İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

NUTRIENT RECOVERY
FROM
SOURCE-SEPARATED HUMAN URINE

Ph.D. Thesis by

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Department :	**Chemical Engineering**
Programme:	**Chemical Engineering**

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KAYNAĞINDA AYRILMIŞ İNSAN İDRARINDAN NUTRİENTLERİN GERİ KAZANILMASI

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PREFACE

The study presented in this thesis was carried out between February 2001 and October 2004 at the Chemical Engineering Department of İstanbul Technical University under the instructions of Prof.Dr. A.Nursen İPEKOĞLU and Prof. Dr. İlhan TALINLI.

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October, 2005 Sibel BAŞAKÇILARDAN-KABAKCI

CONTENTS

ABBREVIATIONS

WHO : World Health Organisation
UNICEF : The United Nations Children's Fund
OECD : Organisation for Economic Co-Operation and Development
EcoSanRes : Ecological Sanitation Research
APHA : American Public Health Association
NH_3-N : Ammonia Nitrogen
PO_4^{3-} -P : Phosphate Phosphorus
COD :Chemical Oxygen Demand
BOD_5 : Biological Oxygen Demand
TSS :Total Suspended Solids
S : Solubility
SI : Saturation Index
IAP : Ion Activity Product
STRV : Struvite
DCPD : Dicalcium Phosphate Dihydrate
DCPA : Dicalcium Phosphate Anhydrate
OCP : Octacalcium Phosphate
TCP : Tricalcium Phosphate
ACP : Amorphous Calcium Phosphate
MAP :Magnesium Ammonium Phosphate Hexahydrate
HAP : Hydroxyapatite
FT-IR : Fourier Transform Infrared Spectroscopy
SEM : Scanning Electron Microscopy
EDS : Energy Dispersive Spectroscopy
ICP : Inductively Coupled Plasma
EFMA : European Fertilizer Manufacturers' Association

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$\mathbf{K_{sp}}$: Solubility product

$\mathbf{K_{(1,2,3)}}$: Acid ionization constants

$\mathbf{K_{h\ (1,2,3)}}$: Hydrolysis constants

$\mathbf{K_{w}}$: Ion-product constant of water

$\mathbf{K_{b}}$: Base ionization constant

$\mathbf{S}$: Solubility

$\boldsymbol{\mu}$: Chemical potential

$\mathbf{N_{O,A}}$: Overall mass transfer rate of A from water to air

$\mathbf{K_{OL,A}}$: Overall mass transfer coefficient

$\mathbf{a}$: Interfacial area per unit volume of liquid

$\mathbf{V_{L}}$: Total volume of liquid

$\mathbf{C_{L,A}}$: Concentration of A in the bulk liquid

$\mathbf{C^{*}_{L,A}}$: Liquid concentration of A in equilibrium with the gas phase concentration

$\mathbf{C_{G,A}}$: Gas phase concentration of A

$\mathbf{K_{L}}$: Overall mass transfer coefficient

$\mathbf{V_{B}}$: Volume of air bubble

$\mathbf{A_{B}}$: Surface area of air bubble

$\mathbf{V_{G}}$: Total volume of all gas in the system

$\mathbf{V_{L}}$: Total volume of liquid

$\mathbf{H_{A}}$: Dimensionless Henry's law constant for substance A

$\mathbf{Q_{G}}$: Gas flow rate

$\boldsymbol{\tau}$: Contact time of the gas bubbles rising through the liquid

$\mathbf{F_{A}}$: Mass transfer rate of compound A

NUTRIENT RECOVERY FROM SOURCE-SEPARATED HUMAN URINE

SUMMARY

In recent years, the utilization of source-separated human urine in agricultural farmlands instead of artificial mineral fertilizers has become a favorite method. Urine, which has a volume less than 1% of the wastewater volume, contributes about 80% of nitrogen and 60% of phosphorus to household wastewater.

Centralized wastewater treatment systems consume high amounts of water which dilute the nutrients and restrict the recovery of nutrients. Therefore, source separation systems (urine separation systems) have been developed to separate and to store the urine for agricultural use. The most important item of source separation system is the specially designed toilet which separates the urine from faeces and transports the mixture of urine and flush water to a storage tank.

Existing urine separation system which is mainly used in Sweden, Germany and China uses the urine in the farmlands without processing. Although source separation system has some benefits, there are some disadvantages and risks which must be minimized before performing the urine-separation system. These disadvantages and risks can be classified as follows;

- Difficulties during the usage of toilets,
- Difficulties in storage,
- Difficulties in transportation,
- Difficulties during the application to farmland,
- Transmission risk of pathogenic bacteria,
- Transmission risk of metabolic residues (pharmaceutical residues and hormones in urine).

This thesis presents a research of nutrient recovery from human urine in order to overcome the difficulties related with the storage and spreading of urine. By transforming the urinary nutrients into solid fertilizer, the amount of urine which is needed to fertilize a farmland decreases and the ammonia which is unstable in the storage tank is stabilized. Thus, urine-based solid fertilizer can be suggested as a promising bio-fertilizer which is superior to urine with respect to its characteristics and composition.

In this study, two different methods were used in order to recover the urinary nutrients from source-separated human urine;

- Macronutrients such as phosphorus and nitrogen were recovered by magnesium ammonium phosphate hexahydrate (struvite) precipitation.
- Urinary ammonia was recovered as ammonium sulphate by stripping and absorption operations.

In the first chapter, the importance of sustainable environment and its relation with sustainable agriculture was introduced. Additionaly, the benefits of urine-separation system and the disadvantages of the total source-separation system were discussed.

In the second chapter, magnesium ammonium phosphate hexahydrate (struvite) was precipitated from fresh urine. The influence of process conditions such as reaction period, reaction pH and initial molar ratio of reactants on precipitation efficiency was examined. Nearly 98% of PO_4^{3-}-P and 40% of NH_3-N was recovered by this method. Optimum reaction pH was found as 9.5. Recovery efficiency of P seemed almost stable and N recovery increased as the initial molar ratio of Mg:P was kept above 1. Excess Mg promoted the formation of struvite and depressed the formation of calcium salts. According to quatitative analyses, K and Zn coprecipitated with struvite. Besides, elements such as Na, Al, Si and S were detected qualitatively by available equipments.

In the third chapter, the behaviour of urine during the storage was investigated and nutrients were recovered as struvite. Urea hydrolysis was found to be the crucial step during the storageof urine. The rate of hydrolysis was found to be directly related with urease activity and dilution. In undiluted urine, the fraction of ammonia nitrogen to total nitrogen was 12% after 6 weeks storage period. When the urine was diluted 4 times, the fraction increased to 72%. Although the pH of stored urine increased slowly on a daily basis, the ammonia concentration increased sharply between pH 9 and 9.54. Spontaneous precipitate formation because of the pH rise caused a decrease in the molar concentrations of Mg, Ca and PO_4^{3-}-P. By the end of the hydrolysis, the pH of the stored urine was higher than 9 and the molar concentration of ammonia nitrogen was much more higher than the molar concentration of phosphorus and magnesium. According to results, optimum pH for precipitation was 9.5 and optimum initial molar N:P:Mg ratio was 1:1:1.13.

In the fourth chapter, urinary ammonia was stripped with air in batch system and the ammonia-air gaseous mixture was bubbled through the sulphuric acid solution. Resultant ammonium sulphate solution was evaporated to obtain ammonium sulphate crystals. The efficiency of stripping was represented in terms of combined mass transfer coefficient $(K_L \times a)$ which is the product of overall mass transfer coefficient (K_L) and interfacial area (a). The value of $(K_L \times a)$ increased from 0.098 h^{-1} to 0.204 h^{-1} as the operational pH was raised from 11 to 12. In contrast, higher operational pH such as 13.5 reduced the value of $(K_L \times a)$ to 0.184 h^{-1}. A direct relationship between the air flow rate and $(K_L \times a)$ was observed during the experiments. Besides, this relation was also valid between air flow rate and mass transfer rate. In other words, the amount of ammonia that was transported from urine to air in a particular period increased, as the air flow rate was increased. Averagely 90% of ammonia (which was stripped with air in the stripping unit) was recovered as ammonium sulphate.

In the fifth chapter, urine based struvite and ammonium sulphate were compared with artificial mineral fertilizers. The advantages and the drawbacks of the production methods were discussed.

In the sixth chapter, overall conclusions about nutrient recovery were presented.

In the seventh chapter, struvite precipitation and stripping/absorption operations were re-evaluated and new project ideas for the future were suggested.

KAYNAĞINDA AYRILMIŞ İNSAN İDRARINDAN NUTRİENTLERİN GERİ KAZANILMASI

ÖZET

Son yıllarda kaynağında ayrılmış insan idrarının tarımsal alanlarda suni gübre yerine kullanılması gözde bir metot haline gelmiştir. Atıksu hacminin %1'inden daha az hacime sahip idrar, evsel atıksuya yaklaşık azotun %80'i ve fosforun %60'ı kadar bir katkı yapmaktadır.

Merkezi atıksu arıtma sistemleri çok fazla miktarda su kullanarak sahip olduğu nutrientleri seyreltir ve nutrientlerin geri kazanılmasını sınırlar. Bu nedenle, kaynağında ayırma sistemleri (idrar ayırma sistemleri) idrarı ayırmak ve tarımsal alanlarda kullanmak üzere depolamak için geliştirilmiştir. Kaynağında ayırma sisteminin en önemli öğesi idrarı dışkıdan ayıran ve idrar-su karışımını depolama tankına taşıyan özel dizayn edilmiş tuvaletlerdir.

Başlıca İsveç, Almanya ve Çin gibi ülkelerde kullanılan kaynağında ayırma sistemi, idrarı hiçbir işleme tabi tutmadan tarımsal alanlarda kullanır. Kaynağında ayırma sisteminin bazı faydaları olmasına rağmen idrar ayırma sistemini hayata geçirmeden önce minimize edilmesi gereken bazı dezavantajlar ve riskler mevcuttur. Bu dezavantajlar ve riskler aşağıda sınıflandırılmıştır;

- Tuvaletlerin kullanılması sırasında karşılaşılan zorluklar,
- Depolamadaki zorluklar,
- Taşımadaki zorluklar,
- Tarımsal alanlara uygulama sırasında karşılaşılan zorluklar,
- Patojen bakterilerin taşınma riski,
- Metabolik kalıntıların taşınma riski (idrardaki ilaç kalıntıları ve hormonlar).

Bu tez, idrarın depolanması ve tarımsal alanlara uygulanması sırasında karşılaşılan zorlukları gidermek üzere insan idrarından nutrientleri geri kazanan bir araştırmayı sunmaktadır. İdrardaki nutrientlerin katı gübre haline dönüştürülmesiyle bir tarımsal alanı gübrelemek için kullanılması gereken idrar miktarı azalır ve depolama süresince kararsız olan amonyak kararlı bir bileşiğe dönüşür. Bu nedenle, idrar bazlı katı gübrenin, karakteri ve bileşimi nedeniyle idrara kıyasla daha üstün ve gelecek vadeden bir bio-gübre olabileceği öne sürülebilir.

Bu çalışmada, kaynağında ayrılmış insan idrarındaki nutrientlerin geri kazanılması için iki farklı yöntem uygulanmıştır:

- Fosfor ve azot gibi makronutrientler magnezyum amonyum fosfat hehzahidrat (struvit) çöktürmesiyle geri kazanılmıştır.
- İdrardaki amonyak, sıyırma ve absorpsiyon operasyonlarıyla amonyum sülfat olarak geri kazanılmıştır.

Birinci bölümde sürdürülebilir çevrenin önemi ve sürdürülebilir tarım ile arasındaki ilişki ortaya konulmuştur. Ek olarak, idrar ayırma sisteminin faydaları ve bütün olarak kaynağında ayırma sisteminin dezavantajları tartışılmıştır.

İkinci bölümde idrardan magnezyum amonyum fosfat hekzahidrat (struvit) çöktürülmüştür. Reaksiyon süresi, optimum pH ve reaktanların başlangıç molar konsantrasyonları gibi proses koşullarının çöktürme verimi üzerine etkisi araştırılmıştır. PO_4^{3-}-P 'un yaklaşık %98'i ve NH_3-N'un %40'ı bu yöntemle geri kazanılmıştır. Optimum reaksiyon pH'sı 9.5 olarak bulunmuştur. Başlangıç molar Mg:P oranı 1'in üstündeyken P geri kazanımı sabit kalmış, N'un geri kazanma verimi artmıştır. Mg'un molar konsantrasyonunun aşırı olması struvit oluşumunu tetiklemiş ve kalsiyum tuzlarının oluşumunu bastırmıştır. Kantitatif analizlere göre K ve Zn struvit ile eşçökmüştür. Ayrıca Na, Al, Si ve S gibi elementler mevcut ekipmanlarla kalitatif olarak saptanmıştır.

Üçüncü bölümde, idrarın depolanma süresince davranımı incelenmiştir ve nutrientler struvit olarak geri kazanılmıştır. İdrarı depolama suresince üre hidrolizinin en önemli adım olduğu saptanmıştır. Hidroliz hızının idrardaki üreaz aktivitesine ve seyrelmeye doğrudan bağlı olduğu belirlenmiştir. Seyreltilmemiş idrarda, 6 haftalık depolama süresinin sonunda amonyak azotunun toplam azota oranı %12'dir. İdrar 4/1 oranında seyreltildiğinde bu oran %72'ye yükselmiştir. Depolanmış idrarın pH'sı günlük bazda yavaş artsa da pH 9 ile 9.54 aralığında amonyak konsantrasyonu hızla yükselmiştir. İdrarın pH'sının artması nedeniyle kendiliğinden oluşan çökelti Mg, Ca ve PO_4^{3-}-P'un molar konsantrasyonlarında düşüşe neden olmuştur. Hidrolizin sonunda idrarın pH'sı 9'dan fazladır ve amonyak azotunun molar konsantrasyonu fosfor ve magnezyumun molar konsantrasyonundan oldukça fazladır. Sonuçlara göre, çöktürme için optimum pH 9.5'tur ve optimum başlangıç molar N:P:Mg oranı 1:1:1.13'tür.

Dördüncü bölümde, idrardaki amonyak kesikli sistemde hava ile sıyrılmıştır ve amonyak-hava gaz karışımı sülfürik asit içinden geçirilmiştir. Amonyum sülfat kristalleri elde etmek için oluşan amonyum sülfat çözeltisi evapore edilmiştir. Sıyırma işleminin verimi tüm kütle iletim katsayısı (K_L) ile arafaz yüzey alanının (a) çarpımı olan birleştirilmiş kütle iletim katsayısı $(K_L \times a)$ ile ifade edilmiştir. İdrar pH'sının 11'den 12'ye çıkarılmasıyla $(K_L \times a)$ 0.098 saat^{-1} değerinden 0.204 saat^{-1} değerine yükselmiştir. Buna karşılık pH 13.5 gibi yüksek bir operasyon pH'sı $(K_L \times a)$ değerini 0.184 saat^{-1}'e indirmiştir. Deneyler sırasında hava akis hızıyla $(K_L \times a)$ arasında doğrudan bir ilişki gözlenmiştir. Ayrıca, bu ilişki hava akış hızıyla kütle transferi hızı arasında da mevcuttur. Diğer bir ifadeyle hava akış hızının artmasıyla idrardan havaya birim zamanda aktarılan amonyak miktarı artmıştır. Sıyırma ünitesinde sıyrılan amonyağın ortalama %90'ı amonyum sülfat olarak geri kazanılmıştır.

Beşinci bölümde idrar bazlı struvit ve amonyum sülfat suni mineral gübrelerle kıyaslanmıştır. Üretim metotlarının avantajları ve dezavantajları tartışılmıştır.

Altıncı bölümde nutrient geri kazanımı ile ilgili tüm sonuçlar sunulmuştur.

Yedinci bölümde struvit çöktürmesi ve sıyırma/absorpsiyon operasyonları tekrar değerlendirilmiştir ve gelecek için yeni proje fikirleri önerilmiştir.

1. URINE SEPARATION AND ITS USAGE AS A FERTILIZER

1.1 Sustainable Wastewater Treatment

The drainage systems used in urban life range from rudimentary, unlined, open-channel drains to highly modified and technically enhanced, piped sewer systems. In both cases, water transports the waste away from the areas of human habitation where it would otherwise cause illness and disease or disrupt the operation of other urban services (Butler and Parkinson, 1997) .

The need for sanitation arose in 15th century in central Europe where the fatal diseases such as typhus, cholera and diarrhoea were detected in many people because of the direct contact with excreta. In the year 1539, nearly all the places in Paris – the heart of the Europe - were degenerated that no one could travel accross the city. To protect the people from getting infected, sewer systems were re-invented which were used centuries ago by the ancient civilizations and Romans. After the flushing toilets were invented in 18th century, the sewer systems were re-designed (Berndtsson and Hyvönen, 2002). But, discharging the wastes and excreta into streams, lakes and sea made changes in characteristics and appearence of receiving surroundings. This undesirable case forced people to think on the treatment of wastewater streams. From that time till today, sophisticated wastewater treatment plants have been built where sewage is treated to a very high degree. According to WHO/UNICEF, 86% of the world's urban population has adequate sanitation (http://www.unicef.org). But in the next 25 years, 1.5 billion people mostly in Asia will need additional sanitation systems (Esrey, 2002).

It is accepted by many researchers that the problem of sanitation in urban area is solved by the conventional wastewater treatment system which is mostly known as centralized wastewater treatment. It consists of a sewer system which collects wastewater from households, small enterprises, industrial plants, institutions and storm water runoff and transports this combined stream to a wastewater treatment plant which is usually located outside of the limits of the city. After treatment, the wastewater is discharged into the closest water body. The main aim of the existing wastewater treatment system is to treat the wastewater to effluent requirements allowing for discharge to the surface water. Originally, the central treatment is oriented towards the removal of organic pollutants (Roeleveld et al., 1997).

In most of the industrialized countries, a huge amount of investment is done to build and maintain the sewer systems and treatment plants. In OECD countries, nearly 64% of the population use the sewer system. But this value is just 17% for Turkey, which is the minimum value among the OECD countries (OECD, Environmental Data Compendium).

In rural areas and semi-urban areas, conventional centralized treatment units are not used because of the high investment rates.Generally, short term solutions for wastewater treatment have been applied in rural area which are majorly neither hygienic nor practicle.

Nowadays low cost decentralized systems have been built and developed complying with environmental and hygienic standards and aiming at a maximum reuse of the available resources (Parkinson and Tayler, 2003). Decentralized wastewater treatment systems are onsite or clustered wastewater systems that are used to treat and dispose of relatively small amounts of wastewater.The decentralized approach leads to treatment and reuse of water, nutrients and by-products of the technology inside an industry or in the vicinity of the settlement in the case of domestic wastewater (Lier and Lettinga, 1999). Adequately managed decentralized wastewater treatment systems are a cost effective and long term option for meeting public health and water quality goals, particularly in less populated areas.

Both of the centralized and decentralized systems have advantages and drawbacks, and the selection of the system depends on the investment that governments can do. Lier and Lettinga (1999), Kärmann (2001) and Berndtsson and Hyvönen (2002) detailed the handicaps of conventional wastewater treatment systems in their study. It was stated that conventional sanitation systems are lacking of the management of the resources such as water, energy and nutrients. Besides, unefficiently or wrongly treated wastewater creates environmental dangers. Even the best treatment plants can not treat nearly 20% of nitrogen, 5% of phosphorus and more than 90% of potassium (Otterpohl et al., 1997). Discharged nutrients are accumulated in water bodies which causes eutrophication. Krebs and Larsen (1997) gave an amazing example for this situation by declaring that urban drainage system in Switzerland, which is used now, may fail with regard to receiving water protection under critical circumstances. According to surveys, the biggest danger in centralized system is stated to be the inefficient removal of excreted pathogens (Berndtsson and Hyvönen, 2002). Besides, the energy demand for the destruction of the organic compounds and for the nitrification is high (Otterpohl et al.,1997).

In many parts of the world, except from the undeveloped countries, conventional sanitary system uses potable water as a transporter medium. Using too much water restricts the recovery of both nutrients and water. Besides, transporting the wastewater with valuable drinking water is nonsense in places where safe drinking water is hardly available (Otterpohl et al., 1997; Lier and Lettinga, 1999; Berndtsson and Hyvönen, 2002). Sewage sludge -one of the main end product of wastewater treatment- is rich in nutrients but also it is rich in pollutants such as heavy metals. Using the sewage sludge as a fertilizer in agricultural farmland is not recommended because of the long term accumulation of heavy metals in the soil (Otterpohl et al., 1997; Berndtsson and Hyvönen, 2002). The latest studies also indicated that treated (waste)water also contains nutrients and persistent compounds (i.e.hormones, pharmaceutical residues...) which in turn results eutrophication and environmental hazards in receiving waters (Sedlak et al., 2000; Berndtsson and Hyvönen, 2002). Furthermore, reuse of centralized treated domestic wastewater requires an additional large distribution network for distributing the effluent to agricultural sites.

Wilderer and Schreff (2000) indicated that decentralized systems can only become advantageous if small decentralized systems provide advanced wastewater treatment and operation and control of the treatment systems are accomplished by trained people. Lier and Lettinga (1999) implied that it may take generations before decentralized concepts will have found application. Acceptance of the decentralized concepts greatly depends on the technical and economical feasibility of the decentralized systems to be developed and it also depends on developments in off-site treatment systems as well.

The drawbacks of centralized and decentralized wastewater treatment systems forced researchers to investigate more efficient sanitation systems. Besides, researchers are discussing on the efficiency and sustainability of conventional wastewater treatment systems nowadays. Butler and Parkinson (1997) declared that sustainability should be one of the objectives of existing treatment systems. Thus, decentralized and centralized wastewater treatment systems should be evaluated with regard to sustainability.

The term “sustainable development” was first published in 1987 in World Commission on Environment Development, which defines the term as: “Development that meets the needs of the present generation without compromising the ability of future generations to meet their own needs” (Larsen and Gujer, 1997; Balkema et al., 2002). The meaning underneath this definition is that all human being whether living today or in future have equal rights. Basicly, sustainable system must not harm the basic life support system of our planet : the air, water and soil, and the biological systems. In other words natural resources of the earth must be used in a cycle economically (Butler and Davies, 2000). Kärrmann (2001) emphasized that the saving of clean water and recycling of nutrients are the major sustainability aspects. According to Otterpohl et al. (1999), sustainable sanitation has to co-operate with agriculture and such a co-operation will surely bring a sustainability to agriculture.

Theoretically, sustainable environmental protection combines effective sanitation and treatment with reuse of treated water and treatment products (Lier and Lettinga, 1999). Hence, sustainable sanitation or sustainable wastewater treatment must comply with the rules listed below:

✓ Wastewater should not be diluted with clean water. The amount of clean water used for transporting the should be lowered,

✓ Recovery and reuse of treated water and products of treatment process should be maximized,

✓ Technologies used in treatment and recovery should be robust, reliable and simple to operate and they should have a long lifetime,

✓ Treatment units should be applicable at any scale,

✓ Total treatment system should be accepted by the public.

Many researchers are trying to assess and quantify the sustainability of the current wastewater treatment systems by using one of the methodologies listed below (Balkema et al., 2002):

- Exergy analysis : Exergy is a measure of the potential to cause change in the environment and its quality (Balocco et al., 2004). It can be considered as a property of the interactions between the open system and its environment. In exergy analysis, just exergy is used as a quantifiable indicator. Hellström and Kärrman (1997) used exergy analysis to compare a centralized wastewater treatment plant with decentralized system. Their study revealed that urine separation from the household wastewater is beneficial with respect to exergy analysis when nitrogen and phosphorus recycling is considered.

- Economic analysis : the sustainability of the system is assessed in terms of money. Economic analysis is better at measuring quantitative impacts than qualitative ones. Tools such as cost-benefit analysis, life cycle costing and total cost assessment balance the expected costs and benefits. Besides, they are often the first step in a project (Balkema et al., 2002). But, it is straightforward to use economic tools to look at trends in production costs or wages. Difficulties in quantifying the social and environmental aspects are the main disadvantages of this method.

- Life cycle assessment : life cycle assessment indicates the environmental and economical impacts that occurs at all life cycle stages of a product (such as processing of raw material, manufacturing, transportation and distribution, use – reuse and waste management). As a quantitative analysis, life cycle assessment calculates energy and material balances at all life cycle stages of a product and then determines and weighs the associated impacts (Roeleveld et al., 1997; Brix, 1999; Balocco et al., 2004). Life cycle assessment of urine-separating systems showed that urine-separating systems has many advantages with regard to nutrient recovery. But the same studies also indicated that the storage, transport and spreading of large amounts of urine negatively affects the system efficiency (Lind et al., 2000; Lind et al., 2001).

- System analysis : system analysis focuses on the comparison of whole systems and uses a multi-dimensional set of sustainability indicators such as material use, emissions, costs and required land area (Balkema et al., 2002).

The analyses listed above are not satisfactory in all areas. It will be more useful if a methodology which combines the features of all analyses is built. Alternatively, Hellström et al. (2000) measured the sustainability of the urban water and wastewater system by using five important criteria. Each criteria listed below is evaluated with indicators which are quantifiable and easy to measure:

- ✓ health and hygiene criteria (measured by: microbial risk assessment),
- ✓ social-cultural criteria (measured by: surveys and assessment scales),
- ✓ environmental criteria (measured by: life cycle assessment, computer based modelling, material flow analysis and exergy analysis),
- ✓ economic criteria (measured by: cost benefit analysis),
- ✓ functional and technical criteria (measured by: functional risk analysis) .

Whether the classical methodology or combined methodology is used, current wastewater systems are found as unsustainable. Practically, selection of sustainable wastewater treatment system which fulfills the requirements of sustainability is a kind of a optimisation problem which should ;

- ✓ minimize the costs,
- ✓ minimize the energy use,
- ✓ minimize the land area required,
- ✓ minimize the loss of nutrients,
- ✓ minimize waste production,
- ✓ maximize products such as clean water, biogas, biomass, fertilizers and compost,
- ✓ maximize the score of qualitative sustainability indicators such as social acceptance, institutional requirements (Balkema et al., 2002).

It is not possible to have a wastewater treatment system that minimises cost, energy use and land area while maximising performance. According to Butler and Parkinson (1997), it is very hard to obtain a sustainable treatment system. But, enhancing the existing wastewater treatment system in order to approach sustainability is more logical. Small decentralized systems with different kinds of treatment can be a better tool instead of obtaining a higher degree of sustainability in current wastewater treatment system (Hedberg, 1999). Using a system which is a combination of decentralized and centralized system can be an alternative. In such a system, household wastewater should be separated from the industrial wastewater and nutrients should be recovered. By doing changes in toilet system, the water used for transportation should be lowered. The last of all, storm water should be collected separately for further usage.

Separate handling of household wastewater streams provides many advantages.Most of the countries (i.e. Sweden, Germany, China, Switzerland...) who are aware of these advantages have been focused on separate collection and processing of household wastewater (Figure 1.1). Separating the streams of household wastewater and processing the streams separately ,

✓ reduces eutrophication,

✓ decreases the production of mineral fertilizers by increasing nutrient recycling,

✓ decreases the amount of fresh water used for flushing,

✓ saves energy.

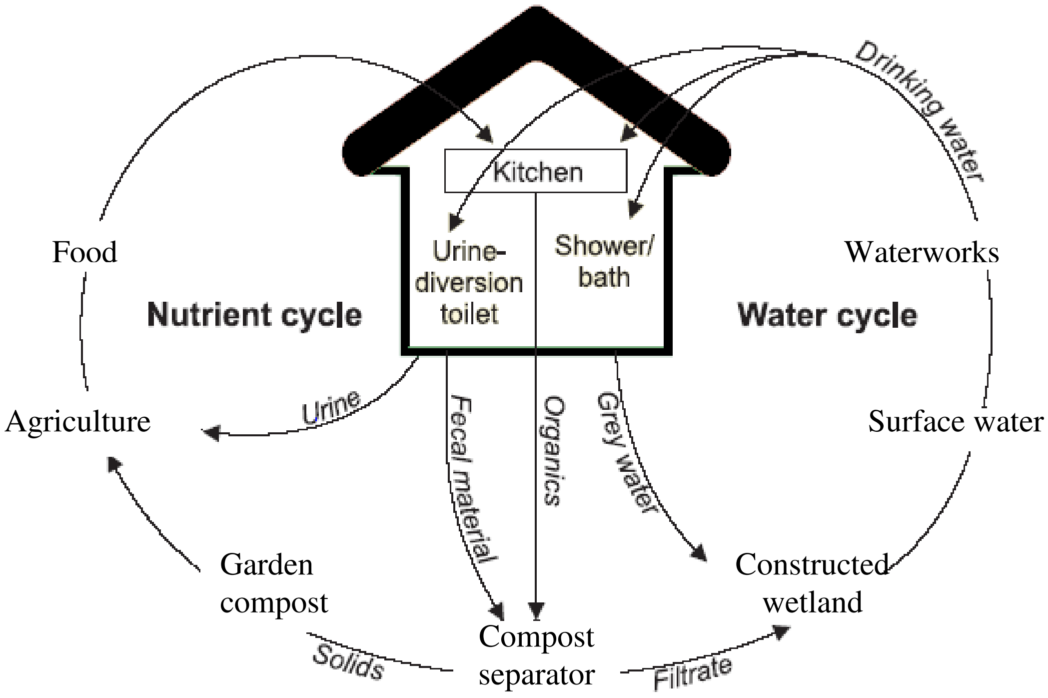

Figure 1.1: Possible ways to close the nutrient and water cycles in households (EcoSanRes, http://www.ecosanres.org).

In terms of flow quantity, household wastewater depends on the human behaviour and habits (Butler et al., 1995). Major fraction of nutrients in wastewater is originated from human excreta. It is declared that human urine is the largest contributor of nutrients to household wastewater which is also seen in Table 1.1 (Almeida et al., 1999; Otterpohl, 2002). Thus, separating the toilet wastewater from the household wastewater and recovering of the nutrients can be an efficient method for attaining a more sustainable system. Besides nutrient recycling is important in order to avoid eutrophication and probably also for decreasing the production of mineral fertilizers. Urine recycling is almost 30% less energy demanding than the one with mineral fertilizer production for a case of 1km transport of urine.

Furthermore, separation of faeces and urine from the domestic wastewater is considered as the most important step towards sustainable water concepts (Otterpohl et al., 1997).

Table 1.1: Contribution of each appliance to the daily discharged household wastewater (% of total volume or mass per 100 capita). (Almeida et al., 1999).

Appliance	Volume	COD	NH_3-N	NO_3-N	PO_4-P	TSS
WC	30.8	43.9	97.1	3.8	79.8	77.4
Kitchen sink	13	23.2	0.3	38	9.4	10.1
Wash basin	12.6	1.7	0.1	10.7	1.3	2.1
Bath	15.7	2.5	0.6	15.3	1.1	1.3
Shower	11.7	6.4	0.7	24.6	4.1	5.1
Washing machine	16.2	22.3	1.2	7.6	4.3	4
Total (per 100 capita per day)	10.23 m^3	11 188 g	237.95 g	36.72 g	668 g	5610 g

1.2 Urine Usage in Farmlands

For many years human excreta which contains considerable amounts of nutrients (Table 1.2) has been used as an agricultural aid in many parts of the world. But during this period, many diseases have been noticed because of the direct contact of excreta. It is obvious that microbial content of faeces depresses the benefits of faecal nutrients. Although the usage of excreta is more convenient, people still do not notice the difference between the urine and faeces. Main nutrients in excreta come from the urine which are also all plant available. The other point is the purity of urine in terms of microbes and viruses. Its high nutrient content and hygienic quality makes urine a much more valuable resource than faeces.

Table 1.2: Average production of urine and faeces and their nutrient content (http://www.ecosanres.org).

	Urine	Faeces
Amount	1.2 $L.person^{-1}.day^{-1}$	150 $g.person^{-1}.day^{-1}$ (wet weight)
Nitrogen ($g.person^{-1}day^{-1}$)	11	2
Phosphorus ($g.person^{-1}day^{-1}$)	1	0.6
Potassium ($g.person^{-1}day^{-1}$)	2.5	0.6

Urine fraction utilised in agriculture for vegetation must be free of faeces. To ensure this criteria, urine and faeces must be separated at source and both of the fractions should be treated and utilized (Heinanen-Tanski and Wijk-Sijbesma, 2005). Urine separating systems used today aims to separate urinary nutrients such as phosphorus, nitrogen and potassium at source. They can be used as concentrated fertilizer, since they are free from heavy metals and undiluted by household wastewater. A schematic representation of source separation system from toilet to field is shown in Figure 1.2.

The major ingredient of urine is water (nearly 95%), the rest is urea, sodium, potassium, phosphates, sulfates, creatinine, uric acid, calcium and magnesium.The total amount of solids in a 24 h urine sample averages around 60g (35g organic, 25g inorganic). The most important organic substances are urea, uric acid and creatinine. Urea is a product formed by the liver from ammonia and carbondioxide. 95% of nitrogen content of urine is in the form of this substance. Uric acid is the end product of the oxidation of purines in the body. By weight, there is normally about 60 times as much urea as uric acid in urine.

