REMOVAL AND RECOVERY OF NUTRIENTS AS STRUVITE FROM ANAEROBIC DIGESTION/CO-DIGESTION RESIDUES OF POULTRY MANURE

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REMOVAL AND RECOVERY OF NUTRIENTS AS STRUVITE FROM ANAEROBIC DIGESTION/CO-DIGESTION RESIDUES OF POULTRY MANURE

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ABSTRACT

REMOVAL AND RECOVERY OF NUTRIENTS AS STRUVITE FROM ANAEROBIC DIGESTION/CO-DIGESTION RESIDUES OF POULTRY MANURE

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The main objective of this study was to investigate the removal and recovery of nutrients from anaerobic digestion residues of poultry manure through struvite ($MgNH_4PO_4.6H_2O$, MAP) precipitation. To this purpose, three sets of laboratory experiments were conducted.

In the first set, separate and co-digestion of poultry manure and sewage sludge were studied in laboratory-scale mesophilic anaerobic batch reactors and subsequent struvite precipitation experiments were conducted with the reactors effluents. The effects of important parameters on struvite precipitation were investigated and it is illustrated that up to 89 % of NH_4-N, 84 % PO_4-P and 42 % COD removals were possible. In the second set, the effluents of a full-scale co-digestion plant utilizing poultry manure and maize silage were subjected to struvite precipitation experiments. Acidic phosphorus-dissolution process was successfully applied to the solid phase effluents to obtain phosphorus-enriched solution. By the addition of external Mg and P more than 90% of NH_4-N and PO_4-P were recovered from phosphorus-enriched solution, whereas the addition of only Mg led to partial recovery of NH_4-N. In the third set, the effluents of a full-scale poultry manure digester were subjected to struvite precipitation experiments. The findings illustrated that Ca has inhibitory effects on the struvite reaction and lead to formation of hydroxlyapatite and amorphous calcium phosphates together with struvite.

Based on the results obtained in this study, it is postulated that, struvite precipitation is a viable option for the recovery of the nutrients in the anaerobically digested poultry manure. This study illustrated that, poultry manure, if managed properly, could meet one-fourth of Turkey's domestic fertilizer demand.

Keywords: Anaerobic Digestion, Poultry Manure, Nutrient Recovery, Struvite, Phosphorus Dissolution.

ÖZ

ANAEROBİK OLARAK TEK BAŞINA/BİRLİKTE BOZUNDURULMUŞ TAVUK GÜBRESİ ARTIKLARINDAN STRÜVİT ŞEKLİNDE NÜTRİENT GİDERİMİ VE GERİ KAZANIMI

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Çalışmanın temel amacı, anaerobik olarak bozundurulmuş tavuk gübresi artıklarından strüvit ($MgNH_4PO_4.6H_2O$, MAP) çöktürmesi yöntemi ile nütrient giderimi ve geri kazanımını araştırmaktır. Bu amaçla, üç set laboratuar deneyi gerçekleştirilmiştir.

Birinci sette, tavuk gübresi ve evsel atık çamurun tek başına ve birlikte bozundurulması laboratuar ölçekli mezofilik anaerobik kesikli reaktörlerde çalışılmış ve reaktör çıktıları ile strüvit çöktürme deneyleri yapılmıştır. Strüvit çöktürmesine etki eden önemli parametrelerin etkileri incelenmiş ve en yüksek olarak NH_4-N'de % 89, PO_4-P'de % 84 ve KOİ'de % 42 giderimin mümkün olduğu gösterilmiştir. İkinci sette, tavuk gübresi ve mısır silajının birlikte bozundurulduğu büyük ölçekli bir tesisin çıktıları ile strüvit çöktürme deneyleri yapılmıştır. Tesisin katı faz çıktısına asitli fosfor çözünmesi prosesi, fosforca zenginleştirilmiş sıvı elde edebilmek amacıyla başarılı bir şekilde uygulanmıştır. Dışarıdan Mg ve P eklenmesi ile fosforca zenginleştirilmiş sıvıdaki NH_4-N ve PO_4-P'nin % 90 dan fazlası geri kazanılırken, yanlızca Mg eklenmesi kısmi NH_4-N geri kazanımına yol açmıştır. Üçüncü sette, büyük ölçekli bir tavuk gübresi bozundurma tesisinin çıktıları ile strüvit çöktürme deneyleri yapılmıştır. Bulgular Ca'nın strüvit reaksiyonu üzerinde inhibe edici etkilerinin olduğunu ve strüvit ile birlikte hidroksilapatit ve amorf kalsiyum fosfatların çökmesine yol açtığını göstermiştir.

Bu çalışmada elde edilen sonuçlar temel alındığında, strüvit çöktürmenin anaerobik bozundurulmuş tavuk gübresinde bulunan nütrientlerin geri kazanımı için uygulanabilir bir seçenek olduğu savunulmaktadır. Bu çalışma, tavuk gübresinin uygun şekilde yönetildiği koşulda, Türkiye'nin yerli gübre ihtiyacının dörtte birini karşılayabileceğini göstermiştir.

Anahtar Kelimeler: Anaerobik Bozundurma, Tavuk Gübresi, Nütrient Gerikazanımı, Strüvit, Fosfor Çözünmesi.

To my brother...

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ABBREVIATIONS

ACP : Amorphous Calcium Phosphate
AD : Anaerobic Digestion
BM : Basal Medium
CA : Citric Acid
COD : Chemical Oxygen Demand
EDS : Energy Dispersive Spectroscopy
F/M : Food to Microorganisms Ratio
GC : Gas Chromatograph
H-Ac : Acetic Acid
HAP : Hydroxylapatite
H-Bu : n-Butyric Acid
H-Pr : Propionic Acid
HRT : Hydraulic Retention Time
H-Va : n-Valeric Acid
LCFAs : Long Chain Fatty Acids
MAP : Magnesium Ammonium Phosphate
METU : Middle East Technical University
MLSS : Mixed Liquor Suspended Solids
MLVSS : Mixed Liquor Volatile Suspended Solids
NH_4-N : Ammonia Nitrogen
OCP : Octa Calcium Phosphate
PAOs : Phosphorus Accumulating Organisms
PDF : Powder Diffraction File
PO_4-P : Orthophosphate
sCOD : Soluble Chemical Oxygen Demand
SEM : Scanning Electron Microscopy
TKN : Total Kjeldahl Nitrogen
TP : Total phosphorus
TS : Total Solids
TSS : Total Suspended Solids

UST	: University of Stuttgart
VFA	: Volatile Fatty Acid
VS	: Volatile Solids
WWTP	: Waste Water Treatment Plant
XRD	: X-ray Diffraction

CHAPTER 1

INTRODUCTION

As the world economy is currently facing a severe global crisis, the world focuses on finding immediate solutions to severe economic challenges. That is why environmental sustainability is taking a secondary position. However, it is obvious that environmental concerns are more urgent now, since long-term prosperity cannot be achieved without sustainable environmental management. A major step for the development of such a system is to shift society's dependence on fossil carbon sources to the use of renewable resources for the production of energy and goods (Angenent et al., 2004; Ragauskas et al., 2006).

Livestock manure as a renewable resource, if managed properly, can serve as a raw material for fertilizer industry. The conventional approaches dealing with livestock manure are the direct land application of the manure, spreading of nutrient rich wastewater on cropland and dumping it directly to the receiving water bodies (Beal et al., 1999; Yılmaz and Demirer, 2008; Yetilmezsoy and Şapçı-Zengin, 2009). However, these practices result in loss of nutrients and lead to severe environmental problems. The most common problems directly linked to the disposal of untreated manure are odor formation, methane and ammonia emissions, the release of nutrients and pathogens that may affect human health and aesthetic problems (Salminen et al., 1999; Yılmaz and Demirer, 2008).

Anaerobic digestion (AD) is an established livestock manure bioconversion technology (Hobson and Wheatley, 1993; Lusk, 1998; Demirer et al., 2000; US Environmental Protection Agency, 2002; Güngör-Demirci and Demirer, 2004; Uludağ-Demirer et al., 2008) and due to high nutrient content, the anaerobic digester effluents can be used as a liquid fertilizer. However, the unavailability of land area to which the liquid fertilizer can be applied, does not enable effective application of AD effluents and cause several environmental problems such as eutrophication. Therefore, in order to avoid adverse environmental impacts due to overapplication of AD effluents on limited land or leaching of liquor into the groundwater, the nutrients must be completely or partially removed.

Moreover, the recovery of nutrients from the anaerobically digested manure is a potential source of revenue. Crystallization of N and P in the form of magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4.6H_2O$, struvite) is one of the possible techniques applicable for this purpose. Because struvite can be used in agriculture as fertilizer and is preferred for numerous reasons, struvite precipitation from AD effluents was investigated in this study.

Although variety of studies about the struvite precipitation and accompanied removal/recovery of P and N from the effluents of anaerobically digested animal manure has been conducted previously by many researchers (Schuiling and Andrade, 1999; Burns et al., 2001; Nelson et al., 2003; Uludağ-Demirer et al., 2005), there is only one study investigating the struvite precipitation process from anaerobically digested poultry manure (Yetilmezsoy and Şapçı-Zengin, 2009). Nutrient recovery from anaerobically digested poultry manure is a viable option because poultry manure is rich in nutrients and large amounts of waste is produced due to the growing demand for poultry production. In order to fill this gap in the literature, this study aimed removal/recovery of nutrients from both the liquid and solid phases of the anaerobically digested poultry manure.

To this purpose, three sets of laboratory experiments were conducted. In the first set, because there is no full-scale poultry manure digester in Turkey separate and co-digestion of poultry manure and sewage sludge were studied in laboratory-scale anaerobic mesophilic batch reactors. Struvite precipitation experiments were conducted in the liquid phase of the reactor effluents. In the second set, effluents of a full-scale biogas plant co-digesting poultry manure and maize silage were subjected to struvite precipitation experiments. The liquid phase of the full scale effluent was directly used in the struvite precipitation experiments whereas the solid phase of the effluent was subjected to phosphorus-dissolution process prior to struvite precipitation experiments. In the third set, struvite precipitation experiments were conducted in both the liquid and solid phases of the effluent of a full-scale biogas plant digesting poultry manure. In the struvite precipitation experiments the effect of molar ratio of constituent ions, pH, phosphorus source, seeding and the presence of foreign ions were investigated.
Additionally in the third set, complexation of foreign ions prior to struvite precipitation experiments was investigated.

CHAPTER 2

LITERATURE REVIEW

2.1 Quantities and Characteristics of Poultry Manure

The poultry and livestock industries are growing rapidly, and this leads to large quantities of animal waste products. According to the US Department of Agriculture and Economic Research Service (2008) US consumption of chicken averaged 39 kg per person in 2006; more than triple the 1960 level. Atuanya and Aigbirior (2002) reported that the poultry production is fastest growing cottage industry and estimated the annual solid waste generation from poultry farms at millions of tons. According to the statistics given by the Ministry of Agriculture, Forestry and Fisheries of Japan, the annual production of chicken manure from layer and broiler farms is about 13 million tons (Abouelenien et al., 2009; MAFF, 2008). Moreover, Güngör-Demirci and Demirer (2004) reported that the production of cattle and poultry manure was approximately 20 million tons dry matter in 2000 in Turkey.

The main constituents of poultry manure are the feces and urine; however feces and urine may be mixed with bedding, hair, feathers, blood, bone, feed wastage and soil. This result in a manure with properties considerably different from fresh manure, which contains only feces and urine (OSU Extension, 2006). The amount and composition of manure excreted per unit of time vary widely according to the total live weight of the animal, animal size and age, feed and water intake etc. (Polprasert, 1996). Simmons et al. (1987) worked on the variability of manure production rates for growing broilers and developed a model for predicting manure production based on bird growth stage. Table 2.1 gives the ratio of fresh manure weight generated daily per animal body weight, along with dry solids level.

Table 2.1 Fresh poultry manure production and characteristics per animal type (Adopted from OSU Extension, 2006)

Animal Type	Animal Size, kg		Nutrient Content					Daily Manure	Daily Nutrients				
		Ratio	TS	VS	N	P	K	weight	TS	VS	N	P_2O_5	K_2O
		Wm/Wa	% db	% db	% db	% db	% db	g/day	g/day	g/day	g/day	g/day	g/day
Layer	1.8	0.065	25	75.4	5.38	4.15	2.46	118	29	23	1.59	1.22	0.73
Broiler	0.9	0.090	26	72.3	4.91	2.99	2.35	82	21	14	1.27	0.64	0.50
Turkey	9	0.045	25	76.0	5.60	4.80	2.40	408	102	77	5.71	4.90	2.45
Duck	2.7	0.055	27	59.6	5.16	4.26	3.14	150	40	23	2.08	1.72	1.27

Wm = daily weight of manure, Wa = average weight of animal during this stage of production, TS = total solids, VS = volatile solids, % wb = percent wet basis, and % db = percent dry basis. To convert manure weights to gallons, divide by 8.3. P_2O_5 = 2.273 x P and K_2O = 1.205 x K.

Poultry manure is regarded as a valuable source of nutrients for crops and can improve soil productivity due to its high nutrient content (Sakar et al., 2009). However, even within a specific operation, the characteristics of the manure will be influenced greatly by the ration, the use of bedding, the manure handling system. Therefore, variations of ±20% can occur in the characteristics of different poultry manures due to high dependency on feed digestibility and nutrient feeding levels of the animal (OSU Extension, 2006). Table 2.1 depicted the characteristics of fresh manure, solids, and quantities of N, P_2O_5, and K_2O produced daily per animal type.

Values in Table 2.1 are averages for individual animals being fed according to National Research Council Guidelines (OSU Extension, 2006). The study of Moffitt and Lander (1997) combined four data bases; namely Midwest Plan Service (MWPS), Natural Resources Conservation Service (NRCS), American Society of Agricultural Engineers (ASAE) and North Carolina State University (NC State) for the characterization of animal manures. Table 2.2 depicted the characteristics of different animal manures adopted from the study of Moffitt and Lander (1997). As depicted in Table 2.2 the highest nutrient content belongs to the poultry manure in comparison to the other animal manures. Apart from nitrogen, phosphorus and potassium, poultry manure contains 10 essential plant nutrients that are used by plants. These include calcium (Ca), magnesium (Mg), copper (Cu), sulphur (S), manganese (Mn), copper (Cu), zinc (Zn), chlorine (Cl), boron (B), iron (Fe) and molybdenum (Mo) (Chastain et al., 2004). These may originate from the feed, supplements, medications, and water consumed by the animals (Chastain et al., 2004).

Table 2.2 Annual as excreted manure (Adopted from Moffitt and Lander, 1997)

Animal Type	Avg wt. (kg)	# animals per AU*	Tons manure per AU	N	P	K
				kg/ton manure		
Dairy						
Milk cow	612	0.74	15.24	4.85	0.87	3.04
Heifers	249	1.82	12.05	2.75	0.59	2.28
Beef						
Steer - Bulls - Calves	295	1.54	10.59	4.98	1.53	3.57
Cows	454	1	11.5	4.97	1.72	3.72
Hogs and Pigs						
Grower	50	9.09	14.69	5.13	1.49	3.61
Breeder	170	2.67	6.11	6.01	1.94	3.56
Sows and litters	-	-	-	-	-	-
Poultry						
Broilers	1.0	454.55	14.97	12.17	3.54	4.76
Layers	1.8	250	11.45	12.22	4.52	4.74
Turkeys	6.8	66.67	8.18	13.77	5.37	5.27
Sheep	36	12.5	7.24	9.99	1.66	7.20

* AU:1000 pound animal unit

2.2. Treatment and Utilization of Poultry Manure

Direct land application of manure is the most preferred method of utilization, but it is not always feasible. If the land to be used for application is distant or the location is sensitive to odor, some type of manure treatment may be required (OSU Extension, 2006). Treatments may help to improve the physical and chemical properties of the waste, solve odor problem, recover nutrients or energy from manure, increase the fertilizer value and reduce the volume and its phytotoxicity (Salminen et al., 2001; OSU Extension, 2006). Treatment processes fall into three categories; physical, chemical, and biological. Physical treatment systems involve such simple processes as settling, filtering, and drying to change the characteristics of the manure. Chemical treatment is basically addition of a chemical to help conditioning manure. Biological treatment made use of naturally occurring microorganisms in the manure to change its properties.

Physical Treatment

The physical treatment methods are mostly applied to achieve solid-liquid separation. The solid-liquid separation may be accomplished by settling, centrifugation and filtering and screening. The solid-liquid separation is applied for the following purposes: (i) to improve the treatment efficiency of vegetative infiltration areas and leach fields, (ii) to reuse manure solids for bedding, (iii) to use the liquids for flushing, (iv) to reduce the volume of the waste to be hauled (Burton and Turner, 2003; OSU Extension, 2006). Drying is another physical treatment method used primarily for volume reduction by making the water to evaporate, concentrating the solids (Burton and Turner, 2003).

Chemical Treatment

The objective of chemical treatment is to eliminate the odor production, to remove pathogens and improve the dewatering characteristics of manure. For this purpose coagulating agents such as ferric chloride, lime, alum and organic polymers are used (OSU Extension, 2006). Chemical treatment is usually achieved by the addition of quick lime (CaO) or hydrated lime (CaOH) to raise the pH of the manure to 12 for 30 minutes, thereby eliminating odor production and limit the spread of disease. One limitation to this treatment is the loss of ammonia via volatilization (OSU Extension, 2006).

Biological Treatment

There are three main classes of biological treatment applied to manure; (i) composting, (ii) aerobic treatment and (iii) anaerobic treatment.

Manure Composting: Composting is a natural process in which organic material undergoes biological degradation to a stable end product. In conventional composting, ingredients are brought together, mixed, and then put into a pile to compost. In general the mix is turned every three or four days, but sometimes every day or only weekly or monthly (Burton and Turner, 2003).

Composting reduces the volume of the parent materials by 40 to 60% and if the process is controlled properly it can be an effective means of reducing pathogens (Martin, 2005; OSU Extension, 2006). High temperatures associated with the composting process are responsible for killing pathogens (Martin, 2005; OSU Extension, 2006). Although composting may be accomplished under anaerobic or aerobic conditions, aerobic composting is used mostly (Tchobanoglous et al., 2003). The process consumes oxygen and releases heat, water, and carbon dioxide. Aerobic composting accelerates material decomposition and lead to higher temperature rise; thereby achieve higher pathogen removal (Tchobanoglous et al., 2003). Composting of manure mixes typically take several months to a year to compost and cure (OSU Extension, 2006).

Aerobic Treatment: It is not common but pilot schemes are being used increasingly in France and Netherlands (Burton and Turner, 2003). A key purpose of aerobic treatment is the removal of unwanted ammonia via the nitrification/denitrification, organic matter removal is also achieved by this treatment (Burton and Turner, 2003). If lagoons are used for the treatment than, large land area is needed for natural aeration (OSU Extension, 2006). If aerators are used for the aeration then the energy requirement will be high.

Anaerobic Treatment: Anaerobic treatment of organic wastes including animal manure has been applied successfully to convert them into profitable by products as well as to reduce the pollution of air, water and soil caused by these wastes (Bousfield et al., 1979; Huangh and Shih, 1981; Demirer et al., 2000; Misi and Forster, 2001; US Environmental Protection Agency, 2002; Cheng and Liu, 2002; Güngör - Demirci and Demirer, 2004; Demirer and Chen, 2005; Yılmaz and Demirer, 2008). However, high ammonia nitrogen concentrations in the effluent of the anaerobic reactors which can be attributed to the anaerobic bioconversion of proteins contained in animal manure into amino acids and then to ammonia make a post-treatment necessary to remove ammonia before discharge into receiving water bodies (Lusk, 1998; Cheng and Liu, 2002; Martin et al., 2003; Demirer and Chen, 2005; Uludağ-Demirer et al., 2008). Since anaerobic digestion is the mostly applied farm animal manure bioconversion technology, more detailed description and literature information on anaerobic digestion, its application to poultry manure and subsequent post-treatment options are represented in the following sections.

2.3 Anaerobic Digestion

In this part, anaerobic digestion (AD) is represented under the following four sub-titles; the process description, stages of AD, important factors controlling AD and anaerobic co-digestion process.

2.3.1 Process Description

Anaerobic digestion (AD) can be defined as the use of microbial organisms, in the absence of molecular oxygen (O_2), for the stabilization of organic matter (substrate) by conversion to methane and some inorganic end products. Anaerobic treatment of wastes results in conversion of organic matter into biogas (20-30 % CO_2, 60-79 % CH_4, 1-2 % H_2S and other gases) and water (Parkin and Owen, 1986; Verma, 2002; Sperling et al., 2007). In the conversion process, a series of interdependent metabolic reactions and different classes of microorganisms take part.

AD of municipal sludges was practiced for more than 100 years ago (Speece, 2008) and the first anaerobic digester is considered to have been built in an Indian leper colony in Bombay in 1859 (Speece, 2008). Being one of the earliest biological waste treatment methods, anaerobic digestion is used for the stabilization of wide array of industrial and agricultural wastes. The feedstocks of anaerobic digesters vary in physical form as well as in chemical composition. Waste activated sludge (Bolzonella et al., 2005; Romano and Zhang, 2008; Demirer and Othman, 2008), organic fraction of municipal solid waste (Hartmann and Ahring, 2005; Dogan et al., 2008), domestic wastewater (Monroy et al., 2000; Ergüder and Demirer, 2008), fruit and vegetable wastes (Bouallagui et al., 2005), animal manure (Güngör-Demirci and Demirer, 2004; Demirer and Chen, 2004; Karim et al., 2005), sugar industry wastes (Hutnan et al., 2001; Farhadian et al., 2007), pulp and paper industry wastes (Grover et al., 1999; Tezel et al., 2001) and food waste (Kim et al., 2006) are among the feedstocks suitable for anaerobic biological treatment.

2.3.2 Stages of Anaerobic Digestion

AD is the consequence of a series of metabolic interactions among various groups of microorganisms. It occurs in four stages; (i) hydrolysis/liquefaction, (ii) acidogenesis, (iii) acetogenesis and (iv) methanogenesis (Figure 2.1). AD is carried out by a group or consortia of bacteria, working together to convert organic matter to gas and inorganic constituents. The bacterial consortia are essentially producing the "bio-enzymes" that accomplish the digestion process. A poorly developed or stressed bacterial consortium will not provide the desired conversion of waste to gas and other beneficial products (Dennis and Burke, 2001).

Hydolysis/liquefaction is the conversion of complex and/or insoluble organics (carbohydrates, proteins, fats, etc.) into simpler forms such as sugars, amino acids and long chain fatty acids (LCFAs). This is accomplished by extracellular, hydrolytic enzymes produced and excreted by the bacterial population for this specific purpose (Parkin and Owen, 1986). Essentially no organic waste stabilization occurs during this step; the organic matter is simply converted into a soluble form that can be utilized by the bacteria. The bacteria responsible for the hydrolysis are composed of both obligate and facultative anaerobes and they are also responsible for removing small amounts of oxygen introduced when feeding the digester (Parawira, 2004).

Once complex organics are hydrolyzed, acidogenesis takes place. During acidogenesis, sugars, amino acids and LFCAs resulting from hydrolysis are used as substrates by fermentative microorganisms to produce organic acids, such as acetic, propionic, butyric and other short-chain fatty acids and alcohols. The hydrolyzed organic materials are also utilized by anaerobic oxidisers to produce H_2 and CO_2 (Kalyuzhnyi et al., 2000; Gerardi, 2003; Parawira, 2004).

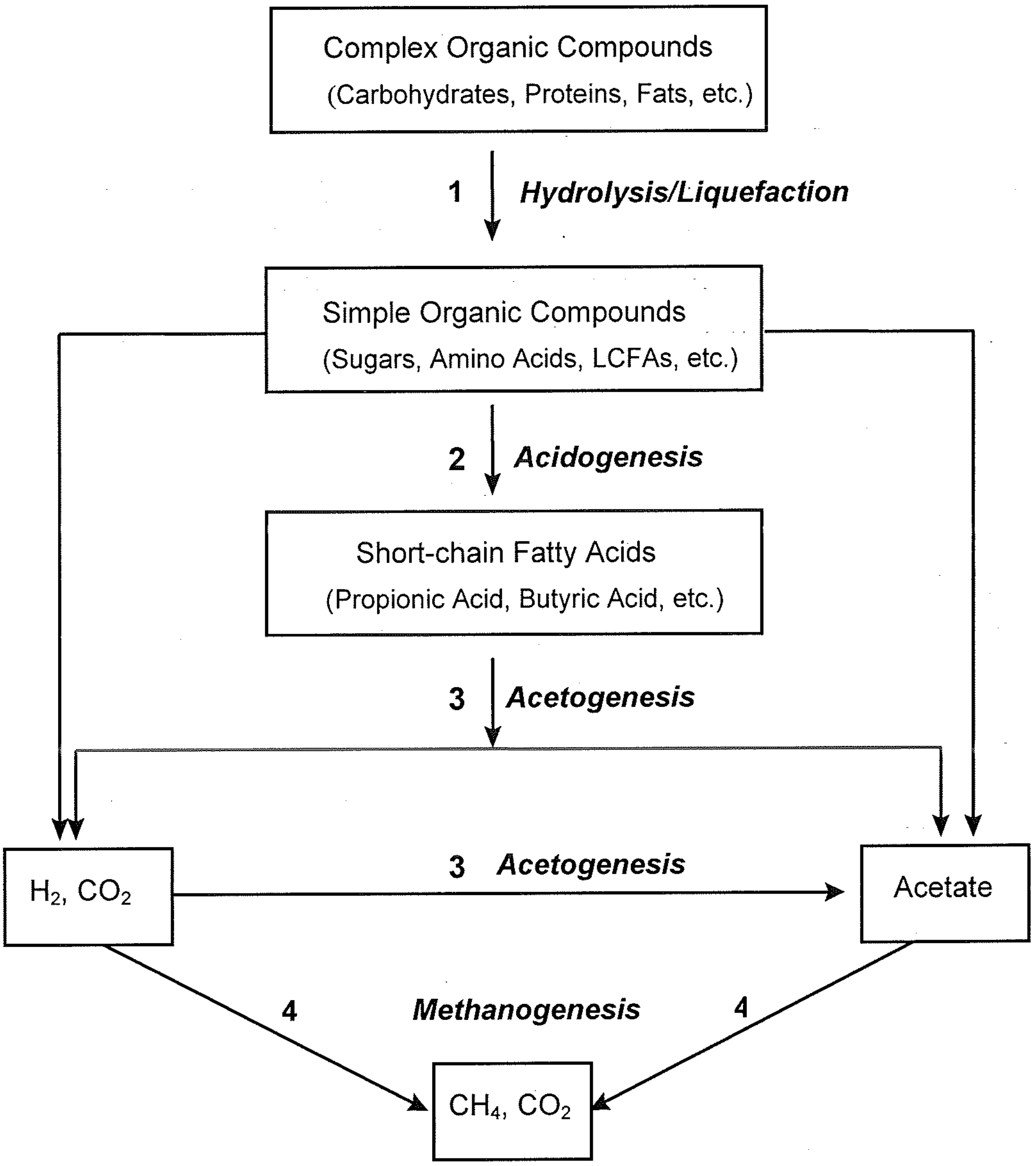

Figure 2.1. Stages of anaerobic digestion (Gerardi, 2003)

The next stage is acetogenesis, which involves the degradation of higher organic acids to acetate, hydrogen and carbondioxide. This intermediate conversion is important for the successful production of biogas because the organic acids produced in the acidogenesis are not utilised directly by the methanogens. The different bacterial species that are capable of acetogenesis are termed as acetogens.

The slow-growing acetogens are sensitive to fluctuations in organic loads and environmental changes (Parawira, 2004).

Final stage of AD is methanogenesis, where waste stabilization takes place. In this stage, methanogens utilize H_2/CO_2 and acetic acid to form methane and carbon dioxide (Parawira, 2004). Methanogens are strict anaerobes to which oxygen is inhibitory and they are sensitive to both operational conditions and environmental changes (Parkin and Owen, 1986).

2.3.3 Important Factors Controlling Anaerobic Digestion

The environmental factors that are important in anaerobic digestion (AD) include temperature, pH and alkalinity, solids retention time, food to microorganism ratio, the availability of nutrients, and the presence of toxic components in the process (Dennis and Burke, 2001; Speece 2008).

Temperature

The anaerobic bacterial consortia function under three temperature ranges: psychrophilic (0-20 °C), mesophilic (20-42 °C), and thermophilic (42-75 °C) (Gerardi, 2003). Several studies in literature depicted that the production of biogas has two optima, one at the mesophilic range at 35 °C and the other one in the thermophilic range at 55 °C (Bouallagui et al., 2004; Speece, 2008). However, the study of Lepistö and Rintala (1996) illustrated that AD is possible at temperatures up to 80 °C.

pH and Alkalinity

Another important parameter to be considered in AD is pH. AD can proceed well within a pH range of 6.6-7.6 (McCarty, 1964a). Components such as CO_2 and volatile fatty acids (VFAs) tend to lower pH. At pH values below 6.2, the efficiency drops off rapidly and the acidic conditions can be quite toxic to methanogens (McCarty, 1964a). In a well-operating anaerobic digester, deviations of pH from desired ranges are buffered by the alkalinity.

Alkalinity concentrations of 2000-4000 mg/L (as $CaCO_3$) are usually required to maintain the pH at or near neutral level (Tchobanoglous et al. 2003). Metabolism-generated alkalinity is the characteristics of many feed stocks. This is the increase of alkalinity in a wastewater resulting from the metabolism of an organic compound. For instance, the degradation of proteins due to the release of ammonium ions lead to the increase of alkalinity concentration in the reactor (inherent alkalinity generation). If the alkalinity is not sufficient to maintain the pH at the desired level, external alkalinity should be added into the reactor (Speece, 2008).

Nutrients

In order for any biological process to operate, inorganic nutrients required by the bacteria for their growth must be supplied. In addition to the two elements (N and P) required for both aerobic and anaerobic microbial systems, some sulfide precursors must be added in anaerobic systems because the methanogens manifest an obligate requirement for sulfide (Speece, 2008). Other than macronutrients (N and P), the micronutrients of iron, cobalt, nickel and zinc are required by methanogens. Due to the much reduced amount of biomass synthesis in anaerobic processes in comparison to aerobic processes, the nutrient requirements are lower in anaerobic processes; however, external nutrient supplementation may still be necessary in some cases.

Toxic Materials

There are many materials, both organic and inorganic, which may be toxic or inhibitory to the anaerobic waste treatment process. Organic chemicals, heavy metals, ammonia nitrogen depending on pH, cations such as Na, K, Ca and Mg, sulfides and some other miscellaneous substances play inhibitory roles (Parkin and Owen, 1986). If there is toxicity, it will be reflected in a reduced initial rate of gas production (Speece, 2008). However, microorganisms usually have the ability to adapt to some extent to inhibitory concentrations of most materials, depending on the concentration of the inhibitory substance (McCarty, 1964b).

Food to Microorganism Ratio (F/M)

The ratio of food [Chemical oxygen demand, COD] to microorganisms [volatile suspended solids (VSS)], i.e., (F/M) expresses the potential food availability to the microbial population (Droste, 1997). F/M is an important parameter which influences the biodegradability of wastes (Grady, 1985). It is reported that a too high value of F/M may be toxic and a too low value may interfere the biodegradation due to the prevention of the induction of the enzyme necessary for biodegradation (Prashanth et al., 2006).

2.3.4 Anaerobic Co-digestion of Wastes

In addition to the operational parameters, the efficiency of AD process highly depends on the waste characteristics. The composition of the starting material in AD is important; there is a need for a suitable ratio between carbon and nitrogen. If the characteristic of the waste is not appropriate for the desired level of treatment, some measures can be taken. Co-digestion of wastes is one of the options used for the improvement of process efficiency in AD.

Anaerobic co-digestion is the use of a co-substrate in the digestion medium, which mostly improves the biogas yields as a result of positive synergism established in the reactor and the supply of missing nutrients by the co-substrates (Mata-Alvarez, 2000). Co-digestion brings several economical benefits due to sharing of equipment, easier handling of mixed wastes and the use of common access facilities. Moreover, the use of a co-substrate can also help to establish the required moisture content in the digester. Apart from these co-digestion becomes an interesting alternative when the amount of one type of organic waste generated at a particular site at a certain time is not sufficient to make AD cost effective (Callaghan et al., 1999). This is of particular importance for animal wastes where small quantities are generated in small farms. Co-digestion as a process has been examined for the treatment of animal waste (Callaghan et al., 1999; Misi and Forster, 2001; Güngör-Demirci and Demirer, 2004, Umetsu et al., 2006; Gelenegis et al. 2007), food industry wastes (Carucci et al. 2005), organic fraction of municipal solid waste (Sundarajan et al., 1997; Hamzawi et al., 1998), fish wastes (Mshandete et al. 2004), potato waste

(Parawira et al, 2004) and wastewater sludge (Romano and Zhang, 2008; Kabouris et al., 2009).

In most of the studies the results of co-digestion were enhancement of AD process by the increase of methane yield. Parawira et al. (2004) reported considerable increase (31-63 %) in the methane yield from batch co-digestion of potato waste and sugar beet leaves compared with that from batch digestion of potato waste alone. During anaerobic batch co-digestion of sisal pulp and fish wastes at ambient temperature (27±1 °C), Mshandete et al. (2004) reported 59 to 94 % increase in the methane yield compared to that obtained for the digestion of pure sisal pulp and fish wastes. Since this work heavily concentrates on poultry manure, literature information on anaerobic digestion and co-digestion of poultry manure is represented in the following section.

2.4 Anaerobic Digestion of Poultry Manure

Adderley et al. (1976) investigated the anaerobic fermentation of chicken manure and reported that the optimal temperature and total solids (by weight) dilution to organic acids as 25°C and 2.5%, respectively. They concluded that the rates of methane production and waste stabilization could be improved by considering the impact of temperature changes on methanogenic microorganisms. Aubart and Fauchille (1983) investigated the continuous anaerobic digestion of poultry wastes diluted with water. The poultry waste was taken from an industrial farm of laying hens without litter. They studied the effect of retention time and total solids content on biogas production, and reported that it was possible to work with very short retention times (4 or 5 days) with a 4% TS concentration. For a digester treating poultry manure; a TS content of 6 % and retention time of 15 days were found to be optimum. In these conditions a noticeable COD reduction (52.6 %) was observed. Moreover, they reported that the fertilizer value of the reactor effluents were high, except the slight deficiency in potash (K_2O). Another study investigated the digestion of the manure of laying hens under thermophilic conditions (Huang and Shih, 1981). A mixed culture was used in the reactors with different retention times and VS contents, and 4 day retention time and 6% volatile solids (VS) were reported to give the maximum gas production. Safley et al. (1987) monitored the performance of a full-scale (587 m^3) poultry anaerobic digester for 3 years. The digester was operated on a 22-day retention time at 35 °C. Biogas production averaged 0.39 m^3/kgVS added and average methane content of the biogas was 58.3%.

In another study the anaerobic treatment of liquid fraction of hen manure was studied in two parallel laboratory 2.6 liter upflow anaerobic sludge blanket (UASB) reactors at 35°C (Kalyuzhnyi et al., 1998). The wastewater was first preacidified by keeping the feeding flasks open at ambient temperature (18-20 °C) for 2 days (micro aerobic preacidification) and then fed to the reactors. The study reported that the biogas production rate at the organic loading rate (OLR) of 11–12 g COD/L.day and hydraulic retention time (HRT) of 1–2 days was about 3.5–3.6 L/L.day with a methane content of 79–81% and an effluent pH of about 8. Under these OLR and HRT, both reactors demonstrated optimal operation stability with a COD removal efficiency of 70–75%.

In order to reduce the cost of treatment by avoiding volume increase due to dilution of poultry manure there have been some efforts to treat poultry manure in its semi-solid form. To this purpose anaerobic digestion of high solids chicken manure was conducted by several investigators (Bujoczek et al. 2000; Abouelenien et al., 2009) Dry anaerobic digestion has some advantages of using smaller reactor size and smaller wastewater treatment facility than those of conventional processes (Abouelenien et al., 2009). However, dry anaerobic digestion studies produced inefficient results due to ammonia inhibition (Bujoczek et al. 2000; Abouelenien et al., 2009). Abouelenien et al. (2009) adopted ammonia stripping process in order to improve the production of methane during dry anaerobic digestion of chicken manure.

Apart from these co-digestion of poultry manure and several wastes was investigated by several investigators (Desai et al., 1994; Callaghan et al., 1999; Misi and Forster, 2001; Güngör-Demirci and Demirer, 2004, Gelenegis et al., 2007). Callaghan et al. (1999) investigated the effect of co-digesting cattle slurries with a range of solid wastes including poultry manure. Compared with their control (cattle slurry alone), co-digestions with poultry manure (7.5 and 15 % of TS) gave higher cumulative methane productions, and the reactor with the lower concentration of poultry manure gave higher specific methane yield. The lower methane yields achieved in the reactors where poultry manure was used as the co-digestate was attributed to the high concentrations of free ammonia which was produced during the digestion. An experimental study was conducted by Güngör-Demirci and Demirer (2004) to investigate anaerobic treatability and biogas generation potential of broiler and cattle manure. The study depicted that the biogas yields were observed to be 180–270 and 223–368 mL gas / gCOD added for initial COD concentrations of 12,000 and 53,500 mg/L, respectively. Total COD removals were in the range of 32–43.3% and 37.9–50% for the initial COD concentrations of 12,000 and 53,500 mg/L, respectively.

2.5 Nutrient Removal and Recovery Processes

Because AD removes mainly carbon, the traditional processes should be sometimes completed for nitrogen and phosphorus removal in order to meet the effluent discharge regulations. In this section the conventional and new processes applied for nutrient removal/recovery are described in detail.

There are biological and physical/chemical processes applied for nitrogen removal. Biological nitrogen removal is achieved by a series of biochemical reactions by which nitrogen transforms from one form to another. Key biological nitrogen removal reactions are nitrification and denitrification. The other related reactions include ammonification (conversion of organic nitrogen to ammonia nitrogen) and nitrogen uptake for cell growth (Jeyanayagam, 2005). Nitrification is the conversion of ammonium NH_4^+, to nitrite, NO^{2-}, and finally to nitrate, NO^{3-} (WEF, 1998). Nitrification in itself is not a significant removal mechanism of nitrogen; it is the conversion of nitrogen from a reduced form (ammonia) to an oxidized form (nitrate). In order to achieve significant nitrogen removal, denitrification must follow nitrification (Tchobanoglous et al., 2003). Denitrification is the reduction of nitrate to nitrogen gas by certain heterotrophic bacteria in the absence of dissolved oxygen (anoxic conditions). Physical/chemical nitrogen removal processes can be listed as stripping NH_3 (g), ion-exchange process and membrane separation (WEF, 1998). However, typically physical/chemical nitrogen removal processes are not used and biological processes have essentially replaced them (WEF, 1998).

Phosphorus removal processes can be grouped into two: chemical processes and biological processes. Chemical phosphorus removal processes are based on precipitation of phosphorus in the form of metal phosphates. Metal salts, specifically aluminum and iron salts are mostly used for chemical phosphorus removal from the wastewaters (Tchobanoglous et al., 2003). Lime can also be used for phosphorus precipitation, however the kinetics of precipitation are very small and some other chemical compounds other than calcium phosphates e.g. $CaCO_3$ (calcite) are formed. Therefore, it is preferred rarely (WEF, 1998). Biological phosphorus removal processes relies on phosphorus uptake by aerobic heterotrophs capable of storing orthophosphate greater than their biological growth requirements (Jeyanayagam, 2005). The microorganisms involved in the uptake of excess phosphorus are called Phosphorus accumulating organisms (PAOs) and the efficiency of a system is directly related to the fraction of PAOs in the mixed liquor suspended solids (MLSS) (Jeyanayagam, 2005). Key process elements are: anaerobic zone with sufficient readily biodegradable organic matter, subsequent aerobic zone, recycling phosphorus-rich return sludge to the anaerobic zone (WEF, 1998; Jeyanayagam, 2005).

Nitrogen and phosphorus removal can be achieved by the use of proper biological process sequence. The typical process configuration of combined systems encompasses an anaerobic tank followed by the anoxic and aerobic zones of a completely mixed oxidation ditch. Most common combined nitrogen and phosphorus removal processes are A_2O, Modified University of Cape Town, Five-stage Bardenpho and the Johannesburg (Jeyanayagam, 2005).

Apart from the conventional nutrient removal and recovery processes there are two new promising processes used for nutrient removal from wastewaters; anammox process and struvite precipitation (van Lier, et al, 2001). Anammox, a process of anaerobic ammonium oxidation, is an innovative technological advancement in the removal of ammonia nitrogen from wastewaters (van Lier, et al, 2001). Anammox process is used for removal of ammonium without oxygen and nitrite is used as the electron acceptor in the process. The costs of conventional ammonium removal via nitrification-denitrification from sludge reject waters are mainly associated with aeration-cost and the addition of an expensive electron donor (e.g. methanol). The anammox process provides an alternative for the nitrification, with no extra electron donor requirement (Shivaraman and Shivaraman, 2003). Struvite precipitation is another promising process applied for nutrient recovery. As the name suggest, anammox process is applicable to ammonia removal only, however, struvite precipitation has the advantage of removing both ammonia and phosphate from the wastewater. The process is based on chemical precipitation principles under certain conditions, ammonia, magnesium and phosphate react to form a precipitate called struvite. This process can be accepted as a sustainable treatment method because it serves to dual purpose; (i) removal and (ii) recovery of nutrients from wastewaters if struvite precipitate is collected and then used as a fertilizer. The following sections include the literature information and details about the struvite precipitation process.

2.6 The Struvite Precipitation Process

In this part, struvite precipitation process is represented under the following six sub-titles; the chemistry of struvite, struvite precipitation, important parameters controlling struvite precipitation, nutrient recovery from AD effluents by struvite precipitation, the uses of struvite and full-scale applications and economics of the process.

2.6.1 The Chemistry of Struvite

Struvite or magnesium ammonium phosphate (MAP) is a white crystalline substance that is formed by the combination of magnesium, phosphate and ammonia in equal molar quantities (Doyle and Parsons, 2002). Struvite forms according to the simplified reaction depicted below:

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O \text{..} (1)$$

Struvite crystals have a rod like orthorhombic structure and can be identified via X-ray diffraction (XRD) analysis by matching the intensity and position of the peaks produced to a database for the crystal structure (Doyle and Parsons, 2002).

The struvite formation is observed when wastewater solution is saturated with respect to struvite ($MgNH_4PO_4.6H_2O$). In addition to the wastewaters, struvite crystals are also found in nature where it has been identified in guano (Whitaker, 1968) as well as in urinary stones due to bacterial infections within the kidneys (Griffith, 1978).

2.6.2 Struvite Precipitation

Struvite precipitation can occur via two distinct pathways: crystal growth and nucleation. Nucleation is the first stage and occurs when constituent ions combine to form crystal embryos. Crystal growth is the second stage and continues until equilibrium is reached (Ohlinger et al., 1999). In literature several researchers investigated the rate of crystal formation; Ohlinger et al. (2000) and Nelson et al. (2003) identified that struvite kinetics of crystal growth followed first order kinetics with rate constants ranging from 3.7 to 12.3 h^{-1}, respectively, depending on the solution pH. While in another study by Türker and Çelen (2007) the reaction kinetics was reported as second order with a higher rate constant.

The formation of crystals (i.e. nucleation) usually occurs spontaneously (homogeneous nucleation) or can be aided by the presence of suitable nuclei e.g. solid impurities in suspension or sites on the pipe walls (heterogeneous nucleation) (Doyle and Parsons, 2002). The time taken for nucleation to occur is called the induction time and has been investigated to identify what controls the formation of a precipitate (Doyle and Parsons, 2002). Several parameters e.g. pH and temperature were reported to have impact on induction time, where increasing pH and temperature lead to a reduction in the induction time (Abbona et al., 1982; Doyle and Parsons, 2002).

2.6.3 Important Parameters Controlling Struvite Precipitation

Struvite precipitation is influenced by chemical composition of the wastewater (organic matter, presence of chealating agents, ionic strenght), pH, the molar ratio of $Mg:NH_4\text{-}N:PO_4\text{-}P$ (Mg:N:P), the degree of supersaturation, temperature, and the presence of foreign ions such as calcium (Schulze-Rettmer, 1991; Doyle and Parsons, 2002).

Molar ratio of Mg:N:P

For intentional struvite precipitation the molar ratio of struvite forming ions (Mg:N:P) should be at least unity. At any given pH level, any increase in the Mg:N:P ratio would increase the degree of saturation with respect to struvite formation, which, in turn would enhance the removal and recovery of PO_4-P and NH_4-N (Adnan et al., 2004; Rahaman et al., 2008). The studies have indicated the importance of molar concentration ratio of Mg, NH_4-N, and PO_4-P (Mg:N:P) as well as the pH of wastewater to achieve considerable removal of the nutrients by struvite formation (Nelson et al., 2003; Münch and Barr, 2001a; Uludağ-Demirer, 2008). The molar concentrations of the struvite forming ions depend on their activities, which are controlled by the ionic strength, pH and composition of the wastewater. Münch and Barr (2001) reported that Mg:P molar ratio of 1.3:1 was an ideal environment for struvite formation, while in another study it was reported that excess amounts of magnesium decreases struvite purity (Demeestere et al., 2001). Furthermore, Nelson et al. (2003) stated that an engineering solution could be devised to facilitate the controlled precipitation and recovery of struvite for the dual purpose of P removal from swine waste and production of a slow-release fertilizer by the optimization of pH and/or Mg:P molar ratio.

pH

In addition to the saturated concentrations of Mg, NH_4-N, and PO_4-P pH of the solution should be the pH of the minimum solubility of struvite to recover the maximum amount of struvite from the wastewater. Theoretically, solubility of struvite decreases as pH increases up to a pH level of 9.0. At a pH level above 9.0, struvite becomes more soluble as a result of decreasing and increasing ion activities of ammonia and phosphate, respectively (Stumm and Morgan, 1970). However, the pH of minimum solubility of struvite may differ due to changing ionic strength and composition of wastewaters. The minimum solubility pH for struvite precipitation reported by a number of researchers displays a range of values, from 8.0 to 10.7 (Stumm and Morgan 1970; Momberg and Oellermann 1992; Ohlinger et al., 1998, Doyle and Parsons, 2002; Nelson et al., 2003).

Presence of Foreign ions

The presence of foreign ions in the wastewater has been shown to affect the rate of formation, the quality and also the purity of the struvite crystals produced (Momberg and Oellermann, 1992; Le Corre et al., 2005). In sludge liquors, where relatively low molar ratios of Mg:Ca can be observed (Table 2.3), calcium ions can interact with phosphate or carbonate ions to form calcium phosphates (usually as hydroxylapatite) or calcium carbonates (usually calcite) according to Eqs. (2) and (3) respectively (Le Corre et al., 2005).

$5Ca^{2+} + 3PO_4^{3-} + H_2O \rightarrow Ca_5(PO_4)3OH + H^+$..(2)

$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$..(3)

Le corre et al. (2005) illustrated that at Mg:Ca molar ratios of 1:1 and above, no crystalline material was produced in the reaction only amorphous sludge. Also in their study Wang et al. (2005) depicted that by varying the Mg:Ca ratio the formation and quality of struvite crystals varied vastly. They revealed that the struvite purity was reduced from 85 % at Mg:Ca ratio of 2:0.5 to 61% at Mg:Ca ratio of 2:1. However, by the addition of Ca ion the residual concentration of PO_4-P is reduced significantly, therefore it is proposed if P removal is the targeted goal and not struvite purity (Wang et al., 2005).

Table 2.3 Average levels of magnesium and calcium in settled sludge liquors of different WWTPs[a] in United Kingdom (Le Corre et al., 2009)

	Magnesium, mg/L	Calcium, mg/L	Molar ratio of Mg:Ca
Barston	46	257	1:3.4
Coleshill	19	94	1:3
Mansfield	52	123	1:1.4
Milcote	34	165	1:3
Oswestry	31	185	1:3.6
Spernal	53	321	1:3.7
Wanlip	41	188	1:2.8

[a] WWTPs:Wastewater treatment plants

Apart from calcium other ions present in wastewater streams also affect the formation of struvite. Kabdaşlı et al. (2006) noted that the presence of sodium, calcium, sulphate and carbonate-bicarbonates ions had an impact on either induction time of struvite formation or crystal morphology and sizes of the particles. Another ion which possibly interferes with struvite formation is potassium, however, it does not have many preferential precipitates over struvite and its co-precipitation would meet the necessity of enhancing the fertilizer quality of the product (Doyle and Parsons, 2002). The major possible precipitate is a struvite analogue called potassium struvite ($MgKPO_4.6H_2O$, KMP). However, several authors have pointed out that potassium struvite could precipitate instead of ammonium struvite, only in the case of low ammonium concentrations. (Schuiling and Andrade, 1999; Wilsenach et al., 2006; Marti et al., 2008). Also, the study of Rontentalp et al. (2007) illustrated that the metals can be incorporated into the crystal lattice or sorbed to the surface of struvite, decreasing the purity of the product. Substitution for magnesium, phosphate and ammonium ions within the struvite molecule is reported in literature. Arsenate (AsO_4^{3-}) can be substitute of phosphate (Rontentalp et al., 2007). Ammonium was reported to be partly substituted by sodium, rubium, caesium and tellenium (Banks et al., 1975; Mathew and Schroeder, 1979). On the other hand, magnesium was also reported to be replaced by other metals such as cadmium (Ravikumar et al., 2002), zinc (Chand and Agarwal, 1991) and nickel (Haferburg et al., 2008).

Temperature

The solubility of struvite has increased by the increase of temperature in the range of 10-50 °C, while the solubility decreased up to 65 °C (Uludağ-Demirer, 2008). In literature it is stated that the structure of struvite has changed as the temperature increased beyond 65 °C (Aage et al., 1997; Uludağ-Demirer, 2008).

Phosphorus source

Ammonia nitrogen is typically in excess relative to Mg and PO_4-P in wastewaters (Schulze-Rettmer, 1991); therefore, the inadequate ions, such as Mg and PO_4-P, have to be added to induce struvite formation in wastewater. For phosphate supplementation, Brionne et al. (1994) proposed phosphoric acid (H_3PO_4) and also tested potassium hydrogen phosphate (K_2HPO_4) and potassium dihydrogen phosphate (KH_2PO_4). Webb and Ho (1992) used potassium dihydrogen phosphate in their studies. Schulze-Rettmer (1991) proposed phosphoric acid and Zdybiewska and Kula (1991) reported better precipitation results when using phosphoric acid with magnesium chloride than using it with magnesium oxide. Numerous investigators reported using sodium phosphate dibasic heptahydrate ($Na_2HPO_4.7H_2O$) as phosphorus source in their studies (Münch and Barr, 2001a; Altınbaş et al., 2002a; Uludağ-Demirer et al., 2005).

2.6.4 Nutrient Recovery from AD Effluents by Struvite Precipitation

The struvite precipitation technique has been applied to various wastewaters, such as swine waste (Burns et. al., 2001; Nelson et al., 2003), agro-industrial effluents (Altınbaş et al., 2002a, Uludağ et al., 2005), landfill leachate (Li et al., 1999; Altınbaş et al.,2002b; Öztürk et al.,2003), calf manure (Schuiling and Andrade, 1999), domestic wastewater, coking plant and nitrogen work effluents (Zdybiewska and Kula,1991), leather tanning (Tünay et al.,1997), poultry manure (Yetilmezsoy and Şapçı-Zengin, 2009), semiconductor wastewater (Warmadewanthi and Liu, 2009), municipal wastewater (Uludağ-Demirer, 2008) and anaerobic digester sidestreams (Battistoni et al., 1997; Battistoni et al.,2000; Münch and Barr, 2001a).

Depending on the composition of the wastewater and the selection of the process parameters, struvite precipitation can be used to remove ammonia nitrogen (NH_4-N), phosphate (PO_4-P) or both. Ammonia nitrogen is typically in excess relative to Mg and PO_4-P in wastewaters (Schulze-Rettmer, 1991); therefore, in order to induce struvite formation the inadequate ions, such as Mg and PO_4-P, have to be added to the reactor. In literature there are various studies focusing on either removal/recovery of phosphorus, ammonia or both. Depending on the chemicals added and the molar concentration ratio of the constituent ions the process can be used for different purposes.

