ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

INVESTIGATION OF PHOSPHORUS RECOVERY FROM ANAEROBIC DIGESTION SUPERNATANT OF DIVERSE WASTES :SAMSUN CASE STUDY

M.Sc. THESIS

Merve ATASOY

Department of Environmental Engineering

Environmental Biotechnology Programme

Thesis Advisor: Prof. Dr. Rüya TAŞLI

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

FARKLI ATIKLARIN ANAEROBİK ÇÜRÜTÜLMESİNİN ÜST SUYUNDAN FOSFORGERİ KAZANIMININ İNCELENMESİ : SAMSUN ÖRNEĞİ

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Merve Atasoy, a **M.Sc.** student of ITU **Graduate School of Science Engineering And Technology** student ID 501121821, successfully defended the **thesis** entitled **"INVESTIGATION OF PHOSPHORUS RECOVERY FROM ANAEROBIC DIGESTION SUPERNATANT OF DIVERSE WASTES : SAMSUN CASE STUDY "**, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : 4 May 2015
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To my family,

FOREWORD

I would like to deeply thank my supervisor Prof. Dr. Rüya Taşlı , for her support and patience in each step of this study. I am also greatful to Assist. Prof. Mahmut Altınbaş for his guidance, help and support during this research. Also, I want to express special thanks to Mehmet Akça for support at laboratory.
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May 2015

Merve ATASOY
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ABBREVIATIONS

EBPR	**:** Enhanced Biological Phosphorus Removal
NH_4 – N	**:** Ammonia Nitrogen
Orto – P	**:** Orthophoshate
PR	**:** Phosphate Rocks
TKN	**:** Total Kjeldahl Nitrogen
TN	**:** Total Nitrogen
TP	**:** Total Phosphorus
TS	**:** Total Solids
VFA	**:** Volatile Fatty Acid
VS	**:** Volatile Solids
WWTP	**:** Wastewater Treatment Plant

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INVESTIGATION OF PHOSPHORUS RECOVERY FROM ANAEROBIC DIGESTION SUPERNATANT OF DIVERSE WASTES : SAMSUN CASE STUDY

SUMMARY

Due to depleting phosphorus reserves and the nonrenewable and irreplaceable nature of phosphorus with another substance, phosphorus recovery has become increasingly important so as one of the significiant problems awaiting emerging solution.
Phosphorus is one of the building blocks of cells and essential for the sustainability of agricultural land as well as it is crucial for the continuation of the life cycle.
Beside of that phosphorus obtained from phosphorus rocks naturally, unnatural phosphorus cycle can also be considered as phosphorus source. Unnatural phosphorus cycle involves extensive applications in a variety of industries and products including detergents, fertilizers, paints, food and baverages, pharmaceuticals also human and animal excrement. Because this cycle is a valuable phosphorus resource, a significiant amount of phosphorus is recovered from this cycle as well as avoiding the excess phosphorus discharge to ecosystem. So, wastewater could be used as a major phosphorus resource.
The aim of this study is to recover phosphorus from anaerobic digester supernatant. In particular, studies showed that high amount of phosphorus could be recovered from enhanced biological phosphorus removal wastewater treatment plants with anaerobic digestion reactor.
Phosphorus recovery methods constitute the largest part of the crystallization process, which is addition of chemicals to the wastewater or sewage sludge, the precipitated phosphorus is provided. Product of recovered phosphorus has ability to be used as fertilizer on agricultural land.
In this study, phosphorus is recovered from the supernatant of an anaerobic digester as sutrivite precipitate. In order to increase both the amount of phosphorus recovered and biogas efficiency, various wastes (sewage sludge, municipal organic waste and leachate) were digested together anaerobically. After anaerobic digestion, phosphorus is recovered as struvite precipitation through pH adjustment with 0,1 M NaOH without any chemical addition. Phosphorus (total phosphorus and ortophosphate) and ammonia nitrogen were analyzed from anaerobic digester supernatant and struvite precipitate that is dissolved in acidic solution to measure the efficiency of recovered phosphorus. 77 % phosphorus recovery with struvite precipitation is achieved.
Although reserves of phosphate rocks have been run out speedily and various studies have been conducted about phosphorus recovery from wastewater treatment plants, current recovery technologies can not cope with the mining the phoshate rocks in terms of price. As well as necessitation of developments at phosphorus recovery studies, restricting phosphorus use to essential uses, improving the efficiency of phosphorus use and increasing the phosphorus recycling should be done.

FARKLI ATIKLARIN ANAEROBİK ÇÜRÜTÜLMESİNİN ÜST SUYUNDAN FOSFORGERİ KAZANIMININ İNCELENMESİ:SAMSUN ÖRNEĞİ

ÖZET

Fosfor rezervlerinin tükenmeye başlamasından ve fosforun yenilenemeyen ve yeri başka bir elementle doldurulamayan yapısından dolayı fosforun geri kazanımı giderek önem kazanan ve çözüm bekleyen önemli problemlerden biridir.

Hücrenin yapı taşlarından birisi olan ve tarım arazilerinin sürdürülebilirliği için büyük önem arz eden fosfor, aynı zamanda yaşam döngüsünün devamlılığı için zorunludur.

Fosforun, doğal kaynağı olan fosfor rezervlerinden çıkarılmasının yanısıra doğal olmayan fosfor döngüsü de fosfor için önemli bir kaynak olarak görülebilir. Doğadaki fosfor döngüsü, karada ve denizde olmak üzere iki ekosistemde gerçekleşmektedir. Ayrıca, bir çok endüstride geniş uygulama alanları olan ve deterjan, gübre, boya, gıda, içki, ilaç gibi ürünlerin yanısıra insan ve hayvan dışkısında bulunan fosfor, doğal olmayan fosfor döngüsünü oluşturmaktadır. Önemli miktarda fosforun bu değerli fosfor kaynağından geri kazanılması ile fazla fosforun ekosisteme deşarjı da önlenebilir. Böylece atıksu, önemli bir fosfor kaynağı olarak kullanılabilir.

Bu çalışmanın amacı, büyük ölçekli olarak uygulanacak bir arıtma çamurunun farklı atıklarla karıştırılıp, anaerobik olarak çürütülmesine dayanan projenin laboratuvar ölçekli halinin incelenmesidir. Çalışma genel olarak, ileri biyolojik atıksu arıtma tesisinden alınacak arıtma çamurunun, katı atık düzenli depolama sahasının girişinden alınacak evsel organik atık ve aynı tesiste oluşan sızıntı suyunun, bir arada anaerobik olarak parçalanmasına dayanmaktadır. Anaerobik parçalanma sonucunda, atık, susuzlaştırma ünitesine gelerek, katı kısım kompost tesisine, sıvı kısımın ise %67' si anaerobik çürütücü girişine geri devredilecek, kalan %33' lük kısım ise sızıntı suyu arıtma tesisine gönderilecektir. Bu çalışmanın asıl amacı ise tüm atıkların beraber anaerobik olarak çürütülmesi sonucunda, çamur çürütücüsü üst suyundan fosfor geri kazanım veriminin incelenmesidir. Fosfor konsantrasyonunun yüksek olduğu atıksu arıtma tesislerinin arıtma çamurları, fosfor geri kazanımı için önemli bir kaynaktır. Bu alandaki çalışmalar, özellikle ileri biyolojik fosfor giderimi ile anerobik çürütücü içeren atıksu arıtma tesislerinden yüksek miktarda fosfor geri kazanılabileceğini göstermiştir.