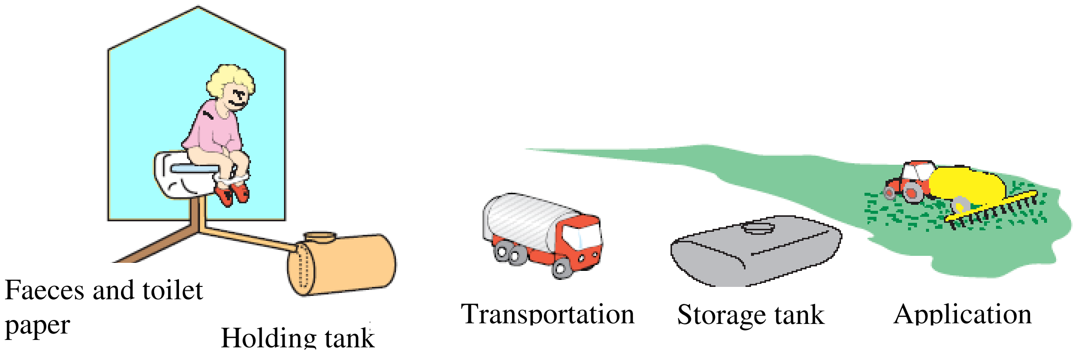

Figure 1.2: Source separation system from toilet to field (illustrated by Kim Gutekunst in the study of Johansson, 2000).

The major inorganic constituents of urine are chlorides, phosphates, sulphates and ammonia. Sodium chloride is the predominant chloride and makes up about half of the inorganic substances. Since ammonia is toxic to the body and lacking in plasma there is very little of it normally present in fresh urine. About 0.3 to 1 g of glucose in a 24 h urine sample would be considered normal excretion. But these values are not the same for all people. The study of Siener and Hesse (2002) declared that eating habits directly affects the concentration of ingredients in urine which is also depicted in Table 1.3.

The second largest conributor of nitrogen and phosphorus to household wastewater is faeces. 17% of faecal nitrogen is contained in the bacterial fraction. About 10% is found as ammonia from the degradation of urea, peptides and aminoacids. The remaining part is found in different organic compounds such as uric acid and different enzymes (Vinnerås and Jönsson, 2002). But only the 50% of nutrients are water soluble or in other words plant available. Pathogenic bacteria content is low in urine when compared with faeces.Consumption of heavy metals from foods is low and the major part of the heavy metals excreted in the faeces (Vinnerås, 2001; Vinnerås and Jönsson, 2002).

Table 1.3: Urine composition of 10 healthy male consuming a self-selected diet, a western type diet, normal mixed diet and a vegetarian diet (Siener and Hesse, 2002).

INGREDIENTS	Self selected diet	Western type diet	Normal mixed diet	Vegetarian diet
Urine volume L (in 24 h)	1.29±0.15	1.48±0.12	2.30±0.12	2.45±0.24
pH	6.01±0.15	5.95±0.11	6.51±0.07	6.80±0.07
Sodium (mmole.day^{-1})	159±0.24	176±13	146±4	102±15
Potassium (mmole.day^{-1})	84±7	60±3	77±5	110±6
Calcium (mmole.day^{-1})	4.68±0.76	4.48±0.39	3.09±0.44	2.46±0.42
Magnesium (mmole.day^{-1})	4.60±0.44	4.63±0.21	5.09±0.35	5.40±0.52
Ammonium (mmole.day^{-1})	30.8±3.9	38.7±1.6	25.6±2.0	18.7±1.9
Chloride (mmole.day^{-1})	164±21	169±12	139±5	106±14
Phosphate (mmole.day^{-1})	32.6±2.6	35.4±1.7	29.4±1.1	25.2±2.0
Sulfate (mmole.day^{-1})	18.5±2.9	22.5±1.0	18.1±0.6	16.1±1.2
Uric acid (mmole.day^{-1})	3.59±0.30	3.91±0.21	2.93±0.10	2.58±0.16
Oxalic acid (mmole.day^{-1})	0.317±0.021	0.281±0.020	0.287±0.018	0.37±0.039
Citric acid (mmole.day^{-1})	2.863±0.315	2.831±0.189	3.226±0.247	4.23±0.356

Western type diet: high energy and alcohol, excess protein and low fluid intake.

Normal mixed diet: low energy, cholesterol, protein and fat.

The degree of separation in toilets is the most critical step in source separation systems. Unlike classical toilets, where both urine and faeces are mixed with water and then grey water, a separating toilet separates the urine and faeces at source. Source separating toilets have two bowls where the urine and a small amount of flush water are collected in the front part of the bowl and the faeces in the back (Figure 1.3). Source separating toilets must not be confused with composting toilets which is originally commercialized in Sweden to provide a solution to sanitation and environmental problems in unsewered, rural and suburban area and in both developed and undeveloped countries (Figure 1.4).

Figure 1.3: The two urine separating toilets used in recycling source separated human urine: on the left, the Dubbletten from BB Innovation&Co AB and, on the right side, the DS toilet from Wost Man Ecology AB (http://www.stockholmvatten.se).

Urine with flush water is piped to a tank which is emptied when it is full. Brown water (faeces+toilet paper+flush water) is transported to separators where the faecal water and solids are separated. The faecal water is transported to on-site treatment system and the separated solids are transported to a composting unit where they are composted together with source separated biodegradable household waste and pellets of sawdust (Vinnerås and Jönsson, 2002).

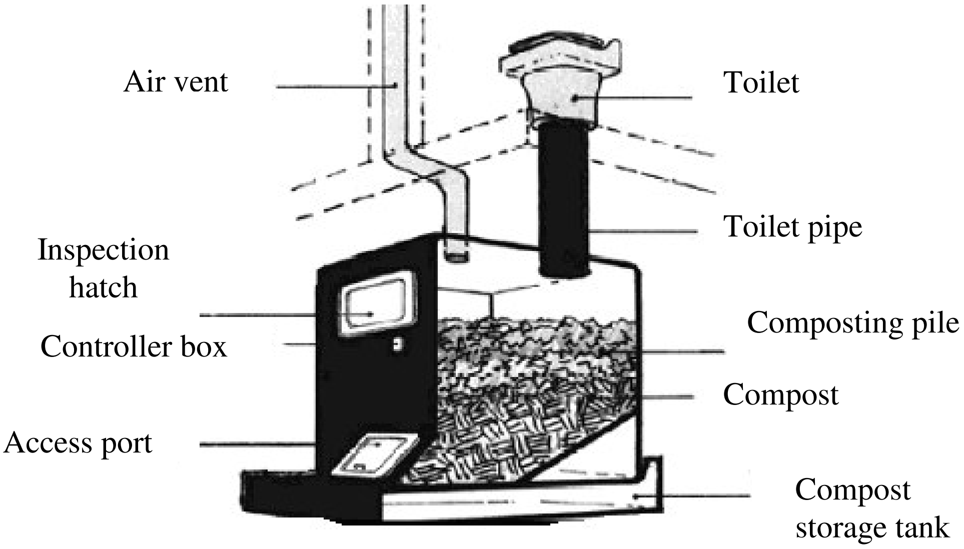

Figure 1. 4: Composting toilet (http://www.stockholmvatten.se).

After the urine is separated in toilets, it passes through a separate pipe system to a holding tank which is connected to one or more households. The urine is collected and transported by a tank truck or suction truck to storage tanks which are often located deep in the ground (Figure 1.5).

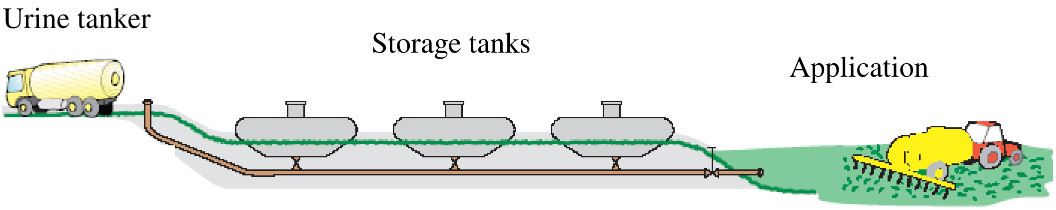

Figure 1.5: Transportation and storage of human urine (illustrated by Kim Gutekunst in the study of Johansson, 2000).

Nowadays, an alternative approach has been explored by the Swiss researchers. Larsen et al. (2001) investigated the probability of using the existing pipeline for transporting the stored urine to a treatment unit. Urine is intended to be transported at nights. The aim of such a strategy is,

- ✓ to level out the ammonia dynamics at the wastewater treatment plant,
- ✓ to avoid combined sewer overflow containing urine,
- ✓ to process the urine (Rauch et al., 2003).

Besides, according to Swiss researchers processing of urine before using as a fertilizer is a necessity and this idea differs them from the other researchers. Whether stored or processed, source separation of urine is beneficial (Wilsenach and Loosdrecht, 2004). Because,

- ✓ Small and simpler treatment units are used,
- ✓ Urine separation reduces nutrient discharges and increases the potential for closing nutrient cycle,
- ✓ Sludge production is low when compared with conventional sewage treatment,
- ✓ Water and energy is saved (Henze, 1997). The amount of water saved may vary between 5-40 L per person per day depending on individual habits and the toilet which the comparison is made with,
- ✓ Amount of chemicals used in conventional sewage treatment is reduced,
- ✓ Nutrients are recovered and reused instead of artificial fertilizers, which in turn saves the natural resources (Larsen et al., 2001; Larsen et al., 2004).

1.3 Evaluation of Source Separation System

Although source separation seems advantageous it does not solve all wastewater treatment problems. Once the urine has been separated, the faeces and greywater must still be treated. Besides, there are some difficulties and risks which must be evaluated before using the urine in the farmlands. These difficulties and risks are classified as follows ;

(1) Difficulties during the usage of the toilets,

(2) Difficulties during the storage,

(3) Difficulties in transportation,

(4) Difficulties in application to farmland,

(5) Risk of pathogenic bacteria transmission,

(6) Risk of pharmaceutical and hormonal residues transmission.

- ➢ Difficulties during the usage of the toilets:

The problems arising from the toilets are extensively discussed in the study of Hanæus et al. (1997) who investigated the urine separation system in an ecological village in Northern Sweden. In their study, the problems are assigned to the design and the use of the toilets and the accuracy of the construction of the sewer system. The most important disadvantages are expressed as the laborious cleaning of the toilets and the unpleasant odor which occur due to poor design and installations that are not water tight. Stoppages that block the toilet seals are reported to be a serious problem that calls for continued research.

- Difficulties during the storage of urine:

As indicated before source separation of human urine is based on toilets equipped with two bowls, a front one for the collection of urine and a rear one for faeces. The urine is collected separately and led through the pipes to a collection tank (storage tank). The study of Höglund et al. (2000) revealed that nitrogen in stored urine is in the form of ammonia due to the rapid ureolysis (urea hydrolysis) in the pipes. Thus, the nitrogen is in the form of ammonia in the storage tank. Handling the ammonia is a problem during storage, transportation and application (Hellström et al., 1999).

- Difficulties during the transportation of urine:

The volume of urine varies with person to person and the amount of flush water used. Besides the residential percentage directly effects the amount of collected urine (Vinneras and Jönsson, 2002; Jönsson et al., 1997). As the urine is collected for about 6 or 8 month , the amount which should be transported is increased (Hellström et al., 1999). The resulting huge amounts are not easily transported.

- Difficulties during the application of urine:

Due to its high ammonia content, nearly 5% of ammonia is lost in the total urine system. Hellström et al. (1999) expressed that losses are small during collection and storage. The main part of ammonia is lost during the application of urine. Because of this, most of the studies focused on the stabilisation of urinary nitrogen by different processing methods (Hellström et al., 1999; Lind et al., 2000; Lind et al.,2001; Behrendt et al., 2002; Udert et al., 2003-c).

- Risk of pathogenic bacteria transmission:

The amount of pathogenic bacteria in urine is reported to be low. The risk of pathogenic bacteria is mainly because of the cross-contamination of faeces in the separating toilet (Höglund et al., 2000; Höglund et al, 2002). The risk is higher in the case of diarrhoea or when children use the toilet (Schönning et al., 2002). The other risk is the human parasitic germs such as helminth eggs or schistosoma miracidia which can enter the soil through the urine of infected people. But, it is also reported that the survival of helminth eggs and schistosoma miracidia will be reduced in urine under the influence of urine salts, the increase in pH through hydrolysis of urea and the increase in temperature (Heinonen-Tanski and Wijk-Sijbesma, 2005).

The risk assessments indicated that risks related to the reuse of source-separated human urine was quite low, except for possible infections from rotavirus when the urine is either unstored or stored at low temperature (4ºC). Survival of microorganisms is governed by the storage conditions, temperature, microbial antagonism and dilution within the naturally elevated pH of stored urine.
According to assessments, risks could be minimised through recommendations regarding occupational precautions, storage conditions and crop restrictions.

- Risk of hormonal and pharmaceutical residues transmission:

Urine is rich in nutrients but it also comprises hormonal residues which might have a potential adverse effect on soil microorganisms and aquatic organism when reach groundwater and surface water. The hormonal residues which are naturally found in human urine is depicted in Table 1.4.

The other potential risk is the transformation of pharmaceutical residues which are excreted via urine after usage. Generally, pharmaceuticals are excreted to a great extent in urine as an active ingredient or as their metabolites. When the urine is used directly in the farmland, these chemicals can reach to soil, surface water, ground water and finally enter the foodchain.

Every year nearly 3000 new active compounds are synthesized but it is very difficult to obtain the exact data of consumption. The predominant therapeutic classes according to local therapeutic practices are analgesics/anti-inflammatories, lipid regulators, antibiotics, β-blockers, anti-epileptics, hormones. Elimination rates of these drugs depend on the drug itself, person who consumes that drug and the dosage. For example amoxacillin, antibiotic, is not metabolized at all by the body and nearly 80-90% of the parent drug is excreted unchanged via urine. The drug which is nearly metabolized in the body may also excreted in a modified form, either hydrolysed or conjugated (Bound and Voulvoulis, 2004). Some of the drugs and their excretion routes are given in Table 1.5 by referring Sedlak and Pinkston (2001).

Table 1.4: Hormones excereted with urine (Tuzcu and Tuzcu, 1992).

Eustrogens (except pregnants)	
Kids	<10 µg.(24 h)$^{-1}$
Men (adult)	15-40 µg.(24 h)$^{-1}$
Women (pre- menopause)	15-80 µg.(24 h)$^{-1}$
Women (post- menopause)	< 20 µg.(24 h)$^{-1}$
Aldosterone	2-16 µg.(24 h)$^{-1}$
Catecholamine fractions (for adults)	
Epinephrine	0-20 µg.(24 h)$^{-1}$
Norepinephrine	15-80 µg.(24 h)$^{-1}$
Dopamine	65-400 µg.(24 h)$^{-1}$
Vanilylmandelic acid	< 9 µg.(24 h)$^{-1}$
Homovanilic acid	< 8 µg.(24 h)$^{-1}$

If urine is used as a fertilizer and applied to agricultural area, urinary pharmaceuticals will surely contact with soil. The amount of pharmaceuticals and their metabolites being introduced into the environment is probably low. However, their continual input into the environment may lead to a high, long-term concentration and promote unnoticed adverse effects on aquatic and terresterial organisms. The fate of the urinary pharmaceutical residues in soil media depends on the lipophilicity or other ability of binding to solids. Drug molecules often have many functional groups e.g. carboxylic acids, aldehydes and amines, which makes the binding capacities of the molecules to solids dependent on pH or other constituents (e.g. complexation) in the solids matrix. Drugs that are mobile in the soil may be a threat to ground water or they can leach to a nearby stream. Depending on the ability of the drug to bind solids either organisms in the terrestrial ecosystem or aquatic ecosystem may be exposed (Jørgensen and Halling-Sørensen, 2000).

Table 1.5: The most known drugs and their excretion profile (Sedlak and Pinkston, 2001).

Name of the drug	**Classification**	**Excretion**
Acetominophen	analgesic	excreted mostly as conjugates
Ibuprofen	analgesic, anti-inflammatory	extensive metabolism, possibly to conjugates
Amoxicillin	antibiotic	excreted mostly in original form (>50%)
Cephalexin	antibiotic	excreted mostly in original form (>50%)
Nabumetone	analgesic, anti-inflammatory	extensive metabolism to active metabolites
Azithromycin	antibiotic	data on metabolism not obtained
Oxaprozin	analgesic, anti-inflammatory	extensive metabolism, possibly to conjugates
Gabapentin	anticonvulsant	excreted mostly in original form (>50%)
Sulfamethoxazole	antibiotic	excreted as mixture of conjugates/original form
Gemfibrozil	cholesterol lowering	excreted mostly in original form (>50%)
Metoprolol	B-blocker	extensive metabolism, possibly to conjugates
Ciprofloxacin	antibiotic	excreted as mixture of conjugates/original form
Mupirocin	antibiotic	extensive metabolism to inactivate metabolites
Erythromycin	antibiotic	little excreted in urine
Atenolol	B-blocker	excreted mostly in original form (>50%)
Sertraline	antidepressant	extensive metabolism to active metabolites
Nefazodone	antidepressant	extensive metabolism to active metabolites
Tetracycline	antibiotic	excreted mostly in original form (80-90%)

Pharmaceutical compounds can also be released into the aquatic environment mostly by effluents from municipal sewage treatment plants. Because several investigations have shown some evidence that substance of pharmaceutical origin are often not eliminated during wastewater treatment and also not biodegraded in the environment (Heberer, 2002; Stuer-Lauridsen et al., 2000). Hence, it is obvious that this kind of chemicals are hardly removed via simple processes.

What has been done to overcome the obstacles ?

The researchers did not give up the idea of using the human urine as a fertilizer after facing with the difficulties and risks. Instead, many of them investigated new methods to overcome the problems. Here, there are some studies that involve the local solutions for particular problem of separating system:

- Lind et al. (2001) tried a simple method to reduce the volume of urine by freezing. They examined if the nutrients were still recovarable after freezing and thawing.Nearly 80% of both nitrogen and phosphorus was concentrated in 25% of the volume.

- Hellström et al.(1999) acidified the urine to prevent the decomposition of urea to ammoniacal nitrogen. Thus, the risk of ammonia evaporation was reduced. Acidification was found to be a useful method where sulphuric acid was more efficient than acetic acid. But the study has to be detailed by repeating the experiments for full-scale systems.

- Höglund et al. (2000, 2002) extensively investigated the microbial risks of source separated human urine as a fertilizer. They found that the risks related to the reuse of source separated human urine was low except for possible infections from rotavirus when the urine is either unstored or stored at low temperature (4°C).

- Jönsson et al. (1997) examined the possible contamination of source separated human urine with faeces. During the study they measured the metal content and faecal concentration of urine and the flush water consumption. According to results, heavy metals and faecal concentration of urine is very low. Besides nearly 50% of the flushwater was saved when compared with conventional toilets.

- Sundin et al. (1999) investigated the use of faecal sterols to measure faecal contamination of the urine. The results reflected that mesurement of faecal matter entering the urine storage tanks over time should be based on amounts of coprostonol rather than its precursor cholesterol.

- Udert et al. (2003a-b) investigated the precipitation potential of urine in pipes during transportation. The growing of urease active bacteria in the pipes was prooved in the study. Besides, precipitation was simulated with a dynamic computer model.

- Larsen et al. (2001) and her team started to study seriously on source separated human urine. Their study included the investigation of the thoughts of Swiss farmers towards source separated human urine and re-construction the idea of using the human urine. The working group focused on the usage of existing sewer network for the transportation of urine to a treatment facility to remove the unwanted species such as pharmaceutical and hormonal residues in urine (Larsen et al., 2004; www.novaquatis.ch).

- Behrendt et al. (2002) processed the urine in order to decrease the amount of urine and to obtain urine based fertilizer. They obtained isobutylaldehyde-di-urea from urine. In another study they stripped the ammonia in urine and absorbed in water. The results were challenging.

- Lind et al. (2000) and Bán and Dave (2004) recovered the urinary ammonia by obtaining magnesium ammonium phosphate (struvite) with wollastonite and zeolite adsorption. They recovered nearly 65-80% of nitrogen with this combined method.

- Adamsson (2000) investigated the potential use of human urine in culturing of green algae. The study suggested that it was possible to culture algae and zooplankton to feed fish larvae.But researcher insisted on doing long term studies to see the further effects of using human urine. Especially the relatively high content of chlorides in urine makes it necessary to carry out field trials for different crops.

- Pahl-Wostl et al. (2003) investigated the consumer attitudes towards a new fertilizer “ human urine”. The results indicated that the whole concept of urine separation is accepted only if the comfort of living and the expenses of the new technology is same as conventional ones. The other important outcome of the survey showed that urine can be accepted as a fertilizer if all the people are convinced that hygienic risks and micropollutant problems are totally solved.

- Bán and Dave (2004) achieved toxicological tests with *Daphnia magna*, in order to evaluate the potential use of the urine in aquaculture systems. It was concluded that fresh and stored urine are highly toxic for *Daphnia magna*. High pH and high ammonia concentration are reported to be the main reasons for the toxicity.

Same study also revealed that, urine which was remained after struvite precipitation and zeolite adsorption was highly toxic for *Daphnia magna*.

- Hanæus et al. (1997) investigated the urine separation system in an ecological village in northern Sweden. According to this study, efficiency of the urine separation system depends on the degree of separation in the toilets and the behaviour of users.

- Jönsson et al. (2002) investigated the benefits and the drawbacks of urine separation systems by using a simulation package named “ORWARE”. According to simulation results, urine separation systems decrease the nitrogen and phosphorus emissions while saving energy.

2. STRUVITE PRECIPITATION FROM FRESH URINE

2.1 Introduction

2.1.1 Urine as a nutrient source

Urine has been a favorite bioresource since it is a complete nutrient solution. The best way of recovering the urinary nutrients is to separate the streams of household wastewater and to collect the urine separately. Urine separating toilets enables the separate collection of urine at the source where the urinary nutrients are partially diluted (Vinnerås and Jönsson, 2002). These toilets have been preffered in rural areas and semi-urban areas where urine is collected in tanks and used in agricultural area as a fertilizer (Günther, 2000; Höglund et al., 2000). Adapting this system to urban area has been a favorite subject to many European initiatives since it is a well studied subject in rural area. But things get harder when the urine separation technique is oriented to urban life. As the population is high in urban area, the amount of urine which needs to be transported increases. The problem of transportation can be eliminated if the urine is concentrated with respect to nutrients. Two methods can be used to concentrate the urine. One of them involves decreasing the urine volume, the other one involves transforming of urinary nutrients into solid state.

According to literature survey, there are a few studies that concentrate on the recovery of urinary nutrients by transforming them into solid form. Lind et al. (2001) froze the urine and recovered 80% of urinary nutrients. Lind et al. (2000) and Bán and Dave (2004) recovered the urinary nutrients by struvite precipitation and adsorption on zeolite. Behrendt et al. (2002) focused on the recovery of urinary nitrogen by isobuthylaldehyde-di-urea precipitation.

The methods mentioned above mainly concentrated on the recovery of urinary nitrogen. But, urine is also a good source of phosphorus and potassium which are all plant available. Thus, the technique which has the aim of decreasing the volume with maximum nutrient recovery should focus on the transforming of urinary nitrogen, phosphorus and potassium into solid form.

In this chapter, nutrients in fresh urine were recovered as magnesium ammonium phosphate hexahydrate (struvite) which is a well known slow release fertilizer.

2.1.2. Struvite precipitation

Magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4.6H_2O$), mostly known as struvite, is a white crystalline compound having magnesium, nitrogen and phosphorus in equal molar concentrations. Apart from being a well known kidney stone, this compound is also known to form scales (Larsson et al., 1984; Wrigley et al., 1992; Grases et al., 1996). Struvite formation on pipes and equipment has been a problem in wastewater treatment industry for decades (Ohlinger et.al., 1998; Ohlinger et al., 1999; Bouropoulos and Koutsoukos, 2000; Babić-Ivančić, 2002; Doyle and Parsons, 2002; Hirasawa et al., 2002; Nelson et.al., 2003).

Nowadays , struvite precipitation is mentioned as an effective method for phosphorus recovery (Morse et al., 1998). Besides, its nitrogen and phosphorus content and its low solubility in water enables it to be used as a slow release fertilizer (Shin and Lee, 1997; Li et.al., 1999; Liberti et al., 2001; Stratful et.al., 2001; Ueno ve Fujii, 2001; Doyle and Parsons, 2002; Hirasawa et al., 2002; Nelson et.al., 2003).

Struvite is precipitated according to the general reaction shown below:

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O \qquad \textbf{(2.1)}$$

Precipitation involves the rapid formation of a sparingly soluble solid phase from a liquid solution phase which generally comprises the simultaneous and rapid occurence of nucleation, crystal growth and other processes such as Ostwald ripening and agglomeration (Karpinski and Wey, 2001). In every precipitation reaction, solubility of the precipitating component must be known in order to determine the driving force for the reaction. When a precipitate coexists in equilibrium with the solution, the appropriate equilibrium constant representing interphase equilibrium is the solubility product.

Struvite is a sparingly soluble salt and the speciation of the components of struvite is pH dependent. Struvite solubility decreases with increasing pH. However, as pH continues to rise above 9, the solubility of struvite begins to increase since the ammonium ion concentration starts to decrease and the phosphate ion concentration starts to increase (Snoeyink and Jenkins, 1980). Because of this behaviour, there must be a definite pH where the precipitation efficiency is maximum. This pH can be obtained if the pH of minimum struvite solubility is calculated theoretically.

It is possible to calculate the solubility of struvite in an aqueous solution by using equilibrium equations between corresponding ions. Equilibrium dissociation of $MgNH_4PO_4.6H_2O$ is:

$$MgNH_4PO_4 \leftrightarrow Mg^{2+} + NH_4^{\ +} + PO_4^{\ 3-} \qquad \textbf{(2.2)}$$

Solubility product for the struvite can be expressed as follows:

$$K_{sp} = \left[Mg^{2+}\right] \times \left[NH_4^{\ +}\right] \times \left[PO_4^{\ 3-}\right] \qquad \textbf{(2.3)}$$

The equilibria of NH_4 in aqueous solution is expressed in equation (2.4):

$$NH_4^{\ +} + H_2O \leftrightarrow NH_3 + H_3O^+ \qquad \textbf{(2.4)}$$

The following equilibria (equation 2.5, 2.6 and 2.7) is observed if the basic properties of PO_4^{3-} is considered:

$$PO_4^{\ 3-} + H_2O \leftrightarrow HPO_4^{\ 2-} + OH^- \qquad \textbf{(2.5)}$$

$$HPO_4^{\ 2-} + H_2O \leftrightarrow H_2PO_4^{\ -} + OH^- \qquad \textbf{(2.6)}$$

$$H_2PO_4^{\ -} + H_2O \leftrightarrow H_3PO_4 + OH^- \qquad \textbf{(2.7)}$$

The other equilibria is the ionisation of pure water, which behave like weak acids or bases,

$$H_2O + H_2O \leftrightarrow H_3O^+ + OH^- \qquad \textbf{(2.8)}$$

The equilibrium constant for equation (2.8) is shown below:

$$K_{eq} = \frac{[H_3O^+] \times [OH^-]}{[H_2O]^2} \qquad \textbf{(2.9)}$$

Since the concentration of water is constant, equation (2.9) can be written as;

$$K_w = K_{eq} \times [H_2O]^2 = [H_3O^+] \times [OH^-] \quad \textbf{(2.10)}$$

Reorganizing the equation (2.10) yields equation (2.11).

$$[OH^-] = \frac{K_w}{[H_3O^+]} \quad \textbf{(2.11)}$$

Solubility product in terms of solubility is denoted as;

$$K_{sp} = \underbrace{\left[Mg^{2+}\right]}_{S} \times \underbrace{\left[NH_4^{\ +}\right]}_{S} \times \underbrace{\left[PO_4^{\ 3-}\right]}_{S} \quad \textbf{(2.12)}$$

Solubility of $MgNH_4PO_4$ in terms of concentrations can be written as:

$$S = \left[Mg^{2+}\right] = [NH_3] + \left[NH_4^{\ +}\right] = \left[PO_4^{\ 3-}\right] + \left[HPO_4^{\ 2-}\right] + \left[H_2PO_4^{\ -}\right] + [H_3PO_4] \quad \textbf{(2.13)}$$

Equilibrium relations for the equations (2.4), (2.5), (2.6) and (2.7) can be written in terms of S. Equations and related equilibrium relations for NH_4^+ are shown below:

$$NH_4^{\ +} + H_2O \leftrightarrow NH_3 + H_3O^+ \Rightarrow K_h = \frac{K_w}{K_b} = \frac{[NH_3] \times [H_3O^+]}{[NH_4^{\ +}]} \quad \textbf{(2.14)}$$

It is possible to re-arrange equation (2.14) in order to find the concentration of $[NH_3]$ in terms of $[NH_4^+]$.

$$[NH_3] = \frac{K_w \times [NH_4^{\ +}]}{K_b \times [H_3 0^+]} \quad \textbf{(2.15)}$$

As previously indicated, total ammonia species in aqueous solution equals to solubility value:

$$S = [NH_3] + [NH_4^{\ +}] \quad \textbf{(2.16)}$$

Thus, substituting equation (2.15) into equation (2.16) yields equation (2.17).

$$S=\frac{K_w}{[H_3O^+]\times K_b}\times[NH_4{}^+]+[NH_4{}^+] \quad \textbf{(2.17)}$$

$$S=[NH_4{}^+]\times\left(\frac{K_w}{[H_3O^+]\times K_b}+1\right) \quad \textbf{(2.18)}$$

Equation (2.18) should be re-arranged in order to use in equation (2.3).

$$[NH_4{}^+]=\frac{S}{(1+\frac{K_w}{K_b\times[H_3O^+]})} \quad \textbf{(2.19)}$$

The hydrolysis of PO_4^{3-} consists of three steps which are detailed below:

$$PO_4{}^{3-}+H_2O\leftrightarrow HPO_4{}^{2-}+OH^-\Rightarrow K_{h1}=\frac{K_w}{K_3}=\frac{[HPO_4{}^{2-}]\times[OH^-]}{[PO_4{}^{3-}]} \quad \textbf{(2.20)}$$

Equation (2.11) is placed in equation (2.20) to obtain equation (2.21).

$$[PO_4{}^{3-}]=\frac{K_3\times[HPO_4{}^{2-}]}{[H_3O^+]} \quad \textbf{(2.21)}$$

Second step of PO_4^{3-} hydrolysis is:

$$HPO_4{}^{2-}+H_2O\leftrightarrow H_2PO_4{}^-+OH^-\Rightarrow K_{h2}=\frac{K_w}{K_2}=\frac{[H_2PO_4{}^-]\times[OH^-]}{[HPO_4{}^{2-}]} \quad \textbf{(2.22)}$$

After substituting equation (2.11) into (2.22), equation (2.23) can be obtained.

$$[HPO_4{}^{2-}]=\frac{K_2\times[H_2PO_4{}^-]}{[H_3O^+]} \quad \textbf{(2.23)}$$

The third step of PO_4^{3-} hydrolysis is shown below:

$$H_2PO_4{}^-+H_2O\leftrightarrow H_3PO_4+OH^-\Rightarrow K_{h3}=\frac{K_w}{K_1}=\frac{[H_3PO_4]\times[OH^-]}{[H_2PO_4{}^-]} \quad \textbf{(2.24)}$$

Equation (2.24) must be modified by using equation (2.11).

$$[H_2PO_4{}^-] = \frac{K_1 \times [H_3PO_4]}{[H_3O^+]} \quad \textbf{(2.25)}$$

Total phosphate species can be written as:

$$S = [PO_4{}^{3-}] + [HPO_4{}^{2-}] + [H_2PO_4{}^-] + [H_3PO_4] \quad \textbf{(2.26)}$$

Equation (2.26) should be arranged to have an equation containing S and [PO_4^{3-}].

$$S = [PO_4{}^{3-}] + \left(\frac{[H_3O^+] \times [PO_4{}^{3-}]}{K_3}\right) + \left(\frac{[H_3O^+]^2 \times [PO_4{}^{3-}]}{K_2 \times K_3}\right) + \left(\frac{[H_3O^+]^3 \times [PO_4{}^{3-}]}{K_1 \times K_2 \times K_3}\right) \quad \textbf{(2.27)}$$

$$[PO_4{}^{3-}] = \left(\frac{S}{1 + \frac{[H_3O^+]}{K_3} + \frac{[H_3O^+]^2}{K_2 \times K_3} + \frac{[H_3O^+]^3}{K_1 \times K_2 \times K_3}}\right) \quad \textbf{(2.28)}$$

Substituting [NH_4^+] from equation (2.19) and [PO_4^{3-}] from equation (2.28) into equation (2.3) gives:

$$K_{sp} = S \times \left(\frac{S}{1 + \frac{K_w}{K_b \times [H_3O^+]}}\right) \times \left(\frac{S}{1 + \frac{[H_3O^+]}{K_3} + \frac{[H_3O^+]^2}{K_2 \times K_3} + \frac{[H_3O^+]^3}{K_1 \times K_2 \times K_3}}\right) \quad \textbf{(2.29)}$$

Equation (2.29) should be rearranged in order to obtain S:

$$S = \left[K_{sp} \times \left(1 + \frac{K_w}{K_b \times [H_3O^+]}\right) \times \left(1 + \frac{[H_3O^+]}{K_3} + \frac{[H_3O^+]^2}{K_2 \times K_3} + \frac{[H_3O^+]^3}{K_1 \times K_2 \times K_3}\right)\right]^{1/3} \quad \textbf{(2.30)}$$

To find out the solubility value, the constants used in the equation must be found from the literature. In this study, the value of constants were taken from the paper of Bouropoulos and Koutsoukos (2000) who studied on the precipitation of magnesium ammonium phosphate hexahydrate.