Generally, in the studies focusing on phosphorus removal/recovery the addition of external phosphorus source was eliminated and only magnesium additions were done so as to adjust the molar ratio of magnesium to phosphorus (Mg:P) keeping the ammonia in excess. Indeed, by this application the purity of the product precipitated is not always guaranteed, due to competition between struvite and other metal phosphates (Le Corre et al., 2009). There are a number of researchers focusing on removal/recovery of phosphorus in their studies. Burns et al. (2001) conducted laboratory and field experiments using magnesium chloride ($MgCl_2$) to force the precipitation of struvite and reduce the concentration of soluble phosphorus in swine waste. By the adjustment of molar concentration ratio of magnesium to total phosphorus to 1.6:1, 76 % removal of soluble phosphorus was achieved. In the same study, the increase of pH to a level of 9.0 increased the reduction of soluble phosphorus to 91% (concentration reduced from 572 to 50 mg/L).

The XRD analysis of the recovered precipitate confirmed the formation of struvite; however the chemical analysis of the precipitate indicated presence of impurities. The removal of NH_4-N achieved by this application was not illustrated in this study. In the study of Münch and Barr (2001a) at a Mg:P ratio of 1.3:1, 94 % and 6 % removal was recorded for PO_4-P and NH_4-N, respectively. This is achieved by the addition of Mg ion only at pH level of 8.5-9.0.

Other studies in literature focused on the removal of ammonia by struvite precipitation process. Çelen and Türker (2001) studied the ammonia removal from the effluent of anaerobic digester treating molasses based industrial wastewater via struvite precipitation. The objective of the study was to investigate the effects of several parameters (molar ratio of Mg:N:P, time, pH, magnesium source and temperature) on the removal efficiency of NH_4-N. Their results indicated that temperature did not significantly affect ammonia removal within the range of 25-40 ^oC. The other conclusions that can be drawn from this study are; the optimum pH of ammonia recovery is 8.5-9.0, slight excess of Mg and P is required to enhance the recovery of ammonia, $MgCl_2.6H_2O$ is a better magnesium source in comparison to MgO. The removal efficiencies of NH_4-N obtained by the use of $MgCl_2.6H_2O$ were within the range of 78.7% to 96.9%, while PO_4-P removals achieved in this study were not depicted.

The study of Uludağ-Demirer et al. (2005) investigated the removal of ammonia through struvite precipitation from the effluents of one- and two-phase anaerobic reactors digesting dairy manure. In the experiments the effects of molar ratio of Mg:N:P and magnesium source on the removal of ammonia was investigated. The results indicated that overdosing of magnesium in excess of molar concentration of ammonium, led to ammonia removal efficiencies higher than 90%. Uludağ-Demirer et al. (2005) also proved that $MgCl_2.6H_2O$ is more efficient as magnesium source than $Mg(OH)_2$ in terms of final ammonia concentrations and the required amount.

Yetilmezsoy and Şapçı-Zengin (2009) studied ammonia recovery via struvite precipitation from upflow anaerobic sludge blanket (UASB) pretreated poultry manure wastewater. They tested three combinations of chemicals including $MgCl_2 \cdot 6H_2O+KH_2PO_4$, $MgSO_4 \cdot 7H_2O+NaHPO_4 \cdot 7H_2O$, and MgO+85% H_3PO_4 at different pH levels. Before the experiments the relevant magnesium and phosphorus containing chemicals were mixed in the pre-determined ratios to adjust the molar ratio of Mg:N:P to 1:1:1. Then, the performance of the struvite precipitation process was evaluated by the measurement of remaining COD, color and ammonia concentrations. Their results indicated that maximum NH_4–N removal, maximum chemical oxygen demand (COD) and color reductions, were obtained as 85.4%, 53.3% and 49.8%, respectively, at pH level of 9.0 with the addition of

$MgCl_2 \cdot 6H_2O + KH_2PO_4$. They also investigated different molar ratios of Mg:N:P by the use of $MgCl_2 \cdot 6H_2O + KH_2PO_4$, and the fertility of the recovered precipitate by conducting pot experiments with three different test plants.

2.6.5 The Uses of Struvite

Struvite can be used as a slow-releasing fertilizer, secondary phosphate ore, and as a phosphate source in other industrial processes (Schuiling and Andrade, 1999). The fertilizer properties of struvite were demonstrated in 1962 by the study of Bridger et al. As a fertilizer, struvite is preferred over other metal ammonium phosphates for numerous reasons. First, nutrients are released at a slower rate compared to other fertilizers; thereby plants can take up most of the nutrients without waste by leaching (Münch and Barr, 2001a). Therefore, less frequent application is required. Second, the production of struvite from wastewater streams offers the immediate advantage of avoiding the environmental impacts associated with production from phosphate rock (Morse et al., 1998). Lastly, the essential nutrients P, N and Mg are applied simultaneously with essentially no unnecessary components in the fertilizer; even though there is deficiency of potassium (Wang et al., 2005).

Struvite can be used as secondary phosphate ore and as compared to sedimentary phosphate ores struvite has some attractive environmental aspects. It is lower in impurities such as fluorine, heavy metals and radioactive elements which makes it advantageous (Schuiling and Andrade, 1999). Struvite is also used as a raw material in phosphate industry for the production of Mg-Phosphate cements in building materials and also in making fire resistant panels (Schuiling and Andrade, 1999; Stratful et al., 2001).

2.6.6 Full-scale Applications and Economics of the Process

There are several examples illustrating the mass production of struvite from wastewater in the world, such as in Japan (Unitika, Hiagari Sewage Treatment Plant), Australia (Oxley Creek Wastewater Treatment Plant, Brisbane), USA (Sacramento Regional Wastewater Treatment Plant), Italy (Treviso Wastewater Treatment Plant).

In all of these plants, sewage sludge digester effluents are used as the raw material (Özden et al., 2007). There is no full-scale application of struvite precipitation technique in livestock industry (Burns and Moody, 2002).

Commercial sales of struvite to industry and the public have been taking place for the past eight years by Unitika Ltd, Japan (Ueno and Fujii, 2001). The fertiliser, under the name of "Green MAP II" has been promoted with focus on its environmental credentials. The selling price of the product was €250/ton in 2001, with transport costs borne by the purchaser. Münch and Barr (2001b) worked on the development of a business plan for the full-scale application and commercialization of struvite precipitation process, and evaluated selling price of the recovered struvite. Based on the N and P content alone, the sales price was estimated as $234/ton when the struvite is used in broad-scale agriculture. However, they stated that the intention is to use struvite as "boutique" fertilizer in specialized applications. For such a case, the sales price is to be higher. For instance, a sales price of $3800/ton has been reported in Japan (Taruya et al, 2000 cited in Münch and Barr, 2001b).

To the best of our knowledge there is no production of struvite from wastewater in Turkey. However, the data taken from Turkish Statistical Institute (TSI) illustrated that there was a significant increase (48.6 %) in the import rate of fertilizers from 2007 to 2008 (Oral, 2009). Therefore, it is postulated that the set up of a full-scale struvite crystallization plant from wastewater would reduce the need to imported fertilizers.

CHAPTER 3

MATERIALS AND METHODS

3.1 Waste Characteristics

The experimental studies performed in this study can be categorized by considering the wastes that were used in three different experimental sets. There were three types of wastes which were subjected to struvite precipitation experiments, namely effluents of lab-scale anaerobic batch reactors, effluent of a full-scale poultry manure co-digester and effluent of a full-scale poultry manure digester.

During the characterization analysis the reliability of the data were tested by calculating the coefficient of variation (CV) of the data points. It is a statistical measure of the dispersion of data points in a data series around the mean. CV is the ratio of standard deviation to the mean, multiplied by 100 and is reported as percentage. Throughout the thesis it is used to measure the reliability of the measurements and a CV of 10% is used as the criteria for rejecting the result of the measurement. In such a case the same analysis were repeated by taking another sub-sample from the stock solution.

3.1.1 Characterization of Waste and Seed Culture used in Set 1

Fresh poultry manure was collected from a commercial farm housing about 500,000 laying hens located in Ankara, Turkey. Sewage sludge was collected from the influent of anaerobic digesters of Greater Municipality of Ankara Central Wastewater Treatment Plant, Turkey. Both wastes were characterized and kept refrigerated at 4°C until used. The composition of poultry manure is summarized in Table 3.1. Before characterization the litters (sawdust, stones, straw etc.) present in the manure are separated manually and the manure was homogenized by thoroughly mixing for half a day.

Except metals other analysis used for the characterization of poultry manure, sewage sludge and digested seed culture were conducted in triplicate i.e. three sub-samples were taken from the continuously mixed stock solution and analyzed. Most of the metal analyses were conducted in duplicate. The details are depicted in the following tables (Table 3.1, 3.2 and 3.3).

Table 3.1. Characterization of poultry manure

Parameter	Poultry Manure
TS, % by weight	70.1±0.1[a]
VS ,% of TS	86.2±0.2
COD, mg/g dry matter	456.0±53.0
TKN, mg N/g dry matter	20±1.0
NH_4-N, mg N/g dry matter	7.6±0.1
NH_4-N,% TKN	45.3±16.2
TP, mg P/g dry matter	6.1±0.1

[a]mean ± std (n=3)

The mixed anaerobic culture obtained from anaerobic sludge digesters of Greater Municipality of Ankara Central Wastewater Treatment Plant was used as seed in the study. The mixed anaerobic culture concentrated by settling and subjected to 10 days of digestion prior to use. The compositions of sewage sludge and digested seed culture are summarized in Table 3.2. In COD analysis; the results were represented as mass/mass for poultry manure because the analysis was conducted by taking a specified mass of manure, whereas the results for sewage sludge and digested seed culture were represented as mass/volume since the analysis were conducted with the liquid phase samples taken from the stock solutions of these wastes.

The effluents of reactors were subjected to solid-liquid separation by means of centrifugation and sieving. The liquid phase obtained after solid-liquid separation of the anaerobic reactor effluents were used in struvite precipitation experiments.

Table 3.2. Characterization of digested seed culture and sewage sludge

Parameter	Digested Seed Culture	Sewage Sludge
TS, % by weight	23.4±0.9[a]	25.6±0.2
VSS, % of TS	50.3±1.8	33.6±0.2
TSS, g/L	22.6±0.8	23.3±0.5
VSS, g/L	11.4±0.2	7.6±0.5
COD, mg/L	18976.4±111.4	27023±1249.8
sCOD, mg/L	78.1±0.0	4453.1±110.5
TKN, mg N/L	1024.8±12	1619.0±103.0
NH_4-N, mg N/L	413.2±8.0	492.1±5.0
TP, mg P/L	505.3±18.5	510.3±54.0
PO_4-P, mg P/L	21.2±0.6	135.4±2.3
Alkalinity, mg $CaCO_3$/L	7500	3000
pH	7.7	6.3

[a]mean ± std (n=3)

Table 3.3. Metal content of poultry manure, digested seed culture and sewage sludge

Metal, mg/g	Poultry Manure	Digested Seed Culture	Sewage Sludge
Al	<0.1	4.87±0.67[a]	3.64±0.42
As	<0.00005	0.0004	0.0004
Ca	41.6±0.0	41.9±0.0	25.0±0.0
Cd	<0.0001	0.007±0.01	0.004±0.007
Co	<0.005	<0.005	<0.005
Cr	0.003±0.007	0.86±0.01	1.37±0.05
Cu	0.02±0.02	0.33±0.03	0.23±0.01
Fe	0.16±0.004	12.45±0.03	8.38±0.07
Hg	0.0007	0.00006	0.0004
K	14.3	4.82	3.88
Mg	3.29±0.01	7.21±0.01	5.86±0.01
Mn	0.18±0.01	0.28±0.01	0.20±0.02
Ni	0.007±0.01	0.07±0.02	0.06±0.03
Pb	0.003±0.02	0.06±0.01	0.04±0.00
Zn	0.22±0.03	2.75±0.03	1.70±0.01

[a]mean ± std (n=2)

Due to the fact that metals can be incorporated into the crystal lattice or sorbed to the surface of struvite (Kamnev et al., 1999; Rontentalp et al.2007), it is important to know the sources of metals and heavy metals in the digested material. For this purpose, both substrates (poultry manure and sewage sludge) and digested seed culture were analyzed for their metal content (Table 3.3).

Basal Medium

The composition of basal medium (BM) used in the experiments was as follows (concentrations of the constituents are given in parentheses as mg/l): NH_4Cl (1200), $MgSO_4·7H_2O$ (400), KCl (400), $Na_2S·9H_2O$ (300), $CaCl_2·2H_2O$ (50), $(NH_4)_2·HPO_4$ (80), $FeCl_2·4H_2O$ (40), $CoCl_2·6H_2O$ (10), KI (10), $MnCl_2·4H_2O$ (0.5), $CuCl_2·2H_2O$ (0.5), $ZnCl_2$ (0.5), $AlCl_3·6H_2O$ (0.5), $NaMoO_4·2H_2O$ (0.5), H_3BO_3 (0.5), $NiCl_2·6H_2O$ (0.5), $NaWO_4·2H_2O$ (0.5), Cysteine (10), $NaHCO_3$ (6000). This BM contained all the necessary micro- and macro-nutrients required for an optimum anaerobic microbial growth (Demirer et al., 2000).

3.1.2 Characterization of Waste used in Set 2

The wastewater sample was taken from a full-scale biogas plant, co-digesting poultry manure and maize silage at a waste mixing ratio of 0.25:0.75 located in Munich, Germany. The biogas plant has three anaerobic digesters; one primary anaerobic digester, connected in series to the two parallel connected secondary anaerobic digester. The sample (designated as FS) was collected from the effluent of primary anaerobic digester and kept frozen during storage. The solids content of the effluent sample were; TS 86.8±2.1 g/kg, VS 75.1 % of TS and was subjected to solid-liquid separation by means of centrifugation and both phases of the effluent were characterized (Table 3.4 and Table 3.5) and kept refrigerated at 4°C until used.

Table 3.4. Characterization of the liquid phase of the FS sample

Parameter	Concentration
TS, g/kg	39±1[a]
VS, % of TS	69±1
COD, mg/L	44208±658
sCOD, mg/L	27366±0
TKN, mgN/L	6173±136
NH_4-N, mgN/L	3907±105
PO_4-P, mgP/L	60.5±0.7
TP, mgP/L	209±1
Al [b], mg/L	6.67
Ca, mg/L	441
Cd, mg/L	<0.025
Co, mg/L	0.2
Cr, mg/L	0.3
Cu, mg/L	3.4
Fe, mg/L	110
Hg, mg/L	0.008
K, mg/L	5380
Mg, mg/L	10.5±1.8
Ni, mg/L	0.3
Pb, mg/L	0.3
Zn, mg/L	15.5
Conductivity, mS/cm	33
pH	7.9

[a] mean ± std (n=2)

[b] The Al, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Ni, Pb, Zn concentrations depict the mean concentration of the duplicate analysis.

Table 3.5. Characterization of the solid phase of the FS sample

Parameter	Concentration
TS, g/kg	175±10[a]
VS, % of TS	79.6±0.6
TKN, mgN/g dry matter	30.1±2.8
TP, mg P/g dry matter	16.1±0.2
Al[b], mg/g	878
Ca, mg/g	40307
Cd, mg/g	<2.3
Co, mg/g	3.12
Cr, mg/g	7.76
Cu, mg/g	113
Fe, mg/g	4715
Hg, mg/g	<0.078
K, mg/g	26235
Mg, mg/g	7849
Ni, mg/g	5.13
Pb, mg/g	<4.66
Zn, mg/g	647

[a] mean ± std (n=2)

[b] The Al, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Ni, Pb, Zn concentrations depict the mean concentration of the duplicate analysis.

3.1.3 Characterization of Waste used in Set 3

The wastewater sample was taken from a full-scale biogas plant, digesting poultry manure generated from a small poultry farm housing 30,000 laying hens located in Forchtenberg, Germany. The biogas plant has one mesophilic anaerobic digester. The sample (designated as MS) was taken from the effluent of the digester. It is kept refrigerated at 4°C during storage. The solids content of the effluent sample (TS 116±20 g/kg, VS 42±7 % of TS) were high and the sample was non-homogenous characteristics. The effluent sample was subjected to solid-liquid separation by means of centrifugation and both phases of the centrifuged effluent were characterized (Table 3.6 and Table 3.7) and kept refrigerated at 4°C until used.

Table 3.6. Characterization of the liquid phase of the MS sample

Parameter	Concentration
TS, g/kg	16.3±0.0[a]
VS, % of TS	57.4±1.9
COD, mg/L	14516±639
sCOD, mg/L	3713±22
TKN, mgN/L	5838±12
NH_4-N, mgN/L	4612±117
PO_4-P, mgP/L	163±0
TP, mgP/L	287±1
Al[b], mg/L	1.39
Ca, mg/L	78.6
Cd, mg/L	<0.025
Co, mg/L	0.067
Cr, mg/L	0.081
Cu, mg/L	0.455
Fe, mg/L	7.24
Hg, mg/L	<0.005
K, mg/L	3112
Mg, mg/L	5.3±0.1
Ni, mg/L	0.21
Pb, mg/L	<0.05
Zn, mg/L	3.11
Conductivity, mS/cm	32.2
pH	8.58

[a] mean ± std (n=2)

[b] The Al, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Ni, Pb, Zn concentrations depict the mean concentration of the duplicate analysis.

Table 3.7. Characterization of the solid phase of the MS sample

Parameter	Concentration
TS, g/kg	273±4[a]
VS, % of TS	31.0±0.6
TKN, mgN/g dry matter	13±0.1
TP, mg P/g dry matter	18.5±0.2
Al[b], mg/g	703
Ca, mg/g	216450
Cd, mg/g	<2.8
Co, mg/g	<1.7
Cr, mg/g	20.9
Cu, mg/g	41.6
Fe, mg/g	1334
Hg, mg/g	<0.089
K, mg/g	11101
Mg, mg/g	9038
Ni, mg/g	12
Pb, mg/g	<5.6
Zn, mg/g	382

[a] mean ± std

[b] The Al, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Ni, Pb, Zn concentrations depict the mean concentration of the duplicate analysis.

3.2 Analytical Methods

The experimental part of this study was conducted at two different universities, Middle East Technical University (METU), Turkey and University of Stuttgart (UST), Germany. Experiments of Set 1 were conducted in METU and experiments of both Set 2 and Set 3 were conducted in UST. Therefore, two different guidelines for standard methods were followed in the analytical methods.

3.2.1 Analytical Methods used in Set 1

All analysis (COD, VSS, TSS, TS NH_4-N, TKN, PO_4-P, TP and metals) were performed according to standard methods (APHA, 2005). The followed standard methods are presented in Table 3.8. Soluble COD analyses were performed by filtering sample through 0.45 μm pore sized filters prior to applying the standard method (APHA, 2005). During the laboratory study, pH levels were measured with a pH meter (HI 8314, Hanna Instruments) and a pH probe (HI 1230, Hanna Instruments).

Table 3.8. The standard methods used in Set 1 (APHA, 2005)

Parameter	APHA Standard method
TS	2540-B Total Solids Dried at 103-105 °C
VS	2540-E Fixed and Volatile Solids Ignited at 550 °C
TSS	2540-D Total Suspended Solids Dried at 103-105 °C
sCOD, COD	5220-B Open Reflux Method
Alkalinity	2320-B Titration Method
TKN	4500-N_{org} B Macro-Kjeldahl Method
NH_4-N	4500-NH_3-C Titrimetric method
TP	4500-P-J, 4500-P-E
PO_4-P	4500-P-E. Ascorbic Acid Method
Hg	3112-B Cold Vapor Atomic Absorption Spectrometric Method
K	3500-K-B Flame Photometric method
As	3114-B Manual Hydride Generation Atomic Absorption Spectrometric Method
Al, Ca,Cr	3111-D Direct Nitrous Oxide-Acetylene Flame Method
Mg,Cd,Co, Cu, Fe, Ni Pb, Zn	3111-B Direct Air-Acetylene Flame Method

Metal Determinations

Concentrations of metals (Al, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn) were performed by means of atomic absoption spectrometry (Perkin Elmer AAnalyst 400 Flame Atomic Absorption Spectrometry) according to standard methods (APHA, 2005). Hg analysis was conducted according to the cold-vapor atomic absorption spectrometry and As analysis were conducted according to standard methods by manual hydride generation method (APHA, 2005). K analysis was conducted as described in standard methods by using flame photometric method using Jenway PFP7 Model Flame Photometer (APHA, 2005). For total metal determinations of reactor effluents, microwave (Berghof MWS-2) digestion was applied by the addition of 10mL 65 % (v/v) HNO_3 and 2 mL 37 % (v/v) H_2O_2 to 1 gram sample in pressure-resistant Teflon tubes. The microwave program applied was in the following order: 160 °C and 800 W for 5 min, 220 °C and 900 W for 40 min, and 20 min of cooling period at about 100 °C without power appliance. Then, the digested material was cooled and filtered through coarse filter and filled up to 25 mL with de-ionised water. For the soluble metal concentration of liquid phase reactor effluents, samples were filtered through 0.45 µm pore sized filters and digested with 65 % (v/v) HNO_3 until the pH of the solution drops below 2.0. Only glassware, thoroughly cleaned with HNO_3, was used.

Orthophosphate

Orthophosphate determinations for the characterization of sewage sludge and seed culture was carried out as described in standard methods (APHA, 2005) and spectrophotometric measurements were performed at 880 nm wavelength by Cole Parmer 1200 Spectrophotometer. All the other orthophosphate determinations were performed by using Aqualytic Photometer and Aqualytic orthophosphate reagent sets. The analyses were carried out as described in Aqualytic PC Multi Direct Instruction Manual (Method number: 323) adopted from standard methods (APHA, 1992).

Biogas Production

Biogas productions in batch reactors were determined by a water displacement device, measured by using a graduated water reservoir (2000 mL) connected directly to the reactor headspace. Acid brine (10% NaCl w/v, 2% H_2SO_4 v/v) was used as displaced water, in order to eliminate the solubilization of the biogas (Tezel et al., 2007). The illustrative photograph of the reactors and the gas collection column can be seen in Figure 3.1.

Figure 3.1. An illustrative photo of glass reactor and gas collection unit

Biogas Compositions

Biogas compositions were determined with a gas chromatograph (Thermo Electron Co.) equipped with a thermal conductivity detector (TCD). Gas samples for gas composition analysis were withdrawn from the reactors by a 100 µL Hamilton gas-tight glass syringe. Produced biogas was separated as hydrogen (H_2), carbon dioxide (CO_2), oxygen (O_2), methane (CH_4) and nitrogen (N_2) by using parallel connected columns (CP-Moliseve 5A and CP-Porabond Q) at a fixed oven temperature of 45 °C. Helium was used as carrier gas at 100 kPa constant pressure. The inlet and detector temperatures were set to 50 °C and 80 °C respectively (Yılmaz and Demirer, 2008).

Volatile Fatty Acids

Volatile fatty acid (VFA) determinations were also conducted using the same gas chromatograph (Thermo Electron Co.).However the column, the detector and the operational conditions were different: Nukol column (Model 25326, 15 m × 0.53 mm) was used to separate VFAs (acetic, propionic, n-butyric, iso-butyric, n-valeric, iso-valeric, n-caproic, iso-caproic and n-heptanoic acids). Flame ionization detector (FID) was used for this purpose which was adjusted to 280 °C as operating temperature. Helium was used as carrier gas with a constant flow rate of 6 mL/min and the inlet temperature was kept at 250 °C. Oven temperature was initially set to 100 °C with 2 min holding time and then increased up to 200 °C with 8 °C/min ramping (Doğan et al., 2008).

XRD analysis

X-ray diffraction (XRD) technique was used to determine the compositional structure of the products and confirm the presence of struvite in the precipitates. The dried precipitate was separated manually from the filter paper and identified using Rigaku D- Max 2000X-ray diffractometer using Cu Kα radiation. The diffractometer was running at 40 kV and 20 mA. The data were collected over the two–theta range of 5-70° using step size of 0.05°, and counts were collected for 1.5 seconds at each step. XRD analysis of the samples and their identification were carried out at the Advanced Analysis Laboratory (İleri Analizler Laboratuvarı) of Istanbul University, Turkey.

Two subsequent steps were followed during qualitative identification of minerals via XRD analysis. At the first step, Jade 6.5 qualitative analysis program (installed to the XRD equipment) with a library of about 120,000 powder diffraction file (PDF) of minerals was used for the automatic match of the XRD patterns of the sample and the standards in the library. (See Appendix A for the PDF cards of the selected minerals.) At the second step, manual search was done for the confirmation of the findings of the program and the match of the minerals predicted to be present in the mixed sample via other indicators e.g. ion analysis. In the second step, the identification was based on a systematic comparison of strong lines of the unknown and standard patterns, which should agree throughout the *d* spacing and two-theta degree (Klug and Alexander, 1967). The unknown material was tentatively identified by finding the file whose three strong lines (including the strongest line) matched in both *d* spacing and two-theta degree the three strong lines of the unknown pattern (Klug and Alexander, 1967). The same method was applied for the identification of each precipitate collected from the experiments.

Both the pattern preparation and the identification of the minerals via XRD were done by people with expertise. However, one limitation of pattern preparation is the nature of the material as a diffractor of X-rays (Klug and Alexander, 1967). Although several researchers state minimum detection limit for XRD of mixed materials to be low, the minimum detection limit for the samples collected from the experiments conducted in this study was not defined by the laboratory. In the literature it is stated that many crystalline substances give such sharp powder patterns that they are detectable when present to the extent patterns of 1 to 2 percent, or less, in a mixture (Klug and Alexander, 1967; Bunn, 2007; Dutrow and Clark, 2009). Other materials give such poor patterns that, although they can be readily identified when not alone, they may be detected when present in a mixture even to the extent of 50 percent (Klug and Alexander, 1967).

In most of the studies focusing on the nutrient recovery via struvite precipitation XRD analysis was used for the confirmation of the presence of struvite in the mixed material (Doyle and Parsons, 2002; Wang et al.,2006; Kim et al., 2006; Çelen et al., 2007). However, several researchers also indicated the limitation of XRD method for the identification of all minerals present in the mixed material as impurities (Burns et al., 2001; Çelen et al., 2007). Scanning electron microscopy (SEM), elemental analysis and energy dispersive spectroscopy (EDS) were the other supportive methods used together with XRD to confirm the presence of struvite in the mixed precipitate and to determine the purity of the product (Münch and Barr, 2001a; Le Corre et al., 2005; Wang et al., 2005). However, in this study the confirmation of the presence of struvite was done by the use of XRD together with ion (NH_4-N, PO_4-P, Mg and other metals) analyses.

3.2.2 Analytical Methods used in Set 2 and Set 3

All analyses (COD, sCOD, VSS, TSS, TS NH_4-N, TKN, TP and metals) except orthophosphate were performed according to the DIN (Deutsches Institut für Normung e.V.) standards (Table 3.9).

Table 3.9. The standard methods used in Set 2 and Set 3 (Deutsches Institut für Normung e.V.)

Parameter	DIN standard method
TS	DIN 38 409 Part 1/1 DEV H 1/1
VS	DIN 38 409 Part 1/3 DEV H 1/3
sCOD, COD	DIN 38 409 Part 41/2 DEB H 41/2
TKN	DIN EN 25 663 DEV H11
NH_4-N	DIN 38 406 Part 5 DEV E5
TP	DIN 38 414 Part 12 DEV S12
PO_4-P	DIN EN ISO 6878
Mg	DIN 38406 Part 3 DEV E3 / DIN EN ISO 11885 E22
Hg	DIN EN ISO 1483 – E12
Al, Ca, Cd, Co, Cr, Cu, Fe, K, Ni, Pb, Zn	DIN EN ISO 11885 E22

COD, sCOD, VSS, TSS, TS NH_4-N, TKN, TP and Mg determinations were performed at the laboratories of Wastewater Technology (AWT) Department of the University of Stuttgart, Germany. Magnesium determinations of the liquid samples were carried out by using Dr. Lange spectrophotometer (CADAS 200) and Hach Lange reagent sets (LCK 326). Magnesium and other metal (Al, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Ni, Pb, Zn) determinations for the solid phase characterization were carried out in the Hydrochemistry Department of the University of Stuttgart as described by DIN standards.pH levels were measure with WTW pH 323 pH meter.

XRD analysis

XRD analysis and subsequent identification of the dried precipitates collected from Experiments FS-P6, FS-P8, MS-P3, MS-P6 and MS-P8 were conducted in the Karlsruhe Research Center, Germany. The dried precipitates collected from these samples were separated manually from the filter paper and subjected to XRD analysis. The XRD analysis of the samples was conducted using Siemens Bruker D5000 X-ray diffractometer using Cu Kα radiation by the Head of the Division of Nanomineralogy of the Karlsruhe Research Center. The data were collected over the two–theta range of 13.5-34.5° using step size of 0.03°, and counts were collected for 10 seconds at each step. The rest of the XRD analyses of the precipitates collected from the experiments of set 2 and set 3 were done as described in Section 3.2.1 (the XRD analysis used for set 1).

3.3 Experimental Sets and Procedures

There were three experimental sets in this study. The schematic representation of the experimental sets is depicted in Figure 3.2.

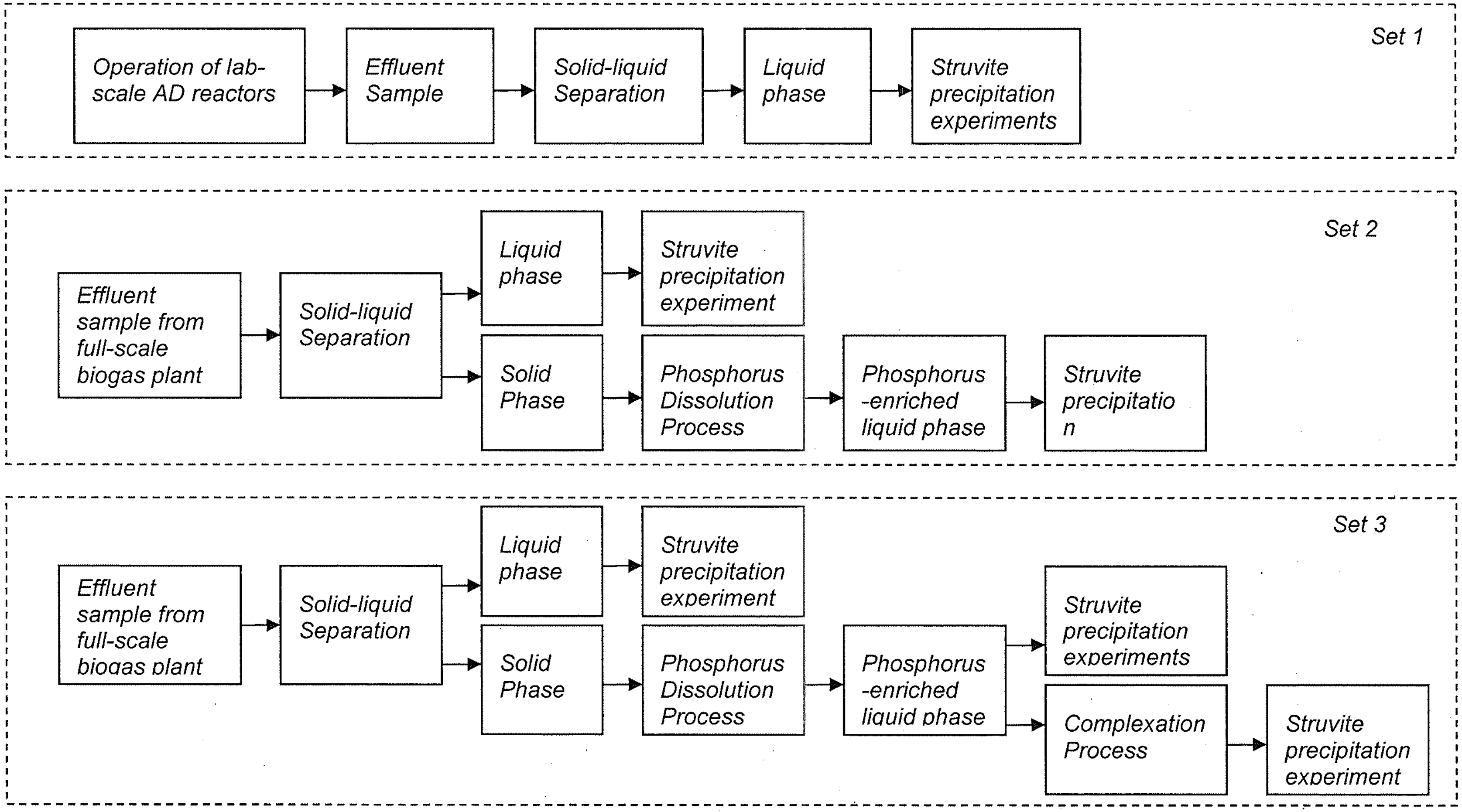

Figure 3.2. Schematic representation of the experimental sets

3.3.1 Set 1: Anaerobic Reactors and Struvite Precipitation from the Reactor Effluents

This set mainly consists of two parts: operation of anaerobic reactors and struvite precipitation experiments with the reactor effluents. In the first part, laboratory scale anaerobic batch reactors co-digesting poultry manure and sewage sludge were operated. After the reactor operations were stopped, reactor effluents were subjected to solid-liquid separation. In the second part, struvite precipitation experiments were conducted with the liquid phase of the reactor effluents.

3.3.1.1 Anaerobic Reactors

A set of mesophilic anaerobic batch reactors co-digesting poultry manure and sewage sludge were operated in the study. In order to determine the effect of waste mixing ratio on biomethanation potentials and effluent nutrient (N and P) concentrations five different waste mixing ratios (poultry manure:sewage sludge as 1.00:0.00, 0.54:0.46, 0.28:0.72, 0.06:0.94, 0.00:1.00) in terms of COD were used in the reactors (Table 3.10). All reactors have a total volume of 5 L with an effective volume of 4.5L. The reactors were incubated with different initial COD concentrations and have different ratio of food (COD) to microorganisms [volatile suspended solids (VSS)], i.e. F/M (Table 3.10).

In order to observe the effect of nutrient and trace metal supplementation on the anaerobic digestion and effluent nutrient concentrations, one reactor with waste mixing ratio of poultry manure to sewage sludge of 0.06:0.94 (Table 3.10) was operated both in the presence and absence of basal medium (BM) [R6 and R4, respectively]. Initial alkalinities of the reactors were measured before incubation of the reactors; in all the reactors alkalinity values exceed 4000 mg/L as $CaCO_3$. Since alkalinity concentrations of the reactors were above the level usually required (2000 - 4000 mg/L as $CaCO_3$) to maintain the pH at or near neutral, external alkalinity was not added to the reactors except R6 (Tchobanoglous et al., 2003).

One control reactor without BM was run during the study in order to determine the background gas production. After the addition of seed culture and BM where necessary, and wastes all reactor were purged with N_2 for 4-5 min to maintain the anaerobic conditions. The reactors were incubated at 35 ± 2 °C in a temperature controlled room. Continual mixing was applied at 180 rpm by the use of magnetic stirrers for 64 days of operation. Biogas productions were measured daily and biogas compositions were recorded periodically. At the end of reactor operations effluents of all reactors were subjected to pH, COD, sCOD, TKN, NH_4-N, TP, PO_4-P and VFA determinations.

Table 3.10. Operating conditions of the reactors

Reactor	Waste mixing ratio (PM:SS)[a]	Initial COD (mg/L)	F/M (mgCOD/mg VSS)
R1	1.00:0.00	14,250	1.1
R2	0.54:0.46	16,500	1.6
R3	0.28:0.72	18,800	2.1
R4	0.06:0.94	27,800	3.8
R5	0.00:1.00	35,000	5.2
R6[b]	0.06:0.94	29,500	4.2

[a] PM: Poultry manure; SS: Sewage sludge

[b] Contained BM supplementation

3.3.1.2 Struvite Precipitation from the Reactor Effluents

The reactor effluents were dark in colour and high in COD concentrations (Section 4.1.1, Table 4.2). Higher COD levels in animal waste slurries correlate to higher total and suspended solids concentrations (Burns et al., 2001). Because waste strength affects struvite solubility (Schulze-Rettmer, 1991; Burns et al., 2001) solid-liquid separation of the reactor effluents was adopted prior to struvite precipitation experiments. Then the liquid phase of each reactor effluent was used for struvite precipitation experiments. Solid-liquid separation of the reactor effluents was achieved by centrifugation (Sorvall Instruments Dupont RC5C) for 15 min at 6000 rpm and sieving through a screen of 0.0139 in (0.355 mm) mesh size. The liquid phase of the reactor effluents were analysed for its struvite forming ions and metals (Table 3.11 and Table 3.12).

After centrifugation, the liquid phase of the effluents was stored at 4°C until used. The experiments were conducted in continuously stirred batch reactors at room temperature (21-22°C).

Table 3.11. Concentration of struvite forming ions, COD, pH and initial Mg:N:P ratio in the liquid phase of reactor effluents

Reactor	Concentration, mg/L			Initial molar	pH	COD
	NH_4-N	PO_4-P	Mg	ratio of Mg:N:P		mg/L
R1	582±1[a]	6.4±0.0	10.7±0.3	12:201:1	8.1	703±27
R2	624±2	9.6±0.0	49.3±4.9	7:144:1	8.2	818±27
R3	669±2	7.4±0.2	67.9±7.2	12:200:1	8.1	970±27
R4	811±4	8.1±0.1	96.7±5.6	15:221:1	8.1	3422±108
R5	900±0	7.1±0.0	69.9±10.6	13:280:1	8.0	3498±108
R6	883±1	10.7±0.3	69.2±7.8	8:183:1	8.1	2395±161

[a] mean±std (n=2)

Table 3.12. Concentration of the metals in the liquid phase of the reactor effluents before the struvite precipitation experiments

Metal[a,b],mg/L	R1	R2	R3	R4	R5	R6
As, mg/L[a]	0.005±0.00[c]	0.004±0.0003	0.008±0.00	0.009±0.00	0.006±0.00	0.006±0.00
Ca, mg/L	98±11	28	19±6	128±6	60±24	133± 4
Cu, mg/L	0.6±0.02	0.35± 0.01	0.2±0.004	<0.001	<0.001	0.2±0.01
Fe, mg/L	0.090±0.001	0.05±0.002	0.04±0.009	0.03±0.01	0.07±0.05	0.2±0.01
Hg, mg/L	0.45	0.40	0.45	0.25	0.4	0.47
K, mg/L	138±20	103±6	102±9	90±18	76±11	107±28
Ni, mg/L	0.25±0.009	0.25±0.006	0.25± 0.001	0.5±0.009	0.3±0.002	0.3±0.009
Pb, mg/L	0.05±0.0007	0.03±0.009	0.04±0.01	0.05±0.04	0.07±0.02	0.1±0.05

[a] Al, Cd, Co, Cr, Mn and Zn concentrations were below the minimum detection limit.
[b] The metal concentrations indicate soluble concentrations.
[c] mean±std (n=2)

Procedure followed in the Struvite Precipitation Experiments in Set 1

Four consecutive steps are followed in the struvite precipitation experiments; (i) addition of chemicals, (ii) mixing, (iii) settling and (iv) filtration (Figure 3.3). Each struvite reactor contained 150 mL of sample. Firstly, Mg and PO_4-P containing chemicals were added into the reactors. The amounts of Mg and PO_4-P ions to be added were calculated considering initial concentrations of these ions in wastewater. In the experiments $MgCl_2.6H_2O$ was used in its solid form as the magnesium source and 85 % H_3PO_4 (v/v) was used as phosphorus source, unless otherwise stated. Following the addition of the chemicals the pH adjustments were made using 25 % NaOH (v/v) solution. Since the volume of NaOH added were very small, dilution effect was neglected. All chemicals used in experiments were analytical grade. Following the addition of the chemicals, the pH of the reactor was adjusted to the desired level. Then, the pH of the reactor content was monitored until observing a constant pH at the adjusted level with a variation of ± 0.01 pH units, which was accepted as an indication for completion of struvite formation. The kinetics of struvite formation is fast and reported equilibrium times are less than or equal to 1h (Çelen and Türker, 2001; Nelson et al., 2003). After the pH of the solution became constant, 30 min of mixing was applied. Reactor content was allowed to settle down for 60 min at the end of mixing period.

After the struvite formation reaction ceased, the reactor content was filtered through coarse filter and the filtrate was analyzed for its PO_4-P, NH_4-N and Mg content. The filter paper was dried in constant temperature room at 35±2°C overnight. The drying temperature was selected to prevent struvite crystals from losing their water of crystallization, which occurs at 60 °C (Ando et al., 1968; Ohlinger et al., 1999). After drying, the precipitate was separated manually from the filter paper and kept at room temperature (21-22°C) until analyzed by X-ray Diffractometry (XRD). In the struvite precipitation experiments the effects of important parameters; molar concentration ratio of the struvite forming ions (Mg:N:P), pH, seeding material addition and the effect of calcium ion were investigated. Table 3.13 depicts the summary of the experiments conducted with the effluent of each reactor.

Table 3.13. Summary of struvite precipitation experiments conducted with the effluent of each reactor

Struvite Precipitation Experiments	Reactor
Molar ratio	R1, R2, R3, R4, R5, R6
pH	R2, R3, R4
Seeding	R1, R3
Foreign ion *(Calcium)*	R3
Ammonia stripping	R2

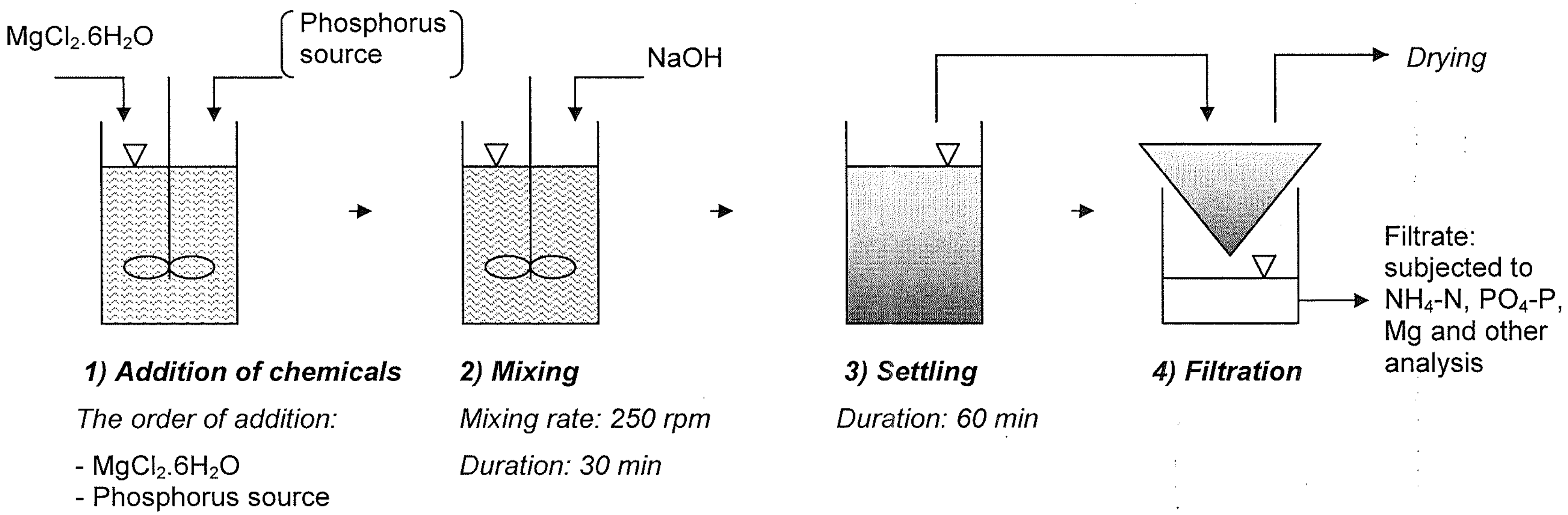

Figure 3.3. Procedure of struvite precipitation experiments

Molar Ratio (Mg:N:P) Experiments

In order to observe the effect of molar concentration ratio of the struvite forming ions (Mg:N:P) four different Mg:N:P ratios (Mg:N:P as 1:1:1, 1.3:1:1,1.5:1:1 and 0.7:1:1) were used. In all of the reactors the initial concentration of the NH_4-N (Table 3.11) was the highest among the three ions. Therefore, its concentration was taken as the basis and total (initial + added) molar concentrations of Mg and PO_4-P were raised to the corresponding molar concentration (42±0.1 - 64±0.0 mM) to obtain a molar ratio of Mg:N:P equal to 1:1:1. The other molar concentration ratios were prepared by adding the calculated amount of chemicals into the reactors, considering the initial concentrations of ions present in wastewater (Table 3.11).

Table 3.14. The experimental setup of molar ratio experiments

Experiment no.	Reactor	Molar ratio of Mg:N:P	Phosphorus source	pH
E1	R1	1:1:1	H_3PO_4	8.5
E2	R1	1.3:1:1	H_3PO_4	8.5
E3	R1	1.5:1:1	H_3PO_4	8.5
E4	R2	1:1:1	H_3PO_4	8.5
E5	R2	1.3:1:1	H_3PO_4	8.5
E6	R2	1.5:1:1	H_3PO_4	8.5
E7	R3	1:1:1	H_3PO_4	8.5
E8	R3	1.3:1:1	H_3PO_4	8.5
E9	R3	1.5:1:1	H_3PO_4	8.5
E10	R4	1:1:1	H_3PO_4	8.5
E11	R4	1.3:1:1	H_3PO_4	8.5
E12	R4	1.5:1:1	H_3PO_4	8.5
E13	R5	1:1:1	H_3PO_4	8.5
E14	R5	1.3:1:1	H_3PO_4	8.5
E15	R5	1.5:1:1	H_3PO_4	8.5
E16	R6	1:1:1	H_3PO_4	8.5
E17	R6	1:1:1	KH_2PO_4	8.5
E18	R6	1.3:1:1	H_3PO_4	8.5
E19	R6	1.5:1:1	H_3PO_4	8.5
E20	R6	1.5:1:1	KH_2PO_4	8.5
E21	R6	1.5:1:1	H_3PO_4	9.5
E22	R6	0.7:1:1	H_3PO_4	8.5

In two of the experiments conducted with R6 two different phosphorus sources, namely KH_2PO_4 and 85 % H_3PO_4 (v/v) were used for comparison. The experimental setup is presented in Table 3.14. Additionally in order to observe the effect of higher pH level at the molar concentration ratio of Mg:N:P of 1.5:1:1, Experiment 21 was conducted at pH level of 9.5.

pH Experiments

In order to determine the effect of pH on the removals of NH_4-N and PO_4-P, experiments were conducted at pH levels 8.0, 8.5 and 9.0 by the use of Mg:N:P molar ratio of 1:1:1 with the liquid phase of R2, R3 and R4 (Table 3.13). The experiments were conducted as described in the procedure (Figure 3.3). The experimental setup is presented in Table 3.15.

Table 3.15. The experimental setup of pH experiments

Experiment no.	Reactor	Molar ratio of Mg:N:P	pH
E23	R2	1:1:1	8.0
E24	R2	1:1:1	9.0
E25	R3	1:1:1	8.0
E26	R3	1:1:1	9.0
E27	R4	1:1:1	8.0
E28	R4	1:1:1	9.0

Seeding Experiments

In order to improve the performance of struvite formation by providing the adequate surface for reaction, seeding material addition was investigated. For this purpose, previously formed struvite was used as the seeding material. The seeding material was obtained from a struvite precipitation experiment conducted with synthetically prepared solution of 1000mg/L NH_4-N, 2214 mg/L PO_4-P and 1714 mg/L Mg concentration. The concentrations of struvite forming ions were adjusted in order to adjust the stoichiometry of struvite (Mg:N:P ratio of 1:1:1).

For the preparation of synthetic solution NH_4Cl, 85 % H_3PO_4 (v/v) and $MgCl_2.6H_2O$ were used. During the experiment the pH level was adjusted to 8.5 by the use of 25 % NaOH (v/v) solution and the experiment was conducted as described in the procedure (Figure 3.3, Section 3.3.1.2). Seeding experiments were conducted with the liquid phase effluents of R1 and R3 (Table 3.13).

All experiments were conducted by the use of Mg:N:P of 1:1:1 and as described in the procedure (Figure 3.3). The addition sequence applied was magnesium source ($MgCl_2.6H_2O$), phosphorus source (H_3PO_4), buffering reagent (NaOH) and seeding material, where necessary. Two levels of seed addition (10 g/L and 20 g/L) were tested and unseeded experiments were also conducted as the control experiments. The experimental setup is presented in Table 3.16.

Table 3.16. The experimental setup of seeding experiments

Experiment no.	Reactor no.	Seeding material (g/L)
E1[a]	R1	0
E29	R1	10
E30	R1	20
E7[a]	R3	0
E31	R3	10
E32	R3	20

[a] Control experiments.

Foreign Ion (Calcium) Experiments

Experiments were conducted in order to observe the effect of Ca ion on the removals of NH_4-N and PO_4-P. For this purpose three experiments were conducted with the liquid phase effluent of R3 at pH level of 8.5 as described in the procedure (Figure 3.3, Section 3.3.1.2). During the experiments $CaCl_2$ was used as the calcium source.

The addition sequence applied was magnesium source ($MgCl_2.6H_2O$), calcium source ($CaCl_2$), phosphorus source (H_3PO_4) and buffering reagent (NaOH). In the experiments three different molar ratio of Mg:Ca were used keeping the molar concentration of NH_4-N in excess (Table 3.17).

Table 3.17. The experimental setup of foreign ion experiments

Experiment no.	Reactor no.	Molar ratio of Mg:Ca:P:N	Total (initial + added) concentration (mg/L)			
			Mg	Ca	PO_4-P	NH_4-N
E33	R3	1:1:1:5	229	382	296	669±2[a]
E34	R3	1:2:1:5	229	764	296	669±2
E35	R3	2:1:1:5	458	382	296	669±2

[a] mean± std (n=2)

Ammonia Stripping Experiments

In order to be able to determine the effect of air stripping on NH_4-N removal, duplicate experiments were conducted with the effluent of R2 at room temperature (21-22°C). The experiments were conducted in batch reactors with continuous mixing as described in procedure (Figure 3.3, Section 3.3.1.2) without addition of any magnesium and/or phosphorus containing chemicals. A 150 mL sample from the liquid phase of the R2 effluent was placed in a beaker with a pH probe (HI 1230, Hanna Instruments). Following up the measurement of initial pH level, pH of the sample was raised to 8.5 by adding 25 % NaOH (v/v) under continuous mixing at 250 rpm. Mixing is applied for 30 min and then the reactor content was allowed to settle down for 60 min (settling period). Sample was withdrawn after the settling period and analyzed immediately to measure NH_4-N concentration.

3.3.2 Set 2: Struvite Precipitation from the Effluent of the Full-scale Co-digestion Plant utilizing Poultry Manure and Maize Silage

In this set, prior to struvite precipitation experiments solid-liquid separation of the biogas plant effluent was adopted. Struvite precipitation experiments were conducted in both the liquid phase and solid phase of the effluent. Prior to solid phase struvite precipitation experiments, phosphorus dissolution process was adopted to obtain phosphorus-enriched liquid phase.

Phosphorus Dissolution Process applied in Set 2 and Set 3

The solid phase obtained after solid-liquid separation of the biogas plant was subjected to phosphorus dissolution process prior to struvite precipitation experiments. Phosphorus dissolution was achieved in four steps; (i) dilution, (ii) acidic dissolution, (iii) mixing and (iv) solid-liquid separation (Figure 3.4). In order to be able to apply continuous mixing, the solid phase was diluted by distilled water till the total solids (TS) concentration became 5-10 %. Then, the pH of the diluted waste was adjusted to 2.0 by the addition of 20 % HCl (v/v). The acidic mixture was mixed at 250 rpm by using jar test apparatus (No: MSR12/180, Geppert Rührtechnik, Dreieich) for two hours. After the dissolution, separation of the phosphorus-enriched liquid phase from the remaining solid phase was achieved either by centrifugation (Sorvall Instruments, Dupont RC6) at 10000 rpm for 15 min and sieving through a screen of 0.022 in (0.56 mm) mesh size or filtering through folded filter of pore size 320 mm (Macherey-Nagel). Then, the filtrate (phosphorus-enriched liquid phase) was characterized and kept refrigerated at 4°C until used.

