UNIVERSITI PUTRA MALAYSIA

CRYSTALLIZATION AND CHARACTERIZATION OF STRUVITE CRYSTALS THROUGH GEL GROWTH TECHNIQUE

AHMAD SALSABILI

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By

AHMAD SALSABILI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

August 2017

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DEDICATION

Dedicated to my beloved parents, lovely wife and cute daughter.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Crystal growth or crystallization is defined as controlled phase or state change to solid state. This state transition might happen from any state of matter, liquid, gas or solid to solid state which are crystals. Crystalline materials produced through chemical reaction in any media can readily be controlled in order to increase the crystal size, yield and change the crystals morphology. However, the gel media is known to be one of the best media for investigating the effects of different operational parameters on crystals size, morphology, yield and purity so far.

Magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4.6H_2O$) which is better known as struvite, is one of the most fascinating inorganic phosphate compounds. There are several reasons associated with the study of struvite crystals. First of all, it is one of most popular scale deposits in wastewater treatment plants. Second of all, struvite is known as one of the major components of urinary calculi.

Crystallization and characterization of struvite crystals grown in gel media has been carried out in the current study. Struvite crystals were grown in two different gels of gelatin and silica gel using both single and double diffusion crystallization techniques. The pH ranged from 6 to 9 for silica gel and gelatin. Different gel densities were practiced ranging from 1.04 to 1.08 for silica gel and 1.04 to 1.11 for gelatin. Totally the crystals grown in silica gel had more variety of morphologies and the silica gel itself demonstrated less number of limitations compare to gelatin gel. Crystals with prismatic, pyramidal, dendritic, star shaped and branched star shaped morphologies were grown through this technique mainly in silica gel. The grown crystals in both gel media have been characterized by SEM, EDX and FTIR sets. The SEM test revealed the inner morphology, crystal size and the volume of cracks inside the crystals. EDX test proved the existence of comprising elements, namely phosphorous, oxygen and magnesium. The FTIR test revealed the internal chemical bonds of N-H, O-H, P-O, water of crystallization and metal-

oxygen bonds. The FTIR results are presented and compare to other studies carried out formerly.

The harvested struvite crystals grown within different operational conditions were analyzed by powder X-ray diffraction (XRD) set. The crystal size was calculated based on Scherrer equation which ranged from 27.9124 to 32.5919 nm. It has been found that struvite crystallizes in the orthorhombic (single-phase) Pmn21 space group with unit cell parameters: a = 6.9550 Å, b = 6.1420 Å, c = 11.218 Å and $\alpha = \beta = \Upsilon = 90°$. Totally, the crystals grown in pH of 8 had larger crystal size. This was also approved by the SEM analysis showing less amount of cracks happening at this pH value.

Struvite crystal habits were analyzed using optical microscopy. All three crystals diaphaneity, transparent, translucent and opaque were noticed in the crystallization of struvite crystals in silica gel. The crystals formed in the acidic pH values (6, 6.5) demonstrated high transparency while the crystals formed at high alkaline pH values had more translucent and opaque diaphaneity. The high alkaline pH value (9) lead to the formation of Liesegang rings which is described in detail in the context.

The solubility of produced crystals were analyzed through solubility test. Proportional portions of the harvested crystals were stirred well for one day at constant rate of 400 RPM and after that dried out in the oven at 35 °C. The solubility results revealed that the minimum solubility happens for the crystals grown in gel with pH of 8 at 392 and 474 mg/l for gel SG of 1.07 and 104 respectively.

An optimization study based on Taguchi model of experiment design has been carried out and the results were announced. The effects of different combination of four process parameters of gel density, gel pH, magnesium molarity and ADP molarity on struvite crystal size were studied and the results were reported. The results of the ANOVA analysis revealed that pH was the most influential parameter in sense of producing bigger crystals with contribution percent of over 65% followed by magnesium dosage (25%), ADP molarity (7%) and gel density (1%).