K_{sp}= 5.495x10^{-14} (@ 25°C)

$K_w = 10^{-14}$, $K_b = 1.76 \times 10^{-5}$ (@ 25°C)

$K_1 = 7.079 \times 10^{-3}$, $K_2 = 6.309 \times 10^{-8}$, $K_3 = 4.265 \times 10^{-13}$ (@ 25°C)

The resultant equation is solved in Microsoft EXCEL programme and the solubility values were drawn against pH which is depicted in Figure 2.1.

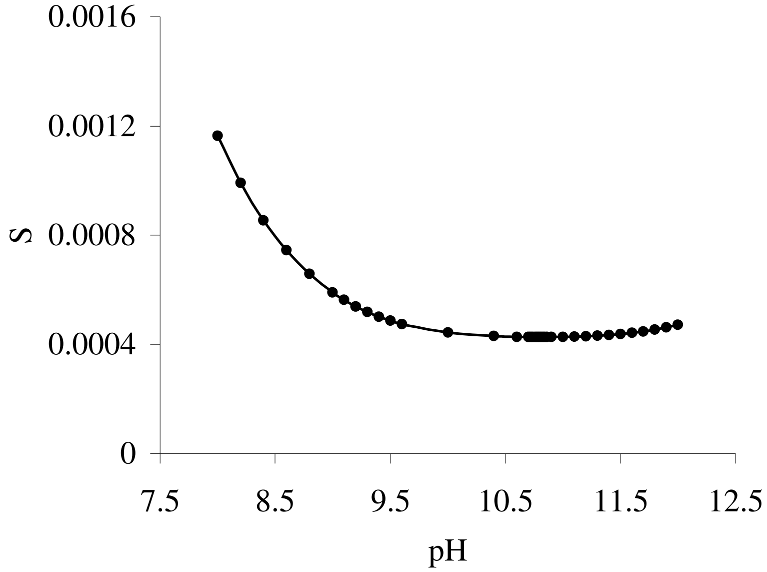

Figure 2.1: Solubility of struvite at different pH values.

The exact pH of minimum struvite solubility can also be found from the graph where the differential of solubility (dS) is drawn against pH. As seen from Figure 2.2, the pH of minimum struvite solubility is 10.8 .

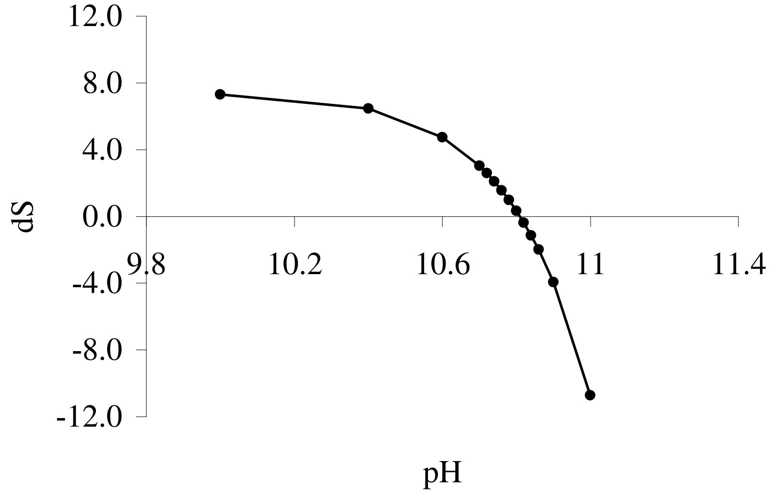

Figure 2.2: Differential of solubility at different pH values.

In literature, there are a few studies concerning the kinetics of struvite precipitation. Nelson et al.(2003) indicated that once nucleation has occured, crystal growth rate exceeds the nucleation rate because of greater activation energy is required for nucleation of non-associated ions as compared to the activation energy for deposition of ions on a crystal surface. Ohlinger et al. (1999) who investigated the kinetics of struvite formation concluded that struvite formation in pure water and in wastewater is controlled by nucleation. Furthermore, nucleation rate is directly affected from the degree of supersaturation and crystal growth is promoted by mixing.

Struvite precipitation from pure water and wastewater has been studied earlier and various results have been obtained up to now. Therefore, it is very difficult to write the optimal reaction conditions required for effective struvite precipitation. In all of these studies, initial molar ratio of N:P:Mg and precipitation pH were optimized. Theoretical calculations indicated that minimum solubility occurred at pH 10.8 whereas Ohlinger et al. (1998) found the pH of minimum struvite solubility as 10.3 in pure solutions. The decrease in the minimum solubility pH resulted from the consideration of magnesium phosphate complexes in equilibrium calculations and from the application of the experimentally determined solubility constant. Studies aimed to find the pH of minimum struvite solubility in wastewater found the pH of minimum solubility between 8.9 to 10.7. According to Schulze-Rettmer (1991), the initial molar N:P:Mg ratio had to be 1:1:1.3 and precipitation had to be achieved between pH 8 and 10. Nelson et.al. (2003) found the pH of minimum struvite solubility between 8.9 and 9.25 in anaerobic swine lagoon liquid. Demeestere et al. (2001) informed that maximum nitrogen removal efficiency was obtained when the initial molar N:P:Mg ratio was adjusted as 1:1.5:1.5 and the pH was fixed at 9. According to Shin and Lee (1997), optimal Mg:N ratio had to be 1.5:1.

Scott et al. (1991) developed a model to understand the optimal conditions for struvite formation which contained various equilibrium equations of components formed from ammonia, phosphate, magnesium and water. According to that model, concentration of phosphorus in solution decreases rapidly with an increase in either magnesium concentration or pH. Maekawa et al. (1995) expressed that the pH of precipitation directly affects the type of the precipitate. It is either acid soluble ($pH<6$) or becomes $Mg_3(PO_4)_2$ in basic conditions ($pH>10$). Furthermore, magnesium can form struvite when the pH is sufficiently high and newberyite

($MgHPO_4.3H_2O$) when the concentration in solution is very large and the pH is rather low (Abbona et al., 1982; Abbona and Lundager-Madsen, 1988). In other words, pH has a great influence on phosphate and ammonia equilibria. Increase in pH will result lower ammonium ion concentration while causing an increase in phosphate ion concentration. As pH increases from 7 to 9 the percent of total NH_3-N present as NH_4^+ decreases from 99% to 64%. In the same pH range, the fraction of total PO_4-P present as the PO_4^{3-} anion increases 250 fold (Nelson et al., 2003).

Precipitation is the nucleation and subsequent growth of a phase from another phase of different composition. This process is only possible if the solution is supersaturated with respect to precipitated compound. A supersaturated solution may be stable for a very long time if the surface tension of the new phase is sufficiently high and the supersaturation is low.

Precipitation (or reactive crystallization) differs from the classical crystallization methods in the way that the supersaturation, no longer results from an action on the physical properties of the solution. It is obtained by a chemical reaction between two soluble components, leading to a less soluble product which crystallizes. Reaction and the crystallization occur simultaneously and both reaction kinetics and crystallization kinetics have to be taken into account. Generally high supersaturation levels are reached in precipitation. The solid phase which crystallizes from the reaction of A^{z+} and B^{z-} can be denoted as,

$$xA^{z+} + yB^{z-} \rightarrow A_xB_y \qquad \textbf{(2.31)}$$

In the case of precipitation of molecular components, the driving force of the crystallization is the difference between the chemical potential of the solute in the supersaturated liquid phase and in the solid. At equilibrium conditions these two chemical potentials are equal. Chemical potentials regarding with the above equation can be written as;

$$\mu=x\mu_A+y\mu_B \qquad \textbf{(2.32)}$$

where

$$\mu_A=\mu_{A0}+RT\ln(a_A) \qquad \textbf{(2.33)}$$

$$\mu_B=\mu_{B0}+RT\ln(a_B) \qquad \textbf{(2.34)}$$

The driving force of the crystallization is in this case,

$$\Delta\mu = RT\ln(a_A^x a_B^y / K_{sp}) \qquad \textbf{(2.35)}$$

In the above equation ($a_A^x a_B^y$) term indicates activity product, K_{sp} indicates the thermodynamic solubility constant. The ratio of ion activities to the thermodynamic solubility product ($a_A^x a_B^y / K_{sp}$) is also known as supersaturation (S). Supersaturation is the most important parameter that characterizes the solution and it considers ion concentration, pH and ionic strength. Sometimes supersaturation is defined as $S' = S^{1/(x+y)}$. This expression should be used in the expressions of the primary nucleation kinetics and growth rate of the formed nuclei, if the reaction kinetics is fast.

Supersaturation is also defined by using saturation index (SI). As previously expressed, precipitation of a phase is only possible if its ion activity product (IAP) is higher than the solubility product (K_{sp}). The relation between the IAP and K_{sp} can be expressed with Saturation Index (SI).

$$SI = LOG\frac{IAP}{K_{sp}} \qquad \textbf{(2.36)}$$

or

$$SI = LOG\frac{[A^{z+}]_{act}^{x} \times [B^{z-}]_{act}^{y}}{K_{sp}} \qquad \textbf{(2.37)}$$

If SI is 0, IAP equals K_{sp} which means that solution is saturated. If SI exceeds 0, IAP also exceeds K_{sp} which means that solution is supersaturated. But if SI is lower than 0, IAP has a lower value than K_{sp} which indicates the unsaturated solution.

Both SI and S are the simplistic measure of saturation. But the main drawback of the definitions is the absence of temperature effects on mineral stability. Furthermore, these definitions does not take into account the slow kinetics and nucleation problems of many reactions. Although SI and S definitions have the drawbacks listed above, they can be used to find out the precipitation potential of minerals that might precipitate from urine.

Undiluted and unhydrolysed human urine contains considerable amounts of NH_3-N, PO_4^{3-}-P, Mg, Ca, K, Na and Cl. Although the concentration of these ions are directly related with the eating habits, the average ratio between them is nearly the same. Average N**:**P**:**Ca**:**Mg ratio in urine is 8**:**6**:**1.1**:**1. Possible phases that might precipitate from Ca-PO_4-NH_3-Mg system are;

Struvite (STRV)	-$MgNH_4PO_4.6H_2O$	(pK_{sp}=13.15@25˚C)
Hydroxyapatite (HAP)	-$Ca_5(PO_4)_3(OH)$	(pK_{sp} =58.33@25˚C)
Dicalcium phosphate dihydrate (DCPD)	-$CaHPO_4.2H_2O$	(pK_{sp} =6.69@25˚C)
Dicalcium phosphate anhydrate (DCPA)	-$CaHPO_4$	(pK_{sp} =6.90@25˚C)
Octacalcium phosphate (OCP)	-$Ca_4H(PO_4)_3$	(pK_{sp} =49.60@25˚C)
Tricalcium phosphate (TCP)	-$Ca_3(PO_4)_2$	(pK_{sp} =26.00@25˚C)
Amorphous calcium phosphate (ACP)	-$Ca_3(PO_4)_2$	(pK_{sp} =26.52@25˚C)

(pK_{sp} values are taken from Montastruc et al., 2003 and Udert et al., 2003).

Equations between (2.39) and (2.53) are used for the calculation of S and SI values,

$$MgNH_4PO_4.6H_2O \rightarrow Mg^{2+} + NH_4^{+} + PO_4^{3-} \qquad \textbf{(2.39)}$$

$$S = \left[\frac{[Mg^{2+}] \times [NH_4^{+}] \times [PO_4^{3-}]}{K_{sp\,STRV}} \right]^{1/3} \qquad \textbf{(2.40)}$$

$$SI = LOG \frac{IAP_{STRV}}{K_{sp\,STRV}} = LOG \frac{[Mg^{2+}] \times [NH_4^{+}] \times [PO_4^{3-}]}{K_{sp\,STRV}} \qquad \textbf{(2.41)}$$

$$Ca_5(PO_4)_3(OH) \rightarrow 5Ca^{2+} + 3PO_4^{3-} + OH^{-} \qquad \textbf{(2.42)}$$

$$S = \left[\frac{[Ca^{2+}]^5 \times [OH^{-}] \times [PO_4^{3-}]^3}{K_{sp\,HAP}} \right]^{1/9} \qquad \textbf{(2.43)}$$

$$SI = LOG \frac{IAP_{HAP}}{K_{sp\,HAP}} = LOG \frac{[Ca^{2+}]^5 \times [OH^{-}] \times [PO_4^{3-}]^3}{K_{sp\,HAP}} \qquad \textbf{(2.44)}$$

$$Ca_4H(PO_4)_3 \rightarrow 4Ca^{2+} + H^{+} + 3PO_4^{3-} \qquad \textbf{(2.45)}$$

$$S = \left[\frac{[Ca^{2+}]^4 \times [H^+] \times [PO_4{}^{3-}]^3}{K_{sp\,OCP}} \right]^{1/8} \tag{2.46}$$

$$SI = LOG \frac{IAP_{OCP}}{K_{sp\,OCP}} = LOG \frac{[Ca^{2+}]^4 \times [H^+] \times [PO_4{}^{3-}]^3}{K_{sp\,OCP}} \tag{2.47}$$

$$CaHPO_4 \rightarrow Ca^{2+} + HPO_4{}^{2-} \tag{2.48}$$

$$S = \left[\frac{[Ca^{2+}] \times [HPO_4{}^{2-}]}{K_{sp\,DCPD}} \right]^{1/2} \tag{2.49}$$

$$SI = LOG \frac{IAP_{DCPD}}{K_{sp\,DCPD}} = LOG \frac{[Ca^{2+}] \times [HPO_4{}^{2-}]}{K_{sp\,DCPD}} \tag{2.50}$$

$$Ca_3(PO_4)_2 \rightarrow 3Ca^{2+} + 2PO_4{}^{3-} \tag{2.51}$$

$$S = \left[\frac{[Ca^{2+}]^3 \times [PO_4{}^{3-}]^2}{K_{sp\,TCP}} \right]^{1/5} \tag{2.52}$$

$$SI = LOG \frac{IAP_{TCP}}{K_{sp\,TCP}} = LOG \frac{[Ca^{2+}]^3 \times [PO_4{}^{3-}]^2}{K_{sp\,TCP}} \tag{2.53}$$

Phases which may precipitate can be interpretted from Figure 2.3 and 2.4.

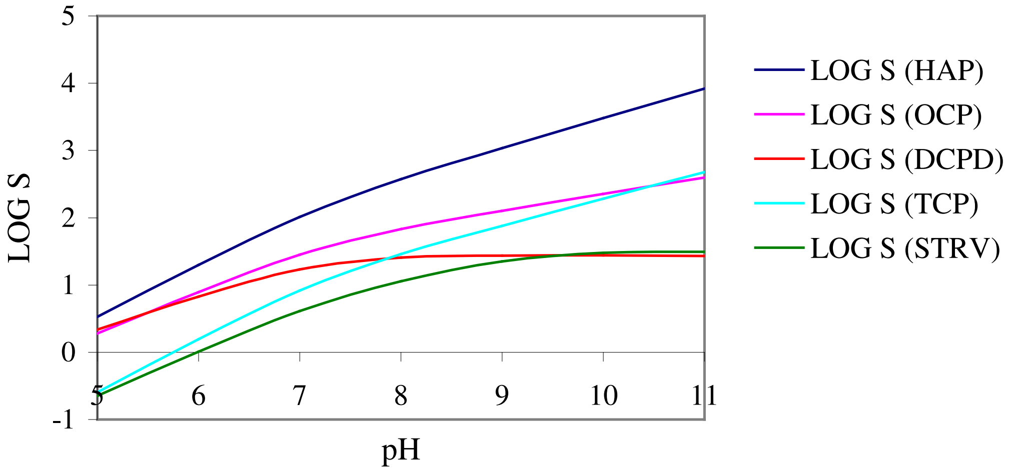

Figure 2.3: Supersaturation of urine with respect to minerals: HAP, OCP, DCPD, TCP , STRV.

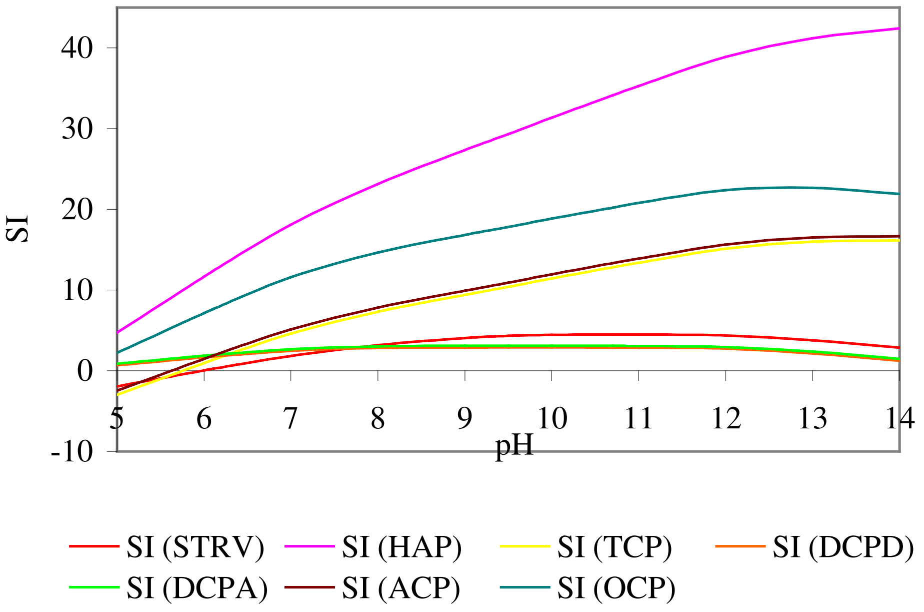

Figure 2.4: Saturation index of the minerals: STRV, HAP, TCP, DCPD, DCPA, ACP, OCP.

As seen from the figures, urine is a supersaturated with respect to all phases above pH 7. In other words, we should expect the formation of all phases when the pH is above 7. But several studies reported that all calcium phosphate compounds can not form at the same time. Although HAP seems to have the highest supersaturation degree among the other calcium phosphates, it does not precipitate directly from supersaturated solutions. According to Liu et al. (2001), formation of HAP crystals involves three steps including OCP formation, ACP transformation and finally HAP transformation. When calcium phosphates are precipitated from aqueous solutions, an amorphous phase is easily obtained as the first phase instead of HAP. Phase transformations into metastable phases are quite common, and systems that do this are sometimes said to obey the Ostwald's rule. In those systems interfacial tension for the metastable phase is lower than for the equilibrium phase (Sear, 2005). As a result, ACP precipitation decreases supersaturation with respect to the other phases, so that the nucleation of other calcium phosphates is hindered. The actual phase that forms under any given conditions is often dictated by kinetic factors rather than thermodynamic considerations. Besides, temperature of solution strongly affects the reaction rate. Moreover, due to the possible occurrence of many different phases, the precipitation process is very complicated. Different solid phases incorporate different ions and complexes. Concentrations of these ions change considerably with the change of calcium, magnesium and phosphorus concentrations, and the solution pH (Arifuzzaman and Rohani, 2004). Furthermore, Mg is known to hinder the nucleation of HAP and promote the formation of TCP and ACP (Abbona and Baronnet, 1996).

In urine which is amended with magnesium, struvite becomes the dominant phase. The major ion that affects the struvite precipitation yield and purity of the precipitate is reported as calcium. According to Abbona et al. (1986), calcium causes much greater effect on the crystallization of the magnesium phosphate solutions than does magnesium on calcium phosphate and the phase which is precipitated from Ca and Mg bearing solution depends on the initial molar ratio of Mg:Ca. Schulze-Rettmer (1991) expressed the formation of hydroxyapatite, dicalcium phosphate and octacalcium phosphate together with struvite where calcium ions are available in wastewater. Jaffer et al. (2002) expressed the existence of hydroxyapatite crystals in precipitates which are formed from Ca bearing solutions. Rensburg et al. (2003) precipitated struvite from anaerobic digester liquor and detected small amounts of amorphous calcium phosphate, newberyite, calcite and magnesite in the precipitate.

In the case of struvite precipitation from human urine, both the precipitation pH and the initial molar concentration of reactants affects the purity of the precipitate. The molar ratio of NH_3-N : PO_4^{3-}-P : Mg in fresh urine is about 9:6:1. The ratio is not constant which mainly depends on eating habits and human metabolism. It is obvious that urine is deficient in magnesium when compared with phosphorus. The molar ratio of urinary Ca:Mg and K:Mg of urine is 1.1:1 and 14:1 respectively. Because the limiting ion for struvite precipitation in human urine is magnesium, urine must be amended with magnesium to enhance the precipitation. Magnesium hydroxide, magnesium oxide and magnesium chloride are the possible sources for this amendments (Li et al., 1999; Li and Zhao, 2003). Among these, magnesium oxide has an advantage of increasing the pH. However studies showed that insolubility of the material causes problems during the precipitation. Magnesium hydroxide is also quite insoluble in water which restricts its usage. Among magnesium sources, magnesium chloride seems to be the best practicle solution with respect to its solubility in water (Jaffer et al., 2002). However, magnesium chloride is acidic therefore additional pH adjustment is a necessity for effective precipitation. Li and Zhao (2003) mentioned that addition of NaOH is more effective than lime or $Mg(OH)_2$. But this method could be expensive depending on the desired pH. Air stripping is another method that can be applied to raise the pH of the solution (Battistoni et al., 2000; Musvoto et al., 2000; Battistoni et al., 2001; Münch and Barr, 2001; Battistoni et al., 2002). CO_2 is stripped out resulting an increase in pH by aerating the wastewater stream. Stratful et al. (2001) suggested a combination of both methods to obtain an effective pH for struvite precipitation.

The scope of this chapter was to study the precipitation reaction in order to determine the optimal reaction conditions and to identify the precipitate.

2.2 Materials and Methods

2.2.1 Characterization of source separated urine

To characterize the urine, 24 hr urine samples were collected from 10 people (aged between 9-55, 5 men-5 women) and mixed in a container. 1000 ml of mixed sample was acidified to pH 1.5 with concentrated H_2SO_4 and stored at 4 °C until the characterization tests were completed. All the analyses were conducted at the chemical engineering laboratory, environmental engineering laboratory and metallurgy engineering laboratory of Istanbul Technical University, by following the standard procedures and methods (APHA, 1992). Elements such as K, Fe, Cd, Cu, Mn, Mg and Ca in urine were determined by atomic absorption spectrometer (Perkin Elmer 1100-B). WTW-Inolab pH meter was used for recording the pH of the urine.

2.2.2 Struvite precipitation

All the precipitation experiments were carried out in 300-500 ml glass beakers. The amount of urine used in the experiments ranged between 50-200 ml. Fresh urine was neither diluted nor filtered before the experiments. Urine was mixed for 5 minutes by magnetic stirrer (IKAMAG-RH) prior to magnesium addition.

Analytically pure $MgCl_2.6H_2O$ was used as the magnesium source. The pH was controlled and recorded during the reaction.1 N NaOH, 5 N NaOH and 1 N HCl was used to maintain the constant pH. Reactions were achieved at room temperature.

All the analyses were run according to standard methods (APHA, 1992). Mg, Ca, K and heavy metals such as Fe, Cd, Cu, Zn, Mn were determined by atomic absorption spectroscopy (Perkin Elmer 1100-B).

In all of the experimental sets, initial PO_4^{3-}-P, Mg, Ca and NH_3-N concentration of urine were determined prior to Mg addition. After the urine was amended with Mg, solution was mixed for 5 min in order to obtain homogen mixture. After reaching the desired pH value, solution is mixed for a certain time which is also known as reaction period. By the end of the reaction period, precipitate was separated from the urine by simple filtration. The volume of filtrate was recorded and samples were taken to analyze PO_4^{3-}-P, Mg, Ca and NH_3-N in residual urine. The amount of PO_4^{3-}-P, Mg, Ca and NH_3-N which were reacted at particular process conditions were calculated. The calculated amount also indicated the amount of reactants (P, N, Ca and Mg) that were recovered by precipitation reaction. Finally, the percentage recovery values of PO_4^{3-}-P, Mg, Ca and NH_3-N were calculated according to equations 2.31,2.32, 2.33 and 2.34 where “in”,“fin”and “V” expressions denote “initial”, “final”and “volume of solution” respectively.

$$NH_3 - N_{recovered}\% = \frac{([NH_3 - N]_{in} \times V_{in}) - ([NH_3 - N]_{fin} \times V_{fin})}{([NH_3 - N]_{in} \times V_{in})} \times 100 \qquad \textbf{(2.54)}$$

$$PO_4^{3-} - P_{recovered}\% = \frac{([PO_4^{3-} - P]_{in} \times V_{in}) - ([PO_4^{3-} - P]_{fin} \times V_{fin})}{([PO_4^{3-} - P]_{in} \times V_{in})} \times 100 \qquad \textbf{(2.55)}$$

$$Mg_{recovered}\% = \frac{([Mg]_{in} \times V_{in}) - ([Mg]_{fin} \times V_{fin})}{([Mg]_{in} \times V_{in})} \times 100 \qquad \textbf{(2.56)}$$

$$Ca_{recovered}\% = \frac{([Ca]_{in} \times V_{in}) - ([Ca]_{fin} \times V_{fin})}{([Ca]_{in} \times V_{in})} \times 100 \qquad \textbf{(2.57)}$$

2.2.2.1 Determination of reaction period

Optimum reaction period was determined by precipitating struvite at two different process pH (pH 9 and pH 10) where the reaction period was set as 30 min, 60 min and 120 min respectively. Initial Mg:P ratio of solution was adjusted as 1 in all experiments where the operational pH was set at desired value by adding 1N and 5N NaOH. NH_3-N, PO_4^{3-}-P, Ca and Mg were analyzed before and after the precipitation.

2.2.2.2 Determination of optimum pH

To determine the optimum pH for struvite precipitation, urine was mixed with $MgCl_2.6H_2O$ and the pH was raised to the desired value with 1 N and 5 N NaOH. Solution was mixed for 60 min and the pH was kept constant during the reaction period. Experiments were achieved at four different pH values (pH 9, 9.5, 10, 10.7) at two different initial molar Mg:P ratio (1.31:1 and 0.43:1). NH_3-N, PO_4^{3-}-P, Ca and Mg were analyzed before and after the precipitation. Precipitate was removed and dried in an oven at 40°C for 48 h, in order to prevent the struvite crystals from losing their water of crystallization which occurs at 60°C (Ohlinger et al., 1998).

2.2.2.3 Effect of initial molar Mg:P ratio

The influence of initial molar ratio of Mg:P on reaction efficiency was investigated. The molarity of magnesium and phosphate were varied in order to obtain the desired molar ratio of Mg:P (Mg:P→0.4, 0.6, 0.7, 0.9,1, 1.2, 1.3, 1.6, 1.8). Each precipitation was achieved by using 50 ml of fresh urine which were not filtered prior to precipitation. Reaction pH was kept constant at 9 and 1N NaOH was added to adjust the pH during the reaction. NH_3-N, PO_4^{3-}-P, Ca and Mg were analyzed before and after the precipitation. Precipitate was removed and dried in an oven at 40°C for 48 h.

2.2.3 Characterization of the precipitate

Solid phase was identified and the degree of crystallinity was measured by X-ray diffraction analysis (Philips-PW1710). Functional groups in the precipitate were identified with FT-IR spectroscopy (Perkin Elmer, SpectrumOne). The qualitative analyses of the precipitate in terms of elements were conducted by energy dispersive spectroscopy (JEOL 2000 EX / TEM-EDS) and ICP. Carbon, hydrogen and nitrogen content of the precipitate was determined with Carlo Erba 1106 Elemental Analyzer.

2.3 Results and Discussion

2.3.1 Characterization of fresh urine

Human urine is a complex aqueous solution containing sodium chloride (NaCl) and urea ($CO(NH_2)_2$) as dominant compounds but also potassium (K), calcium (Ca), sulfate (SO_4) and phosphate (PO_4) in low concentrations. There is no detailed information about urine composition since it is mainly the subject of medication. In our study, urine was characterized in terms of wastewater parameters. The results were compared with the data which was previously obtained by other researchers (Table 2.1).

Table 2.1: Characterization of urine (with comparison)

Parameter		This study	Udert et al., (2003-d)	Fittschen and Hahn, (1998)
NH_3-N	(mg N.L^{-1})	531	480	364
Urea-N	(mg N.L^{-1})	Not analyzed	7700	10700
TKN	(mg N.L^{-1})	11413	Not analyzed	6879
PO_4^{3-} -P	(mg P.L^{-1})	800	740	592
Calcium	(mg.L^{-1})	240	190	Not analyzed
Magnesium	(mg.L^{-1})	75	100	Not analyzed
Sodium	(mg.L^{-1})	Not analyzed	2800	Not analyzed
Potassium	(mg.L^{-1})	2400	2200	1656
Sulphate	(mg.L^{-1})	Not analyzed	1500	Not analyzed
Chloride	(mg.L^{-1})	Not analyzed	3800	Not analyzed
COD	(mg.L^{-1})	8475	Not analyzed	8261
BOD_5	(mg.L^{-1})	Not analyzed	Not analyzed	3860
Cr	(mg.L^{-1})	0.30	Not analyzed	Not analyzed
Cu	(mg.L^{-1})	0.06	Not analyzed	Not analyzed
Cd	(mg.L^{-1})	0.01	Not analyzed	Not analyzed
Mn	(mg.L^{-1})	0.1	Not analyzed	Not analyzed
Zn	(mg.L^{-1})	0.4	Not analyzed	Not analyzed
Ni	(mg.L^{-1})	0.11	Not analyzed	Not analyzed
Fe	(mg.L^{-1})	0.21	Not analyzed	Not analyzed
pH	-	6.10	6.2	Not analyzed

2.3.2 Optimum reaction period

In order to find the optimum reaction period, precipitation processes were run in 30, 60 and 120 min respectively. Experiments were achieved at two different pH values (pH 9 and pH 10) where the initial molar ratio of Mg:P was kept as 1. Figure 2.5 depicts the effect of reaction period on percentage recovery of the constituent ions of struvite and urinary calcium at pH 9. Similarly, Figure 2.6 depicts the effect of reaction period on percentage recovery of P, N, Mg and Ca at pH 10.

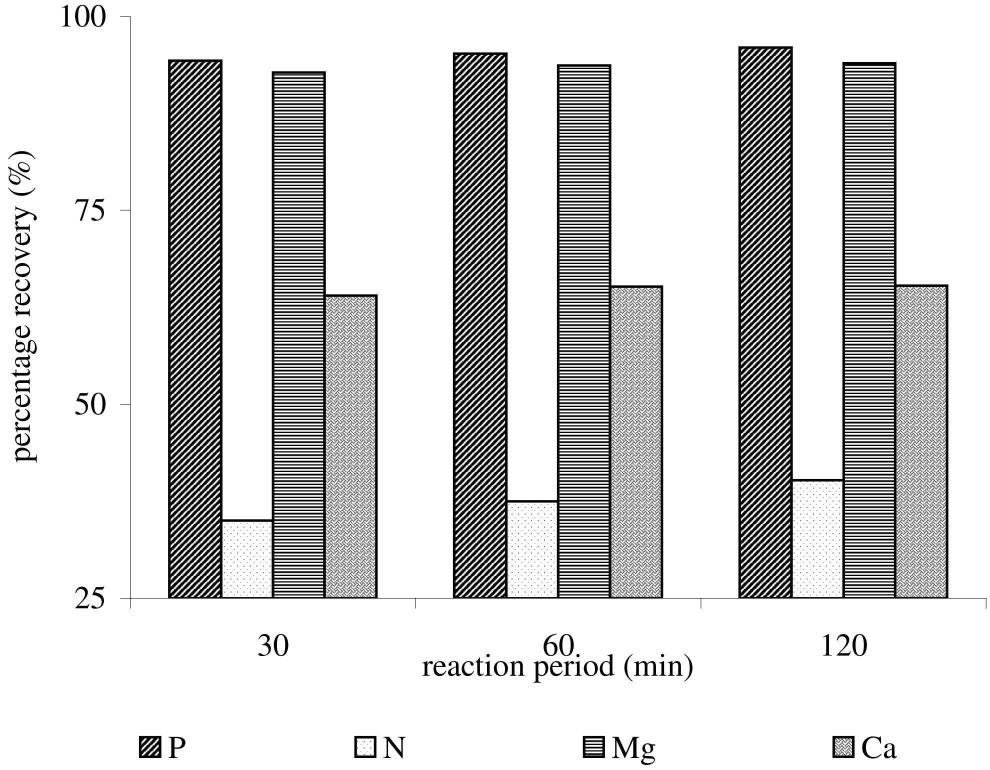

Figure 2.5: Percentage recovery of the constituent ions of struvite and urinary calcium at different reaction periods, ($(Mg:P)_{in}$ = 1:1, pH= 9).

As seen from the figures, reaction period had a negligible effect on the percentage recovery of urinary N, P, Ca and Mg. The amount of P that formed precipitate increased with time, but this increase was not so sharp. For example at pH 10, 96.2% of PO_4^{3-} -P was precipitated in 30 min, while 97.3% of PO_4^{3-}-P formed precipitate in 60 min and 97.5% of PO_4^{3-}-P formed precipitate in 120 min. The same behaviour was also valid for NH_3-N recovery. At pH 9, 35% of NH_3-N was recovered in 30 min and the recovery percentage of N was calculated as 40.2% when the reaction period was 120 min.

