



**Nutrient Removal and Recovery by the Precipitation
of Magnesium Ammonium Phosphate**

By

Guangan Jia

School of Chemical Engineering

Faculty of Engineering, Computer and Mathematical Sciences

The University of Adelaide

Adelaide South Australia

**A Thesis Submitted for the Degree of
Master of Philosophy**

DECLARATION

NAME: Guangan JIA

PROGRAM: Master of Philosophy

This work contains no materials which have been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due references have been made in the text.

I give consent to this copy of my thesis, when deposited in the University Library, being available for loan and photocopying, subject to the provisions of the Copyright ACT 1968.

I also give permission for the digital version of my thesis to be made available on the web, via the University's digital research repository, the Library catalogue, the Australian Digital Thesis Program (ADTP) and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

SIGNATURE:

DATE:

ACKNOWLEDGEMENTS

I have to say it has been a long and windy journey to get to the completion of this project. At times, there were huge obstacles that I had to deal with and without help and support from the research group and The School of Chemical Engineering, this thesis would not have been possible. I would like to extend my gratitude to the following people for their contribution throughout this project:

- My supervisors Associate Professor Bo Jin (The School of Chemical Engineering, The University of Adelaide), Associate Professor Joerg Krampe (South Australia Water Corporation), Dr. Hu zhang (The School of Chemical Engineering, The University of Adelaide) and Associate Professor Sheng Dai (The School of Chemical Engineering, The University of Adelaide). Thank you for your patience with and faith in me.
- This project would not have been possible without support from South Australia Water Corporation and United Water in Bolivar, thanks very much for providing centrate and data of wastewater.
- I also want to thank research group members: Lijuan Wei, Ming Dai, Dr Guiseppe Laera, Frank Fan, Xing Xu, and Cuong Tran from The School of Chemical Engineering, The University of Adelaide, thank you for your sincere help and useful suggestions.
- The staff at School of Chemical Engineering who would happily assist with my queries.
- Fellow post-graduate colleagues at School of Chemical Engineering, I appreciated the time spent with these great research students, it was a real pleasure doing research in this university.

- The staff at Adelaide Microscopy, in particular Ken.
- My parents, my wife, and my two sons for their patience and emotional support and constant faith in me, without their support, I would go nowhere.

ABSTRACT

Phosphate and ammonium are the main nutrient sources in wastewater, contributing to eutrophication of water bodies. Removal of these nutrients from wastewater using conventional technologies is a challenge in water industry. Many processes have been developed to remove these two nutrients. On the other hand, phosphorus from nature is not infinite, which will be running out in about 50 – 100 years. Therefore recycling phosphorus is becoming an issue, as well as a challenge, for researchers all over the world.

This research is to investigate a chemical process technology to recover the nutrients by the precipitation of magnesium ammonium phosphate (MAP), which is valuable product and nutrient fertiliser. This is a new process based on the chemical equilibrium, which is greatly affected by pH of the solution, concentrations of Mg^{2+} , NH_4^+ , PO_4^{3-} , and other ions and organic matters included in the wastewater. In order to implement this process, the optimal pH, and the best molar ratio of Mg^{2+} , NH_4^+ and PO_4^{3-} must be adequately studied.

In this thesis, the optimal pH and optimization of the molar ratio of $Mg^{2+}:NH_4^+:PO_4^{3-}$, were studied based on synthetic wastewater. It was found that the best pH range was 9-9.5, and the best molar ratio was $Mg^{2+}:NH_4^+:PO_4^{3-}=1.3:1:1.1$. Visual MINTEQ 3.0 software was then introduced to predict the possible solids precipitated and additional alkaline required in order to maintain the optimal pH value during experiments. Laboratory scale experiments were carried out under the same conditions of model input. Struvite yielded from laboratory experiments was tested and confirmed by SEM and X-ray diffraction. The results indicated that the experimental results agreed well with that of model prediction within the error deviation. Reagent addition rate and temperature were also tested in terms of removal

efficiency and morphology of the precipitates. These two factors can affect size and morphology of crystals, but have limited impact on the removing efficiency compared to pH and concentration.

The main advantages of this technology are to recover nutrients and to prevent eutrophication. Preliminary results of operational factors of laboratory scale MAP system have been discussed and presented. Conclusions and recommendations were also made in this work.