The kinetics and growth mechanism of struvite crystallization in gel media has been studied in this thesis. For this purpose, both pseudo first and second-order kinetic models were applied to the experimental data. The tests were carried out on the amount of magnesium concentraton changes over time and rate of struvite crystals formation assuming equamolar reaction (consumption) of 1:1:1 for Mg:NH4:PO4. The magnesium concentration was measured at certain intervals and based on the concentration reduction of magnesium, the kinetic rate constants (K1, K2) and rates of reaction (R) for samples grown in various operational conditions were calculated and reported. Based on the results of the kinetic study the experimental data better fits with second-order kinetic model with minimum and maximum R2 over 97% and 99% compare to first-order kinetic model with minimum and maximum R2 of 89% and 95% respectively. The obtained pseudo first and second-order rate constants can be used to explain the struvite crystallization behavior.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

KAJIAN PENGHABLURAN DAN PENCIRIAN KRISTAL STRUVITE DITANAM MELALUI TEKNIK PERTUMBUHAN GEL

Oleh

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Pertumbuhan kristal atau penghabluran juga ditakrifkan sebagai fasa kawalan atau perubahan keadaan kepada keadaan pepejal. Peralihan keadaan yang mungkin berlaku dari mana-mana keadaan jirim, cecair, gas atau pepejal kepada keadaan pepejal yang kristal.

Bahan kristal dihasilkan melalui tindak balas kimia dalam mana-mana media dengan mudah boleh dikawal untuk meningkatkan saiz kristal, hasil dan perubahan morfologi kristal. Walau bagaimanapun, media gel dikenali sebagai salah satu media yang terbaik untuk mengkaji kesan parameter operasi yang berbeza pada saiz kristal, morfologi, hasil dan ketulenan setakat ini.

Magnesium ammonium fosfat heksahidrat ($MgNH_4PO_4.6H_2O$) yang lebih dikenali sebagai struvite, adalah salah satu sebatian fosfat bukan organik yang paling menarik. Terdapat beberapa sebab-sebab yang berkaitan dengan kajian kristal struvit. Pertama sekali, ia adalah salah satu kapur yang paling popular dalam rawatan loji air sisa. Kedua, struvite dikenali sebagai salah satu komponen utama kalkuli urinari.

Penghabluran dan pencirian kristal struvite ditanam di media gel telah dijalankan dalam kajian ini. Kristal struvite telah ditanam dalam dua gel yang berbeza gelatin dan gel silika menggunakan kedua-dua teknik penyebaran penghabluran tunggal dan berganda. pH adalah di antara 6-9 untuk gel silika dan gelatin. Kepadatan gel yang berbeza telah diamalkan antara 1.04-1.08 untuk gel silika dan 1.04-1.11 untuk gelatin. Secara keseluruhannya, kristal ditanam di gel silika mempunyai morfologi yang lebih pelbagai dan gel silika itu sendiri menunjukkan jumlah kekurangan yang kurang berbanding dengan gel gelatin. Kristal dengan prisma, piramid, dendritik, berbentuk bintang dan morfologi berbentuk bintang bercabang telah ditanam melalui teknik ini terutamanya dalam gel silika. Kristal di kedua-dua media gel telah dicirikan oleh set SEM, EDX dan FTIR. Ujian SEM

mendedahkan morfologi dalaman, saiz kristal dan jumlah retak dalam kristal. Ujian EDX membuktikan kewujudan unsur yang terdiri daripada fosforus, oksigen dan magnesium. Ujian FTIR mendedahkan ikatan kimia dalaman N-H, O-H, P-O, penghabluran air dan bon logam-oksigen. Keputusan FTIR dibentangkan dan dibandingkan dengan kajian lain yang dijalankan sebelum ini.

Kristal struvite dituai ditanam dalam keadaan operasi yang berbeza dianalisis dengan set serbuk pembelauan sinar-X (XRD). Saiz kristal dikira berdasarkan persamaan Scherrer yang iaitu di antara 27.9124-32.5919 nm. Ia telah didapati bahawa struvite menghablur dalam otorombik (fasa tunggal) kumpulan ruang Pmn21 dengan parameter sel unit: a = 6.9550 Å, b = 6.1420 Å, c = 11.218 Å dan $\alpha = \beta = \Upsilon = 90°$. Secara keseluruhannya, kristal ditanam di pH 8 mempunyai saiz kristal yang lebih besar. Ini juga telah dibuktikan oleh analisis SEM yang menunjukkan kurang jumlah keretakan berlaku pada nilai pH ini.