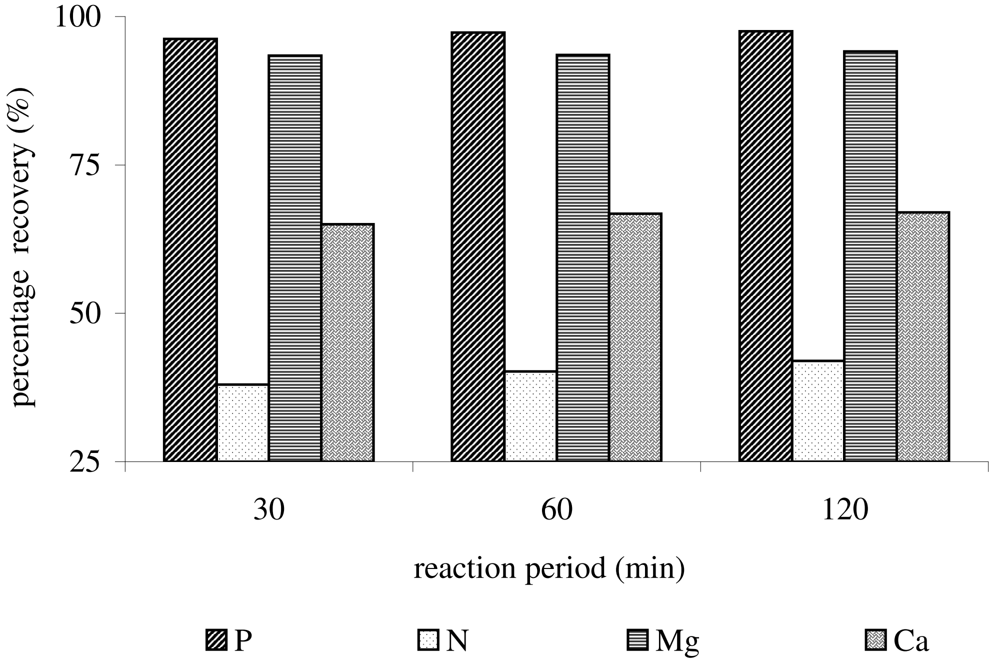

Figure 2. 6: Percentage recovery of the constituent ions of struvite and urinary calcium at different reaction periods, ((Mg:P)$_{in}$=1:1, pH =10)).

It was obvious that nucleation was rapid. Therefore, longer reaction periods were unnecessary since they all gave similar results. Same observations were obtained by Demeestere et al. (2001) who found out that the mass of the struvite after precipitation was nearly the same where the reaction period was kept as 20, 30, 40, 50 and 60 min separately. Stratful et al. (2001) who investigated the operational conditions for effective struvite precipitation also concluded that reaction period had a negligible effect on efficiency. But the same study revealed that reaction period had a strong effect on crystal size; crystal size increased with time and maximum crystal size was obtained when the reaction period was chosen as 60 min.

2.3.3 Optimum reaction pH

The average pH of urine was 6, which decreased immediately after addition of $MgCl_2.6H_2O$. Raising the pH above 6.9-6.95 resulted unstable nuclei formation. It was obvious that precipitation began at about pH 7 and spontaneous decrease in pH was observed as the struvite formation started. Grases et al. (1997) who investigated the precipitation of phosphates from urine like liquors also concluded that the precipitate appears instantaneously at pH 7.5 and above; it starts within minutes at pH 7 and the solids are visible after a long period of time below pH 7. The same behaviour was detected by Doyle and Parsons (2002) who concluded that struvite precipitation is very slow where the operational pH is lower than 8. Bouropoulos and Koutsoukos (2000) reported that rapid desupersaturation or pH changes during the crystal growth may influence not only the mechanism but also the physicochemical characteristics of the crystalline precipitate. Therefore, pH adjustment during the precipitation reaction is advantageous.

Although equilibrium based calculations indicated that the pH of minimum struvite solubility was 10.7, many researchers found different optiumum pH values for struvite precipitation from wastewater. In this study the pH range was held between 9 and 10.7 which are thought to be the border values for efficient precipitation. The results of the experiments are depicted in Figure 2.7 and Figure 2.8.

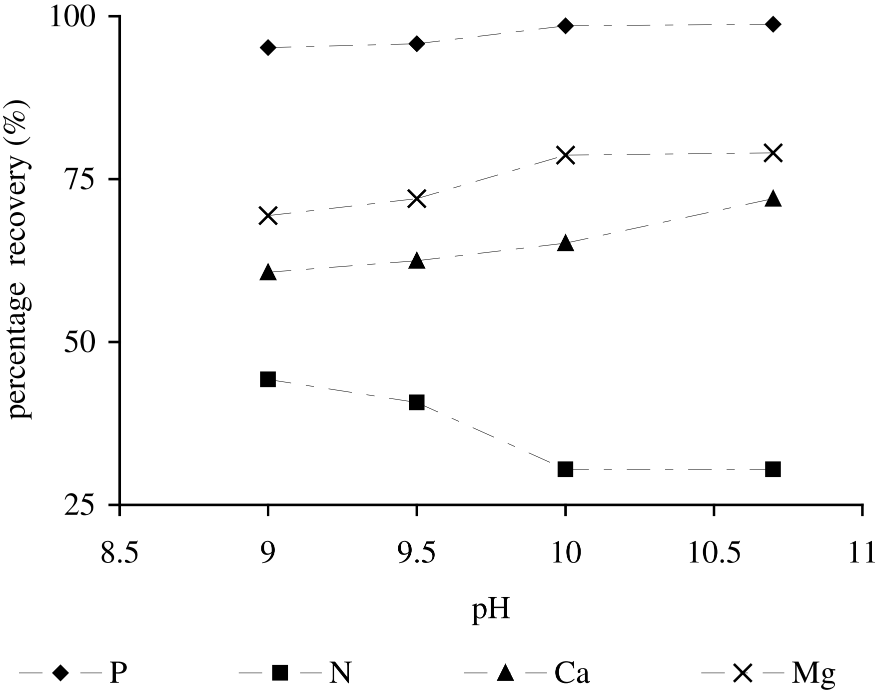

Figure 2. 7: The effect of pH on percentage recovery of the constituent ions of struvite and urinary Ca. ($(\text{Mg:P})_{in} = 1.31:1$, period=60 min).

The residual concentrations of PO_4^{3-}-P, Mg and Ca in urine decreased remarkably with the rise in pH. Higher than 90% of urinary PO_4^{3-}-P was recovered between pH 9 and 10.7 in both of the sets where the molar ratio of Mg:P was set as 1.31:1 and

0.43:1. The difference between the recovery efficiencies at each pH was not so high, but positive effect of high pH values on PO_4^{3-}-P recovery was easily detected.

The amount of Ca that was coprecipitated with struvite was high at higher pH values. The effect of high pH was more important in experiments where the mole ratio of Mg:P was 0.43. Higher than 90% of urinary Ca contributed to the precipitate where the process pH was kept above 9. This was caused by Ca precipitation with PO_4^{3-}. But, in experiments where the initial mole ratio of Mg:P was 1.31, nearly 69-79% of urinary calcium was coprecipitated with struvite.

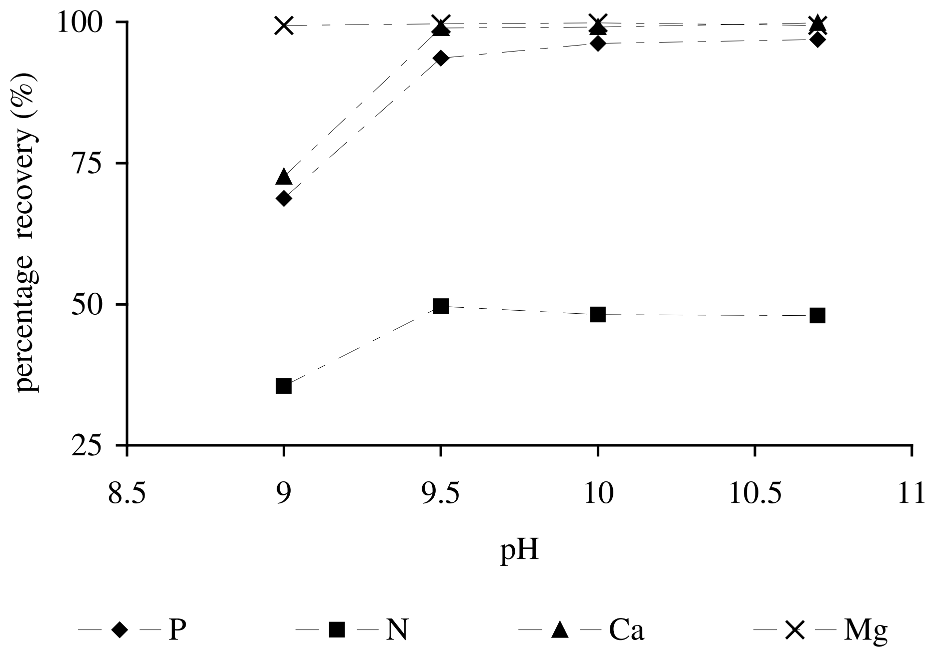

Figure 2.8: The effect of pH on percentage recovery of the constituent ions of struvite and urinary Ca. ((Mg:P $)_{in}$ = 0.43:1, period=60 min).

The contribution of Ca to precipitate is also mentioned by various studies. Jaffer et al. (2002) precipitated struvite from centrifuge liquors and concluded that struvite formation was rapid at pH 9 where the Mg :P ratio was 1.05:1. Below this ratio, the precipitate was a mixture of hydroxyapatite and struvite. Abbona and Boistelle (1979) expressed that struvite as a kidney stone was seldom found in the pure state, being almost always associated with varying amounts of apatite compounds. Grases et al. (1997) indicated the formation of hydroxyapatite during the struvite precipitation at pH 8.

The amount of Mg that formed precipitate increased as the operation pH was raised. Higher than 99% of Mg was precipitated above pH 9 where the initial molar Mg:PO_4^{3-} ratio was 0.43. Because Mg is the limiting component of struvite in that ratio, it was not easy to determine the effect of pH on Mg consumption. When the initial molar Mg:P ratio was 1.31, the positive effect of pH on struvite formation was easily detected.

According to results, only NH_3-N showed an inconsistent behaviour due to pH changes. It might be resulting from the ammonia volatilization above pH 9.3. Above this pH, characteristic odor of urine combined with ammonia and created a serious operational problem.

At constant initial molar Mg:P ratio (0.43:1), the amount of precipitate increased as the pH was raised, which can be seen in Figure 2.9. Coprecipitation of other salts such as magnesium phosphate, hydroxyapatite or carbonate apatite at higher pH values can be probable. Although the amount of precipitate increased with pH, they were all below the theoretical amount of precipitate which was calculated according to NH_3-N depletion in reactions. Therefore, ammonia volatilization during the struvite precipitation could be pronounced.

Similar results were obtained by Demeestere et al. (2001) who investigated the influence of pH on the amount of precipitate. According to their study, the amount of struvite in the precipitate which was expected on a stochiometric basis was not formed at all pH values. The same study also proved the coprecipitation of other salts by declaring that the amount of struvite in the precipitate was always lower than the amount of precipitate.

According to quantitative analyses of the precipitates which were obtained at constant initial molar ratio (Mg:P=0.43:1), the percentage weight of K in the precipitate was calculated as 0.76%, 1.56% and 1.04% at pH 9, 9.5 and 10.7 respectively. At the same pH values, the percentage weight of Ca in the precipitates were found as 6.07%, 8.32% and 6.47% respectively. At this initial molar Mg:P ratio and at each pH, the percentage weight of Mg in the precipitate was always lower than its stoichiometric value.

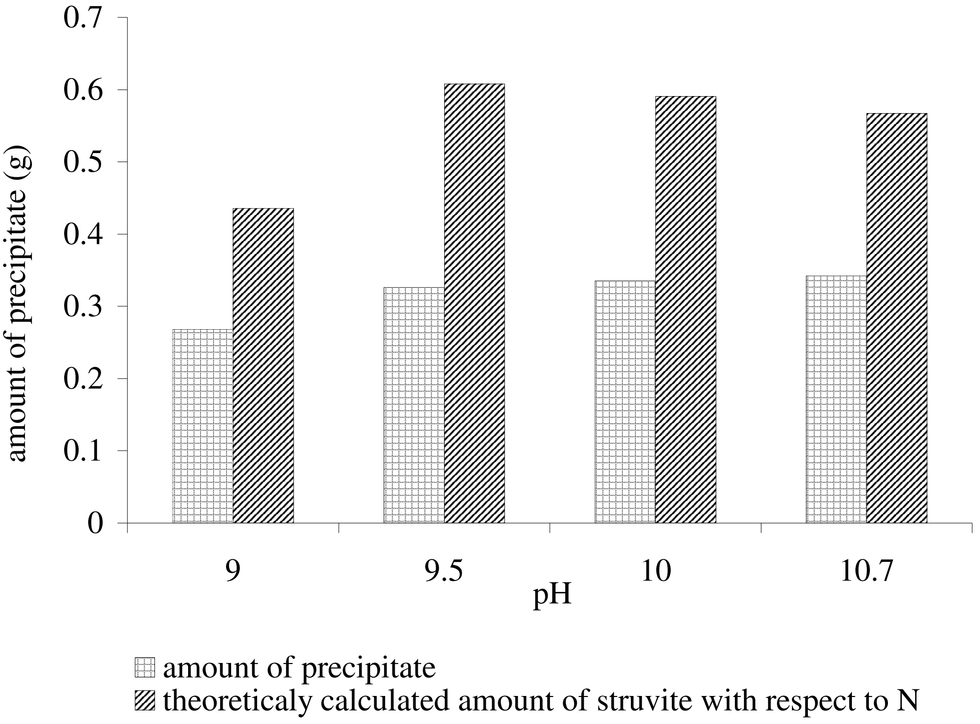

Figure 2.9: The amount of precipitate and theoreticaly calculated amount of precipitate obtained at different pH values.

Consequently, higher amounts of precipitate formed at higher pH values which indicated the coprecipitation of other salts. According to Demeestere et al. (2001), the optimal pH for struvite precipitation ranged between 8.5 and 9 with respect to the amount of struvite in the precipitate.

2.3.4 Optimum initial molar Mg:P ratio

Figure 2.10 implies the effect of initial molar Mg:P ratio on percentage recovery of constituent ions of struvite and urinary Ca. Nearly 92-98% of PO_4^{3-}-P could be recovered from fresh urine where the initial molar Mg:P ratio was adjusted between 0.6 and 1.82 by adding appropriate amounts of $MgCl_2.6H_2O$. Approximately 40-45% of urinary NH_3-N was recovered in this Mg:P range. Urinary NH_3-N recovery was slightly influenced from the initial reactant concentrations when the initial molar Mg:P ratio was adjusted below 1. NH_3-N recovery started to increase as the initial molar Mg:P ratio got higher values (Mg:P>1). Furthermore, higher than 60% of urinary calcium coprecipitated with struvite at all initial molar Mg:P values.

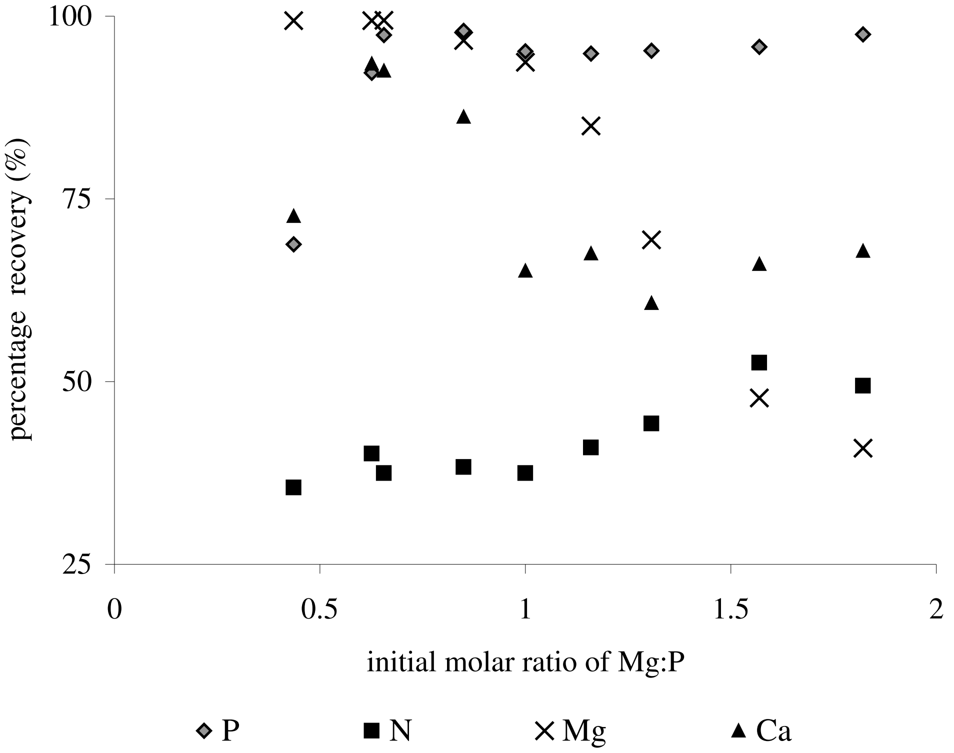

Figure 2.10: Effect of initial mole ratio of Mg:P on percentage recovery of the constituent ions of struvite and urinary calcium (t_{opt}: 60 min, pH_{opt}:9).

Our findings from the previous experiments aiming to find optimum pH showed us that urinary calcium was always precipitating at all pH values. Urinary calcium coprecipitation could not be prevented but raising the molar concentration of magnesium decreased the amount of calcium that formed precipitate. When the number of moles of P, Mg and Ca in the precipitate were calculated, it was seen that the total number of moles of calcium and magnesium were nearly equal with the number of moles of phosphorus. This situation was completely true for the experiments where the initial mole fraction of magnesium was lower than phosphorus. When the initial molar ratio of Mg:P was increased, the amount of calcium in the precipitate decreased. But the total number of moles of magnesium and calcium in the precipitate was higher than phosphorus.

Excessive magnesium did not affect the PO_4^{3-} -P recovery, because it was already ranging between 92-98% at selected initial molar Mg:P ratios. But higher magnesium enhanced struvite formation and depressed calcium contribution. Therefore, it can be concluded that excess magnesium affected the PO_4^{3-}-P recovery indirectly. As seen from Figure 2.10, studying with the initial molar Mg:P ratios higher than 1.5 is not recommended since the residual magnesium tend to increase and phosphorus recovery stays the same. Same result was also declared by Burns et al. who precipitated struvite from swine manure slurries. It is concluded that molar Mg:P ratio of 1.6:1 was efficient and studying at higher molar ratios was meaningless.

The amount of urinary K in the precipitate increased as the initial molar Mg:P ratio was increased. The percentage weight of K in the precipitates ranged between 0.76% (where the initial molar Mg:P ratio was 0.43) and 1.58% (where the initial molar Mg:P ratio was 1.16). But surprisingly, the percentage weight of Mg in the precipitate was 8.3% which was below the stoichiometric value (9.9%), even though the initial molar Mg:P ratio was 1.16.

2.3.5 Characterization of the precipitate

Struvite which was precipitated from fresh urine was white crystalline powder although urine was dark brown in color. Besides, urine based struvite is odorless. Surprisingly, it is impossible to differentiate the urine-based struvite from pure struvite. Photograph of urine based struvite samples is shown in Figure 2.11.

Figure 2.11: Picture of urine based struvite.

The X-ray diffractions of precipitates (Figure 2.12-2.13) were compared with the standard X-ray diffraction patterns of struvite (Figure 2.14-2.15) and HAP (Figure 2.16). According to X-ray diffractions, the main phase in the precipitate is crystalline struvite since the diffractions which belonged to precipitates were matched with standard diffraction patterns of struvite. HAP crystals can not be defined clearly because of the similarities in diffraction patterns. The main effect of Ca was the formation of amorphous calcium phosphate phase which was easily noticed from the X-ray diffraction patterns.

The X-ray diffractions of precipitates which were obtained at different initial molar Mg:P ratios are shown in Figure 2.12. The characteristic peaks of struvite were obvious in all of the samples which was an indicator of the phase dominancy. Amorphous calcium phosphate formation is much more significant when the initial Mg:P ratio is below 1. Intensity of the peaks lowered and most of the peaks combined to yield just one peak. But as the Mg:P ratio is held above 1, the intensity of characteristic peak of struvite increased and separate peaks were detected.

Figure 2.13 depicts the X-ray diffractions of struvite precipitated at different pH values where the initial molar ratio of Mg:P was 0.43. In this figure, characteristic peaks of struvite were detectable in all the samples but there was a significant widening of the peaks which could be explained by the excessive nuclei formation rather than crystal growth at pH values higher than 9.

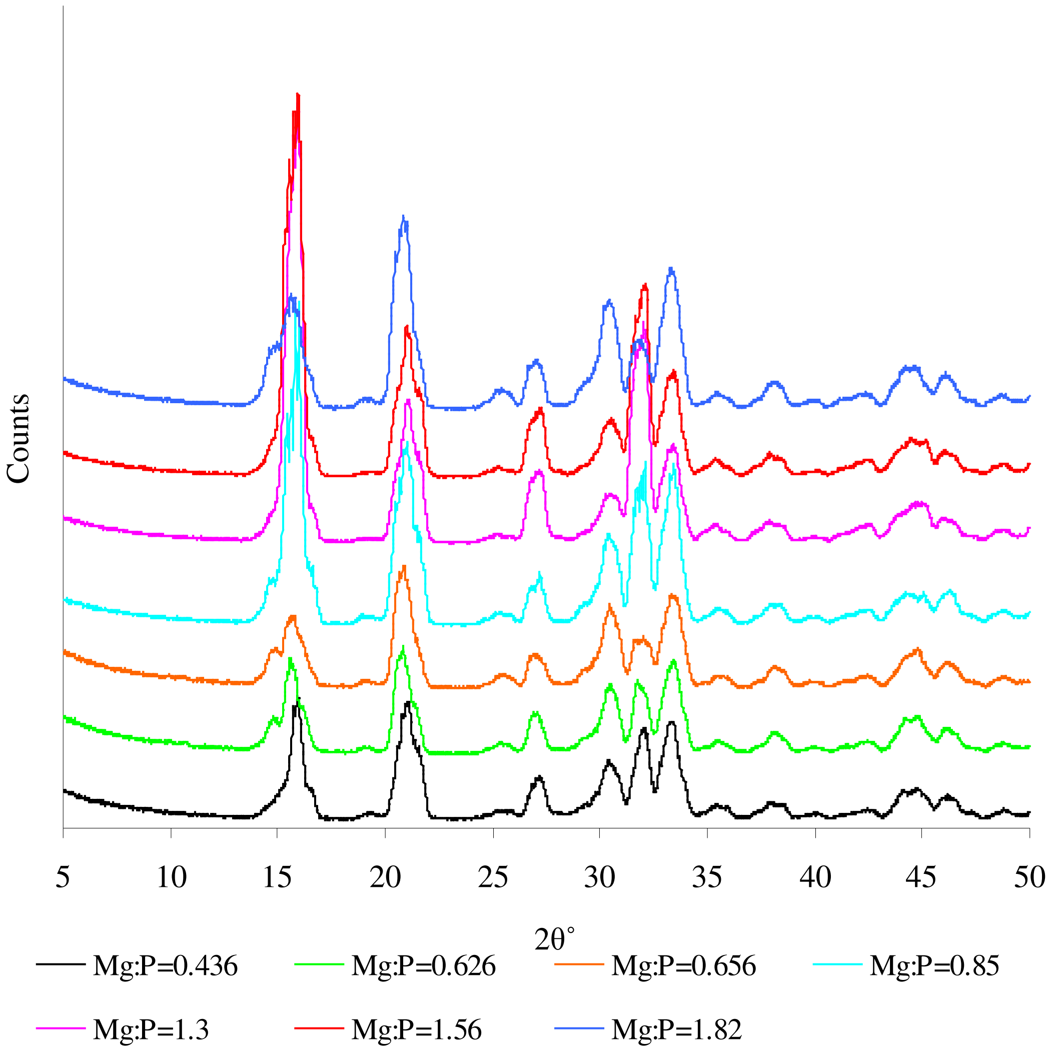

Figure 2.12: Powder X-ray diffractograms of urine-based struvite which was precipitated at constant pH (pH 9).

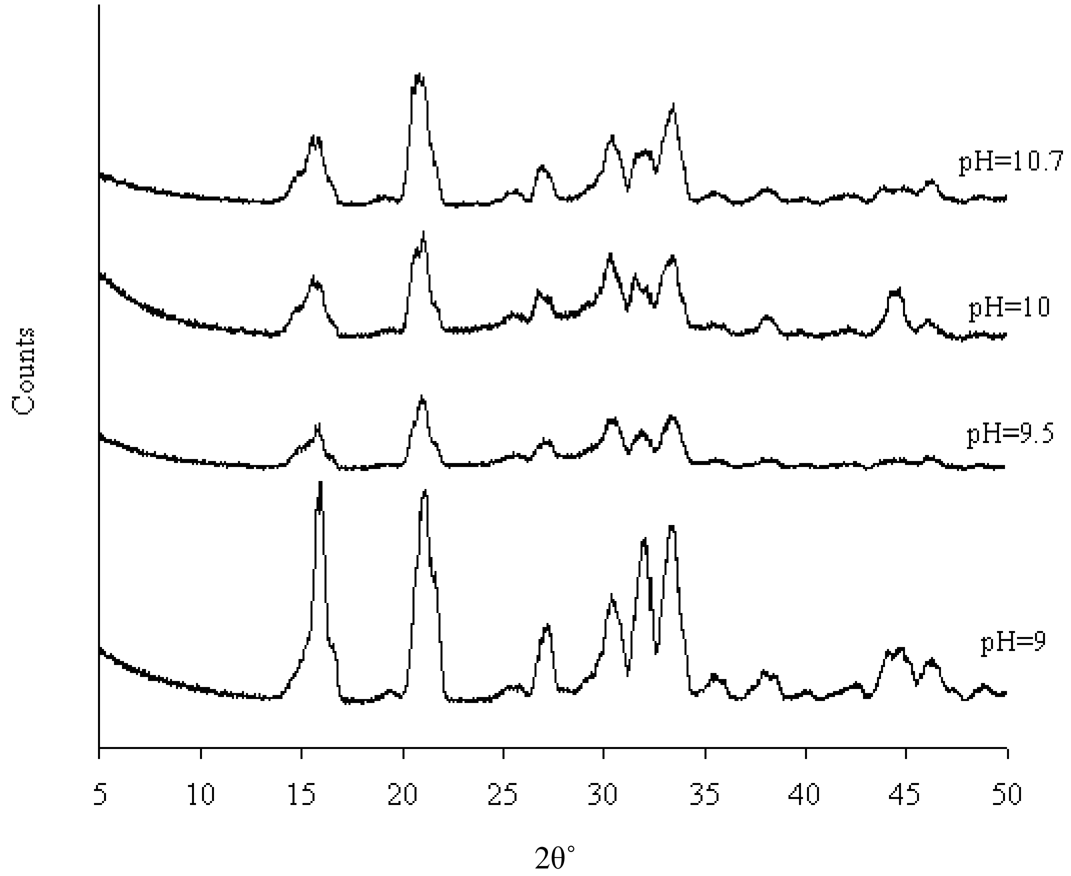

Figure 2.13: Powder X-ray diffractograms of urine-based struvite which was precipitated at constant initial molar Mg:P ratio (Mg:P=0.43).

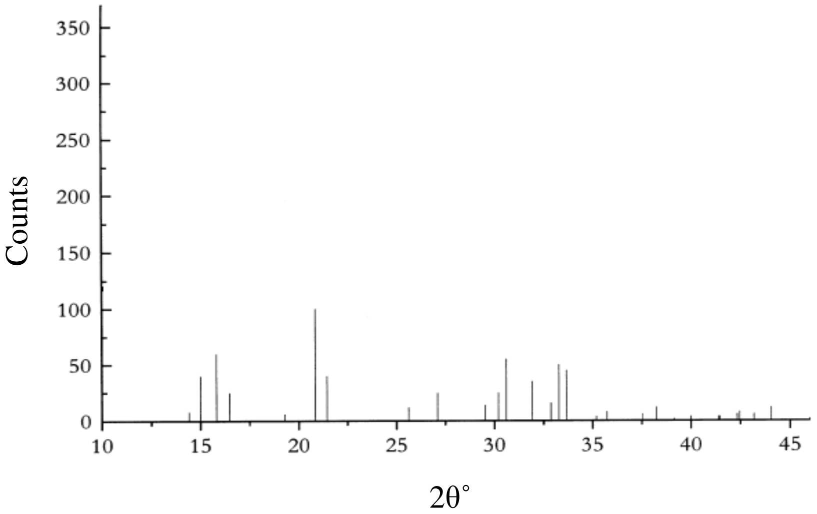

Figure 2.14: Reference diffraction lines of struvite (Bouropoulos and Koutsoukos, 2000).

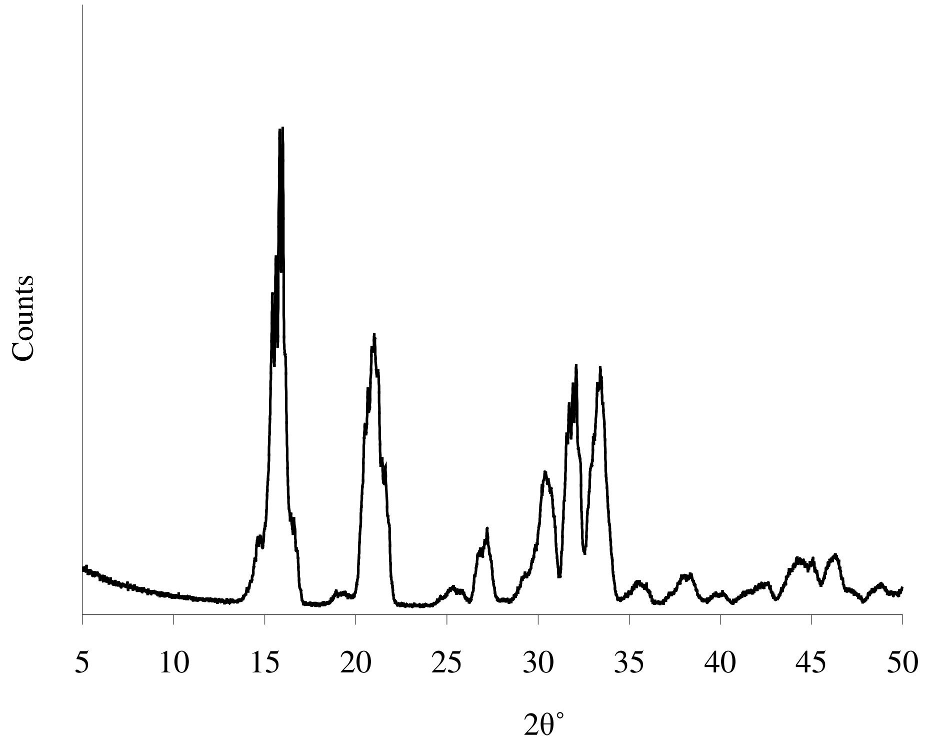

Figure 2.15: Reference diffraction lines of struvite which was precipitated from pure solution.

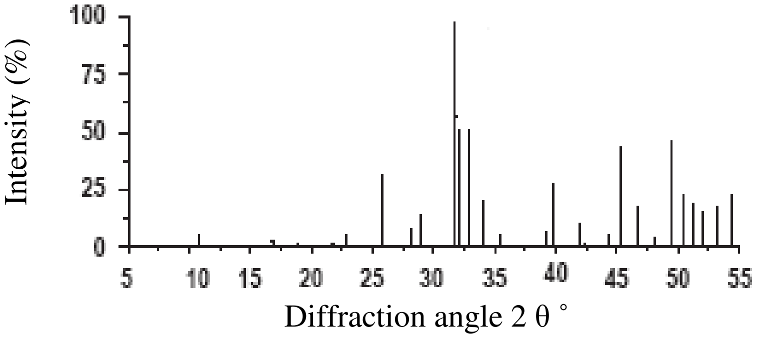

Figure 2.16: Reference diffraction lines of hydroxyapatite (Rusu et al., 2005).

FT-IR spectra of the precipitates revealed that there was no other functional group that belonged to another compound (Figure 2.17). All the precipitates showed the same patterns with standard struvite FT-IR spectra (Figure 2.18). The weak band at 963 cm^{-1} is assigned to P-O symmetric stretching, the strong one centered at 1032-1096 cm^{-1} is due to P-O antisymmetric vibration, and the narrow band at 3000-3571 cm^{-1} is assigned to OH stretching.