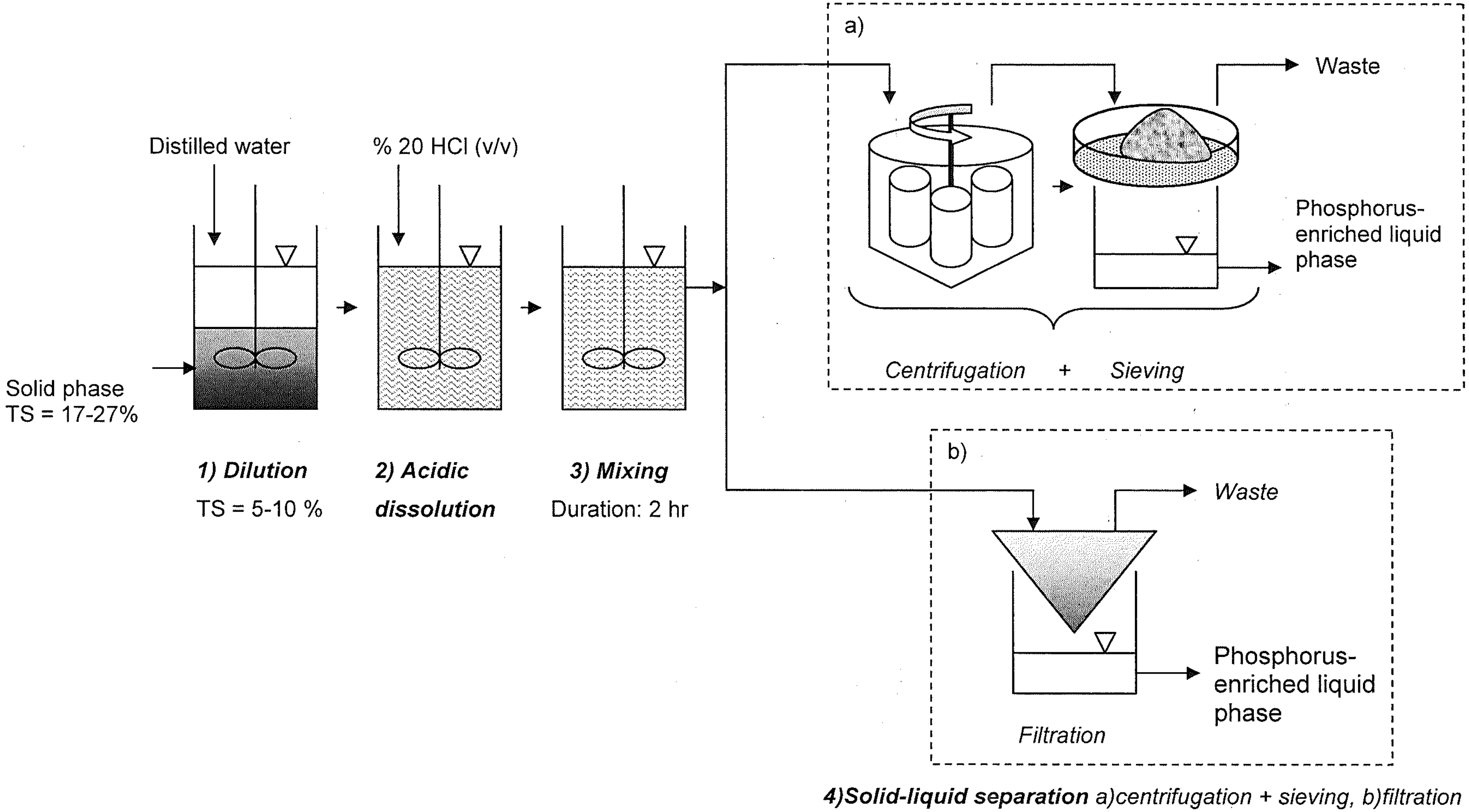

Figure 3.4 The schematic representation of the phosphorus dissolution process

Struvite Precipitation Experiments

The struvite precipitation experiments were conducted using the effluent of the full-scale poultry manure co-digestion plant located in Munich, Germany. The effluent of the biogas plant (designated as FS) was subjected to solid-liquid separation before the struvite precipitation experiments. Solid-liquid separation was achieved by centrifugation (Sorvall Instruments, Dupont RC6) for 15 min at 10000 rpm and sieving through a screen of 0.022 in (0.56 mm) mesh size. The liquid phase obtained after centrifugation was used directly for struvite precipitation experiments, whereas the solid phase was subjected to phosphorus dissolution process before the struvite precipitation experiments. After solid-liquid separation, both phases were characterized and stored at 4°C until used.

Procedure followed in the Struvite Precipitation Experiments in Set 2 and Set 3

Four consecutive steps are followed in the struvite precipitation experiments conducted with the liquid phase and phosphorus-enriched phase of the biogas plant effluents; (i) addition of chemicals, (ii) mixing, (iii) settling (iv) filtration (Figure 3.3, Section 3.3.1.2). The struvite precipitation experiments were conducted in continuously stirred batch reactors at room temperature (21-22°C). Each struvite reactor contained 150 mL of sample, unless otherwise stated, and was continuously mixed using a magnetic stirrer. During the experiments mixing speed was kept constant at 250 rpm.

The concentration of NH_4-N was kept constant at its original level in all experimental runs. After adding Mg containing chemical, PO_4-P containing chemical, where necessary, was added to the reactor. The amounts of Mg and PO_4-P ions to be added were calculated considering initial concentrations of these ions in wastewater. In the experiments $MgCl_2.6H_2O$ was used in its solid form as the magnesium source and 75 % H_3PO_4 (v/v) was used as phosphorus source, unless otherwise stated.

The pH adjustments were made using 20 % NaOH (v/v) solution. Since the volume of NaOH added were very small, dilution effect was neglected. All chemicals used in the experiments were analytical grade.

The pH of the reactor content was monitored until observing a constant pH at the adjusted level with a variation of ± 0.01 pH units, which was accepted as an indication for completion of struvite formation. After the pH of the solution became constant at the desired level, 30 min of mixing was applied and at the end of mixing period, reactor content were allowed to settle down for 60 min (Figure 3.3, Section 3.3.1.2). After the struvite formation reaction ceased, the reactor content was filtered through folded filter of pore size 320 mm (Macherey-Nagel) and the filtrate was analyzed for its PO_4-P, NH_4-N and metal content. The precipitates were dried in constant temperature room at 30±2°C overnight. After drying the precipitate was separated manually from the filter paper and kept at room temperature (21-22°C) until analyzed for XRD.

3.3.2.1 Liquid Phase Experiments of Full-scale Co-digestion Plant

Initial composition of the liquid phase contained a molar concentration ratio of 1:612:5 of Mg:N:P indicating that Mg ion is the limiting reactant for NH_4-N and PO_4-P removal by struvite precipitation (Table 3.4, Section 3.1.2). Therefore, it had to be added in all experiments to initiate struvite formation. Similarly, the concentration of PO_4-P (2.0±0.0 mM) was not adequate for higher removals of NH_4-N and it was necessary to add phosphorus to improve NH_4-N removal. In order to observe the effect of molar concentration ratio of the struvite forming ions (Mg:N:P) three different Mg:N:P ratios (Mg:N:P as 1:1:1, 1.3:1:1 and 1.5:1:1) were used. In the experiments, the concentration of NH_4-N was taken as the basis and total (initial + added) molar concentrations of Mg and PO_4-P were raised to the corresponding molar concentration (279±7.5 mM) to obtain a molar ratio of Mg:N:P equal to 1:1:1. The other molar concentration ratios were prepared by adding the calculated amount of chemicals into the reactors, considering the initial concentrations of the ions in the sample (Table 3.4, Section 3.1.2).

To observe the effect of phosphorus source on the removals of NH_4-N and PO_4-P, two different phosphorus containing chemicals (H_3PO_4 and $NaH_2PO_4.2H_2O$) were used in the experiments. These experiments were conducted keeping all other parameters, except the phosphorus source, the same. The experimental setup of the liquid phase experiments is presented in Table 3.18.

Table 3.18. The experimental set-up of the liquid phase experiments of FS sample

Experiment no.	Molar ratio of Mg:N:P	Phosphorus source
FS-L1[a]	1:1:1	H_3PO_4
FS-L2[a]	1.3:1:1	H_3PO_4
FS-L3[a]	1.5:1:1	H_3PO_4
FS-L4	1:1:1	$NaH_2PO_4.2H_2O$
FS-L5	1.3:1:1	$NaH_2PO_4.2H_2O$
FS-L6	1.5:1:1	$NaH_2PO_4.2H_2O$

[a] Experiments conducted with 200 mL of sample.

3.3.2.2 Solid Phase Experiments of Full-scale Co-digestion Plant

During the phosphorus dissolution process the solid phase of FS sample was diluted to 5 % TS, in order to allow continuous mixing. At the end of the mixing period the solid-liquid separation was achieved by centrifugation and sieving (Figure 3.4, Section 3.3.2). The phosphorus-enriched liquid phase was characterized (Table 4.8, Section 4.2.2) and kept refrigerated at 4°C until used. The phosphorus-enriched liquid phase was subjected to struvite precipitation experiments following the procedure described for Set 2.

In the struvite precipitation experiments conducted with the phosphorus-enriched liquid phase, the effects of molar concentration ratio of Mg, NH_4-N, PO_4-P (Mg:N:P) and molar concentration ratio of Mg to PO_4-P (Mg:P) were investigated, separately. In order to observe the effect of molar concentration ratio of the struvite forming ions (Mg:N:P) on the recovery of NH_4-N and PO_4-P, three different Mg:N:P ratios (1:1:1, 1.3:1:1 and 1.5:1:1) were used. In the phosphorus-enriched liquid phase initial molar concentration of the NH_4-N (Table 4.8, Section 4.2.2) was the highest among the three struvite forming ions and the initial molar ratio of Mg:N:P was 1:6:2. Therefore, in order to adjust the molar concentration ratio of Mg:N:P to the desired value, concentration of NH_4-N was taken as the basis (Table 3.19). Total (initial + added) molar concentrations of Mg and PO_4-P were raised to the corresponding molar concentration of NH_4-N (106±0.3 mM) to obtain a molar ratio of

Mg:N:P equal to 1:1:1. The other molar concentration ratios were prepared by adding the calculated amount of ions (Mg and PO_4-P) into the reactors considering the initial concentrations of these ions in the solution (Table 4.8, Section 4.2.2).

In order to investigate the effect of molar concentration ratio of magnesium to phosphate (Mg:P) on the recovery of PO_4-P and NH_4-N, three different Mg:P ratio, namely, 1:1, 1.3:1 and 1.5 :1 were used in the experiments. For the adjustment of Mg:P ratio, initial PO_4-P concentration in the solution was taken as the basis (Table 3.19). By the consideration of the initial molar concentration of PO_4-P (26.7±0.0 mM), the total (initial + added) molar concentration of Mg was raised accordingly. The experimental set-up of the phosphorus-enriched liquid phase of FS sample is presented in Table 3.19.

Table 3.19. Experimental set-up of the phosphorus-enriched liquid phase of the FS sample

Exp. no	Molar ratio tested	Basis of chemical addition	Molar ratio	Chemicals added	pH
FS-P1	Mg:N:P	NH_4-N	1:1:1	H_3PO_4, $MgCl_2.6H_2O$	8.5
FS-P2	Mg:N:P	NH_4-N	1.3:1:1	H_3PO_4, $MgCl_2.6H_2O$	8.5
FS-P3	Mg:N:P	NH_4-N	1.5:1:1	H_3PO_4, $MgCl_2.6H_2O$	8.5
FS-P4	Mg:P	PO_4-P	1:1	$MgCl_2.6H_2O$	8.5
FS-P5	Mg:P	PO_4-P	1.3:1	$MgCl_2.6H_2O$	8.5
FS-P6	Mg:P	PO_4-P	1.5:1	$MgCl_2.6H_2O$	8.5
FS-P7	-[a]	-	1:2[b]	na[c]	8.5
FS-P8	-	-	1:2	na	9.5

[a] Not applicable
[b] Initial Mg:P ratio
[c] No addition

To observe the effects of additions of magnesium and phosphorus, two experiments (Experiment FS-P7 and FS-P8) were conducted without addition of any chemical except NaOH (20 % v/v) to adjust the pH of the solution. These experiments were carried out similar to other struvite precipitation experiments except the addition of chemicals other than NaOH, by just increasing the pH level of the reactors to 8.5 and 9.5 (Experiment FS-P7 and FS-P8, respectively).

3.3.3 Set 3: Struvite Precipitation from the Effluents of Full-scale Poultry Manure Digester

Similar to the previous two sets, prior to struvite precipitation experiments solid-liquid separation of the biogas plant effluent was done. Struvite precipitation experiments were conducted in both the liquid phase and solid phase of the effluent. Prior to struvite precipitation experiments in the solid phase, phosphorus dissolution process was adopted to obtain phosphorus-enriched liquid phase. Additionally, metals present in the phosphorus-enriched liquid phase were complexed by the addition of citric acid and subsequent struvite precipitation experiments were conducted with the resulting solution.

Struvite Precipitation Experiments

Struvite precipitation experiments were conducted in both phases of the solid-liquid separated biogas plant effluent. The procedure followed during struvite precipitation experiments was the same as described for the second set (Section 3.3.2).

3.3.3.1 Liquid Phase Experiments of Poultry Manure Digester

Initial composition of the liquid phase contained a molar concentration ratio of 1:1510:24 of Mg:N:P indicating that Mg ion with a concentration of 5.3±0.1 mg/L is the limiting reactant for NH_4-N and PO_4-P removal by struvite precipitation (Table 3.6). Therefore, it had to be added in all experiments to initiate struvite formation. Similarly, the concentration of PO_4-P (5.3±0.0 mM) was not adequate for higher removals of NH_4-N and it was necessary to add phosphorus to improve NH_4-N removal. In order to observe the effect of acidic dissolution the liquid phase was subjected to phosphorus dissolution as described in detail in Section 3.3.2. However, the Mg and PO_4-P concentrations in the remaining solution were 11.1±0.42 mg/L and 212.0±0.0 mg/L, respectively. The adoption of phosphorus dissolution process to the liquid phase did not provide a significant advantage because the concentrations of Mg and PO_4-P were still not adequate for higher removals of NH_4-N. Therefore, the struvite precipitation experiments were conducted with the original liquid phase, the characterization of which was provided in Table 3.6.

In the experiments, the concentration of NH_4-N was taken as the basis and total (initial + added) molar concentrations of Mg and PO_4-P were raised to the corresponding molar concentration of NH_4-N (329±8 mM) to obtain a molar ratio of Mg:N:P equal to 1:1:1. To observe the effect of pH on the removals of NH_4-N and PO_4-P, three different pH levels (8.0, 8.5 and 9.0) were used in the experiments by the use of Mg:N:P of 1:1:1. These experiments were conducted keeping all other parameters the same, except the pH level. In order to observe the effect of molar concentration ratio of the struvite forming ions (Mg:N:P) three different Mg:N:P ratios (Mg:N:P as 1:1:1, 1.3:1:1 and 1.5:1:1) were used. The molar concentration ratios were adjusted by adding the calculated amount of ions into the reactors considering the initial concentrations of the ions in wastewater (Table 3.6). The experimental set-up of the liquid phase experiments of MS sample is depicted in Table 3.20.

Table 3.20. The experimental set-up of the liquid phase experiments of MS sample

Experiment no.	Molar ratio of Mg:N:P	pH
MS-L1	1:1:1	8.0
MS-L2	1:1:1	8.5
MS-L3	1:1:1	9.0
MS-L4	1.3:1:1	8.5
MS-L5	1.5:1:1	8.5

3.3.3.2 Solid Phase Experiments of Poultry Manure Digester

The solid phase of the full-scale biogas plant digesting poultry manure was subjected to the phosphorus dissolution process as described previously (Figure 3.4, Section 3.3.2). Unlike the FS sample, the solid phase of MS sample was diluted by distilled water till the TS concentration becomes 10 %, in order to provide continuous mixing during the third step of the phosphorus dissolution process.

As described in the procedure of the phosphorus dissolution process solid-liquid separation can be achieved by two techniques a) centrifugation and sieving, b) filtration (Figure 3.4, Section 3.3.2). Both of the techniques were tested in this set of experiments. In the struvite precipitation experiments conducted with the phosphorus-enriched liquid phase, the effects of molar concentration ratio of Mg, NH_4-N, PO_4-P (Mg:N:P) and molar concentration ratio of Mg, PO_4-P (Mg:P) were investigated, separately. In order to observe the effect of molar concentration ratio of the struvite forming ions (Mg:N:P) on the recovery of NH_4-N and PO_4-P, three different Mg:N:P ratios (1:1:1, 1.3:1:1 and 1.5:1:1) were used.

In the phosphorus-enriched liquid phase initial molar concentration of the NH_4-N (Table 4.13, Section 4.3.2) was the highest among the three struvite forming ions and the initial molar ratio of Mg:N:P was 1:4:2. Therefore, the concentration of NH_4-N was taken as the basis in order to adjust the molar concentration ratio of Mg:N:P to the desired value (Table 3.21). Total (initial + added) molar concentrations of Mg and PO_4-P were raised to the corresponding molar concentration of NH_4-N (141±5 mM) to obtain a molar ratio of Mg:N:P equal to 1:1:1. The other molar concentration ratios were prepared by adding the calculated amount of ions (Mg and PO_4-P) into the reactors considering the initial concentrations of these ions in the solution (Table 4.13, Section 4.3.2).

In order to investigate the effect of molar concentration ratio of magnesium to phosphate (Mg:P) on the recovery of PO_4-P and NH_4-N, three different Mg:P ratio, namely, 1:1, 1.3:1 and 1.5 :1 were used in the experiments. For the adjustment of Mg:P ratio, initial PO_4-P concentration in the solution was taken as the basis (Table 4.13, Section 4.3.2). By the consideration of the initial molar concentration of PO_4-P (57.4±0.1 mM), the total (initial + added) molar concentration of Mg was raised accordingly. The experimental set-up of the phosphorus-enriched liquid phase of the MS sample is depicted in Table 3.21.

Table 3.21. Experimental set-up of the phosphorus-enriched liquid phase of the MS sample

Experiment No	Molar ratio tested	Basis of chemical addition	Molar ratio	Chemicals added	pH
MS-P1	Mg:N:P	NH_4-N	1:1:1	H_3PO_4, $MgCl_2.6H_2O$	8.5
MS-P2	Mg:N:P	NH_4-N	1.3:1:1	H_3PO_4, $MgCl_2.6H_2O$	8.5
MS-P3	Mg:N:P	NH_4-N	1.5:1:1	H_3PO_4, $MgCl_2.6H_2O$	8.5
MS-P4	Mg:P	PO_4-P	1:1	$MgCl_2.6H_2O$	8.5
MS-P5	Mg:P	PO_4-P	1.3:1	$MgCl_2.6H_2O$	8.5
MS-P6	Mg:P	PO_4-P	1.5:1	$MgCl_2.6H_2O$	8.5
MS-P7	-[a]	-	1:2[b]	na[c]	8.5
MS-P8	-	-	1:2	na	9.5

[a] Not applicable
[b] Initial Mg:P ratio
[c] No addition

To observe the effects of additions of magnesium and phosphorus, two experiments (Experiment MS-P7 and MS-P8) were conducted without addition of any chemical except NaOH (20 % v/v) to adjust the pH of the solution. These experiments were carried out similar to other struvite precipitation experiments except the addition of chemicals, by just increasing the pH level of the reactors to 8.5 and 9.5 (Experiment FS-P7 and FS-P8, respectively).

Complexation of Metals

The phosphorus-enriched liquid phase was subjected to complexation process in order to prevent co-precipitation of interfering metals together with struvite. In order to form insoluble complexes with the metals present in the phosphorus-enriched liquid phase citric acid monohydrate [CA, $C_6H_8O_7.H_2O$] was used as the complexing agent. The complexation of metals was adopted after the phosphorus-dissolution process the procedure of which was illustrated in Figure 3.4.

Complexation of metals was achieved in four steps; (i) mixing, (ii) pH adjustment, (iii) settling and (iv) solid-liquid separation (Figure 3.5). Similar to the struvite precipitation experiments for the complexation of the metals was carried out at room temperature (21-22°C) with 150 mL of phosphorus-enriched liquid. The previously calculated amount of solid CA was added to the continuously mixed reactor. Following the addition of the CA, the reactor content was mixed continuously for 20 min at 250 rpm. Then, the pH of the solution was adjusted to 8.5 with the addition of 20 % NaOH (v/v) and then the mixing was stopped for 30 min and the reactor was left open to atmosphere (settling period). At the end of the settling period, the reactor content was filtered through folded filter of pore size 320 mm (Macherey-Nagel) and the filtrate was analyzed for its PO_4-P, NH_4-N and Mg content.

Depending on the molar concentrations of the metals Mg, Fe, Al, K and Ca the amount of CA to be added to the solution was calculated. In the complexation process two molar concentration of CA was tested. In the first case the amount of CA added was equal to the sum of the molar concentrations of the metals namely Mg, Fe, Al, K and Ca (molar ratio of CA:metals of 1:1) and in the second case the amount added was 1.5 times the sum of the molar concentrations of the metals (molar ratio of CA:metals of 1.5:1). The resulting solutions were then analyzed for their struvite forming ions and metals. Struvite precipitation experiments were conducted with the solution obtained after the complexation process by the use of CA:metals molar ratio of 1.5:1.

3.3.3.3 Struvite Precipitation Experiments conducted with the Remaining Solution after Complexation Process

In total three experiments were conducted with the solution obtained after the complexation process by the use of CA:metals molar ratio of 1.5:1. One experiment was conducted by the adjustment of struvite stoichiometry through addition of Mg and PO_4-P (Experiment MS-C3) and two experiments were conducted with the original solution through addition of only Mg by taking initial PO_4-P concentration as the basis to adjust the molar ratio of Mg:P to 1:1 (Experiment MS-C1) and 1.5:1 (Experiment MS-C2).

Table 3.22. Experimental set-up of the complexed phosphorus-enriched liquid phase of FS sample

Experiment no.	Molar ratio used	Basis of chemical addition	Molar ratio	Chemicals added
MS-C1	Mg:P	PO_4-P	1:1	$MgCl_2.6H_2O$
MS-C2	Mg:P	PO_4-P	1.5:1	$MgCl_2.6H_2O$
MS-C3	Mg:N:P	NH_4-N	1:1:1	H_3PO_4, $MgCl_2.6H_2O$

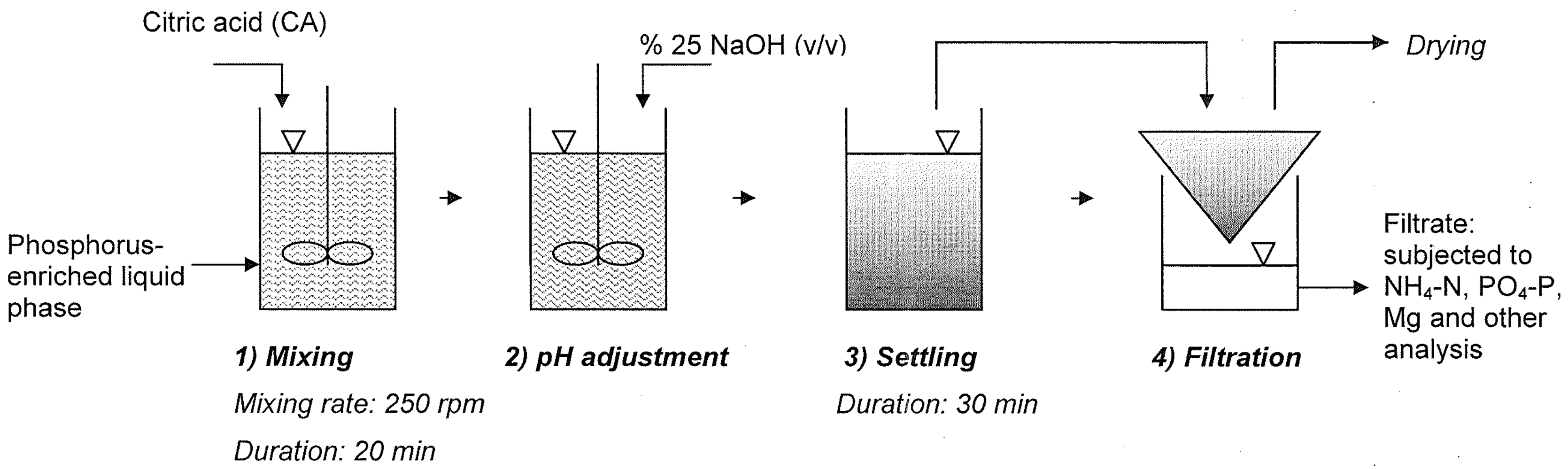

Figure 3.5. The schematic representation of the complexation process

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Anaerobic Reactors and Struvite Precipitation Experiments from the Reactor Effluents

The experimental results of Set 1 is presented under two main parts; (i) anaerobic batch reactors and (ii) struvite precipitation experiments with the liquid phase of reactor effluents.

4.1.1 Performance of the Anaerobic Reactors

The performance of anaerobic batch reactors were evaluated in terms of the biogas production, COD, NH_4-N, TKN, and TP removal efficiencies and soluble COD and VFA concentrations.

Biogas Production

Reactors were operated until the variation in daily gas production was less than 15 % for a two-week period. The gas production values of the reactors are depicted in Figure 4.1. Most of the gas production in R1, R2 and R3 was completed within first 13 days of operation. During the stated period, R1, R2 and R3 produced 68, 72 and 70 % of their total biogas productions (as of day 64), respectively (Figure 4.1a). Sung and Dague (1995) stated that, high F/M ratio, established right after feeding of a batch reactor, provides a high driving force for methanogenic activity and elevated biogas production rates. So, as biodegradation proceeded with time, depletion of available substrates resulted in the decrease in biogas production rates, which was an expected result. However, within first 13 days of operation R4, R5 and R6 produced 22, 27 and 25 % of their total biogas productions, which suggest there is an inhibitory condition within the reactors. Even so, reactors with higher initial COD concentrations (R4, R5 and R6) were superior to the reactors having lower initial COD concentrations in terms of total amount of biogas. The same behavior was observed with the net methane generations of the reactors (Figure 4.1b).

The methane yields and average methane content of total biogas productions are given in Table 4.1. Experimental values are compared to the theoretical methane yields (395mL CH_4/g COD added at 35 °C) given by Speece (2008). Methane yields of R1, R2 and R3 were (228, 206 and 189 mL CH_4/g COD added, respectively) and the results were similar to the average specific methane yield (210 mL CH_4/ g COD added) recorded in the study of Salminen and Rintala (1999) in which substrate was a combination of poultry slaughterhouse and food packing plant wastes. Lower specific methane yields in R4, R5 and R6 support the presence of partial inhibition due to ammonia toxicity in these reactors.

Table 4.1. Methane yield and content, COD, NH_4-N, TKN, and TP removal efficiencies for reactors

Reactor no	Methane yield mL CH_4/g COD_{added}	Methane Content, %	Percent Removals			
			COD	TKN	NH_4-N	TP
R1	228	61±0.4[a]	63	-(33)	-(57)	-(3)
R2	206	63±1.0	60	-(19)	-(52)	0
R3	189	60±1.0	52	15	-(49)	9
R4	146	55±1.0	43	8	-(54)	1
R5	157	62±0.6	44	19	-(52)	11
R6	153	53±0.5	44	8	-(58)	-(18)

[a] mean± std (n=2)

In order to compare the supplementation of nutrient and trace metals on gas productions, two of the reactors (R4 and R6) were run with the same waste mixing ratio and similar operating conditions i.e. initial COD and F/M (Table 3.10) except BM supplementation. While R4 was run without BM; R6 was run with BM. Both specific methane yields and COD removals (Table 4.1) of these reactors were close to each other; specific methane yield and COD removal in R4 were 146 mL CH_4/g COD added and 43 %, respectively whereas the same performance parameters in R6 were 153 mL CH_4/g COD added and 44% in R6. This indicated that nutrient supplementation did not improve the digestion performance.

As stated in literature domestic sludge usually contains sufficient quantities of nitrogen (in the form of protein, urea and ammonia), phosphorus and other micro nutrients for efficient digestion (Parkin and Owen, 1986). Moreover, the study of Güngör-Demirci and Demirer (2004) indicated that nutrients present in poultry manure are enough for anaerobic microbial growth. Considering the low COD removals and methane yields in both reactors it can be interpreted that the deficiency of nutrients is not the reason of low biogas production.

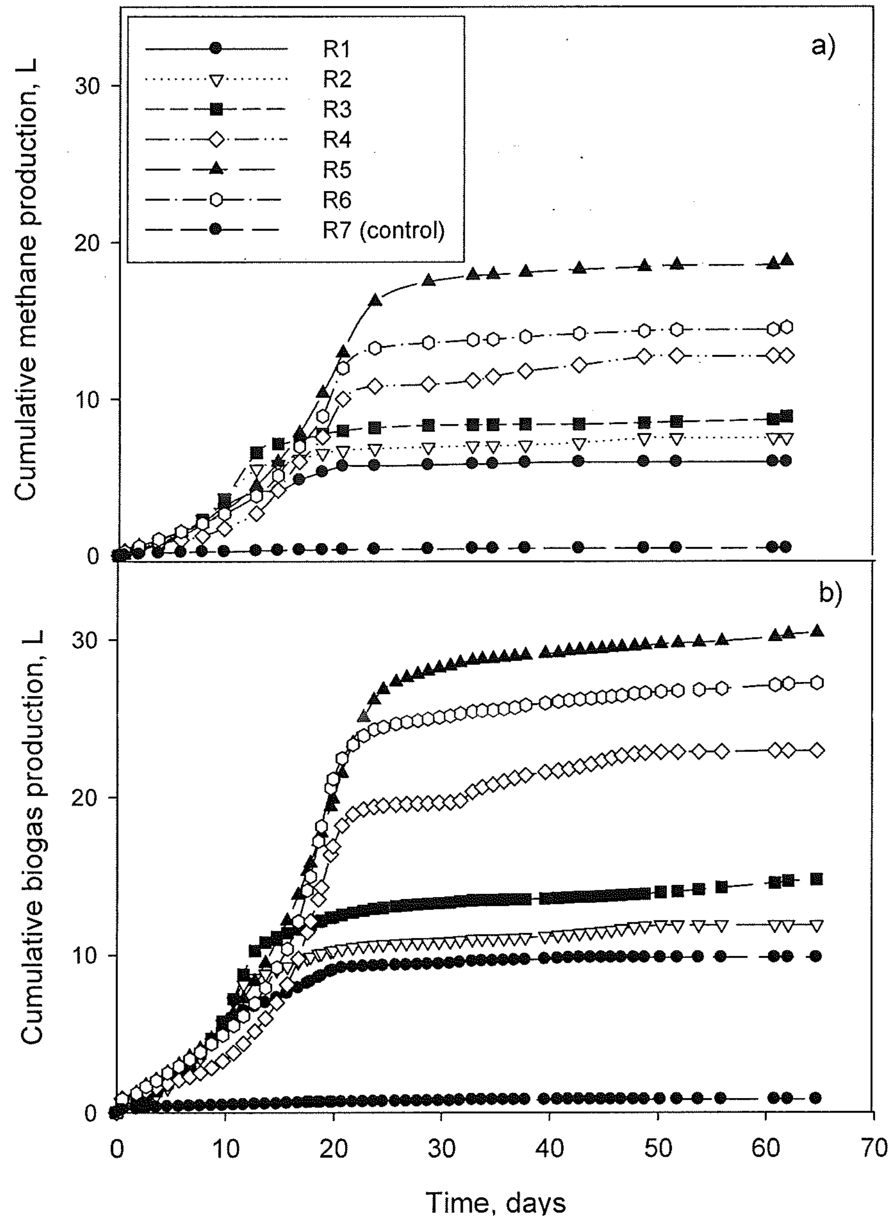

Figure 4.1. Cumulative gas production values of the reactors (a) Cumulative net methane production. (b) Cumulative biogas production

Table 4.2. Initial and final concentrations of COD, TKN, TP, PO_4-P, TS, NH_4-N, VFA and pH

				Initial				
Reactor	pH	COD (mg/L)	sCOD (mg/L)	TKN (mgN/L)	NH_4-N (mgN/L)	TP (mgP/L)	PO_4-P (mgP/L)	VFA (mgHAc/L)
R1	7.4	14,250	716±28[a]	708±14	281±4	303±8	16.3±0.8	373±11
R2	7.3	16,500	586±55	869±18	324±4	354±11	24.7±0.3	522±38
R3	7.4	18,800	1191±28	1030±30	368±4	405±17	22.9±0.2	584±49
R4	7.1	27,800	1396±14	1183±43	409±4	454±24	43.5±1.3	823±71
R5	7.1	35,000	1494±14	1356±58	457±5	508±31	45.3±0.3	909±52
R6	7.0	29,500	2217±207	1146±41	397±4	442±23	50.3±1.3	575±30
				Final				
Reactor	pH	COD (mg/L)	sCOD (mg/L)	TKN (mgN/L)	NH_4-N (mgN/L)	TP (mgP/L)	PO_4-P (mgP/L)	VFA (mgHAc/L)
R1	8.1	9579±288	340±28	942±1	650±2	312±10	5.8±0.1	63.1±11.2
R2	8.2	10848±232	428±6	1071±4	671±2	354±3	2.1±0.0	63.7±0.6
R3	8.1	12625±658	572±6	879±17	715±4	370±3	1.3±0.0	94.4±3.6
R4	8.1	18546±808	2575±13	1089±29	892±0	449±15	1.3±0.0	907±39
R5	8.0	22440±170	3288±28	1103±7	942±3	451±1	2.5±0.0	1080±22
R6	8.1	19477±704	2265±26	1050±4	939±2	520±6	2.3±0.0	728±4

[a] mean± std (n=2)

COD, NH_4-N, TKN, and TP removal efficiencies

The observed COD, NH_4-N, TKN, and TP removal efficiencies of the reactors are given in Table 4.1. The COD removal efficiencies observed in R1, R2 and R3 were ranging 52-63 % and more or less within the typical performance level of anaerobic digesters treating poultry manure. The removals were similar to the removal efficiencies (32-56 %) reported by Aubart and Fauchille (1983), lower than the removal efficiencies (75-94 %) reported by Yetilmezsoy et al. (2009) and higher than some of the removal efficiencies reported by other researchers in literature (Bousfield et al., 1979; Huang and Shih, 1981; Güngör-Demirci and Demirer, 2004). On the other hand, in literature percent COD removals in sewage sludge digesters are recorded as ranging from 40-60 % (Parkin and Owen, 1986) the removals observed in R4, R5 and R6 were 43, 44 and 44%, respectively (Table 4.1). Lower COD removals indicated incomplete and inefficient digestion in these reactors.

In the reactors, 63 to 89 % of nitrogen was ammonificated at the end of digestion period, which is an expected result (Field et al., 1985; Krylova et al., 1997).The negative values observed of TKN and NH_4-N removal correspond to an increase in the reactor. This is an observation also reported by other researchers (Cheng and Liu, 2002; Martin et al., 2003; Demirer and Chen, 2005) and can be attributed to the anaerobic bioconversion of proteins contained in wastes into amino acids and then to ammonia.

Table 4.2 depicts the final concentrations of ammonia nitrogen measured in the reactors which were reached inhibitory levels in R4, R5 and R6. Ammonia is a nutrient for bacteria involved in the anaerobic digestion process, but at concentrations exceeding the critical concentration levels it inhibits methanogenesis. The work of Koster and Lettinga (1984) revealed that the maximum methanogenic activity was not affected by ammonium nitrogen concentrations of 680 mg/L, it was reduced to 59% at ammonium nitrogen concentrations of 853 mg/L. Concentrations of ammonium nitrogen in R4, R5 and R6 were 892±0, 942±3 and 939±2 mg /L, respectively (Table 4.2). As reported in literature, the excess of ammonium can inhibit the destruction of organic compounds, accumulation of VFA, and methanogenesis (Krylova et al. 1997). Since methanogens are the most sensitive bacteria among the complex population involved in anaerobic digestion, their activity is inhibited (Speece, 2008).

Other than high ammonia concentrations, F/M was influential on the treatment of the reactors. F/M was increased in the reactors in the increasing order of sewage sludge fraction in the reactors (Table 3.10, Section 3.3.1.1). F/M in R4, R5 and R6 were 3.8, 5.2 and 4.2 mg COD/mg VSS, respectively which may lead to toxic conditions in the reactors. This finding is in accordance with the literature, since Prashanth et al. (2006) reported that high value of F/M may be toxic and result in reduction of treatment efficiencies and methane yields. The low treatment efficiencies observed for TP are also expected since anaerobic digesters are known to reduce negligible amounts of nutrients (Lusk, 1998).

Soluble COD and VFA Concentrations

The inhibitory conditions that were observed in R4, R5 and R6 were confirmed with the results of sCOD (Figure 4.2a) and VFA measurements (Figure 4.2b). The initial sCOD concentrations in R4, R5 and R6 were 1396±14, 1494±14 and 2217±207 mg/L, respectively. At the end of digestion period concentrations of sCOD reached to level of 2575±13, 3288±28 and 2265±26 mg/L in R4, R5 and R6, respectively (Table 4.2).

Similar to the case of sCOD there is accumulation of VFA (Figure 4.2b) in R4, R5 and R6, the concentrations were 907±39, 1080±21.8 and 728±3.8 mg HAc/L, respectively (Table 4.2). As stated by Speece (2008), commonly the volatile acids concentration in the effluent from anaerobic treatment is less than 100 – 300 mg HAc/L. Moreover, Parkin and Owen (1986) reported that volatile acids levels above 500mg/L usually indicate incomplete and inefficient digestion. The levels of VFA in all three reactors (R4, R5 and R6) were higher than the normal range, suggesting partial inhibition in these reactors. Increasing levels of sCOD and total VFAs indicated the abundance and/or activity of acetogens and methanogens were insufficient to convert the VFAs produced. Similar observation was reported in the study of Angenent et al. (2002). The reason of this phenomenon may be explained by relatively high concentrations of ammonia nitrogen present in these reactors

(Table 4.2). The release of ammonia nitrogen resulted in accumulation of VFA because of the need to maintain the pH at 8.0-8.2 (Krylova et al., 1997).

Moreover, as stated previously high F/M (Table 3.10, Section 3.3.1.1) may lead to toxic conditions in R4, R5 and R6. On the other hand in R1, R2 and R3 sCOD concentrations were reduced below to their initial concentrations at the end of the digestion period and there is a significant reduction in total VFAs, without any indication of an inhibition (Table 4.2).The pH values were above 8.0 in all reactors despite the high total VFA levels present in R4, R5 and R6 (Table 4.2).

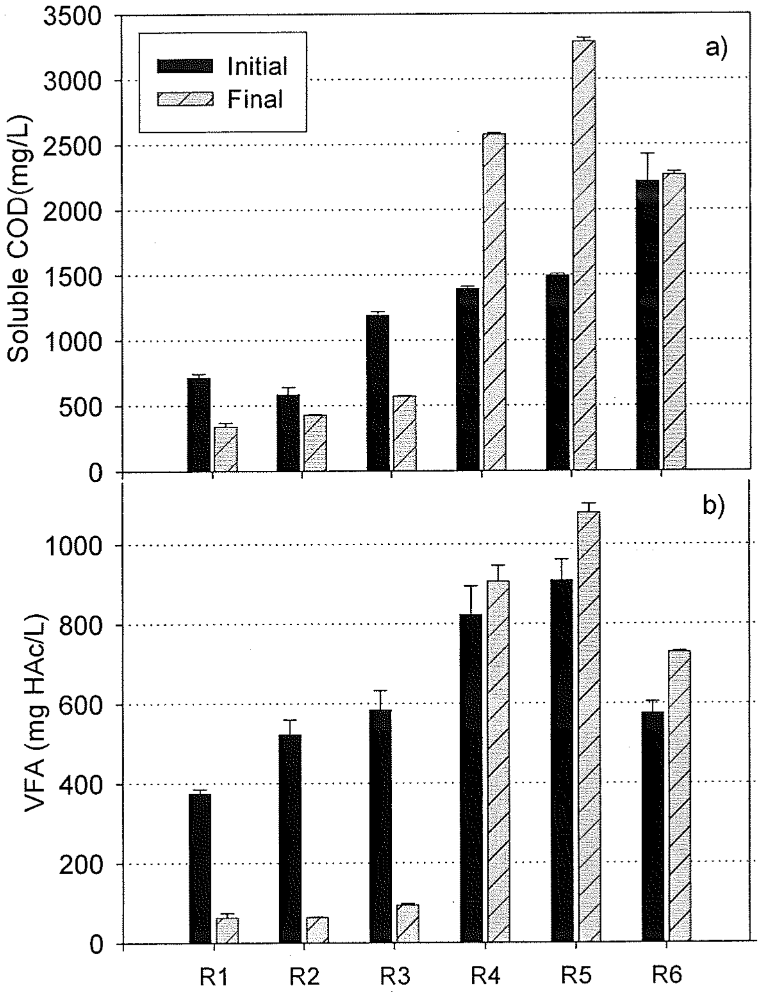

Figure 4.2. a) Initial and final concentrations of sCOD in the reactors b) Initial and final concentrations of VFA

Similar high pH values with high ammonium nitrogen concentrations have been reported by several authors (Webb and Hawkes, 1985; Salminen and Rintala, 1999; Angenent et al. 2002), the high pH being supposedly due to the buffering capacity of ammonia produced in the system.

4.1.2 Struvite Precipitation from the Liquid Phase of Reactor Effluents

In the struvite precipitation experiments the effect of molar ratio of Mg:N:P, pH, seeding and presence of calcium ion were investigated.

The effect of molar ratio of Mg:N:P

Ammonia nitrogen is in excess in all of the reactor effluents (Table 3.11, Section 3.3.1.2) and addition of magnesium and phosphorus from external sources is necessary. This is because the molar ratio of struvite forming ions (Mg:N:P ratio) should be at least unity for intentional struvite precipitation. Whereas higher magnesium can enhance the struvite precipitation process and increase the removal of PO_4-P and NH_4-N from the wastewater (Rahaman et al., 2008). At any given pH level, any increase in the Mg:N:P ratio would increase the degree of saturation with respect to struvite formation, which, in turn would enhance the removal and recovery of PO_4-P and NH_4-N (Adnan et al., 2004; Rahaman et al., 2008). In this study, in order to maximize nitrogen and phosphorus removals, four different total (initial + added) molar concentration ratios of the struvite forming ions Mg:N:P of 1:1:1, 1.3:1:1, 1.5:1:1 and 0.7:1:1 were used (Table 3.14, Section 3.3.1.2).

The results of the experiments in terms of residual concentrations and percent removals of the struvite forming ions were depicted in Table 4.3. In order to represent the actual removal of the ions from the wastewater, the removals are reported considering the initial concentrations of the ions present in wastewater but not the total concentrations. The results of the experiments conducted by the use of Mg:N:P molar ratio of 1:1:1 (E1, E4, E7, E10, E13, E16 and E17) indicated the use of struvite stoichiometry (Mg:N:P of 1:1:1) was not sufficient to decrease the residual PO_4-P concentrations (Figure 4.3) down to their initial concentrations (6.4±0.0 mg/L – 10.7±0.3 mg/L). This is due to its addition into the wastewater to initiate the struvite formation, which led to further contamination of wastewater by PO_4-P. In 4 out of 6 experiment conducted by the use of Mg:N:P molar ratio of 1.3:1:1, residual PO_4-P concentrations (3.9±0.2 - 10.3±1.4mg/L) drop down to their initial concentrations, resulting in removals of 41.8 – 59.8 % (Figure 4.3). Yet, in all of the experiments conducted by the use of Mg:N:P molar ratio of 1.5:1:1, PO_4-P concentrations (2.3±1.4 - 5.0±0.1 mg/L) were lower than initial concentrations so that higher PO_4-P removals (47.6-71.3%) were obtained (Figure 4.3).

Table 4.3. The results of the molar ratio experiments

Reactor no	Experiment no.	Molar ratio of Mg:N:P	Residual Concentration, mg/L				Percent removals[a]			
			NH_4-N	PO_4-P	Mg	COD	NH_4-N	PO_4-P	Mg	COD
	E1	1:1:1	137	11.6±0.6[b]	109	441±0	83.7	-[c]	-	37.2
R1	E2	1.3:1:1	101	9.3±0.4	271	510±17	82.7	-	-	27.3
	E3	1.5:1:1	70.0	3.4±0.1	353	nd[d]	88.0	47.6	-	nd
	E4	1:1:1	145±0	10.5±0.7	32.9±2.4	nd	76.7	-	33.3	nd
R2	E5	1.3:1:1	161±10	3.9±0.2	171	nd	74.2	59.8	-	nd
	E6	1.5:1:1	137 ±12	2.8±0.9	64.0	nd	78.0	71.3	-	nd
	E7	1:1:1	136±2	77.5±3.5	39.4±0.9	566±6	79.7	-		41.6
R3	E8	1.3:1:1	123	10.3±1.4	271	nd	81.6	-	-	nd
	E9	1.5:1:1	150±10	2.3±1.4	365	nd	77.6	69.6	-	nd
	E10	1:1:1	125±2	11.5±0.7	101	nd	84.6	-	-	nd
R4	E11	1.3:1:1	176±0	3.9±0.2	328±4	nd	78.2	52.1	-	nd
	E12	1.5:1:1	157	2.4±0.1	369	nd	80.8	70.4	-	nd
	E13	1:1:1	95.2	47.5±3.5	78.6	nd	89.4	-	-	nd
R5	E14	1.3:1:1	122±6	4.1±0.2	327	nd	86.5	41.8	-	nd
	E15	1.5:1:1	104	3.7±0.1	323	nd	88.5	48.6	-	nd
	E16	1:1:1	169±1	28.5±0.7	50.8	nd	80.9	-	26.6	nd
	E17[e]	1:1:1	160	54.0±5.7	123±6	nd	81.9	-	-	nd
	E18	1.3:1:1	112±4	5.6±0.1	382	nd	87.6	47.7	-	nd
R6	E19	1.5:1:1	118	5.0±0.1	487± 34	nd	86.6	53.3	-	nd
	E20[e]	1.5:1:1	120	3.6±0.0	280	nd	86.4	66.4	-	nd
	E21[f]	1.5:1:1	170±10	1.7±0.0	406	nd	80.8	84.1	-	nd
	E22	0.7:1:1	371±25	531±2	32.8	nd	58.0	-	52.6	nd

[a] Percent removals were calculated considering the initial concentrations of the ions at the influent of struvite reactor (Table 3.11, Section 3.3.1.2).

[b] mean±std (n=2)

[c] "-" means no removal i.e. final concentration is higher than initial concentration.

[d] nd: Not determined.

[e] KH_2PO_4 was used as the phosphorus source (Table 3.14, Section 3.3.1.2).

[f] Conducted at pH level of 9.5 (Table 3.14, Section 3.3.1.2).

The results of the molar ratio experiments imply that to drive higher portion of the available phosphate from solution, an excess of magnesium is required. This is mainly due to the chemical composition of the wastewater being investigated. The use of Mg at a concentration greater than the stoichiometric amount needed to achieve the desired removal efficiency of PO_4-P has also been reported in other studies (Beal et al., 1999; Münch and Barr, 2001a; Stratful et al., 2001; Adnan et al., 2003; Nelson et al., 2003; Uludağ-Demirer, 2008; Rahaman et al., 2008). This can be explained by the presence of the complexing agents, which have the potential of forming soluble complexes with Mg thereby reducing the activity of Mg and making it unavailable to the struvite reaction (Beal et al., 1999; Nelson et al., 2003; Burns et al., 2003).

Ionic strength, presence of other cations (e.g. Ca, K) and pH are the other factors affecting the activity of the ions in the wastewater (Uludağ-Demirer et al., 2005). Because the complete analysis of wastewater is not known, it is difficult to discuss the effects of ionic strength and complexing agents on the activities of ions. However, based on the above discussions, it may be speculated that there is high amount of the complexing agents present in R1 and R3 in comparison to the other reactor effluents. In all experiments conducted by the use of Mg:N:P molar ratio of 1:1:1 residual concentration of NH_4-N reduced below to its initial concentration with a minimum percentage removal of 74.2 % (Figure 4.3). As described in the study of Uludağ-Demirer and Othman (2009) there are two major mechanisms of NH_4-N removal in systems with high concentrations of Mg and PO_4-P, namely struvite precipitation and air stripping. Even though struvite precipitation leads to formation of other minerals containing Mg and/or PO_4-P (e.g. hydroxylapatite, newberyite, monenite) examination of all the possible species indicated that the only specie containing NH_4^+ in its composition is struvite (Uludağ-Demirer and Othman, 2009).

To be able to determine the effect of air stripping on NH_4-N removal, duplicate experiments were conducted with the effluent of R2 at room temperature (21-22°C). In ammonia stripping experiments conducted with the effluent of R2, average NH_4-N removal were 2.3 % suggesting at pH level of 8.5 there is negligible loss of ammonia to atmosphere. This finding contradicts with the finding of Çelen and Türker (2001) who observed 11% loss of ammonia to air at pH level of 8.5. However, the difference can be explained by higher operational temperature (37°C) adjusted during the experiments conducted by Çelen and Türker (2001), which is one of the important parameters increasing the rate of ammonia stripping (Tchobanoglous et al., 2003). Therefore, the high ammonia nitrogen removals (Table 4.3) observed in the experiments can be accepted as an indication of formation of struvite in the system. Unlike the PO_4-P removals in the case of NH_4-N removals there was not a trend followed in each experiment.

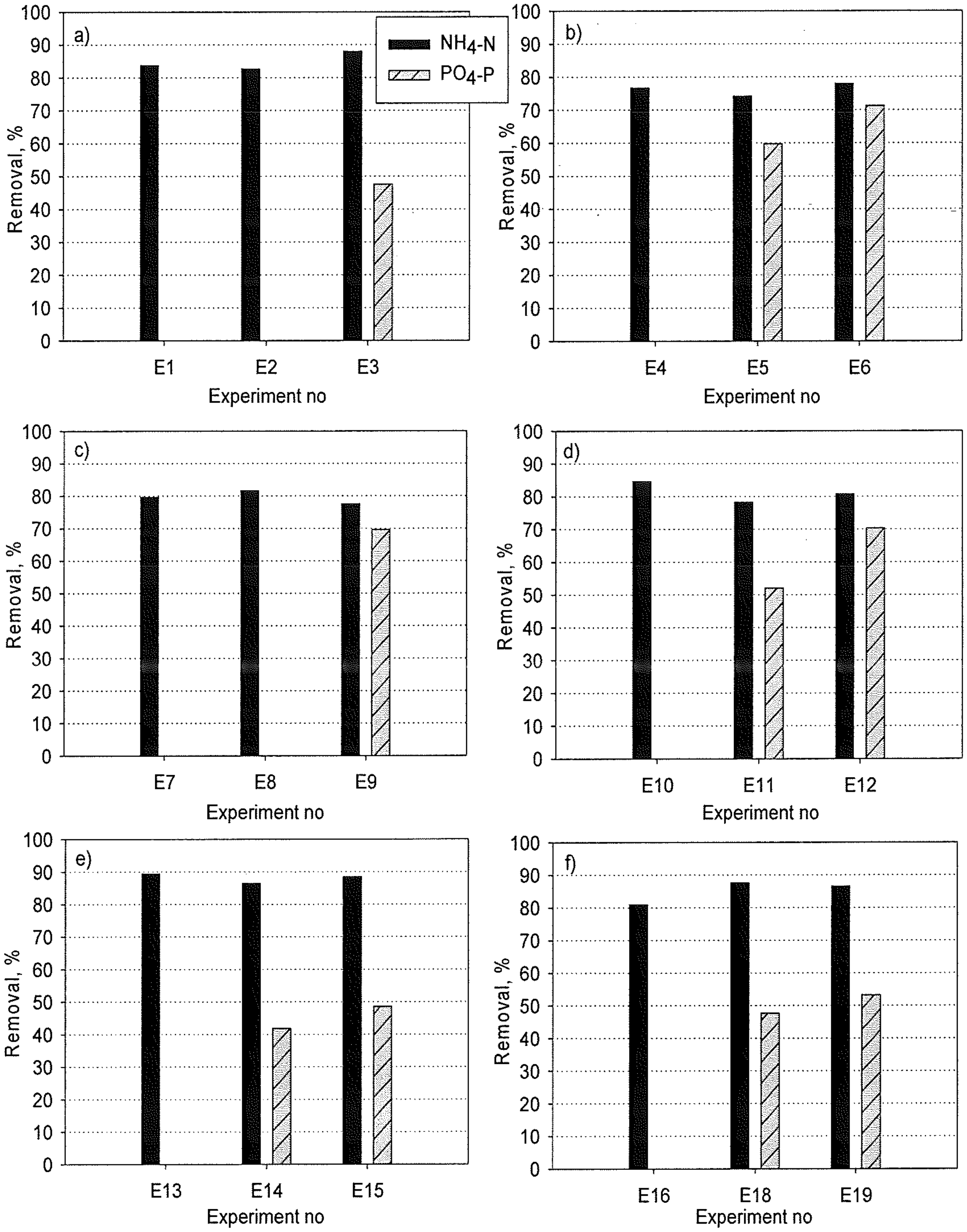

Figure 4.3. NH_4-N and PO_4-P removals versus molar ratio experiments conducted with the effluent of a) R1, b) R2, c) R3, d) R4, e) R5, f) R6

In the experiments conducted with the effluents of R1, R2, R4 and R5 the variation of the molar of Mg:N:P from 1:1:1 to 1.3:1:1 lowered NH_4-N removals slightly, up to maximum of 6.4 % in R4 (Figure 6 a, b, d and e). On the other hand, the variation of the molar ratio of Mg:N:P from 1.3:1:1 to 1.5:1:1 increased the NH_4-N removals, up to maximum of 5.3 % in R1 (Figure 4.3). In the experiments conducted with the effluents of R3 and R6, the variation of the molar of Mg:N:P from 1:1:1 to 1.3:1:1 enhanced the NH_4-N removals slightly, at a maximum of 6.7 % in R6, whereas further increase of molar ratio of Mg:N:P to 1.5:1:1 reduced the removals of NH_4-N (Figure 4.3). These may be explained by alternative removal mechanisms of magnesium and/or phosphate e.g. formation of other competitive minerals such as newberyite [$MgHPO_4.3H_2O$], althausite [$Mg_2PO_4(OH)$] in the reactor.