Tabiat kristal struvite dianalisis dengan menggunakan mikroskop optik. Diaphaneity, ketelusan, lut dan legap ketiga-tiga kristal telah dikenalpasti dalam penghabluran kristal struvite dalam gel silika. Kristal terbentuk dalam nilai pH berasid (6, 6.5) menunjukkan ketelusan yang tinggi manakala kristal terbentuk pada nilai pH alkali yang tinggi mempunyai diaphaneity lebih lut dan legap. Nilai pH alkali yang tinggi (9) membawa kepada pembentukan cincin Liesegang yang diterangkan secara terperinci dalam konteks.

Kebolehlarutan kristal yang dihasilkan dianalisis melalui ujian kelarutan. Bahagian berkadar kristal dituai telah dikacau dengan baik untuk satu hari pada kadar malar 400 RPM dan selepas itu dikeringkan di dalam ketuhar pada suhu 35 °C. Hasil kelarutan mendedahkan bahawa kelarutan minimum berlaku pada kristal ditanam di gel dengan pH 8 pada 392 dan 474 mg/l untuk gel SG 1.07 dan 104 masing-masing.

Satu kajian pengoptimuman berdasarkan reka bentuk eksperimen model Taguchi telah dijalankan dan keputusan telah diumumkan. Kesan kombinasi yang berbeza daripada empat parameter proses ketumpatan gel, pH gel, kemolaran magnesium dan kemolaran ADP kepada saiz kristal struvite dikaji dan keputusan telah dilaporkan. Keputusan analisis ANOVA menunjukkan bahawa pH adalah parameter yang paling berpengaruh dalam menghasilkan kristal yang lebih besar dengan sumbangan peratus lebih daripada 65% diikuti oleh dos magnesium (25%), kemolaran ADP (7%) dan ketumpatan gel (1%).

Kinetik dan mekanisme pertumbuhan penghabluran struvite dalam media gel telah dikaji dalam tesis ini. Bagi tujuan ini, kedua-dua model kinetik tertib pseudo-pertama dan kedua telah diaplikasikan ke atas data eksperimen. Ujian telah dijalankan ke atas jumlah kepekatan magnesium berubah dari masa ke masa dan kadar pembentukan kristal struvite dengan andaian reaksi sama molar (penggunaan) 1: 1: 1 untuk Mg:NH4:PO4. Kepekatan magnesium diukur pada tempoh tertentu dan berdasarkan pengurangan kepekatan magnesium, pemalar kadar kinetik (K1, K2) dan kadar tindak balas (R) untuk sampel ditanam dalam pelbagai keadaan operasi telah dikira dan dilaporkan. Berdasarkan hasil kajian kinetik data eksperimen berpadanan lebih baik dengan model kinetik tertib kedua dengan minimum dan maksimum R2 lebih 97% dan 99% berbanding dengan model kinetik tertib pertama dengan minimum dan maksimum R2 sebanyak 89% dan 95% masing-masing. Kadar pemalar tertib pseudo-pertama dan kedua yang diperolehi boleh digunakan untuk menerangkan tingkah laku penghabluran struvite.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

MAP	Magnesium Ammonium Phosphate
XRD	X-ray Powder Diffraction
XRF	X-ray Fluorescence
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
EDX	Energy-dispersive X-ray Spectroscopy
SMS	Sodium meta-silicate
ADP	Ammonium Dihydrogen Phosphate
SG	Specific Gravity
IUPAC	International Union of Pure and Applied Chemistry
JCPDS	Joint committee of powder diffraction standards
EDTA	Ethylenediaminetetraacetic Acid
FWHM	Full Width at Half Maximum
SLR	Single-lens Reflex Camera
DSLR	Digital Single-lens Reflex Camera
ASTM	American Society for Testing and Materials
θ	Bragg's angle
b	Full wave half width maximum
t	Crystals size (Calculated based on Scherrer equation)
Å	Angstrom (one hundred-millionth of centimiter, 10^{-10} meter

CHAPTER 1

INTRODUCTION

1.1 Background information

Crystallization is considered as one of the most important unit operations in chemical industries where solids with desired physical and chemical properties are separated from a solution, gas or even solid (Ariyanto, 2013). Crystal growth techniques are numerous. They ranges from such simple and inexpensive processes to complicated and expensive processes (Robert S. Feigelson, 2004). The time of crystallization also might take from minutes, hours or days to months and years. The applications of crystallization are so vast from fertilizer industry to pharmaceuticals and catalyst.