Fosfor geri kazanım metodlarının büyük bir kısmı, atıksuya veya arıtma çamuruna kimyasal ilave edilerek fosforun çöktürülmesi işlemi olan kristalleştirme metoduna dayanmaktadır. Kristalleştirme metodu; atıksuya veya arıtma çamuruna kimyasal ilave ederek, ortamdaki fosforun çökmesi prensibine dayanmaktadır. Çöktürme sonucunda, fosfor, ya strüvit denilen; azot, magnezyum, fosfor içeriğine sahip bir bileşik oluşturmakta ya da kalsiyum ile bileşik oluşturarak çökelmektedir. Ancak, kalsiyumun genellikle ortamda yeterli miktarda bulunmayışı ve dışarıdan ilave edilmesinin maliyeti arttırması nedeniyle strüvit çöktürmesi çok daha fazla kullanılan bir yöntem olmuştur. Ayrıca, strüvit yöntemi ile geri kazanılan fosfor, direk olarak tarım arazilerinde gübre olarak kullanılabilmektedir. Bu nedenle, bu çalışmada da strüvit çöktürmesi kullanılacaktır.

Bu çalışmada, hem geri kazanılan fosfor miktarını hem de anaerobik çürütücünün biyogaz verimini arttırmak amacıyla, çeşitli atıklar (arıtma çamuru, organik atık ve sızıntı suyu) anaerobik olarak birlikte çürütülmüştür. Anaerobik çürütme, 250 ml' lik şeffaf şişelerde, 37°C' de elli gün boyunca, her gün şişelerin basınçları ölçülerek takip edilmiştir. Anaerobik çürümenin gerçekleştiği beş şişeden, ilk üç şişe, atıkların

tamamını, belli oranlarda (%11 arıtma çamuru, %11 sızıntı suyu, %11 evsel organik atık ve %67 aşı çamuru) içermekte, kalan iki şişe ise aşı çamurunun takibi amacıyla yalnızca (%100 aşı çamuru) aşı çamurundan oluşmaktadır. Anaerobik çürüme verimi, hem ölçülen gaz miktarının, ideal gaz yasasına göre, biyogazın molar oranı hesaplanarak hem de birinci gün ve ellinci günde, karışımın toplam katı ve uçucu katı içeriği ölçülerek, takip edilmiştir. Atıkların anaerobik olarak çürütülmesi sonucunda, tüm atıkların belirli oranlarda bulunduğu, birinci, ikinci ve üçüncü şişelerde, ortalama olarak %44 uçucu katı maddenin çürümesi sağlanmıştır. Bunun yanı sıra, anaerobik çürütmenin ellinci gününde, kümülatif biyogaz miktarı 850 ml hacime ulaşmıştır.

Anaerobik çürütmenin ardından, dışarıdan kimyasal eklenmeden yalnızca 0,1 M NaOH ilavesiyle pH ayarlanarak, fosfor strüvit çöktürmesiyle geri kazanılmıştır. Strüvit çöktürmesine etki eden en önemli noktalardan birisi pH' dır. Ve bu çalışmada, üç farklı pH aralığı (pH: 8,8; pH: 9,8 ve pH: 10,8) kullanılarak, çöken strüvit miktarı incelenmiştir. Çökelmenin en fazla olduğu, pH: 9,8' de, 100 ml anaerobik çamur çürütücüsü üst suyundan, 8,26 gram strüvit elde edilmiştir. Geri kazanılan fosforun verimini bulmak amacıyla fosfor (toplam fosfor ve ortofosfat) ve amonyum azotu, anaerobik çürütücünün üst suyunda ve çöktürülen strüvitin asidik çözeltide çözündürülmesi ile elde edilen solüsyonda, analiz edilmiştir.

Fosfor geri kazanımının yanı sıra, çalışmanın diğer bir önemli noktası; Samsun Doğu İleri Biyolojik Atıksu Arıtma Tesisi' nin anaerobik çamur çürütücüsünün girişinden alınan arıtma çamurlarının, aynı şekilde Samsun Avdan Enerji Düzenli Katı Atık Depolama Tesisi' nden alınan evsel organik atık ve sızıntı suyu ile beraber anaerobik olarak çürütülmesidir. Bu çürütme ile hem arıtımı zor olan atıkların bertarafı mümkün olmuş hem de bu arıtmadan biyogaz elde edilmiştir. Fosfor geri kazanım potansiyeli ve anerobik çürütücünün biyogaz üretim verimini incelemek amacıyla; anaerobik çürütücü kurulmadan önce tüm atıklarda, çürütücünün kurulduğu birinci gün karışımda, anaerobik çürümenin stabil hale geldiği ellinci günde karışımda, struvit çöktürmesinden elde edilen çökeltinin asidik solüsyonda çözülmesi ile elde edilen sıvıda ve çöktürmeden arta kalan filtratta; toplam katı madde, uçucu katı madde, toplam fosfor, orto – fosfat, toplam kjeldahl azotu ve amonyum azotu analizleri yapılmıştır. Yapılan analizler sonucunda, atıkların oluşturduğu karışımda (birinci, ikinci ve üçüncü şişelerde), anaerobik çürütme ile girişteki toplam fosforun %50' si, orto – fosfatın %77' si giderilmiştir. Bununla beraber, çamur çürütücüsü üst suyunda yapılan strüvit çöktürmesi ile %75,7 toplam fosfor, %75 orto – fosfat strüvit olarak geri kazanılmıştır.

Deneysel analizlerin dışında, atıkların karakterizasyon değerleri kullanılarak, anaerobik çürütücünün birinci ve ellinci gün değerleri teorik olarak da hesaplanmıştır.

Karadeniz Bölgesinin en büyük atıksu arıtma tesisi olan, Samsun Doğu İleri Biyolojik Atıksu Arıtma Tesisi, biyolojik olarak azot ve fosforu arıtan proseslere sahiptir. Ön arıtma ve biyolojik arıtma sonucunda, birincil çöktürme ve son çöktürme tanklarından elde edilen arıtma çamurları, anaerobik olarak çürütülmektedir. Arıtılan atıksu ise derin deniz deşarjı ile yeniden doğaya dönmektedir. Çalışmada, numunesi kullanılan diğer bir tesis ise; Samsun Avdan Enerji Düzenli Katı Atık Depolama Tesisi' dir ve hem Samsun İlinden hem de çevre illerden toplanan evsel katı atıkların düzenli depolama ile uzaklaştırıldığı bir tesistir.

Fosfat kayaçlarının hızla tükenmesi ve fosforun atıksudan geri kazanımı üzerine bir çok çalışma yürütülmesine karşın varolan geri kazanım teknolojileri, fosfat rezervleriden elde edilen fosforun maliyetinden çok daha yüksektir. Dolayısıyla, fosfor

geri kazanım çalışmalarının geliştirilmesinin zorunlu olmasının yanı sıra fosforun kullanımına kısıtlamalar getirilmeli, fosfor kullanım verimi yükseltilmeli ve ekonomide fosforun geri dönüşümü arttırılmalıdır. Aynı zamanda, fosfor geri kazanımında kullanılan kimyasal maddeler hem maliyeti yükseltmekte hem de fosfor geri kazanımını sınırlamaktadırlar. Bu nedenle, yeni teknolojilerin, kimyasal kullanımını en aza indirmesi gerekmektedir. Bu da; ihtiyaç duyulan kimyasal maddelerin atıklardan sağlanması ile mümkün olacaktır. Bu çalışmanın amaçlarından birisi de, yüksek azot içeriğine sahip sızıntı sularının, strüvit çöktürmesinde gerekli olan azot, magnezyum ve fosfat molar oranının 1:1:1 olmasını sağlamaktır. Sızıntı suyu kullanımı, gerekli olan azot miktarını karşılamakla kalmayıp, sızıntı sularının arıtımının da anaerobik olarak gerçekleşmesine olanak vermiştir. Aynı şekilde, çalışmada kullanılan evsel organik atıkların hem fosfor hem de organik madde içeriğinin zengin oluşu, anaerobik arıtmanın biyogaz üretim potansiyelini arttırmak ve fosfor konsantrasyonunu yükseltmekle kalmayıp, bu atıkların arıtımını da sağlamıştır.