Table of Contents

Declaration	I
Acknowledgements	II
Abstract	IV
List of Figures	X
List of Tables	X VII
List of Abbreviations	X VIII
List of Equations	X X
Chapter 1 Introduction	1
1.1 Background.....	2
1.2 Aim and objectives.....	5
1.3 Thesis outline	6
Chapter 2 Literature review	8
2.1 Introduction.....	9
2.2 Wastewater treatment process.....	9
2.2.1 Physical treatment.....	10
2.2.2 Biological treatment.....	10
2.2.3 Tertiary treatment.....	15
2.3 NH_4^+ and PO_4^{3-} recovery by the precipitation of magnesium ammonium phosphate.....	23
2.4 Factors influencing struvite precipitation process.....	30
2.5 Characteristics of struvite.....	38

2.6 Economic value of struvite.....	41
2.7 Modelling of precipitation process of magnesium ammonium phosphate.....	45
2.8 Summary.....	50
Chapter 3 Materials and experiments	52
3.1 Experiment setup	53
3.2 Materials.....	53
3.3 Preparation of solutions required.....	54
3.3.1 Ammonium preparation	54
3.3.2 Magnesium (Mg^{2+}) preparation	54
3.3.3 Phosphate (PO_4^{3-}) preparation	55
3.4 Wastewater from Bolivar wastewater treatment plant.....	55
3.5 Analysis methods and procedure	56
3.5.1 Analysis methods.....	56
3.5.2 Analysis procedure.....	57
3.5.3 Instruments used.....	57
3.6 Experiments.....	60
3.6.1 Sample preparation.....	60
3.6.2 Experiments without pH control.....	61
3.6.3 Experiments with pH control.....	61
3.6.4 Feeding rate.....	62
Chapter 4 Optimisation of pH and molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}	63

4.1 Introduction.....	64
4.2 Materials and methods	67
4.2.1 Materials.....	67
4.2.2 Struvite precipitation system and its operation.....	68
4.2.3 Characterization of crystals precipitated.....	69
4.2.4 Analysis of chemicals and data.....	69
4.3 Results and discussion	70
4.3.1 Optimization of operation pH.....	70
4.3.2 Magnesium and phosphate sources.....	78
4.3.3 Effect of Mg^{2+} : NH_4^+ : PO_4^{3-} molar ratio.....	82
4.3.4 The effect of feeding rate.....	94
4.3.5 The effect of temperature	96
4.4 Conclusions.....	100
References.....	102
Chapter 5 Modelling of struvite precipitation process.....	109
5.1 Introduction.....	110
5.2 Materials and methods.....	112
5.2.1 Materials.....	112
5.2.2 Struvite precipitation test.....	113
5.2.3 Characterization of precipitated crystals.....	113
5.2.4 Analytical methods and procedures.....	113
5.3 Chemical modelling.....	114

5.4 Visual MINTEQ3.0 setup and Model revising.....	116
5.4.1 Thermodynamic chemical equilibrium.....	116
5.4.2 Model revising.....	116
5.4.3 Model operation conditions.....	118
5.5 Results and discussion.....	122
5.5.1 Model output	122
5.5.2 Experimental results.....	126
5.5.3 Mass balance analysis.....	131
5.5.4 X-ray diffraction results.....	132
5.6 Comparison of experimental data with modelling results.....	135
5.7 Summary.....	139
References.....	140
Chapter 6 Conclusions and recommendations.....	146
6.1 Conclusions.....	147
6.2 Recommendations.....	149
References	151
Appendix 1.....	170
Appendix 2.....	172

List of figures

Figure 1.1 Eutrophication problems (Algae).....	4
Figure 1.2 Consequences of eutrophication problems.....	4
Figure 2.1 A typical large scale sewage treatment plant.....	10
Figure 2.2 Process diagram of anaerobic digestion (Gerardi et al., 2003).....	14
Figure 2.3 Nitrogen cycle in WWTP (Starmen et al., 2009).....	16
Figure 2.4 Nitrogen shortcut in enhanced BNR (Starmen et al., 2009).....	16
Figure 2.5 Air stripping process	18
Figure 2.6 Cone aerators	19
Figure 2.7 Draft aerator	19
Figure 2.8 Cascade aerator	20
Figure 2.9 Spray aerator	20
Figure 2.10 Scheme of the A ² /O simulated plant for simultaneous C/N/P removal. Javier Guerrero et al., (2010).....	22
Figure 2.11 Representative integrated constructed wetland system 11 in winter 2006: (a) sedimentation tank; (b) site overview; and (c) inlet arrangement to the first ICW cell.....	23
Figure 2.12 Reactor used by Jaffer et al., (2001).....	24
Figure 2.13 Reactor fabricated by Etter et al.,(2011)	27
Figure 2.14 Reactor used by Korchef (2011)--dissolved carbonate removal technique.....	28
Figure 2.15 Crystallization pilot plant developed by Martí et al., (2010).....	28