Crystal growth or crystallization is also defined as controlled phase or state change to solid state. This state transition might happen from any state of matter, liquid, gas or solid to solid state which are crystals. These crystal growth techniques are named melt growth, vapor growth and solid growth respectively. However, in most system of interest crystallization is the separation of salt from aqueous solution (Britton, 2002a; Robert S. Feigelson, 2004; Dhakal, 2008) or purification (Botsaris and Toyokura, 1997). Basically, the crystallization process happens in solution mode and means that the concentration of dissolved solid which is called solute exceeds the equilibrium (saturated) solute concentration in the solvent which is the medium in which the process happens (Mullin, 2001a; Le Corre, 2006; Le Corre et al., 2009a; Ariyanto, 2013). This sort of solution is called a supersaturated solution which will be further discussed in the following chapters of this thesis.

Generating non-equilibrium supersaturated conditions in solution can be possibly achieved through the following approaches (Mullin, 2001a):

- Changing the medium temperature
- Solvent evaporation
- Chemical reaction
- Changing the composition of the solvent
- Addition of other solutes

The method in which supersaturation is generated through chemical reaction is called precipitation. In this method, two or more reactants are mixed together in appropriate amounts to form an insoluble solid inside the mixture. Manipulating the mixture pH together with the varying the reactants concentrations are known to be the most influential parameters in both precipitation and crystallization processes.

Crystalline materials produced through chemical reaction in any media can readily be controlled in order to increase the crystal size, yield and change the crystals morphology.

However, the gel media is known to be one of the best media for investigating the effects of different operational parameters on crystals size, morphology, yield and purity so far. Gel growth technique is a technique of chemical reaction method, which enables the researchers to monitor the effects of change of different operational parameters easier and spot the optimum growth conditions. The gel growth technique is one sort of modified version of solution growth technique. In this technique, growth happen due to the reaction between two solutions in a gel medium or through achieving supersaturation by diffusion in gel media. Controlled diffusion of reactants in gel media can mimic the real condition in human body in a broad sense (Chauhan, 2011).

Single and double diffusion gel growth technique are simplified *in vitro* models of highly complex growth of urinary calculi *in vivo* (Natarajan et al., 1997a; Kanchana and Sundaramoorthi, 2008; Chauhan and Joshi, 2013). Crystallization and growing crystals with different morphologies is quite common in bio-crystallization through gel growth technique.

Magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4.6H_2O$) which is better known as struvite, is one of the most fascinating inorganic phosphate compounds. There are several reasons associated with the study of struvite crystals. First of all, it is one of most popular scale deposits in wastewater treatment plants. Second of all, struvite is known as one of the major components of urinary calculi.

Degradation of solids in an anaerobic digestion unit in wastewater treatment plants results in releasing magnesium, ammonium and phosphate ions. These dissolved wastewater constituents can combine and react under certain physio-chemical conditions and form struvite precipitates which is commonly known as a nuisance and the source of scale deposition in wastewater treatment plants. Primarily, struvite was known by wastewater companies as something unwanted. It was known as stiff and hard to remove scale forming at points of high turbulence. Pipe walls, pumps and centrifuges are the major parts prone to fouling by struvite deposition in wastewater treatment plants. At the same time, as struvite is globally known as a slow-release fertilizer (Doyle and Parsons, 2002a; Doyle et al., 2003) which makes it a valuable and marketable byproduct in wastewater treatment industry. Predicting struvite precipitation potential is quite critical for operators and designers. The possibility of struvite removal and recovery and enhancing the struvite recovery yield encourages wastewater treatment companies to further study the struvite crystallization and precipitation. Struvite crystallization would also allow reduction of sludge volumes, hence sludge handling and disposal, compared to other phosphorous removal techniques.