1. INTRODUCTION

"We may be able to substitute

nuclear power for coal,

and plastics for wood,

and yeast for meat,

and friendliness for isolation,

but for phosphorus there is neither substitute nor replacement "

Isaac Asimov (1920 bis 1992)

First published 1959 (Life's bottleneck)

Beside of phosphorus is the fundamental part of the biochemical reactions in nature, it is an essential nutrient as a fertilizer in agriculture. Nevertheless, remaining phosphorus rock reserves will diminish in 50 – 100 years (Steen, I., 1998). Hence, we need to recover phosphorus as much as possible. One of the main sources of phosphorus is wastewater containing human excrement and detergents. Phosphorus recovery from wastewater not only ensures the sustainability of the phosphorus but also improves biological nutrient removal operations and reduces the amount of the sewage sludge.

1.1 Aim of The Thesis

In recent years, few studies have been conducted for phosphorus recovery from wastewater treatment plants cause of that phosophorus is an irreplaceable and non – renewable element and it's reserves have began to run out. Additionaly, wastewater is a valuable phosphorus source due to it contains high amount phosphorus via human excreta and detergent. Therefore, aim of the thesis is to evaluate the phosphorus recovery systems and find out the potentially amount

of phosphorus recovery from anaerobic digester supernatant that consist of municipal organic waste, leachate and sewage sludge.

1.2 Scope of the Thesis

The major objective of this study is to evaluate the phosphorus recovery as struvite precipitation from anaerobic digester supernatant, for this purpose a lab scale anaerobic digester containing municipal organic waste, leachate and sewage sludge which have high amount of phosphorus contents was conducted 50 days. The thesis consists of 5 parts. In the first part, aim and scope of the thesis are briefly explained. Second part is consisted of literature review with three parts mainly, which are phosphorus recovery, anaerobic digester and applications of phosphorus recovery from anaerobic digester supernatant. Material and methods are defined at the third part, This part presents the methodology of experiments and descriptions of operating conditions. In addition, the forth part involves results of the potential phosphorus recovery via struvite precipitation and performance of anaerobic digester in terms of solids removal, biogas production and process stability. Conclusions and recommendations for future study are presented in the fifth part.

2. LITERATURE REVIEW

Phosphorus (P) is an essential nutrient for all life forms, which includes:

- Key player in fundamental biochemical reactions that occurs in enzymes which catalyze chemical reactions of biosynthesis (Tisdale et al., 1985),
- A part of genetic materials (DNA, RNA) which form the backbones of nucleic acids and imparts structure to the molecules,
- The key element of the energy supplier ATP (adenosine triphosphate) is a nucleotide which is involved in intracellular energy generated during photosyentesis abd respiration; the energy is used in other bioprocesses,
- In structural support of organisms provided by membranes (phospholipids) is important in the formation of biological membranes and in some signal transduction pathway,
- A compound of bone and teeth of of animal's structure (the bio mineral hydroxyapatite)

Beside these functions, a sufficient amount of phosphorus is essential for growth and development of all organisims. Plants, animals and bacteria are dependent on a reliable access to phosphorus to thrive we get our phosphorus through the food we eat. Thus, phosphorus is an important part of food chain too.

As a vital cell component, phosphorus can not be replaced by any other element. At the same time, phosphorus has found extensive applications in a variety of industries and products including detergents, fertilizers, paints, food and baverages, pharmaceuticals (Cisse and Mrabet, 2004). For these reasons, phosphorus needs to be recovered for sustainability of life cycle.

2.1 Phosphorus Cyle

Phosphorus passes through several interconnected cycles in nature. There are two main cyclesthat are organic and inorganic phosphorus cycles. Inorganic cycle can be described as a global cycle that involves four major components (K.C. Ruttenberg, 2003).

- Techtonic uplift and exposure of phosphorus – bearing rocks to the forces of weathering,
- Physical erosion and chemical weathering of rocks producing soils and providing dissolved particulate phosphorus to rivers,
- Riverine transport of phosphporus to lakes and the ocean,
- Sedimentation of phosphorus associated with organic and mineral matter and burial in sediments.

The cycle begins anew with uplift of sediments into the weathering regime. Briefly, the inorganic cycle (Fig. 2.1) describes the cycle from erosion, transport to the oceans, sedimentation, tectonic uplift and alteration of phosphate – containing rocks into plant – available phosphates in soil (Emsley, 1980; Filipelli, 2002). This cycle time is several million years in human spaces of times phosphate transported into the oceans can be considered as "lost" for agricultural use (P. Cornel and C. Shaum, 2009).

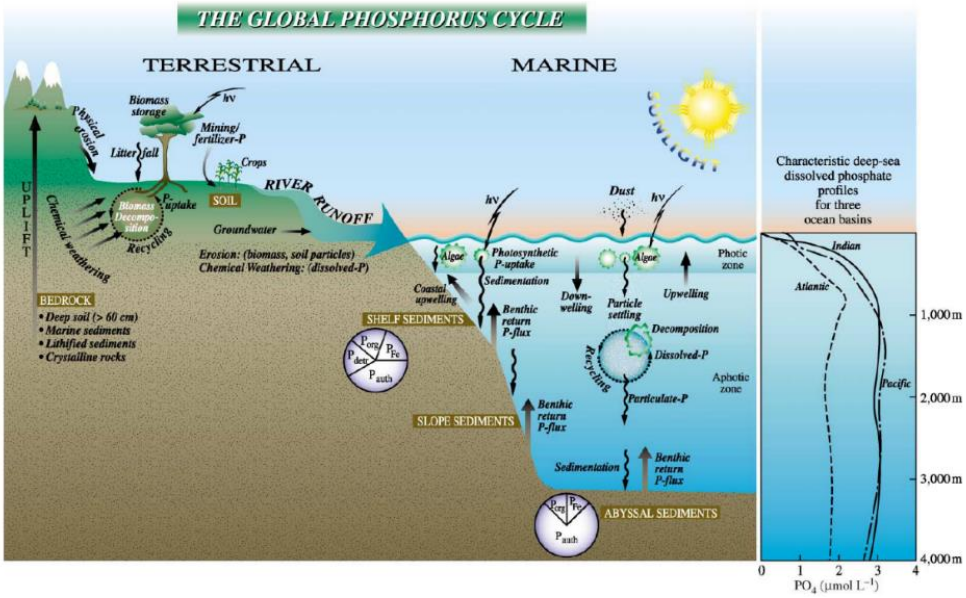

Figure 2.1 : Global Phosphorus Cycles.

There are two organic phosphorus cycles, as well as the inorganic phosphorus cycle. One of the cycles takes places on land (soil-plants-humans/animals-organic waste-soil) and another in water. The cycle time of these cycles is between a few weeks and up to one year. (Emsley 1980; Bennett&Carpenter 2002). The phosphorus cycles both of organic and inorganic are described at Figure 2.2.

