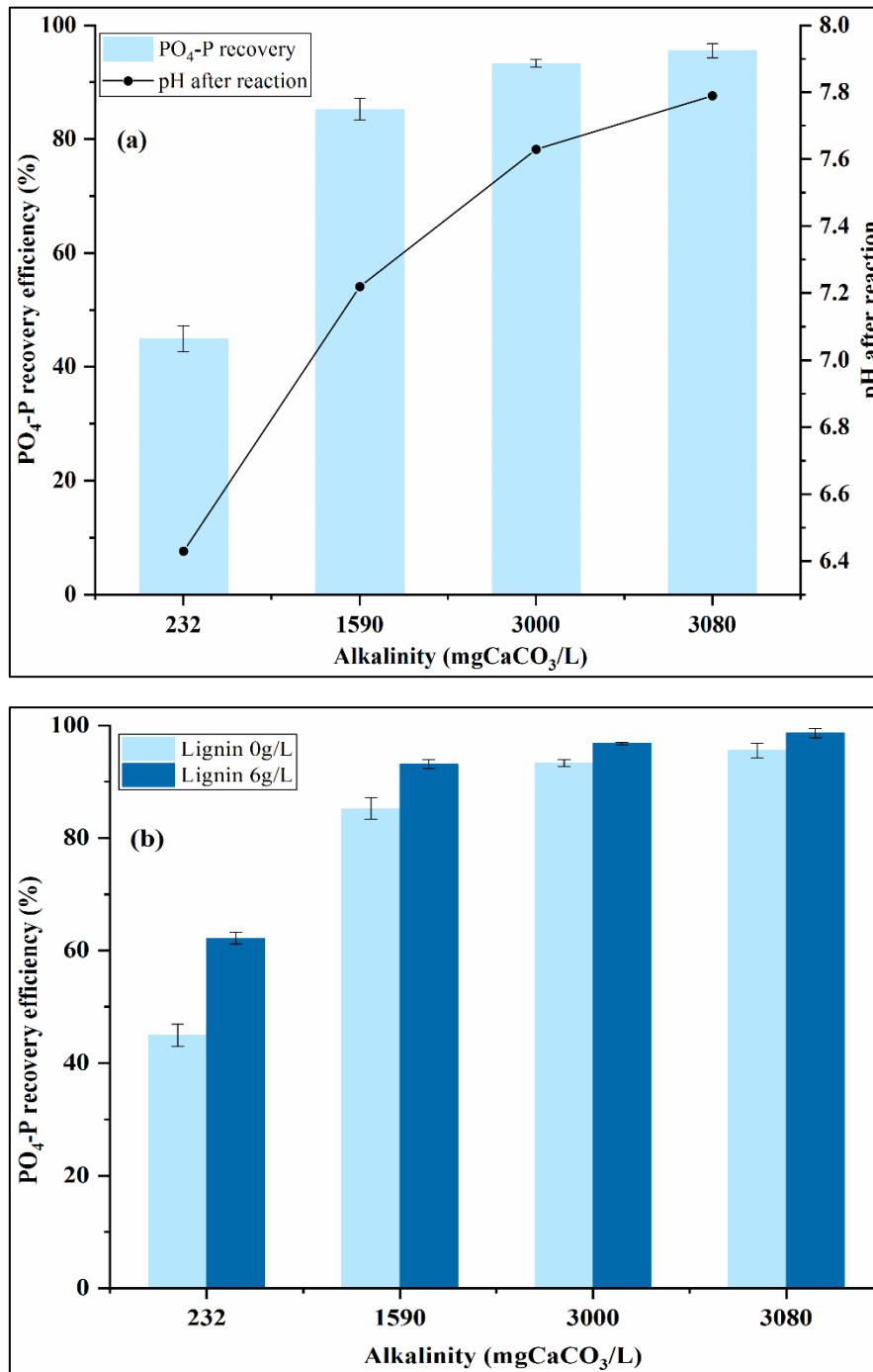
Afterwards, we prepared the synthetic biosolid digestate supernatant with the different alkalinity to investigate the effect of alkalinity on PO<sub>4</sub>-P recovery.