Struvite was later on identified by wastewater treatment companies as a premium slow-release fertilizer (Doyle and Parsons, 2002b; Rahman et al., 2014). In addition to represent an approach of limiting phosphorous mining and representing a novel method of removal and recovery of nutrients (N, P) from wastewater streams. The composition of struvite makes it a potentially valuable and marketable product for the fertilizer industry (Ghosh et al., 1996; Barak and Stafford, 2006; El Diwani et al., 2007; Uysal et al., 2010; Karak and Bhattacharyya, 2011; Latifian et al., 2012; Rahman et al., 2013a;

Rahman et al., 2014). NPK (nitrogen phosphate potash) fertilizer is known globally as a good and reliable fertilizer due to the concurrent presence of nitrogen phosphorous and potassium elements (Saïdou et al., 2003). Struvite as a fertilizer has two of these three elements which are quite vital for the growing plants and crops, nitrogen and phosphorus in the form of ammonium and phosphate respectively. As it contains essential nutrients that plants need, therefore, it can be readily used as fertilizer (Britton, 2009; Rahman et al., 2013b).

Besides the useful fertilizer properties of struvite, there are other reasons associated with the study of struvite crystals. First of all, it is one of most popular scale deposits in wastewater treatment plants. Second of all, in an entirely different scenario struvite is known as one of the major components of urinary calculi. Majority of urinary calculi are composed of phosphates and calcium salts (Terai et al., 1996; Minevich, 2001; Chou et al., 2007; Wisener et al., 2010; Bindhu and Thambi, 2012; Fry, 2013; Komyakov et al., 2013). Struvite is also one of the major components of urinary calculi (Terai et al., 1996; Bernardo and Smith, 2000; Bindhu and Thambi, 2012; Chauhan and Joshi, 2013; Honey et al., 2013). Struvite stones are normally formed inside both human and animals kidneys. It is also known as urine sand or urease stone by physicians. Struvite stones are known as infection stones as they mainly happen due to the urinary tract infections. Growing struvite stones in gel media is suggested as the best technique to mimic the growth conditions occurring in a human body in a simplified approach. C. K. Chauhan et. al. (Chauhan, 2011; Chauhan and Joshi, 2013)declared that the gel growth technique is the best and most suitable technique for the development and study of the struvite crystals in order to simulate the real conditions and environment of kidney tissue (Banks et al., 1973; Kanchana and Sundaramoorthi, 2008; Chauhan et al., 2009b; Chauhan, 2011). As mentioned, Struvite features and characteristics like fertilizer properties, being urinary calculi major components and as scale deposits in the wastewater treatment plant in conjunction with its crystallization in gel media make their study quite precious.

1.2 Problem statement

Nowadays, there are plenty of fertilizers known with different characteristics. Ghosh et.al (1996) carried out several comparative studies between struvite as fertilizer and other well-known fertilizers such as urea, formaldehyde, superphosphate and ammonium nitrate. Within his studies he concluded that struvite responded much better (even double) than other fertilizers like superphosphate.

Magnesium ammonium phosphate hexahydrate i.e. struvite, is globally known as a fertilizer (Barak and Stafford, 2006; Latifian et al., 2012; Rahman et al., 2013a; Mukhlesur Rahman et al., 2013). However the rate of leaching loss together with the crystal size of the struvite crystals are the two main factors which determine the final level of suitability of struvite as a fertilizer. The lower the leaching rate means the longer the fertilizer would last (Bizier and DeBarry, 2004; Latifian et al., 2012; Liu et al., 2012; Rahman et al., 2013a; Rahman et al., 2014). The more the crystal last means the longer the plant will receive essential nutrients for growth purposes (Ghosh et al., 1996; Barak and Stafford, 2006; Rahman et al., 2013a).

Besides, struvite crystal size plays an important role in the stability and mechanical strength of the struvite as final product (Mullin, 2001a; Hanhoun et al., 2013; Rudolph, 2015) . The stronger crystals with higher mechanical strength will demonstrate better stability in contact with water as solution medium. Le Corre et al., (2006; 2009b) declared that the tiny crystals are normally washed off during the harvesting step. They concluded that particle (group of crystals) size plays an important role in the final quality of harvested crystals. So far, there is no comprehensive dissolution study of struvite crystals grown through gel growth technique. Subsequently there is no detailed comparison between the solubility results of struvite crystals grown trough other techniques and those grown in gel media.