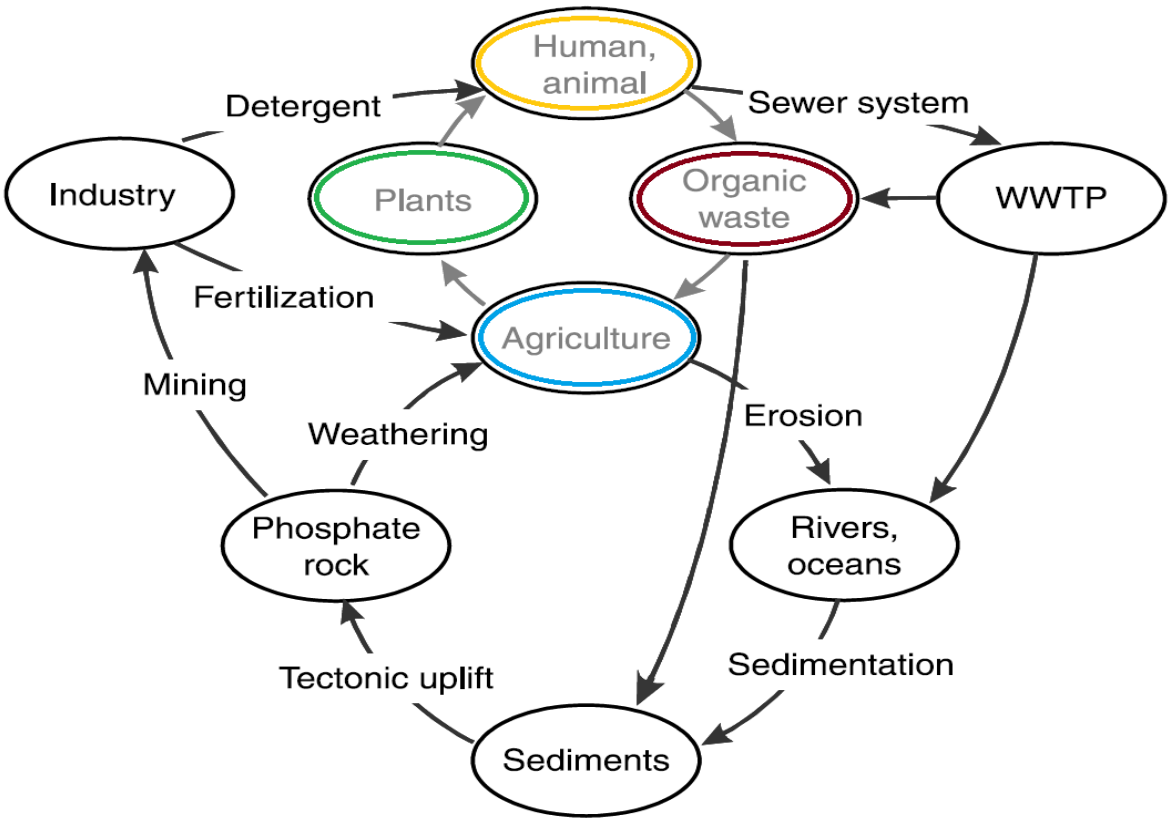

Figure 2.2 : Human Impacts of Phosphorus Cycle.

In addition, it showed the human impacts to the phosphorus cycle. According to the Fig. 2.2, if phosphorus compounds in animal and human excrements are not used in fertilization, phosphate contained in wastewater is partly transported to the oceans via the discharge systems.

Frequently, phosphorus exists in municipal and industrial wastewaters as three froms, which are orthophosphates, condensed phosphates (pyro-, meta- and other polyphosphates) and as originally bound in phosphorus. Ortophosphates and polyphosphates (condensed phosphates) constitue the total inorganic phosphorus. However, polyphosphates are converted to orthophosphates easily thus orthophosphate is the most dominant forms among these species (Orhon and Artan, 1994).

2.2 Sources of Phosphorus

Due to the phosphorus cannot transform gas form naturally; it has two main cycles in nature, which are in aquatic systems and on land. The main source of phosphorus is the phosphate rocks in nature. Phosphate transfers to the soil in inorganic form via meteorological factors. Plants

convert to organic form of inorganic phosphorus in soil. Then organic phosphate participates to herbivorous and carnivorous structure. The organic phosphate in the structure of animals, return to the soil result of animal mortality by the help of metabolic functions of bacteria and fungi. This cycle is similar with the aquatic phosphorus cycle beside there is effects of jeological and tectonic processes at cycle. Consequently, the main phosphorus source is phosphate rocks in nature. However, this source is non-renewable and limited. Nonetheless, phosphorus has not only naturally sourceses but also manmade sourceses that are domestic or industrial sewage treatment effluents represent a major source of phosphorus input into water bodies (Bennett et al., 2001).

In the way of natural phosphorus sourceses, another important issue is quality of the phosphate rocks. Due to phosphorus high reactivity, P is always found in combination with other elements. Thus, it has various types of mineral rocks, which are given at Table 2.1 with P contents of rocks. P is mainly found as apatites.

Table 2.1 : P – Bearing Minerals and their P content.

Mineral	Chemical Formula	P Content (%)
Apatite (fluorapatite)	$Ca_5(PO_4)_3F$	18,6
Chlorapatite	$Ca_5(PO_4)_3Cl$	18,0
Hydroxylapatite	$Ca_5(PO_4)_3OH$	16,1
Monazite	$Sm.(PO_4)$	12,7
Rhabdophane	$(Ce,La)PO_4.H_2O$	12,6
Strengite	$FePO_4.2H_2O$	16,7
Turquoise	$CuAl_6(PO_4)_4(OH)_8.4(H_2O)$	15,4
Variscite	$AlPO_4.2H_2O$	19,8
Vivianite	$Fe_3(PO_4)_2.8H_2O$	12,5
Wavellite	$Al_3(PO_4)_2(OH)_3.5H_2O$	14,8
Xenotime	$YbPO_4$	11,7
Vivianite	$Fe_3(PO_4)_2.8H_2O$	12,5

The quality of phosphate rock not only depends on its phosphate concentration but also its concentration of other harmful subtances, cadminium and uranium particularly (Kratz, 2004). It also found that the content of metallic contaminants in rocks is increasing steadily, such as cadmium, uranium, nickel, chromium, copper and zinc (Driver J. et all., 1999). Although, the

world phosphate rocks reserve stands around 71 billion tons (Table 2.1), with current technology, it is not possible to economically extract deposits in inaccessible locations and deposits with high levels of radioactive or heavy metal contamination (Vaccari, 2009). Reginal phosphate deposits vary distinctively. Presently, two thirds of the phosphate rocks are mined in USA, Morrocco and China approximately. In addition, note worthly amounts are mined in Russia, Brazil, Israel, Jordan, South Africa and Tunisia (P. Cornel and C. Shaum, 2009). Phosphate rocks (PR) reserve and production with respect to countries are given at Table 2.2 However, for those countries, such as Japan, having insufficient phosphate revervior; the phosphorus recovery is a practical way for securing a sustainable phosphorus supply.

Table 2.2: Phosphate Rocks Reserve and Production Globally Estimated.