##### *5.4.4.1 Phosphorus recovery efficiency*

According to Wei et al. (2019), alkalinity is another important parameter affecting PO<sub>4</sub>-P recovery efficiency. Without lignin addition, as Figure 5.3(a) shows, the PO<sub>4</sub>-P recovery enhances significantly as the alkalinity of synthetic wastewater increases gradually. When the alkalinity increases from 232 to 1590 mg/L as CaCO<sub>3</sub> at the initial pH of 7.9, the PO<sub>4</sub>-P recovery efficiency increases by 40.28% ( $p < 0.05$ ). The PO<sub>4</sub>-P recovery efficiency under 3080 mg/L as CaCO<sub>3</sub> is higher than 95%, so alkalinity may be the main reason for the high PO<sub>4</sub>-P recovery efficiency of the real lagoon supernatant. The pH of the supernatant after the reaction is measured and the results are also shown in Figure 5.3(a). The pH after the reaction is 6.43 and 7.79, respectively, when the alkalinity is 232 and 3080 mg/L as CaCO<sub>3</sub>. As the alkalinity increases, a stronger buffering capacity prevents the pH from dropping. Therefore, under higher alkalinity, struvite crystallization and aggregation processes can last longer and lead to a higher PO<sub>4</sub>-P recovery efficiency.

While at a pH of 9.0, it shows a decreasing trend of phosphate removal with the increase of alkalinity in the wastewater in the previous study (Wei et al., 2019), because the co-existing carbonate can react with the Mg<sup>2+</sup> and form more magnesite at a higher pH.

The effect of lignin addition under different alkalinity was also investigated and the result is shown in Figure 5.3(b). Although the PO<sub>4</sub>-P recovery efficiency is enhanced with the lignin addition at different alkalinity, the increment of PO<sub>4</sub>-P recovery efficiency decreases as alkalinity increases. Since the PO<sub>4</sub>-P recovery efficiency is already very high at higher alkalinity without lignin addition, the effect of lignin becomes insignificant. Therefore, in this study, lignin is more efficient in enhancing the PO<sub>4</sub>-P recovery efficiency at a lower alkalinity.