To understand this, collected precipitates from the reactors were analyzed by the XRD technique. The XRD analysis of the precipitates collected from the experiments conducted with the liquid phase of R3 by the use of three different molar ratio of Mg:N:P (1:1:1, 1.3:1:1 and 1.5:1:1 corresponding to the Experiments E7, E8 and E9, respectively) were conducted. The qualitative identification of the precipitate was conducted as described in Section 3.2.1, see Appendix B for the application of the described method for the identification of the sample collected from Experiment E7. From the results of XRD analysis, it is determined that the precipitate was mainly struvite. In a similar manner, the precipitates collected from Experiments E8 and E9 were identified as struvite using the same method (Figure C.2 and C.3 in Appendix C, respectively). The patterns of the samples and struvite which was retrieved from the data base in the software installed to the equipment match almost exactly showing also the purity of struvite was high. The XRD pattern of the samples did not match with any other mineral, which may be due to the corresponding mineral, may have dissolved to be below the detection of XRD.

The results of the molar ratio experiments illustrated that the influence of excess Mg in the removal of NH_4-N and PO_4-P (Figure 4.3) was significant; however, it was obvious that excess Mg has a greater influence on residual PO_4-P concentration, which was also observed by other researchers (Uludağ-Demirer, 2008; Uludağ-Demirer and Othman, 2009). The only reactor effluent, in which Mg is limiting condition (Mg:N:P molar ratio of 0.7:1:1) and pH level of 9.5 tested was R6 (E22 and E21, respectively). The result of Experiment E22 indicated that Mg limitation in the system resulted in higher residual concentrations of both NH_4-N and PO_4-P (Table 4.3) compared to the residual concentrations recorded in experiments conducted with the effluent of R6 without magnesium limitation (E16-E20). There was addition of extra phosphorus to induce struvite precipitation; as a result the residual concentration of PO_4-P (531±2 mg/L) was much higher than the initial concentration of the PO_4-P (10.7±0.3 mg/L) which is unfavorable from contamination point of view.

Comparison of the experiments E19 and E21 illustrated the effect of pH on the removals of NH_4-N and PO_4-P. Although increasing the pH level from 8.5 to 9.5 resulted in significant increase in PO_4-P removal (from 53.3 to 84.1 %), it lowered NH_4-N removal (from 86.6 to 80.8 %). Even though the decrease in NH_4-N removal seems to be small with the consideration of higher ammonia stripping rate at pH level of 9.5, the difference would be more significant indicating the existence of alternative removal processes of PO_4-P as discussed previously. Table 3.12 depicts the metal content of the reactor effluents subjected to struvite precipitation experiments. There were trace amounts of foreign ions (metals) present in the solutions except calcium and potassium. This may imply that other minerals precipitating in the system were calcium phosphates [$Ca_3(PO_4)_2$, $Ca_8(HPO_4)_2(PO_4)_4.5H_2O$, $Ca_5(PO_4)_3OH$] resulting in lower residual PO_4-P concentrations in the resulting solution.

The residual concentration of Mg in E19 was 487± 34 mg/L whereas it was 406 mg/L in E21 (Table 4.3). The difference between the residual Mg concentrations in these two experiments may be attributable to formation of other interfering salts e.g. $Mg_3(PO_4)_2$ and $MgHPO_4$, leading to further reduction of in PO_4-P concentration in the reactor. Demeestre et al. (2001) stated that $Mg_3(PO_4)_2$ had lower solubility at 25 °C than struvite, yet it is mainly formed at higher pH levels. Also in the same study of Demeestre et al. (2001) it is stated that formation of $MgHPO_4$ is possible but due to relatively high solubility of this salt, the mass of its precipitate will be limited. In order to confirm the precipitated minerals in experiments E19 and E21, XRD analysis of the precipitates collected from these experiments were conducted (Figure C.3 and Figure C.5 in Appendix C, respectively). The XRD patterns of the two samples only matched with the XRD pattern of the struvite (which is obtained from the library of the equipment), indicating that the precipitates were mainly struvite. Although not matched with other minerals, there are a number of unassigned peaks in the XRD patterns of the samples, which cannot be determined neither by the software nor by the personnel with expertise. Based on the above discussions, it may be speculated that the amount of minerals other than struvite were below the detection limit of XRD. In literature the detection limit of XRD for mixed materials is given as about 2% of the sample (Klug and Alexander, 1967; Dutrow and Clark, 2009).

In order to determine the effect of phosphorus source on the removal of NH_4-N and PO_4-P two experiments were conducted with the effluent of R6. During these experiments, KH_2PO_4 was used as the phosphorus source and the results were compared with the experiments conducted using H_3PO_4 as the phosphorus source. Comparison of E16 and E17 revealed that the use of KH_2PO_4 as phosphorus source led to an increase in the residual PO_4-P concentration (from 28.5±0.7mg/L to 54.0±5.7mg/L); when Mg:N:P molar ratio was 1:1:1. However, comparison of the results of E19 and E20 indicated that the use of KH_2PO_4 slightly reduced the residual PO_4-P concentration (from 5.0±0.1 mg/L to 3.6±0.0 mg/L) in excess magnesium conditions (Mg:N:P of 1.5:1:1). The difference may be attributed to the addition of K^+ ion together with phosphorus to the reactor and formation of other precipitating minerals e.g. potassium struvite ($KMgPO_4.6H_2O$) in the reactor together with struvite.

The enhancement of PO_4-P removal achieved in E20 was not significant, and the residual PO_4-P concentration observed in experiment E17 was doubled. Based on the results, it can be concluded that the use of KH_2PO_4 has a disadvantage when stoichiometric molar ratio of 1:1:1 is used, and it provides slightly better results in terms of phosphorus when excess magnesium is present in the system. Overall the disadvantages are more pronounced and thus, the use of H_3PO_4 is recommended as it does not contain any other ion that can have an impact on the precipitation (Schulze-Rettmer, 1991).

COD removals

Struvite precipitation not only remove NH_4-N and PO_4-P, but also lead to COD removal from the wastewater (Tünay and Kabdaşlı, 2001; Öztürk et al., 2003; Kabdaşlı et al., 2008, Yetilmezsoy and Şapçı-Zengin, 2009). To test this in three of the experiments (E1, E2 and E7), the effluent quality in terms of residual COD was also determined (Table 4.3). Results indicated that struvite precipitation not only helps to remove ammonia and phosphate, but also achieved considerable COD removals with a maximum removal efficiency of 42 % (Table 4.3).

The removal of COD during the precipitation of struvite may be attributed to the adsorption onto the struvite surface (Kabdaşlı et al., 2008). Confirming this, the presence of carbon in the elemental composition of the precipitated mineral was determined by the chemical analysis in other studies (Schulze-Rettmer, 1991; Nelson et al., 2003). Nelson et al. (2003) also reported gray discoloration of the precipitates compared with pure (white) struvite mineral and attributed this to the presence of organic C originating from the lagoon effluent. Similar to the observation of Nelson et al. (2003) there was light brown or gray discoloration of the precipitates (depending on the waste mixing ratio of the reactors) compared with pure (white) struvite mineral, indicating co-precipitation of organic materials together with struvite.

In literature higher COD removal efficiencies were reported; Yetilmezsoy and Şapçı-Zengin (2009) reported maximum COD removals of 54 % while Öztürk et al. (2003) reported average COD removals of 50 %. Slightly lower COD removals achieved in this study can be explained by lower initial COD concentrations and different chemical composition of the wastewaters.

The effect of pH

Similar to the molar ratio of struvite forming ions pH is an important factor to be considered in the struvite precipitation reactor due to its effects on the activities of the struvite forming ions and also on the solubility of struvite. In literature the minimum solubility of struvite has been observed between pH of 8.0 and 10.7 in different water or wastewater systems (Doyle and Parsons, 2002; Nelson et al., 2003). In order to determine the effect of pH on the removals of NH_4-N and PO_4-P, three different pH levels (8.0. 8.5 and 9.0) were used in the experiments keeping the molar ratio of Mg:N:P at 1:1:1.

The experiments were conducted with the liquid phase of R2, R3 and R4 (Table 3.15). In these experiments the maximum level of pH was set to 9.0 to avoid the loss of NH_4^+ by ammonia stripping. The results of the experiments in terms of residual concentrations and percent removals of the struvite forming ions were depicted in Table 4.4. In order to represent the actual removal of the ions from the wastewater; the removals are reported considering the initial concentrations of these ions present in wastewater (Table 3.11) but not the total (initial + added) concentrations.

Table 4.4. The results of the pH experiments

Reactor no	Experiment No	pH	Residual Concentration (mg/L)			% removal[a]		
			NH_4-N	PO_4-P	Mg	NH_4-N	PO_4-P	Mg
R2	E23	8.0	145±5[b]	28.5±3.5	32.8	76.8	-[c]	33.5
	E4	8.5	146±0	10.5±0.7	32.9±2.4	76.7	-	33.3
	E24	9.0	125±2	21.0±0.0	37.0	80.0	-	24.9
R3	E25	8.0	148	33±1.4	66.2	77.8	-	2.5
	E7	8.5	136±2	77.5±3.5	39.4±0.9	79.7	-	42.0
	E26	9.0	125	173±2.8	37.2	81.3	-	45.2
R4	E27	8.0	174	12.5±0.7	55.8	78.6	-	-
	E10	8.5	125±2	11.5±0.7	101	78.2	-	-
	E28	9.0	133±2	1.0±0.0	54.8	83.6	87.7	-

[a] All removals were calculated considering the initial concentrations of the ions at the influent of struvite reactor (Table 3.11).

[b] mean±std (n=2)

[c] "-" means no removal i.e. final concentration is higher than initial concentration.

In all of the experiments the increase in pH level led to higher NH_4-N removals (Table 4.4), which is also reported by other researchers (Çelen and Türker, 2001; Uludağ-Demirer, 2008). However in the case of PO_4-P removals, results were somewhat different regarding the pH. In the experiments conducted with effluent of R4, the increase in pH led to an increase in the PO_4-P removals. Similar results were reported in the literature, indicating that higher PO_4-P removals were achieved by the increase of pH (Beal et al., 1999; Münch and Barr, 2001a; Stratful et al., 2001; Pastor et al., 2007; Rahaman et al., 2008). The level of enhancement observed in PO_4-P was not followed by NH_4-N removals, which may imply the precipitation of other minerals together with struvite during the experiments (Schulze-Rettmer, 1991). As discussed previously based on the chemical composition of the wastewater (Table 3.12) other minerals precipitating in the system could be calcium phosphates. However, NH_4-N removal efficiencies were high (77-84 %), indicating formation of struvite in the reactors.

In the experiments conducted with the effluent of R3, a reverse relation between pH level and residual PO_4-P concentration was observed (Figure 4.4b). Higher residual PO_4-P concentration was observed by the increase of pH level from 8.0 to 9.0. This may be explained by an increase in struvite solubility at higher pH levels, which is also reported by Nelson et al. (2003).

The molar ratio of Mg:N:P in the resulting solutions of E25, E7 and E26 were 3:10:1, 1:6:2 and 1:4:6, respectively. This indicated that the limiting component in the resulting solution of Experiment E25 was PO_4-P, whereas the limiting component in the resulting solutions of experiments E7 and E26 was Mg. These results suggest that in Experiments E7 and E26, probably there were formation of magnesium containing minerals together with struvite at pH levels higher than 8.0. The study of Demeestre et al. (2001) supports this finding, however it is stated that depending on the solubility of the minerals the mass of the precipitates, if any, may be limited.

The results of the XRD analysis for the precipitate collected from experiment E25, E26 and E7 indicated formation of struvite mainly (Figure C.5 and Figure C.6 in Appendix C; Figure B.1 in Appendix B, respectively). Comparison of Figure C.5 and Figure C.6 (Appendix C) revealed that X-ray diffraction of the precipitate of Experiment E26 produced higher number of additional peaks. These peaks indicated the presence of other minerals together with struvite in the sample.

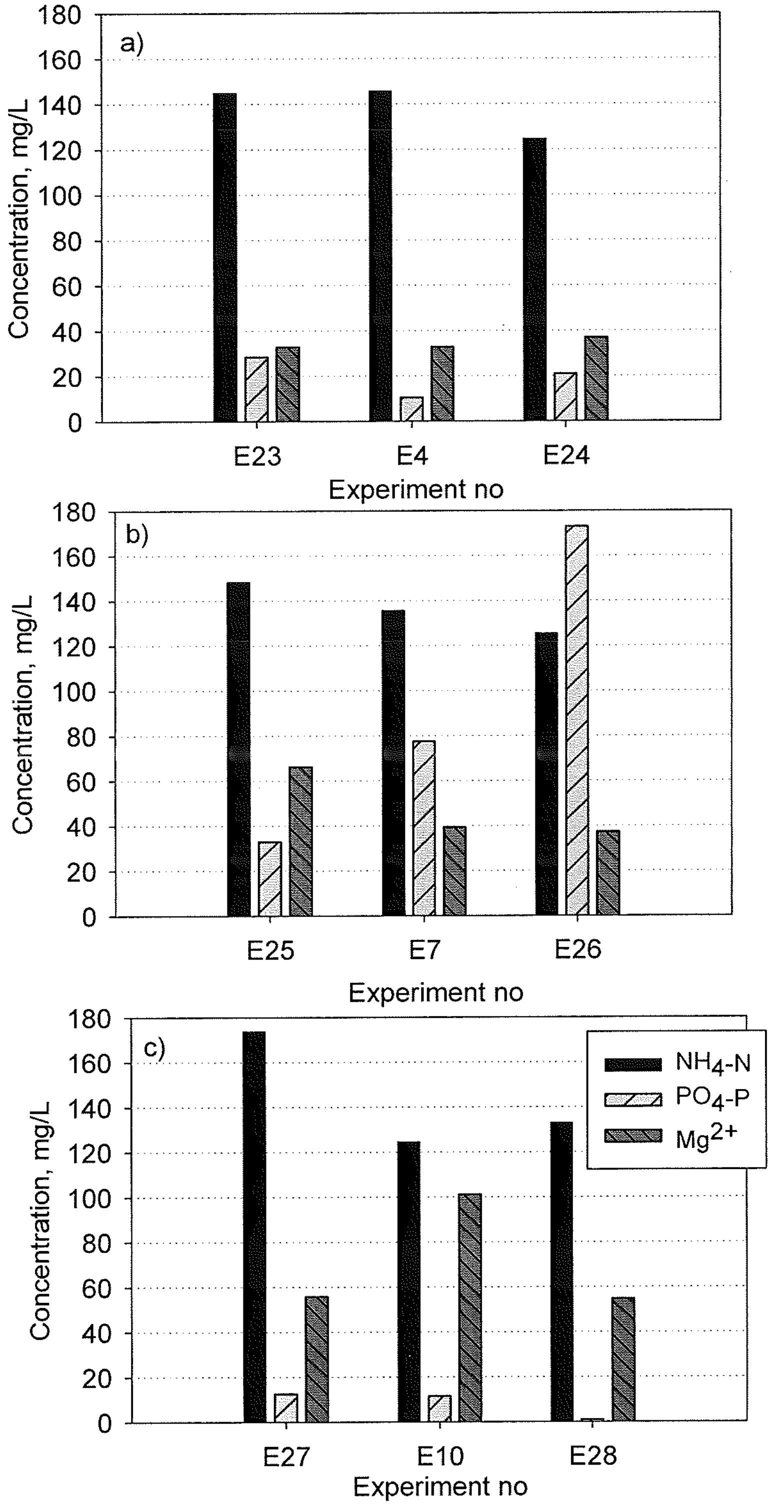

Figure 4.4. Residual concentrations of NH_4-N, PO_4-P and Mg versus pH experiments conducted with the effluents of a) R2, b) R3, c) R4

In a similar manner the variation in residual PO_4-P concentrations (Figure 4.4a) observed in experiments of R2 may be explained by different minimum solubility pH levels of competitive minerals precipitating together with struvite.

The effect of seeding material addition

In order to improve the performance of struvite formation by providing the adequate surface for reaction, seeding material addition was investigated. The effect of seeding material addition was investigated in several studies to enhance the crystallization process and it is emphasized that the seeding material should have a larger specific surface area and similar crystal structure with the precipitating mineral (Wang et al., 2006; Rahaman et al. 2008). For this purpose, synthetically formed struvite was used as the seeding material in this study. Experiments were conducted with effluents of R1 and R3 to reveal the effect of the seeding with synthetically formed struvite (Table 3.16). The results of the experiments are summarized in Table 4.5.

Table 4.5. The results of the seeding experiments

Reactor no	Experiment no	Seed (g/L)	Residual Concentration (mg/L)			% removal[a]		
			NH_4-N	PO_4-P	Mg	NH_4-N	PO_4-P	Mg
R1	E1	0	137	11.6±0.6	108	76.4	-[c]	-
	E29	10	131.6	26.5±0.7	86.2	77.4	-	-
	E30	20	109.2	75.3±3.9	54.2	81.3	-	7.4
R3	E7	0	136±2	77.5±3.5	39.4±1.0	79.7	-	42.0
	E31	10	137	46.5±2.1	22.4	79.5	-	67.0
	E32	20	137	23.0±0.0	35.9±2.7	79.5	-	47.1

[a] All removals were calculated considering the initial concentrations of the ions at the influent of struvite reactor (Table 3.11).

[b] mean±std (n=2)

[c] "-" means no removal i.e. final concentration is higher than initial concentration.

In experiments conducted with the effluent of R1, seeding led to further reduction of residual NH_4-N concentration while increasing residual PO_4-P concentrations (Figure 4.5a), thereby increasing the pollution load of the wastewater. A similar observation was recorded by Kim et al. (2007), which is attributable to the dissolution of the non-equilibrium precipitates of struvite. In R3 experiments (E7, E31 and E32), it was observed that the effect of seeding on residual NH_4-N concentrations was minimal whereas its effect on residual PO_4-P concentrations was significant. In these experiments increasing the amount of synthetically formed struvite addition, reduced residual PO_4-P concentrations from 77.5±3.5mg/L to 23.0±0.0 mg /L (Figure 4.5b). Similar observation was reported by Wang et al. (2006) and attributed to the enhancement of settling in the reactor. They reported without seeding the struvite crystals formed in the reactor exist mostly as colloidal particles and their low settling velocities make sedimentation of these particles negligible, thereby reducing the efficiency of phosphorus removal via struvite precipitation (Wang et al., 2006).

For the effluent of R3 in this current study, it may be speculated that equilibrium is reached after the growth was taken place on the surface of the seed particles and thus improved settling characteristics were achieved in the reactor. This led to lower residual PO_4-P concentrations in comparison to unseeded experiment. In the literature, other investigators reported that the addition of seeding material has no significant effect on residual PO_4-P concentration or PO_4-P removals (Burns et al., 2003; Adnan et al. 2004; Rahaman et al. 2008). This phenomenon is explained by smaller surface area provided by the seeding material in comparison to the surface area of the fresh produced nuclei. More studies need to be conducted to better understand the seeding process in order to improve the results.

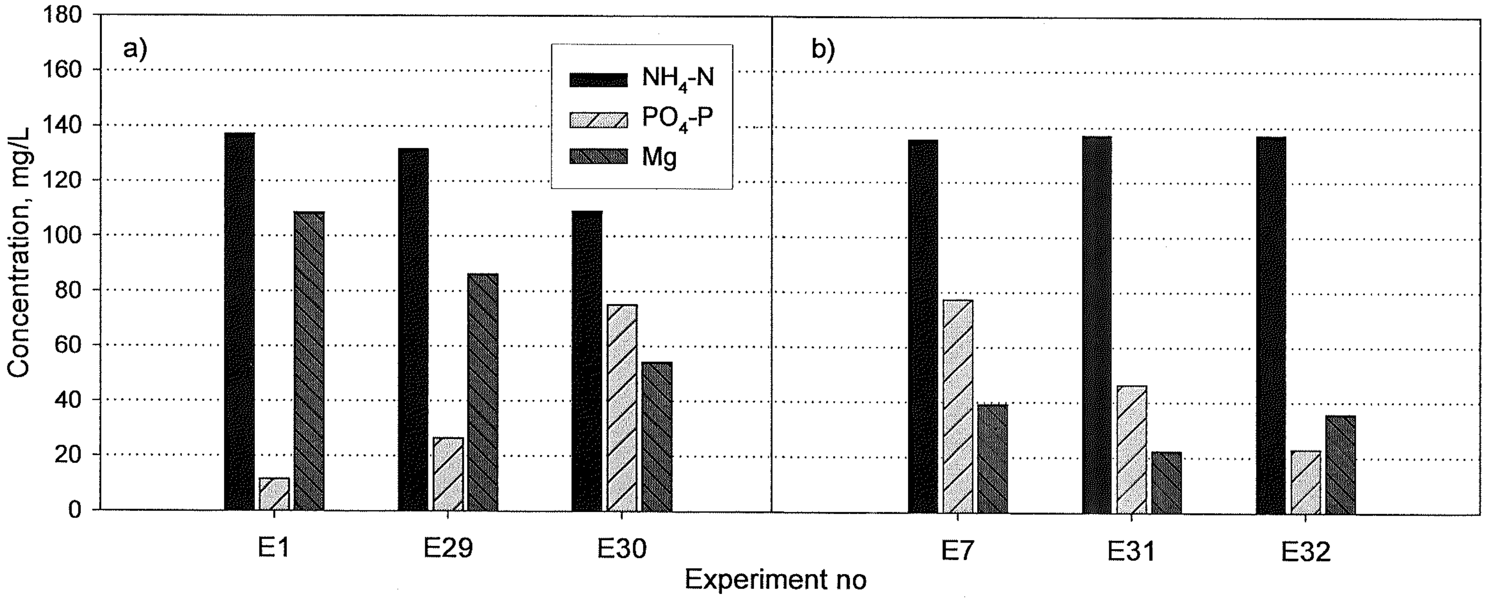

Figure 4.5. Residual concentrations of NH_4-N, PO_4-P and Mg versus seeding experiments conducted with the effluents of a) R1, b) R3

The effect of calcium ion

As stated in literature, the presence of other ions present in the wastewater affects the purity of the precipitating mineral (Schulze-Rettmer, 1991; Le Corre et al., 2005; Wang et al., 2005; Rontentalp et al., 2007). Table 3.12 in Section 3.3.1.2 depicts that calcium and potassium were the two ions present in high concentrations in reactor effluents except struvite forming ions. Both K and Ca are the interfering ions to struvite formation leading the formation of other competing species, such as, potassium struvite (K-MAP, $KMgPO_4.6H_2O$), calcium phosphates [$Ca_3(PO_4)_2$, $Ca_8(HPO_4)_2(PO_4)_4.5H_2O$, $Ca_5(PO_4)_3OH$], calcium carbonates ($CaCO_3$). During anaerobic digestion along with Ca and Mg, K is released due to the Poly-P hydrolysis (Marti et al., 2008).

In the literature different authors (Schuiling and Andrade, 1999; Wilsenach et al., 2006) have pointed out that potassium struvite could precipitate instead of ammonium struvite (MAP), only in the case of low ammonium concentrations. For this reason; the effect of potassium ion was not investigated in the experiments because the reactor effluent having the lowest ammonium concentration was R1 with a concentration of 582±1 mg/L which is quite high.

The effect of calcium ion have been studied by several investigators to enhance phosphorus removal and it is postulated that the relative concentrations of Mg and Ca are the major factor determining phosphorus removal performance and degree of struvite formation (Battistoni et al., 2000; Wang et al., 2005). Recent research predicted that calcium is the major ion interfering struvite formation, and product purity can be greatly decreased when the molar ratio of Mg:Ca ratio is smaller than 1:1 (Wang et al., 2005). For example, at a molar ratio of Mg:Ca of 0.5:1, almost all the phosphorus precipitated in the form of amorphous calcium phosphate (Pastor et al., 2008). In this study three different molar ratios of Mg:Ca were adjusted keeping the molar concentration of NH_4-N in excess (Table 3.17). Experiments were conducted with the effluent of R3 as described in the procedure Section 3.3.1.2 (Figure 3.3) and the results are summarized in Table 4.6.

Table 4.6. Results of calcium ion experiments

Experiment	Molar ratio	Residual Concentration (mg/L)				% removal			
no	Mg:Ca:P:N	NH_4-N	PO_4-P	Mg	Ca	NH_4-N[a]	PO_4-P[a]	Mg[b]	Ca[b]
E33	1:1:1:5	568	5.75±0.35[c]	64.8±3.1	149±14	15.1	22.4	71.7	61.1
E34	1:2:1:5	636	3.25±0.35	121	108	5.0	56.1	47.1	85.9
E35	2:1:1:5	560	1.50±0.00	201	87.6±6.7	16.3	79.8	56.1	77.1

[a] Removals were calculated considering the initial concentrations of the ions at the influent of struvite reactor (Table 3.11).

[b] Removals were calculated considering the total (initial + added) concentrations of the ions in the struvite reactor (Table 3.17)

[c] mean±std (n=2)

In literature it is stated that struvite precipitates at neutral and higher pH levels and at Mg:Ca molar ratios > 0.6:1 (Musvoto et.al., 2000) and a molar ratio higher than 1:1 this will affect the purity of the product (Wang et al., 2005). In E33 the molar ratio of Mg:Ca was 1:1 and the removal of Ca ion from the solution in E33 was 61.1 % (Table 4.6), which imply that there are precipitates containing calcium in the reactor. The precipitate collected from Experiment E33 was analyzed by XRD. Results overlaid with the database standards revealed that together with struvite there were newberyite ($MgHPO_4.3H_2O$) and hydroxylapatite [HAP, $Ca_5(PO_4)_3(OH)$] in the reactor (Figure C.7 in Appendix C). The presence of other minerals together with struvite indicated a decrease in the purity of the product. This can be attributable to the presence of Ca ions because they can influence struvite formation, either by competing for phosphate ions or by interfering with the crystallization of struvite (Le Corre et al., 2005).

As discussed previously, the removal of NH_4-N indicates formation of struvite in the reactor. In E34 NH_4-N removal (5%) were lower in comparison to the NH_4-N removal recorded in E33 (15.1 %) indicating the inhibition of struvite formation by the adjustment of molar ratio of Mg:Ca to 0.5:1. Although the removal of NH_4-N was lowered by the presence of Ca ion, indicating the inhibition of struvite formation, the PO_4-P removal was higher (56.1%) in comparison to the removal achieved in E33 (22.4 %). This difference indicated the presence of alternative removal mechanism of PO_4-P from the wastewater e.g. formation of phosphate containing minerals other than struvite. A similar observation was reported by Pastor et al. (2008) who confirmed precipitating mineral being amorphous calcium phosphate at a molar ratio of Mg:Ca of 0.5:1 through XRD analysis. The XRD analysis of the precipitate collected from Experiment E34 indicated the presence of calcite ($CaCO_3$) and newberyite ($MgHPO_4.3H_2O$) together with struvite (Figure C.8 in Appendix C). The presence of newberyite in the precipitate confirmed that there was an alternative removal mechanism of PO_4-P from the wastewater. The high recovery efficiency of calcium (85.9%) indicated the formation of calcium containing minerals in the reactor. XRD analysis confirmed this finding and proved the presence of calcite in the reactor.

In the literature, it is stated that calcite is thermodynamically stable at ambient temperature and atmospheric pressures and have high precipitation potential depending on the chemical composition of the anaerobic digester effluents (Parsons et al., 2001; Musvoto et al., 2000). The initial alkalinity concentrations of the reactors were exceeding 4000 mg $CaCO_3$/L, due to the biodegradation of nitrogenous organic compounds during the AD, the alkalinity of the reactors were expected to increase above the initial level (Speece, 2008). This will result high bicarbonate concentrations in the reactor effluents, favoring the precipitation of calcite in the reactor (Speece, 2008).

When the ratio of Mg:Ca was 2:1 (Experiment E35) NH_4-N removal enhanced slightly (form 15.1 to 16.3 %) in comparison to experiment E33, whereas the removal efficiency of PO_4-P increased significantly (from 22.4 to 79.8 %). This is expected due to the increase in the degree of saturation with respect to struvite which is observed in the molar ratio experiments of this study and in literature (Beal et al., 1999; Münch and Barr, 2001a; Stratful et al., 2001). Similar observations were recorded in the molar ratio experiments conducted with the effluent of R1, R2 and R6. Another reason may be an alternative removal mechanism of PO_4-P from the reactor e.g. formation of magnesium and/or calcium phosphates. However, the results of the XRD analysis confirmed formation of only calcite together with struvite in the reactor (Figure C.9 in Appendix C). This observation may be due to the amount of the precipitate other than calcite and struvite being limited. The removal of calcium in E35 is 77.1 % and higher than calcium removal recorded in E33 (61.1 %). This may indicate formation of higher amount of calcite in Experiment E35 which is identifiable through the XRD.

The comparison of experiments E9 and E35 indicated different uses of the struvite precipitation technique. In E9 there were additions of magnesium and orthophosphate to adjust the molar ratio of Mg:N:P to 1.5:1:1 and the removal efficiencies of NH_4-N and PO_4-P were 77.6 % and 69.6 %,respectively (Table 4.3). In E35 there were addition of magnesium, orthophosphate and calcium (molar ratio of Mg:Ca:P:N was 2:1:1:5), the removals of NH_4-N and PO_4-P were 16.3 % and 79.8 %, respectively (Table 4.6). This indicated that the addition of calcium ion increased the removal efficiency of PO_4-P and lowered the magnesium source and phosphorus source requirements. However, the disadvantage in this case is that the removal efficiency of NH_4-N is lower and the purity of the product is poorer.

The results of the calcium ion experiments indicated that Ca has inhibitory effects of the struvite reaction. The presence of Ca led to formation of calcite and hydroxlyapatite that were detectable through XRD. The results of the experiments indicated that the addition of magnesium ion above the molar concentration of PO_4-P together with Ca ion helped to remove most of the phosphorus even in low phosphorus wastewaters. If P removal and recovery was the only target, then addition of calcium along with magnesium would be recommended.

4.2 Struvite Precipitation from the Effluents of Full-scale Co-digestion Plant utilizing Poultry Manure and Maize Silage

In this part of the study the removal and/or recovery of nutrients (N and P) from the effluents of a full-scale poultry manure co-digester (designated as FS) was investigated. For the removal and recovery of the nutrients both the liquid and the solid phases of the biogas plant effluent were used. In the liquid phase experiments, struvite precipitation led to "removal and recovery" of the already existing nutrients from the wastewater in the form of struvite. Therefore, the reductions in the concentrations of the ions are referred as "removal". While in the solid phase experiments, a pre-treatment step was adopted to the system in order to make the nutrients available for struvite reaction. Therefore, the removal of the nutrients from the phosphorus-enriched liquid phase is referred as "recovery" but not removal.

4.2.1 Struvite Precipitation from the Liquid Phase Effluent of the Co-digestion Plant

In the struvite precipitation experiments conducted with the liquid phase of the FS sample, the effects of molar concentration ratio of Mg:N:P and phosphorus source on the removals of NH_4-N and PO_4-P were investigated.

The effect of molar concentration ratio of Mg:N:P

Ammonia nitrogen is in excess in most of the AD supernatants and addition of magnesium and phosphorus from external sources is necessary. This is because the molar ratio of struvite forming ions (Mg:N:P ratio) should be at least unity for intentional struvite precipitation. Whereas higher magnesium can enhance the struvite precipitation process and increase the removal of PO_4-P and NH_4-N from the wastewater (Rahaman et al., 2008). At any given pH level, any increase in the Mg:N:P ratio would increase the degree of saturation with respect to struvite formation, which, in turn would enhance the removal and recovery of PO_4-P and NH_4-N (Adnan et al., 2004; Rahaman et al., 2008).

In this study, in order to maximize nitrogen and phosphorus removals, three different total (initial + added) molar concentration ratios of the struvite forming ions Mg:N:P of 1:1:1, 1.3:1:1, 1.5:1:1 were used (Table 3.18, Section 3.3.2.1). For comparison two different chemicals were used for phosphate supplementation; in three of the experiments (Experiment FS-L1, FS-L2 and FS-L3) H_3PO_4 was used, while in the other three experiments (Experiment FS-L4, FS-L5 and FS-L6) $NaH_2PO_4.2H_2O$ was used. The results of the experiments in terms of residual concentration and percent removals of the struvite forming ions were depicted in Table 4.7. In order to represent the actual removal of the ions from the wastewater; the removals are reported considering the initial concentrations of these ions present in wastewater (Table 3.4, Section 3.1.2) but not the total (initial + added) concentrations.

In contrary to the experiments conducted with the effluents of laboratory scale anaerobic reactors the use of Mg:N:P of 1:1:1 (Section 4.1.2) led to a significant removal of PO_4-P in addition to the NH_4-N; 90% and 89 % by the use of H_3PO_4 and $NaH_2PO_4.2H_2O$, respectively. This can be attributed to the different chemical compositions of the wastewaters investigated. In the literature it is stated that Ca is one of the important ions interfering with the precipitation of struvite (Momberg and Oellermann, 1992; Battistoni et al., 2000; Wang et al., 2005) and the calcium contents of the wastewaters were quite different. The concentration of Ca in the liquid phase of the FS sample was 11 mM whereas Ca concentrations in the effluent of the lab-scale anaerobic reactors were ranging between 0.5-3.3 mM, which were at least three fold lower.

As also reported in literature, the organic matter content also affect the struvite precipitation process (Schuiling and Andrade, 1999; Burns et al., 2001; Uludağ-Demirer et al., 2005), the COD concentrations of the liquid phase of the FS sample subjected to struvite precipitation experiments was 44208±658 mg/L whereas the maximum COD concentration observed in the lab-scale anaerobic reactor effluents subjected to struvite precipitation experiments was 3498±108 mg/ L (Table 3.11). The ionic strength, the concentrations of other foreign ions, the presence of complexing agents and organic acids are the other factors may play roles in different behavior of the struvite precipitation process (Schulze-Rettmer, 1991; Uludağ-Demirer et al., 2005).

The results of the experiments indicated that the variation of Mg:N:P from 1:1:1 to 1.3:1:1 led to a considerable increase in the removal of PO_4-P; from 90.3 % to 97.8 % and from 88.8 % to 97.8 %, by the use of H_3PO_4 and $NaH_2PO_4.2H_2O$, respectively. However, the difference in the removal of PO_4-P was minimal by the variation of Mg:N:P from 1.3:1:1 to 1.5:1:1 (from 97.8 % to 98.4 % and from 97.0 % to 98.1 %, by the use of H_3PO_4 and $NaH_2PO_4.2H_2O$, respectively). A similar trend was observed by other researchers (Rahaman et al., 2008). The NH_4-N removals obtained in these experiments ranged between 67-75 % (Figure 4.6), indicating precipitation of struvite in the reactors based on the possible removal mechanisms of NH_4-N discussed previously (see Section 4.1.2) and recorded in the study of Uludağ-Demirer and Othman (2009). The XRD analysis conducted for the precipitate collected from FS-L6 confirmed the presence of struvite, no other minerals were detected (Figure C.10, in Appendix C).

The effect of phosphorus source

In literature, typical chemicals used to add Mg and PO_4-P ions were reviewed for several studies and listed in Uludağ-Demirer et al. (2005). Especially for Mg supplementation, there are several alternatives, such as, MgO, $Mg(OH)_2$, $MgCl_2.6H_2O$ and the effect of Mg source on the removal of NH_4-N by struvite precipitation has been investigated by Çelen and Türker (2001). They reported that the use of MgO provided lower ammonia recovery than that when $MgCl_2.6H_2O$ was used as an Mg ion resource. A comparison of the performance of $MgCl_2.6H_2O$ and $Mg(OH)_2$ as Mg ion additives was accomplished in the study of Uludağ-Demirer et al. (2005), and their results also indicated higher NH_4-N removals from the effluent of the anaerobic digestion of the dairy manure in the reactors spiked by $MgCl_2.6H_2O$

than the reactors treated with $Mg(OH)_2$. For this reason; $MgCl_2.6H_2O$ was used as the source of magnesium and the effect of using different magnesium containing chemicals was not investigated in this study.

For phosphate supplementation, Brionne et al. (1994) tested dipotassium hydrogen phosphate (K_2HPO_4), phosphoric acid (H_3PO_4) and potassium dihydrogen phosphate (KH_2PO_4) and used H_3PO_4 for economical reasons. Webb and Ho (1992) used KH_2PO_4 in their studies. Schulze-Rettmer (1991) proposed H_3PO_4 and Zdybiewska and Kula (1991) reported better precipitation results when using H_3PO_4 with $MgCl_2$ than using it with MgO. On the other hand numerous investigators reported using $Na_2HPO_4.7H_2O$ as phosphorus source (Uludağ-Demirer et al., 2005). However, the comparison of different phosphorus sources were not fully investigated in the literature, therefore in this study two different phosphorus containing chemicals (H_3PO_4 and $NaH_2PO_4.2H_2O$) were used for comparison.

The percentage removals obtained by the use of different phosphorus sources were close to each other (Table 4.7). Following the addition of the phosphorus source to the reactors significant amount of foam formation was observed in the reactors, which may affect the mixing behavior of the reactors. The different NH_4-N and PO_4-P removals recorded by the use of the same molar ratio may also be attributable to the different mixing intensities adjusted during the experiments. The effect of phosphorus source on the removals of NH_4-N and PO_4-P removals was not considerable; however the use of different chemicals may affect the composition of the resulting solution in terms of salinity (Schulze-Rettmer, 1991).

Unlike to the magnesium source, there is no considerable advantage and/or disadvantage of any phosphorus source over each other from nutrient removal point of view (Çelen and Türker, 2001; Uludağ-Demirer et al. 2005).

Table 4.7. Results of the liquid phase experiments of the FS sample

	Molar ratio of	Phoshorus	Residual concentration, mg/L			% removal[b]		
Experiment no	Mg:N:P	source	NH_4-N	PO_4-P	Mg	NH_4-N	PO_4-P	Mg
FS-L1[a]	1:1:1	H_3PO_4	1079±8[c]	5.89±0.05	68.8±2.4	72.4	90.3	-[d]
FS-L2[a]	1.3:1:1	H_3PO_4	1288±8	1.31±0.07	1355±7	67.0	97.8	-
FS-L3[a]	1.5:1:1	H_3PO_4	1152±16	0.95±0.04	2080±28	70.5	98.4	-
FS-L4	1:1:1	$NaH_2PO_4.2H_2O$	1011±23	6.75±0.07	209±0	74.1	88.8	-
FS-L5	1.3:1:1	$NaH_2PO_4.2H_2O$	1025±42	1.85±0.28	1323±3	73.8	97.0	-
FS-L6	1.5:1:1	$NaH_2PO_4.2H_2O$	989±14	1.15±0.07	2240±28	74.7	98.1	-

[a] Experiments conducted with 200 mL of wastewater.

[b] All removals were calculated considering the initial concentrations of the ions at the influent of struvite reactor (Table 3.4).

[c] mean±std (n=2)

[d] “-“ means no removal i.e. final concentration is higher than initial concentration.

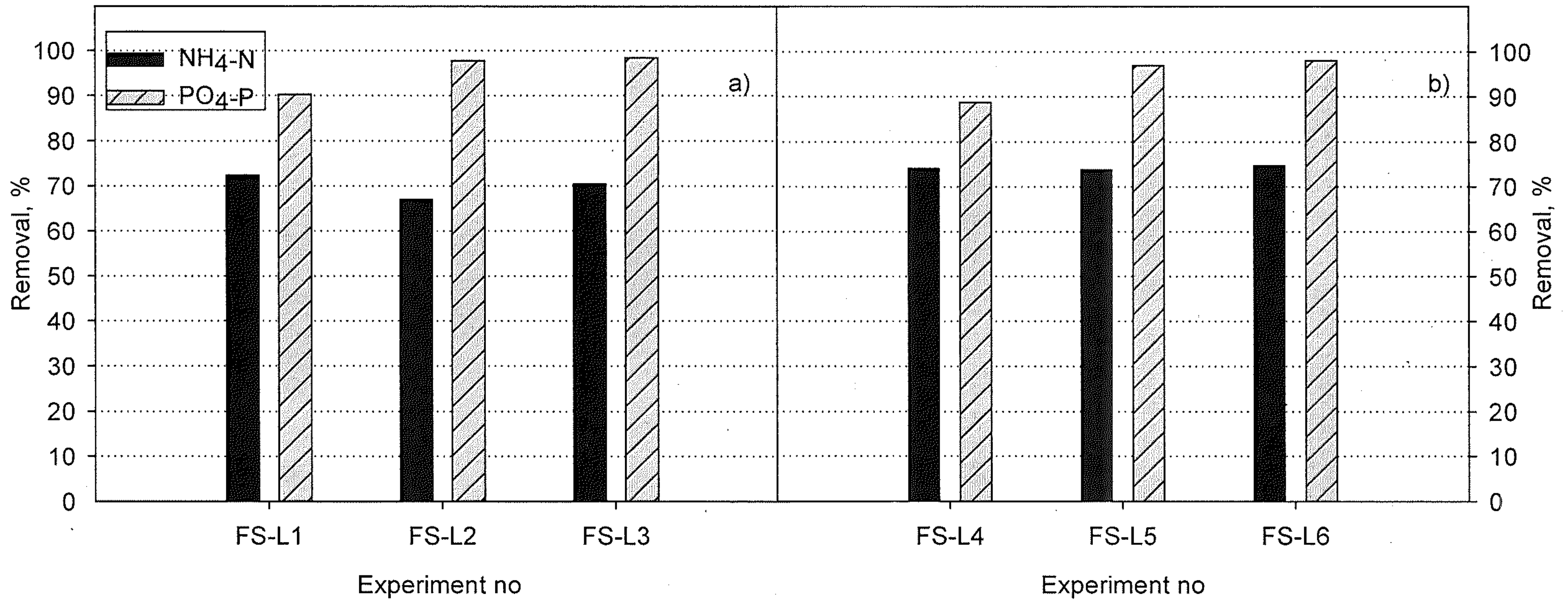

Figure 4.6. NH_4-N and PO_4-P removals versus liquid phase experiments of FS sample a) by the use of H_3PO_4 as the phosphorus source of b) by the use of $NaH_2PO_4.2H_2O$ as the phosphorus source

4.2.2. Recovery of the Nutrients Available in the Solid phase of the Co-digestion Plant

The remaining solid phase obtained after solid-liquid separation process was rich in nitrogen and phosphorus (Table 3.5, Section 3.1.2) and the usual operation applied in practice was dumping it to landfill, incineration or land application (OSU Extension, 2006; Shaffer, 2005). However, the applications of the first two options lead to the loss of nutrients, whereas the third option lead to some problems associated with health, odor and environmental problems. The objective of conducting solid phase experiments was to recover the nutrients (N and P) present in the solid phase and make them available for safe use in agricultural activities.

The recovery of nitrogen and phosphorus can only be done by using the dissolved fraction, but most of the nutrients are located in solid form. For this purpose, the solid phase was subjected to phosphorus dissolution process (Figure 3.4, Section 3.3.2). Müller et al. (2004) stated that sludge cells can be dissolved by acidic or alkali treatment at low or ambient temperatures. In the study of Weidelener et al. (2005) acidic and alkaline dissolution were compared for three different wastewater treatment plant sludges and it is reported that the efficiency of the acidic dissolution was higher than the alkaline dissolution. Therefore, for the purpose of phosphorus dissolution acidic dissolution was applied in this study (Figure 3.4).

The applied process led to the transformation of available phosphates into the orthophosphate. This can be attributable to the disintegration of the cell walls and mineralization of the microbial cells; similar results were reported in other studies (Neyens et al., 2003; Weidelener et al., 2005). Table 4.8 depicts the concentration of metals present in the phosphorus-enriched liquid phase. The phosphorus-enriched liquid phase was analyzed for the metals and heavy metals that were present in high quantities in the solid phase (Table 3.5). In addition to the increase of orthophosphate concentration, acidic dissolution resulted in the release of the metals which were normally integrated in organic complex molecules into the liquid phase (Neyens et al., 2003). Due to the fact that metals can be incorporated into the crystal lattice or sorbed to the surface of struvite (Kamnev et al., 1999; Rontentalp et al., 2007), it is important to know the concentrations of the metals and heavy metals in the wastewater subjected to struvite precipitation experiments.

Table 4.8.Characterization of the phosphorus-enriched liquid phase of the FS sample before struvite precipitation experiments

Parameter	Concentration
NH_4-N, mgN/L	1484±4[a]
PO_4-P, mgP/L	827±3
Mg, mg/L	406±1
Al[b], mg/L	2.11
Ca, mg/L	1581
Cd, mg/L	<0.025
Cu, mg/L	0.284
Fe, mg/L	122
K, mg/L	1439
Ni, mg/L	0.136
Zn, mg/L	15.3

[a]mean ± std

[b]The Al, Ca, Cd, Cu, Fe, K, Ni, Zn concentrations depict the mean concentration of the duplicate analysis.

The effect of molar concentration ratio Mg:N:P

To determine the effect of molar ratio of Mg:N:P on the recovery of NH_4-N and PO_4-P three Mg:N:P ratios were used (Table 3.19, Section 3.3.2.2). The results of the experiments in terms of residual concentration and recovery efficiencies of the struvite forming ions were depicted in Table 4.9. In order to represent the actual recovery of the ions in the wastewater; the recovery efficiencies are reported considering the initial concentrations of the ions present in wastewater (Table 4.8), but not the total (initial + added) concentrations.

In Experiment FS-P1 considerably high recovery efficiencies of the struvite forming ions were achieved (Table 4.8). The analysis of the resulting solution from Experiment FS-P1 revealed that the molar ratio of Mg:N:P was 1:27:11, illustrating the limiting component being magnesium. This may imply the precipitation of magnesium containing minerals in the reactor. To test this XRD analysis of the precipitate collected from Experiment FS-P1 was conducted. The results confirmed the presence of newberyite [$MgHPO_4.3H_2O$] together with struvite (Figure C.11, in Appendix C). The comparison of the results of Experiment FS-P1 and FS-P2 indicated that, Mg at a concentration higher than the stoichiometric ratio was required in order to achieve higher recovery efficiencies of NH_4-N and PO_4-P (Figure 4.7). The requirement of excess magnesium can be attributable to the presence of complexing agents in the wastewater which form soluble complexes with magnesium, thereby making it unavailable for struvite reaction (Beal et al., 1999; Nelson et al., 2003; Burns et al., 2003).

However, the comparison of the Experiment FS-P2 and FS-P3 indicated that the variation of Mg:N:P ratio from 1.3:1:1 to 1.5:1:1 no longer affect PO_4-P recovery efficiency and it is leveled out at about 99 %, which is considerably high (Table 4.9). Similar findings were reported by other investigators (Rahaman et al. 2008; Uludağ-Demirer and Othman, 2009). On the other hand, NH_4-N recovery efficiency was slightly increased (from 90.5 to 92.3 %) by the variation of the molar ratio of Mg:N:P ratio from 1.3:1:1 to 1.5:1:1. This is expected due to the increase in the degree of saturation of solution with respect to the struvite formation (Rahaman et al., 2008). XRD analysis of the precipitate collected from Experiments FS-P3 confirmed precipitation of mainly struvite in the reactor and no other mineral were detected (Figure C.12, Appendix C).

Table 4.9. Results of the solid phase experiments of FS sample conducted by the use of different Mg:N:P molar ratios

Exp.	Molar ratio	Residual concentration, mg/L			% recovery[a]		
no	of Mg:N:P	NH_4-N	PO_4-P	Mg	NH_4-N	PO_4-P	Mg
FS-P1	1:1:1	161±5[b]	151±2	10.3±0.4	89.1	81.8	97.5
FS-P2	1.3:1:1	141±1	6.83±0.00	452±9	90.5	99.2	-[c]
FS-P3	1.5:1:1	114±0	6.43±0.08	740±28	92.3	99.2	-

[a] All recovery efficiencies were calculated considering the initial concentrations of the ions at the influent of struvite reactor (Table 4.8).
[b] mean±std (n=2)
[c] "-" means no recovery i.e. final concentration is higher than initial concentration.

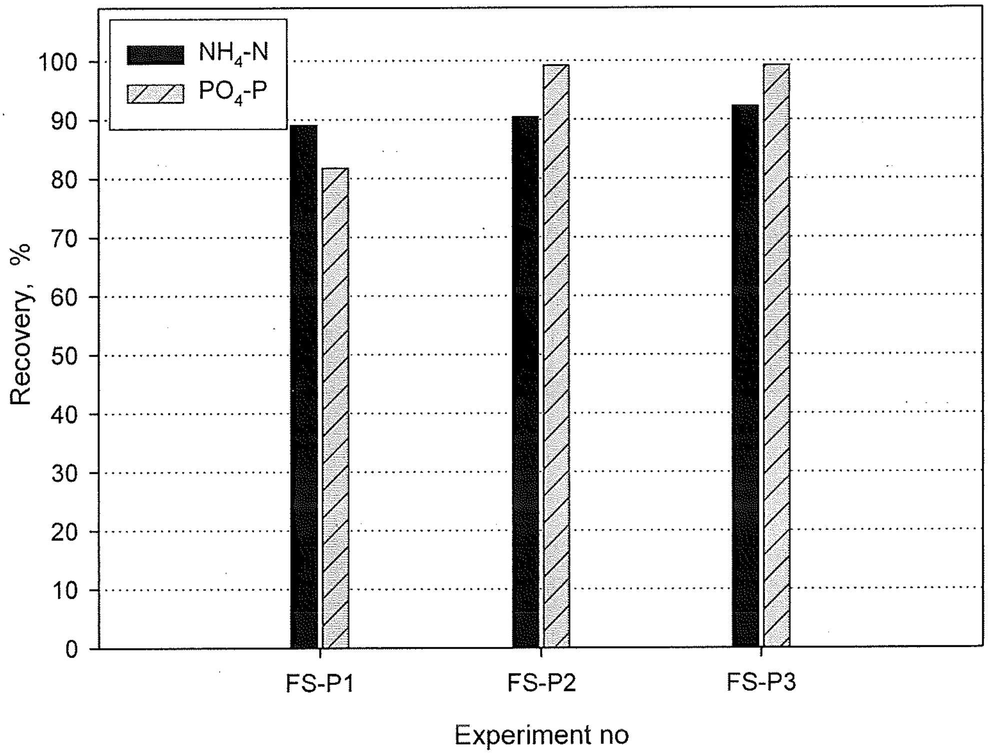

Figure 4.7. NH_4-N and PO_4-P recovery efficiencies versus solid phase experiments of FS sample conducted by the use of different Mg:N:P molar ratios

The effect of molar concentration ratio of Mg:P

The initial molar concentration of Mg:N:P in the phosphorus-enriched liquid phase of the FS sample was 1:6:2. In order to investigate the effect of the molar concentration ratio of Mg:P, three experiments were conducted by addition of Mg containing chemical ($MgCl_2.6H_2O$) only. The amount of Mg to be added to the reactor was determined by taking the PO_4-P concentration as the basis. In these experiments the external phosphorus addition was eliminated, aiming complete recovery of the available PO_4-P. In order to observe the effect of molar concentration ratio of Mg:P on the recovery of PO_4-P and NH_4-N three molar ratio of Mg:P (1:1, 1.3:1 and 1.5:1) were tested (Table 3.19).