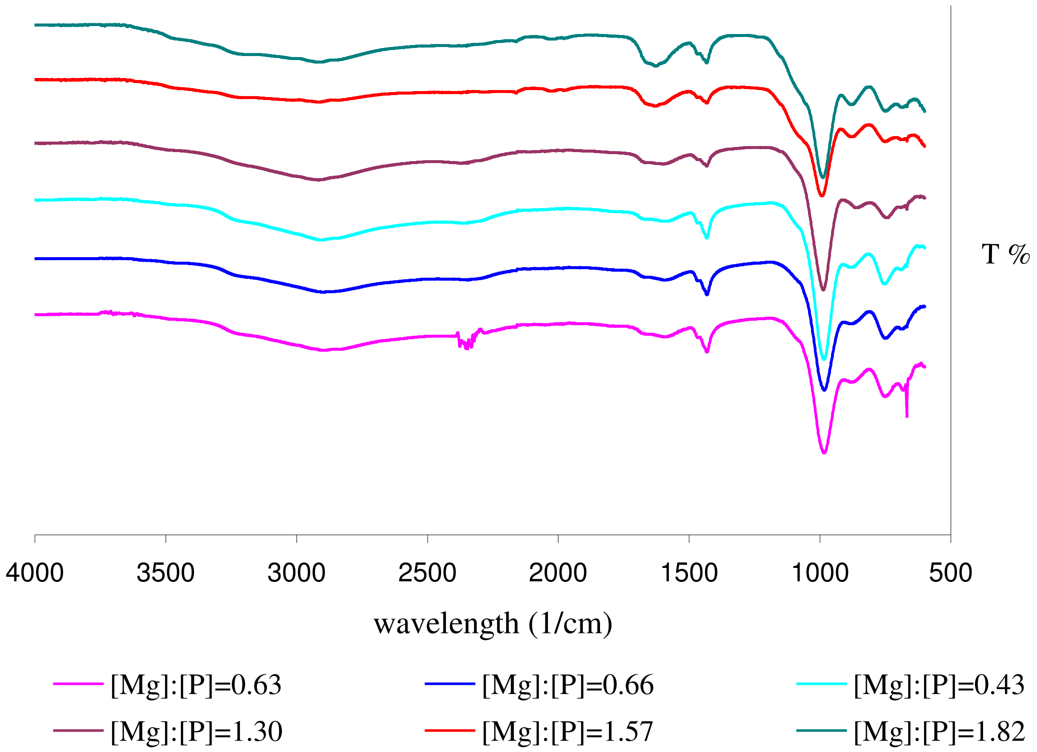

Figure 2.17: FT-IR spectra of precipitates obtained at different initial molar Mg:P ratios.

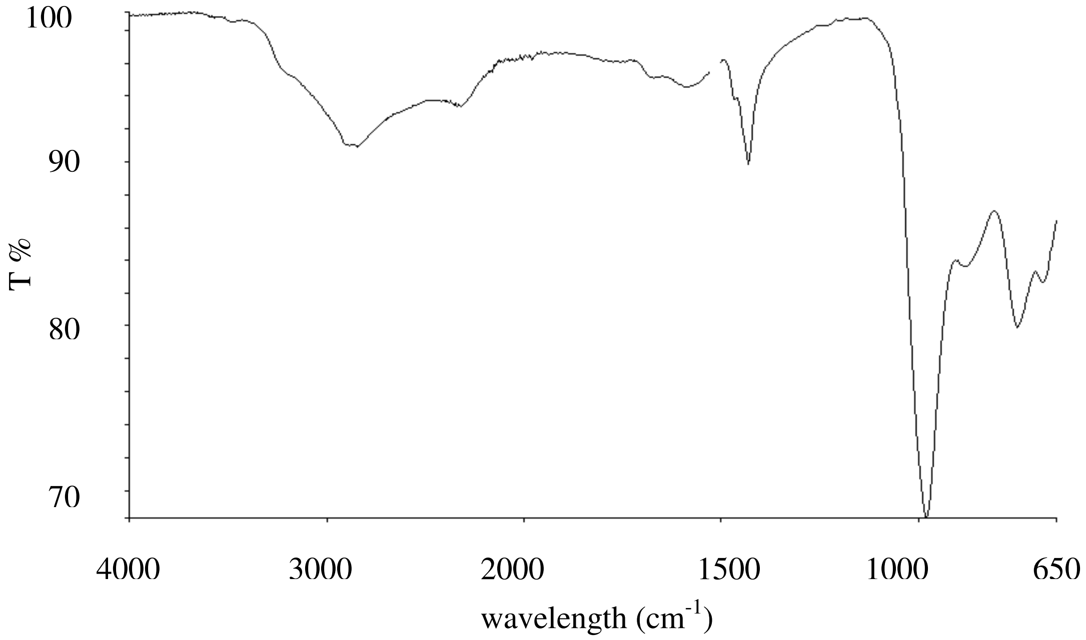

Figure 2.18: FT-IR spectra of struvite obtained from pure solution.

These spectrums could not give us information about the phases that included ammonia, phosphate and hydroxy bands since they have been detected in struvite. But, we can conclude that organic impurities were not detected with respect to FT-IR analysis.

Urinary Ca, K and Zn were detected in all of the precipitates. The presence of K is remarkable in precipitate and it is thought to be found as K-struvite ($KMgPO_4.6H_2O$). The contribution of K can not be prevented. Because, it has the same ionic state with ammonium ions which results the formation of mixed crystals (Usanmaz, 1991). But the presence of K is beneficial since the struvite obtained from the human urine is introduced as a fertilizer. Zn which was detected in the precipitate was thought to be found as Zn-struvite like K-struvite. But, the presence of both K-struvite and Zn-struvite could not be detected from the X-ray diffractions.

Quantitative analyses of precipitates could not detect Fe, Cr, Cu, Mn, Ni and Cd. But the net counts of elements which were determined with SEM-EDS gave us a detailed qualitative analyses. According to results, the elements in the precipitates ranged as P>Mg>Ca>K>Na>Cl .The presence of Cu, S, Zn, Fe, Mn was detected but their net counts were relatively small.

The results of C, H and N analyses which are depicted in Table 2.2 and Table 2.3 indicated that all precipitates contained carbon and the weight percentage of N and H was lower than theoretical amount. The presence of carbon can be resulted from carbonate apatite or it can be resulted from the adsorption of carbon based urinary compounds such as hormonal residues. But the adsorption of highly hydrophobic hormone residues onto inorganic surfaces has not been detected by the other researchers. Besides, organic impurities were not detected in FT-IR spectra of the precipitates.

Table 2.2: Weight percentage of C, H and N of urine-based struvite where the initial molar Mg:P is 0.43.

	pH 9	pH 9.5	pH 10	Theoretical percentage
C (%)	0.75	3.18	3.41	0
H (%)	5.53	4.25	3.27	6.5
N (%)	4.55	4.88	5.23	5.7

Table 2.3: Weight percentage of C, H and N of urine-based struvite where the pH is 9.

	Mg:P =0.43	Mg:P =0.63	Mg:P =0.7	Theoretical percentage
C (%)	0.75	0.67	0.75	0
H (%)	5.53	5.69	5.72	6.5
N (%)	4.55	4.56	4.67	5.7

Qualitative analyses of struvite precipitated at different conditions are depicted in Table 2.4 and Table 2.5. Although the precipitates were analyzed for all of the elements, only the elements that were detected were placed in Table 2.4 and 2.5.

According to results, it is very hard to find a relationship between the process conditions and the elements in the precipitate. Because, the precipitates which were obtained at different pH contained the same elements. Similarly, the precipitates which were obtained at different initial molar Mg:P ratios comprised the same elements. Furthermore, elements such as Si, Ba and Cu showed an inconsistent behaviour which can not be attributed to the process conditions. It might be because of their concentration in urine. But it can be generalized that urinary struvite contains Na, Al, S, Zn, Sr and Ba which all come from urine and the presence of these elements in the precipitate is not affected from the process conditions.

Table 2.4: Results of the qualitative analyses of urine-based struvite (constant initial molar Mg:P ratio, Mg:P = 0.43).

	pH 9	pH 9.5	pH 10	pH 10.7
Na	√	√	√	√
Mg	√	√	√	√
Al	√	√	√	√
Si	-	√	√	√
P	√	√	√	√
S	√	√	√	√
K	√	√	√	√
Ca	√	√	√	√
Cu	√	-	-	-
Zn	√	√	√	√
Sr	√	√	√	√
Ba	√	√	-	√

√ : detected
- : not detected

Table 2.5: Results of the qualitative analyses of urine-based struvite (constant pH, pH 9).

	Mg:P =0.43	Mg:P =0.63	Mg:P =0.7	Mg:P=1.30
Na	√	√	√	√
Mg	√	√	√	√
Al	√	√	√	√
Si	-	-	√	-
P	√	√	√	√
S	√	√	√	√
K	√	√	√	√
Ca	√	√	√	√
Cu	√	-	-	√
Zn	√	√	√	√
Sr	√	√	√	√
Ba	√	√	√	√

√ : detected
- : not detected

2.4. Conclusions

Chapter-2 comprised the nutrient recovery from fresh urine where urinary PO_4^{3-}-P, NH_3-N and Mg were recovered as magnesium ammonium phosphate hexahydrate by adding suitable amounts of $MgCl_2.6H_2O$. Based on the results presented in this chapter, the following conclusions can be drawn:

✓ Higher than 95 % of urinary PO_4^{3-}-P and nearly 45 % of urinary NH_3-N were recovered by struvite precipitation method.

✓ Struvite precipitation did not need long reaction periods. 1 hr was found to be enough for high recoveries.

✓ The efficiency of the precipitation depended on the process pH and initial molar Mg:P ratio.

✓ It was clear that precipitating struvite at pH 10.7 (pH of minimum struvite solubility) was unnecessary since it gave nearly the same recovery efficiency with those achieved at below pH 10.7.

✓ Optimum process pH for struvite precipitation from fresh urine was 9 and optimum process pH was not affected from initial Mg:P ratio.

✓ The process pH influenced not only the reacted N, P, Mg, Ca but also the amount of precipitate and the composition of the precipitate.

✓ Higher initial molar Mg:P ratio enhanced the formation of struvite and lowered the amount of calcium which was coprecipitated with struvite.

✓ All the precipitates were positively identified as crystalline struvite. The presence of hydroxyapatite crystals was not clear.

✓ All the precipitates contained considerable amounts of potassium and calcium.

✓ Urinary struvite was found to be free from organic impurities with respect to FT-IR analyses.

✓ Heavy metal content of the precipitate was too low. This situation is anticipated since the primary route of heavy metal excretion is through faces.

✓ C content of struvite was directly affected from the process pH. Higher pH resulted higher C contribution to the precipitate.

✓ N content of urine based struvite was always lower than its calculated theoretical value due to other phosphate phases in precipitate.

In this study, fresh urine was used as a phosphorus and nitrogen source where the mole ratio of NH_3-N:PO_4^{3-}-P was nearly 1.5. The study proved that, a valuable slow release fertilizer was obtained from the urinary nitrogen, phosphorus and magnesium at this mole ratio. But in real collecting systems, hydrolysis of urea starts while passing through the pipes. As a result of the hydrolysis, the mole ratio of NH_3-N:PO_4^{3-}-P increases. Hence, new process conditions should be determined in order to recover nitrogen and phosphorus from the stored urine. As a conclusion, struvite precipitation from fresh urine will be applicable only if the hydrolysis is prevented and if the urine is immediately transported for processing.

3. HYDROLYSIS OF UREA AND STRUVITE PRECIPITATION FROM STORED URINE

3.1 Introduction

Sustainable sanitation -an alternative for conventional sewarage system- aims to save water, nutrient and energy which is achieved by separating household wastewater streams as yellow water (urine with or without flush water), brown water (feces with flush water) and grey water (washing water from kitchen, bathrooms, laundry etc.) at source (Li et al., 2001).

In recent years, separate collection of human urine and its usage as a fertilizer has been investigated by many scientists (Hellström et al., 1999; Höglund et al., 2000; Lind et al., 2000; Larsen et al., 2001; Lind et al., 2001; Vinnerås and Jönsson, 2002). Results indicated that urine separation is a promising method for the recovery of urinary nutrients only if the disadvantages related with micropollutant content of urine and storage were eliminated (Hellström et al., 1999; Lind et al., 2000; Lind et al., 2001).

Urine separating toilets have been commercialized and many models have been developed. Mainly, the toilets have two bowls, front bowl for urine and rear bowl for faeces and toilet paper. The major advantage of urine separating toilets is the economy in flush water.

Once the urine is separated from the brown water, it is transported to a storage tank which is emptied periodically by farmers to use in farmland as a fertilizer. Larsen et al. (2001) suggested a new idea of using existing sewer system at nights for transport and treatment of separately collected urine. But this system also needs storage tanks to store the urine daily.

During the aging of human urine, calcium oxalate monohydrate is precipitated in acidic pH range, whitlockite (β-$Ca_3(PO_4)_2$) is formed between pH 6 and pH 7, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is dominant around pH 7 and struvite is precipitated in alkaline conditions (Grases et al., 1996).

Whether the urine is used by the farmers or transported through the sewarage system for further processing, urine has to be stored for a period of time. In fresh urine, 80 % of N is found as urea-N, 7 % of N is found as ammonia-N, 6 % of N is found as creatine-N and the rest of the N is in the form of shorter peptides and free aminoacids (Vinnerås, 2001). Urea hydrolysis (ureolysis) starts as the urine flows through the pipes and the hydrolysis continues in the storage tank (Jönsson et al., 1997; Udert, 2002).

As the hydrolysis starts, the formation of ammonium and bicarbonate ions begin according to Equation 3.1 (Hellström et al., 1999).

$$CO(NH_2)_2+3H_2O \rightarrow 2NH_4^+ + HCO_3^- + OH^- \qquad \textbf{(3.1)}$$

Ammonium ion is in equilibrium with dissolved ammonia which results an increase in pH. Above pH 9.3, the equilibrium between the dissolved ammonia and gaseous ammonia is forced to form gaseous ammonia which can be pronounced as ammonia volatilization.

$$NH_4^+ + OH^- \longleftrightarrow NH_{3\,(aq)} + H_2O \qquad \textbf{(3.2)}$$

$$NH_{3\,(aq)} \longleftrightarrow NH_{3\,(g)} \qquad \textbf{(3.3)}$$

The hydrolysis which is catalyzed by the urease enzyme disturbs the equilibria between some of the ions. While ammonia formation takes place, the concentration of PO_4^{3-}-P decreases because of the precipitate formation with Ca and Mg ions. These reactions are mentioned by Bichler et al. (2002) as shown below :

$$6H_2O+Mg^{2+}+NH_4^++PO_4^{3-} \longleftrightarrow MgNH_4PO_4.6H_2O \ (pH=7.2) \qquad \textbf{(3.4)}$$

$$CO_3^{2-}+10Ca^{2+}+6PO_4^{3-} \longleftrightarrow Ca_{10}(PO_4)6CO_3 \ (pH=6.8) \qquad \textbf{(3.5)}$$

Udert et al. (2003 a-b) investigated the precipitate formation in a urine collecting system and identified struvite, hydroxyapatite and calcite compounds which were formed because of the pH rise. Precipitate formation and ammonia generation result higher N:P ratios.

Due to the high pH and NH_3-N fraction of stored urine, ammonia losses will be seen during the storage and application. To overcome these problems, urinary nitrogen should be stabilized. Struvite precipitation seems to be a solution for this problem. Urinary NH_3-N is reacted with P and Mg source to form struvite which is a well known slow release fertilizer (Bouropoulos and Koutsoukos, 2000; Lind et al., 2000; Stratful et al., 2001; Li and Zhao, 2003; Nelson et al., 2003).

Detailed information about struvite chemistry and kinetics were given in previous chapter. Struvite precipitation from separately collected fresh urine was studied in Chapter 2 and the parameters that affected the precipitation efficiency were found as process pH and initial molar ratio of Mg:P and Ca:Mg. Because the constituents of urine change during the storage, new optimum process conditions that affect the precipitation yield should be determined.

The main target of the study was to investigate the applicability of struvite precipitation for the recovery of urinary nitrogen and phosphorus from separately collected and stored urine. To reach this target, hydrolysis period was also observed and the parameters that affected the hydrolysis rate were identified.

3.2 Materials and Methods

3.2.1 Hydrolysis of urea

To investigate the hydrolysis of urea, urine samples from 7 people (aged between 24-27, 4 women-3 men) were collected freshly and equal amounts of urine samples were mixed in a container. Initial pH, NH_3-N and total-N were determined. 50 ml of mixed urine was retrieved and placed in a glass jar which had a volume of 350 ml (Figure 3.1). This procedure was repeated 3 times. First jar was labelled, initial pH and NH_3-N content was recorded. Urine in the second jar was diluted 1.5 times with deionized water. After dilution the initial pH and NH_3-N concentration was determined. Third jar was labelled and urine was diluted 3 times with deionized water. Initial pH and NH_3-N concentration were recorded. Urine in the last jar was diluted 4 times with deionized water. Initial pH and NH_3-N concentration were recorded. Tightly sealed jars were opened once a week and they were sealed immediately after sampling. Two days after the urine samples were placed in jars, a visible turbidity was noticed. After 1 week, a visible precipitate formation was seen. To eliminate their effect on analyses, the samples which were analyzed for NH_3-N were filtered through filter paper before analysis.

Figure 3.1: Picture of jars filled with urine.

In the second part of the experiments, hydrolysis behaviour of 4 times diluted urine was investigated during storage by using urine from 5 different volunteer group. Urine from each group was collected and mixed in different containers. 50 ml of urine was retrieved from each mixture and diluted 4 times with deionized water. Initial pH and NH_3-N were recorded for each group and the reactors were tightly closed to prevent ammonia loss.

3.2.2 Struvite precipitation

Precipitation experiments aiming to find the optimum process conditions were carried out in 250 ml glass beakers. In all of the experiments, urine was filtered prior to precipitation. The amount of urine used in the experiments ranged between 50-100 ml.

Analytically pure $MgCl_2.6H_2O$ and $NaH_2PO_4.2H_2O$ were used as reactants. During the reactions the pH was recorded with pH meter (WTW-Inolab pH meter). 1N and 5N NaOH was used to maintain the constant pH. All the reactions were achieved at room temperature. The beakers were not sealed during the reaction.

In our previous study, struvite precipitation from fresh urine was achieved and the optimum process conditions were identified. It was seen that reaction period had no effect on recovery efficiency but initial molar Mg:P ratio and process pH were the deterministic parameters. Therefore in this study, reaction period was chosen as 60 minutes which was found from the previous chapter. During the hydrolysis of urea, urinary PO_4^{3-}-P formed precipitate with Ca and Mg which resulted a decrease in the concentration of PO_4^{3-}-P and Mg. Because of that reason, additional Mg and P had to be added to precipitate the NH_3-N as struvite. For this aim, stored urine was reacted with $MgCl_2.6H_2O$ and $NaH_2PO_4.2H_2O$ at pH 9, 9.5, 10 and 10.7, where the initial mole ratio of N:P:Mg was adjusted as 1.1:1:1.1. After optimum pH determination, stored urine was reacted with $MgCl_26H_2O$ and $NaH_2PO_4.2H_2O$ where the initial mole ratio of N:P:Mg was adjusted to have 1:1:1, 1:1:1.13, 1:1.2:1, 1.24:1:1 respectively.

In all of the experimental sets, initial PO_4^{3-}-P, Mg and NH_3-N concentration of stored urine were determined prior to P and Mg addition. After the urine was amended with P and Mg, solution was mixed for 5 min. At the end of the reaction period, the precipitate was separated from the residual urine by simple filtration. The volume of filtrate was recorded and samples were taken to analyze PO_4^{3-}-P, Mg and NH_3-N in residual urine. The amount of PO_4^{3-}-P, Mg and NH_3-N which were reacted at particular process conditions were calculated. The calculated amount also indicated the amount of reactants that were recovered by precipitation reaction. Finally, the results were expressed in terms of percentage recovery of PO_4^{3-}-P, Mg and NH_3-N.

All the analyses were run according to standard methods (APHA, 1992). PO_4^{3-}-P was analyzed with 4500-P Vanadomolybdophosphoricacid colorimetric method, NH_3-N was analyzed with 4500 NH_3-B and C preliminary distillation and titrimetric method. Elements such as Mg, Ca, K, Fe, Cd, Cu, Zn, Mn were determined by atomic absorption spectroscopy (Perkin Elmer 1100-B).

3.2.3. Characterization of the precipitate

After each precipitation, suspension was filtered and the precipitate was dried in an oven at 40 ˚C for 48 hr. All crystal samples were analyzed using powder X-ray diffractometry (Philips PW 1710). The samples were identified by analyzing the results against the crystalline struvite standard. Functional groups in precipitate were identified with FT-IR spectroscopy (Perkin Elmer, SpectrumOne). The qualitative analyses of the precipitate were conducted by ICP. Carbon, hydrogen and nitrogen content of the precipitate was determined with Carlo Erba 1106 Elemental Analyzer.

3.3 Results and Discussion

3.3.1 Hydrolysis of urea

In real systems, urine from specially designed toilets flows through the pipes and fills the storage tank. In our laboratory, such a system could not be prepared. Because of this reason, urine samples which were collected from people were stored in reactors.

In all of the experimental sets, ammonia formation and increase in pH were detected although no bacteria or sewage was added from the outside. Besides, hydrolysis of urea was observed in each sample and the positive effect of dilution on hydrolysis rate was obvious (Figure 3.2). This result indicated us that urease enzyme was always found in urine. But obviously, urease enzyme which is responsible for urea hydrolysis is not effective alone.

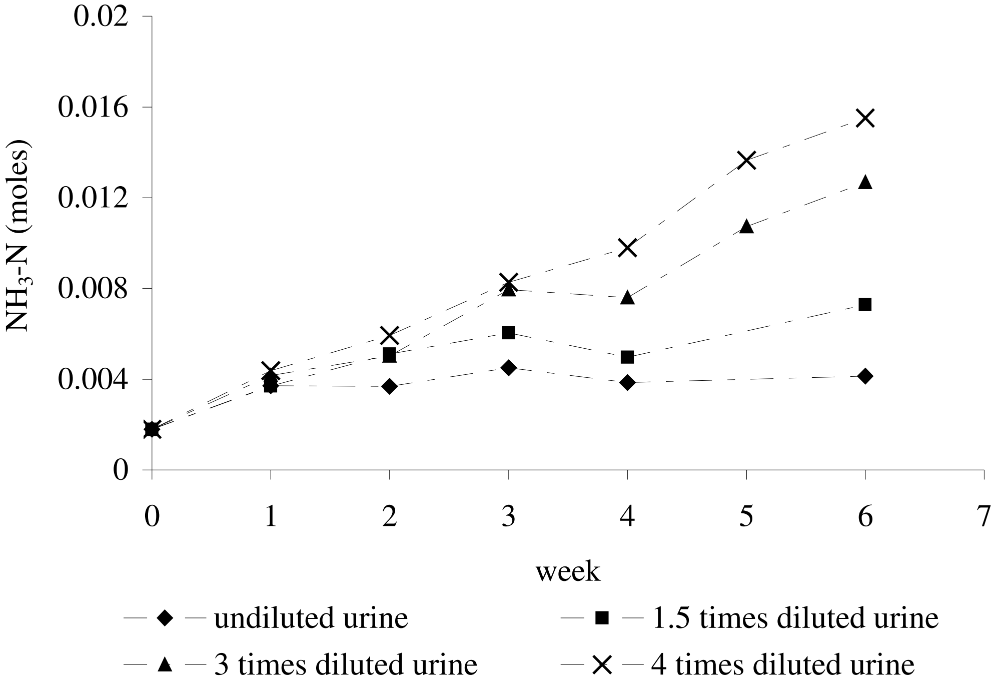

Figure 3.2: NH_3-N content of stored urine on a weekly basis.

Hydrolysis of urea increased the NH_3-N concentration of urine, which in turn raised the pH. NH_3-N concentration of 4 times diluted urine is graphed versus time which is shown in Figure 3.3. The final concentration of stored urine at the end of the 101day was 16 times of its initial concentration. The pH of urine increased sharply in 20 days and then became stable, which is easily seen in Figure 3.4.

By the end of the storage period (101 days) the pH was 9.54 and only 72% of total-N was in the form of NH_3-N. The pH of the solution was found to be directly related with dissolved ammonia concentration in the solution. The same result was obtained by Hellström et al. (1999) who found out that the increase in pH was proportional to the fraction of ammonia nitrogen until a fraction of about 50% was achieved.

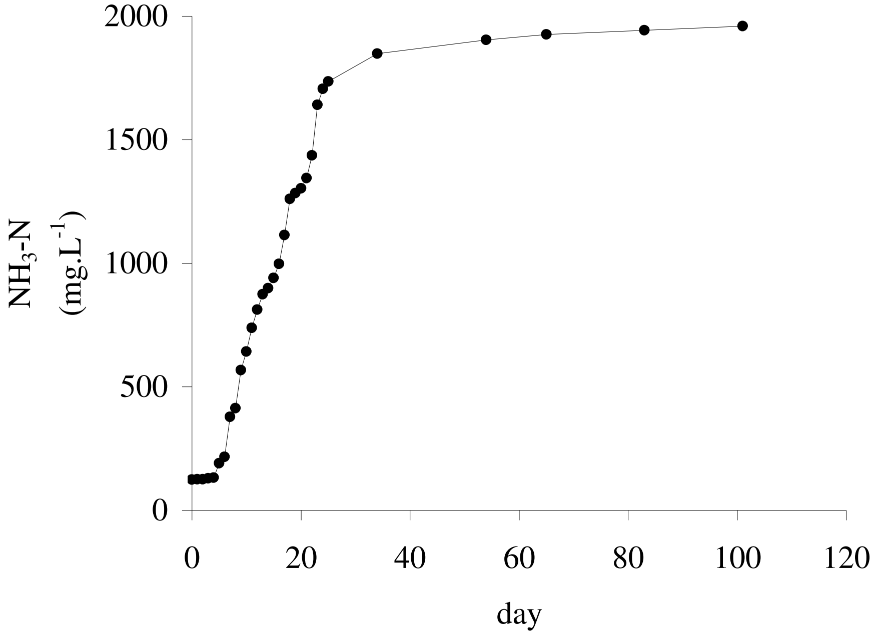

Figure 3.3: NH_3-N concentration of 4 times diluted urine during storage period.

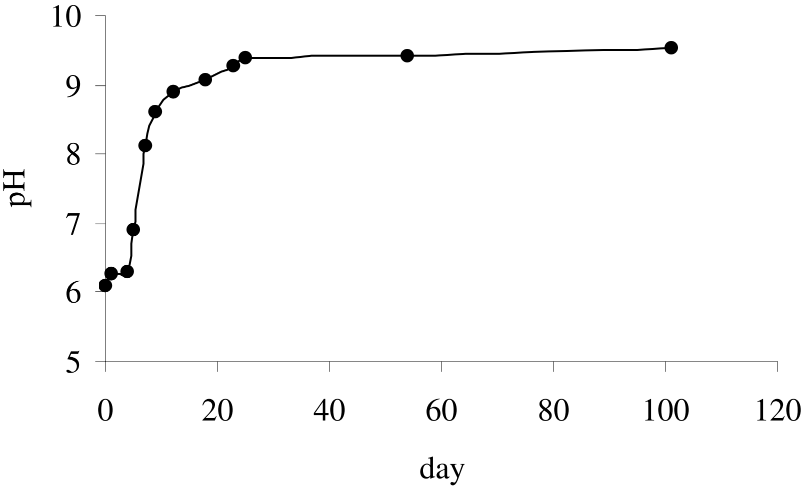

Figure 3.4: pH of 4 times diluted urine during storage period.

Because, urine content differs from person to person, hydrolysis rate changes in all urine combinations. The samples collected from different volunteer groups indicated that hydrolysis rate was changing from group to group (Figure 3.5). Only one sample (urine mixture of group-5) did not show any hydrolysis behaviour during the storage. A volunteer in group-5 who had been using antibiotics while giving urine samples was thought to be the reason for this unexpected behaviour. The residual antibiotic in the urine was expected to inhibit urease activity.

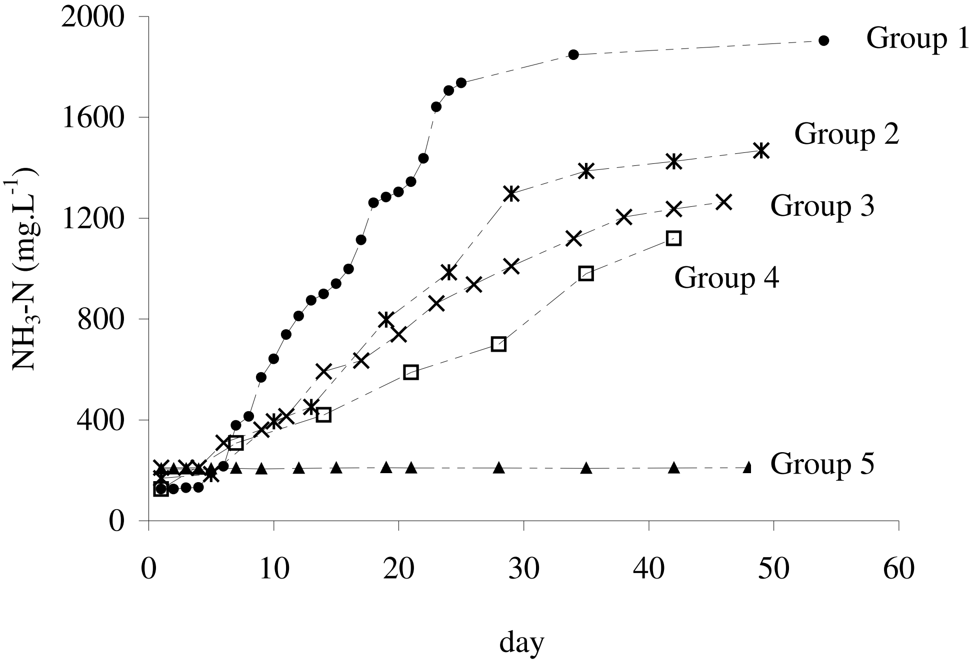

Figure 3.5: NH_3-N concentration in different urine combinations.

As indicated before, in real collecting systems the behaviour of hydrolysis is different. Jönsson et al. (1997) took samples from collection tanks and found that 85% of nitrogen was in the form of ammonia nitrogen. Udert et al.(2003 a-b) expressed that urease active bacteria primarily grew in the pipes which were then transported to collection tank with urine. According to Udert et al. (2003 a-b), urea was completely hydrolyzed in the collection system in 1 day.

3.3.2 Struvite precipitation

For the struvite precipitation, 4 times diluted and stored urine samples were used. Crystals which occured as a result of spontaneous precipitation of phosphate salts were easily seen at the bottom and inner surface of each reactor. Analytical results indicated that nearly 90% of urinary Mg and Ca precipitated spontaneously during the storage period. Besides, nearly 30% of urinary PO_4^{3-}-P precipitated during the storage. It was obvious that the precipitate which was formed during the storage was a mixture of calcium and magnesium phosphates. Grases et al. (2002) also indicated that higher pH values in urine resulted hydroxyapatite, brushite and struvite formation.

The average N:P ratio was 11.7 by the end of the storage period. This ratio was not constant which mainly depended on the hydrolysis rate. At the end of the storage period the resultant pH of the samples was nearly 9.4-9.6. After adding $MgCl_2.6H_2O$ and $NaH_2PO_4.2H_2O$, the pH value dropped below 6. Precipitation started above pH 7.2 and the amount of precipitate was increased as the process pH was raised. The same behaviour was observed in experiments where struvite was precipitated from fresh urine.

The effect of pH on percentage recovery of the constituent ions of struvite is depicted in Figure 3.6. Higher than 85% of NH_3-N was recovered in all precipitation reactions which were achieved above pH 9. Recovery percentages of PO_4^{3-}-P and Mg were higher than 98% in this pH range.

Percentage recovery of N, P and Mg at each pH values between pH 9 and 10.7 were nearly the same. For example, 85.4% of NH_3-N was recovered at pH 9, while it was 86.68% at pH 9.5 and 86.73% at pH 10. But, the amount of NH_3-N that formed precipitate decreased when the pH was set as 10.7.

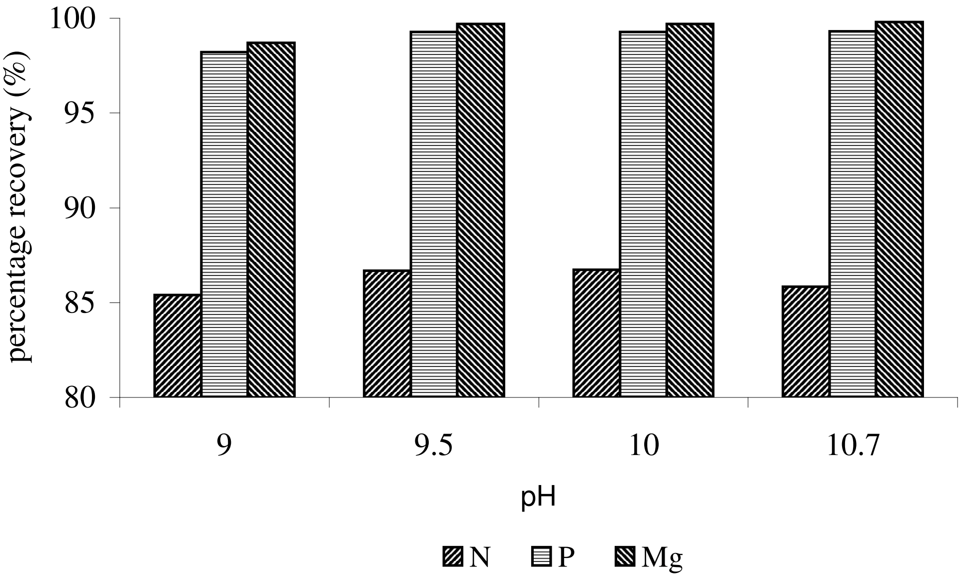

Figure 3.6: The effect of pH on percentage recovery of the constituent ions of struvite.