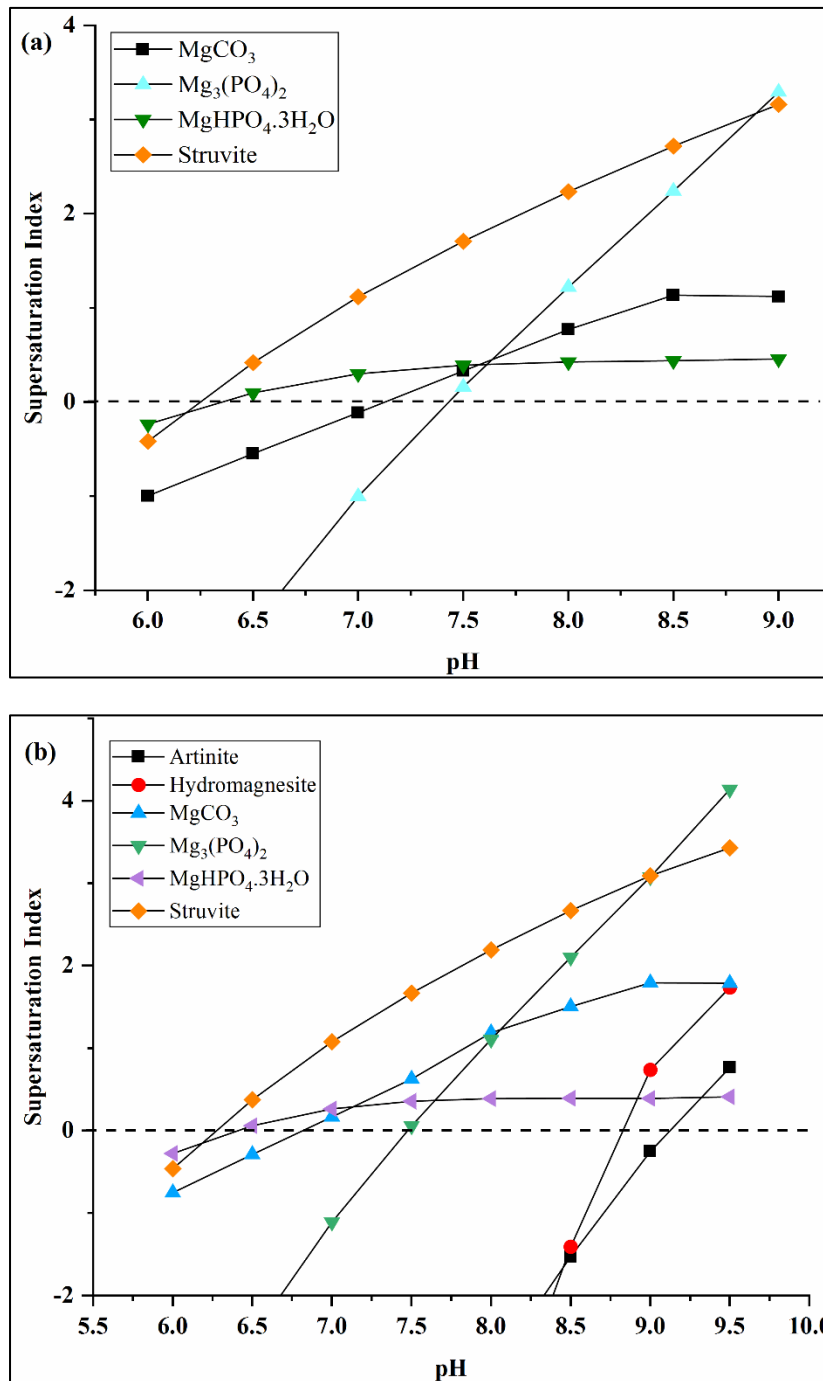


**Figure 5.3** Impact of alkalinity on PO<sub>4</sub>-P recovery efficiency and corresponding pH after the reaction (a) without and (b) with lignin addition (initial pH=7.9, Mg/P molar ratio= 1.5, [PO<sub>4</sub>-P] = 250 mg/L, [NH<sub>4</sub>-N] = 1000 mg/L).

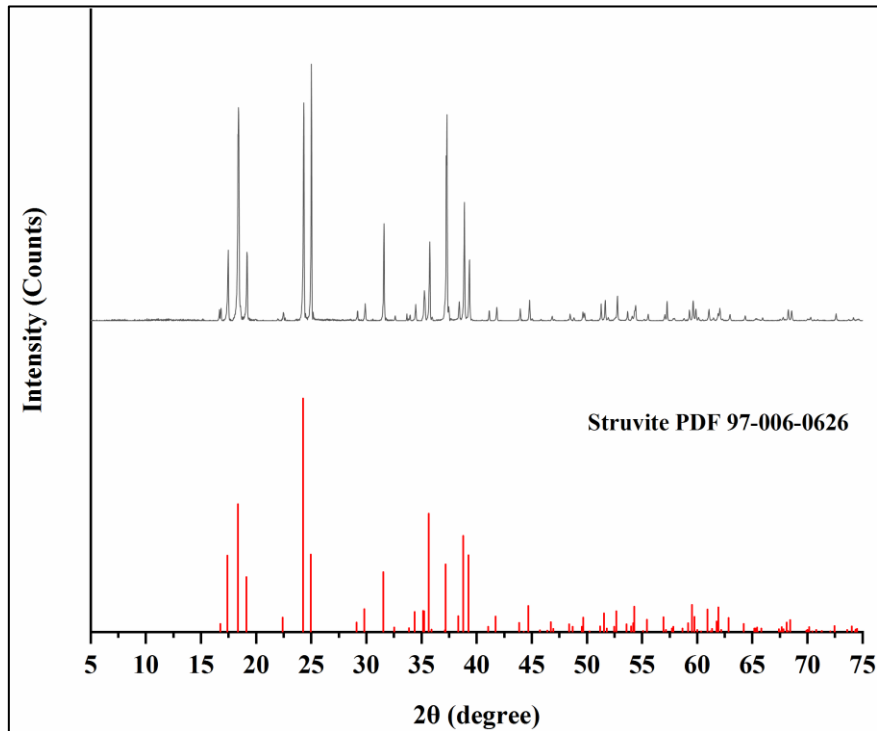
#### 5.4.4.2 Compositions of precipitate