Moreover, surface area has direct relation with dissolution rate, as increasing the effective surface area increases the dissolution rate (Nyvlt et al., 1985; Mullin, 2001a; Myerson, 2002; Ariyanto, 2013).

The main gap here, which became the main motivation to study the crystallization of struvite crystals in gel media was, firstly the importance of studying and investigating struvite crystallization in gel media, secondly to determine the optimum and most influential operational conditions leading to longer lasting fertilizer (lower solubility) and finally running a comprehensive kinetic study on the struvite crystallization in gel media. Last but not the least, the gel growth technique itself provides a 3-dimensional spatial matrices which enables the single crystals to grow mature enough and reach their optimum size. It provides an ambient which increases crystallization and minimizes the sedimentation and precipitation. Compare to other crystallization techniques, as gel growth technique minimizes or in most cases eliminates the convective transport, better crystalline products are expected.

So far, there is no comprehensive study over the participating process parameters in the crystallization in gel media. Moreover, the level of their effect is not clearly known and subsequently the most effective process parameters are not known yet. Due to the mentioned reasons, it has become important to study the principles of struvite crystals solubility, nucleation and growth to evaluate the effects of various controlling parameters on struvite crystallization.

1.3 Research questions

Throughout this research it has been a struggle to answer fundamental as well as practical questions regarding struvite crystallization in gel media. Struvite is globally known as a slow-release fertilizer which its properties has been studied and characterized by other researcher. However, the effects of different operational parameters on struvite crystals growth rate and size are still missing. The optimum conditions in which the biggest crystals are formed are not known yet. The lack of sufficient studies to determine the most influential parameters are quite sensible.

The majority of researches carried out on the growth of struvite crystals previously discusses the formation of struvite crystals within solution modes. As stated earlier, in the solution state mode of crystal formation, nucleation and growth rate are difficult to monitor due to the high pace of reaction. At the same time evaluating the effects of changes in operational conditions on crystallization process is also difficult to evaluate due to the rapid pace of reaction in solution mode.

There are various advantages associated with the growth of struvite crystals in gel media. For instance, it is suggested to be a suitable ambient for growing urinary type struvite crystals due to its similarities with the human kidney tissue. Moreover, gel acts as a reliable framework holding the crystals and provide them with the chance of 3D growth (in all crystal face). The technique also enables the researchers to step-by-step monitor the crystals growth. Throughout this study, it has been tried to grow struvite crystals in different gel media and characterize the resulting crystals in order to spot the best gel for growing struvite crystals.

It is struggled in this study to determine the key parameters affecting the struvite crystals formation, crystal size and morphology and spot the optimum operational conditions in which the biggest crystals with various morphologies can be grown and harvested. Hopefully, spotting the optimum operational and process conditions which leads to different types, size ranges and morphologies of struvite crystals *in vitro* might be used by other scientists to assess these experienced conditions in order to minimize or inhibit the *in vivo* formation of urinary calculi (including struvite stones).

Furthermore, through the kinetic study carried out in this research, the scientists would be enabled to have a clearer and brighter overview of the kinetics of magnesium diffusion in gel media.

1.4 Objectives of the study

The purpose of this study is to widen the understanding of struvite crystallization principles in order to improve struvite formation in terms of characteristics (shape, morphology and size). As it was stated earlier, crystal size and morphology plays an important role in fertilizer properties of struvite (Latifian et al., 2012). Moreover, the outcome of this thesis can be used by other researchers researching in the fields related to urinary tract stones. Consequently, the objectives envisaged to be achieved during the course of current study are as follows:

- To evaluate the feasibility of growing struvite crystals through gel growth technique, study and characterize their physico-chemical properties.
- To study the kinetics of struvite formation through magnesium consumption at different operational conditions using Nelson's mathematical model to predict the effluent concentration of magnesium knowing the initial value.