The results of the experiments i.e. the residual concentrations and recovery efficiencies of struvite forming ions and the metals (Al, Ca, Fe, K and Zn) initially present in considerable amounts in the phosphorus-enriched liquid phase (Table 4.8) were depicted in Table 4.10. The concentrations of Cd, Cu and Ni in the remaining solution were not determined as they were already in trace concentrations in the original solution (Table 4.8).

Table 4.10. Results of the solid phase experiments of FS sample conducted by the use of different Mg:P molar ratios

Experiment	Molar ratio	Residual Concentration, mg/L							
no	of Mg:P	NH_4-N	PO_4-P	Mg	Al	Ca	Fe	K	Zn
FS-P4	1:1	1229±25[a]	1.50±0.00	311±14	0.14	549	0.23	984	0.25
FS-P5	1.3:1	1241±4	1.30±0.00	417±4	nd[b]	nd	nd	nd	nd
FS-P6	1.5:1	1250±10	1.20±0.00	448±12	0.15	528	0.30	965	0.24
FS-P7	1:2[c]	1251±1	6.83±0.00	197±6	nd	nd	nd	nd	nd
FS-P8	1:2[c]	1286±5	0.90±0.00	215±5	0.21	375	0.49	1421	0.38

Experiment	Molar ratio	Recovery[d], %							
no	of Mg:P	NH_4-N	PO_4-P	Mg	Al	Ca	Fe	K	Zn
FS-P4	1:1	17.2	99.8	23.5	93.4	65.3	99.8	31.6	98.4
FS-P5	1.3:1	16.4	99.8	-[e]	nd	nd	nd	nd	nd
FS-P6	1.5:1	15.8	99.9	-	92.9	66.6	99.8	32.9	98.4
FS-P7	1:2[c]	15.7	99.2	51.5	nd	nd	nd	nd	nd
FS-P8	1:2[c]	13.4	99.9	47.2	90.0	76.3	99.6	1.3	97.5

[a] mean±std (n=2)

[b] nd: Not determined.

[c] Initial molar ratio in the solution i.e. no addition of chemicals

[d] All recovery efficiencies were calculated considering the initial concentrations of the ions at the influent of struvite reactor (Table 4.8).

[e]“-“ means no recovery i.e. final concentration is higher than initial concentration.

The results of the experiments (Experiment FS-P4, FS-P5 and FS-P6) illustrated that residual PO_4-P concentrations ranging between 1.50±0.00 mg/L to 1.20±0.00 mg/L were achievable by the addition of Mg only. Although the residual PO_4-P concentrations were quite low, because of the very high residual NH_4-N concentrations, there should be post treatment of this ion down in the stream to meet the discharge regulations. For instance, if the objective is to use the treated water for irrigation, ammonia nitrogen concentration should be below 50 mg/L as specified in the Technical Bulletin of Water Pollution Control Regulation of Turkey (MoEF, 1991). Moreover, depending on the location of the plant if it is combined with the treatment plant of the poultry processing unit, then more stringent criteria is to be met. For example, the effluent discharge criteria specified by the World Bank Group for poultry processing is 10 mg/L total nitrogen and 2 mg/L for total phosphorus (IFC, 2007) and the similar criteria required by the Water Pollution Control Regulation of Turkey (Official Gazette: 31 December 2004, No.25687) is 15 mg/L for ammonia nitrogen and 2 mg/L for orthophosphate (MoEF, 2004).

The results from XRD analysis for the precipitate collected from the reactor containing phosphorus-enriched solution with molar ratio of Mg:P of 1.5:1 (Experiment FS-P6) depicted clearly that the precipitate was mainly struvite (Figure C.13 in Appendix C). The pattern of the sample and struvite (designated by straight lines in Figure C.13 in Appendix C) which was retrieved from the data base in the software installed to the equipment match almost exactly showing also the purity of struvite was high. The unassigned peaks that are present in the pattern of the sample indicate the presence of some other minerals as impurities.

The variation of the molar ratio of Mg:P from 1:1 to 1.5:1 slightly lowered the recovery of NH_4-N, while the recovery efficiency of PO_4-P (Table 4.10) leveled out at about 99 %, which is considerably high. Moreover, the recovery efficiency of the Ca ion was 66.6 % in Experiment FS-P6, which is quite high. Based on these results, it may be speculated that there were formation of calcium containing minerals e.g. hydroxylapatite [HAP, $Ca_5(PO_4)3OH$], calcite ($CaCO_3$) in the reactor together with struvite as impurities.

The high recovery efficiencies of Al, Fe and Zn (Table 4.10) indicated their precipitation together with struvite. Similar observation was recorded by other researchers (Kamnev et al., 1999; Rontentalp et al., 2007), who illustrated that the metals can be incorporated into the crystal lattice or sorbed to the surface of struvite decreasing the purity of the product. However, because the initial molar concentration ratios of Al:P, Fe:P and Zn:P were 0.003:1, 0.08:1 and 0.009:1 they did not lead to formation of significant quantities of other minerals e.g. berlinite ($AlPO_4$), iron phosphate ($FePO_4$), and zinc ammonium phosphate hexahydrate ($ZnNH_4PO_4.6H_2O$) that were detectable by XRD analysis.

In the literature different authors (Schuiling and Andrade, 1999; Wilsenach et al., 2006) have pointed out that potassium struvite could precipitate instead of ammonium struvite (MAP), only in the case of low ammonium concentrations. Based on this, the low recovery efficiencies of potassium (Table 4.10) may be attributable to the high NH_4-N concentration of the phosphorus-enriched liquid phase.

To observe the effect of phosphorus and magnesium additions and pH, two experiments (Experiment FS-P7 and FS-P8) were conducted (Table 3.19). Because of the release of metals together with nutrients during acidic dissolution, re-precipitation of nutrients together with metals (Mg and Ca) occurred while adjusting the pH level. The results of Experiment FS-P7 indicated that addition of magnesium is required to obtain lower residual concentrations of PO_4-P at a pH level of 8.5 (Table 4.10). In experiment FS-P8, slightly higher residual Mg concentrations than experiment FS-P7 was observed (Table 4.10). Also, the lowest residual concentration of Ca was observed in experiment FS-P8 (Table 4.10). This may indicate precipitation of Ca in the reactor due to higher pH level (9.5) adjusted during the experiment. In the phosphorus-enriched liquid phase the molar ratio of Ca:Mg was 2.2:1. In the literature it is stated that the purity of the precipitate decreased when Ca:Mg ratio is higher than 1:1 (Wang et al., 2005).

Numerous researchers have investigated the optimum pH values and concluded that the optimum pH values for the precipitation of hydroxyapatite [HAP, ($Ca_5(PO_4)_3OH$)] occurs at pH levels above 9.5, whereas effective struvite precipitation occurs at pH at 8.0 and above (Wang et al., 2005). Moreover, the very low (0.90±0.00 mg/L) residual concentration of PO_4-P suggest alternative removal mechanisms of PO_4-P from the reactor e.g. formation of other competitive minerals together with struvite. The collected precipitate from Experiment FS-P8 was analyzed with XRD to confirm the mineral present in the precipitate (Figure C.14 in Appendix C).

For the precipitate that was formed at pH level of 9.5 in experiment FS-P8, a broad hump centered at approximately 30° is apparent, which is due to amorphous materials in the sample. A similar observation was recorded in the study of Wang et al. (2005), in which the presence of amorphous phase was attributed to the presence of amorphous calcium precipitates. From the match of the XRD pattern of the sample and the pattern of the struvite (which is retrieved from the data base installed to the XRD equipment), the existence of struvite crystals is clear (Figure C.14 in Appendix C).

The results of the experiments conducted by the addition of both magnesium and phosphorus (Experiment FS-P1, FS-P2 and FS-P3) and the experiments conducted by the addition of magnesium only (Experiment FS-P4, FS-P5 and FS-P6) indicated that Mg concentration was an important factor in the removal of NH_4-N and PO_4-P. However, it was clear from the results that PO_4-P concentration controls the removal of NH_4-N significantly. This is because the major removal mechanism of NH_4-N was by struvite precipitation, while PO_4-P removal is by the precipitation of several minerals including struvite. Uludağ-Demirer (2008) reported similar results using statistical methods to determine the significance of concentration of struvite forming ions and pH on the removal of NH_4-N and PO_4-P. Another study of Uludağ-Demirer and Othman (2009) also reported similar findings.

By changing the initial concentrations of Mg and PO_4-P in the solution, the effects of Mg:N:P and Mg:P ratios on recovering NH_4-N and PO_4-P were analyzed. There were two extreme compositions of the solution as one corresponding to the original solution with Mg:P ratio of 1.5:1 (Experiment FS-P6) and the other simulating struvite formation stoichiometry in the solution with addition of extra Mg at a Mg:N:P ratio of 1.5:1:1 (Experiment FS-P3). The two different compositions also indicated the use of struvite formation for different purposes.

The molar concentration ratio of the solution, with the final composition of the solution, advantages and disadvantages of the technique for each case are summarized in Table 4.11. As seen from Table 4.11, the concentration of NH_4-N can be reduced from 1484±4 mg/L to 1250±10 mg/L in a solution containing Mg molar concentration equal to half of initial NH_4-N concentration at pH of 8.5 by struvite precipitation. This is achieved in Experiment FS-P6 by keeping the concentrations of NH_4-N and PO_4-P as in the original wastewater, which is preferred over the addition of PO_4-P. The same conditions, however, yielded considerably high removal of PO_4-P (99.9 %) by reducing its concentration from 827±3 mg/L to 1.20±0.00 mg/L. As discussed before, the difference between the removal of NH_4-N and PO_4-P may indicate the formation of other species containing PO_4-P as impurities. However XRD results (Figure C.13 in Appendix C) indicated formation of mainly struvite. Since NH_4-N recovery (15.8 %) is poor in this case, struvite formation in wastewater composition with excess NH_4-N can be used to recover PO_4-P only.

It was also illustrated that increasing the pH level to 9.5 without addition of any magnesium and/or phosphorus containing chemical (Experiment FS-P8) led to complete recovery of PO_4-P (99.9%), reducing its concentration down to 0.90±0.00 mg/L. However, XRD analysis of the precipitate confirmed the presence of other minerals as impurities, reducing the purity of the struvite which in turn reduces its market value (Wang et al., 2005). Moreover, the residual concentration of NH_4-N was very high (1286±5 mg/L), thus, just the increase of pH can be applied for the recovery of PO_4-P, only. On the other hand, the recovery efficiencies of NH_4-N and PO_4-P in the wastewater simulating struvite stoichiometry with excess Mg (Experiment FS-P3) were close to each other 92.3 % and 99.2 %, respectively, indicating formation of almost pure struvite. The XRD analysis confirmed this finding, because the peaks in the XRD pattern of the sample matched well with the standard struvite peaks obtained from the data base of the instrument.

Table 4.11. Maximum recoveries of NH_4-N and PO_4-P by struvite precipitation from phosphorus-enriched liquid of FS sample

Wastewater composition	Exp. no.	Molar ratio of Mg:N:P	Final Concentration (mg/L)		Advantages	Disadvantages	Proposed Application
			NH_4-N	PO_4-P			
Original with addition of extra Mg	FS-P6	1.5:3:1	1250±10	1.20±0.00	No addition of PO_4-P, high recovery of PO_4-P,struvite purity is higher in comparison to FS-P8	Addition of Mg, poor recovery of NH_4-N, high concentration of NH_4-N in effluent	Only for the recovery of PO_4-P
Original with pH increase to 9.5	FS-P8	1:6:2 [a]	1286±5	0.90±0.00	No addition of Mg and PO_4-P,high recovery of PO_4-P,	Purity of struvite is poor, high concentration of NH_4-N in effluent, poor recovery of NH_4-N	Only for the recovery of PO_4-P
Simulating struvite stoichiometry with excess Mg	FS-P3	1.5:1:1	114±0	6.43±0.08	High recoveries of PO_4-P and NH_4-N, purity of struvite is high, nearly four times higher amount of precipitate was obtained	Addition of PO_4-P and excess Mg	For the recovery of both NH_4-N and PO_4-P

[a] Initial molar ratio of the phosphorus-enriched liquid phase

4.3 Struvite Precipitation from the Effluent of the Full-scale Poultry Manure Digester

In this part of the study the removal/recovery of nutrients (N and P) from the effluents of a full-scale poultry manure digester (designated as MS) was investigated.

4.3.1 Struvite Precipitation from the Liquid Phase Effluent of the Poultry Manure Digester

In the struvite precipitation experiments conducted with the liquid phase of the MS sample, the effects of molar concentration ratio of Mg:N:P and pH on the removals of NH_4-N and PO_4-P were investigated.

The effect of molar concentration ratio of Mg:N:P

The molar ratio of Mg:N:P in the liquid phase of the poultry manure digester (MS sample) was 1:1510:24. As expected ammonia nitrogen is in excess and addition of magnesium and phosphorus from external sources is necessary. For intentional struvite formation the molar ratio of Mg:N:P should be at least unity, whereas higher magnesium can enhance the struvite precipitation process and increase the removal of PO_4-P and NH_4-N from the wastewater (Rahaman et al., 2008). Therefore, in order to maximize nitrogen and phosphorus removals, three different total (initial + added) molar concentration ratios of the struvite forming ions Mg:N:P of 1:1:1, 1.3:1:1, 1.5:1:1 were used (Table 3.20). During the molar ratio experiments pH level was kept constant at 8.5.

The results of the experiments in terms of residual concentrations and percent removals of the struvite forming ions were depicted in Table 4.12. In order to represent the actual removal of the ions from the wastewater; the removals are reported considering the initial concentrations of these ions present in wastewater (Table 3.6) but not the total (initial + added) concentrations.

Table 4.12. Results of the liquid phase struvite precipitation experiments of the MS sample

Experiment no	Molar ratio of Mg:N:P	pH	Residual concentration, mg/L			% removal[a]		
			NH_4-N	PO_4-P	Mg	NH_4-N	PO_4-P	Mg
MS-L1	1:1:1	8.0	630±4[b]	3293±1	10.6±1.9	86.3	-[c]	-
MS-L2	1:1:1	8.5	646±35	3679±1	5.65±0.92	86.0	-	-
MS-L3	1:1:1	9.0	606±0	3235±1	9.55±0.35	86.9	-	
MS-L4	1.3:1:1	8.5	158±0	1203±4	45.5±1.7	96.6	-	-
MS-L5	1.5:1:1	8.5	121±3	112±4	344±7	97.4	31.6	-

[a] All removals were calculated considering the initial concentrations of the ions at the influent of struvite reactor (Table 3.6).

[b] mean±std (n=2)

[c] “-“ means no removal i.e. final concentration is higher than initial concentration.

The result of experiment MS-L2 indicated that the adjustment of molar ratio of Mg:N:P of 1:1:1 at a pH level of 8.5 was not sufficient to decrease the residual concentration of PO_4-P (3293±1 mg/L) down to its initial concentration (163±0 mg/L). This is because of its addition into the wastewater to initiate the struvite formation; however, this led to further contamination of wastewater by PO_4-P (Table 4.12). A similar finding was recorded by the experiment conducted with the effluent of lab-scale anaerobic reactor digesting poultry manure (R1) (Experiment E1, Section 4.1.2). However, the difference between the initial and the residual concentrations of PO_4-P in experiment MS-L1 were high compared to the difference observed in the experiments conducted with the effluent of R1 (Experiment E1, Section 4.1.2). This is due to the lower initial NH_4-N concentrations (582.4±0.8 mg/L) of R1 compared to the NH_4-N concentration of liquid phase of MS sample (4612±117 mg/L).

The removal of NH_4-N was 86.3 % which was quite high and attributable to struvite formation based on the possible removal mechanisms of NH_4-N discussed previously and recorded in the study of Uludağ-Demirer and Othman (2009). XRD analysis of the sample collected from Experiment MS-L2 depicted the presence of struvite; no other minerals were detected from the XRD patterns of the sample (Figure C.15 in Appendix C).

The variation of molar ratio of Mg:N:P from 1:1:1 to 1.3:1:1 at pH level of 8.5 enhanced the removal of NH_4-N (Table 4.12) and lowered the residual concentration of PO_4-P, however, the residual PO_4-P concentration (1203±4 mg/L) was still higher than its initial concentration (163±0 mg/L). The result of experiment MS-L5 illustrated that further addition of Mg to the reactor (the use of Mg:N:P ratio of 1.5:1:1) led to reduction of residual PO_4-P concentration (112±4 mg/L) down to its initial concentration (163±0 mg/L). The use of molar ratio of Mg:N:P of 1.5:1:1 (Experiment MS-L5) led to NH_4-N removal of 97.4 % and PO_4-P removal of 31.6 %, whereas the use of the same Mg:N:P (Experiment E1, Section 4.1.2) led to NH_4-N removal of 88 % and PO_4-P removal of 47.6 %. From these two set of results, it may be concluded that nutrient removal/recovery in the form of struvite from the effluent of poultry manure digester is a viable option for NH_4-N removal/recovery.

Moreover, excess Mg was required to reduce the PO_4-P concentration down to its initial concentration thereby leading to actual removal of the ion from the wastewater. The requirement of excess Mg for the enhancement of PO_4-P removal can be explained by the presence of the complexing agents in the wastewater, which have the potential of forming soluble complexes with Mg thereby reducing the activity of Mg and making it unavailable to the struvite reaction (Beal et al., 1999; Nelson et al., 2003; Burns et al., 2003). Based on these discussions, it may be speculated that there is considerable amount of complexing agents in the effluents of poultry manure digesters.

Among the experiments conducted with the liquid phase effluent of the poultry manure digester, the highest NH_4-N removal efficiency (97.4 %) was achieved in Experiment MS-L5. The concentration of NH_4-N was reduced from 4612±117 mg/L to 121±3 mg/L via struvite formation. The precipitate collected from Experiment MS-L5 was confirmed as struvite by means of XRD analysis (Figure C.16 in Appendix C).

From the experiments conducted with the liquid phase of the MS sample, in average 83±2 g/L precipitate was obtained.

The effect of pH on the removals of pH

Apart from molar ratio of struvite forming ions pH is an important factor to be considered in the struvite precipitation reactor because it has effect on the activities of the ions and also on the solubility of struvite. In literature the minimum solubility of struvite has been observed between pH of 8.0 and 10.7 in different water or wastewater systems (Doyle and Parsons, 2002; Nelson et al., 2003). In order to determine the effect of pH on the removals of NH_4-N and PO_4-P, two additional experiments were conducted at pH levels 8.0 and 9.0 by the use of Mg:N:P molar ratio of 1:1:1 (Table 3.20). The maximum level of pH was set to 9.0 to avoid the loss of NH_4^+ into atmosphere by the mechanism of ammonia stripping.

The results of the experiments in terms of residual concentration and percent removals of the struvite forming ions were depicted in Table 4.12. In order to represent the actual removal of the ions from the wastewater; the removals are reported considering the initial concentrations of these ions present in wastewater (Table 3.6) but not the total (initial + added) concentrations. In the three experiments conducted at different pH levels (Experiment MS-L1, MS-L2 and MS-L3), NH_4-N removals (86.3%, 86.0% and 86.9%) were similar (Figure 4.8). As expected, pH 9.0 was the level of higher removal of NH_4-N. However, the difference between the NH_4-N removals observed at different pH levels were lower in comparison to the experiments conducted with the effluents of lab-scale anaerobic reactors by the use of molar ratio of Mg:N:P of 1:1:1 at different pH levels (Table 4.4, Section 4.1.2). As the solution becomes more saturated with respect to the ions forming struvite, the change in free ion concentrations becomes less effective in the pH range studied, thereby reducing the effect of pH on the removal of NH_4-N. Similar finding was recorded by Uludağ-Demirer and Othman (2009) who studied the effect molar ratio at pH levels of 8.0, 8.5 and 9.0.

The variation in residual PO_4-P concentrations observed in experiments at different pH levels may be explained by different minimum solubility pH levels of competitive minerals precipitating together with struvite.

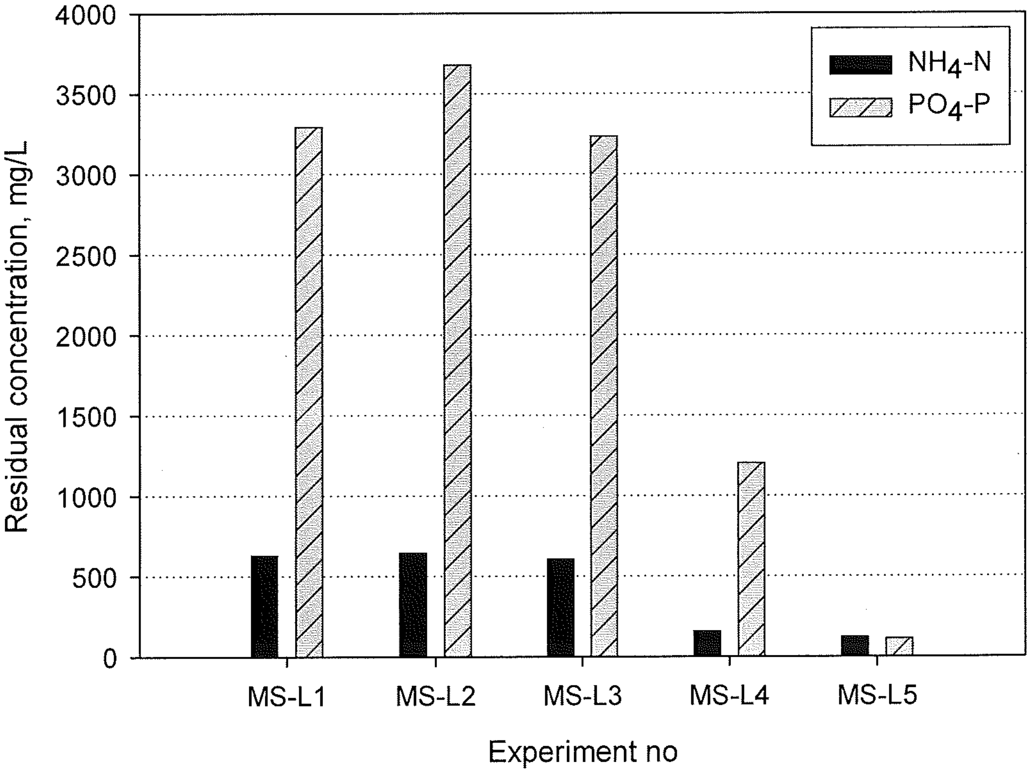

Figure 4.8. Residual concentrations of NH_4-N, PO_4-P and Mg versus struvite precipitation experiments conducted with the liquid phase of MS sample

4.3.2 Recovery of the nutrients available in the Solid phase of the Poultry Manure Digester

In a similar manner the solid phase of the poultry manure digester (MS sample) was subjected to the phosphorus-dissolution process (Figure 3.4). As described in the procedure of the phosphorus dissolution process solid-liquid separation can be achieved by two different techniques a) centrifugation and sieving, b) filtration (Figure 3.4). Both of the techniques were tested with the MS sample. The phosphorus-enriched liquid phase was analyzed for its NH_4-N, PO_4-P and Mg concentrations after each solid-liquid separation process (Table 4.13).

The concentrations of the struvite forming ions in the two phosphorus-enriched solutions were close to each other. However, because filtration was time consuming, the subsequent struvite precipitation experiments were conducted with the solution in which the first solid-liquid separation technique (centrifugation and sieving) was used. Therefore, the metal analyses were conducted with the phosphorus-enriched solution subjected to struvite precipitation experiments (Table 4.14).

Table 4.13. Concentration of struvite forming ions in the phosphorus-enriched liquid phase of MS sample

Concentration, mg/L					
Filtration			Centrifugation and Sieving		
NH_4-N	PO_4-P	Mg	NH_4-N	PO_4-P	Mg
1975±45[a]	1786±2	743±10	1969±74	1778±2	806±1

[a] mean±std (n=2)

PO_4-P concentration in the phosphorus-enriched liquid phase of the FS sample was 827±3 mg/L (Table 4.8) whereas PO_4-P concentration in the phosphorus-enriched liquid phase of the MS sample was 1778±2 mg/L (Table 4.13). The difference between PO_4-P concentrations can be attributable to different chemical compositions of the wastes. Also the reason of the lower PO_4-P concentration of the FS sample may be attributable to the lower total solids (TS) concentration of the slurry adjusted before the acidic dissolution process (Figure 3.4). In order to provide continuous mixing of the reactor content solid phase of the FS sample was diluted till the TS content became 5%, whereas dilution of MS sample up to 10% of TS was sufficient for continuous mixing.

Table 4.14. Concentration of the metals in the phosphorus-enriched liquid phase of the MS sample subjected to struvite precipitation experiments

Metal [a]	Concentration,mg/L
Al	4.06
Ca	5152
Cd	<0.025
Co	<0.015
Cr	0.208
Cu	0.109
Fe	37.9
K	1057
Ni	0.230
Pb	<0.05
Zn	8.03

[a]The Al, Ca, Cd, Cu, Fe, K, Ni, Zn concentrations depict the mean concentration of the duplicate analysis.

The effect of molar concentration ratio Mg:N:P

To determine the effect of molar ratio of Mg:N:P on the recovery of NH_4-N and PO_4-P three Mg:N:P ratios, namely 1:1:1, 1.3:1:1 and 1.5:1:1 were used in the experiments (Table 3.21). The results of the experiments in terms of residual concentration and recovery efficiencies of the struvite forming ions were depicted in Table 4.15. In order to represent the actual recovery of the ions in the wastewater; the recovery efficiencies are reported considering the initial concentrations of the ions present in wastewater (Table 4.13), but not the total (initial + added) concentrations.

The results of experiment MS-P1 illustrated that the use of molar ratio of Mg:N:P of 1:1:1 was sufficient for complete PO_4-P recovery reducing its concentration from 1778±2 mg/L to 0.88±0.03 mg/L (Table 4.15). However, the recovery efficiency of NH_4-N was 61.5 % which is lower in comparison to the PO_4-P recovery. Based on the previous discussions the recovery of NH_4-N can be attributed to the formation of struvite, while PO_4-P removal may be due to formation of several insoluble species including struvite (Uludağ-Demirer and Othman, 2009).

The different recovery efficiencies of NH_4-N and PO_4-P recorded in the experiments where Mg:N:P ratio is 1:1:1 may indicate formation of other PO_4-P containing species as impurities together with struvite. To test this XRD analysis of the precipitate collected from Experiment MS-P1 was conducted and the presence of hydroxlyapatite [HAP, $Ca_5(PO_4)_3(OH)$] together with struvite was confirmed (Figure C.17 in Appendix C).

Table 4.15. Results of the solid phase experiments of MS sample conducted by the use of different Mg:N:P molar ratios

Experiment	Molar ratio	Residual concentration, mg/L			% recovery[a]		
no	of Mg:N:P	NH_4-N	PO_4-P	Mg	NH_4-N	PO_4-P	Mg
MS-P1	1:1:1	760±2[b]	0.88±0.03	621±27	61.5	100.0	19.8
MS-P2	1.3:1:1	720±1	0.80±0.05	1325±49	63.5	100.0	-[c]
MS-P3	1.5:1:1	678±4	0.57±0.04	1738±4	65.6	100.0	-

[a] All recovery efficiencies were calculated considering the average concentrations of the ions at the influent of struvite reactor (Table 4.14).

[b] mean±std (n=2)

[c] "-" means no recovery i.e. final concentration is higher than initial concentration.

The recovery efficiencies of NH_4-N recorded in the Mg:N:P experiments were lower in comparison to the recovery efficiencies of NH_4-N conducted with the phosphorus-enriched liquid phase of FS sample by the use of the same Mg:N:P ratios (Figure 4.7, Section 4.2.2). This can be attributed to the different chemical compositions (organic matter, ionic strength, Ca and other metal concentrations) of the wastewaters investigated. In the literature it is stated that Ca is one of the important ions interfering with the precipitation of struvite and the removal of PO_4-P (Momberg and Oellermann, 1992; Battistoni et al., 2000; Wang et al., 2005). The concentration of Ca in the phosphorus-enriched liquid phase of the MS sample was 5152 mg/L, three times the Ca concentration in the phosphorus-enriched liquid phase of the FS sample (1581 mg/L). The effect of Ca ion have been studied by several investigators to enhance phosphorus removal and it is postulated that the relative concentrations of Mg and Ca is the major factor determining phosphorus removal performance and degree of struvite formation (Battistoni et al., 2000; Wang et al., 2005). Musvoto et al. (2000) reported that struvite precipitates at neutral and higher pH levels and at Mg:Ca molar ratios > 0.6:1. In experiment MS-P1 the molar ratio of Mg:Ca based on the total (initial + added) concentrations is 1.1, the XRD analysis confirmed precipitation of hydroxlyapatite together with struvite, reducing the residual PO_4-P concentration. The precipitation of hydroxylapatite together with struvite was also confirmed in Experiment E33 (Section 4.1.2), which is conducted by the use of Mg:Ca molar ratio of 1.

In all the experiments PO_4-P was completely recovered, however, higher recovery efficiencies of NH_4-N were recorded by the increase of Mg concentration (Table 4.16). The increase in NH_4-N recovery efficiency indicated precipitation of higher amount of struvite in the reactor. The Mg:Ca molar ratio in Experiment MS-P3 by the use of Mg:N:P ratio of 1.5:1:1, was 1.6:1, favoring precipitation of struvite instead of hydroxylapatite (Wang et al., 2005), which is confirmed by XRD analysis. The XRD patterns of the sample were matched only with struvite (Figure C.18 in Appendix C). However, similar to the XRD patterns of the precipitate collected from Experiment FS-P8 (Section 4.2.2), the broad hump centered at approximately 30^o may indicate formation of poorly crystallized phosphorus containing materials. This may explain the complete recovery of PO_4-P from the solution.

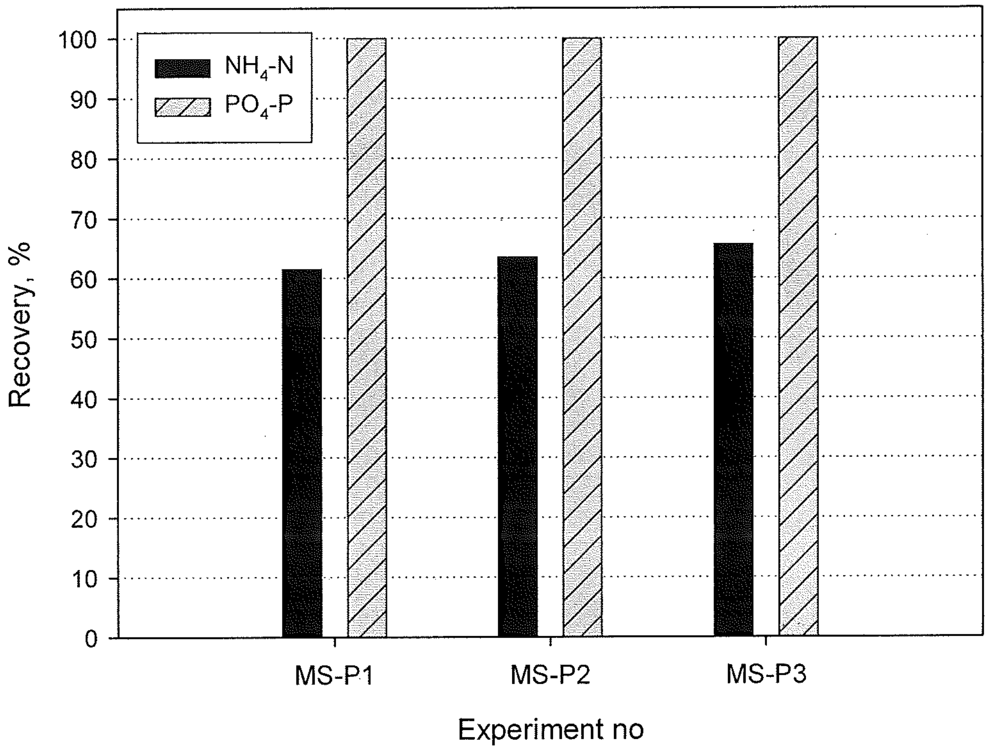

Figure 4.9. NH_4-N and PO_4-P recovery efficiencies versus solid phase experiments of MS sample conducted by the use of different Mg:N:P molar ratios

The effect of molar concentration ratio of Mg:P

The initial molar concentration of Mg:N:P in the phosphorus-enriched liquid phase of the MS sample was 1:4:2. In order to observe the effect of molar concentration ratio of Mg:P on the recovery of PO_4-P and NH_4-N three molar ratio of Mg:P (1:1, 1.3:1 and 1.5:1) were tested (Table 3.21). The experiments were conducted by addition of Mg containing chemical ($MgCl_2.6H_2O$) only. The amount of Mg to be added to the reactor was determined by taking the PO_4-P concentration as the basis. Unlike the Mg:N:P experiments, in these experiments external phosphorus was not added, aiming complete recovery of the available PO_4-P.

The results of the experiments i.e. the residual concentrations and recovery efficiencies of struvite forming ions and the metals (Al, Ca, Fe, K and Zn) initially present in considerable amounts in the phosphorus-enriched liquid phase (Table 4.14) were depicted in Table 4.16.

All recovery efficiencies depicted in Table 4.16 were calculated considering the initial concentrations of the corresponding ions in the wastewater, but not the total (initial + added) concentrations. The concentrations of Cd, Cu, Co, Pb, Cr and Ni in the remaining solution were not determined as they were already in trace concentrations in the original solution (Table 4.14).

The results of the experiments (Experiment MS-P4, MS-P5 and MS-P6) illustrated that residual PO_4-P concentrations ranging between 1.20±0.03 mg/L to 1.00±0.04 mg/L were achievable by the addition of Mg only. However, since the residual concentrations of NH_4-N were quite high there should be post treatment of this ion down in the stream to meet the discharge regulations.

Comparison of experiment MS-P4 and MS-P5 indicated that the addition of Mg at a concentration higher than the stoichiometric ratio of PO_4-P lowered the recovery efficiency of NH_4-N (Table 4.16). However, there was complete recovery of PO_4-P in both of the experiments. Similar findings were reported in the experiments conducted with the phosphorus-enriched liquid phase of the FS sample. The high recovery efficiencies of calcium ion observed in Experiment MS-P5, MS-P6 and MS-P7 when considered together with the high initial concentration of Ca of 5152 mg/L (Table 4.14) indicated the formation of calcium containing minerals in the reactor.

To determine the precipitating mineral XRD analysis were conducted for the precipitates collected from experiment MS-P5 and MS-P6. The XRD patterns of the samples collected from the experiments MS-P5 and MS-P6 match both the patterns of the struvite and hydroxyapatite [HAP, $Ca_5(PO_4)_3(OH)$] which were retrieved from the database in the software installed to the equipment (Figure C.19b and C.19c in Appendix C, respectively). The presence of HAP together with struvite confirmed the presence of alternative removal mechanism of PO_4-P from the system, leading complete recovery of PO_4-P.

Table 4.16. Results of the solid phase experiments of MS sample conducted by the use of different Mg:P molar ratios

Experiment no	Molar ratio of Mg:P	Residual Concentration, mg/L							
		NH_4-N	PO_4-P	Mg	Al	Ca	Fe	K	Zn
MS-P4	1:1	1844±2[a]	1.20±0.03	1023±15	nd[b]	nd	nd	nd	nd
MS-P5	1.3:1	1885±6	1.03±0.01	1244±7	0.203	1944	<0.088	1056	nd
MS-P6	1.5:1	1878±4	1.00±0.04	1229±4	nd	1995	nd	1039	nd
MS-P7	1:2[c]	1906±11	7.90±0.00	598±25	0.14	1310	0.26	757	0.19
MS-P8	1:2[c]	1640±36	0.11±0.00	710±7	0.221	nd	0.07	1036	0.87

Experiment no	Molar ratio of Mg:P	Recovery[d], %							
		NH_4-N	PO_4-P	Mg	Al	Ca	Fe	K	Zn
MS-P4	1:1	6.5	99.9	-[e]	nd	nd	nd	nd	nd
MS-P5	1.3:1	4.4	99.9	-	95.0	62.3	>99.8	0.1	nd
MS-P6	1.5:1	4.8	99.9	-	nd	61.3	nd	1.7	nd
MS-P7	1:2[c]	3.3	99.6	25.8	96.6	74.6	99.3	28.4	97.6
MS-P8	1:2[c]	16.9	100.0	11.9	94.6	nd	99.8	2.0	89.2

[a] mean±std (n=2)

[b] nd: Not determined.

[c] Initial molar ratio in the solution i.e. no addition of chemicals

[d] All recovery efficiencies were calculated considering the initial concentrations of the ions at the influent of struvite reactor (Table 4.13 and Table 4.14).

[e]“-“ means no recovery i.e. final concentration is higher than initial concentration.

Experiment MS-P7 and MS-P8 were conducted without addition of any chemical except the buffering reagent used for the increase of the pH to 8.5 and 9.5, respectively. The XRD analysis of the precipitate collected from the Experiment MS-P8 depicted that there was a small amount of crystalline material formed in the reactor, and most of the precipitate was in amorphous form (Figure C19a in Appendix C). The peaks that are formed during the analysis of the sample collected from the experiment MS-P8 indicated the formation of HAP and struvite. However there are a number of peaks that could be identified by the XRD.

According to the literature there are five calcium phosphate crystalline species that can precipitate from solutions containing Ca and P. These are HAP, tricalcium phosphate (whitlockite) [TCP, $Ca_3(PO_4)_2$], octacalcium phosphate [OCP, $Ca_8(HPO_4)_2(PO_4)_4.5H_2O$], monenite [DCP, $CaHPO_4$] and dicalcium phosphate dihydrate (brushite) [DCPD, $CaHPO_4.2H_2O$] (Musvoto et al., 2003; Wang et al., 2005; Çelen et al., 2007; Uludağ-Demirer and Othman 2009). Among them, thermodynamically the most stable phase is HAP and could be expected to precipitate (Snoeyink and Jenkins, 1980; Musvoto et al., 2000). However, it has been established that a number of species act as precursors to the precipitation of HAP, such as amorphous calcium phosphate (ACP, with approximate formulation $Ca_3(PO_4)_2.\ xH_2O$], but with no structured crystalline order (Blumenthal et al., 1977; Betts et al., 1981; Musvoto et al., 2000), octacalcium and brushite. With time these species may transform to HAP (Musvoto et al., 2000). However, as reported in the study of Musvoto et al. (2000) the formation of the precursor species is a relatively fast process whereas the growth of HAP is a very slow such that the conversion takes a long time (from a minimum of one month to a number of years).

Also the presence of Mg in solution strongly affects the conversion process (Arvin, 1983). Based on these discussions it may be speculated that there is formation of ACP in the reactor, which act as precursor of HAP formation. However, the transformation of ACP to HAP process did not end up at the time the analysis was conducted. Similarly, XRD analysis of Experiment FS-P8 indicated presence of amorphous materials in the precipitate collected from the reactor in which pH was raised to 9.5 without addition of any chemical (Section 4.2.2). On the other hand, the lower residual Mg concentration observed in Experiment MS-P7 in comparison to

MS-P8 indicated the inhibition of struvite formation by the increase of pH from pH 8.5 to 9.5. Higher NH_4-N recovery efficiency observed in Experiment MS-P8 may seem contradictory to this finding; however it can be attributable to ammonia stripping by the increase of pH.

Comparison of Experiment MS-P7 with the experiments conducted by the addition of Mg at pH level of 8.5 indicated the effect of addition of Mg. The Ca recovery efficiency recorded in experiment MS-P7 was 74.6 % whereas the Ca recovery efficiencies recorded in experiments conducted by the addition of Mg at a concentration higher than the molar concentration of initial PO_4-P were 62.3% and 61.3 % in Experiment MS-P5 and MS-P6, respectively. This indicated that the increase of Mg concentration in the solution suppress the precipitation of Ca containing minerals. This finding is supported by other studies reporting that the magnesium ion kinetically hinders the nucleation and subsequent growth of HAP (Çelen et al., 2007) and OCP (Abbona, 1990; Çelen et al., 2007).

Table 4.16 depicted the recovery efficiencies of the other ions (Al, Fe, K and Zn). The high recovery efficiencies of Al, Fe and Zn indicated their precipitation together with struvite. Similar observation was recorded in the study of Rontentalp et al. (2007), which illustrated that the metals can be incorporated into the crystal lattice or sorbed to the surface of struvite decreasing the purity of the product. However, because the molar concentration ratio of the molar concentration ratios of Al:P, Fe:P and Zn:P were 0.003:1, 0.03:1 and 0.002:1 they did not lead to formation of significant quantities of other minerals e.g. berlinite ($AlPO_4$), iron phosphate ($FePO_4$) and zinc ammonium phosphate hexahydrate ($ZnNH_4PO_4.6H_2O$) that were detectable by XRD analysis. Recovery efficiencies of potassium were lower in comparison to the recovery efficiencies of other metals (Table 4.16). This may be attributable to the high NH_4-N concentration of the phosphorus-enriched liquid phase (Schuiling and Andrade, 1999; Wilsenach et al., 2006).

Table 4.17. Maximum recoveries of NH_4-N and PO_4-P by struvite precipitation from phosphorus-enriched liquid

Wastewater composition	Exp. no.	Molar ratio of Mg:N:P	Final Concentration (mg/L)		Advantages	Disadvantages	Proposed Application
			NH_4-N	PO_4-P			
Original with addition of extra Mg	MS-P6	1.5:2:1	1878±4	1.00±0.04	No addition of PO_4-P, high recovery of PO_4-P	Addition of Mg, poor recovery of NH_4-N, high concentration of NH_4-N in effluent	Only for the recovery of PO_4-P
Original with pH increase to 9.5	MS-P8	1:4:2 [a]	1640±36	0.11±0.00	No addition of Mg and PO_4-P,high recovery of PO_4-P,	Purity of struvite is poor, high concentration of NH_4-N in effluent, poor recovery of NH_4-N	Only for the recovery of PO_4-P in the form of ACP
Simulating struvite stoichiometry with excess Mg	MS-P3	1.5:1:1	678±4	0.57±0.04	High recoveries of PO_4-P and NH_4-N, purity of struvite is relatively higher, nearly two times higher amount of precipitate was obtained	Addition of PO_4-P and excess Mg, there calcium containing impurities in the product	For recovering NH_4-N and PO_4-P

[a] Initial molar ratio of the phosphorus-enriched liquid phase

By changing the initial concentrations of Mg and PO_4-P in the solution, the effects of Mg:N:P and Mg:P ratios on the recovery efficiencies of NH_4-N and PO_4-P were analysed. There are two extreme compositions of the solution as one corresponding to the original solution with Mg:P ratio of 1.5:1 (Experiment MS-P6) and the other simulating struvite formation stoichiometry in the solution with addition of extra Mg at a Mg:N:P ratio of 1.5:1:1 (Experiment MS-P3). The two different compositions also indicate the use of struvite formation for different purposes.

The molar concentration ratio of the solution, with the final composition of the solution, advantages and disadvantages of the technique for each case are summarized in Table 4.17. As seen from Table 4.17, if the concentrations of NH_4-N and PO_4-P are kept as in the original wastewater (Experiment MS-P6), which is preferred over the addition of PO_4-P, the concentration of NH_4-N can be reduced from 1969±74 mg/L to 1878±4mg/L in a solution containing with a molar concentration ratio of Mg:NH_4-N of 0.75:1 at a pH level of 8.5 by struvite precipitation. The same conditions, however, yielded considerably high removal of PO_4-P (99.9 %) by reducing its concentration from 1778±2 mg/L to 1.00±0.04mg/L. As discussed before, the difference between the removal of NH_4-N and PO_4-P may indicate the formation of other species containing PO_4-P as impurities. As expected XRD results indicated formation of struvite and HAP, reducing the purity of the product. Since NH_4-N recovery (4.8 %) is poor in this case, struvite formation in wastewater composition with excess NH_4-N can be used to recover PO_4-P only.

It was also illustrated that increasing the pH level to 9.5 without addition of any magnesium and/or phosphorus containing chemical (Experiment MS-P8) led to complete recovery of PO_4-P (100.0 %), reducing its concentration down to 0.11±0.00 mg/L. XRD analysis of the precipitate confirmed that the purity of the struvite was poor and there were precipitation of HAP together with struvite, reducing its market value (Wang et al., 2005). Moreover, the residual concentration of NH_4-N was also very high (1640±36 mg/L), thus, just the increase of pH can be applied for the recovery of PO_4-P only. On the other hand, the recovery efficiencies of NH_4-N and PO_4-P in the wastewater simulating struvite stoichiometry with excess Mg (Experiment MS-P3) were 65.6 % and 100.0 %, respectively, leading to the complete recovery of PO_4-P and considerably high recovery of NH_4-N.

The results of the experiments conducted by the addition of both magnesium and phosphorus (Experiment MS-P1, MS-P2 and MS-P3) and the experiments conducted by the addition of magnesium only (Experiment MS-P4, MS-P5 and MS-P6) indicated that Mg concentration was an important factor in the removal of NH_4-N and PO_4-P. However, it was clear from the results that PO_4-P concentration controls the removal of NH_4-N significantly. Similar finding was reported in the experiments conducted with the phosphorus-enriched phase of the FS sample and also in other studies conducted by other researchers (Uludağ-Demirer, 2008, Uludağ-Demirer and Othman, 2009).

4.3.3 Complexation and Subsequent Struvite Precipitation Experiments

As discussed previously the high recovery efficiencies of other ions Al, Fe, Zn and Ca indicated their precipitation together with struvite, thereby reducing the purity of the product. Experiment MS-P7 indicate that just the increase of pH to the level of 8.5 led to precipitation of 96.6 % of aluminum, 74.6 % of calcium, 99.3 % of iron, 28.4 % of potassium and 97.6 % of the zinc (Table 4.16). To prevent the co-precipitation of other phosphate forms together with struvite, while adjusting the pH level, these ions have to be either removed or inactivated through complexation before the pH adjustment.

Other researchers used several complexing agents e.g. citric acid (CA), sodium citrate for the purpose of inactivating interfering ions prior to struvite precipitation experiments (Weidelener, 2005; Taşdelen, 2008). Taşdelen (2008) reported using both sodium citrate and CA for the complexation of the metals and reported better results by the use of CA. Therefore, in order to inactivate other interfering metals CA was used as the complexing agent. To test the effect of the concentration of CA, two different molar ratios of CA:metals (K, Ca, Fe, Al and Mg) namely 1:1 and 1.5:1 were used. The resulting samples (CS1 and CS2) were analyzed for their NH_4-N, PO_4-P and Mg concentrations and the results were summarized in Table 4.18. CS1, the resulting solution of the complexation process in which the molar concentration ratio of CA:metals was 1:1, was analyzed for its struvite forming ions before and after the pH adjustment (Figure 3.5).

The objective of the complexation was to prevent the loss of the struvite forming ions especially PO_4-P, by the formation of precipitates other than struvite. However, as depicted in Table 4.18 the concentrations of NH_4-N, PO_4-P and Mg at the end of complexation process were lowered down to their initial concentrations (Table 4.13). These reductions are referred as "loss" because they are not available anymore for the subsequent struvite precipitation reaction. The percent losses of the struvite forming ions versus the resulting samples of complexation process were presented in Figure 4.10. The reduction in the concentrations of PO_4-P and Mg after the pH adjustment indicated their precipitation in the reactor (Table 4.18). Confirming this, a visible precipitate was formed at the bottom of the reactor subjected to complexation process by the use of molar ratio of CA:metals of 1:1. The amount of precipitate was limited and the physical observation of it was not possible.

The percent losses of the struvite forming ions were lower when the molar ratio of CA:metals were 1.5:1 in the resulting solution of CS2 (Figure 4.10). Similar findings were reported by Taşdelen (2008) who tested different molar concentration ratio of CA:metals in his study. The smaller the percent loss of the ions, the lower their requirement to initiate struvite precipitation, therefore struvite precipitation experiments were conducted with the sample in which the losses were minimal, namely CS2.

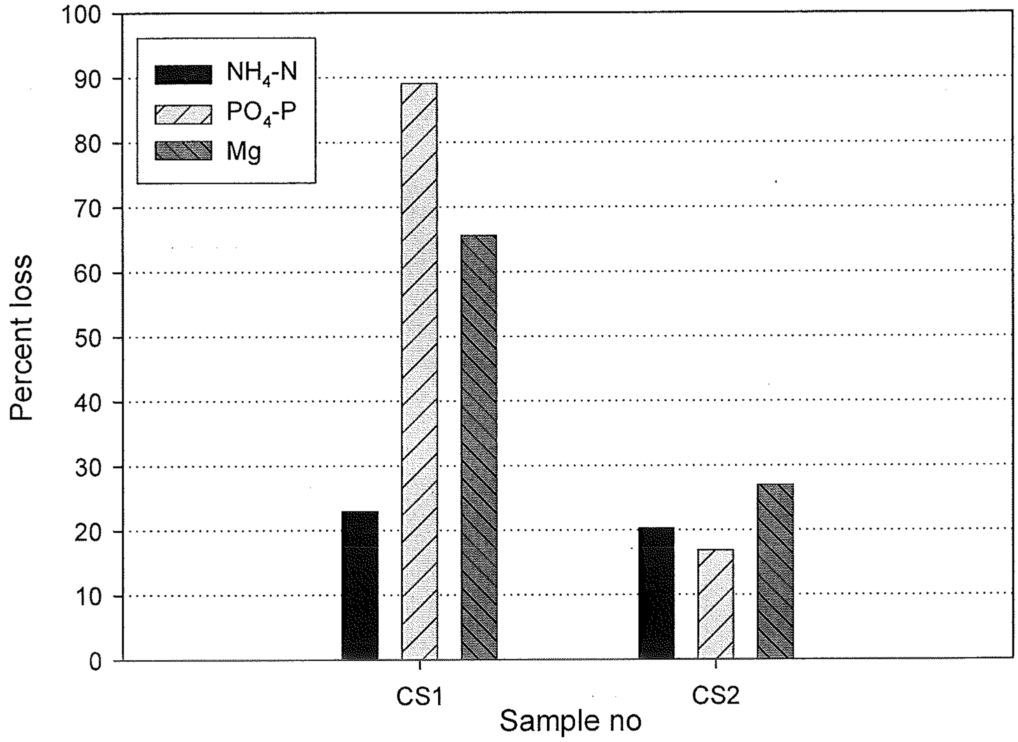

Figure 4.10. Percent loss of ions versus complexation process

In total three experiments were conducted with CS2. One experiment was conducted by the adjustment of struvite stoichiometry through addition of Mg and PO_4-P containing chemicals (Experiment MS-C3) and two experiments were conducted with the addition of only Mg by taking initial PO_4-P concentration as the basis to adjust the molar ratio of Mg:P to 1:1 (Experiment MS-C1) and 1.5:1 (Experiment MS-C2). The results of the experiments were summarized in Table 4.19. In order to represent the actual recovery of the ions from the phosphorus-enriched liquid phase; the recovery efficiencies are reported considering the initial concentrations of these ions in phosphorus-enriched liquid phase (Table 4.13) but not the total (initial + added) concentrations.

The results of the experiments indicated that there were no or limited struvite precipitation in the experiment MS-C1 and MS-C2. The residual concentrations of

NH_4-N and PO_4-P lowered below their initial concentration levels in the phosphorus-enriched liquid phase (initial concentrations of NH_4-N and PO_4-P were 1969±74mg /L and 1778±2 mg/L, respectively). However, there was very limited amount of precipitate, which was slightly visible. Physically in order to analyze the precipitate either by XRD or for its composition, the dried precipitates have to be separated from the filter paper manually. However, the separation of the limited amount of precipitates from Experiment MS-C1 and MS-C2 were not possible, thus they could not be analyzed with XRD.