The PO<sub>4</sub>-P recovery efficiency increases with the increasing alkalinity, while the composition of the collected precipitation may also change at the higher alkalinity. The prediction of possible precipitates under different alkalinity (1590 and 3000 mg/L as CaCO<sub>3</sub>) by Visual MINTEQ is shown in Figure 5.4. As alkalinity increases, the SI of struvite and MgCO<sub>3</sub> increase simultaneously while the SI of Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and MgHPO<sub>4</sub>·3H<sub>2</sub>O decrease, which indicates that struvite is more likely to crystallize under higher alkalinity. Moreover, as pH rises gradually from 8.5 to 9.5 when alkalinity is 3000 mg/L as CaCO<sub>3</sub> (Figure 5.4(b)), more impurities may start to appear such as Artinite (Mg<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>·3H<sub>2</sub>O) and Hydromagnesite (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O), causing the reduction of the produced struvite purity.

At pH of 7.9, the dominant precipitate may still be struvite for both alkalinity of 1590 and 3000 mg/L as CaCO<sub>3</sub>, as the SI of struvite is the highest among all the potential precipitates. It is also proved by XRD analysis of the precipitates at the alkalinity of 3000 mg/L as CaCO<sub>3</sub>, as shown in Figure 5.5. Struvite crystal is examined and confirmed by comparison with the struvite reference card from the Inorganic Crystal Structure Database (ICSD). For the other precipitates, they cannot be detected in this XRD analysis, which is likely due to their small amounts. The other co-precipitates may be determined by the following SEM and EDS analysis.



**Figure 5. 4** Supersaturation index (SI) of different compounds that can be formed from ions present in the synthetic supernatant as a function of pH (without lignin addition) with an alkalinity of (a) 1590 mg/L and (b) 3000 mg/L as CaCO<sub>3</sub>.



**Figure 5. 5** XRD analysis of solid precipitate at an alkalinity of 3000 mg/L as  $\text{CaCO}_3$  (initial pH = 7.9, Mg/P molar ratio = 1.5,  $[\text{PO}_4\text{-P}] = 250$  mg/L,  $[\text{NH}_4\text{-N}] = 1000$  mg/L, lignin = 0 g/L).

#### 5.4.4.3 Morphology and elemental analysis

The morphology characteristics of the precipitate under various alkalinities are obtained by SEM. Different magnification views for the samples at alkalinity 1590 and 3000 mg/L  $\text{CaCO}_3$  are shown in Figure 5.6.