Country	**PR Production** (kiloton, kt)	**PR Reserve** (megaton, Mt)	**Nature of PR**
Australia	2700	250	Sedimentary – carbonate – fluorapatite
Brazil	6200	310	Igneous – hydroxyl – fluorapatite
China	72,000	3700	Sedimentary – carbonate – fluorapatite
Israel	3200	180	Sedimentary – carbonate – fluorapatite
Jordan	6200	1500	Sedimentary – carbonate – fluorapatite
Morocco	27,000	50,000	Sedimentary – carbonate – fluorapatite
Russia	11,000	1300	Igneous – hydroxyl – fluorapatite; Sedimentary – carbonate – fluorapatite
Syria	3100	1800	Sedimentary – carbonate – fluorapatite
South Africa	2500	1500	Igneous – hydroxyl – fluorapatite; Sedimentary – carbonate – fluorapatite
USA	28,000	1400	Sedimentary – carbonate – fluorapatite
Tunisia	5000	100	Sedimentary – carbonate – fluorapatite
Others	74,000	500	
World Total	191,000	71,000	

There are many different predictions for how long the remaning phosphate reservers will last. The main challenge of making predictions of how long the phosphate rocks will last that is difficult to get good data on the amount of phosphate rock left (Gilbert, 2009). However, according to the United States Geological Survey in 1996 around 38 million tonnes of phosphate (P_2O_5) are exctracted each year globally. The known globally phosphate reserves were 3600 – 8000 million tonnes at 1999. At the same time, it is estimated that there are 7000 million tons of phosphate rocks as P_2O_5 remaining in the reserves that could be economically

mined. The human population consumes 40 million tons of P as P_2O_5 each year (Florida Institue of Phosphate Research, 2005). It is predicted that P demand will increase by 1,5% each year (Steen, 1998). Estimates are that the resource could be exhausted in as little as 100 – 250 years (European Fertilizer Manufacturers Association, 2000).

Moreover, another investigation shows that based on the current consumption rate, the present world reserves of phosphate may be exhausted within the next 50 – 100 years (Steen, I., 1998).

Having said that with these assumptions and predictions, regardless of many years the remaining rock phosphates will last the current use of phosphorus is unsustainable.

Cordell et al. (2011) presented a suggestion to sustainable scenario of future phosphorus use, which can be seen at Fig. 2.3.

According to the Fig. 2.3 that is important, a lot study can be done with agriculture efficiency, food chain efficiency and changing dies to decrease the demand of phosphorus. However, phosphorus recovery from human excreta (and thus wastewater) is also an essential part of achieving a sustainable phosphorus future.

Based on the average phosphorus load of 1.8 g phosphorus per capita per year in raw wastewater (approximately it is involved 0.6 kg phosphorus per capita per year from human wastes.
0,3 kg P per capita per year from laundry detergents and 0,1 kg P per capita per year from household detergents and other cleaners (Sedlak, 1991)) with German boundary conditions and a per capita wastewater flow of 200 L per capita per day the inflent concentration is around 9 mg/L (ATV-DVWK, 2000). An average of approximately 11% of the incoming phosphorus load is removed with the primary sludge during primary settlement (ATV-DVWK, 2000). In biological wastewater treatment, approximately 28% of the incoming phosphorus load are incoorpareted into the biomass and removed with the surplus sludge, even without specific P removal process. Moreover, phosphorus is one of the limiting nutrients in most fresh water and marine ecosystems cause of its concentration is considered a measure of the biological productivitiy or trophic state. The level of phosphorus has a close relationship with algal growth in terms of eutrophication that is the development of blue – green algae blooms. Under warm temperatures and darkness, these blooms die and decompose, which results in the depletion of dissolved oxygen (DO), offensive odor and killing of aquatic lives including fish.

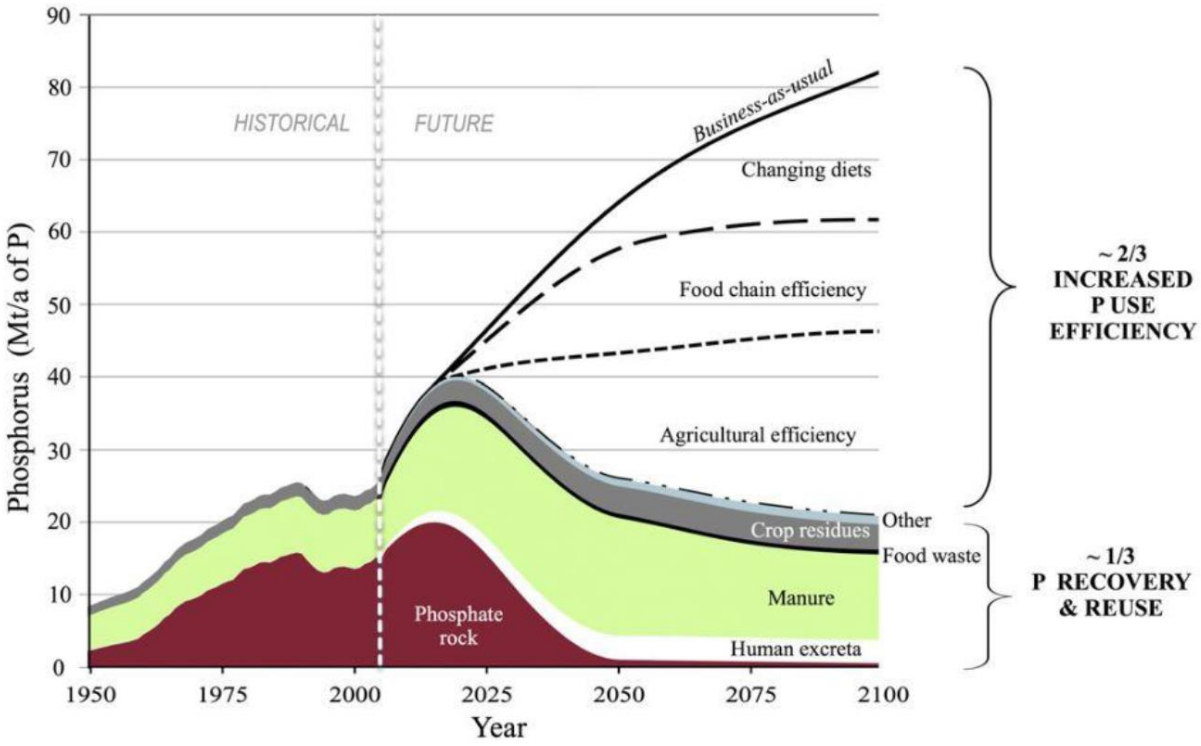

Figure 2.3: A Sustainable Scenario for Meeting Long Term Future Phosphorus Demand.

In addition, decreased depths of water bodies by progressive silting; reduced transparency, recreational and conservation value of waters due to the coloring (green to brown) and the smell of the water; loss of livestock and the possible lethal effect of algal toxins on drinking water (Henze et al., 1997; Jiang and Graham, 1998). Phosphorus is usually considered as the limiting nutrient for algae growth in most freshwater systems as atmospheric nitrogen can serve as infinite source for aquatic biota. Thus, to control phosphorus inputs is the key to control algae blooms (Gong and Zhao, 2014). For that reason, phosphorus discharge is limited by regulations. For example, the European Union Urban Wastewater Treatment Directive 91/271, obligated the removal of P from domestic and industrial discharged into sensitive areas (Commision of the European Comminities, 1991). Additionaly, approximately 48% of the European population has subjected to phosphorus removal requirement since 1991. In Canada, some regions are P sensitive thus, P concentration in municipal effluent discharge limit on total P ranges from 2 to 0,1 mg/l in North America.Additionally, addition, it is 2 mg/l in Turkey too (T.C. Environment and Urban Ministry, Water Pollution Control Regulations, 2004).

Furthermore, phosphorus removal technologies are strictly depend on the phosphorus recovery technologies.

2.3. Phosphorus Removal Technologies

Due to the efficiency of phosphorus recovery technologies are strictly depend on the phosphorus removal systems in the wastewater, the principle of the phosphorus removal technologies will be discussed in this part.