The comparison of the residual concentrations of NH_4-N and PO_4-P in experiment MS-C1 and MS-C2 (Table 4.19) with their concentrations in the complexed solution CS2 (NH_4-N and PO_4-P of 1569±6 mg/L and 1478±2 mg/L, respectively) also confirmed that the precipitation of the struvite was inhibited by the presence of CA. A recent study conducted by Kofina et al. (2007) confirmed this finding. Kofina et al. (2007) investigated the effect of the presence citrate and phosphocitrate ions in the spontaneous precipitation of struvite from synthetic wastewater solutions supersaturated with respect to struvite at 25 °C and pH 8.5. The presence of citrate caused reduction of the rate of struvite precipitation and increase the induction time and Kofina et al. (2007) reported that the inhibition due to the presence of citrate may be attributable to its adsorption on the crystal surface, thereby blocking of the active crystal growth sites. In a similar manner, the study of Van der Houwen and Valsami-Jones (2001) depicted the inhibition of hydroxlyapatite formation by the presence of CA and it was attributed to binding of citrate on the active sites of newly formed nuclei. Also the presence of CA may lead to formation of magnesium-citrate complexes and make the added Mg unavailable for struvite reaction, thereby preventing the formation of struvite.

Unlike the experiments (Experiments MS-C1 and MS-C2) conducted by the addition of Mg only, the addition of both Mg and PO_4-P to adjust the stoichiometry of the struvite (Mg:N:P of 1:1:1) led to recovery of NH_4-N and PO_4-P in the form of struvite. The recovery efficiencies of NH_4-N and PO_4-P were 72.6% and 89.7 %, respectively. Based on the above discussions it may be speculated that the increase in the degree of saturation with respect to struvite formation may be sufficient to overcome the inhibition caused by the citric acid. However, XRD analysis of the precipitate collected from Experiment MS-C3 confirmed the presence of whitlockite [$Ca_9(MgFe)(PO_4)6PO_3OH$] together with struvite (Figure C.20 in Appendix C). Due to the inhibition of struvite there was formation of another mineral in detectable amounts via XRD, resulting in a decrease in the purity of the product.

In experiment MS-P1 conducted with the phosphorus-enriched liquid phase by the use of Mg:N:P ratio of 1:1:1 without complexation, the recovery efficiencies of NH_4-N and PO_4-P were 61.5 % and 100.0 %, respectively. The comparison of the results of experiments conducted by the use of Mg:N:P of 1:1:1, with and without complexation (Experiment MS-C3 and MS-P1, respectively) indicated that the adoption of complexation enhanced the recovery efficiency of NH_4-N (from 61.5% to 72.6%), whereas, lowered the recovery efficiency of PO_4-P (from 100.0% to 89.7 %). Based on the results of these two experiments, adoption of the complexation process may be proposed under the circumstances where the recirculation of the effluent stream was possible for the recovery of the remaining PO_4-P and the purity of the product is not a concern. Results of XRD analysis indicated that the presence of CA did not lead to formation of pure struvite, as intended. Therefore, the use of CA as the complexing agent should be investigated further, so that its potential for inhibition is prevented.

Table 4.18. The NH_4-N, PO_4-P and Mg concentration of the complexed solutions

Sample no	Molar ratio of citric acid : metals	Concentration pre-pH adjustment, mg/L			Concentration post-pH adjustment[a], mg/L		
		NH_4-N	PO_4-P	Mg	NH_4-N	PO_4-P	Mg
CS1	1:1	1971±8[b]	1209±2	624±7	1516±13	193±1	277±2
CS2	1.5:1	nd[c]	nd	nd	1569±6	1478±2	588±4

[a] Subjected to struvite precipitation experiments

[b] mean±std (n=2)

[c] Not determined

Table 4.19. Results of the experiments conducted by the complexed phosphorus-enriched liquid phase of the MS sample

Experiment no	Molar ratio of Mg:N:P	Residual concentration, mg/L			% recovery[a]		
		NH_4-N	PO_4-P	Mg	NH_4-N	PO_4-P	Mg
MS-C1	1:2:1	1589±8[b]	1560±3	1810±14	19.3	12.3	-[c]
MS-C2	1.5:2:1	1547±25	1521±15	2328±18	21.4	14.5	-
MS-C3	1:1:1	538±7	184±0	815±35	72.7	89.7	-

[a] Recovery efficiencies were calculated considering the initial concentrations of the ions in the phosphorus-enriched liquid phase (Table 4.13).

[b] mean±std (n=2)

[c] "-" means no recovery i.e. final concentration is higher than initial concentration.

4.3.4 The Yield of Struvite Precipitation Process

To the best of our knowledge there is not any full-scale poultry manure digestion/co-digestion plant in Turkey, therefore lab-scale anaerobic reactors digesting/co-digesting poultry manure were operated in Set 1. However, the comparison of the nutrient concentrations of the effluent streams of Set 1 with the nutrient concentrations of the effluent samples used in Set 2 and Set 3 depicted that the concentrations in full-scale plants were much higher than lab-scale reactor effluents. Therefore, in order to calculate the yield and potential of struvite formation from the anaerobically digested poultry manure, the data collected from Set 3 was used, because it represents the data obtained from full-scale poultry manure digester. The proposed action is to collect the fresh poultry manure from laying hens and broilers, subject to anaerobic digestion and apply solid-liquid separation as conducted in Set 3. At the end of phase separation both phases are to be undergone struvite precipitation process. The procedure of the proposed action is depicted in Figure 4.11. The assumptions and the data used from Set 3 were depicted in the figure.

According to the data given in Table 2.1 (Section 2.1), the average annual manure production from laying hens and broilers is 0.037 tons. The number of laying hens and broiler is given as 244,280,376 for 2008 (TURKSTAT, 2008). Using this information the annual production of poultry manure (from laying hens and broilers) were calculated as about 9 million tons.

Considering a dilution ratio of 1/3, the volume of wastewater (diluted poultry manure will be approximately 27 million tons, which is proposed to be undergone anaerobic digestion. At the end of digestion process, similar to the application in Set 3 phase separation is to be done. At the end of phase separation nearly 60% (w/w) of the digested effluent will remain in the liquid phase and about 40% (w/w) will be in the solid phase. The results of the experiments conducted with the liquid phase of MS sample, illustrated that 83±2 g/L precipitate can be obtained (Section 4.3.1). Considering the same figure applicable for the other poultry manure digesters, it is found that out of 16.2 million ton/year digested liquid phase in average 1.34 million tons of precipitate could be obtained.

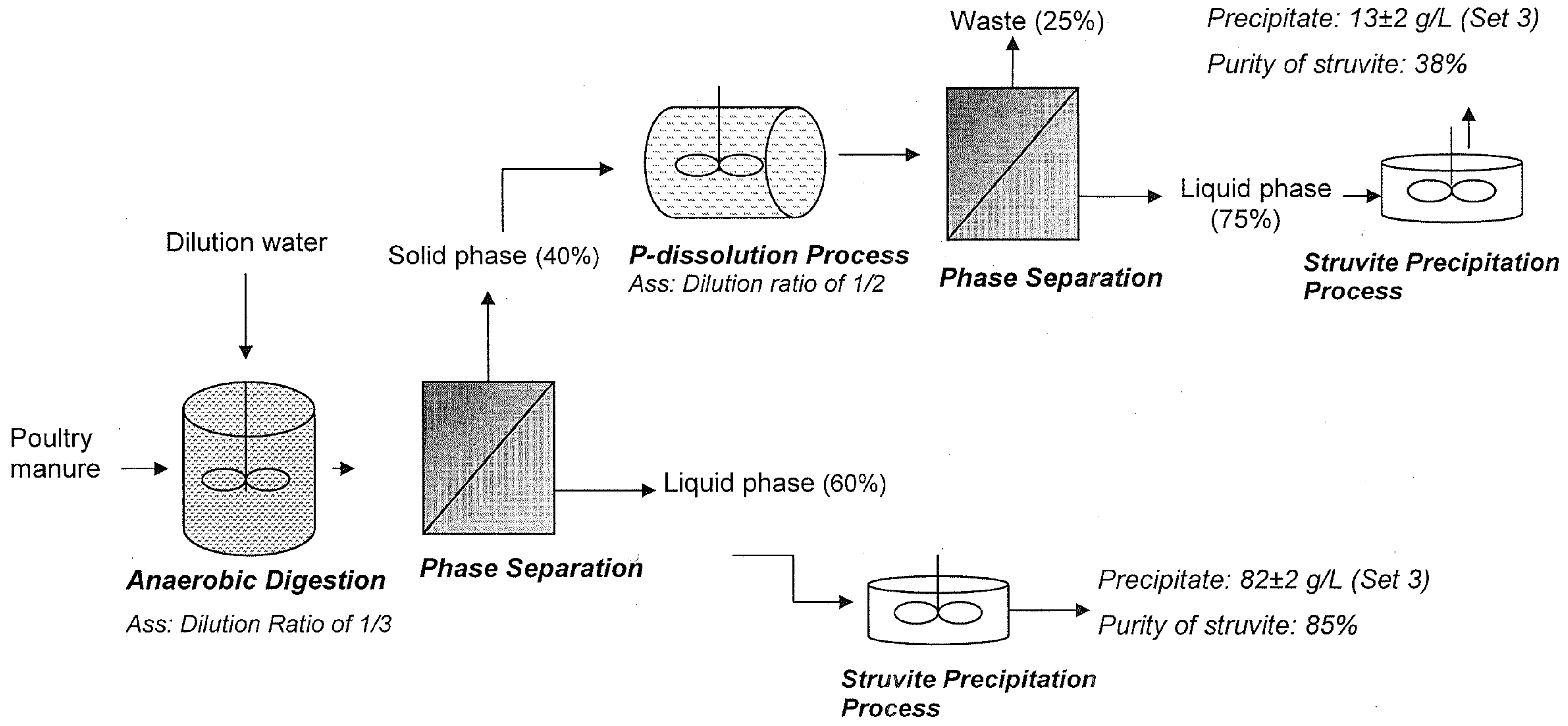

Figure 4.11. The proposed treatment scheme used for yield calculation

On the other hand, considering a dilution ratio of 1/2 for phosphorus dissolution process, there would be 21.6 million tons of solution is to be subjected to phosphorus dissolution process. With the assumption of 75% (w/w) remaining in the liquid phase after phase separation, in total 16.2 million tons of phosphorus-enriched liquid phase could be obtained in one year. By using the data of Set 3 (13±2 g/L), the average amount of precipitate can be calculated as 0.21 million tons per year.

As stated previously, throughout this thesis the purity of the precipitates were not detected. Therefore, the exact amount of struvite production could not be calculated. However, for the purpose of the calculation of the yield of the process, the purity of the struvite in the precipitates collected from the experiments conducted with MS sample are assumed to be same as given in the study of Wang et al. (2005). In the study of Wang et al. (2005), the chemical compositions of the effluents from two anaerobic lagoons utilizing piggery wastes were investigated. According to the measured values, five synthetic wastewater solutions were then formulated to mimic typical magnesium, calcium, ammonium, and phosphate concentrations that could be expected in the effluent of anaerobic lagoons. Struvite precipitation experiments were conducted with those solutions and the precipitates collected from the experiments were analyzed for their struvite fraction. Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) were used together with XRD to study the deposit structure and elemental composition of the precipitates. The results indicated that the maximum struvite purity was 85 % with Ca:Mg molar ratio 0.5:2, whereas the struvite purity was reduced to 38% with Ca:Mg molar ratio of 2:2. As depicted previously the critical point determining the purity of the struvite in the precipitates is Ca:Mg molar ratio.

As depicted in Table 3.6 (Section 3.1.3) the calcium concentration in the liquid phase of MS sample was 2mM (78.6 mg/L) and was quite low in comparison to NH_4-N concentration of 329 mM (4612±117mg/L). Since the concentration of Mg was raised at least to the level of NH_4-N to adjust the desired molar ratio of Mg:N:P, in all the experiments the Ca:Mg molar ratio were close to zero (≤0.006). Therefore, with a rough estimation the purity of the struvite in the precipitates collected from the liquid phase experiments of Set 3, were considered to be 85 % as given in Wang et al. (2005). Therefore, out of 1.34 million tons of precipitate 1.14 million tons of struvite could be obtained.

In a similar manner, the purity of the struvite in the precipitates collected from the experiments conducted by the addition of Mg (Experiment MS-P4, MS-P5 and MS-P6) were taken as 38% with a conservative estimation. Since the molar ratio of Ca:Mg were <1:1 in all of these experiments. With this estimation it is calculated that out of 0.21 million tons of precipitate 0.08 million tons of struvite could be obtained. Combining the results of liquid and solid phase experiments; it can be concluded that out of 1 kg of poultry manure, 0.1 kg of struvite could be obtained.

To sum up, the calculations indicated that if the poultry manure generated from laying hens and broilers in Turkey were subjected to the proposed treatment scheme (Figure 4.11), with a gross estimation 1.22 million tons of struvite could be obtained annually. Considering the annual fertilizer consumption of Turkey being 5.15 million tons in 2007 (DRT International, 2008), it can be concluded that poultry manure, if managed properly, could meet 23.7 % of annual fertilizer demand of Turkey.

CHAPTER 5

CONCLUSIONS

The main objective of this study was to investigate the removal and recovery of nutrients from both the liquid and solid phases of the anaerobically digested/co-digested poultry manure through struvite precipitation. The following conclusions can be drawn from the obtained results of experimental sets (Set 1, 2, 3):

Antagonistic interactions were found when mixtures of poultry manure and sewage sludge were digested with high F/M and high initial COD concentrations. Performances of the co-digestion reactors decreased as the fraction of poultry manure decreased. This is contradictory to the findings of other investigators (Misi and Forster 2001; Güngör-Demirci and Demirer, 2004). The possible mechanisms which are thought to play roles in this observation can be listed as follows: different F/M ratio and initial COD concentrations for the reactors (Table 3.10, Section 3.3.1.1). There were indications of partial inhibition by ammonia nitrogen which needs to be further investigated.

Nutrient supplementation did not improve the digestion performance in the reactors having waste mixing ratio of 0.06:0.94 (poultry manure: sewage sludge) in terms of COD. As stated in literature, domestic sludge usually contains sufficient quantities of nitrogen (in the form of protein, urea and ammonia), phosphorus and other micro nutrients for efficient digestion (Parkin and Owen, 1986). Moreover, the study of Güngör-Demirci and Demirer (2004) indicated that nutrients present in poultry manure are enough for anaerobic microbial growth.

The results of the struvite precipitation experiments illustrated that the influence of excess Mg in the removal of NH_4-N and PO_4-P (Figure 4.3, Section 4.1.2) was significant; however, it was obvious that PO_4-P concentration controls NH_4-N removal by struvite formation.

Unlike to the magnesium source (Çelen and Türker, 2001; Uludağ-Demirer et al. 2005) the effect of phosphorus source on the removals of NH_4-N and PO_4-P removals is not considerable.

Struvite precipitation not only helps to remove ammonia and phosphate, but also achieved considerable COD removals with a maximum removal efficiency of 42 % (Section 4.1.2).

Increasing the pH level from 8.0 to 9.0 enhanced NH_4-N removals in all experiments; however the effect on residual PO_4-P concentrations was highly dependent on the chemical composition of the wastewater being studied. As the solution becomes more saturated with respect to the struvite forming ions, the change in free ion concentrations becomes less effective in the pH range (8.0 - 9.0) studied, thereby reducing the effect of pH on the removal of NH_4-N.

The use of acidic phosphorus dissolution process was applicable to the solid phase of the full-scale biogas plants and can be used as a preliminary step of struvite precipitation experiments to obtain a nutrient rich solution. In this study solutions with considerably high concentrations of nutrients (1484±4mg/L NH_4-N and 827±3mg/L PO_4-P in Set 2; 1969±74 mg/L NH_4-N and 1778±2 mg/L PO_4-P in Set 3) were obtained. Comparison of the concentration of the nutrients available in the phosphorus-enriched liquid phase obtained in Set 2 and Set 3 indicated the significance of the total solids concentration of the solid phase subjected to the phosphorus-dissolution process. The limiting condition in the phosphorus-dissolution process is continuous mixing of the slurry phase. If continuous mixing of the high solids systems were possible than higher PO_4-P and NH_4-N concentrations would be attainable.

In the experiments conducted with the phosphorus-enriched liquid phase of poultry manure co-digestion plant (Set 2) by the addition of external phosphorus and magnesium, high recovery efficiencies (>90%) of NH_4-N and PO_4-P were observed. Whereas in the experiments conducted by the addition of only magnesium, almost complete recovery of PO_4-P and partial recovery of NH_4-N were attained. The obtained results of the experiments indicated that struvite precipitation process can be used for different purposes e.g. recovery of PO_4-P only or recovery of both NH_4-N and PO_4-P.

The findings of this study indicated that Ca has inhibitory effects on the struvite reaction. The presence of Ca led to formation of calcite, hydroxlyapatite and amorphous calcium phosphates that were detectable through XRD. The results of the experiments indicated that the addition of magnesium ion above the molar concentration of PO_4-P together with Ca ion helped to remove/recover most of the phosphorus even in low phosphorus wastewaters. If only P removal and recovery was the only target, then addition of calcium along with magnesium would be recommended.

The results of experiments conducted with the liquid phase effluent of lab-scale poultry manure digester (R1, Set 1) and the experiments conducted with the liquid phase of full-scale poultry manure digester (Set 3) were similar. The results illustrated that for the reduction of the residual concentration of PO_4-P down to its initial concentration (to attain actual removal of PO_4-P) excess Mg is required. This can be due to the presence of organic ligands present in the effluent of the poultry manure digesters.

The results obtained from this study indicated that the struvite precipitation process can be successfully applied to anaerobic digestion/co-digestion residues of poultry manure. The proposed treatment order for the recovery of nutrients from poultry manure is in the following order: anaerobic digestion, phase separation, if liquid phase struvite precipitation; if solid phase phosphorus dissolution, phase separation and as the final step struvite precipitation process. The calculaton of the yield of the process indicated that if the poultry manure generated from laying hens and broilers in Turkey were subjected to the proposed treatment scheme, with a gross estimation 1.22 million tons of struvite could be obtained annually.

Based on the results obtained in this study, it is postulated that, struvite precipitation is a viable option for the recovery of the nutrients in the anaerobically digested poultry manure. Considering the huge amount of poultry manure generation, it can be concluded that there is high potential of struvite production from poultry manure in Turkey. This study illustrated that, poultry manure, if managed properly, could meet one-fourth of Turkey's domestic fertilizer demand.

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APPENDIX A

POWDER DIFFRACTION CARDS OF SELECTED MINERALS

Table A.1 PDF card of struvite

```
                                  PDF_71-2089
PDF#71-2089: QM=Calculated; d=Calculated; I=(Unknown)
Struvite
MgNH4PO4(H2O)6
Radiation=CuKa1 Lambda=1.5406   Filter=
Calibration=    2T=14.421-89.112        I/Ic(RIR)=0.97
Ref: Level-1 PDF

Orthorhombic,  Pmn21(31)        Z=2     mp=
CELL: 6.941 x 6.137 x 11.199 <90.0 x 90.0 x 90.0>       P.S=
Density(c)=1.7  Density(m)=     Mwt=    Vol=477.0
Ref: Ibid.

Strong Lines: 4.25/X  5.60/7  5.90/5  2.92/4  2.69/4  2.66/4  4.14/3  2
```

Table A.1 PDF card of struvite (cont'd)

2-Theta	d(Å)	I(f)	(h k l)	Theta	1/(2d)	2pi/d	n^2
14.421	6.1370	6.3	(0 1 0)	7.210	0.0815	1.0238	
15.004	5.8997	46.2	(1 0 1)	7.502	0.0847	1.0650	
15.814	5.5995	65.9	(0 0 2)	7.907	0.0893	1.1221	
16.457	5.3819	29.1	(0 1 1)	8.229	0.0929	1.1675	
19.290	4.5976	3.9	(1 1 0)	9.645	0.1088	1.3666	
20.869	4.2531	100.0	(1 1 1)	10.434	0.1176	1.4773	
21.464	4.1364	31.0	(0 1 2)	10.732	0.1209	1.5190	
25.040	3.5533	3.6	(1 1 2)	12.520	0.1407	1.7683	
25.647	3.4705	9.2	(2 0 0)	12.824	0.1441	1.8105	
27.100	3.2877	23.0	(1 0 3)	13.550	0.1521	1.9111	
27.952	3.1893	1.2	(0 1 3)	13.976	0.1568	1.9701	
29.077	3.0685	2.3	(0 2 0)	14.538	0.1629	2.0476	
29.545	3.0209	10.6	(2 1 0)	14.773	0.1655	2.0799	
30.173	2.9594	8.0	(0 2 1)	15.087	0.1690	2.1231	
30.273	2.9499	12.2	(2 0 2)	15.137	0.1695	2.1300	
30.626	2.9167	44.8	(2 1 1)	15.313	0.1714	2.1542	
31.939	2.7998	29.8	(0 0 4)	15.969	0.1786	2.2442	
32.873	2.7223	8.2	(1 2 1)	16.436	0.1837	2.3080	
33.267	2.6909	44.2	(0 2 2)	16.634	0.1858	2.3349	
33.683	2.6587	38.3	(2 1 2)	16.841	0.1881	2.3633	
35.204	2.5472	1.9	(0 1 4)	17.602	0.1963	2.4667	
35.758	2.5090	5.8	(1 2 2)	17.879	0.1993	2.5043	
37.583	2.3913	4.0	(1 1 4)	18.791	0.2091	2.6276	
37.925	2.3705	0.3	(0 2 3)	18.963	0.2109	2.6506	
38.297	2.3483	11.6	(2 1 3)	19.148	0.2129	2.6756	
39.155	2.2988	1.2	(2 2 0)	19.577	0.2175	2.7332	
39.748	2.2658	0.4	(3 0 1)	19.874	0.2207	2.7730	
40.005	2.2519	3.4	(2 2 1)	20.003	0.2220	2.7902	
40.166	2.2432	2.1	(1 2 3)	20.083	0.2229	2.8009	
41.402	2.1791	3.0	(2 0 4)	20.701	0.2295	2.8834	
41.685	2.1649	2.5	(3 1 0)	20.843	0.2310	2.9023	
42.368	2.1316	3.2	(1 0 5)	21.184	0.2346	2.9477	
42.473	2.1266	6.4	(2 2 2)	21.236	0.2351	2.9546	
42.950	2.1040	0.4	(0 1 5)	21.475	0.2376	2.9862	
43.732	2.0682	2.8	(0 2 4)	21.866	0.2418	3.0380	
44.063	2.0535	10.2	(2 1 4)	22.031	0.2435	3.0598	
44.239	2.0457	6.1	(0 3 0)	22.120	0.2444	3.0715	
44.849	2.0193	2.6	(3 1 2)	22.425	0.2476	3.1116	
44.983	2.0136	9.0	(1 1 5)	22.491	0.2483	3.1204	
45.737	1.9821	3.5	(1 2 4)	22.869	0.2523	3.1700	
46.119	1.9666	3.4	(3 0 3)	23.059	0.2542	3.1950	
46.227	1.9622	6.1	(1 3 0)	23.114	0.2548	3.2021	
46.347	1.9574	11.7	(2 2 3)	23.173	0.2554	3.2099	
46.973	1.9328	0.8	(1 3 1)	23.487	0.2587	3.2509	
47.267	1.9215	3.9	(0 3 2)	23.633	0.2602	3.2700	
48.574	1.8728	5.1	(3 1 3)	24.287	0.2670	3.3550	
48.747	1.8665	3.2	(0 0 6)	24.374	0.2679	3.3663	
49.160	1.8518	1.5	(1 3 2)	24.580	0.2700	3.3930	
49.285	1.8474	2.8	(3 2 0)	24.643	0.2707	3.4011	
49.997	1.8227	2.4	(3 2 1)	24.999	0.2743	3.4471	
50.400	1.8091	3.7	(0 2 5)	25.200	0.2764	3.4731	
50.697	1.7992	11.4	(2 1 5)	25.348	0.2779	3.4922	
50.856	1.7940	11.6	(0 3 3)	25.428	0.2787	3.5024	

Table A.1 PDF card of struvite (cont'd)

PDF_71-2089

51.107	1.7857	1.4	(0 1 6)	25.553	0.2800	3.5185
51.387	1.7767	0.6	(2 2 4)	25.693	0.2814	3.5365
51.836	1.7623	9.9	(2 3 0)	25.918	0.2837	3.5653
52.208	1.7506	1.7	(1 2 5)	26.104	0.2856	3.5891
52.523	1.7409	5.6	(2 3 1)	26.261	0.2872	3.6092
52.706	1.7352	12.2	(1 3 3)	26.353	0.2881	3.6209
52.898	1.7294	6.1	(1 1 6)	26.449	0.2891	3.6331
53.457	1.7126	6.3	(3 1 4)	26.729	0.2919	3.6687
54.545	1.6810	3.9	(2 3 2)	27.273	0.2974	3.7377
55.385	1.6575	2.3	(4 0 2)	27.693	0.3017	3.7908
55.449	1.6557	2.3	(3 2 3)	27.725	0.3020	3.7948
55.602	1.6515	3.1	(0 3 4)	27.801	0.3027	3.8045
55.885	1.6438	1.4	(2 0 6)	27.943	0.3042	3.8223
57.195	1.6093	1.3	(3 0 5)	28.598	0.3107	3.9044
57.391	1.6042	2.7	(2 2 5)	28.696	0.3117	3.9166
57.551	1.6001	2.8	(4 1 2)	28.776	0.3125	3.9266
57.768	1.5947	5.6	(0 2 6)	28.884	0.3135	3.9401
58.039	1.5879	6.8	(2 1 6)	29.019	0.3149	3.9570
59.220	1.5590	1.1	(1 0 7)	29.610	0.3207	4.0303
59.318	1.5566	1.5	(3 1 5)	29.659	0.3212	4.0364
59.421	1.5542	2.6	(1 2 6)	29.711	0.3217	4.0428
59.940	1.5419	1.0	(3 2 4)	29.970	0.3243	4.0748
60.347	1.5325	0.7	(0 4 0)	30.173	0.3263	4.0999
60.709	1.5243	0.1	(4 1 3)	30.355	0.3280	4.1221
60.968	1.5184	0.3	(0 4 1)	30.484	0.3293	4.1381
61.299	1.5110	2.8	(1 1 7)	30.650	0.3309	4.1583
62.191	1.4914	1.2	(2 3 4)	31.096	0.3352	4.2128
62.498	1.4849	2.9	(1 4 1)	31.249	0.3367	4.2315
62.740	1.4797	1.7	(0 4 2)	31.370	0.3379	4.2462
62.812	1.4782	1.4	(3 3 2)	31.406	0.3383	4.2506
62.966	1.4749	2.0	(1 3 5)	31.483	0.3390	4.2600
63.767	1.4583	3.6	(4 2 2)	31.883	0.3429	4.3085
64.316	1.4472	0.4	(1 4 2)	32.158	0.3455	4.3416
64.975	1.4341	0.2	(4 1 4)	32.488	0.3487	4.3813
65.434	1.4252	1.3	(3 2 5)	32.717	0.3508	4.4088
65.820	1.4177	1.5	(0 2 7)	32.910	0.3527	4.4319
66.024	1.4138	1.2	(2 1 7)	33.012	0.3536	4.4441
66.768	1.3999	2.1	(4 2 3)	33.384	0.3572	4.4884
67.177	1.3923	0.7	(2 4 1)	33.588	0.3591	4.5126
67.312	1.3899	1.6	(1 4 3)	33.656	0.3597	4.5206
67.990	1.3777	0.8	(0 3 6)	33.995	0.3629	4.5608
68.719	1.3648	0.3	(0 1 8)	34.359	0.3663	4.6037
68.930	1.3612	3.1	(2 4 2)	34.465	0.3673	4.6161
69.347	1.3540	0.6	(5 1 0)	34.673	0.3693	4.6405
69.440	1.3524	0.5	(1 3 6)	34.720	0.3697	4.6460
69.925	1.3442	4.4	(3 3 4)	34.962	0.3720	4.6743
70.226	1.3392	1.4	(1 1 8)	35.113	0.3734	4.6918
70.823	1.3293	0.6	(4 2 4)	35.412	0.3761	4.7265
71.196	1.3233	1.3	(4 3 0)	35.598	0.3778	4.7482
71.346	1.3209	0.8	(1 4 4)	35.673	0.3785	4.7568
71.657	1.3159	1.0	(5 1 2)	35.829	0.3800	4.7748
71.840	1.3130	4.7	(2 4 3)	35.920	0.3808	4.7854
72.598	1.3011	0.7	(5 0 3)	36.299	0.3843	4.8289
72.787	1.2982	0.7	(2 0 8)	36.393	0.3851	4.8398
73.550	1.2866	1.0	(4 3 2)	36.775	0.3886	4.8834
73.902	1.2814	1.5	(2 3 6)	36.951	0.3902	4.9034
74.086	1.2787	0.9	(3 4 0)	37.043	0.3910	4.9139
74.430	1.2736	1.7	(0 2 8)	37.215	0.3926	4.9334
74.648	1.2704	7.8	(3 4 1)	37.324	0.3936	4.9458
75.356	1.2602	1.3	(0 3 7)	37.678	0.3968	4.9858
75.597	1.2568	1.2	(5 2 1)	37.799	0.3978	4.9994
75.761	1.2545	0.9	(2 4 4)	37.881	0.3986	5.0086
75.889	1.2527	1.7	(1 2 8)	37.945	0.3991	5.0158
76.280	1.2472	1.3	(4 3 3)	38.140	0.4009	5.0376
76.426	1.2452	1.3	(1 4 5)	38.213	0.4015	5.0458
76.810	1.2399	1.3	(1 3 7)	38.405	0.4032	5.0673
77.271	1.2337	0.6	(5 2 2)	38.635	0.4053	5.0929
77.938	1.2248	0.2	(1 0 9)	38.969	0.4082	5.1299

Table A.1 PDF card of struvite (cont'd)

PDF_71-2089

78.340	1.2195	0.9	(0 1 9)	39.170	0.4100	5.1522
79.125	1.2094	2.2	(3 2 7)	39.563	0.4134	5.1954
79.778	1.2011	1.5	(1 5 1)	39.889	0.4163	5.2311
80.036	1.1979	1.1	(0 5 2)	40.018	0.4174	5.2452
80.218	1.1956	1.3	(4 3 4)	40.109	0.4182	5.2551
80.746	1.1891	0.1	(2 4 5)	40.373	0.4205	5.2838
81.068	1.1852	0.8	(0 4 6)	40.534	0.4219	5.3012
81.383	1.1814	0.5	(1 5 2)	40.691	0.4232	5.3182
81.507	1.1799	0.7	(5 0 5)	40.754	0.4237	5.3250
81.879	1.1755	1.2	(3 1 8)	40.940	0.4253	5.3450
81.995	1.1742	1.8	(4 2 6)	40.998	0.4258	5.3512
82.494	1.1683	0.1	(1 4 6)	41.247	0.4280	5.3780
82.695	1.1660	0.6	(0 5 3)	41.347	0.4288	5.3887
82.946	1.1631	0.6	(3 4 4)	41.473	0.4299	5.4021
83.329	1.1587	1.3	(5 1 5)	41.665	0.4315	5.4225
83.467	1.1572	2.5	(2 5 0)	41.733	0.4321	5.4298
83.634	1.1553	1.4	(0 3 8)	41.817	0.4328	5.4387
83.824	1.1531	1.4	(0 2 9)	41.912	0.4336	5.4488
83.869	1.1526	0.9	(5 2 4)	41.934	0.4338	5.4512
84.115	1.1499	1.1	(1 5 3)	42.058	0.4348	5.4642
84.768	1.1427	0.4	(4 4 1)	42.384	0.4376	5.4986
85.078	1.1393	0.3	(1 3 8)	42.539	0.4389	5.5149
85.242	1.1375	0.9	(1 2 9)	42.621	0.4395	5.5235
85.645	1.1332	1.2	(2 5 2)	42.822	0.4412	5.5445
85.853	1.1310	0.7	(6 1 1)	42.927	0.4421	5.5554
86.334	1.1259	1.0	(4 4 2)	43.167	0.4441	5.5804
86.507	1.1241	0.5	(0 5 4)	43.254	0.4448	5.5894
86.748	1.1216	0.8	(2 4 6)	43.374	0.4458	5.6019
86.914	1.1199	0.5	(0 0 10)	43.457	0.4465	5.6105
87.321	1.1157	0.3	(3 2 8)	43.660	0.4481	5.6315
87.483	1.1141	1.2	(6 1 2)	43.741	0.4488	5.6398
87.842	1.1105	1.2	(3 4 5)	43.921	0.4503	5.6582
88.151	1.1073	0.7	(0 4 7)	44.076	0.4515	5.6741
88.216	1.1067	0.6	(3 3 7)	44.108	0.4518	5.6774
88.759	1.1013	0.3	(0 1 10)	44.380	0.4540	5.7051
89.112	1.0979	1.2	(5 3 3)	44.556	0.4554	5.7230

Table A.2 PDF card of newberyite

```
                                        PDF_72-0023
PDF#72-0023: QM=Calculated; d=Calculated; I=(Unknown)
Newberyite
MgHPO4(H2O)3
Radiation=CuKa1 Lambda=1.5406    Filter=
Calibration=    2T=14.896-71.875        I/Ic(RIR)=0.52
Ref: Level-1 PDF

Orthorhombic,  Pbca(61) Z=8     mp=
CELL: 10.215 x 10.681 x 10.014 <90.0 x 90.0 x 90.0>     P.S=
Density(c)=2.123        Density(m)=     Mwt=     Vol=1092.6
Ref: Ibid.

Strong Lines: 5.94/X  4.71/X  3.46/8  3.04/7  5.34/7  3.09/6  4.50/4  4.14/4

2-Theta    d(A)    I(f)   ( h k l)    Theta  1/(2d)   2pi/d  n^2
 14.896  5.9422  100.0   ( 1 1 1)    7.448  0.0841  1.0574
 16.586  5.3405   65.6   ( 0 2 0)    8.293  0.0936  1.1765
 17.348  5.1075    9.7   ( 2 0 0)    8.674  0.0979  1.2302
 17.699  5.0070    0.8   ( 0 0 2)    8.850  0.0999  1.2549
 18.816  4.7123   96.7   ( 0 2 1)    9.408  0.1061  1.3334
 19.247  4.6078   30.5   ( 2 1 0)    9.623  0.1085  1.3636
 19.730  4.4960   38.8   ( 1 0 2)    9.865  0.1112  1.3975
 20.742  4.2789    0.5   ( 1 2 1)   10.371  0.1169  1.4684
 21.426  4.1438   38.0   ( 1 1 2)   10.713  0.1207  1.5163
 24.090  3.6912   12.7   ( 2 2 0)   12.045  0.1355  1.7022
 24.348  3.6527   14.4   ( 0 2 2)   12.174  0.1369  1.7201
 24.882  3.5755   13.9   ( 2 0 2)   12.441  0.1398  1.7573
 25.701  3.4634   83.9   ( 2 2 1)   12.850  0.1444  1.8142
 25.883  3.4394   23.6   ( 1 2 2)   12.942  0.1454  1.8268
 26.263  3.3906    2.3   ( 2 1 2)   13.131  0.1475  1.8531
 27.972  3.1872   15.7   ( 1 3 1)   13.986  0.1569  1.9714
 28.906  3.0862   58.2   ( 3 1 1)   14.453  0.1620  2.0359
 29.340  3.0415   68.3   ( 1 1 3)   14.670  0.1644  2.0658
 30.052  2.9711    3.5   ( 2 2 2)   15.026  0.1683  2.1148
 30.583  2.9207    0.6   ( 2 3 0)   15.291  0.1712  2.1512
 31.582  2.8306    2.5   ( 0 2 3)   15.791  0.1766  2.2198
 31.754  2.8156   18.6   ( 3 0 2)   15.877  0.1776  2.2315
 31.890  2.8039   12.6   ( 2 3 1)   15.945  0.1783  2.2409
 32.040  2.7912   28.3   ( 1 3 2)   16.020  0.1791  2.2511
 32.869  2.7226   35.3   ( 1 2 3)   16.435  0.1836  2.3078
 33.112  2.7032    9.0   ( 2 1 3)   16.556  0.1850  2.3243
 33.532  2.6702    4.9   ( 0 4 0)   16.766  0.1872  2.3530
 34.741  2.5801   37.0   ( 0 4 1)   17.370  0.1938  2.4352
 35.111  2.5538    4.0   ( 4 0 0)   17.555  0.1958  2.4604
 35.555  2.5229   11.1   ( 2 3 2)   17.777  0.1982  2.4905
 35.868  2.5015    5.4   ( 0 0 4)   17.934  0.1999  2.5117
 36.134  2.4837    4.1   ( 4 1 0)   18.067  0.2013  2.5297
 36.254  2.4758    2.6   ( 2 2 3)   18.127  0.2020  2.5379
 36.937  2.4315    7.3   ( 1 0 4)   18.469  0.2056  2.5840
 37.268  2.4107   11.5   ( 4 1 1)   18.634  0.2074  2.6064
 37.608  2.3897   14.2   ( 3 3 1)   18.804  0.2092  2.6293
 37.918  2.3709   13.8   ( 1 1 4)   18.959  0.2109  2.6501
 37.993  2.3664   14.5   ( 2 4 0)   18.997  0.2113  2.6552
 38.671  2.3264    1.1   ( 3 1 3)   19.336  0.2149  2.7008
 39.065  2.3039    2.2   ( 4 2 0)   19.532  0.2170  2.7272
 39.207  2.2959    2.7   ( 1 4 2)   19.604  0.2178  2.7368
 39.582  2.2749    3.1   ( 4 0 2)   19.791  0.2198  2.7619
 39.731  2.2668    1.8   ( 0 2 4)   19.865  0.2206  2.7718
 40.128  2.2452    0.7   ( 2 0 4)   20.064  0.2227  2.7984
 40.509  2.2250    1.3   ( 4 1 2)   20.254  0.2247  2.8239
 40.739  2.2130    3.4   ( 1 2 4)   20.370  0.2259  2.8393
 40.826  2.2085    5.2   ( 3 3 2)   20.413  0.2264  2.8450
 40.994  2.1998   10.1   ( 2 1 4)   20.497  0.2273  2.8563
 41.449  2.1767    7.4   ( 3 2 3)   20.725  0.2297  2.8866
 42.205  2.1395    6.1   ( 2 4 2)   21.102  0.2337  2.9368
 43.189  2.0930    8.9   ( 4 2 2)   21.594  0.2389  3.0021
 43.359  2.0852    5.1   ( 0 4 3)   21.679  0.2398  3.0133
 43.650  2.0719    7.3   ( 2 2 4)   21.825  0.2413  3.0326
```

Table A.2 PDF card of newberyite (cont'd)

				PDF_72-0023		
43.996	2.0564	4.0	(3 4 1)	21.998	0.2431	3.0554
44.299	2.0430	12.7	(1 4 3)	22.150	0.2447	3.0754
44.554	2.0320	2.5	(4 3 1)	22.277	0.2461	3.0922
45.116	2.0079	0.2	(1 3 4)	22.558	0.2490	3.1292
45.482	1.9926	0.3	(4 1 3)	22.741	0.2509	3.1532
45.740	1.9820	6.4	(3 1 4)	22.870	0.2523	3.1702
46.015	1.9708	3.2	(2 5 0)	23.008	0.2537	3.1882
46.096	1.9675	2.5	(5 1 1)	23.048	0.2541	3.1935
47.058	1.9295	17.8	(2 4 3)	23.529	0.2591	3.2564
47.383	1.9170	1.2	(4 3 2)	23.692	0.2608	3.2776
47.812	1.9008	1.5	(2 3 4)	23.906	0.2630	3.3055
47.938	1.8961	4.3	(4 2 3)	23.969	0.2637	3.3137
48.059	1.8916	2.8	(5 0 2)	24.030	0.2643	3.3216
48.187	1.8869	8.4	(3 2 4)	24.093	0.2650	3.3299
48.528	1.8744	9.9	(0 2 5)	24.264	0.2667	3.3521
48.856	1.8626	1.1	(5 1 2)	24.428	0.2684	3.3733
49.336	1.8456	0.2	(4 4 0)	24.668	0.2709	3.4044
49.589	1.8368	0.5	(2 1 5)	24.794	0.2722	3.4207
50.224	1.8150	0.1	(4 4 1)	25.112	0.2755	3.4618
50.738	1.7978	12.2	(1 4 4)	25.369	0.2781	3.4949
51.045	1.7877	4.5	(4 0 4)	25.523	0.2797	3.5146
51.189	1.7830	2.6	(5 2 2)	25.595	0.2804	3.5238
51.531	1.7720	1.2	(1 5 3)	25.766	0.2822	3.5458
51.807	1.7632	5.7	(4 1 4)	25.904	0.2836	3.5635
51.898	1.7604	6.3	(2 2 5)	25.949	0.2840	3.5693
52.070	1.7549	9.9	(3 3 4)	26.035	0.2849	3.5803
52.823	1.7317	1.8	(4 4 2)	26.411	0.2887	3.6284
52.963	1.7275	1.4	(1 6 1)	26.481	0.2894	3.6373
53.220	1.7197	7.7	(5 1 3)	26.610	0.2907	3.6536
53.801	1.7025	2.4	(6 0 0)	26.900	0.2937	3.6906
53.987	1.6971	2.0	(2 5 3)	26.994	0.2946	3.7024
54.546	1.6810	14.8	(6 1 0)	27.273	0.2974	3.7378
54.676	1.6773	8.7	(0 6 2)	27.338	0.2981	3.7460
54.918	1.6705	7.9	(5 3 2)	27.459	0.2993	3.7613
55.374	1.6578	7.2	(2 6 1)	27.687	0.3016	3.7901
55.470	1.6552	6.2	(1 6 2)	27.735	0.3021	3.7961
55.763	1.6472	1.1	(1 0 6)	27.881	0.3036	3.8146
55.930	1.6426	1.2	(3 2 5)	27.965	0.3044	3.8251
56.083	1.6385	7.6	(4 5 0)	28.041	0.3052	3.8347
56.480	1.6279	0.6	(1 1 6)	28.240	0.3071	3.8596
56.702	1.6221	0.4	(6 2 0)	28.351	0.3082	3.8736
56.896	1.6170	1.6	(4 5 1)	28.448	0.3092	3.8857
57.094	1.6119	1.6	(6 0 2)	28.547	0.3102	3.8981
57.367	1.6048	3.3	(1 5 4)	28.684	0.3116	3.9151
57.510	1.6012	6.8	(5 4 1)	28.755	0.3123	3.9240
57.650	1.5976	5.9	(4 3 4)	28.825	0.3130	3.9328
57.833	1.5930	6.5	(2 6 2)	28.916	0.3139	3.9442
58.095	1.5864	6.9	(2 0 6)	29.048	0.3152	3.9605
58.241	1.5828	6.0	(1 4 5)	29.120	0.3159	3.9696
58.600	1.5740	0.6	(1 2 6)	29.300	0.3177	3.9919
58.795	1.5692	2.0	(2 1 6)	29.397	0.3186	4.0040
58.939	1.5657	8.0	(5 1 4)	29.469	0.3193	4.0129
59.292	1.5573	1.9	(3 6 1)	29.646	0.3211	4.0348
59.456	1.5533	1.3	(3 3 5)	29.728	0.3219	4.0449
59.660	1.5485	1.2	(2 5 4)	29.830	0.3229	4.0575
59.890	1.5431	0.7	(5 4 2)	29.945	0.3240	4.0717
60.200	1.5359	1.2	(6 3 0)	30.100	0.3255	4.0908
60.512	1.5287	0.2	(2 4 5)	30.256	0.3271	4.1100
60.863	1.5208	1.3	(2 2 6)	30.431	0.3288	4.1316
60.978	1.5182	0.8	(6 3 1)	30.489	0.3293	4.1387
61.276	1.5115	0.8	(4 2 5)	30.638	0.3308	4.1569
61.585	1.5047	1.7	(3 6 2)	30.792	0.3323	4.1758
61.735	1.5014	2.0	(6 1 3)	30.868	0.3330	4.1850
61.859	1.4986	1.0	(3 0 6)	30.929	0.3336	4.1926
62.153	1.4923	5.0	(1 7 1)	31.077	0.3351	4.2105
62.466	1.4855	0.6	(4 4 4)	31.233	0.3366	4.2296
63.279	1.4684	1.6	(6 3 2)	31.640	0.3405	4.2790
63.367	1.4666	1.5	(3 5 4)	31.684	0.3409	4.2843

Table A.2 PDF card of newberyite (cont'd)

PDF_72-0023

63.588	1.4620	2.0	(2 7 0)	31.794	0.3420	4.2976
63.737	1.4589	1.4	(5 4 3)	31.869	0.3427	4.3067
64.221	1.4491	1.8	(3 4 5)	32.111	0.3450	4.3359
64.422	1.4451	4.1	(4 6 1)	32.211	0.3460	4.3480
64.622	1.4411	2.6	(4 3 5)	32.311	0.3470	4.3600
64.902	1.4355	1.4	(1 6 4)	32.451	0.3483	4.3769
65.133	1.4310	0.8	(7 1 1)	32.566	0.3494	4.3907
65.374	1.4263	0.2	(3 6 3)	32.687	0.3506	4.4052
65.948	1.4153	8.6	(5 5 2)	32.974	0.3533	4.4395
66.343	1.4078	2.3	(6 0 4)	33.172	0.3552	4.4631
66.523	1.4044	3.8	(1 1 7)	33.261	0.3560	4.4738
66.708	1.4010	2.8	(1 4 6)	33.354	0.3569	4.4848
66.919	1.3971	2.1	(4 0 6)	33.459	0.3579	4.4973
66.992	1.3957	1.9	(6 1 4)	33.496	0.3582	4.5017
67.088	1.3940	1.8	(7 2 1)	33.544	0.3587	4.5074
67.355	1.3891	5.4	(7 1 2)	33.677	0.3599	4.5232
67.565	1.3853	4.1	(4 1 6)	33.783	0.3609	4.5356
67.775	1.3815	4.1	(5 2 5)	33.887	0.3619	4.5481
67.906	1.3792	2.0	(3 7 1)	33.953	0.3625	4.5558
68.134	1.3751	2.6	(1 7 3)	34.067	0.3636	4.5692
68.367	1.3710	1.5	(4 5 4)	34.183	0.3647	4.5830
68.637	1.3662	0.5	(2 1 7)	34.319	0.3660	4.5989
68.921	1.3613	0.8	(5 4 4)	34.460	0.3673	4.6155
69.159	1.3572	1.2	(4 4 5)	34.579	0.3684	4.6295
69.279	1.3551	0.8	(7 2 2)	34.640	0.3690	4.6366
69.486	1.3516	0.6	(4 2 6)	34.743	0.3699	4.6487
70.084	1.3415	1.5	(3 7 2)	35.042	0.3727	4.6836
70.225	1.3392	1.1	(2 7 3)	35.112	0.3734	4.6918
70.471	1.3351	1.3	(0 8 0)	35.235	0.3745	4.7061
70.545	1.3339	1.4	(2 2 7)	35.273	0.3748	4.7104
70.749	1.3305	4.9	(0 6 5)	35.375	0.3758	4.7222
70.983	1.3267	4.9	(5 3 5)	35.491	0.3769	4.7358
71.189	1.3234	2.0	(0 8 1)	35.594	0.3778	4.7477
71.478	1.3188	1.9	(1 6 5)	35.739	0.3791	4.7645
71.629	1.3163	3.9	(1 3 7)	35.815	0.3798	4.7732
71.875	1.3125	2.0	(1 8 1)	35.937	0.3810	4.7874

Table A.3 PDF card of hydroxylapatite

```
                                   PDF_74-0566
PDF#74-0566: QM=Calculated; d=Calculated; I=(Unknown)
Hydroxylapatite
Ca10(PO4)6(OH)2
Radiation=CuKa1 Lambda=1.5406   Filter=
Calibration=    2T=10.831-89.527          I/Ic(RIR)=1.06
Ref: Level-1 PDF

Hexagonal,  P63/m(176)  Z=1     mp=
CELL: 9.424 x 9.424 x 6.879 <90.0 x 90.0 x 120.0>       P.S=
Density(c)=3.152         Density(m)=     Mwt=    Vol=529.1
Ref: Ibid.

Strong Lines: 2.81/X  2.72/6  2.78/5  3.44/4  1.84/3  1.94/3  2.63/2  2.26/2

2-Theta    d(Å)    I(f)  ( h k l)   Theta  1/(2d)   2pi/d  n^2
 10.831  8.1614    17.0  ( 1 0 0)    5.416  0.0613  0.7699
 16.842  5.2599     4.6  ( 1 0 1)    8.421  0.0951  1.1946
 18.817  4.7120     2.3  ( 1 1 0)    9.408  0.1061  1.3334
 21.761  4.0807     6.5  ( 2 0 0)   10.881  0.1225  1.5397
 22.857  3.8874     6.3  ( 1 1 1)   11.429  0.1286  1.6163
 25.356  3.5096     2.3  ( 2 0 1)   12.678  0.1425  1.7903
 25.882  3.4395    35.7  ( 0 0 2)   12.941  0.1454  1.8268
 28.130  3.1695     8.8  ( 1 0 2)   14.065  0.1578  1.9824
 28.920  3.0847    16.0  ( 2 1 0)   14.460  0.1621  2.0369
 31.765  2.8147   100.0  ( 2 1 1)   15.882  0.1776  2.2323
 32.194  2.7781    51.5  ( 1 1 2)   16.097  0.1800  2.2617
 32.896  2.7205    61.3  ( 3 0 0)   16.448  0.1838  2.3096
 34.062  2.6299    21.0  ( 2 0 2)   17.031  0.1901  2.3891
 35.454  2.5298     3.9  ( 3 0 1)   17.727  0.1976  2.4836
 38.167  2.3560     0.2  ( 2 2 0)   19.083  0.2122  2.6669
 39.196  2.2964     5.0  ( 2 1 2)   19.598  0.2177  2.7360
 39.790  2.2636    20.5  ( 1 3 0)   19.895  0.2209  2.7758
 40.435  2.2289     1.8  ( 2 2 1)   20.218  0.2243  2.8190
 40.844  2.2075     0.4  ( 1 0 3)   20.422  0.2265  2.8463
 41.985  2.1502     5.6  ( 1 3 1)   20.992  0.2325  2.9222
 42.324  2.1337     1.1  ( 3 0 2)   21.162  0.2343  2.9447
 43.874  2.0618     4.5  ( 1 1 3)   21.937  0.2425  3.0474
 44.360  2.0404     1.1  ( 4 0 0)   22.180  0.2451  3.0794
 45.328  1.9990     3.5  ( 2 0 3)   22.664  0.2501  3.1431
 46.380  1.9561     0.7  ( 4 0 1)   23.190  0.2556  3.2121
 46.693  1.9437    28.1  ( 2 2 2)   23.347  0.2572  3.2326
 48.080  1.8908    12.2  ( 1 3 2)   24.040  0.2644  3.3230
 48.585  1.8724     4.0  ( 2 3 0)   24.293  0.2670  3.3558
 49.489  1.8403    31.3  ( 2 1 3)   24.744  0.2717  3.4143
 50.474  1.8066    16.1  ( 3 2 1)   25.237  0.2768  3.4778
 51.253  1.7810    11.6  ( 1 4 0)   25.627  0.2807  3.5280
 52.074  1.7548    11.7  ( 4 0 2)   26.037  0.2849  3.5805
 53.218  1.7198    14.0  ( 0 0 4)   26.609  0.2907  3.6535
 54.482  1.6828     1.0  ( 1 0 4)   27.241  0.2971  3.7338
 55.861  1.6445     5.9  ( 3 2 2)   27.931  0.3040  3.8208
 56.316  1.6323     0.2  ( 5 0 0)   28.158  0.3063  3.8493
 57.132  1.6109     3.7  ( 3 1 3)   28.566  0.3104  3.9004
 58.026  1.5882     1.5  ( 5 0 1)   29.013  0.3148  3.9562
 58.163  1.5848     1.1  ( 2 0 4)   29.081  0.3155  3.9647
 58.293  1.5815     1.0  ( 4 1 2)   29.147  0.3161  3.9729
 58.736  1.5707     0.8  ( 3 3 0)   29.368  0.3183  4.0003
 59.923  1.5424     4.3  ( 2 4 0)   29.961  0.3242  4.0737
 60.402  1.5313     3.2  ( 3 3 1)   30.201  0.3265  4.1033
 61.569  1.5050     3.2  ( 2 4 1)   30.785  0.3322  4.1749
 61.702  1.5021     5.0  ( 1 2 4)   30.851  0.3329  4.1830
 62.980  1.4747     7.9  ( 5 0 2)   31.490  0.3391  4.2608
 63.403  1.4658     1.6  ( 5 1 0)   31.701  0.3411  4.2864
 63.997  1.4536     7.4  ( 3 0 4)   31.998  0.3440  4.3224
 64.163  1.4503     9.3  ( 3 2 3)   32.082  0.3448  4.3324
 64.998  1.4337     6.9  ( 5 1 1)   32.499  0.3488  4.3826
 66.410  1.4066     2.1  ( 1 4 3)   33.205  0.3555  4.4671
 67.357  1.3891     0.1  ( 2 2 4)   33.679  0.3600  4.5233
 68.459  1.3694     0.4  ( 3 1 4)   34.230  0.3651  4.5884
```