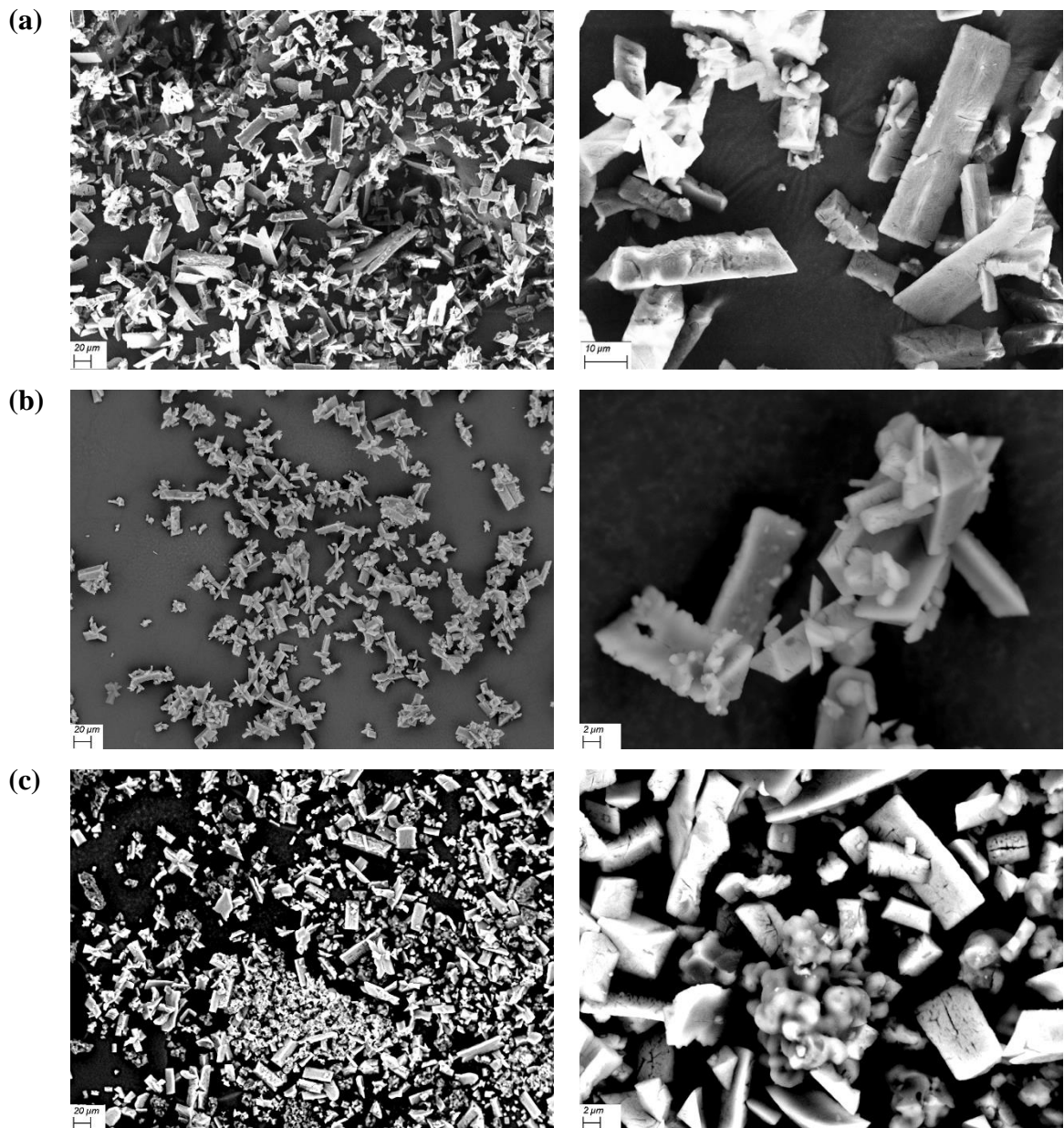
Without lignin addition, under higher alkalinity, the struvite still remains typical orthorhombic morphology while some irregular cluster crystals are attached to the struvite surface. The EDS results shown in Figure 5.7(a) indicates that the cluster crystals are likely to be carbonate compounds, such as magnesium carbonates ( $\text{MgCO}_3$ )