Two main phosphorus removal systems in wastewater is present, which are chemical and enhanced biological phosphorus removal (EBPR) technologies. While chemical phosphorus removal technologies has been used widely in the past, EBPR technologies is becoming most popular recently due the lower chemical costs, lower sludge production and increased potential for phosphorus recovery (Morse et al., 1998). Nonetheless, chemical phosphorus removal technologies still is used as a supplement to EBPR or the sole method of phosphorus removal (Orhon and Artan, 1994).

2.3.1. Chemical phosphorus removal

Chemical phosphorus removal is achieved by adding metal ions for the precipitation of dissolved orthophosphate as metal phosphate. Generally, aluminuim and iron salts such as alum, sodium, aluminate, ferric chloride, ferrous chloride and ferrous sulfate are used as precipitating agents (Orhon and Artan, 1994). The basic precipitation reactions for aluminum iron and calcium is given at Table 2.3.

These reactions should be considered together with many other competing reactions. Moreover, the metal salts will react with other compounds in the water as well so increase the consumption of metal salts. These reactions should be considered together with many other competing reactions. Moreover, the metal salts will react with other compounds in the water as well so increase the consumption of metal salts.

Table 2.3 : Metal ions used for chemical phosphorus removal.

Name	Metal Ion	Basic Precipitation Reaction
Aluminum	Al^{3+}	$Al^{3+}+H_nPO_4^{3-n} \longleftrightarrow AlPO_4+nH^+$
Iron	Fe^{3+}	$Fe^{3+}+H_nPO_4^{3-n} \longleftrightarrow FePO_4+nH^+$
Calcium	Ca^{2+}	$10Ca^{2+}+6PO_4^{3-}+2OH^- \longleftrightarrow Ca_{10}(PO_4)_6(OH)_2$

Therefore, the second process is the simultaneous precipitation that metal salts are added in the biological reactor, however, it can be added in influent, effluent, in the return sludge etc. well.

The phosphorus is then removed together with the secondary sludge. The process that gives the highest efficiency in phosphorous removal for that reason, it has been the most popular method. Removal efficiency can reach 95%, and P concentration in the effluent can be lower than 0,5 mg/l . The third one is post – precipition, the metal salts are added after secondary sedimentation tank (Tchobanoglous et al. 2014).

Chemical phosphorus removal is simple to operate, also phosphorus levels below 1 mg P/l can be achieved in the effluent. In addition, combined with good particle separation process can be achieve lower phosphorus concentration in the effluent. Nonetheless, a significiant increase in the sludge production, cost of chemicals and heavy metal concentration via metal ions, is the main handicap (WEF, 2011).

Chemical phosphorus removal has three main processes configuration, which are related to the location of the addition metal salt. Figure 2.4 displays the schematically chemical phosphorus removal configurations in the wastewater treatment plant. According to the figure, first system is pre – precipitation that is the general category of chemical precipitation processes. Metals

salts are added in the primary treatment and the phosphorus is removed together with the primary sludge.

2.3.2. Enhanced biological phosphorus removal

EBPR relies on the selection and proliferation of a microbial population capable of uptaking orthophosphate in greater amounts than their normal biological growth requirements (Wisconsin Department of Natural Resources, The Wisconsin Department of Natural Resources, Introduction to Phosphorus Removal Study Guide, 2009). Beside the point of phosphorus recovery, EBPR is more favorable technology than chemical phosphorus removal cause of that (Janssen et al. 2002):

- Process does not require chemicals
- System has lower sludge production
- The sludge contains less metals

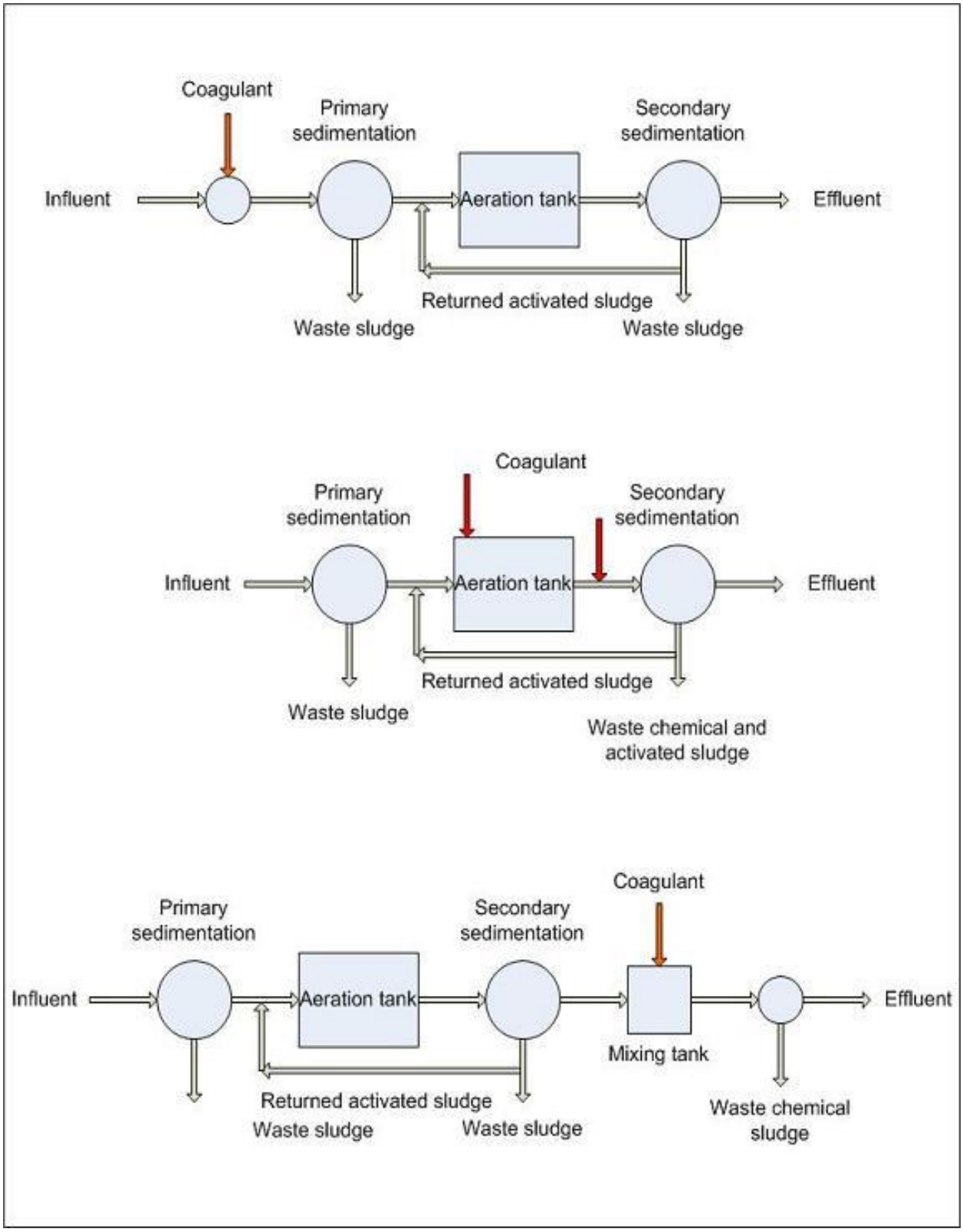

Figure 2.4 : Basic configurations of chemical phosphorus removal.