Figure 2.16 Reactor designed by Münch et al., (2001)	29
Figure 2.17 Picture of pure struvite crystals.....	38
Figure 2.18 SEM Images of struvite obtained by Korchef et al.,(2011) in his experiments.....	38
Figure 2.19 SEM Image of struvite obtained by Ye et al., (2010) in his experiments.....	39
Figure 2.20 SEM Image of struvite recovered from swine wastewater by Rahman et al., (2011).....	40
Figure 2.21 SEM Image of struvite recovered from landfill leachates by Zhang et al., (2009)	40
Figure 2.22 Reactor designed by Rahman et al., (2011) to recover N and P....	42
Figure 2.23 A model flow designed by Harada et al., (2006)	48
Figure 2.24 Model procedure developed by Gadekar et al., (2010)	49
Figure 3.1 Experiment process setup	53
Figure 3.2 SHIMADZU, AA-6300, Atomic absorption spectrophotometer.....	58
Figure 3.3 LIUV-201 UV/Vis spectrometer	58
Figure 3.4 Colorimeter HACH.....	59
Figure 3.5 X-ray Diffraction, Miniflex 600	59
Figure 3.6 Philips XL 30 Scanning electron microscopy	60
Figure 4.1 pH variation from 8 to 11 during the course of precipitation reaction without pH control. The molar ratio of Mg^{2+} : NH_4^+ : PO_4^{3-} was 1:1:1.....	71

Figure 4.2 Impact of MAP formation and ammonium removal efficiency in laboratory scale experiments without pH control (molar ratio of Mg^{2+} : NH_4^+ : PO_4^{3-} was 1:1:1).....	72
Figure 4.3 Mass profile of crystals and residuals of ammonium and phosphate at a controlled pH range (8-11) (molar ratio of Mg^{2+} : NH_4^+ : PO_4^{3-} was 1:1:1).....	73
Figure 4.4 XRD pattern of the struvite, magnesium phosphate and brucite precipitated at Mg^{2+} : NH_4^+ : PO_4^{3-} molar ratio 1:1:1 at initial pH 9 without pH control. 1. Standard pattern PDF# 15-0762. 2. Standard pattern PDF#35-0134. 3. Standard pattern PDF#44 1482.....	76
Figure 4.5 XRD pattern of the struvite precipitated at Mg^{2+} : NH_4^+ : PO_4^{3-} molar ratio 1:1:1 at initial pH 9 with pH control. 1. Standard pattern PDF# 15-0762.....	77
Figure 4.6 SEM image of struvite obtained from synthetic wastewater at initial pH 9 without pH control, the molar ratio of Mg^{2+} : NH_4^+ : PO_4^{3-} was 1:1:1.....	77
Figure 4.7 SEM image of struvite obtained from synthetic wastewater at initial pH 9 with pH control, the molar ratio of Mg^{2+} : NH_4^+ : PO_4^{3-} was 1:1:1.....	78
Figure 4.8 Mass of crystals and removal efficiency of ammonium and phosphate at different pH value 8.5, 9 and 9.5 with the molar ratio of Mg^{2+} : NH_4^+ : PO_4^{3-} =1:1:1.....	79
Figure 4.9 System profiles of crystal mass and NH_4^+ -N removal efficiency using MgO and H_3PO_4 (85%) and $MgCl_2 \cdot 6H_2O + KH_2PO_4$ at pH 8.5, 9, and 9.5.....	80
Figure 4.10 XRD shows the struvite precipitated at Mg^{2+} : NH_4^+ : PO_4^{3-} molar ratio 1:1:1 at initial pH 9 with MgO as resource. 1. Standard pattern PDF# 15-0762.....	81