Higher than 98% of PO_4^{3-}-P and Mg were precipitated at pH 9 and the percentage recovery of these ions increased above 99% at pH 9.5. But pH values higher than 9.5 did not affect the percentage recovery of PO_4^{3-}-P and Mg. Besides, higher pH values enhanced the ammonia volatilization, which restricted the efficiency and created an operational problem due to characteristic ammonia odor. Because of these outcomes, precipitating struvite from stored urine above pH 9.5 is not recommended.

Experiments which were achieved at constant pH by using different initial molar N:P:Mg ratios revealed that initial reactant concentrations influenced the efficiency of precipitation. The effect of initial N:P:Mg ratio on percentage recovery of N, P and Mg is depicted in Figure 3.7.

Higher than 85% of NH_3-N was recovered as struvite in all the experiments. But percentage recovery of NH_3-N could not exceed 92% even the initial molar ratio of reactants were changed.

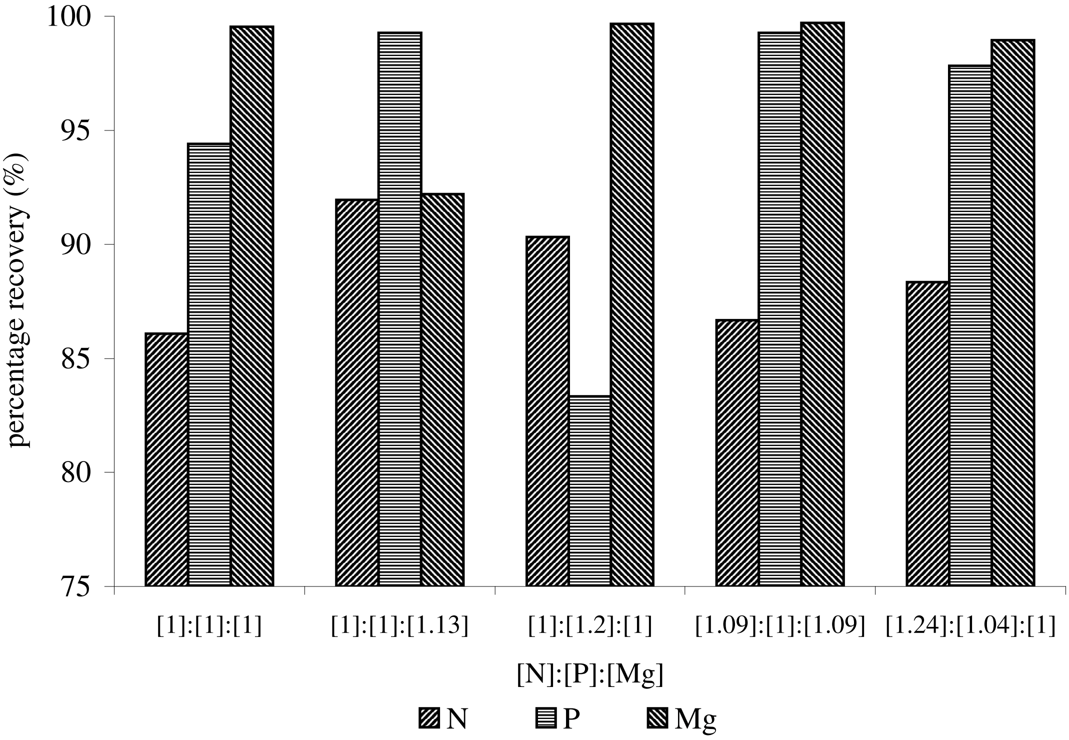

Figure 3.7: The effect of initial molar N:P:Mg ratio on percentage recovery of the constituent ions of struvite.

The amount of NH_3-N that formed precipitate was higher when the initial concentration of P or Mg was in excess. For example, 86% of NH_3-N was recovered at equimolar concentrations, while 90.32% of NH_3-N formed precipitate as the initial N:P:Mg ratio was 1:1.2:1. This value increased to 91.95% when the initial N:P:Mg ratio was adjusted as 1:1:1.13.

It was clear that excess Mg had a positive effect on PO_4^{3-}-P and NH_3-N recovery. The same result was also obtained in our previous study which aimed to recover urinary PO_4^{3-}-P. But in that study, the effect of excess magnesium on phosphate recovery was not as sharp as it did on nitrogen recovery.

Consequently, the effect of higher initial Mg:P ratio is important from a practical standpoint since PO_4^{3-}-P consumption can be increased with an increase in pH. Therefore practically, initial molar concentration of magnesium should be in excess to achieve efficient struvite precipitation. The initial N:Mg ratio should be lower than 1.13 in order to have an acceptible residual Mg concentration. Because nearly 7.8% of Mg was left in urine as a residue at this initial molar ratio.

3.3.3 Characterization of the precipitate

Urine becomes very dark brown in color at the end of the storage period. On the other hand, the characteristic odor of urine combined with ammonia which created an undesirable process condition. In spite of these conditions, the precipitates obtained from stored urine was white crystalline powder and completely odorless.

In order to identify the phase, X-ray diffractions of precipitates were compared with the standard X-ray diffraction patterns of struvite (Figure 3.13-3.14) and hydroxyapatite (Figure 3.15). All the precipitates were identified as crystalline struvite.

According to X-ray diffractions of precipitates (Figure 3.8, 3.9 and 3.10), it is possible to speak of the existence of hydroxyapatite crystals. In these figures, the diffraction lines which are seen between 50-55 (2θ°) angles supported this presume. But it was obvious that the main phase in all of the precipitates was magnesium ammonium phosphate hexahydrate.

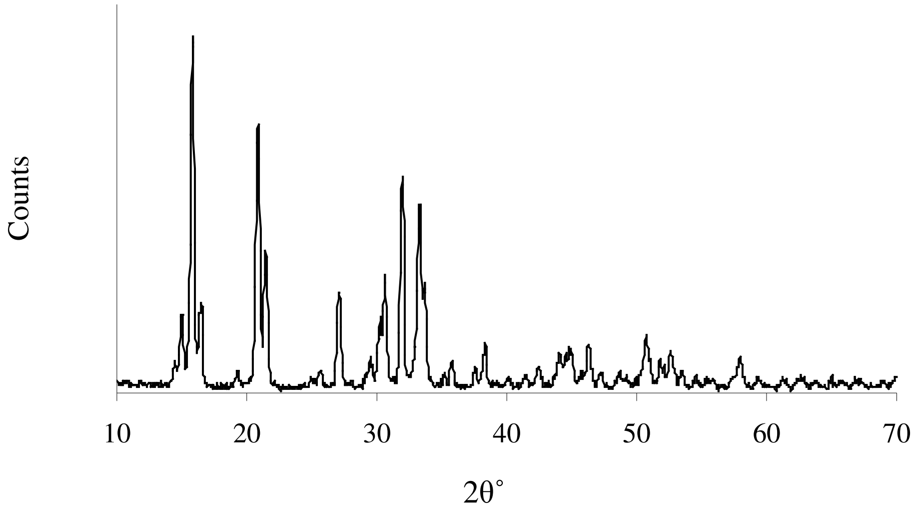

Figure 3.8: X-ray diffraction of urine-based struvite where the initial molar N:P:Mg ratio is 1:1:1.

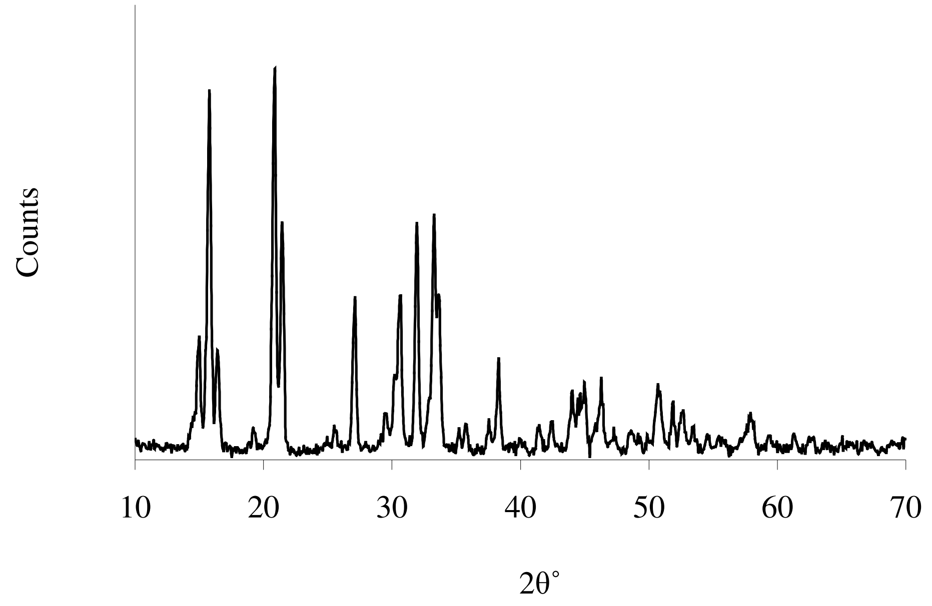

Figure 3.9: X-ray diffraction of urine-based struvite where the initial molar N:P:Mg ratio is 1:1:1.13.

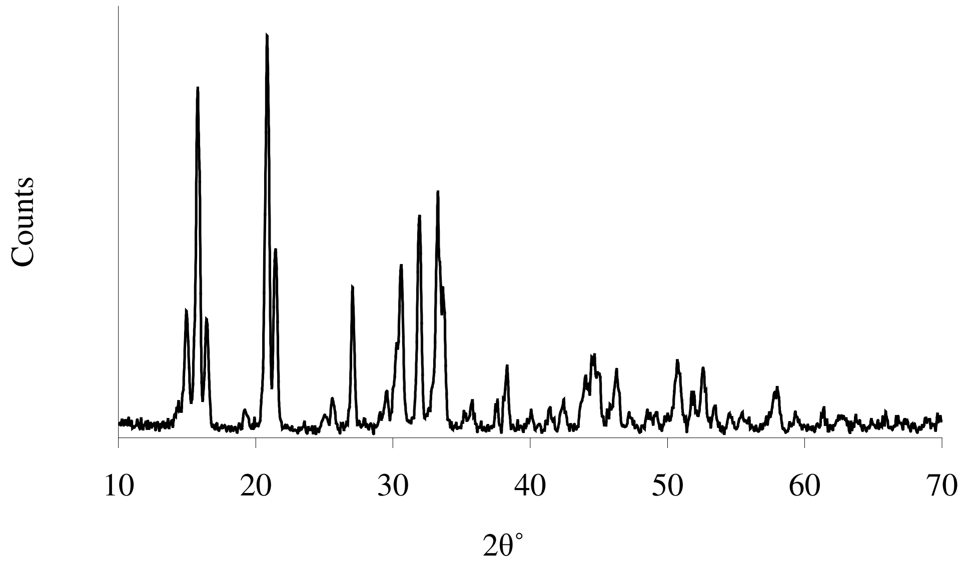

Figure 3.10: X-ray diffraction of urine-based struvite where the initial molar N:P:Mg ratio is 1:1.2:1.

Although the initial molar concentration of reactants were different, the X-ray diffractions of the urine based struvite were similar. The patterns obtained at excess Mg and excess P conditions showed peaks which belonged to struvite and hydroxyapatite. Similar results were obtained by Suzuki et al. (2002) and Burns et al. (2003) who precipitated a mixture of hydroxyapatite and struvite from swine wastewater.

Excess ammonia nitrogen in stored urine forced the reaction to form struvite which is also detectable from the X-ray patterns (Figure 3.11). The characteristic peak of struvite was strong and other small peaks were absent when compared with the previous patterns. The precipitate is totally free from hydroxyapatite. This result is in agreement with other studies, which proved that excess of ammonia relative to Mg and PO_4^{3-} drove the reaction to form a relatively pure precipitate in terms of struvite (Stratful et al., 2001).

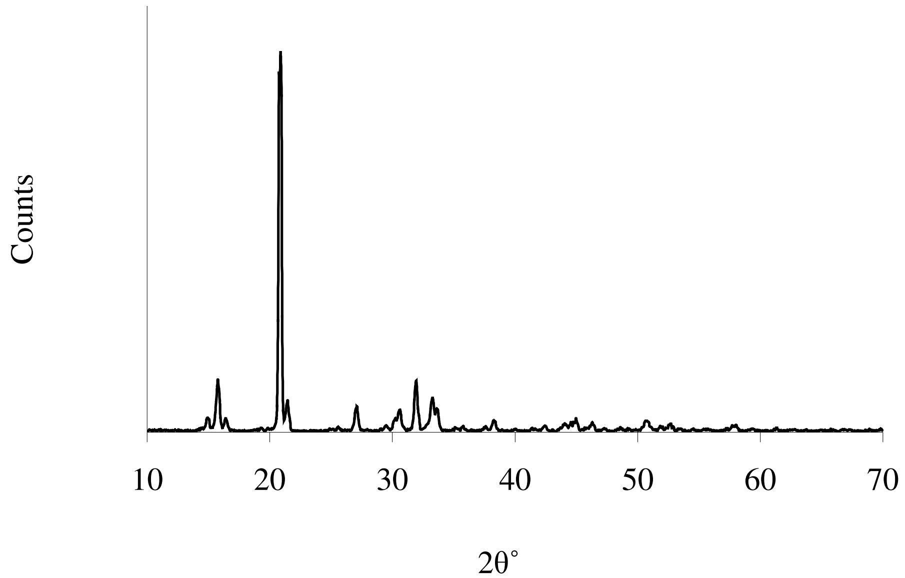

Figure 3.11: X-ray diffraction of urine-based struvite where the initial molar N:P:Mg ratio is 1.24:1:1.

Struvite which were precipitated at pH 10 and 10.7 gave the same patterns (Figure 3.12). Therefore, it can be generalized that crystalline struvite formation was observable in all pH values between 9 and 10.7. The main difference was the widening of the peaks which might be occurred because of the excessive nuclei formation at higher pH values.

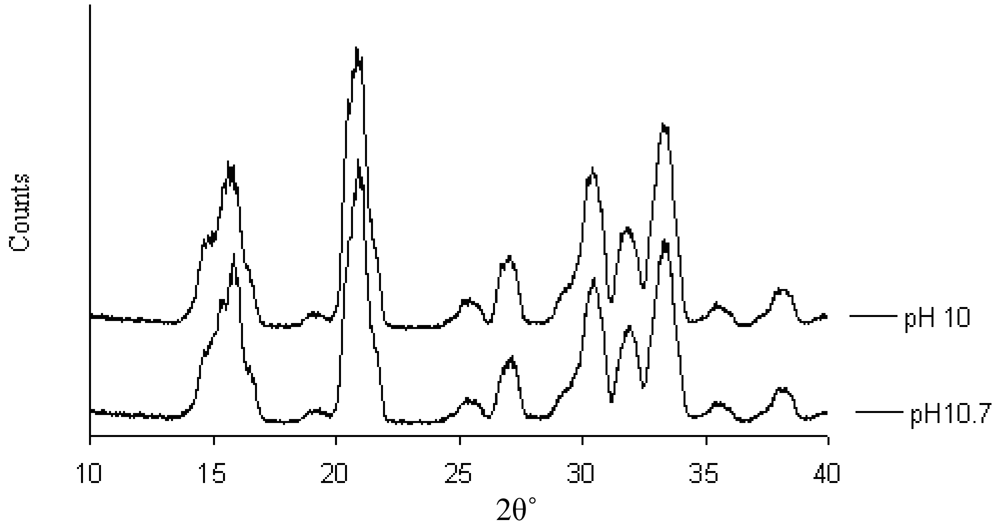

Figure 3.12: X-ray diffractograms of urine-based struvite samples which were precipitated at pH 10.7 and 10.

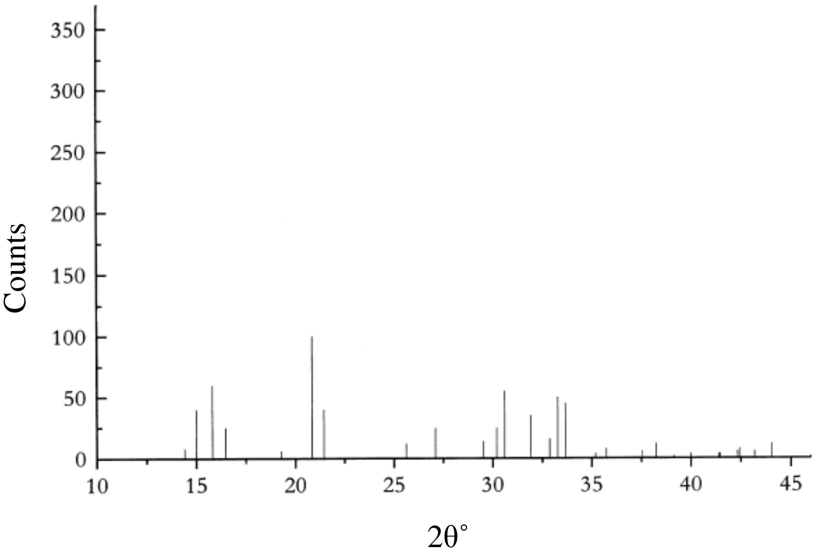

Figure 3.13: Reference diffraction lines of struvite (Bouropoulos and Koutsoukos, 2000).

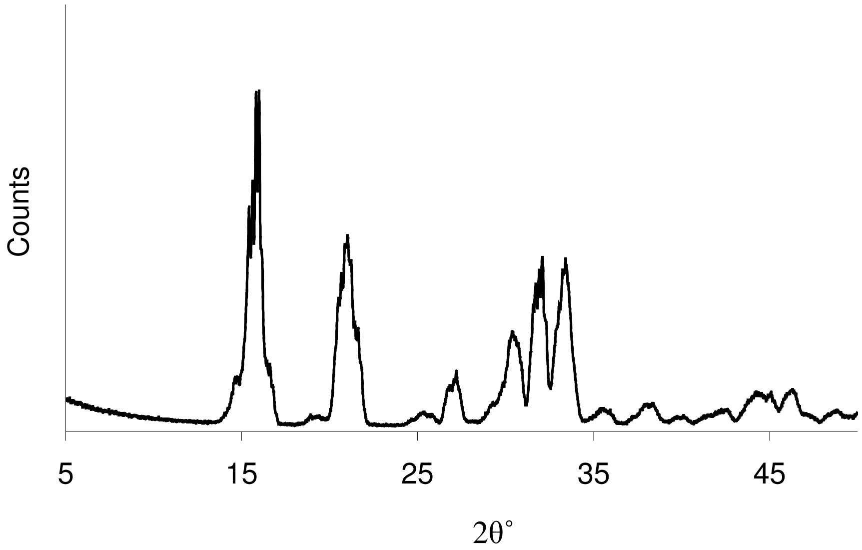

Figure 3.14: Reference diffraction lines of struvite which was precipitated from pure solution.

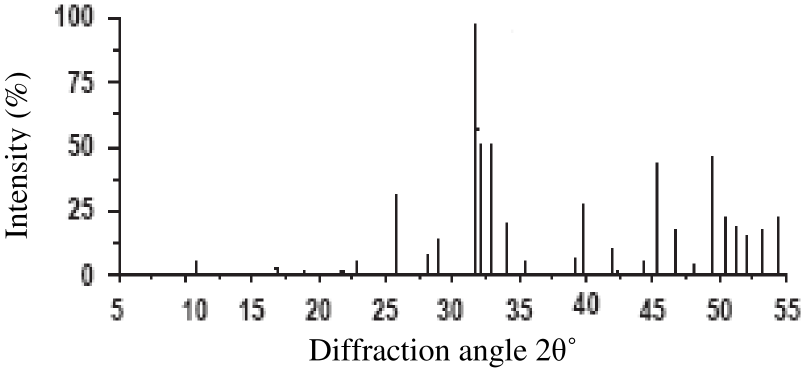

Figure 3.15: Reference diffraction lines of hydroxyapatite (Rusu et al., 2005).

The functional groups in urine-based struvite were identified with FT-IR (Figure 3.16) and the results were compared with patterns which belonged to pure struvite (Figure 3.17). FT-IR patterns of urine based struvite were identical with the patterns of pure struvite. The existence of other groups could not be observed with respect to FT-IR patterns. Thus, it is possible to say that the urine based struvite is free from organic impurities.

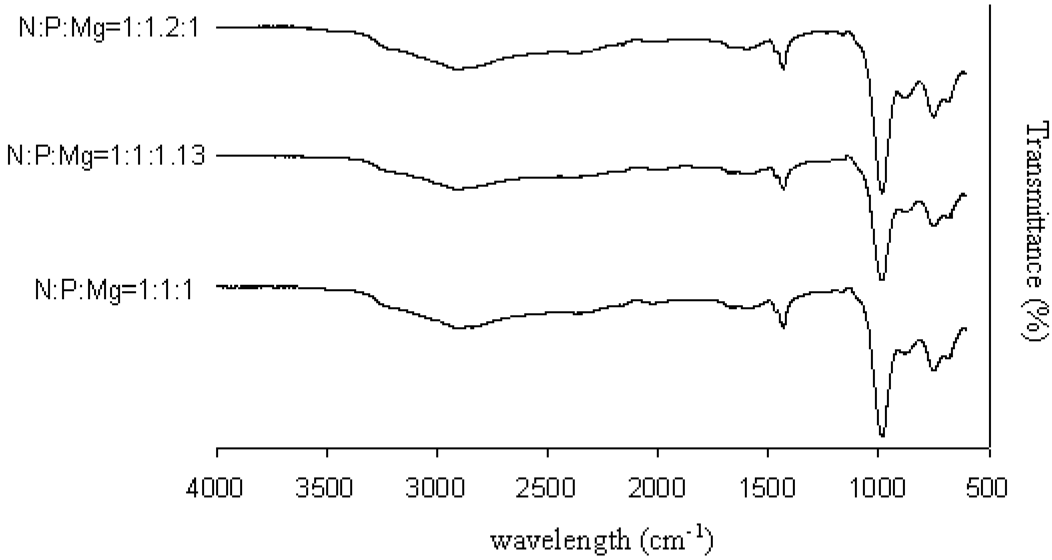

Figure 3.16: FT-IR patterns of struvite crystals precipitated at different initial reactant concentrations.

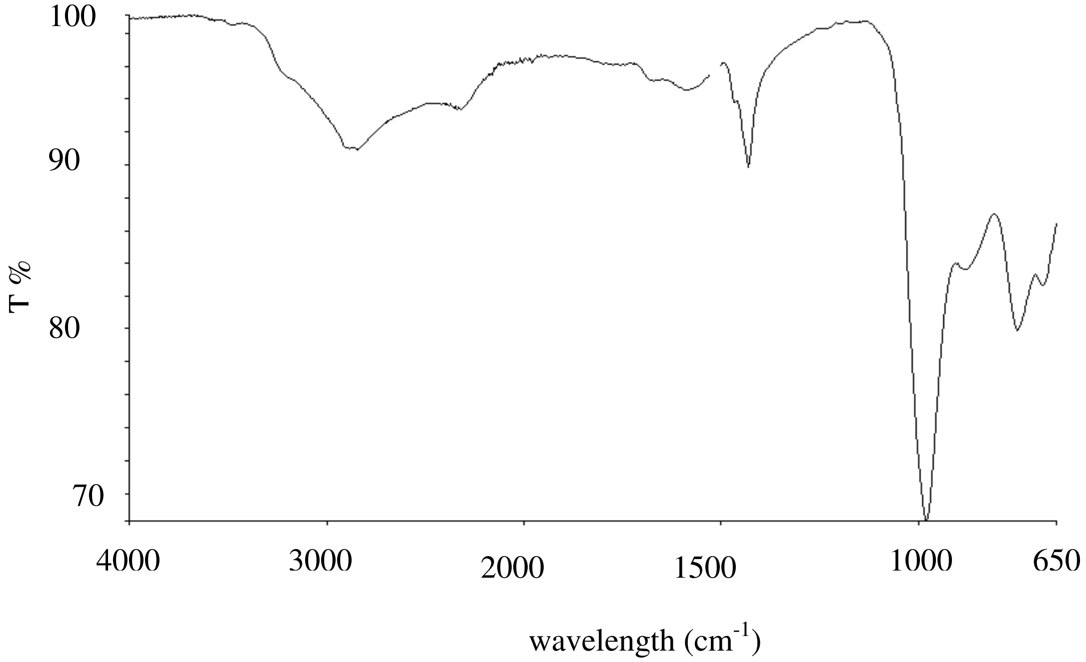

Figure 3.17: FT-IR patterns of pure struvite.

Precipitates were analyzed for their carbon (C), hydrogen (H) and nitrogen (N) content. The weight percentages of C, H and N were compared with their theoretical value (Table 3.1 and Table 3.2).

The purity of the precipitate in excess ammonia conditions is also detectable from the results of C, H and N analysis (Table 3.1). Struvite which was precipitated in excess NH_3-N conditions (1.24:1:1) contained 6.28% H, which must be 6.5% in pure struvite and 5.18% N, which must be 5.7% in pure struvite.

Table 3.1: Weight percentage of C, H and N of urine-based struvite which were precipitated at different initial molar N:P:Mg ratios.

N:P:Mg→	1:1:1	1:1:1.13	1:1.2:1	1.24:1:1	Theoretical percentage of C,H and N in struvite
C (%)	0.22	0.26	0.18	0.17	0
H (%)	5.56	5.91	6.21	6.28	6.5
N (%)	4.53	5.01	4.79	5.18	5.7

The major difference between the struvite precipitated from hydrolyzed urine and struvite precipitated from fresh urine is the carbon content. Carbon content is between 0.17-0.26 in struvite precipitates obtained from hydrolyzed urine which should be zero in pure struvite precipitates.

Table 3.2: Weight percentage of C, H and N of urine-based struvite which were precipitated at pH 10 and 10.7.

pH→	10	10.7	Theoretical percentage of C,H and N in struvite
C (%)	0.64	0.28	0
H (%)	6.17	6.22	6.5
N (%)	5.08	4.83	5.7

Urinary heavy metals could not be detected in the precipitates. The major impurity was found as K and Ca. But the main difference between this study and the study in the previous chapter was the amount of Ca in the precipitates. Precipitate obtained from fresh urine contained considerable amounts of calcium. But precipitate obtained from stored urine had lower amounts of calcium. The main reason for this difference is the spontaneous precipitation of calcium and magnesium salts which occurs during the hydrolysis of urinary urea. Besides, struvite from stored urine was free from heavy metals which precipitated spontaneously as the pH of the urine increased. Because of this reason, the precipitate obtained from stored urine is more pure than the precipitate obtained from fresh urine.

Although most of the metals could not be determined quantitatively in precipitates, metals such as Na, Al, Si, Mn, Fe and Ba were detected qualitatively. The results of the analyses are represented in Table 3.3 and Table 3.4.

Table 3.3: Results of the qualitative analyses of urine-based struvite (constant pH, pH 9.5).

N:P:Mg →	1:1:1	1:1:1.13	1:1.2:1	1.24:1:1
Na	√	√	√	√
Mg	√	√	√	√
Al	-	√	√	√
Si	√	√	√	√
P	√	√	√	√
S	-	-	-	√
K	√	√	√	√
Ca	√	√	√	√
Zn	√	-	-	-
Mn	√	√	√	√
Fe	-	√	√	√
Ba	-	√	√	√

√ : detected
- : not detected

Table 3.4: Results of the qualitative analyses of urine-based struvite (constant initial molar N:P:Mg ratio, N:P:Mg=1.1:1:1.1).

pH→	9	9.5	10	10.7
Na	√	√	√	√
Mg	√	√	√	√
Al	√	√	√	√
Si	√	-	√	√
P	√	√	√	√
S	-	√	√	√
K	√	√	√	√
Ca	√	√	√	√
Zn	-	-	-	√
Mn	√	√	√	√
Fe	√	√	√	√
Ba	√	√	√	√

√ : detected
- : not detected

3.4. Conclusions

Chapter 3 contained the studies about the urea hydrolysis during the storage and nutrient recovery in the form of struvite. According to results expressed in this chapter, the following conclusions can be declared :

- ✓ Urea, the major contributor of urinary N to fresh urine, was hydrolyzed during the storage period in all the experimental sets.
- ✓ Antibiotic residues hinder the hydrolysis of urea by inhibiting the free urease enzyme in urine.
- ✓ NH_3-N content and pH of stored urine increased due to hydrolysis of urea.

- ✓ Ca, Mg and PO_4^{3-} salts precipitated spontaneously, because of the pH increasement during the storage period.
- ✓ It was adviced to keep the reaction pH around 9.5 in order to achieve an efficient NH_3-N recovery.
- ✓ Excess Mg was a necessity to increase the contribution of both N and P to struvite.
- ✓ Holding the initial molar Mg:N ratio higher than 1.13 was not adviced due to increase in residual Mg concentration .
- ✓ Although excess Mg was recommended to enhance the effectiveness, urine based struvite which was precipitated in excess NH_3-N conditions was more pure in terms of struvite.
- ✓ The precipitates obtained at each experimental set were identified as crystalline struvite. Small amounts of hydroxyapatite could be detected which was also related with the calcium content of raw urine.
- ✓ Compounds other than struvite and hydroxyapatite could not be detected by the available instruments.
- ✓ Organic impurities were not found in the precipitates according to FT/IR analyses.
- ✓ Carbon content of urine based struvite was too low.
- ✓ Nitrogen content of urine based struvite was always lower than its theoretical value.
- ✓ All the precipitates contained very small amounts of Al, Mn, Ba, Zn and Fe. But, urine based struvite was completely free from Cd and Cr.

In this study, the change in urine composition due to urea hydrolysis was investigated and the urinary nutrients in stored urine were transformed to magnesium ammonium phosphate hexahydrate, in order to obtain a slow release urine-based fertilizer. The ratio of N:P in stored urine was considerably high which required additional P source to achieve effective nitrogen recovery. But, phosphate deficiency of stored urine becomes a disadvantage with respect to production costs. Besides, addition of phosphorus salts might contaminate the urine based struvite by contributing metals such as Cd and Cr. Therefore, it will be much more suitable to propose the struvite precipitation method as a preliminary step of nutrient recovery from stored urine. In other words, phosphate in stored urine might be recovered by struvite precipitation which only need magnesium addition. Afterwards, ammonia nitrogen which remains in urine might be recovered by stripping /absorption processes.

4. NITROGEN RECOVERY FROM URINE BY STRIPPING AND ABSORPTION OPERATIONS

4.1 Introduction

4.1.1 Urine Separation

Existing wastewater treatment system, which is majorly oriented towards the removal of organic pollutants, aim to treat the wastewater to effluent requirements allowing for discharge to the surface water (Roeleveld et al., 1997). In recent years, the changes in the quality of the surface waters have led people to think about the efficiency of the treatment works. Many studies indicated that existing wastewater treatment systems had handicaps which may create severe problems in the future (Otterpohl et al., 1997; Lier and Lettinga, 1999; Sedlak et al., 2000; Kärrmann, 2001; Berndtsson and Hyvönen, 2002).

The main disadvantage of existing wastewater treatment system is the insufficient management of water, energy and nutrients which restricts the saving of water and the recovery of nutrients. These drawbacks can be eliminated by doing changes in existing wastewater treatment systems. Proposed changes must save the clean water and enable to recover or reuse the nutrients.

Water which is the main transporter medium in conventional sanitary systems can be saved if the quantity of water used for transportation is reduced. Water can also be recovered if the stormwater and grey water (household wastewater except from toilet wastewater) are separately collected and processed. The methods aiming to save the water also saves the energy. Because, higher amounts of water in treatment units consume more energy. Recovery of nutrients is possible only if the nutrient rich part of the wastewater is separately collected. Among the wastewater streams, household wastewater comprises the most nutrient rich part. Nearly 60% of nitrogen in household wastewater comes from urine (Jönsson et al., 1997).

It is very hard to achieve the three savings together doing just one modification to existing wastewater treatment. But in recent years, separate collection of urine and using the stored urine directly in the farmland as a fertilizer is proposed as a promising method. Furthermore, many studies proved that separate handling of urine save water and energy while recovering the nutrients (Hanæus et al., 1997; Otterpohl et al., 1997; Kärrmann, 2001; Balkema et al., 2002; Jönsson, 2002).

Obviously, urine separation has disadvantages which are related with the total toilet system and the potential risks (Höglund et al., 2002). Technical problems about the total toilet system including toilets, pipes and storage tanks can be overcome with further designs. But, the risks of urinary micropollutant and pathogenic bacteria transmission should be eliminated before accepting the urine as a fertilizer. To overcome these obstacles, urinary ammonia which is the major compound at the end of the storage period can be transported to a more acceptable ammonia based compound.

In this study, urinary ammonia is stripped with air and the air-ammonia gaseous mixture is bubbled through sulphuric acid. Furthermore, the efficiency of the combined process is related with mass transfer terms.

4.1.2 Stripping and Absorption

Stripping is a physicochemical operation where a volatile compound in a liquid is transferred into a gaseous phase. The reverse of the operation is defined as absorption and both of the operations are based on the equilibrium between the gas and liquid phase.

Ammonia equilibrium in aqueous solution is pH and temperature dependent, and free ammonia concentration is expressed with the following equation :

$$[NH_3] = \frac{[NH_3 + NH_4^+]}{1 + \frac{[H^+]}{K_a}} \qquad \textbf{(4.1)}$$

In equation (4.1), $[NH_3]$ indicates free ammonia concentration, $[NH_3+NH_4^+]$ indicates total ammonia concentration, K_a indicates ionisation constant. Operation pH, which is the most important parameter in NH_3-NH_4^+ equilibrium can be increased by addition of the $Ca(OH)_2$ or NaOH. Minocha and Rao (1988) stated that using NaOH is more beneficial than using $Ca(OH)_2$.