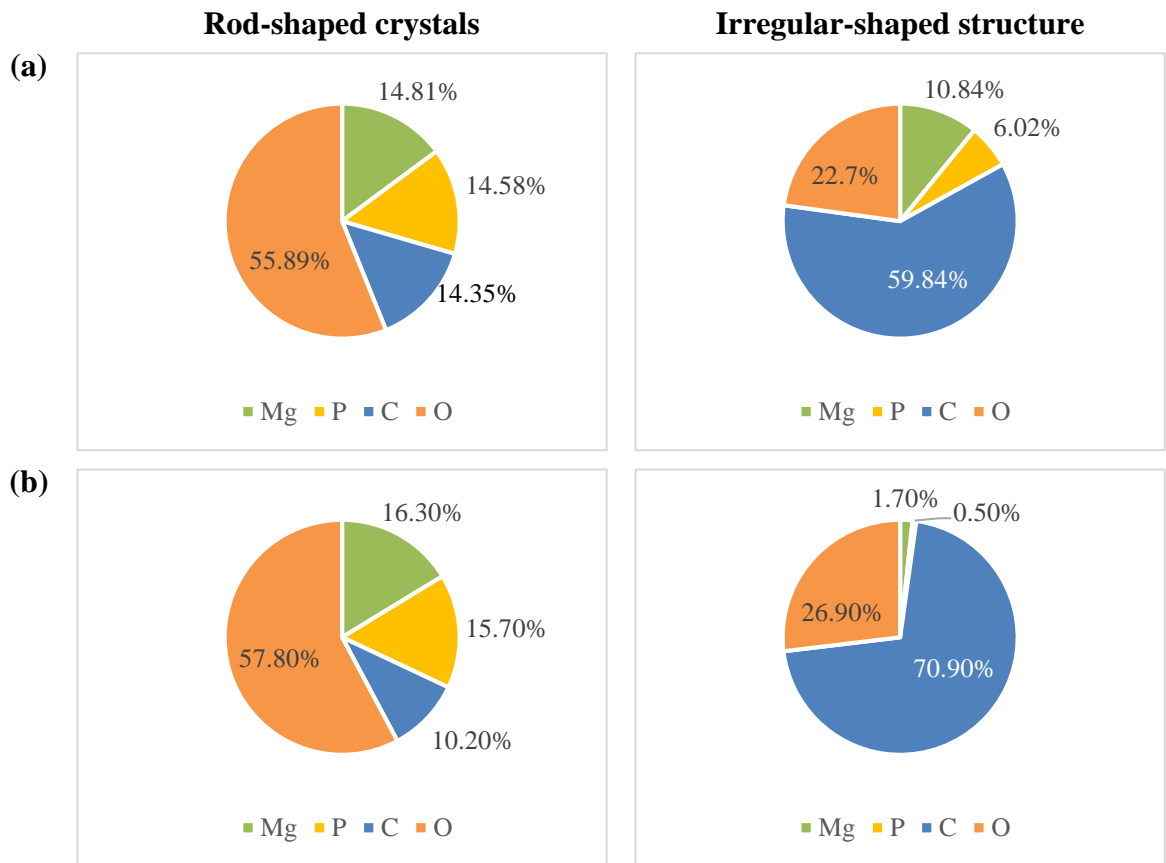
simultaneously co-precipitated with struvite, which is consistent with the precipitation tendency predicted by Visual MINTEQ (Figure 5.4).

Compared to struvite at the alkalinity of 232 mg/L as CaCO<sub>3</sub>, the size of the struvite produced under higher alkalinity 3000 mg/L as CaCO<sub>3</sub> is much smaller (decreasing from 30 μm to around 10 μm), which is consistent with the previous study (Xueyu Liu et al., 2015). A possible reason may be that higher alkalinity stabilizes the pH at a relatively high level which leads to a higher supersaturation, thus the nucleation rate is higher than the growth rate and more fine particles form (Ghosh et al., 2019b; Xiaoning Liu et al., 2013). Therefore, although higher alkalinity results in higher PO<sub>4</sub>-P recovery, more fine crystals and co-precipitates are likely to form, which reduce the purity of the struvite collected.

Compared to the precipitate without lignin addition at the alkalinity of 3000 mg/L as CaCO<sub>3</sub> ( Figure 5.6(b)), with 6 g/L lignin addition (Figure 5.6(c)) the lignin-struvite clusters are observed and nearly all the crystals are orthorhombic morphology, which indicates that the purity of struvite is higher. The EDS (Figure 5.7(b)) also shows that Mg/P atom ratio of the crystals are all around 1.0, which confirmed that lignin still reduces the potential of co-precipitates under higher alkalinity.



**Figure 5. 6** SEM images of the precipitate from synthetic wastewater at pH = 7.9 with an alkalinity of (a) 232 mg/L as CaCO<sub>3</sub>, lignin = 0 g/L, (b) 3000 mg/L as CaCO<sub>3</sub>, lignin = 0g/L, and (c) 3000 mg/L as CaCO<sub>3</sub>, lignin = 6 g/L.



**Figure 5. 7** EDS analysis (Atom%) of rod-shaped crystal and irregular structure observed in SEM images of precipitate based on point analysis from synthetic wastewater (pH = 7.9, Alkalinity = 3000 mg/L as CaCO<sub>3</sub>) with lignin of (a) 0 g/L (b) 6 g/L.