Table A.3 PDF card of hydroxylapatite (cont'd)

PDF_74-0566

68.983	1.3602	0.2	(6 0 0)	34.491	0.3676	4.6192
69.191	1.3567	0.2	(1 0 5)	34.595	0.3686	4.6314
69.671	1.3485	2.0	(5 1 2)	34.835	0.3708	4.6595
70.073	1.3417	0.4	(4 3 0)	35.036	0.3727	4.6829
70.514	1.3344	0.1	(6 0 1)	35.257	0.3747	4.7086
70.797	1.3298	0.2	(5 0 3)	35.398	0.3760	4.7250
71.359	1.3207	0.4	(1 1 5)	35.680	0.3786	4.7576
71.594	1.3169	3.7	(4 3 1)	35.797	0.3797	4.7712
72.230	1.3069	2.8	(5 2 0)	36.115	0.3826	4.8078
72.433	1.3037	1.7	(2 0 5)	36.217	0.3835	4.8195
72.945	1.2958	0.3	(3 3 3)	36.472	0.3859	4.8488
73.732	1.2839	1.9	(5 2 1)	36.866	0.3894	4.8938
74.009	1.2798	3.8	(2 4 3)	37.005	0.3907	4.9095
74.913	1.2666	1.3	(2 3 4)	37.457	0.3948	4.9608
75.029	1.2649	1.1	(6 0 2)	37.514	0.3953	4.9673
75.619	1.2565	4.5	(2 1 5)	37.810	0.3979	5.0006
76.083	1.2500	2.4	(3 4 2)	38.041	0.4000	5.0266
76.471	1.2446	1.8	(6 1 0)	38.235	0.4017	5.0483
77.018	1.2371	5.0	(1 4 4)	38.509	0.4042	5.0789
77.172	1.2350	4.4	(5 1 3)	38.586	0.4048	5.0874
77.717	1.2277	0.2	(3 0 5)	38.859	0.4073	5.1177
77.944	1.2247	0.9	(1 6 1)	38.972	0.4083	5.1303
78.177	1.2217	5.6	(2 5 2)	39.088	0.4093	5.1432
80.834	1.1881	0.3	(2 2 5)	40.417	0.4209	5.2886
81.177	1.1839	0.5	(5 0 4)	40.589	0.4223	5.3071
81.671	1.1780	1.7	(4 4 0)	40.835	0.4244	5.3338
81.867	1.1757	1.2	(1 3 5)	40.934	0.4253	5.3443
82.321	1.1703	0.6	(1 6 2)	41.160	0.4272	5.3687
82.701	1.1659	0.7	(7 0 0)	41.350	0.4288	5.3890
83.120	1.1611	1.0	(4 4 1)	41.560	0.4306	5.4114
83.238	1.1598	1.0	(3 3 4)	41.619	0.4311	5.4177
83.388	1.1580	3.6	(4 3 3)	41.694	0.4318	5.4257
84.265	1.1482	3.4	(2 4 4)	42.132	0.4355	5.4721
84.421	1.1465	1.7	(0 0 6)	42.210	0.4361	5.4803
84.950	1.1407	0.2	(4 0 5)	42.475	0.4383	5.5082
85.440	1.1354	1.7	(5 2 3)	42.720	0.4404	5.5338
85.779	1.1318	0.9	(2 6 0)	42.889	0.4418	5.5515
87.335	1.1156	2.3	(5 1 4)	43.668	0.4482	5.6322
87.491	1.1140	4.1	(4 4 2)	43.745	0.4488	5.6402
88.018	1.1087	2.4	(2 3 5)	44.009	0.4510	5.6673
88.468	1.1042	5.8	(3 5 2)	44.234	0.4528	5.6903
89.527	1.0939	0.3	(1 6 3)	44.764	0.4571	5.7440

Table A.4 PDF card of calcite

```
                                    PDF_72-1652
PDF#72-1652: QM=Calculated; d=Calculated; I=(Unknown)
Calcite
CaCO3
Radiation=CuKa1 Lambda=1.5406    Filter=
Calibration=    2T=23.069-86.648        I/Ic(RIR)=3.2
Ref: Level-1 PDF

Hexagonal,  R-3c(167)   Z=6     mp=
CELL: 4.99 x 4.99 x 17.002 <90.0 x 90.0 x 120.0>        P.S=
Density(c)=2.719        Density(m)=     Mwt=    Vol=366.6
Ref: Ibid.

Strong Lines: 3.03/X  1.87/2  2.28/2  1.91/2  2.09/1  2.49/1  3.85/1  1.60/1

2-Theta    d(Å)    I(f)   ( h k  l)    Theta  1/(2d)   2pi/d  n^2
 23.069  3.8523     9.8   ( 0 1  2)   11.534  0.1298  1.6310
 29.451  3.0303   100.0   ( 1 0  4)   14.726  0.1650  2.0734
 31.547  2.8337     2.1   ( 0 0  6)   15.773  0.1764  2.2173
 35.965  2.4950    13.9   ( 1 1  0)   17.983  0.2004  2.5183
 39.428  2.2835    18.4   ( 1 1  3)   19.714  0.2190  2.7515
 43.163  2.0942    14.5   ( 2 0  2)   21.582  0.2388  3.0004
 47.145  1.9261     6.3   ( 0 2  4)   23.572  0.2596  3.2621
 47.645  1.9071    18.4   ( 0 1  8)   23.822  0.2622  3.2946
 48.579  1.8726    19.3   ( 1 1  6)   24.289  0.2670  3.3554
 56.558  1.6259     3.2   ( 2 1  1)   28.279  0.3075  3.8645
 57.399  1.6040     8.8   ( 1 2  2)   28.700  0.3117  3.9171
 58.268  1.5821     1.0   ( 1 0 10)   29.134  0.3160  3.9713
 60.691  1.5247     4.8   ( 2 1  4)   30.346  0.3279  4.1210
 61.112  1.5152     2.1   ( 2 0  8)   30.556  0.3300  4.1469
 61.520  1.5061     2.6   ( 1 1  9)   30.760  0.3320  4.1718
 63.091  1.4723     2.0   ( 1 2  5)   31.546  0.3396  4.2676
 64.652  1.4405     5.7   ( 3 0  0)   32.326  0.3471  4.3618
 65.867  1.4168     3.2   ( 0 0 12)   32.933  0.3529  4.4347
 69.265  1.3554     1.1   ( 2 1  7)   34.632  0.3689  4.6357
 70.408  1.3362     1.8   ( 0 2 10)   35.204  0.3742  4.7025
 72.994  1.2951     2.4   ( 1 2  8)   36.497  0.3861  4.8516
 73.720  1.2841     0.5   ( 3 0  6)   36.860  0.3894  4.8931
 76.262  1.2475     1.0   ( 2 2  0)   38.131  0.4008  5.0366
 77.395  1.2320     1.7   ( 1 1 12)   38.697  0.4058  5.0998
 78.432  1.2183     0.1   ( 2 2  3)   39.216  0.4104  5.1572
 80.222  1.1956     0.1   ( 1 3  1)   40.111  0.4182  5.2553
 80.937  1.1868     0.5   ( 3 1  2)   40.468  0.4213  5.2941
 81.681  1.1779     2.1   ( 2 1 10)   40.840  0.4245  5.3343
 82.423  1.1691     0.3   ( 0 1 14)   41.212  0.4277  5.3742
 83.785  1.1536     3.7   ( 1 3  4)   41.893  0.4334  5.4467
 84.854  1.1417     1.8   ( 2 2  6)   42.427  0.4379  5.5031
 85.911  1.1304     0.1   ( 3 1  5)   42.955  0.4423  5.5584
 86.648  1.1227     0.5   ( 1 2 11)   43.324  0.4454  5.5967
```

Table A.5 PDF card of whitlockite

```
                                   PDF_70-1786
PDF#70-1786: QM=Calculated; d=Calculated; I=(Unknown)
Whitlockite
Ca18.19Mg1.17Fe0.83H1.62(PO4)14
Radiation=CuKa1 Lambda=1.5406   Filter=
Calibration=    2T=10.971-81.811        I/Ic(RIR)=1.11
Ref: Level-1 PDF

Hexagonal,  R3c(161)    Z=3      mp=
CELL: 10.33 x 10.33 x 37.103 <90.0 x 90.0 x 120.0>        P.S=
Density(c)=3.12 Density(m)=      Mwt=     Vol=3428.8
Ref: Ibid.

Strong Lines: 2.86/X  2.58/8  3.18/6  5.16/5  3.43/4  1.71/4  6.44/3  2.73/3

2-Theta    d(Å)    I(f)   ( h k l)    Theta   1/(2d)   2pi/d   n^2
 10.971  8.0581     7.7   ( 0 1 2)    5.485  0.0620  0.7797
 13.741  6.4392    34.7   ( 1 0 4)    6.870  0.0776  0.9758
 14.311  6.1838     1.9   ( 0 0 6)    7.156  0.0809  1.0161
 17.154  5.1650    49.3   ( 1 1 0)    8.577  0.0968  1.2165
 18.602  4.7661     1.4   ( 1 1 3)    9.301  0.1049  1.3183
 20.407  4.3484     0.3   ( 2 0 2)   10.203  0.1150  1.4449
 21.564  4.1175     2.3   ( 0 1 8)   10.782  0.1214  1.5260
 22.044  4.0290    14.3   ( 0 2 4)   11.022  0.1241  1.5595
 22.409  3.9641     0.4   ( 1 1 6)   11.205  0.1261  1.5850
 25.977  3.4272    37.4   ( 1 0 10)  12.988  0.1459  1.8333
 26.447  3.3673    10.9   ( 2 1 1)   13.224  0.1485  1.8659
 26.778  3.3265     7.9   ( 1 2 2)   13.389  0.1503  1.8888
 27.663  3.2220     4.6   ( 1 1 9)   13.831  0.1552  1.9501
 28.065  3.1768    62.8   ( 2 1 4)   14.032  0.1574  1.9778
 28.852  3.0919     1.0   ( 0 0 12)  14.426  0.1617  2.0321
 28.996  3.0769     2.2   ( 1 2 5)   14.498  0.1625  2.0420
 29.939  2.9820    11.3   ( 3 0 0)   14.970  0.1677  2.1070
 31.297  2.8557   100.0   ( 0 2 10)  15.648  0.1751  2.2002
 32.750  2.7322    29.7   ( 1 2 8)   16.375  0.1830  2.2996
 33.330  2.6860     7.3   ( 3 0 6)   16.665  0.1861  2.3392
 33.758  2.6529     6.9   ( 1 1 12)  16.879  0.1885  2.3684
 34.707  2.5825    82.5   ( 2 2 0)   17.354  0.1936  2.4330
 35.292  2.5411     2.9   ( 0 1 14)  17.646  0.1968  2.4727
 35.480  2.5280     3.3   ( 2 2 3)   17.740  0.1978  2.4855
 35.903  2.4992     9.8   ( 2 1 10)  17.952  0.2001  2.5141
 36.256  2.4757     5.3   ( 1 3 1)   18.128  0.2020  2.5380
 36.506  2.4593     0.6   ( 3 1 2)   18.253  0.2033  2.5549
 37.491  2.3969     1.8   ( 1 3 4)   18.745  0.2086  2.6214
 37.717  2.3830     6.6   ( 2 2 6)   18.859  0.2098  2.6366
 38.215  2.3531     0.8   ( 3 1 5)   19.108  0.2125  2.6701
 39.490  2.2801     2.2   ( 2 0 14)  19.745  0.2193  2.7557
 40.137  2.2448     7.3   ( 1 3 7)   20.069  0.2227  2.7991
 40.397  2.2309     3.0   ( 1 1 15)  20.199  0.2241  2.8164
 40.596  2.2204     1.9   ( 0 4 2)   20.298  0.2252  2.8297
 41.214  2.1885     1.9   ( 2 2 9)   20.607  0.2285  2.8709
 41.364  2.1810     1.6   ( 2 1 13)  20.682  0.2293  2.8809
 41.499  2.1742     6.3   ( 4 0 4)   20.749  0.2300  2.8899
 42.062  2.1464    11.2   ( 3 0 12)  21.031  0.2329  2.9273
 43.343  2.0859     3.2   ( 1 2 14)  21.672  0.2397  3.0123
 43.859  2.0625     4.1   ( 1 3 10)  21.930  0.2424  3.0464
 44.158  2.0492     2.8   ( 3 2 1)   22.079  0.2440  3.0661
 44.371  2.0399     5.4   ( 2 3 2)   22.185  0.2451  3.0801
 44.961  2.0145    11.7   ( 0 4 8)   22.480  0.2482  3.1190
 45.212  2.0039     5.2   ( 3 2 4)   22.606  0.2495  3.1355
 45.336  1.9987     3.7   ( 3 1 11)  22.668  0.2502  3.1437
 45.738  1.9821     6.6   ( 2 2 12)  22.869  0.2523  3.1700
 45.835  1.9781     4.5   ( 2 3 5)   22.917  0.2528  3.1764
 46.479  1.9522     1.3   ( 4 1 0)   23.239  0.2561  3.2185
 47.089  1.9283     2.1   ( 1 4 3)   23.544  0.2593  3.2584
 47.424  1.9154    25.7   ( 4 0 10)  23.712  0.2610  3.2803
 48.462  1.8768    14.7   ( 2 3 8)   24.231  0.2664  3.3478
 48.581  1.8725     8.7   ( 1 3 13)  24.290  0.2670  3.3555
 48.884  1.8616    12.2   ( 1 4 6)   24.442  0.2686  3.3751
```

Table A.5 PDF card of whitlockite (cont'd)

PDF_70-1786

49.678	1.8337	0.2	(1 2 17)	24.839	0.2727	3.4265
50.181	1.8165	3.4	(0 1 20)	25.090	0.2753	3.4590
50.336	1.8113	2.3	(3 1 14)	25.168	0.2760	3.4689
50.796	1.7959	9.5	(3 2 10)	25.398	0.2784	3.4986
51.254	1.7809	4.3	(5 0 2)	25.627	0.2808	3.5280
51.771	1.7644	2.9	(4 1 9)	25.886	0.2834	3.5612
52.010	1.7568	10.8	(0 5 4)	26.005	0.2846	3.5765
52.122	1.7533	6.4	(2 3 11)	26.061	0.2852	3.5836
53.154	1.7217	2.8	(3 3 0)	26.577	0.2904	3.6495
53.424	1.7136	35.3	(2 0 20)	26.712	0.2918	3.6666
53.572	1.7092	19.4	(0 4 14)	26.786	0.2925	3.6761
54.037	1.6956	6.9	(3 0 18)	27.018	0.2949	3.7055
54.195	1.6910	4.6	(2 1 19)	27.098	0.2957	3.7156
54.960	1.6693	4.4	(1 1 21)	27.480	0.2995	3.7640
55.177	1.6632	4.5	(2 4 4)	27.589	0.3006	3.7777
55.392	1.6573	2.2	(3 3 6)	27.696	0.3017	3.7912
55.633	1.6507	2.8	(4 1 12)	27.816	0.3029	3.8064
56.074	1.6387	0.8	(3 1 17)	28.037	0.3051	3.8341
56.536	1.6264	0.8	(1 2 20)	28.268	0.3074	3.8632
56.679	1.6227	3.0	(2 3 14)	28.340	0.3081	3.8721
57.174	1.6098	3.9	(2 2 18)	28.587	0.3106	3.9031
57.351	1.6053	2.2	(5 1 1)	28.676	0.3115	3.9141
57.527	1.6008	0.5	(1 5 2)	28.764	0.3124	3.9251
58.006	1.5887	2.8	(3 3 9)	29.003	0.3147	3.9549
58.227	1.5832	2.7	(5 1 4)	29.113	0.3158	3.9687
58.434	1.5781	1.4	(0 2 22)	29.217	0.3168	3.9816
58.748	1.5704	0.4	(1 5 5)	29.374	0.3184	4.0011
59.769	1.5460	0.5	(0 0 24)	29.885	0.3234	4.0643
60.090	1.5385	14.2	(2 4 10)	30.045	0.3250	4.0841
60.260	1.5345	8.6	(1 3 19)	30.130	0.3258	4.0945
60.975	1.5182	3.1	(1 5 8)	30.488	0.3293	4.1385
61.380	1.5092	1.9	(2 1 22)	30.690	0.3313	4.1633
61.606	1.5042	1.7	(3 3 12)	30.803	0.3324	4.1771
62.211	1.4910	3.8	(6 0 0)	31.106	0.3353	4.2140
62.455	1.4858	2.0	(3 1 20)	31.228	0.3365	4.2289
62.677	1.4810	0.7	(1 1 24)	31.339	0.3376	4.2424
62.990	1.4744	0.2	(5 1 10)	31.495	0.3391	4.2614
63.223	1.4696	0.4	(4 3 1)	31.611	0.3402	4.2755
63.389	1.4661	0.5	(3 4 2)	31.694	0.3410	4.2856
64.050	1.4526	4.0	(4 3 4)	32.025	0.3442	4.3256
64.203	1.4495	2.4	(0 6 6)	32.102	0.3450	4.3348
64.543	1.4427	0.9	(3 4 5)	32.271	0.3466	4.3553
65.056	1.4325	1.2	(5 2 0)	32.528	0.3490	4.3861
65.294	1.4279	4.6	(0 4 20)	32.647	0.3502	4.4004
65.545	1.4230	2.5	(5 2 3)	32.773	0.3514	4.4155
65.837	1.4174	1.8	(1 4 18)	32.919	0.3528	4.4329
65.978	1.4147	1.2	(3 2 19)	32.989	0.3534	4.4413
66.658	1.4019	3.9	(3 4 8)	33.329	0.3567	4.4818
67.002	1.3956	7.4	(5 2 6)	33.501	0.3583	4.5023
68.070	1.3762	1.9	(2 3 20)	34.035	0.3633	4.5655
68.282	1.3725	2.0	(0 3 24)	34.141	0.3643	4.5780
68.581	1.3672	1.3	(4 3 10)	34.290	0.3657	4.5956
68.804	1.3633	1.7	(1 6 1)	34.402	0.3667	4.6087
68.963	1.3606	1.0	(6 1 2)	34.482	0.3675	4.6180
69.396	1.3532	0.5	(2 5 9)	34.698	0.3695	4.6434
69.596	1.3497	0.7	(1 6 4)	34.798	0.3704	4.6551
69.691	1.3481	0.9	(3 4 11)	34.845	0.3709	4.6606
69.785	1.3466	0.6	(4 0 22)	34.892	0.3713	4.6661
69.996	1.3430	0.7	(6 0 12)	34.998	0.3723	4.6784
70.384	1.3365	0.1	(4 2 17)	35.192	0.3741	4.7010
71.001	1.3264	0.6	(1 1 27)	35.500	0.3769	4.7368
71.356	1.3207	1.0	(1 6 7)	35.678	0.3786	4.7574
71.730	1.3147	1.1	(1 2 26)	35.865	0.3803	4.7790
71.979	1.3108	1.8	(1 0 28)	35.989	0.3814	4.7934
72.199	1.3074	1.0	(4 3 13)	36.100	0.3825	4.8060
72.478	1.3030	1.1	(3 2 22)	36.239	0.3837	4.8221
72.686	1.2998	2.4	(5 2 12)	36.343	0.3847	4.8340
73.245	1.2912	3.3	(4 4 0)	36.622	0.3872	4.8660

Table A.5 PDF card of whitlockite (cont'd)

PDF_70-1786

73.470	1.2878	2.0	(5 0 20)	36.735	0.3882	4.8789
73.595	1.2860	1.1	(3 4 14)	36.797	0.3888	4.8860
73.965	1.2804	0.3	(1 6 10)	36.983	0.3905	4.9071
74.181	1.2773	1.8	(2 4 19)	37.091	0.3915	4.9193
74.335	1.2750	2.5	(5 3 2)	37.168	0.3922	4.9281
74.640	1.2705	1.2	(0 2 28)	37.320	0.3935	4.9453
74.794	1.2683	0.4	(2 3 23)	37.397	0.3942	4.9541
74.950	1.2660	0.6	(7 0 4)	37.475	0.3949	4.9628
75.093	1.2640	0.6	(6 1 11)	37.546	0.3956	4.9709
76.112	1.2496	5.1	(4 2 20)	38.056	0.4001	5.0282
76.661	1.2420	1.2	(3 5 7)	38.331	0.4026	5.0590
76.752	1.2407	1.5	(5 1 19)	38.376	0.4030	5.0640
76.966	1.2378	2.4	(2 6 2)	38.483	0.4039	5.0760
77.044	1.2368	2.4	(3 1 26)	38.522	0.4043	5.0803
77.392	1.2321	2.5	(0 7 8)	38.696	0.4058	5.0997
77.574	1.2296	3.5	(1 6 13)	38.787	0.4066	5.1098
77.754	1.2272	1.5	(0 5 22)	38.877	0.4074	5.1198
78.029	1.2236	0.3	(2 6 5)	39.014	0.4086	5.1350
78.330	1.2197	0.1	(3 4 17)	39.165	0.4100	5.1516
78.723	1.2146	0.5	(1 5 20)	39.361	0.4117	5.1733
78.924	1.2120	1.4	(4 1 24)	39.462	0.4126	5.1843
79.226	1.2081	2.1	(6 0 18)	39.613	0.4139	5.2009
79.627	1.2030	0.6	(0 4 26)	39.814	0.4156	5.2229
79.991	1.1985	0.2	(2 6 8)	39.995	0.4172	5.2427
80.261	1.1951	0.5	(5 3 11)	40.131	0.4184	5.2575
80.552	1.1915	1.0	(4 4 12)	40.276	0.4196	5.2733
81.093	1.1849	1.6	(7 1 0)	40.546	0.4220	5.3026
81.542	1.1795	0.6	(7 1 3)	40.771	0.4239	5.3269
81.811	1.1763	4.2	(2 5 18)	40.905	0.4250	5.3413

APPENDIX B

THE QUALITATIVE IDENTIFICATION OF THE PRECIPITATES

Table B.1 The match of *d* spacing and 2-theta of the struvite and the precipitate collected from Experiment E7 Patterns

Strongest lines of Struvite[a,b]		Experiment E7 Patterns	
d spacing (Å)	2-Theta (°)	d spacing (Å)	2-Theta (°)
4.2531	20.869	4.2485	20.892
5.5995	15.814	5.5876	15.848
5.8997	15.004	5.8913	15.026
2.9167	30.626	2.9178	30.615
2.6909	33.267	2.6882	33.302
2.6587	33.683	2.6580	33.691
4.1364	21.464	4.1305	21.496
2.7998	31.939	2.7957	31.986

[a] Retrieved from PDF card 71-2089

[b] The full PDF card is presented in Table A.1 in Appendix A.

Table B.1 indicated the match of the eight strongest lines of standard struvite obtained from the PDF card of struvite, and with the lines of the sample collected from Experiment E7. As indicated in Table B.1 the *d* spacing and the 2-theta values of the struvite and the unknown sample match almost exactly. This clearly illustrates the presence of struvite in the unknown sample. Also the match of the *d* spacing values can be observed from Figure B.1. No other mineral was found by this method. The identification of the precipitates collected from other minerals was done by the same method.

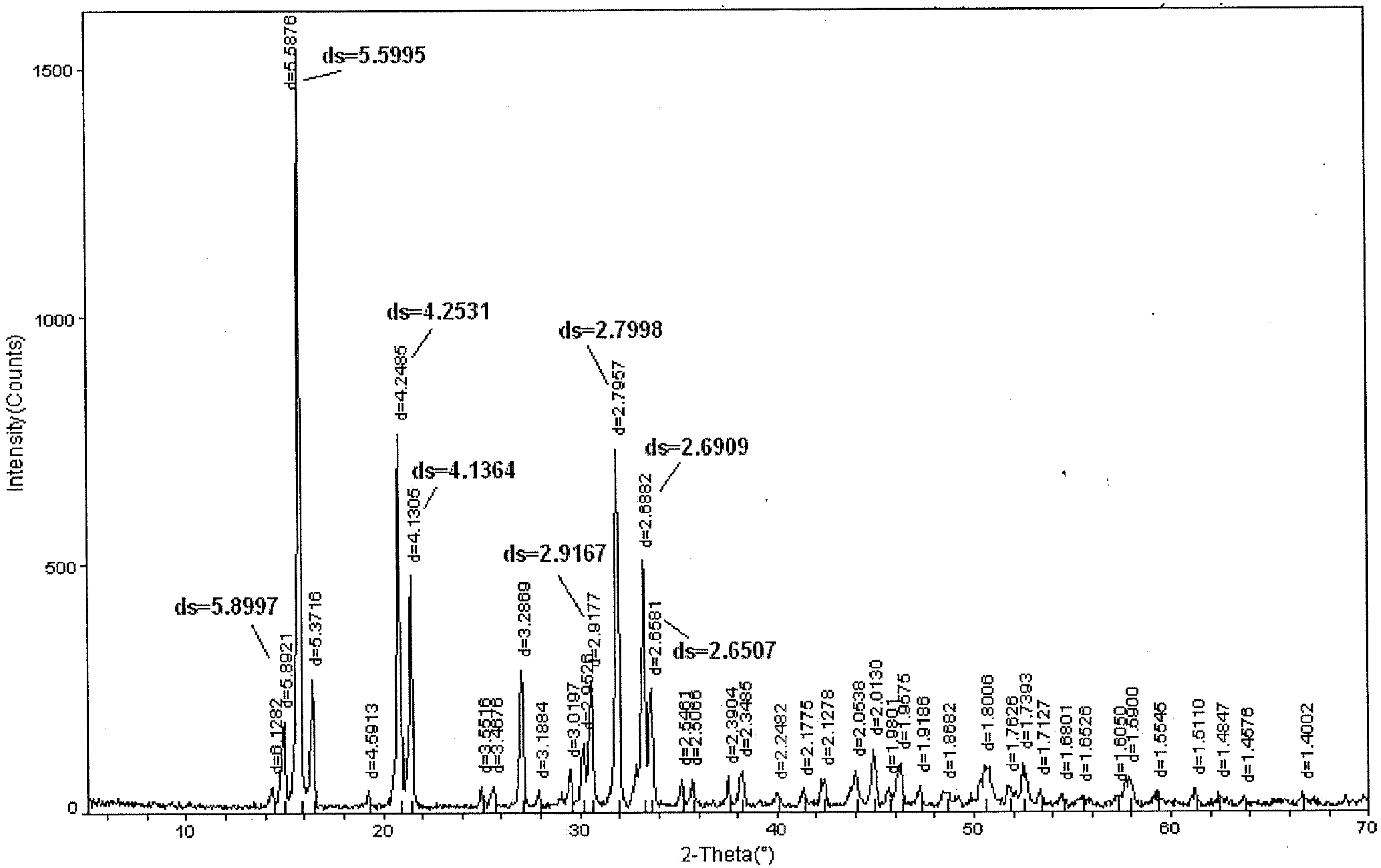

Figure-B.1 The match of *d* spacing of struvite and the precipitate collected from Experiment E7

APPENDIX C

XRD PATTERNS OF THE PRECIPITATES

In this section the XRD patterns of the precipitates collected from the experiments are presented. From Figure C1-C9 the XRD patterns of the precipitates collected from the experiments conducted in Set 1 are presented. From Figure C10-C14 the XRD patterns of the samples of Set 2 and from Figure C15-C20 the XRD patterns of the precipitates collected from Set 3 are represented.

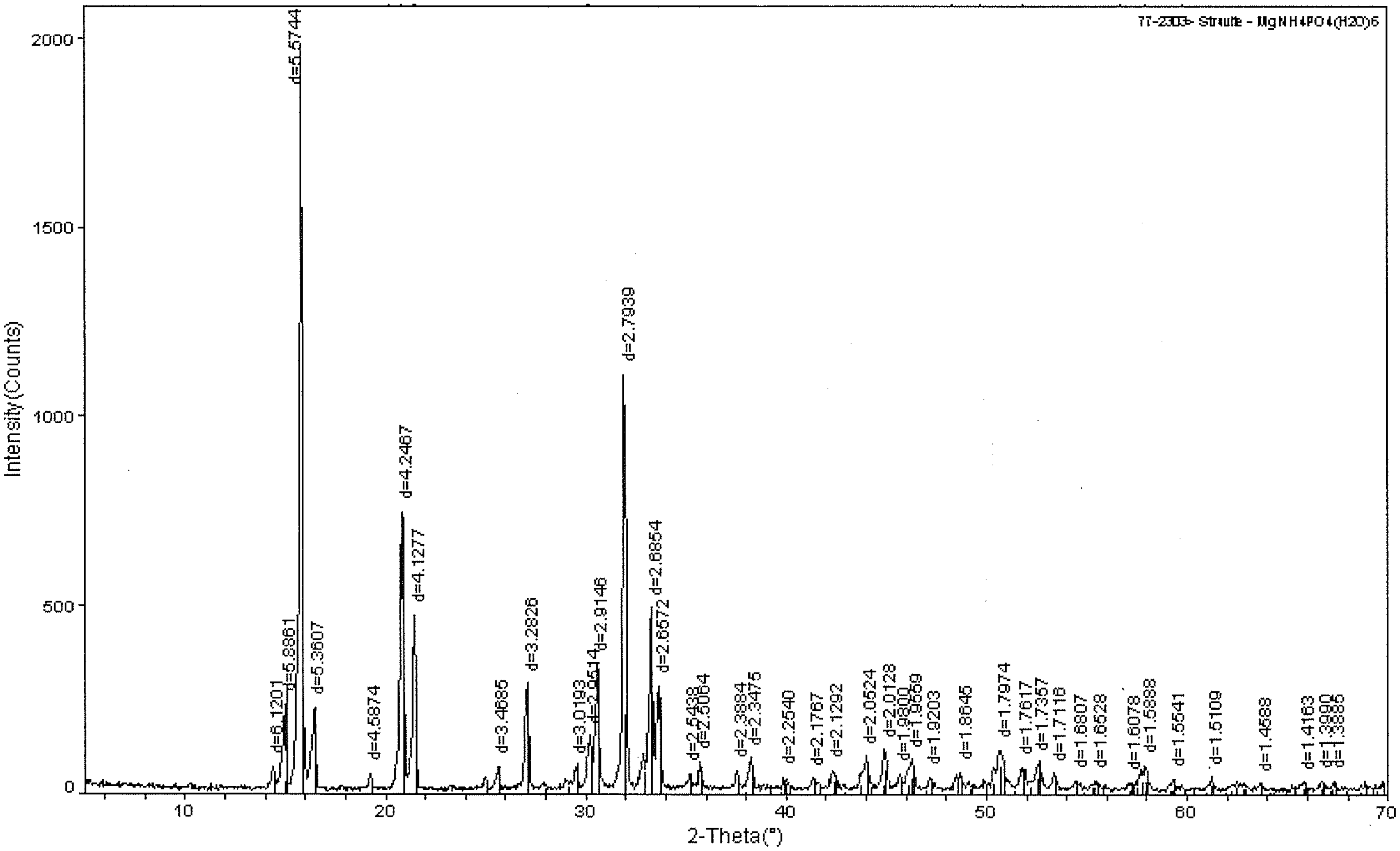

Figure C.1 XRD analysis of the precipitate collected from the molar ratio Experiment E8 of set 1

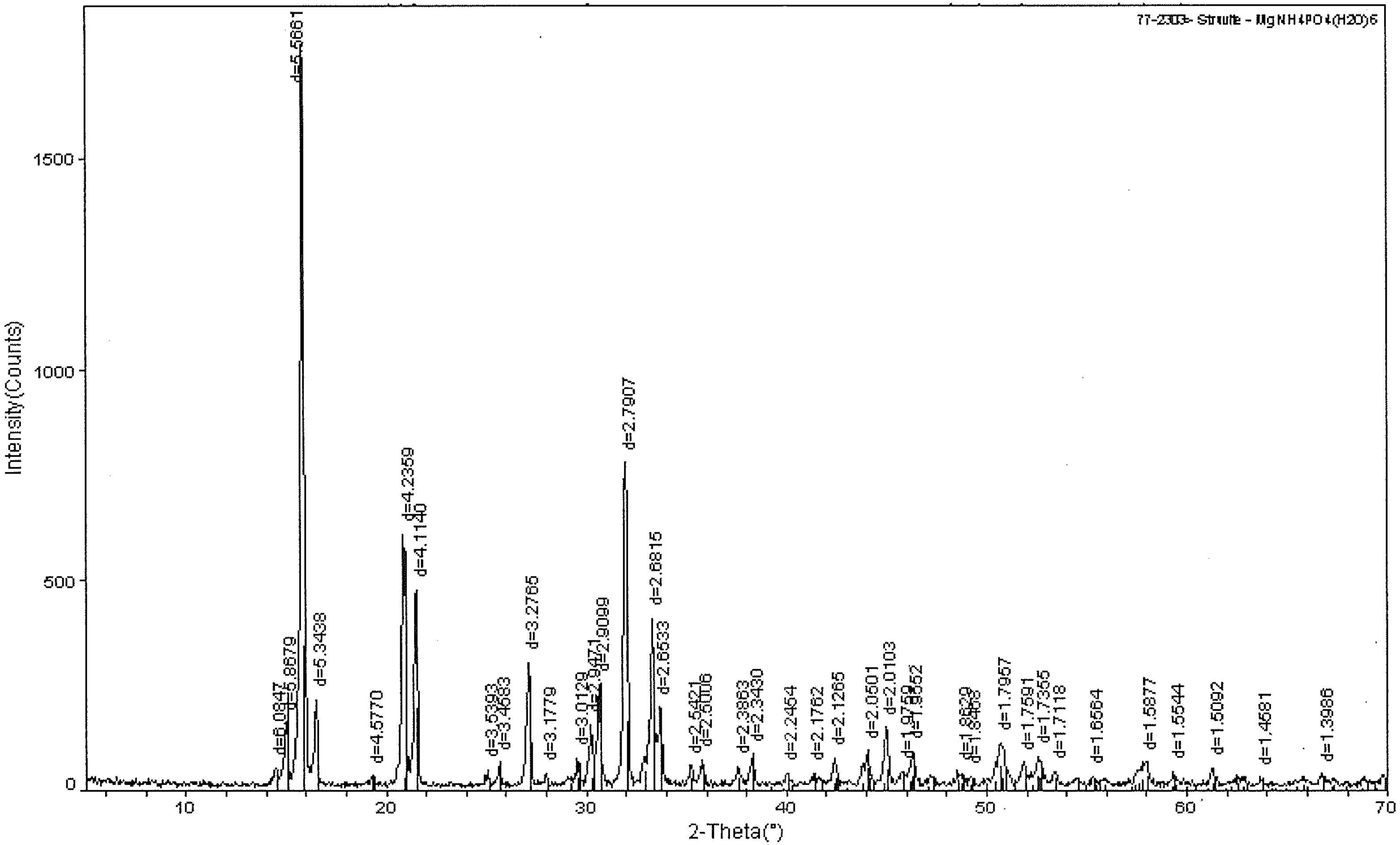

Figure C.2 XRD analysis of the precipitate collected from the molar ratio Experiment E9 of set 1

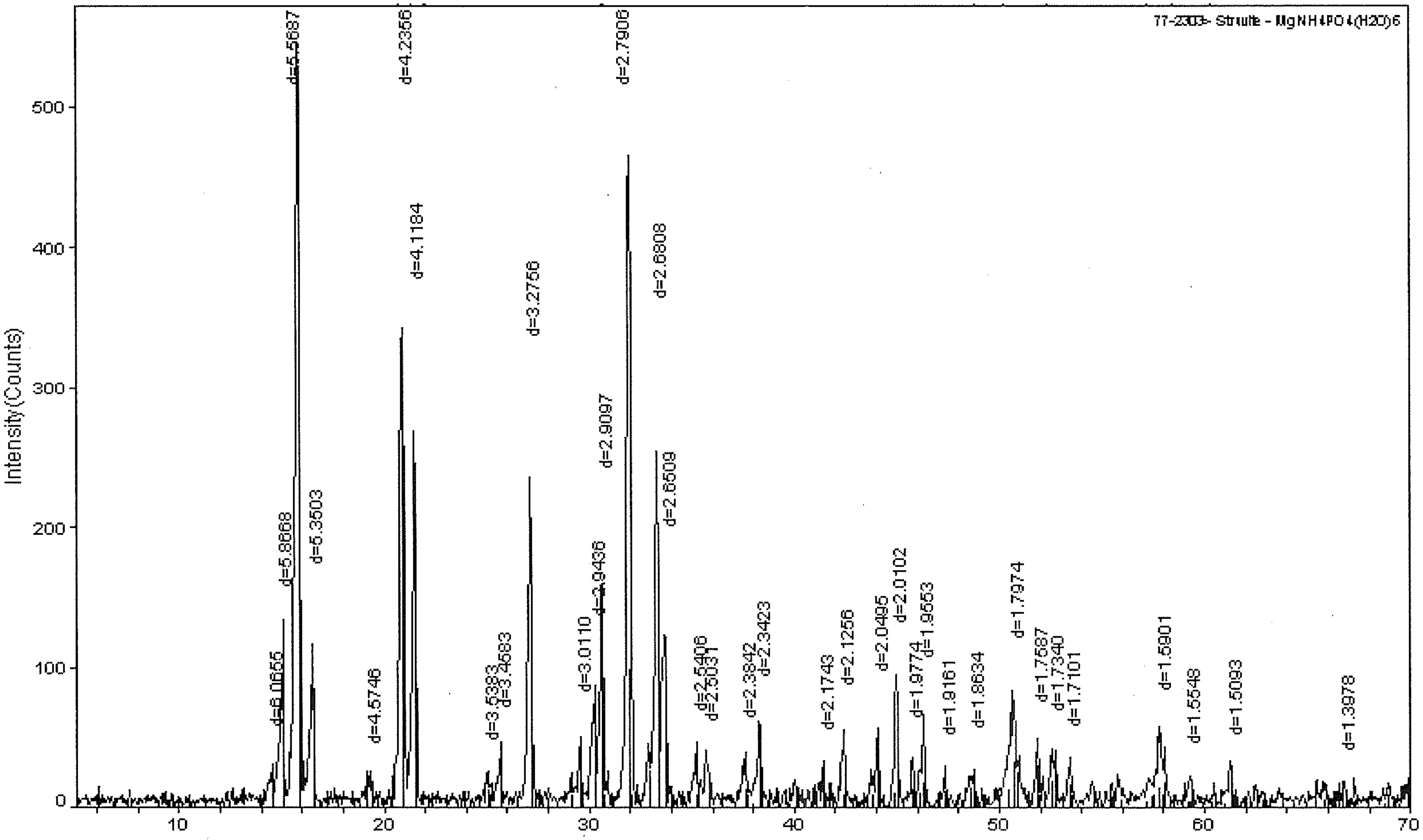

Figure C.3 XRD analysis of the precipitate collected from the molar ratio Experiment E19 of set 1

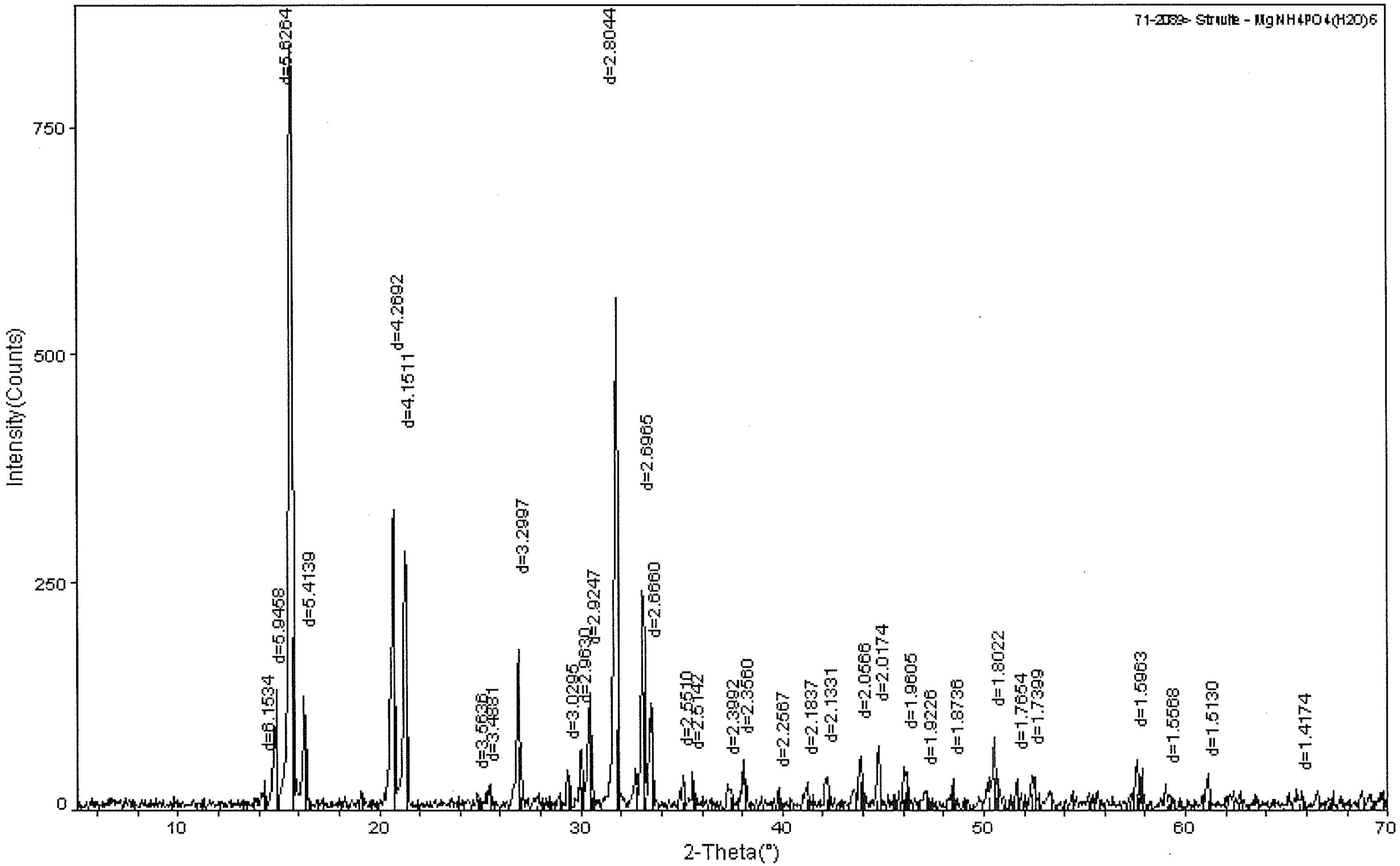

Figure C.4 XRD analysis of the precipitate collected from the molar ratio Experiment E21 of set 1

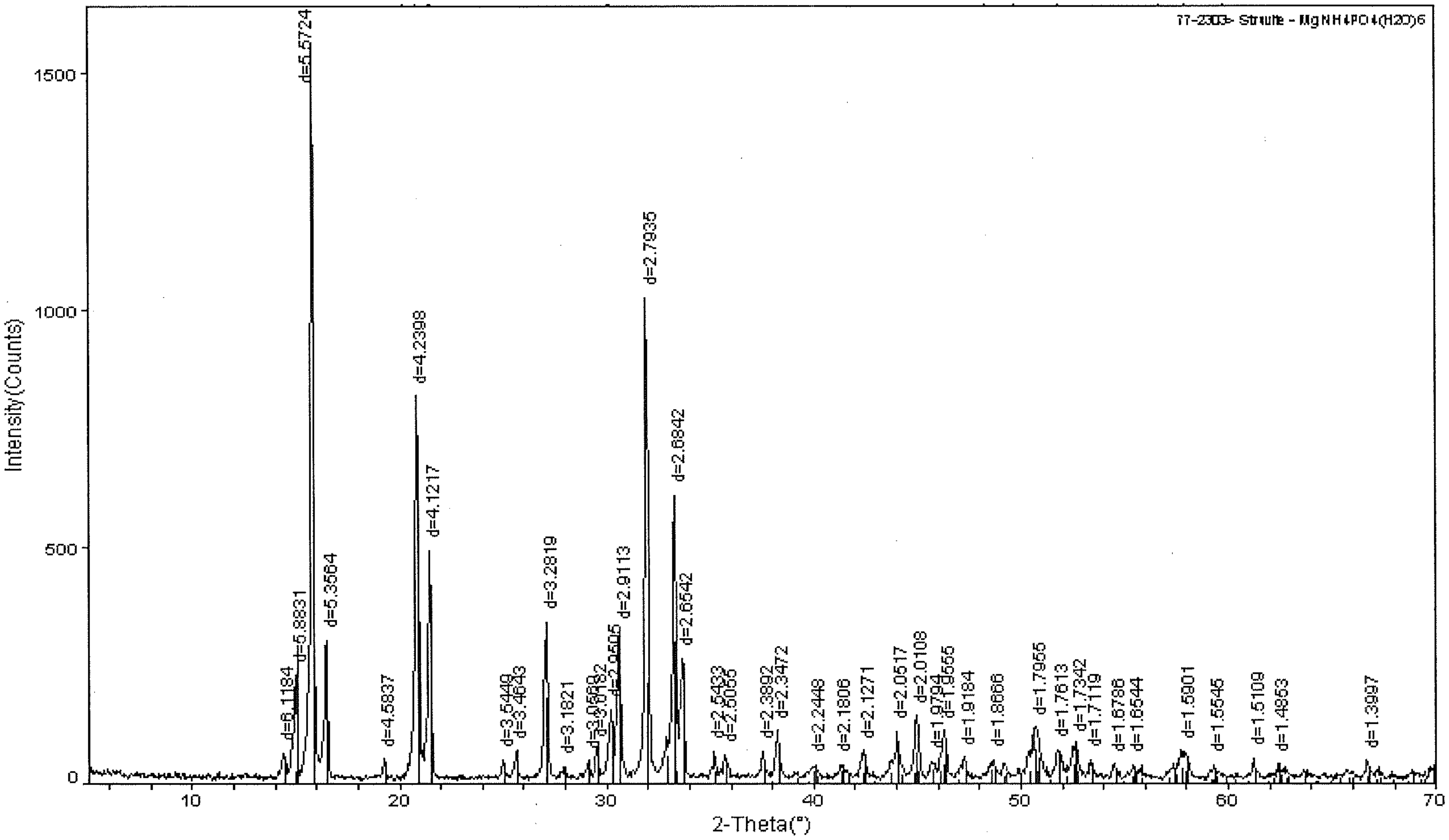

Figure C.5 XRD analysis of the precipitate collected from the pH Experiment E25 of set 1

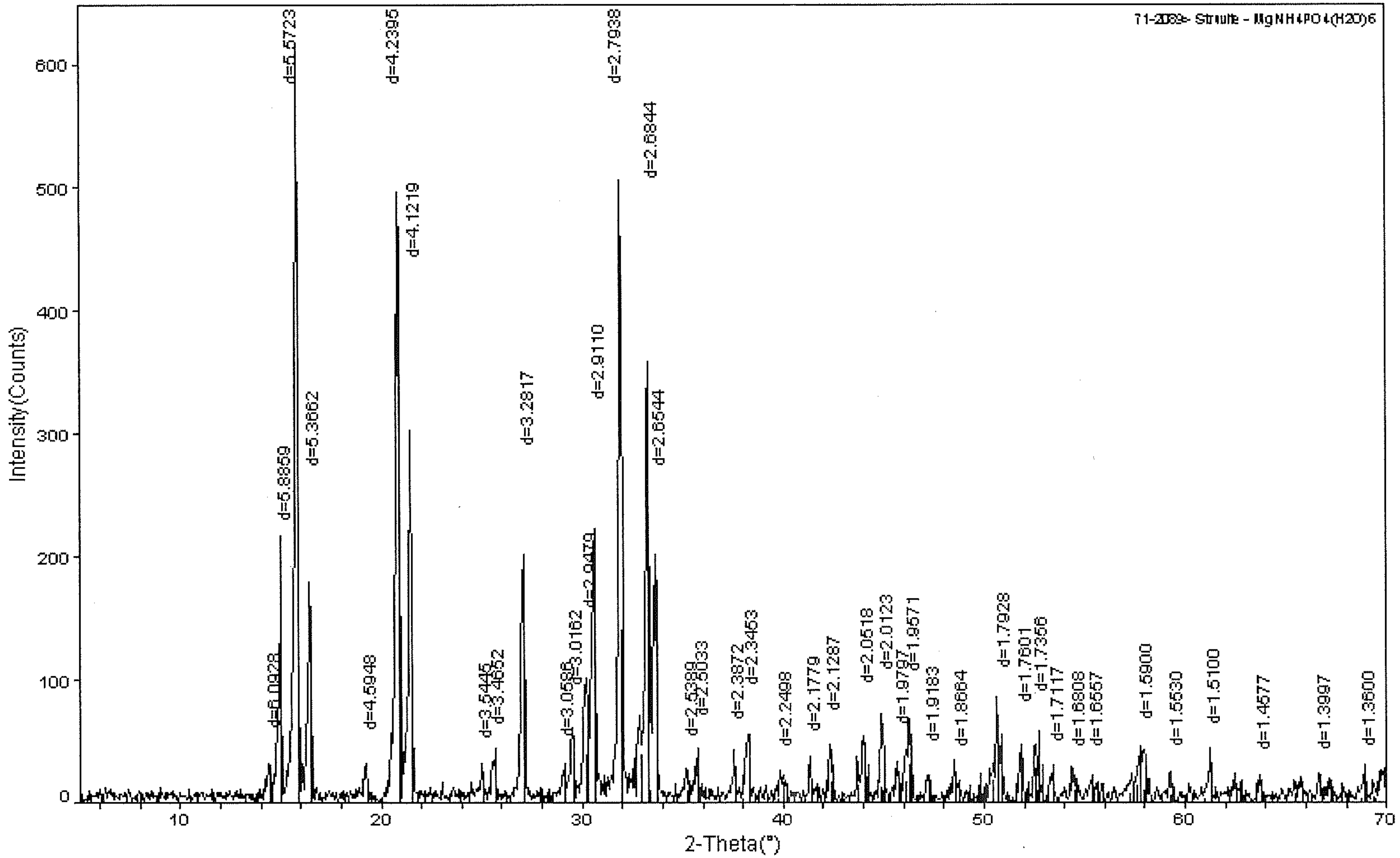

Figure C.6 XRD analysis of the precipitate collected from the pH Experiment E26 of set 1