- Excess sludge is a valuable fertilizer

Nevertheless, EBPR process has some deficiencies that are (Petzet et al. 2013):

- Process is strictly depend on the wastewater characteristics
- Less stable and flexible compared to chemical precipitation
- Process control is complex
- Large reactor volume requirement

Phosphorus is removed by the microorganisms as they use it as a nutrient for growth in activated sludge systems. However, mechanism of EBPR process relies on the specific group of bacteria that called polyphosphate accumulating organisms (PAOs) are able to take up more phosphorus than they require for cellular growth under alterning anaerobic and aerobic/anoxic conditions (Orhon and Artan, 1994).

According to the Fig. 2.5, three intracellular polymers, which are the key biochemical reactions of EBPR system, namely polyphosphate (Poly-P), glycogen and polyhydroxyalkanoates (PHAs) are central to the PAO metabolism (Yuan et al, 2012). Firstly, the hydrolysis of polyphosphate enables PAOs to gain energy under anaerobic conditions. This unique metabolism provides PAOs advatages over most other organisms in terms of able to use carbon sources anaerobically. The reducing equivalents for the conversion of volatile fatty acids (VFAs) to PHA is primarily by the hydrolysis of glycogen, although the oxidation of VFAs

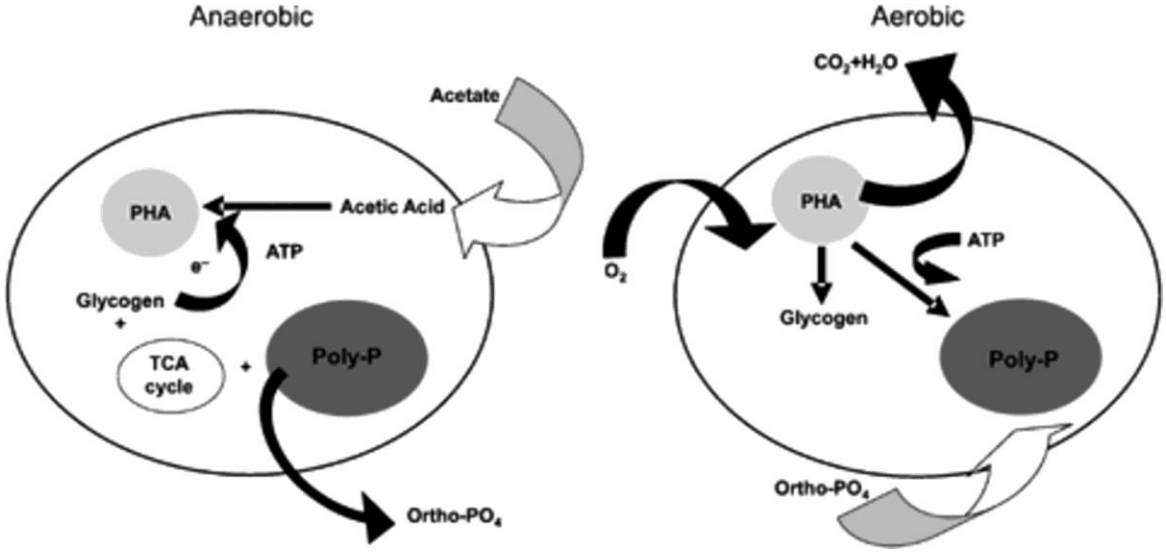

Figure 2.5 : The main biochemical model for EBPR process.

through the full or partial tricarboxylic acid (TCA) cycle could also supply part of the reducing equivalents, particularly when glycogen is limiting (Zhou et al, 2010).

Under the subsequent aerobic/anoxic conditions, PHAs stored anaerobically are oxidized to produce energy for phosphorus uptake, glycogen replenishment and cell growth. The mechanism with variation of quantity the compounds (Orthophosphate, VFAs, PHAs, Glycogen and Polyphosphate) are summarized for liquid phase and biomass in anaerobic and aerobic reactors at Figure 1.6. (Janssen et al, 2002).

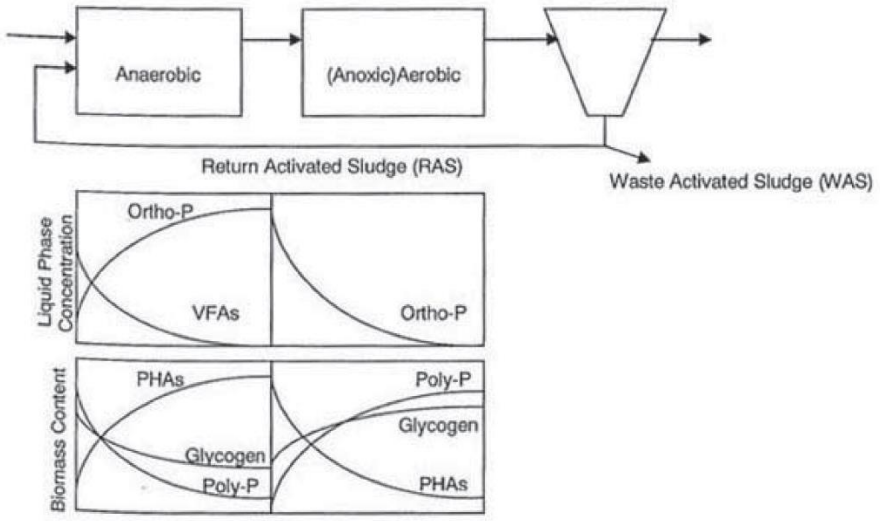

Figure 2.6 : Concentrations of participating compounds in anaerobic and aerobic reactor.

2.4 Stages of Phosphorus Recovery at Wastewater Treatment Plants

Various technologies are developed to recover phosphorus from different locations in the wastewater treatment plants. According to the technologies, phosphorus would be recovered from liquid phase, sewage sludge and sewage sludge ash in the wastewater treatment plant (WWTP).

As an example, in Figure 2.7, the phosphorus balance for a typical German municipal wastewater treatment plant with phosphorus removal is illustrated schematically.Phosphorus recovery rate is given for primary sludge, surplus sludge and enhanced biological phosphorus removal (EBPR) stages. It is able to seen the most recovery rate is possible at the EBPR and precipitation stages.

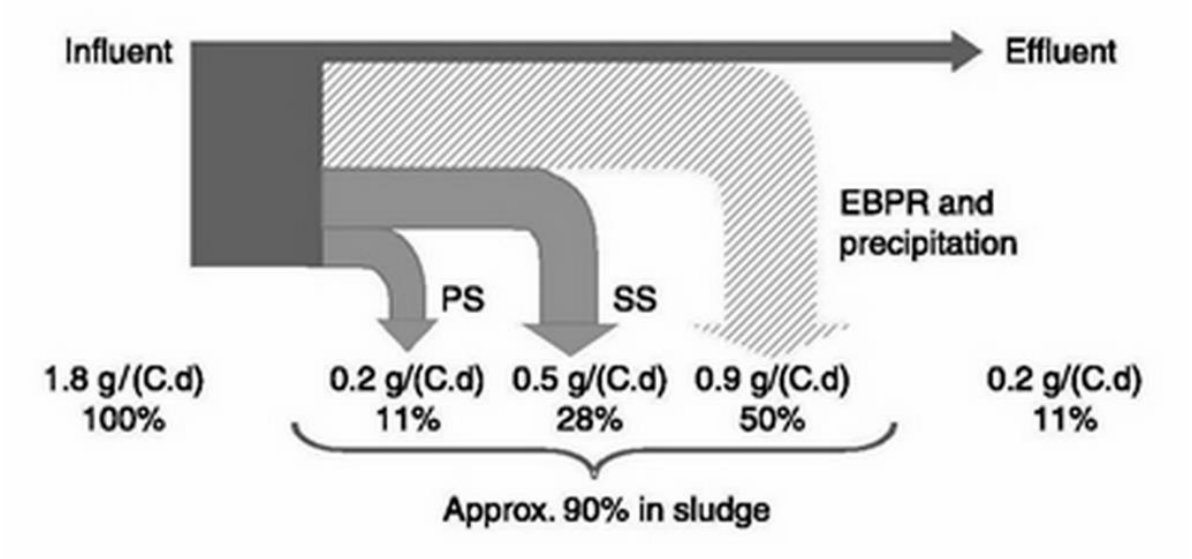

Figure 2.7 : Phosphorus balance for a typical municipal wastewater treatment plant in Germany with biological phosphorus removal and/or precipitation (PS:rimary sludge, SS: surplus sludge, EBPR: enhanced biological phosphorus removal).