Ammonia is very soluble which means that very small amounts of ammonia desorb from the liquid into the gas phase without any application. Because of this, to strip out the ammonia, large amounts of air must be contacted with liquid.

Absorption can be either physical or chemical. In physical absorption the gas is dissociated because of its solubility. In chemical absorption, the gas to be removed reacts with solvent. Although absorption method is a well studied subject by many researchers, environmental application of this method is rare. Ammonia is highly soluble in water and also very reactive against sulphuric acid. In the case of ammonia absorption, chemical absorption seems more advantageous. Minocha and Rao (1988) recovered ammonia as ammonium phosphate from urea fertilizer plant waste. Bonmati and Flotats (2003) absorbed ammonia in sulphuric acid to recover ammonia from pig slurry. Saracco and Genon (1994) recovered ammonia from process liquid wastes by absorption with sulphuric acid.

Calculation of both absorption and stripping is based on material and enthalpy balances and gas-liquid equilibrium data. Besides, both of the methods are conducted in trayed towers, packed columns, spray towers, bubble columns, centrifugal contactors, agitated vessels. The design approach is completely different in all types of the gas-liquid contactors. In bubble aeration systems, mass transfer rate depends on the volumetric gas flow rate, partial pressure of gas and the mass transfer coefficient.

Mass transfer in a diffused aeration system is a dynamic process in which the local equilibrium concentrations (the driving force) change as bubbles rise through the liquid column (Hsieh et al., 1994).

Mass transfer in aerated systems is mainly modelled using the two film theory. In two film theory, each film possesses a resistance to mass transfer but concentrations in the two fluids at the interface are in equilibrium (Seader and Henley, 1998). Therefore, there is no additional interfacial resistance to mass transfer (Figure 4.1).

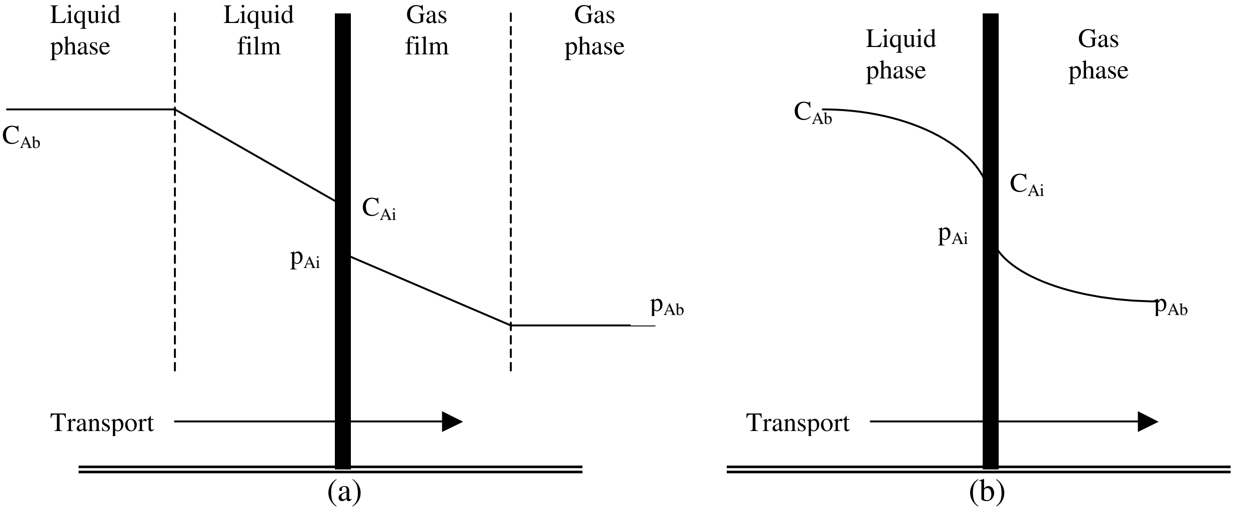

Figure 4.1: Concentration gradients theory: (a) film theory, (b) more realistic gradients (Seader and Henley, 1998).

In aeration systems the "two film model" can be expressed in terms of an overall mass transfer coefficient and an overall concentration difference as shown below :

$$N_{O,A} = -K_{OL,A} \times a \times V_L \times (C_{L,A} - C^*_{L,A}) \tag{4.2}$$

$N_{O,A}$: Overall mass transfer rate of A from water to air [M.t^{-1}].

$K_{OL,A}$: Overall mass transfer coefficient [L.t^{-1}].

a : Interfacial area per unit volume of liquid [L^2.L^{-3}].

V_L : Total volume of liquid [L^3].

$C_{L,A}$: Concentration of A in the bulk liquid [M.L^{-3}].

$C^*_{L,A}$: Liquid concentration of A in equilibrium with the gas phase concentration [M.L^{-3}].

Müller et al. (1981) built and generalized a model for gas transfer to rising air bubbles. In this study, overall mass transfer coefficient was obtained by using Müller's approach.

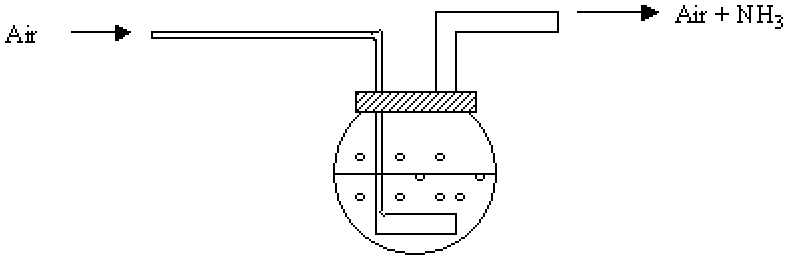

Figure 4.2: Schematic representation of the experimental set of stripping unit.

As seen from the Figure 4.2, air bubbles are passed through a homogeneous liquid. If we assume that there is no change in pressure and volume of the air bubbles, we can write the mass balance for a single rising air bubble.

$$V_B \times \frac{dC_{G,A}}{dt} = K_L \times A_B \times (C_{L,A} - C^*_{L,A}) \qquad \textbf{(4.3)}$$

where,

$C_{G,A}$: Gas phase concentration of A, [M.L^{-3}].

K_L : Overall mass transfer coefficient [L.t^{-1}].

V_B : Volume of air bubble [L^3].

A_B : Surface area of air bubble [L^2].

We can assume that the interfacial area per unit volume of liquid is related with the bubble volume and surface area.

$$\frac{A_B}{V_B} = \frac{a \times V_L}{V_G} \qquad \textbf{(4.4)}$$

V_G : Total volume of all gas in the system [L^3].

V_L : Total volume of liquid [L^3].

In order to start the formulations we should make the equation (4.3) more proper:

$$\frac{dC_{G,A}}{dt} = K_L \times \frac{A_B}{V_B} \times (C_{L,A} - C^*_{L,A}) \qquad \textbf{(4.5)}$$

Equation (4.5) can be rewritten by using equation (4.4)

$$\frac{dC_{G,A}}{dt} = K_L \times (\frac{a \times V_L}{V_G}) \times (C_{L,A} - C^*_{L,A}) \qquad \textbf{(4.6)}$$

Gas phase concentration of substance A is related to the $C^*_{L,A}$ according to Henry's law.

$$C_{G,A} = C^*_{L,A} \times H_A \qquad \textbf{(4.7)}$$

H_A : Dimensionless Henry's law constant for substance A, [-].

By using equation (4.7) in equation (4.6), it is possible to obtain the equation shown below :

$$\frac{dC^*_{L,A}}{dt} = \frac{K_L \times a \times V_L}{V_G \times H_A} \times (C_{L,A} - C^*_{L,A}) \qquad \textbf{(4.8)}$$

Equation (4.9) can be obtained by organizing the equation (4.8):

$$\frac{dC^*_{L,A}}{(C_{L,A} - C^*_{L,A})} = \frac{K_L \times a \times V_L}{V_G \times H_A} \times dt \qquad \textbf{(4.9)}$$

Integrating equation (4.9) with the initial conditions $C^*_{L,A}=0$ at t=0 and assuming that $C_{L,A}$ remains constant during the residence time of a single bubble yields equation (4.10).

$$\ln \frac{(C_{L,A} - C^*_{L,A})}{C_{L,A}} = -\frac{K_L \times a \times V_L}{V_G \times H_A} \times t \qquad \textbf{(4.10)}$$

Rewriting the equation yields :

$$\frac{(C_{L,A} - C^*_{L,A})}{C_{L,A}} = \exp(-\frac{K_L \times a \times V_L}{V_G \times H_A} \times t) \qquad \textbf{(4.11)}$$

$$\frac{C^*_{L,A}}{C_{L,A}} = 1 - \exp(-\frac{K_L \times a \times V_L}{V_G \times H_A} \times t) \qquad \textbf{(4.12)}$$

Müller et al. (1981) included the contact time of gas bubbles by assuming that

$$\frac{V_G}{Q_G} = \tau \qquad \textbf{(4.13)}$$

Q_G : Gas flow rate $[L^3.t^{-1}]$

τ : Contact time of the gas bubbles rising through the liquid [t].

Equation (4.13) can be placed in equation (4.12) :

$$\frac{C^*_{L,A}}{C_{L,A}} = 1 - \exp\left(-\frac{K_L \times a \times V_L}{Q_G \times H_A} \times \frac{t}{\tau}\right) \quad \textbf{(4.14)}$$

Equation (4.14) expresses that the ratio $C^*_{L,A}/C_{L,A}$ is a function of time for different values of the dimensionless group $\left(\frac{K_L \times a \times V_L}{Q_G \times H_A}\right)$.

By assuming that experimentally determined K_L values are average values for an entire system, it is possible to write the mass transfer rate of compound A out of an aeration system as:

$$F_A = Q_G \times C_{G,A} \quad \textbf{(4.15)}$$

where t= τ .

Equation (4.15) can be rewritten by using equation (4.7) to obtain $C_{G,A}$. By using this term, equation (4.16) is obtained:

$$F_A = Q_G \times C_{L,A} \times H_A \times [1 - \exp(-\frac{K_L \times a \times V_L}{Q_G \times H_A})] \quad \textbf{(4.16)}$$

Müller et al. (1981) extended the theory of batch stripping and wrote an expression by assuming that no process other than stripping removed component A from a batch reactor.

$$V_L \times \frac{dC_{L,A}}{dt} = F_A \quad \textbf{(4.17)}$$

Equation (4.16) can be used in equation (4.17), in order to obatin equation (4.18).

$$V_L \times \frac{dC_{L,A}}{dt} = Q_G \times C_{L,A} \times H_A \times [1 - \exp(-\frac{K_L \times a \times V_L}{Q_G \times H_A})] \quad \textbf{(4.18)}$$

Equation (4.18) can be rewritten to obtain equation (4.19),

$$\frac{dC_{L,A}}{C_{L,A}} = \frac{1}{V_L} \times Q_G \times H_A \times [1 - \exp(-\frac{K_L \times a \times V_L}{Q_G \times H_A})]dt \quad \textbf{(4.19)}$$

Integrating equation (4.19) at initial conditions $C_{L,A}=C_{L,A0}$ at t=0 yields equation (4.20).

$$-\ln\frac{C_{L,A}}{C_{L,A0}}=\frac{Q_G\times H_A}{V_L}\times[1-\exp(-\frac{K_L\times a\times V_L}{Q_G\times H_A})]\times t \qquad \textbf{(4.20)}$$

A plot of the negative logaritm of the concentration ratio versus time gives a linear relationship with the slope which can be written as :

$$slope=\frac{Q_G\times H_A}{V_L}\times[1-\exp(-\frac{K_L\times a\times V_L}{Q_G\times H_A})] \qquad \textbf{(4.21)}$$

Mass transfer coefficient can be drawn from equation (4.21).

$$(slope)\times\frac{V_L}{Q_G\times H_A}=[1-\exp(-\frac{K_L\times a\times V_L}{Q_G\times H_A})] \qquad \textbf{(4.22)}$$

$$\ln(1-(slope)\times\frac{V_L}{Q_G\times H_A})=-\frac{K_L\times a\times V_L}{Q_G\times H_A} \qquad \textbf{(4.23)}$$

$$K_L\times a=-\frac{Q_G\times H_A}{V_L}\times\ln(1-(slope)\times\frac{V_L}{Q_G\times H_A}) \qquad \textbf{(4.24)}$$

If the exit gas is saturated with the volatile compound, $\left(\frac{K_L\times a\times V_L}{Q_G\times H_A}\right)$ is much more higher than 1 where $-\ln\frac{C_{L,A}}{C_{L,A0}}=\frac{Q_G\times H_A}{V_L}\times t$ is valid. Thus, this situation is not yielding the value of $(K_L\times a)$. If the volatile compound has a large H_A value or the gas flow rate is too high, the exit gas will be far from saturation. In most of the air bubbling operations, liquid is contacted with large amounts of air which yields unsaturated gas phase. This time, the value of $\left(\frac{K_L\times a\times V_L}{Q_G\times H_A}\right)$ is much more smaller than 1 where $-\ln\frac{C_{L,A}}{C_{L,A0}}=K_L\times a\times t$ is valid. Hence, the batch data from the experiments can be used directly to obtain $(K_L\times a)$.

In this chapter, urinary ammonia was stripped with air and ammonia-air mixture was bubbled through dilute sulphuric acid. The efficiency of the stripping was expressed in terms of combined mass transfer coefficients. Furthermore, overall mass transfer rates in stripping operation were obtained and the percentage of urinary nitrogen recovery as ammonium sulphate was calculated.

4.2 Materials and Methods

4.2.1 Urine samples

Fresh urine samples which were collected from 7 people were mixed in a container. For each experimental set, 50 ml of mixed urine sample was retrieved and placed in a cylindirical reactor where it was diluted 4 times. Reactors were tightly closed and stored for 8 weeks.

4.2.2 Air stripping and ammonia absorption

In this part of the study ammonia stripping with air was achieved in batch conditions. Urine was placed in a glass reactor having 1 L available volume. A connection tube was used to carry the ammonia-air gaseous mixture from stripping unit to absorption unit.0.5M of H_2SO_4 was placed in absorption unit. The amount of the acid was determined after finding the initial NH_3-N concentration of the urine mixture. Air-ammonia gaseous mixture from the stripping unit was bubbled through sulphuric acid. Schematic representation of the laboratory set is shown in Figure 4.3.

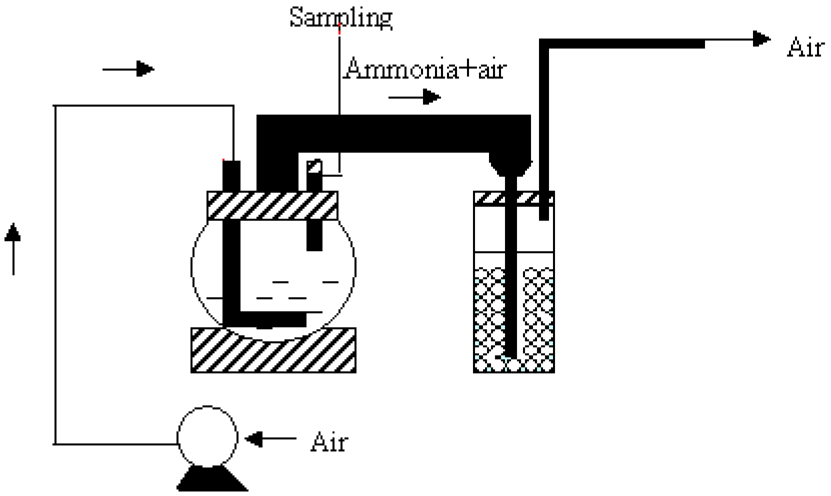

Figure 4.3: Schematic representation of bench scale stripping/absorption set.

Figure 4.4: Picture of stripping/absorption unit.

Six experiments which were repeated twice were conducted to find out the effect of pH and air rate on $K_L \times a$ values.

The effect of pH was determined by running the experiments at constant air flow rate (0.12 $m^3.h^{-1}$) where the pH was adjusted as 11, 12 and 13.5 respectively. During the experiments the pH was controlled and kept nearly constant. Three more experiments were done at constant pH (pH 12) where the air rates were set as 0.12, 0.21, 0.27 $m^3.h^{-1}$ respectively. In all these experiments mentioned above, samples were collected at certain intervals from the sampling part of stripping reactor. Three more experiments were done at constant pH (pH 12) where the air rate was adjusted as 0.09, 0.15 and 0.21 $m^3.h^{-1}$ respectively. In these experiments the samples were collected at the begining and at the end of the period which was set as 5 h. The results were used for the calculation of overall mass transfer rate.

4.2.3 Analyses

All the analyses were run according to standard methods (APHA, 1992). NH_3-N was analyzed using standard 4500 NH_3-B and C preliminary distillation and titrimetric method. At the end of the experiment, absorption unit was separated from the set and the solution was carefully evaporated to dryness. The crystals were weighed and identified by X-ray diffraction (Philips PW 1710) and FT-IR (Perkin Elmer, SpectrumOne).

4.3. Results and Discussion

4 times diluted urine had some changes in concentration during 8 weeks. Although complete hydrolysis could not be detected, the average NH_3-N concentration of the stored urine was 1899 mg.L^{-1} and the average pH was 9.6. Thus, the amount of NaOH needed to adjust the pH for stripping was little. But, throughout the experiments, it was observed that, pH of the urine in the stripping unit decreased spontaneously. On the other hand, ammonia equilibrium in aqueous solutions is pH and temperature dependent. Thus, both of the parameters were kept constant through out the experiment.

Urine has a tendency for foaming during the air bubbling. Thus, using a few drops of surface active reagent was a necessity.

4.3.1 Determination of $(K_L \times a)$

$(K_L \times a)$ is determined by using both batch and equilibrium data . Equilibrium data for ammonia-water-air system is shown in Table 4.1.
Assuming that stripping was the only mechanism for ammonia removal in the stripping unit, equation (4.20) was used to calculate the overall mass transfer coefficient. The slope of the straight line $\left(\frac{Q_G \times H_A}{V_L} \times \left[1-\exp\left(-\frac{K_L \times a \times V_L}{Q_G \times H_A}\right)\right]\right)$ was easily obtained by plotting the natural logaritm of concentration ratio $-Ln\frac{C_{L,A}}{C_{L,A_0}}$ versus time. Where,

$C_{L,A}$ = ammonia concentration at time t,

C_{L,A_0} =inititial ammonia concentration.

Fig 4.6 and 4.7 shows the plots of $-Ln\dfrac{C_{L,A}}{C_{L,A_0}}$ for different pH levels and air flowrates. The value of $\left(\dfrac{Q_G \times H_A}{V_L}\times\left[1-\exp\left(-\dfrac{K_L \times a \times V_L}{Q_G \times H_A}\right)\right]\right)$ at each condition was determined by the slope of best-fit line.

As previously indicated, $(K_L \times a)$ can only be calculated if the exit gas is far from saturation. In other words, exit gas is unsaturated with respect to ammonia if $\left(\dfrac{K_L \times a \times V_L}{Q_G \times H_A}\right)$ is far below 1. Therefore before calculating the value of $(K_L \times a)$, saturation of exit gas (gaseous phase exitting from the stripping unit) was controlled by using equation (4.25),

$$\frac{K_L \times a \times V_L}{Q_G \times H_A} = -Ln\left[1-(slope)\times\frac{V_L}{Q_G \times H_A}\right] \tag{4.25}$$

According to calculations, the ammonia-air gaseous mixture was far from saturation at each stripping condition.

Table 4.1: Equilibrium data for NH_3-H_2O-air system (Geankoplis, 1983).

Partial pressure of ammonia (mmHg)	Mole fraction of ammonia in liquid x_A	Mole fraction of ammonia in vapor y_A
12	0.0208	0.0158
15	0.0258	0.0197
18.2	0.0309	0.0239
24.9	0.0405	0.0328
31.7	0.0503	0.0416
50	0.0737	0.0657
69.6	0.096	0.0915
114	0.137	0.15

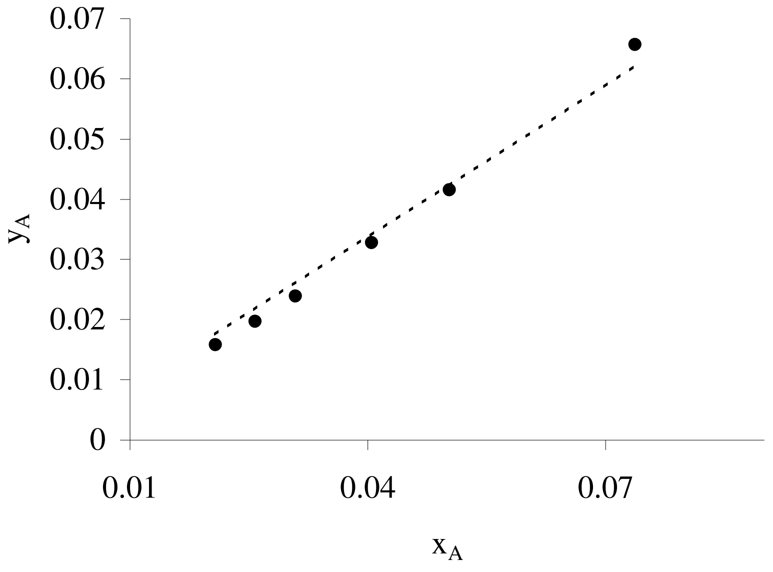

Figure 4.5: Equilibrium line (NH_3-H_2O-air system), (Geankoplis, 1983).

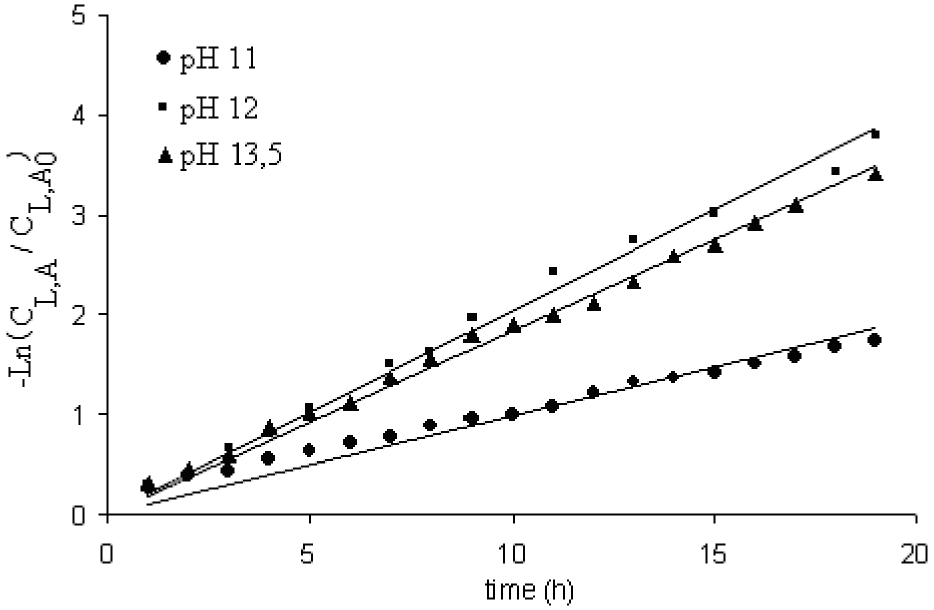

Figure 4.6: The slopes at constant air flow rate (0.12 $m^3.h^{-1}$).

As seen from Figure 4.6, the value of $(K_L \times a)$ and the efficiency of the stripping got higher as the operational pH increased from 11 to 12. But, studying at high pH values such as 13.5 decreased the value of $(K_L \times a)$ and efficiency. The results are also given in Table 4.2 which implies that an operational pH higher than 12 is unnecessary due to its lowering effect to $(K_L \times a)$ value.

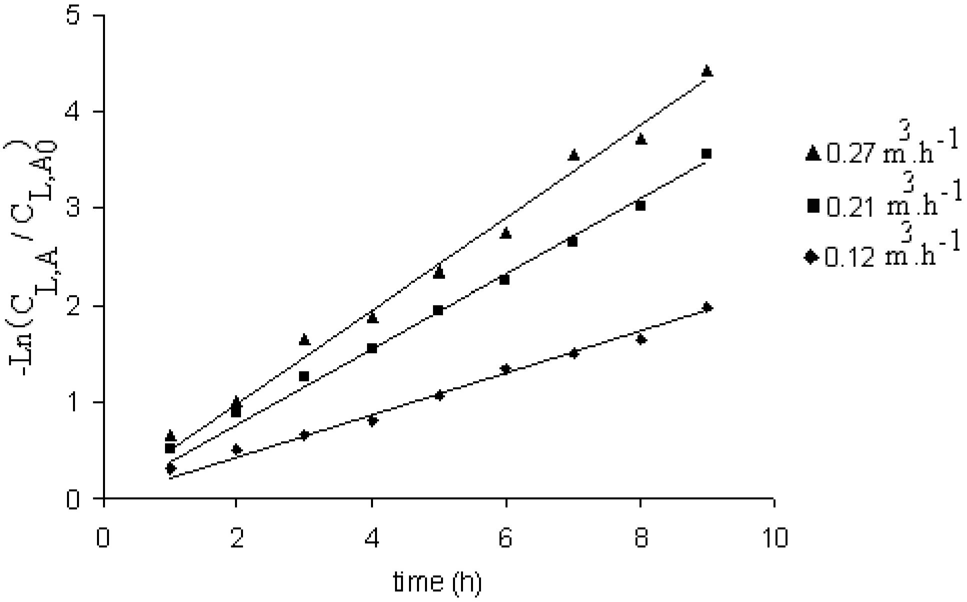

Figure 4.7: The slopes at optimum pH (pH 12).

The promoting effect of higher air rates on stripping efficiency is seen in Figure 4.6 and Table 4.3. The value of $(K_L \times a)$ increased 2.3 times as the air rate was raised from 0.12 to 0.27 $m^3.h^{-1}$.

Table 4.2: $(K_L \times a)$ values at constant air flow rate (0.12 $m^3.h^{-1}$).

pH	$(K_L \times a)$, h^{-1}
11	0.098
12	0.204
13.5	0.184

Table 4.3: $(K_L \times a)$ values at constant pH (pH 12).

Q_G ($m^3.h^{-1}$)	$(K_L \times a)$, h^{-1}
0.12	0.204
0.21	0.393
0.27	0.477

Table 4.2 and 4.3 reveals that the effect of air rate on stripping efficiency is more impressive than the effect of pH. Because, pH is already high enough to shift the ammonium-ammonia equilibrium towards ammonia formation. Thus, higher air flow rates determines the transferring of ammonia from urine to air.

The positive effect of air flow rate on ammonia stripping is anticipated since it has a high solubility in water. Large volumes of air per unit volume of water is a need for this kind of components whose mass transfer is mainly controlled by the gas film (Minocha and Rao, 1988; Arogo et al., 1999). Higher air rates reduces the film thickness which presents a resistance to mass transfer. As a result of this reduction the mass transfer coefficients and overall mass transfer rate increases.

4.3.2 Determination of optimum pH and air flow rate

Figure 4.8 and 4.9 depicts the decrease in ammonia concentration with time at different operation conditions. In both of the figures, the concentration of ammonia in the stripping unit greatly decreased with time.

At constant air flowrate conditions, 82% of NH_3-N was stripped when the pH was 11. At pH 12, 98% of NH_3-N was stripped and it decreased to 97% when the pH was 13.5 . Studying at pH higher than 12 was not beneficial. This result was expected since pH 12 was already high enough to convert all of the ammonium ion to dissolved ammonia gas.

Although pH 12 could be the optimum pH, 19 hours which was the period needed for 97% of ammonia stripping was too long (Figure 4.8). To lessen the period, air rate was increased.

The positive effect of higher air flowrates can be explained by the high solubility of ammonia in water. Solubility is known to be the main reason of the resistance to mass transfer from liquid to the gas phase. Therefore, higher air rates are required to force the mass transfer and to reduce the thickness of the boundary layer that shows a resistance to mass transfer in the liquid side.

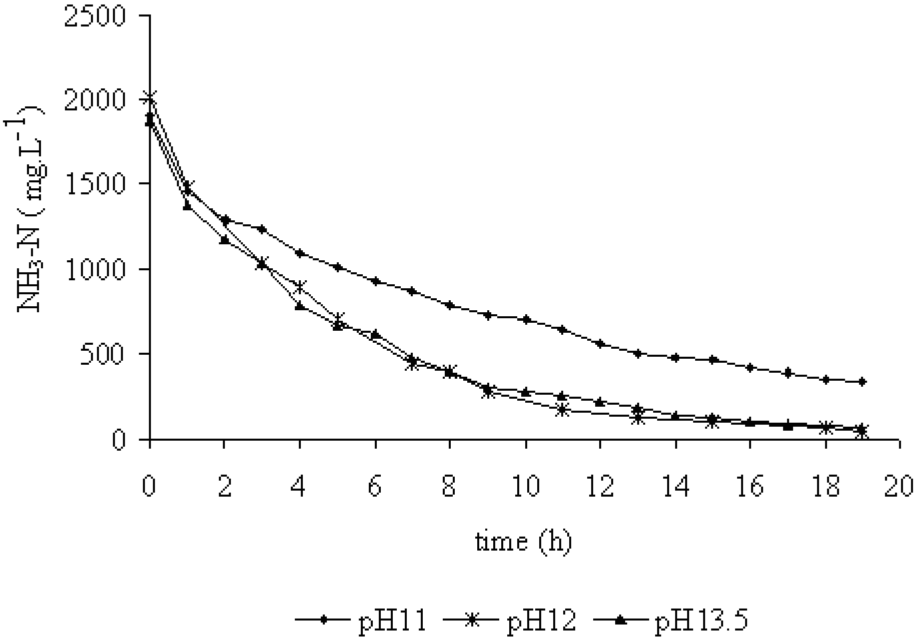

Figure 4.8: NH_3-N concentration in the stripping unit with time at constant air flow rate (0.12 $m^3.h^{-1}$) where the operational pH was varied as pH 11, 12 and 13.5 .

As the air rate used for stripping was increased, the period needed to have the same stripping yield was shortened (Figure 4.9).

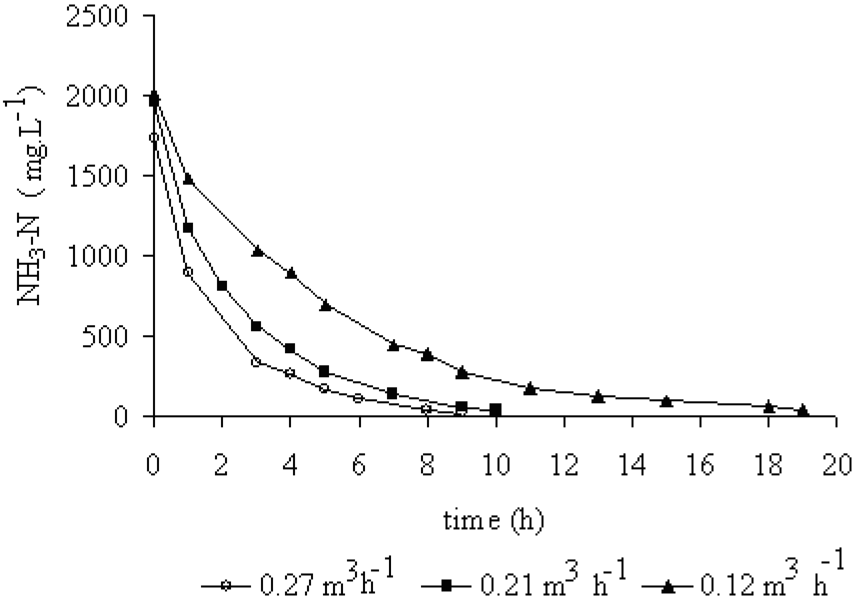

Figure 4.9: NH_3-N concentration in the stripping unit with time at constant pH (pH 12) where the air rate was varied as 0.12, 0.21 and 0.27 $m^3.h^{-1}$.

Nearly 97.7% of NH_3-N was stripped in 19 hours when the air rate was adjusted as 0.12 $m^3.h^{-1}$. As the air rate was selected as 0.21 $m^3.h^{-1}$, about 98% of NH_3-N was stripped in 10 hours. When the air rate was 0.27 $m^3.h^{-1}$, 98.8% of NH_3-N was stripped in 9 hours. Hence, optimizing the air rate as 0.27 $m^3.h^{-1}$ is not adviced since the stripping efficiency increases very slowly after 0.21 $m^3.h^{-1}$.

The positive effect of higher air flow rate on stripping efficiency was also observed by Cheung et al. (1997), who noticed high ammonia removal performance at high air flow rate, regardless of the composition of leachate used.

In all experiments initial volume, sampling volume, number of sampling and final volume of the urine in the stripping unit was measured. By using these data, the volume of water which was lost during the experiments were detected. It was seen that in the experimental set where the air rate was 0.27 $m^3.h^{-1}$, about 5.1% of water was lost in 9 h. As the air rate was adjusted as 0.21 $m^3.h^{-1}$, 1.9% of water was lost in 10 h. Furthermore, nearly 2.3% of water was lost in 19 hours when the air rate was adjusted as 0.12 $m^3.h^{-1}$.