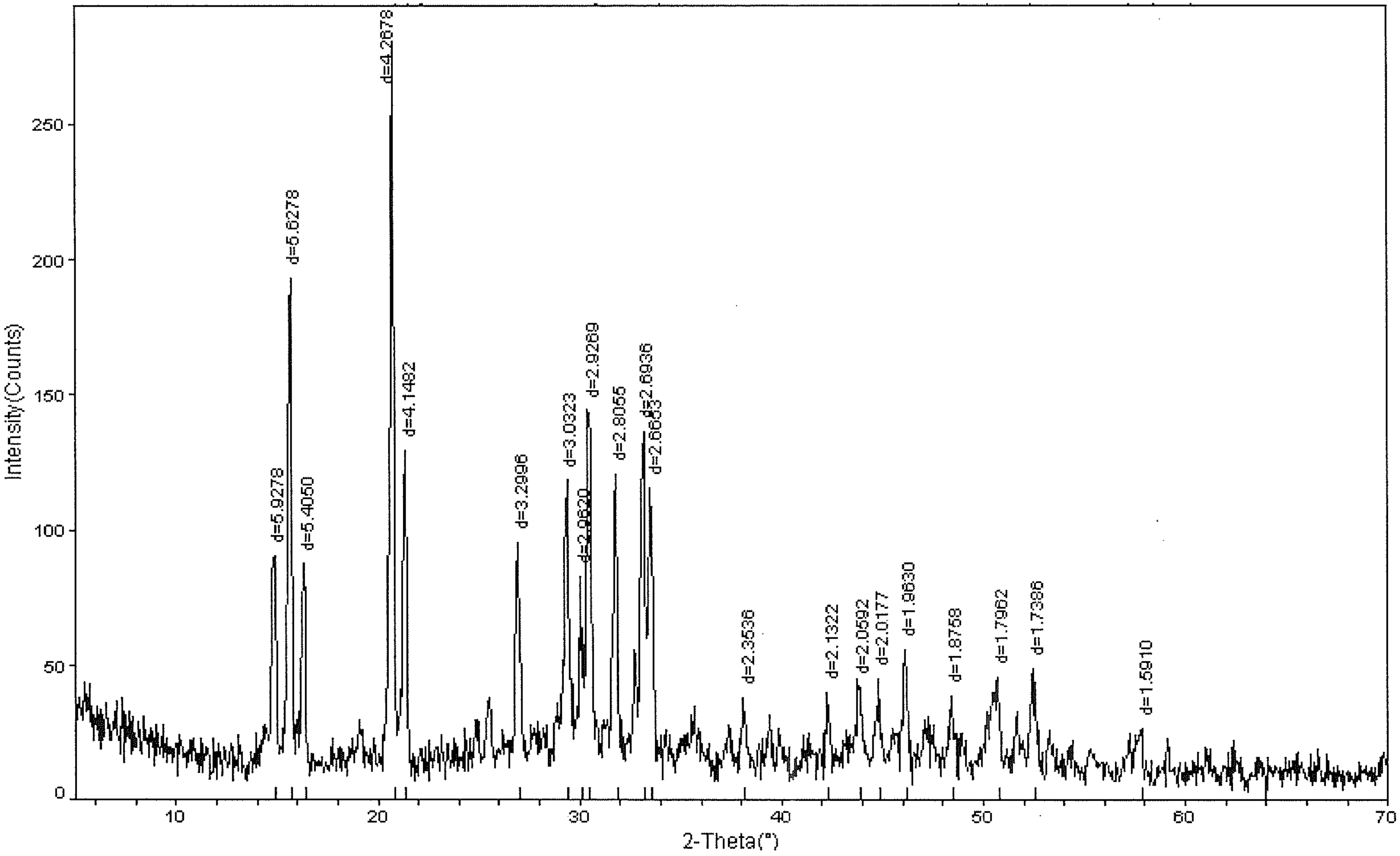

Figure C.7 XRD analysis of the precipitate collected from the calcium ion Experiment E33 of set 1

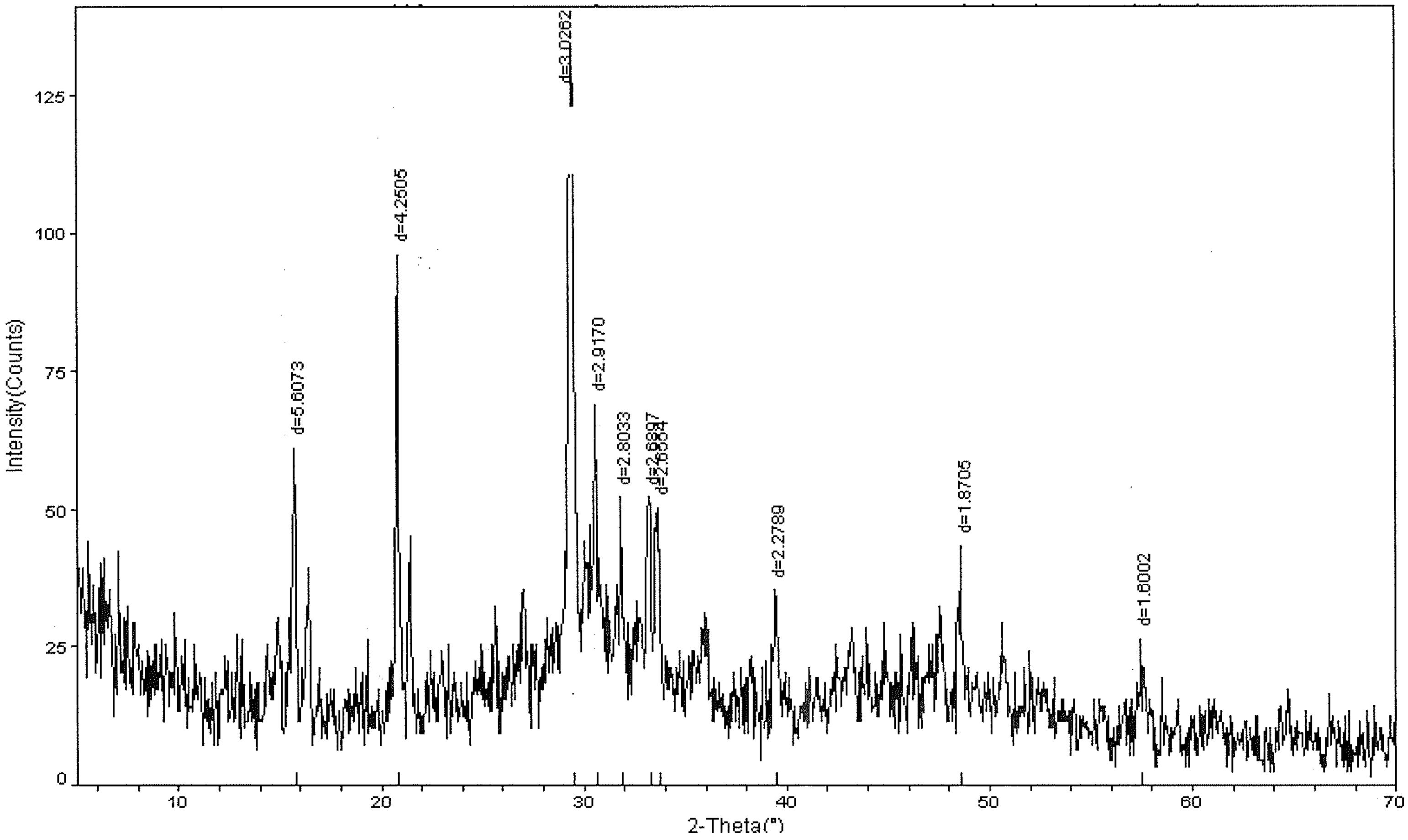

Figure C.8 XRD analysis of the precipitate collected from the calcium ion Experiment E34 of set 1

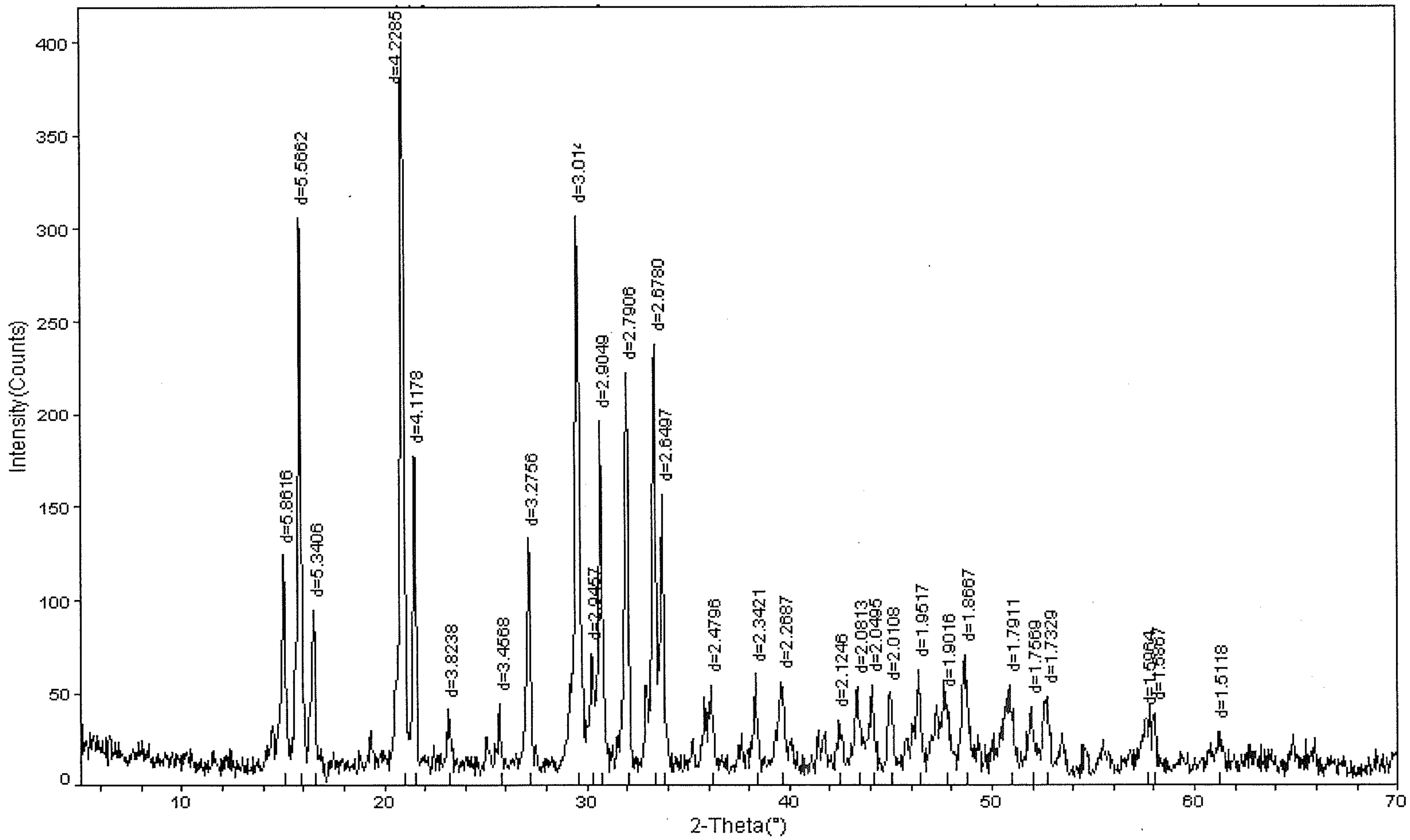

Figure C.9 XRD analysis of the precipitate collected from the calcium ion Experiment E35 of set1

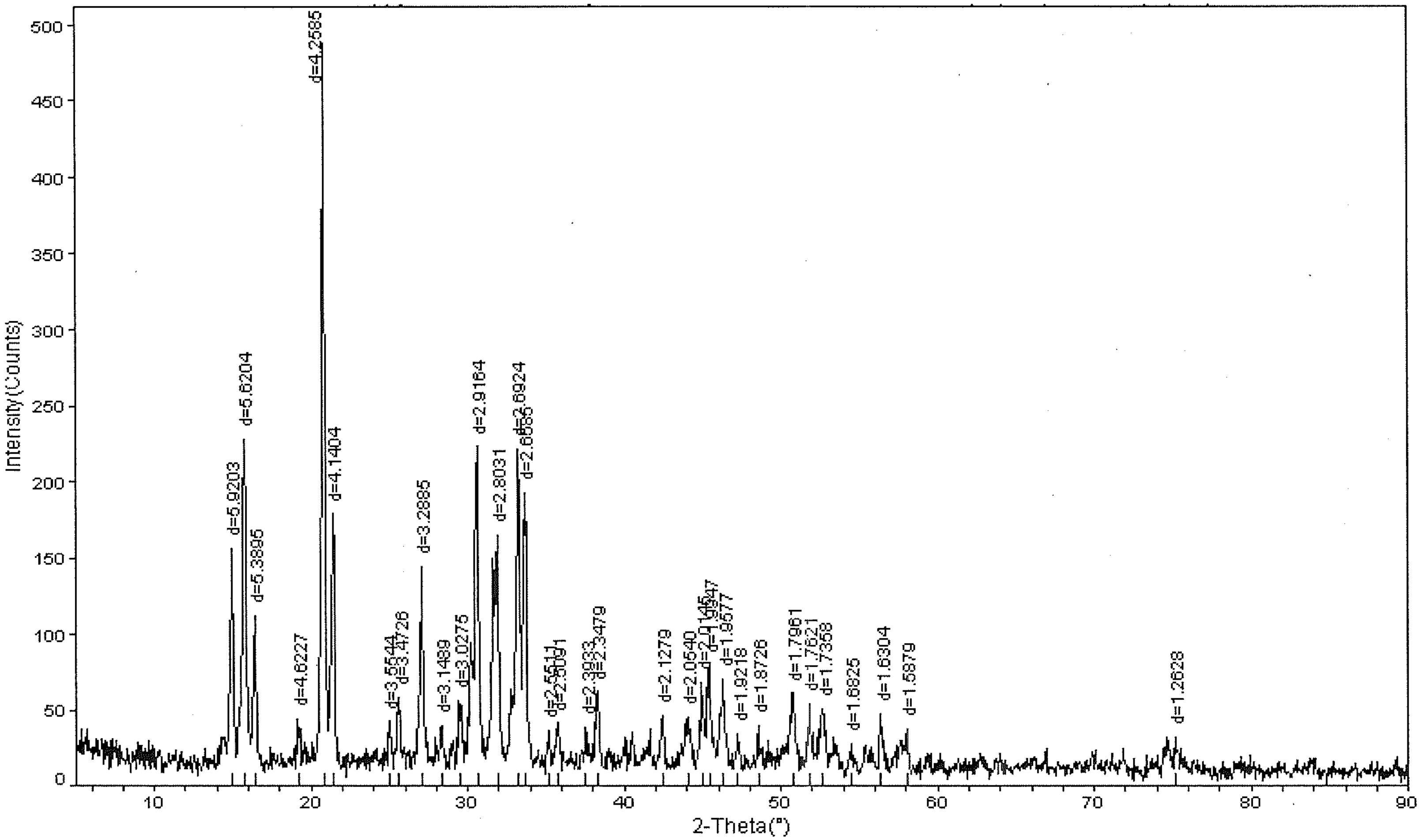

Figure C.10 XRD analysis of the precipitate collected from the Experiment FS-L6 of set 2

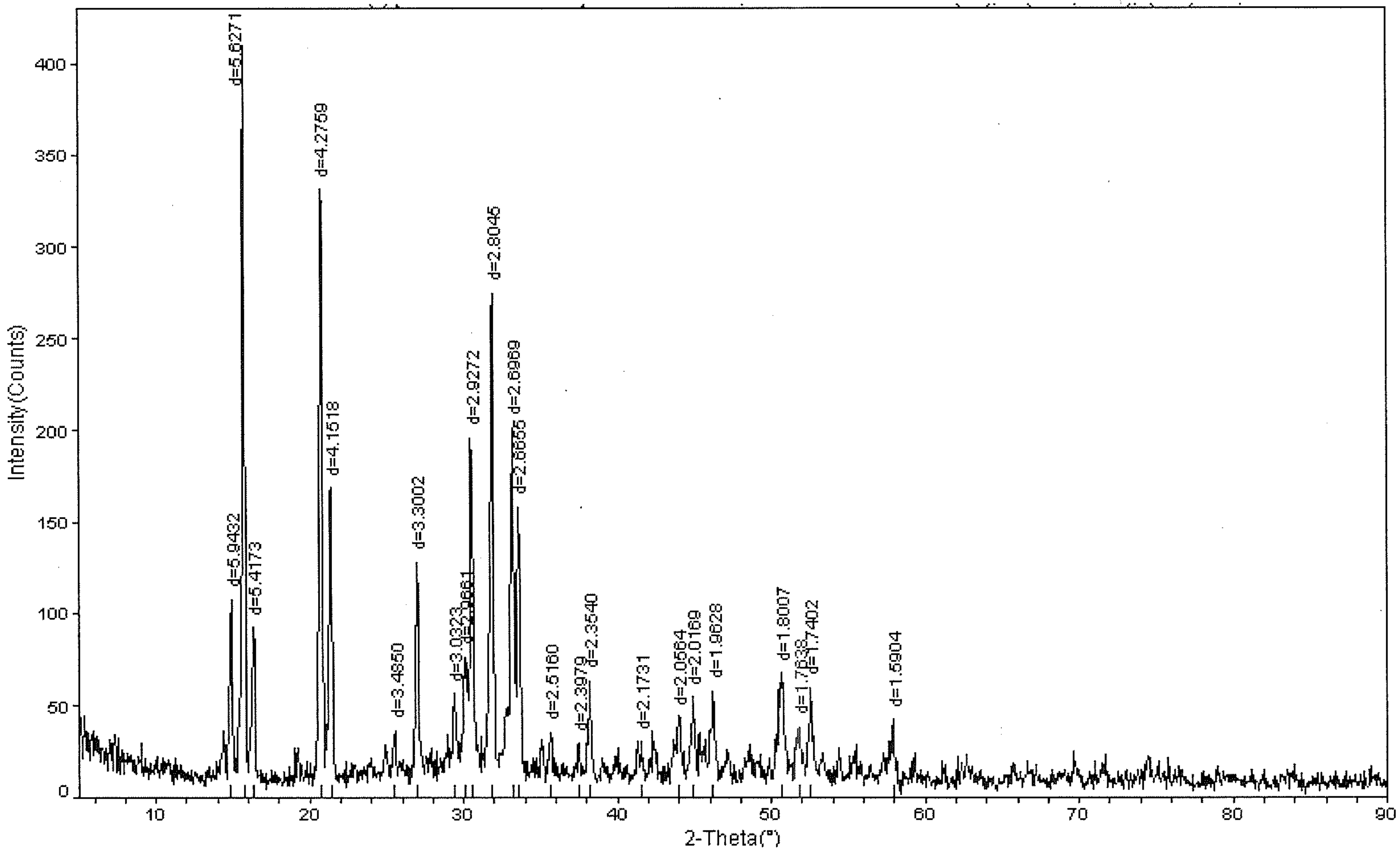

Figure C.11 XRD analysis of the precipitate collected from the Experiment FS-P1 of set 2

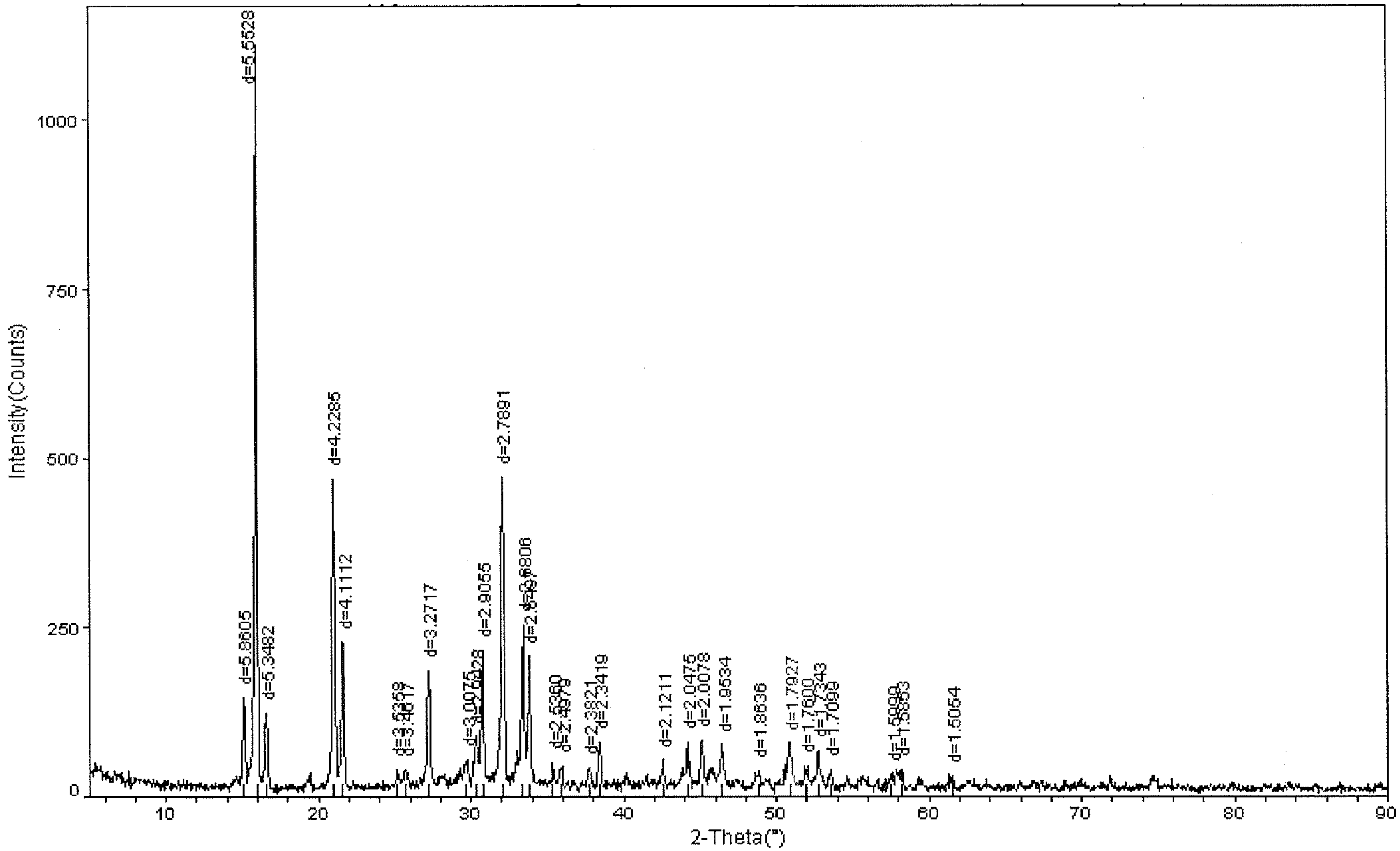

Figure C.12 XRD analysis of the precipitate collected from the Experiment FS-P3 of set 2

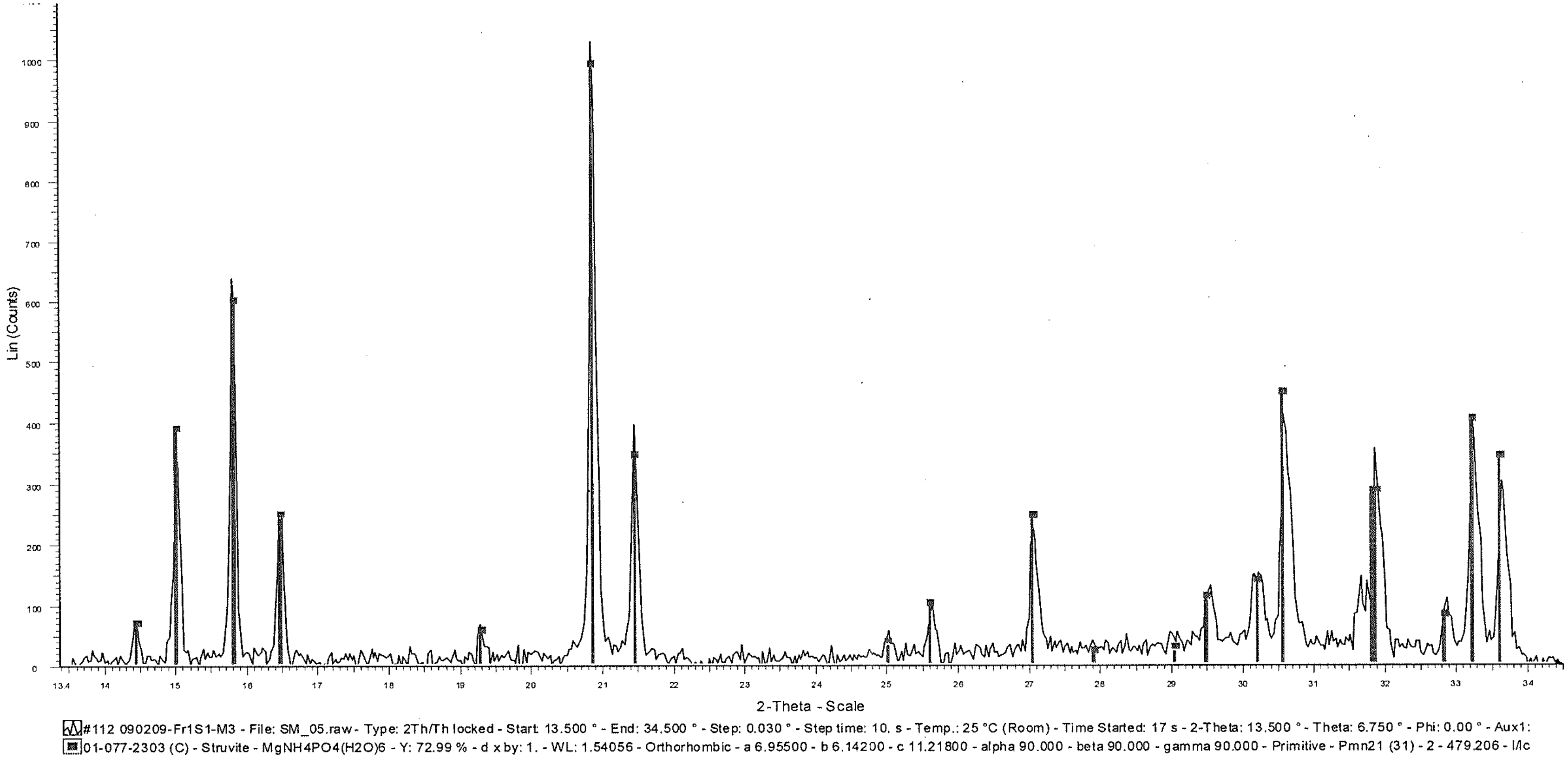

Figure C.13 XRD analysis of the precipitate collected from the Experiment FS-P6 of set 2

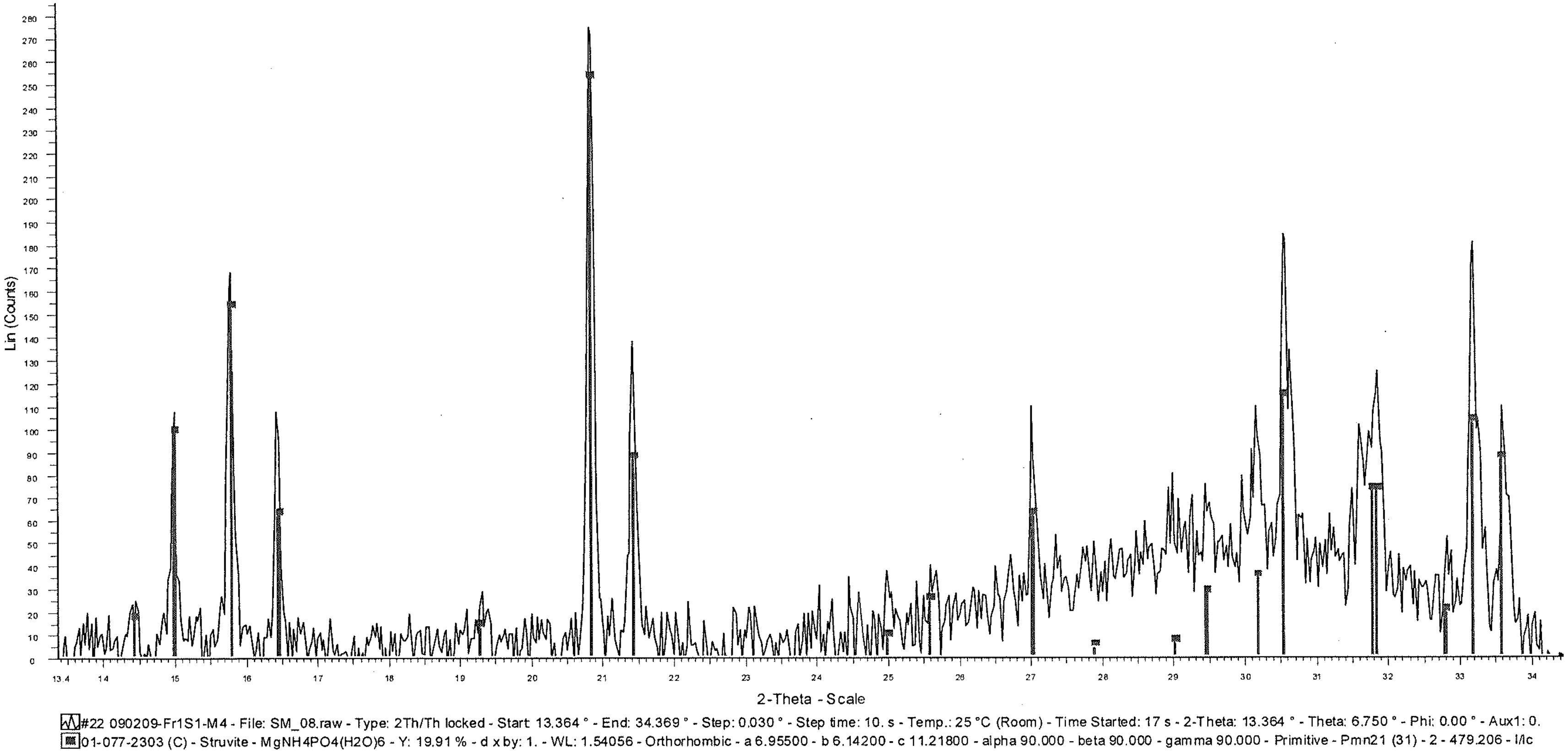

Figure C.14 XRD analysis of the precipitate collected from the Experiment FS-P8 of set 2

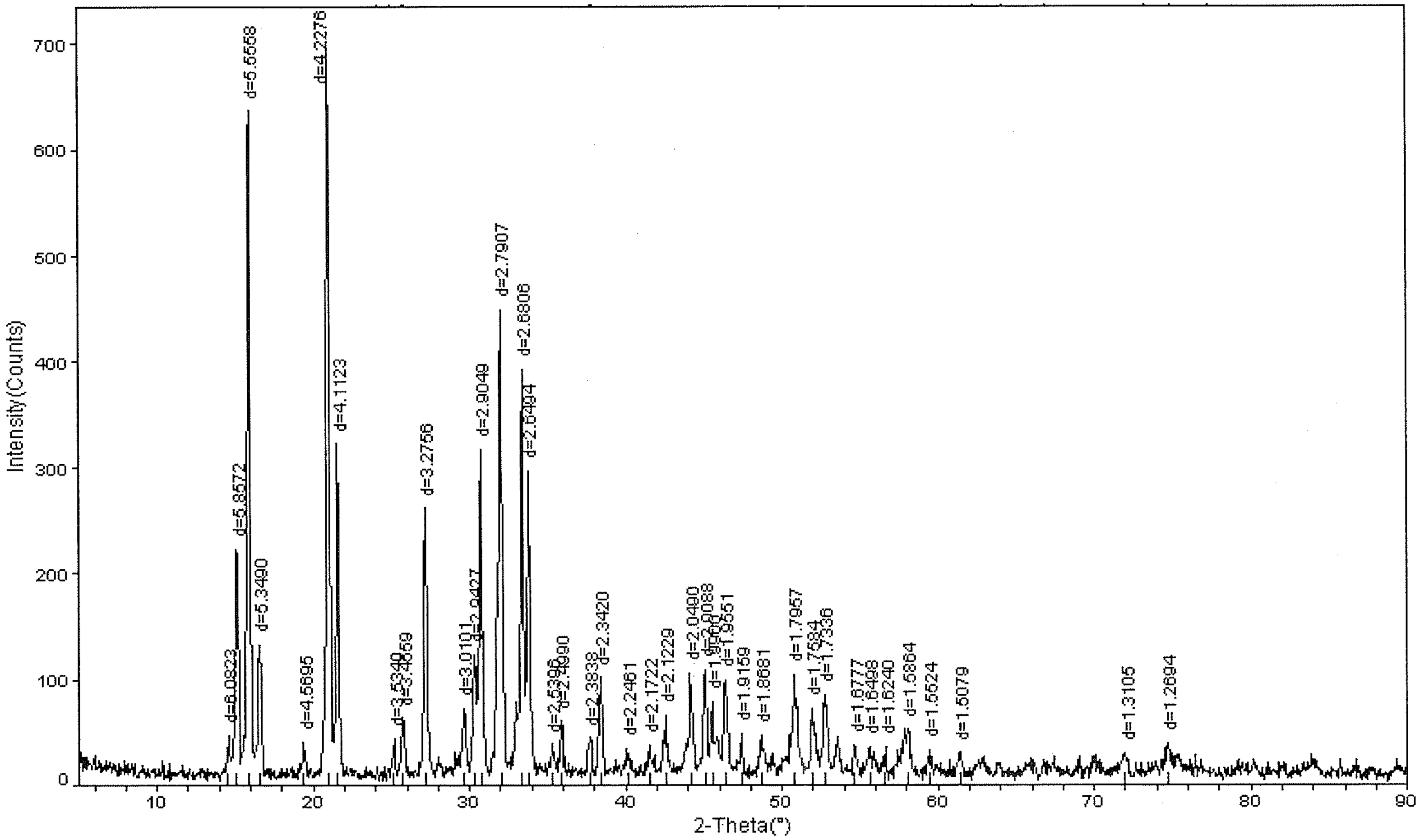

Figure C.15 XRD analysis of the precipitate collected from the Experiment MS-L2 of set 3

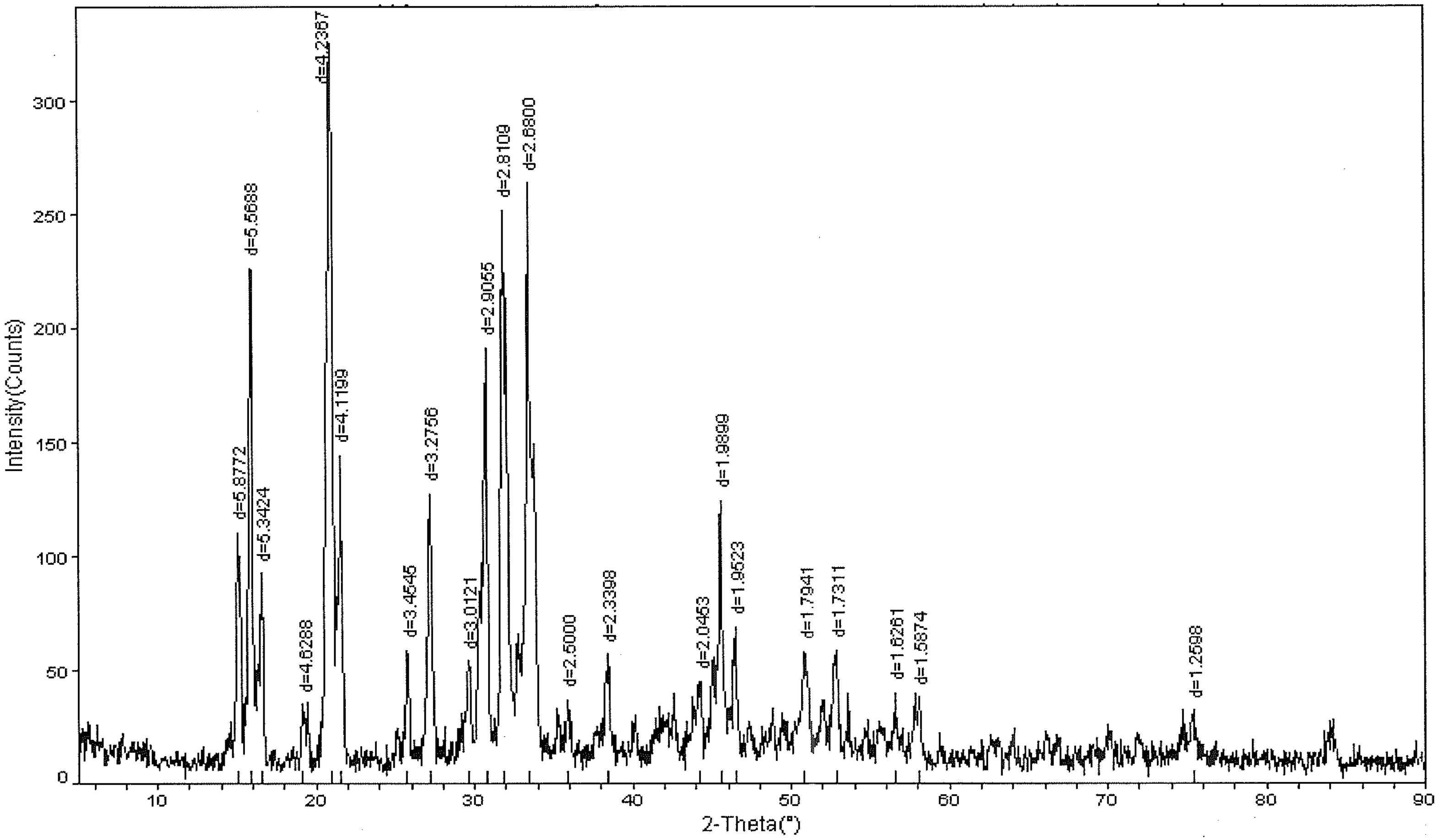

Figure C.16 XRD analysis of the precipitate collected from the Experiment MS-L5 of set 3

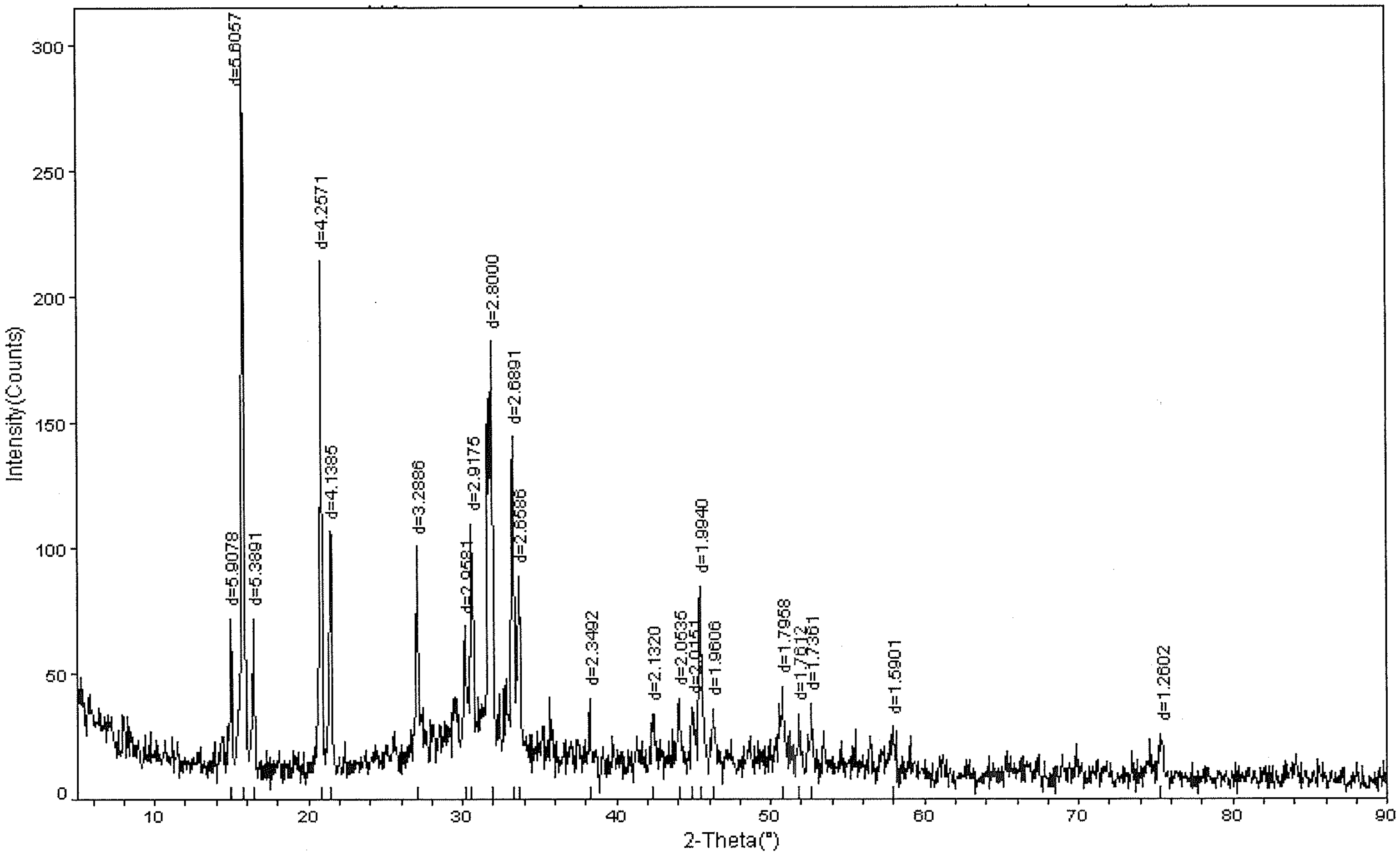

Figure C.17 XRD analysis of the precipitate collected from the Experiment MS-P1 of set 3

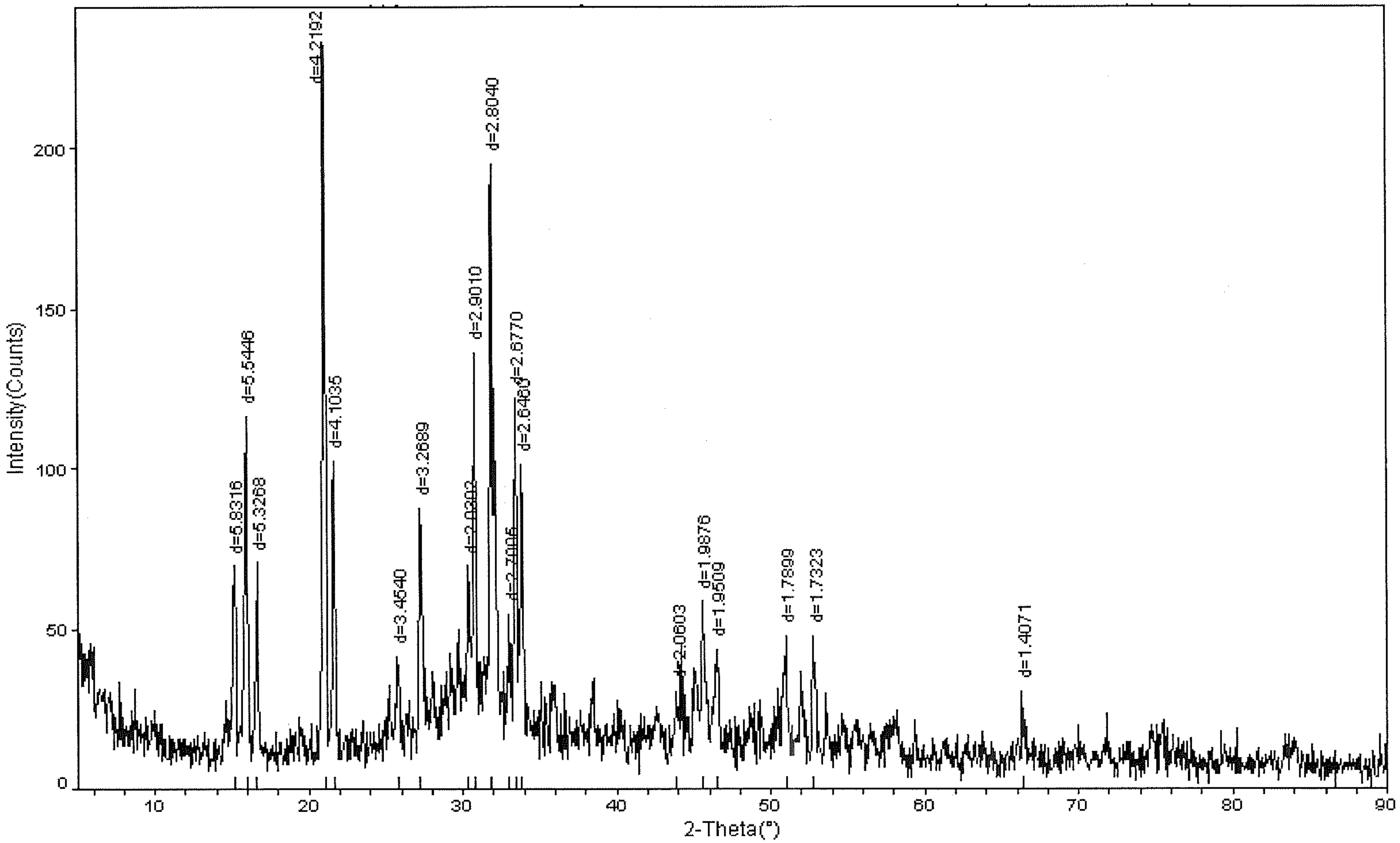

Figure C.18 XRD analysis of the precipitate collected from the Experiment MS-P3 of set 3

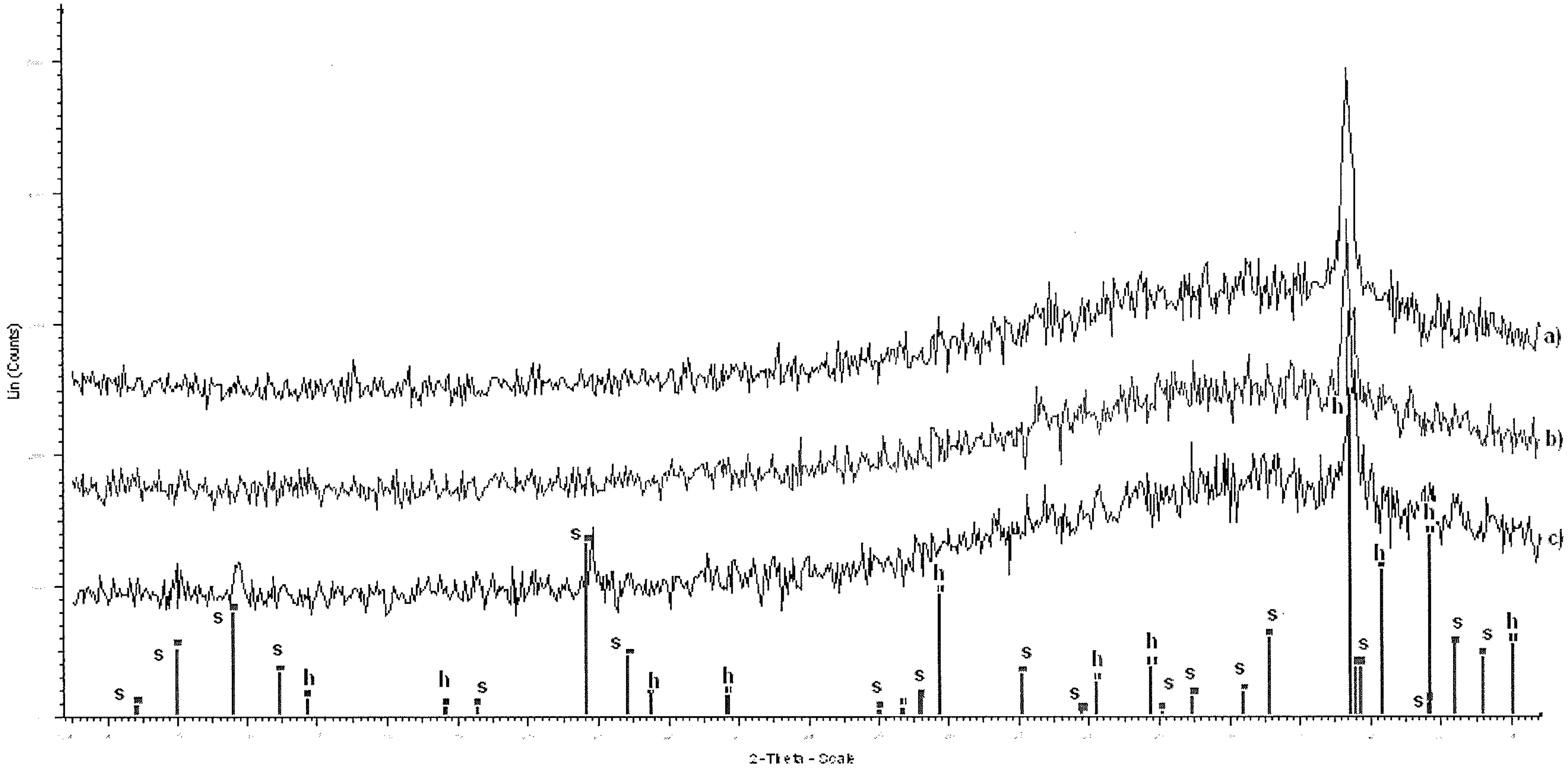

Figure C.19 XRD analysis of the precipitates collected from the a) Experiment FS-P8, b) Experiment FS-P5, c) Experiment FS-P6 of set 2 (s: struvite, h: hydroxylapatite)

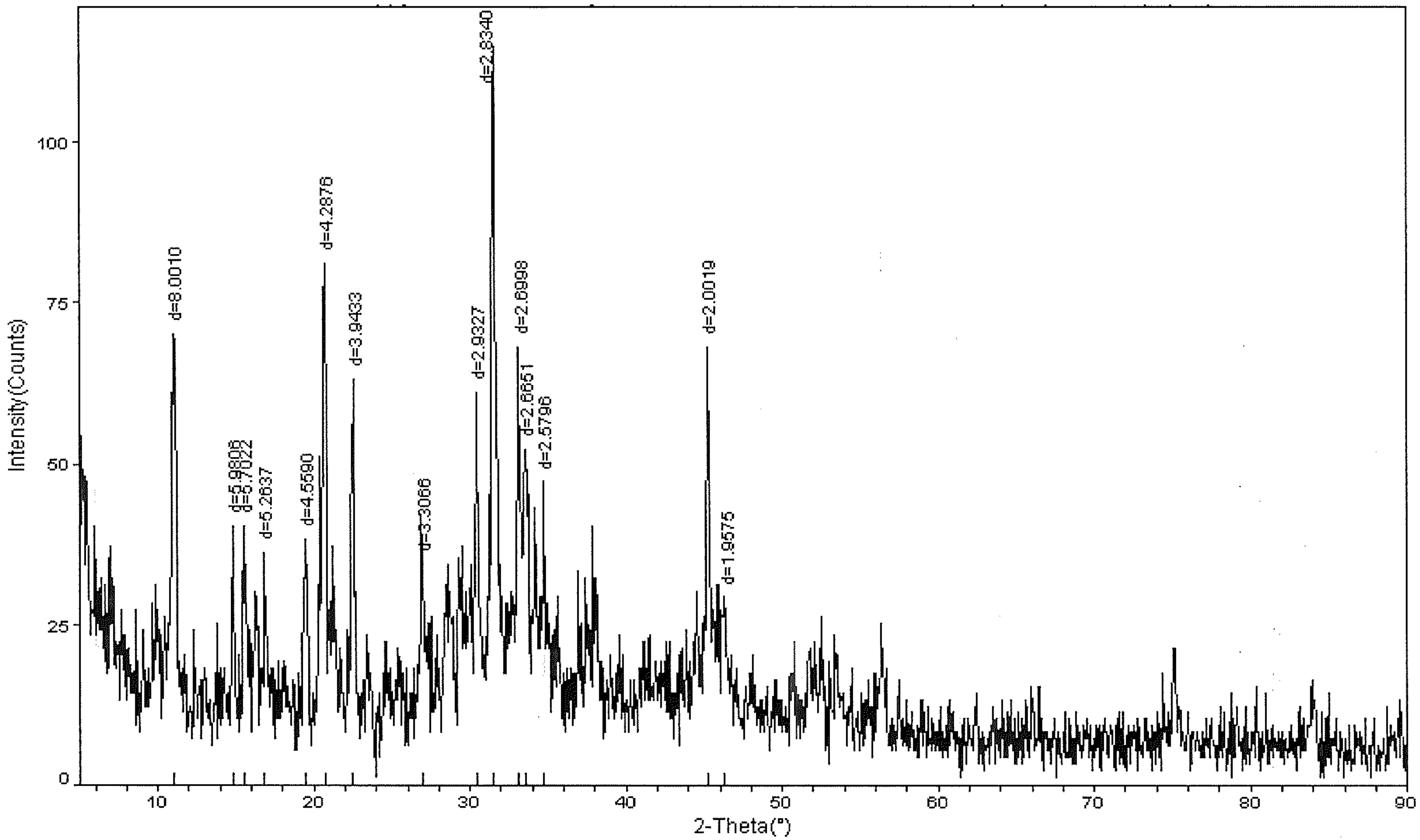

Figure C.20 XRD analysis of the precipitate collected from the Experiment MS-C3 of set 3