Figure 4.11 SEM image of crystal precipitated by using MgO as resource at pH 9, molar ratio of $Mg^{2+}: NH_4^+: PO_4^{3-} = 1:1:1$	82
Figure 4.12 Removal efficiency of ammonium and phosphate at different molar ratio of $Mg^{2+}: NH_4^+: PO_4^{3-}$ with pH at 9.....	84
Figure 4.13 Mass of crystals at different molar ratio of $Mg^{2+}: NH_4^+: PO_4^{3-}$ under pH at 9 at stirring rate of 200 rps.....	84
Figure 4.14 Removal efficiency of ammonium and phosphate at different molar ratio of $Mg^{2+}: NH_4^+: PO_4^{3-}$ with pH at 9 and the stirring rate was 200 rps.....	87
Figure 4.15 Mass of crystals at different molar ratio of $Mg^{2+}: NH_4^+: PO_4^{3-}$ under pH at 9 at stirring rate of 200 rps.....	87
Figure 4.16 Removal efficiency of ammonium and phosphate at different molar ratio of $Mg^{2+}: NH_4^+: PO_4^{3-}$ with pH at 9.....	89
Figure 4.17 Mass of crystals at different molar ratio of $Mg^{2+}: NH_4^+: PO_4^{3-}$ under pH 9.....	90
Figure 4.18 Comparison of ammonium removal efficiency obtained by different researchers with different molar ratio of $Mg^{2+}: NH_4^+: PO_4^{3-}$ at pH 9 with $MgCl_2 \cdot 6H_2O$ as Mg resource.....	90
Figure 4.19 XRD pattern of the struvite precipitated at $Mg^{2+}: NH_4^+: PO_4^{3-}$ molar ratio 1:1:1 at initial pH 9 with pH control. 1. Standard pattern PDF# 15-0762.....	92
Figure 4.20 XRD of struvite obtained at pH 9 with molar ratio of 1:1:1.2 ($Mg^{2+}: NH_4^+: PO_4^{3-}$). 1. Standard pattern PDF# 15-0762.....	92
Figure 4.21 SEM image of struvite obtained at room temperature with the molar ratio of $Mg^{2+}: NH_4^+: PO_4^{3-} = 1:1:1.2$ at pH 9, stirring rate was 200rps.....	93
Figure 4.22 Mass of Crystals and removal efficiency of ammonium and phosphate at different feeding rate.....	95

Figure 4.23 XRD of struvite obtained at pH 9 with molar ratio of 1.3:1:1.1 (Mg^{2+} : NH_4^+ : PO_4^{3-}) and reagent addition rate at 7.1 mL/min. 1. Standard pattern PDF# 15-0762.....	95
Figure 4.24 SEM image of struvite obtained at 25 °C with the molar ratio of Mg^{2+} : NH_4^+ : PO_4^{3-} = 1.3:1:1.1 at pH 9, reagent addition rate at 7.1 mL/min.....	96
Figure 4.25 Mass of crystals and removal efficiency of ammonium and phosphate at different temperature.....	97
Figure 4.26 XRD of struvite obtained at pH 9 with molar ratio of 1.3:1:1.1 (Mg^{2+} : NH_4^+ : PO_4^{3-}) and reagent addition rate at 7.1 mL/min, temperature was 30 degree. 1. Standard pattern PDF# 15-0762.....	99
Figure 4.27 SEM image of struvite obtained at 30 °C with the molar ratio of Mg^{2+} : NH_4^+ : PO_4^{3-} = 1.3:1:1.1 at pH 9, stirring rate was 200rps.....	99
Figure 4.28 SEM image of struvite obtained at 35 °C with the molar ratio of Mg^{2+} : NH_4^+ : PO_4^{3-} = 1.3:1:1.1 at pH 9, stirring rate was 200rps.....	100
Figure 5.1 The main page of Visual MINTEQ 3.0.	119
Figure 5.2 Management tool of Visual MINTEQ 3.0 is used to add or delete possible solids to output.....	119
Figure 5.3 The components concentration page to input the different concentrations of ions.....	121
Figure 5.4 Model output of pH, ionic strength, solids and concentration of different ions.....	122

Figure 5.5 Crystals different shape and size in stage A and stage B detected by Sun et al., (2011).....	130
Figure 5.6 XRD of struvite-K studied by Zhang et al (2011).....	131
Figure 5.7 XRD pattern of struvite, struvite-(K), monetite, and magnesite confirmed under Condition 3. (1. Struvite, Standard pattern PDF# 15-0762; 2. Struvite-(K), Standard pattern PDF# 35-0812; 3. Monenite, Standard pattern PDF# 09-0080; 4. Magnesite, Standard pattern PDF# 08-0479.).....	133
Figure 5.8 SEM image of struvite under Condition 3.....	133
Figure 5.9 SEM image of struvite-(K) under Condition 4.....	134
Figure 5.10 Comparison of ammonium removal efficiency obtained by different researchers with different molar ratio of Mg^{2+} : NH_4^+ : PO_4^{3-} at pH 9 with $MgCl_2 \cdot 6H_2O$ as Mg resource.....	138
Figure A1.1 Standard curve of PO_4^{3-} by LIUV-201 UV/vis spectrometer.....	170
Figure A1.2 Standard curve of NH_4^+ by DR/890 colorimeter HACH, Amver TM HACH Test 'N Tube High Range Ammonium Reagent Set.	170
Figure A1.3 Standard curve of Mg^{2+} by SHIMADZU, AA-6300, Atomic absorption spectrophotometer.....	171
Figure A2.1 SEM image of struvite at pH 8.5 with molar ratio of Mg^{2+} : NH_4^+ : PO_4^{3-} =1:1:1.....	172
Figure A2.2 SEM image of struvite at pH 9 with molar ratio of Mg^{2+} : NH_4^+ : PO_4^{3-} =1.2:1:1.....	172