In mass transfer rate experiments the initial pH was adjusted as 12 and no more pH adjustments were done afterwards. In other words, the system was not disturbed during the stripping period which was set as 5 h. Experimental mass transfer rates indicated that there was a direct relationship between air rate and mass transfer rate (Table 4.4). In other words the amount of ammonia that was transported from the urine to air increased, as the ratio of air rate/initial urine volume was raised.

Table 4. 4: Experimental mass transfer rates of ammonia out of urine.

Air Rate ($m^3.h^{-1}$)	$\frac{\text{Air Rate } (m^3.h^{-1})}{V_{urine,initial}(m^3)}$	% Stripped NH_3-N	Mass transfer rate ($g.h^{-1}$)
0.09	511.4	81.8	0.0363
0.15	833.3	92.4	0.0764
0.21	1166.7	93.2	0.0855

As seen from Table 4.4, higher than 80% of ammonia was stripped out in all of the experiments where the operation period was 5 h. It is obvious that the efficiency would be higher if the period was selected longer like the previous ones. Although higher air flow rates enhances the mass transfer, it increases the amount of water which is lost during the air bubbling. The amount of water which is lost during the stripping operation is important since the residual urine gets more concentrated as the loss increases.

In mass transfer rate experiments, nearly 11% of water was lost when the air rate was 0.15 $m^3.h^{-1}$. This water loss was lower (about 9%) in conditions when the air rate was decreased to 0.09 $m^3.h^{-1}$. When the air rate was adjusted as 0.21 $m^3.h^{-1}$,only 11% of water was lost.

In each experiment, urinary ammonia was transported from stripping to absorption unit with the air. In the absorption unit, ammonia was reacted with sulphuric acid. The resultant ammonium sulphate solution was evaporated to dryness to crystallize ammonium sulphate. Picture of crystallized ammonium sulphate is shown in Figure 4.10. Crystallinity was directly related with the evaporation rate and the way of evaporation. Because of this, FT-IR results were more reliable if the crystals were assessed in terms of impurity. FT-IR spectra of the crystal samples can be seen in Figure 4.11. The patterns were compared with standard ammonium sulphate FT-IR spectrum (Figure 4.12). All the samples showed the same patterns with standard spectra.

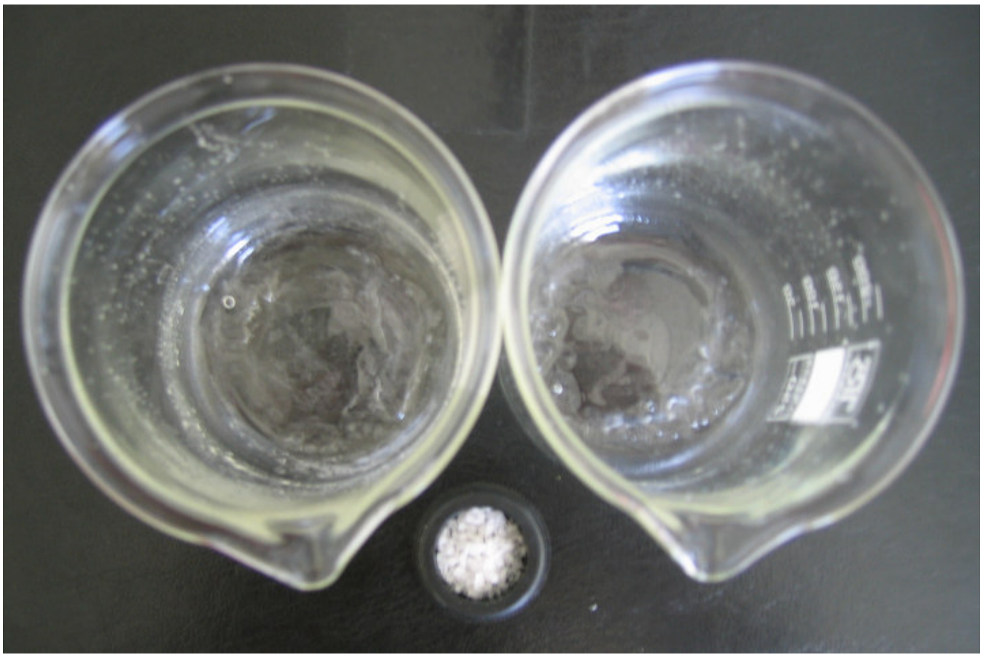

Figure 4.10: Picture of crystallized ammonium sulphate samples.

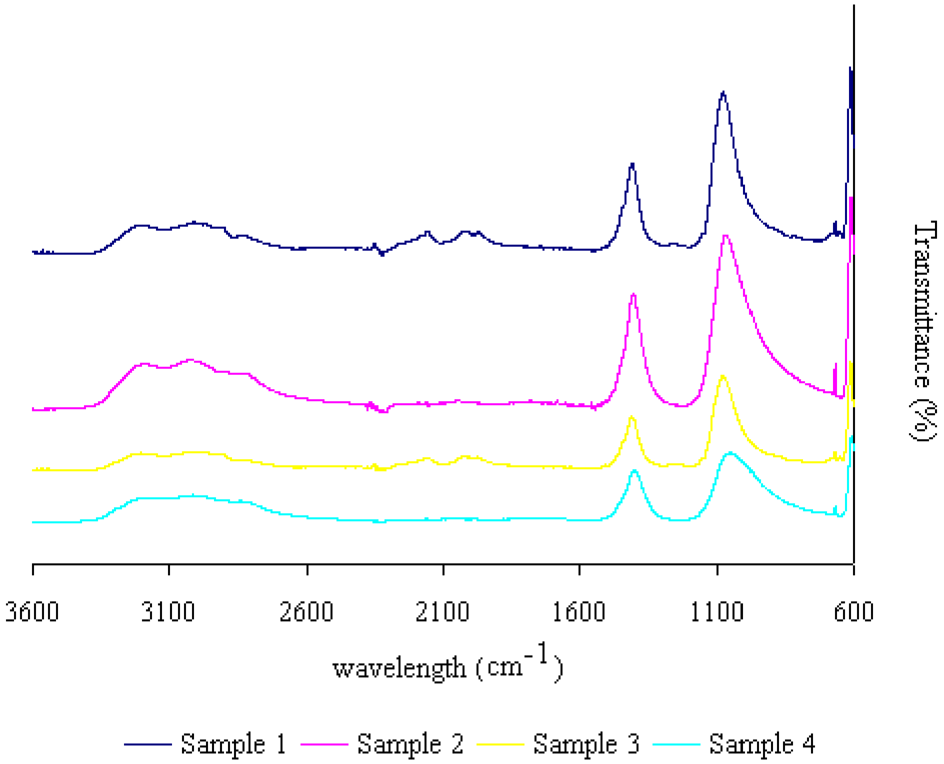

Figure 4.11: FT-IR spectra of urine-based ammonium sulphate crystal samples.

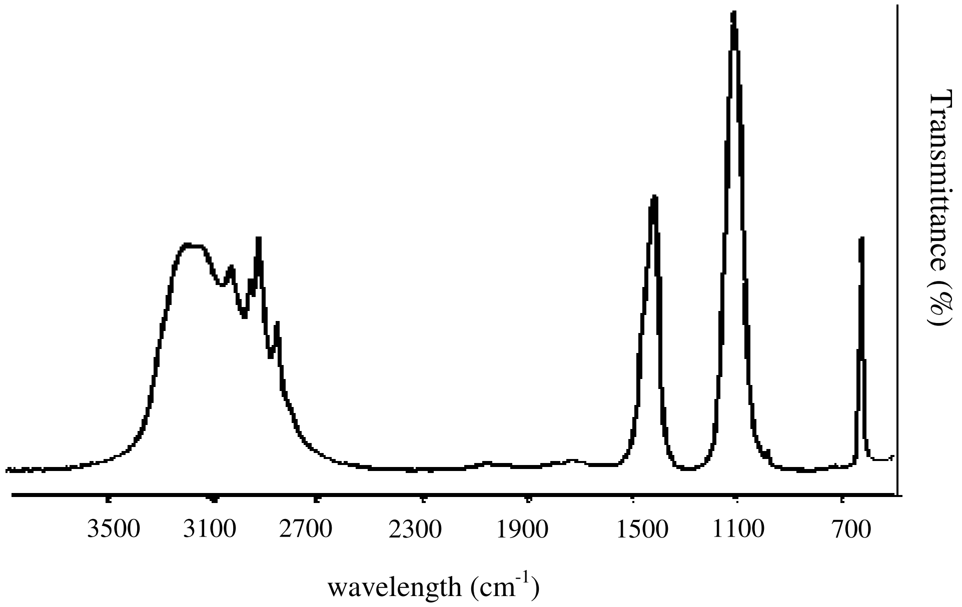

Figure 4.12: Standard FT-IR spectra of ammonium sulphate.

The amount of ammonia that was recovered in the absorption unit was calculated from the amount of ammonium sulphate crystals. This value was compared with the theoretical amount of ammonium sulphate which was calculated by using the amount of ammonia that was stripped in the stripping unit. The difference of the two calculations gave the ammonia loss during the experiment. 90-92% of ammonia (which was stripped with air in the stripping unit) was recovered as ammonium sulphate.

Similar results were obtained by researchers who studied with different kinds of ammonia sources. Minocha and Rao (1988) who recovered nearly 90% of ammonia from urea containing wastewater. Liao et al. (1995) recovered 90-93% of ammonia from swine wastewater.

4.4 Conclusions

In this chapter, urinary ammonia was stripped with air which was bubbled through sulphuric acid solution to obtain ammonium sulphate solution. The amount of ammonia which was recovered as ammonium sulphate was directly related with the stripping efficiency. Lower stripping efficiency resulted lower recovery percentages. In this study, the efficiency of stripping is determined in terms of the product of overall mass transfer coefficient and interfacial area $(K_L \times a)$ and mass transfer rate (F_A). Based on the results, following conclusions can be expressed:

✓ An increase in operational pH resulted higher $(K_L \times a)$ values and higher overall mass transfer rates.

✓ Combined mass transfer coefficient $(K_L \times a)$ increased from 0.098 h^{-1} to 0.204 h^{-1} as the operational pH was raised from 11 to 12. Higher operational pH such as 13.5 reduced the value of $(K_L \times a)$. Therefore, optimum pH was determined as 12.

✓ A direct relationship between the air flow rate and $(K_L \times a)$ was observed during the experiments.

✓ An increase in air flow rate reduced the time needed for efficient stripping at room temperature.

✓ The amount of ammonia that was transported from urine to air in 1 h was higher than 0.085 g, when the air rate was 0.21 $m^3.h^{-1}$. It can be generalized that higher air flow rates enhanced the desorption of ammonia which resulted higher mass transfer rates.

✓ Nearly 93% of urinary ammonia was stripped in 5 h, when the initial pH was 12 and the air rate was adjusted as 0.21 $m^3.h^{-1}$.

In this study, stripping and absorption operations were introduced for the recovery of the urinary ammonia. Ammonium sulphate which is a valuable fertilizer was easily obtained in crystalline form. Using the ammonium sulphate solution as a liquid fertilizer can be suggested in order to prevent the loss from the crystallization process. Besides, the total cost of the recovery system can be lowered.

Consequently, a pilot scale is suggested where the ammonia nitrogen in storage tanks can be transported with air fans to a nearby absorption unit where it can react with sulphuric acid to yield ammonium sulphate. The total system can easily be operated and maintained by using simple controlling items.

5. COMPARISON OF URINE-BASED FERTILIZERS WITH COMMERCIAL FERTILIZERS

The main aim of the present study was to obtain a urine-based fertilizer (a bio-fertilizer) which would be an alternative for artificial mineral fertilizers. Thus, struvite precipitated from urine and ammonium sulphate obtained from stored urine should be compared with artificial mineral fertilizers. Because of this, a general introduction about mineral fertilizers and their environmental effects is given below, in order to make a fair comparison between the artificial mineral fertilizers and urine-based fertilizers.

Plants live, grow and reproduce by taking carbon dioxide from the air, energy from the sun, water and mineral substances from the soil. Plants contain practically all (92) of the elements known to occur in nature, but only 16 are needed for good growth and, of these, 13 are absolutely essential. These mineral nutrients are often classified as either major plant nutrients (nitrogen, phosphorus, potassium, calcium, magnesium and sulphur) because they are required in large amounts, or “micro nutrients” (boron, chlorine, copper, iron, manganese, molybdenum and zinc) which are only required in trace amounts. Soils to which plant nutrients have never been added will invariably be unable to supply enough nutrients to produce optimum yields. To meet this requirement, fertilizers should be added, because healthy plants require a balanced nutrition (EFMA, 2000-a).

Numerous mineral fertilizers have been developed to supplement soil nutrients and to meet the high requirements of crops. They are generally mineral salts, except for some organic chemicals such as urea which are easily converted into salts.

In recent years, there has been concern that the quantitiy of mineral fertilizers used in agriculture is having adverse effects on the environment. Attention has been drawn to the fact that when nutrients are applied to crops they are not all taken up by the plants immediately. There is also concern that some farmers might be applying inappropriate quantities of fertilizer. The nutrients applied may leak to environment where they can cause pollution (EFMA, 1997). The problems of fertilizer usage can be classified as follows;

- Dangerous or even toxic substances in fertilizer can accumulate in soil. Most of the artificial fertilizers used today are produced from the phosphate rocks. Phosphate rocks contain various heavy metals such as cadmium and chromium and their presence in the rock depend on the geological origin and the mining location (Al-Shawi and Dahl, 1999). But high price of the high quality phosphate rock lead people to use low quality phosphate rock which contains heavy metals rather than phosphate (De-Bashan and Y. Bashan, 2004).
- Nutrients which are leached from soil causes eutrophication of surface water, with its negative effect on oxygen supply (damaging to fish and other forms of animal life) (Zhang et al., 2003; McDowell and Sharpley, 2004).
- Nitrogen based fertilizers mainly causes nitrate accumulation in groundwater while diminishing the quality of drinking water (Maeda et al., 2003).
- Excessive or wrongly placed N fertilizer causes unwanted enrichment of the atmosphere with ammonia (Bouwman and Van Der Hoek, 1997; Goebes et al., 2003).

5.1 Struvite As A Fertilizer

Struvite is a well known but rarely utilized slow release fertilizer (De-Bashan and Y. Bashan, 2004). In slow release fertilizers nutrients are released at a slower rate throughout the season and plants are able to take up most of the nutrients without waste by leaching. Because of this, slow release fertilizers are excellent alternatives to soluble fertilizers.

The presence of magnesium in struvite makes it attractive for a few crops like sugar beets that require magnesium. It is also reported that mixing the struvite with phosphoric acid might yield a superior fertilizer (De-Bashan and Y. Bashan, 2004).

Although struvite is known to be a non-burning slow release fertilizer, the commercial production of struvite for agriculture is rare (Liberti et al, 2001). The cost of the production is reported to be the main obstacle that the producers face with. The cost of the production can be decreased by using the wastewater as a source of phosphorus and nitrogen. The only full scale plant for the production of struvite from wastewater is in Japan. "Shimane Prefecture Lake Shinji East Clean Centre" has been producing struvite from wastewater and it has been selling this product under the brand names of "AGRIYUKI MAP AJIGEN" and "HIYAKU-MAP"(Ueno and Fujii, 2001). These fertilizers are reported to be used on paddy rice, vegetables and flowers. Struvite based fertilizer products used in Japan are illustrated in Figure 5.1 and 5.2.

- Good Lustre, Good taste, Good flavour
- Matured amino-acid fertilizer plus MAP
- Specialist fertilizer for good taste rice
- Authentic granular fertilizer combination of MAP, a non-stress fertilizer and amino-acid fertilizer
- 20 kg bag
- Guaranteed content (%)
- Nitrogen (of which organic-N and MAP-N)-Phosphorus –Magnesium 10 (of which 2.5 and 1.0)-10-10-2.5

Figure 5.1: Struvite fertilizer produced in Japan (Ueno and Fujii, 2001).

- Chemical fertilizer No.8 containing MAP and organic
- Authentic granular organic fertilizer combination of MAP, a non-stress fertilizer and amino-acid fertilizer.
- Guaranteed content (%)
- Nitrogen (of which organic-N and MAP-N)-Phosphorus- Potassium-Magnesium 8 (of which 3 and 1.5)-10-8-4

Figure 5.2: Struvite fertilizer produced in Japan (Ueno and Fujii, 2001).

Although there are many studies that concerns struvite precipitation from various media such as wastewater, swine manure, anaerobic liquors etc.; there are no studies that concern short and long term effects of struvite on soil.

It is clear that structure of struvite is not a stranger to soil chemistry. But, if the struvite is obtained from complex liquors such as urine, the composition of the struvite can differ from the original pure struvite. In this situation, struvite must be characterized and compared with commercial fertilizers. The complete characterization of struvite obtained from both fresh and stored urine was detailed in Chapter 2 and Chapter 3.

The cost of the production of urine-based struvite depends if the urine is fresh or stored. Actually, we have no chance to choose. Because in real urine-separation systems, urea hydrolysis starts in the pipes and ends in the tank in one day. Therefore, most of the nitrogen in urine is in the form of ammonia. But the spontaneous precipitation of Ca and Mg salts only happens during the storage. For the struvite precipitation from fresh urine , the main production cost comes from the raw materials such as magnesium source and sodium hydroxide. In the case of struvite from stored urine, the cost of the production depend on the cost of raw materials such as magnesium and phosphorus salts.

Struvite obtained from urine is odorless and white in color although urine has a characteristic odor and dark brown color. These physical characteristics also make the urine-based struvite preferable against urine.

Whether stored or fresh urine is used as a source of nutrients, urine-based struvite always contains impurities such as Ca, K and Zn. But, the presence of Ca, K and Zn in struvite is not a problem since these elements are essential for plant nutrition. Other elements such as Na, Al, Si and Mn are also detected qualitatively. We know that these impurities come from urine itself. Because of that, the concentrations of these metals in struvite is so low and can not be measured quantitatively. But their presence does not creat a problem since they have a very little amount in struvite.

The main advantage of urine-based struvite is its purity with respect to heavy metals such as chromium and cadmium. Most of the low quality phosphate rocks contain high amounts of heavy metals. Using that kind of fertilizer in agriculture results heavy metal accumulation in plants. But, urine-based struvite is nearly free from the heavy metals.

Urine might contain pharmaceutical residues and these residues might adsorb on precipitate or make complexes with constituent ions. Literature survey indicates that among the drug families only bisphosphonates, quinolones and tetracyclines are susceptible to form stable complexes with Mg^{2+} and Ca^{2+} (Brion et al., 1981; Novák-Pékli et al., 1996; Vartanian et al., 1998; Tolls, 2001; Hamscher et al., 2002; Turel, 2002; El-Kommas et al., 2003). It is obvious that among these drugs mentioned above antibiotics possess a higher risk for ecology. Many studies concerning the fate of antibiotics in the soil media indicates that residues of pharmaceutical antibiotics can provoke resistance in pathogens (Thiele-Bruhn, 2003). The resulting antibiotic residues and resistant microorganisms can affect the natural soil microbial community and soil functions and may even harm animals and humans via the food chain (Thiele-Bruhn, 2003). Because of these risks, tetracyclines and quinolones are the compounds that must be investigated in order to find out their transmission risks. But the precipitation studies with tetracyclines revealed that this compound can not coprecipitate with struvite easily (Başakçılardan-Kabakcı et al, in preparation).

As a conclusion, urine-based struvite can be suggested as a good bio-fertilizer. Because, urine-based struvite;

- ✓ has a low solubility,
- ✓ contains considerable amounts of N, P and Mg,
- ✓ contains Ca, K and Zn in small amounts,
- ✓ is almost free from heavy metals such as Cd and Cr,
- ✓ is thought to be free from pharmaceutical residues,
- ✓ is thought to be free from microorganisms which die off at high pH values,
- ✓ is produced from urine which reduces the cost.

5.2 Ammonium Sulphate As A Fertilizer

Ammonium sulphate is a well known commercial fertilizer which is produced by three different processes:

- as a by-product of caprolactam ($(CH_2)_5COHN$) production,
- synthetic manufacture from pure ammonia and concentrated sulphuric acid,
- as a coke oven byproduct.

Among these processes, manufacturing from pure ammonia and sulphuric acid is the most frequently used. Ammonia is produced basically from water, air and energy. Two main types of production process for ammonia synthesis gas are currently in operation in Europe:

- Steam reforming of natural gas or other light hydrocarbons (natural gas liquids, liquified petroleum gas, naphtha)
- Partial oxidation of heavy fuel oil or vacuum residue.

The energy source is usually hydrocarbons, thus providing hydrogen as well, but may also be coal or electricity. Steam reforming of light hydrocarbons is the most efficient route, with about 77% of world ammonia capacity being based on natural gas (EFMA, 2000-b).

Ammonia is reacted with sulphuric acid under certain conditions. After formation of the ammonium sulphate solution, manufacturing operations of each process which are given in the first paragraph are similar. Ammonium sulphate crystals are formed by circulating the ammonium sulfate liquor through an evaporator. Evaporation of the water thickens the solution. Ammonium sulphate crystals are separated from the liquor in a centrifuge.

Ammonium sulphate production from ammonia synthesis gas and sulphuric acid is not easy and cost effective. Besides, production of ammonia always depends on the natural sources. Based on the known resources of fossil raw materials, it is likely that natural gas will dominate as the feedstock for ammonia for the next 50 years at least. In the very long term, 50-200 years, one might expect coal to take over, based on world reserves and consumption rate. Heavy oil may be attractive under special environmental concerns, when natural gas is not available and the partial oxidation process could solve a waste problem (EFMA, 2000-b).

The other disadvantage of ammonium sulphate production is the emissions and wastes that are generated during the production. The major emissions into air come from steam reforming plants. The most important ones are indicated below:

- Flue gas from the primary reformer.
- Vent gases from CO_2 removal.
- Breathing gas from oil buffers (tracer of NH_3, synthesis gas and lube oil).

- Fugitive emissions (diffuse emissions from flanges, stuffing boxes etc.).
- Purge and flash gases.

The other emission sources are heat exchange reforming and partial oxidation plants. Besides, pollution problems related to water occur due to process condensates or due to the scrubbing of waste gases containing ammonia.

It is obvious that production of ammonium sulphate from natural sources is not environmental friendly and economic. On the other hand, a nitrogen rich stream is produced everyday as a result of human metabolism. Source separation system presents a great chance to recycle the urinary nutrients to agriculture. Besides, there is no need for energy (except the energy need for air pumping) and natural resource consumption.

Ammonium sulphate production from urine is not easy but small on-site units next to urine storage tanks can be a good approach. With the results that we had in Chapter 4, we can propose a production unit which produces urine-based ammonium sulphate. The schematic representation of the proposed system is shown in Figure 5.3.

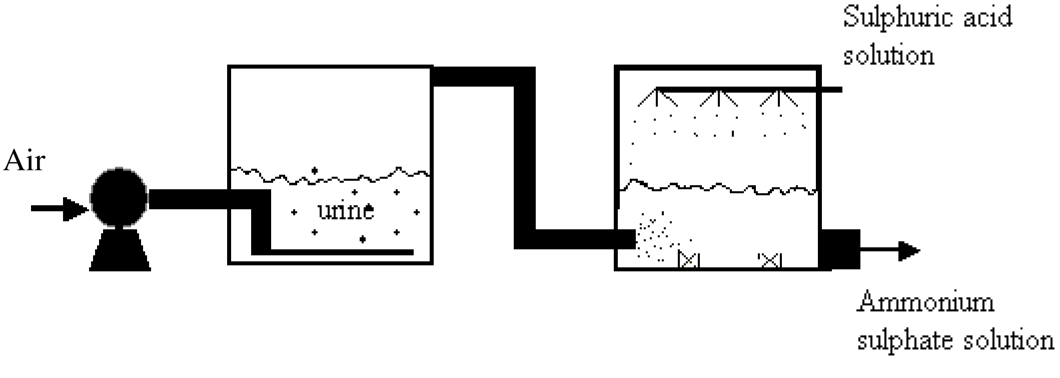

Figure 5.3: Schematic representation of the proposed system of urinary ammonium sulphate production.

Proposed system consists of two tanks which are connected together by a pipe. First tank, which should have a level and pressure controller store the urine. An air blower should be connected to the first tank which introduces the air bubbles.

When the urine reaches a desired level, the air should be pumped and ammonia-air mixture should be transported to the second tank where it is washed with dilute sulphuric acid (or water). The schematic representation of the proposed system is shown in Figure 5.3.

The system should work when the urine level reaches a desired value. Otherwise, obtained ammonia-air mixture may have a lower concentration with respect to ammonia. Urine residue in the first tank can be pumped into trucks and emptied to a land. This residue must not be used for the agricultural purposes, it may be a good biomass for energy production.

The absence of an evaporator is logical since the proposed system is thought to be installed on farmlands. Adjusting the ratio of dilute sulphuric acid: ammonia needs special care but it is still beneficial instead of using evaporator. The proposed system will also have disadvantages such as difficulties in maintainance but its advantages for rural area are more attractive.

There are many advantages of producing urine-based ammonium sulphate. Because,

✓ ammonium sulphate is an efficient fertilizer if it is used in correct amounts and in appropriate seasons,

✓ ammonium sulphate solution obtained from urine is free from heavy metals and other contaminants such as pharmaceutical residues,

✓ urine is a very cheap resource for the production of ammonia,

✓ there is no need for fossil fuel, air and water to produce ammonia. Only source separation system (toilets, pipes and tanks) and controllers are enough,

✓ the cost of production is not affected from the oil prices. Thus, the cost of the production is stable,

✓ farmers can produce their own fertilizer without paying any money for commercial ones.

6. CONCLUSION

This thesis introduced struvite precipitation process and stripping/absorption operation in order to transform the urinary nutrients into valuable fertilizer.

As previously indicated, struvite precipitation process was applied to both waterless fresh urine and diluted-stored urine. In Table 6.1, optimum process conditions of precipitation reactions that were achieved in both waterless fresh urine and diluted-stored urine were compared. Same illustration also compares the purity of the precipitates.

Table 6.1: Comparison of struvite precipitation in fresh urine and diluted-stored urine.

	Struvite precipitation in fresh urine	**Struvite precipitation in diluted-stored urine**
Handling conditions	Waterless fresh urine is used.	Diluted and stored urine is used.
Aim of the process	Struvite precipitation from fresh urine aims to recover urinary phosphorus.	Struvite precipitation from stored urine aims to recover ammonia nitrogen.
Optimum pH	pH 9 is the optimum pH.	pH 9.5 is the optimum pH.
Optimum initial molar ratio of reactants	Mg:P ratio affects the precipitation efficiency. Because it directly controls the formation of amorphous calcium phosphate phase.In order to force the formation of struvite, Mg:P ratio should be maintained between 1 and 1.5. Excess Mg is a necessity to depress amorphous calcium phosphate phase.	N:P:Mg ratio affects the contribution of reactants. But this effect is not as strong as it was observed in undiluted waterless fresh urine due to calcium absence in stored urine. In order to enhance the contribution of reactants to struvite, N:P:Mg ratio should be 1:1:1.3. Excess Mg increases the contribution of both N and P.

Recovery percentages	Under prescribed conditions (pH:9, t_{opt}:1 hr, Mg:P=1.5), 95% of P, 45% of N and 60% of Ca is recovered.	Under prescribed conditions (pH:9.5, t_{opt}:1hr, N:P:Mg = 1:1:1.13), 98 % of P (urinary P + reactant based P), 92% of urinary N is recovered.
Precipitate	Struvite and amorphous calcium phosphate are the main phases found in the precipitate.	Struvite is the main phase that exists in the precipitate.
C, H and N content of precipitate	Due to amorphous calcium phosphate phase contribution, the N content of the precipitate is below its theoretical value. Nearly 4.7% of precipitate is N, 5.7% of precipitate is H and 0.75% of precipitate is C.	Since the main phase is struvite, the weight percentages of H and N are close to their theoretical values. Nearly 6.3% of precipitate is H, 5.2% of precipitate is N and 0.17% of precipitate is C.
Inorganic impurities	Na, Al, S,K, Ca, Zn, Sr and Ba are detected in the precipitate.	Na, Al, S, K, Ca, Zn, Sr, Ba, Mn and Fe are detected in the precipitate.
Further treatment	Struvite precipitation from waterless fresh urine is not a complete solution for the recovery of nutrients since urinary urea and small portion of ammonia nitrogen is left. Therefore, there must be another treatment which involves the recovery of nitrogen.	Struvite precipitation from stored urine involves the recovery of ammonia nitrogen and also phosphorus. Thus, residual urine is poor with respect to N and P. But the residual urine which is rich in K, Na and Cl needs further treatment.

According to results, struvite precipitation process can be regarded as a suitable technology to recover phosphorus and nitrogen from urine. It is clear that struvite obtained from hydrolyzed urine is superior to struvite that is obtained from waterless fresh urine. Another advantage is that the residual hydrolyzed urine (hydrolyzed urine which is left after precipitation reaction) does not require further nutrient removal. The main drawback of the method is the cost of amendments ($MgCl_2.6H_2O$, $NaH_2PO_4.2H_2O$) which becomes much more significant if hydrolyzed urine is used as a source of ammonia nitrogen.

As summarized in Chapter 3, ureolysis is observed in all source separation system which is the combination of toilet, collecting pipes, holding tank and storage tank.

Although acid addition is suggested to slow the ureolysis reaction, it is not an efficient method to prevent ureolysis. Thus, the recovery of urinary nutrients must be achieved in hydrolyzed urine. In real urine collecting systems urea is completely hydrolyzed in one day and almost all of the nitrogen is in the form of dissolved ammonia. Due to high pH and high ammonia content, struvite precipitation and stripping/absorption processes seem to be the efficient methods to recover ammonia nitrogen. To decide which of the methods is the best applicable, struvite precipitation process and ammonia stripping/absorption operations were achieved in diluted-stored urine. Table 6.2 compares struvite precipitation in hydrolyzed urine and stripping / absorption operations in terms of optimum operational conditions and percentage recovery of the constituent ions.

Table 6.2: Comparison of struvite precipitation and stripping/absorption operations.

	Struvite precipitation from stored urine	**Stripping of urinary ammonia / ammonia absorption in sulphuric acid**
Handling conditions	4 times diluted and stored urine is used.	4 times diluted and stored urine is used.
Aim of the process	Struvite precipitation from stored urine aims to recover ammonia nitrogen.	Stripping/absorption operations aim to recover ammonia nitrogen.
Optimum pH	pH 9.5 is the optimum pH.	pH 12 is the optimum pH for stripping of ammonia.
Parameters that affect the efficiency	Only reaction pH and Mg:P ratio affect the precipitation efficiency. Optimum Mg:P ratio is between 1 and 1.5.	Stripping efficiency is directly affected from the pH and air flow rate. Optimum air flow rate is 0.21 $m^3.h^{-1}$.
Recovery percentages	Under prescribed conditions (pH: 9.5, t_{opt}:1h, N:P:Mg =1:1:1.13), 92% of urinary N is recovered.	Under prescribed conditions (pH:12, air rate per unit volume of urine = 1166 h^{-1}), 90% of urinary ammonia nitrogen is recovered.

Precipitate/ Crystal	Struvite is the main phase that exists in the precipitate.	Ammonium sulphate is crystallized by simple evaporation and cooling.
Further Treatment	Struvite precipitation from stored urine involves the recovery of ammonia nitrogen and also phosphorus. Thus, residual urine is poor with respect to N and P. But the residual urine which is rich in K, Na and Cl needs further treatment.	After stripping and absorption processes, urine is still containing P and K. Furthermore, stripping operation brings evaporation problems due to high air flow rates. Thus, the residual urine is also concentrated with respect to P, K, Na and Cl.

Obviously both of the methods yield satisfying results. Although they both aim nitrogen recovery, struvite precipitation becomes much more beneficial with its capability to recover phosphorus. As indicated in 4th chapter, resultant ammonium sulphate solution can be used as in solution form or as in crystal form. Crystallizing ammonium sulphate from ammonium sulphate solution requires subsequent heating and cooling which brings additional cost to the system. But if aqueous ammonium sulphate is preferred, storage and transportation problems will likely occur. Therefore struvite precipitation from hydrolyzed urine is again one step front of stripping/absorption operations.

7. RECOMMENDATIONS AND FUTURE WORK

This thesis presented a research of nutrient recovery from human urine in order to overcome the difficulties related with the storage and spreading of urine.

Struvite precipitation was introduced as a promising method for the recovery of urinary nutrients. Because, urinary ammonia, phosphate and magnesium were recovered as struvite which is a well known slow release fertilizer. Furthermore, struvite precipitation also gave us a great chance to recover K, Ca and Zn.

Stripping-absorption-crystallization methods were declared as an efficient combined method for the recovery of ammonia in stored urine. This combined method gained a greater importance since the storage of human urine is a necessity, which lowers the available concentration of phosphates and increases the ratio of N:P. In other words, this combined method which focused on ammonia recovery was introduced as an alternative for struvite precipitation from the stored urine.

Although this research extensively investigated the nutrient recovery, there are still gaps in total source separation system. Following the investigations described in this thesis, a number of projects could be progressed in the future. Some of these research topics which are related with struvite precipitation and stripping/absorption are listed below:

- Finding an appropriate treatment method for the residual urine which remains after struvite precipitation process and stripping/absorption operations.
- Investigating a method in order to recover phosphate and potassium from stored urine before the stripping/absorption operations.
- Using the urine-based fertilizers (urine-based struvite and urine-based ammonium sulphate) in a pilot area to observe their fertilizing ability.
- Building a pilot scale ammonium sulphate and struvite production plant in an ecological village that uses source-separation system.

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