## 5.5 Conclusion

The lignin-induced struvite crystallization is influenced by initial  $\text{PO}_4\text{-P}$  and  $\text{NH}_4\text{-N}$  concentrations, TSS and alkalinity of the wastewater. The phosphorus recovery of lignin-induced struvite precipitation increases with increasing concentrations of  $\text{PO}_4\text{-P}$ ,  $\text{NH}_4\text{-N}$  or alkalinity. At a lower wastewater pH of 7.9, the effects of lignin on enhancing struvite precipitation and  $\text{PO}_4\text{-P}$  recovery are still significant under different  $\text{PO}_4\text{-P}$  and  $\text{NH}_4\text{-N}$  concentrations. Moreover, lignin is more efficient to promote  $\text{PO}_4\text{-P}$  recovery under relatively lower alkalinity and still effective to reduce the potential of co-precipitates under higher alkalinity. Also, the result indicates that increasing TSS concentration to 205 mg/L does not show the significant effect on phosphorus recovery efficiency ( $p > 0.05$ ). Therefore, the effect-stability and availability of lignin in promoting phosphorus recovery from synthetic wastewaters with different characteristics is confirmed furthermore in this study.

## 5.6 Acknowledgement

The authors acknowledge the funding from Alberta Innovates-Alberta Bio Future Lignin Challenge 1.0 Program and Alberta Bio Future Lignin Pursuit Program, Canada Research Chair (CRC) in Future Community Water Services (Liu, Y.), Natural Sciences and Engineering Research Council of Canada (NSERC) Discovery Grant (Lu, Q.) and the Start-up Fund from the University of Calgary (Lu, Q.).

## Chapter 6 Conclusion and Future Work

### 6.1 Conclusion

The major focus of this study was to establish the feasibility of adding lignin as seeds to enhance the phosphorus recovery efficiency from synthetic wastewater. Although the precipitation of struvite in wastewater is not a new process, novel seed materials that promote phosphorus recovery are receiving increasing attention.

Several operation conditions will affect the physical and chemical nature of collected struvite. Based on the results of the batch experiments, the effect of lignin on promoting PO<sub>4</sub>-P recovery is significant especially at lower pH (pH = 7.9, Mg/P molar ratio = 1.5:1, lignin dosage = 6 g/L). Compared with other non-struvite seed materials, lignin shows its superiority in eco-friendliness and effectiveness for enhancing phosphorus recovery efficiency. While compared with struvite seed, lignin mitigates the production of co-precipitate and reduces the need to adjust pH thus saves the cost of alkali. The thermodynamic software modeling result predicts the variability of possible co-precipitates under different pH, which is further confirmed by XRD results. The morphology and elemental analysis also indicate that some struvite grows onto lignin to form a larger cluster, which is likely due to the aggregation of lignin and in-situ-pH-favorable nucleation sites provided by lignin with the large surface area.

The effect-stability and availability of lignin performance are also evaluated. The effect of lignin is still significant at different synthetic wastewater with different characteristics. At lower pH, the effect of lignin on enhancing struvite precipitation and

phosphorus recovery efficiency is still significant under different  $\text{PO}_4\text{-P}$  and  $\text{NH}_4\text{-N}$  concentrations. Moreover, lignin is more efficient to increase phosphorus recovery under relatively lower alkalinity. Under higher alkalinity, according to the morphology and elemental analysis, lignin could reduce the co-precipitates potential, while smaller-size struvite and more co-precipitates will appear without lignin addition. As for the total suspended solids (TSS), the results show that the effect of TSS on phosphorus recovery efficiency is not significant ( $p > 0.05$ ).

Overall, this study indicates the availability and effect-stability of lignin in promoting struvite crystallization and proposes a new possible use of lignin and makes struvite recovery more cost-effective afterward.

## **6.2 Future Work**

The phosphorus recovery efficiency increases with the increasing pH, however, at the higher pH the effect of lignin will be reduced due to the higher solubility of Kraft lignin. Therefore, the modification of lignin to reduce the solubility at higher pH is required to obtain more efficient lignin seed material.

Furthermore, as the experiments were conducted in a batch system, which are not completely reflective of a reactor or pilot-scale system. The reactor running with real biosolid digestate supernatant wastewater will help determine if similar optimizations are observed under larger scale and more complex feed.

The evaluation of biological and chemical hazards and solubility product values for different struvite samples collected at varying wastewaters could also be conducted.

This could help strengthen the optimization conditions to form a more efficient struvite product as a slow-release fertilizer.

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**v1.10 Last updated September 2015**

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