Figure A2.3 SEM image of struvite with molar ratio of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ =1.2:1:1.2.....	173
Figure A2.4 SEM image of struvite with molar ratio of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ =1.4:1:1.4.....	173
Figure A2.5 SEM image of struvite at pH 9 with molar ratio of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ =1.6:1:1.....	174
Figure A2.6 SEM image of struvite with molar ratio of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ =1.6:1:1.4.....	174
Figure A2.7 SEM image of struvite at pH 9.5 with molar ratio of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ =1.3:1:1.1.....	175

List of Tables

Table 2.1 Experiments designed by Kim (2006) to determine the effect of feeding sequence.....	34
Table 2.2 The kinetic parameters calculated for MAP formation in different studies.....	37
Table 2.3 Summary of costs for a full-scale plant. Jaffer et al., (2001).....	44
Table 2.4 Economical comparison of phosphorous removal process (Unitika Japan).....	45
Table 3.1 Characteristics of centrate from Bolivar wastewater treatment plant, Adelaide.....	56
Table 5.1 Characteristics of raw wastewater from Bolivar wastewater treatment plant, ADELAIDE.....	112
Table 5.2 Modelling process to measure the dosage of NaOH needed to reach pH 9.....	123
Table 5.3 Model outputs of different ions, removal efficiency of NH_4^+ -N and PO_4^{3-} -P, and solid phase predicted under different conditions.....	124
Table 5.4 Table 5.4 Experimental results of different ions, removal efficiency of N and P, and crystals confirmed under condition 1, 2, and 3.....	128
Table 5.5 Table 5.5 Experimental results of different ions, removal efficiency of N and P, and crystals confirmed under condition 4, 5, and 6.....	129
Table 5.6 Mass balance analysis from condition 4.....	132
Table 5.7 Comparison of modelling outputs and experimental results under different conditions.....	137

List of Abbreviations

STPs: Sewage treatment plants

SDE: Sludge dewatered effluent

WWTP: wastewater treatment plant

MAP: Magnesium ammonium phosphate

SEM: Scanning electron microscopy

XRD: X-ray diffraction

AD: Anaerobic digestion

LCFAs: Long chain fatty acids

EPA: Environmental protection agency

BNR: Biological nutrient removal

PAOs: Polyphosphate accumulating organisms

A²/O: Anaerobic-aerobic-oxic

ICW: Integrated constructed wetland

SBRs: Sequencing bench reactors

UASB: Upflow anaerobic sludge blanket

RSM: Response surface technology

CCD: Central composite design

TS: Total solids

PS: Solubility product

HAP: Hydroxyapatite

OCP: Octacalcium phosphate

TCP: Tricalcium phosphate

DCP: Monetite

DCPD: Brushite

CBA: Cost-benefit analysis

List of Equations

Equation 2.1 Typical ion-exchange reactions	20
Equation 2.2 Magnesium ammonium phosphate reaction equation.....	30
Equation 2.3 Two ways for ammonium removal reactions.....	33
Equation 2.4 The first order reaction expression.....	35
Equation 2.5 The linear first order equation.....	35
Equation 2.6 The kinetics of chemical process.....	36
Equation 2.7 The first order reaction by Zhang et al., (2009).....	36
Equation 2.8 The second order reaction by Zhang et al., (2009).....	36
Equation 2.9 The third order reaction by Zhang et al., (2009).....	36
Equation 2.10 The equation to calculate net profit.....	44
Equation 2.11 The equation for calculating benefit.....	44
Equation 2.12 Equation to calculate species ionic strength.....	47
Equation 2.13 Equation to calculate species ionic strength.....	47
Equation 4.1 Magnesium ammonium phosphate reaction equation.....	65
Equation 5.1 Magnesium ammonium phosphate reaction equation.....	110