- To study and evaluate the most influential parameters and the optimum operational conditions for struvite crystallization process using Taguchi method.

1.5 Significance of study

Struvite crystallization within different media has been studied by several researchers. The resulted crystals have also been characterized for their properties. My study contributes to this literature by considering struvite crystallization in gel media.

The contribution of the current study would be of great interest to scholars in chemical and environmental engineering as well as to researchers studying the urinary calculi, particularly struvite stones formation in human body. Studies on the impacts of different operational conditions on the struvite crystals growth rate, size and morphologies plus spotting the key parameters for struvite crystallization and finding out the most suitable environment to mimic the real situation of struvite crystals' growth *in vitro* plus the kinetic study of magnesium diffusion in gel media, are the core areas of the present research in the field of crystallization and crystallography, to which my study would be significant.

So far, the majority of the researches on struvite crystallization has been carried out in aqueous mode. Throughout this research the struvite crystal size grown in different process conditions in gel media together with kinetic study of magnesium consumption in crystallization process would be investigated and discussed in details. The optimization study will enable the other scientists to have better image of the operational conditions' effects and the optimum combination of process parameters leading to bigger crystals formation. The results of this research would be presented in the form of suggestions for optimum operational conditions in sense of bigger crystal size and longer lasting fertilizer.

1.6 Thesis plan

This thesis contains 5 chapters, in which only the fourth chapter presents the experimental work. Each chapter opens with a slightly brief introduction section which states the whole structure and motivation of each individual chapters. Based on the conventional thesis structure set by UPM the main 5 chapters headings are, introduction, literature review, materials and methodology, results and discussions and finally the general conclusions and recommendations.

Chapter 1: Introduction

This work begins with a brief review of the literature on fundamentals and principles of crystallization followed by struvite precipitation and crystallization. In this chapter the brief background and purpose of the study together with the objectives, research questions and significance of the study are presented. Some of the terms used in the thesis have been briefly defined which will be discussed in detail in the subsequent chapters.

Chapter 2: Literature review

The aim and purpose of this chapter is to describe the general background of the study which includes the definition of all terms used in this thesis, processes of struvite formation, common wastewater treatment options and wastewater as a novel option, short literature on urinary calculi, detailed explanation about crystallization and mechanism of nucleation and crystal growth. Current methods of phosphorous removal and recovery are named, explained, discussed and compared. Struvite formation and chemistry is discussed and the major operational conditions known to have impacts on struvite crystallization within different media is discussed as well. A detailed description is presented in this chapter on various techniques of crystallization particularly gel growth technique is described in detail. Pros and cons of crystallization in gel media are discussed and struvite crystallization in gel media are explained and its advantages and disadvantages are further discussed. Different crystallization models are introduced and briefly discussed in this chapter.

Chapter 3: Materials and methods

In order to minimize the errors in the results of the crystallization experiments both experimental and analytical phases of the study must be accurately defined. Within this chapter the crystallization technique used in the study together with the whole process of experiments and analysis have been clearly described. Preparation of the reactants, preparation of all glassware, reaction dosage and technique, reaction conditions, crystals harvesting, analytical methods used for characterization of the samples together with a review on literature of each characterization technique was fully introduced and discussed in this chapter. This chapter opens with a flowchart introducing the whole procedure of the study from literature review to experimental analytical phases and finally leads to the conclusion and recommendation part. Models which were already introduce and incorporated in this study are clearly defined.

Chapter 4: Results and discussions

This chapter systematically discusses all the results gained from all experiments carried out during the study. All analytical results are presented in the form of pictures, charts and diagrams and the key features are subsequently discussed. Further discussions are made over the gained results and it has been tried by the author to demonstrate the results in the form of diagrams to make them more understandable. This chapter consists of both pure and analyzed results gained from characterization sets along with the results of modelling part. Validation of results obtained from experimental phase and modelling part is the final part of this chapter. Some of the results are compared to other researchers' results in order to demonstrate the accuracy of the study.

Chapter 5: Conclusions and recommendations

The general conclusions of the study based on the results of carried out experiments and tests plus the model results are presented in this chapter. Further recommendations for future studies in related fields are also presented in this final chapter.

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