Furthermore, different applications of potential phosphorus recovery processes are displayed via the scheme of a model WWTP at Figure 2.8.

The possible locations in a conventional biological treatment plant for recovery phosphorus from the WWTP could be seen in Fig. 2.8. In addition, P recovery from liquid phase is represented with A1, A2 and A3 in Figure 2.8. Additionally, B1, B2, B3, B4 and B5 show the

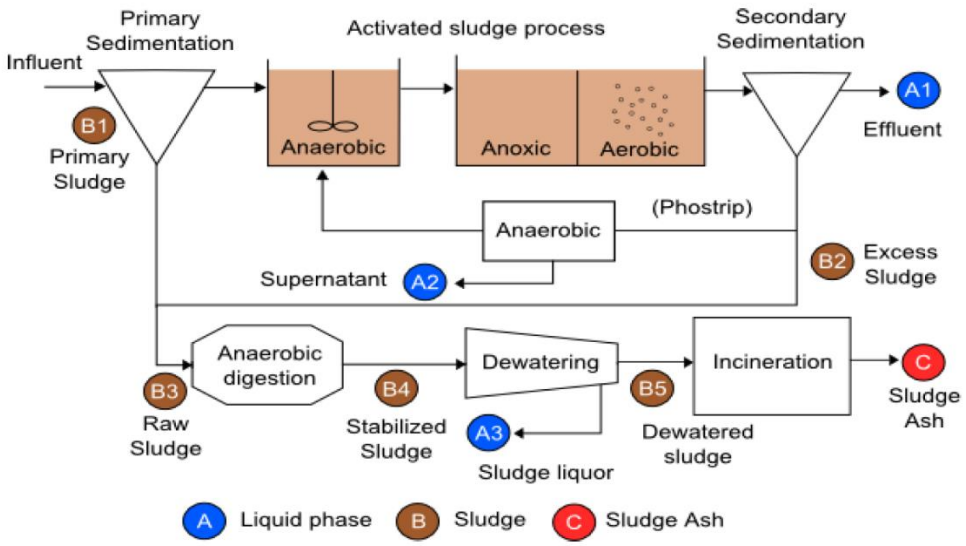

Figure 2.8 : Locations of phosphorus recovery in WWTP.

locations where phosphorus can be recovered from sludge. C also represents the sewage sludge ash after incineration. Moreover, P recovery potentials, phosphorus concentraions based on the volume/mass flows and relative volume/mass flows rates for each stage is given at Table 2.4.

Table 2.4 : Phosphorus recovery potential from different locations in WWTP.

	Volume/mass Flow	**Relative volume/mass flow**	**Concentration of phosphorus**	**Bond**	**Recovery Potential**
Effluent	200 l/cap/d	100%	< 5 mg/l	Dissolved	Max. 55%
Sludge liquor	1-10 l/cap/d	0,5-5%	20-100 mg/l	Dissolved	Max. 50%
Dewatered sludge	0,15 l/cap/d	0,075%	~10 g/kg	Biological /Chemical	~90%
Sewage sludge ash	0,03 kg/cap/d	0,015%	64 g/kg	Chemical	~90%

Since in wastewater treatment plants without phosphorus removal, 90-95% of the incoming phosphorus load is contained in the sewage sludge, the therotical recovery potential is significiantly higher than with separation processes from the aqueous phase.

2.4.1 Recovery from liquid phase

Phosphorus recovery from liquid phase which are effluent, supernatant, and sludge liquor of dewatering is limited to about <50-60% of the incoming phosphorus as rest of the phosphorus is removed together with the sludge.

In general, the recovery is from 10-40% (Cornel and Schaum, 2009). EBPR system most often used as phosphorus needs to be easily released from the sludge by using phosphorus rich side stream. The recovered product is either struvite or calcium phosphate via crystallization technology. In addition, recovery from the liquid phase has a small treatment step typically, which is the main advantage of the system cause of it can be easily installed at existing plants. As with all these processes, the phosphorus removed with the sewage sludge is “lost”, the theoretical recovery potential from liquid phase in common activated sludge plant is limited to <50-60% (P. Cornell, 2009).

2.4.2 Recovery from sewage sludge

The most common recovery stage is sewage sludge cause of its high phosphorus concentration. As 90-95% of the incoming P is incorporated into, the sludge that would be recovered 90-95% potentially. Unfortunately, it is not without problems as sludge, typically contains contaminats such as heavy metals, pathogens and organic pollutants. Therefore, technologies that recover P from sewage sludge must be able to handle these contaminants. For that reason, crystallization and wet chemical technologies have been developed to attempt for recovering phosphorus from sludge.

2.4.3 Recovery from sewage sludge ashes

Sewage sludge ash is the final residue of the incinerated sludge, which is neither directly used nor landfilled. Only mono-incinerated sludge is suitable for phosphorus recovery as co-incinerated sludge often lower the P concentrations and increase the contaminant levels. At the same time, if sludge is incinerated the volume of the sludge is greatly reduced as well as

as organic pollutants and pathogens are destroyed.

Sewage sludge ashes contains about 90% of the phosphorus which is load to the WWTP. Moreover, sewage sludge ashes have a small volume and are easy to transport therefore makes an attractive source for phosphoru (Petzet and Cornel, 2013).

The sewage sludge ashes could also potentially be used directly as a fertilizer, if the heavy metal contents satisfy the fertilizer legislation.

2.5 Phosphorus Recovery Technologies

Phosphorus recovery technologies from WWTPs have received increased attention in the recent decade and as a result, various technologies have been developed. Over 30 different technologies were provided by Hermann (2009) and about 20 of them were identified by Sartorius et al. (2011). These evaluations shows, there is a significiant increase in phosphorus recovery technologies. Nevertheless, only a few processes have been implemented on an industrial scale. Although, there are various technologies for phosphorus recovery, many of them were builded on the same principle. For that reason, just main principles of technologies will be discussed at the next part.

2.5.1 Crystallization

Crystallization principle is depended on the chemical precipitation. For treating high nutrient side streams, technologies based on crystallization of struvite has become a promising method, with several plants in full – scale operation.

Crystallization can be used for treating phosphorus rich side streams, such as water from anaerobic digesters or dewatering. In addition, it is used in combination with chemical technologies as well. The development of this technology has been started in the 1970s for producing a more marketable end product (Morse et al., 1998). On the basis at pilot tests at the Yamato (Japan) WWTP, Joko (1984) found that crystallization was able to reduce the P level from 1 to 4 mg/l in a biologically treated wastewater down to 0,3 – 1,0 mg/l and the removal efficiency was improved in the presence of seed crystals (Gong and Zhao, 2014).

All crystallization technologies are based on three fundamental stages, which are;

1) Supersaturation
2) Primary and secondary nucleation
3) Crystal growth

Nucleation is the process where ions come together to form a solid in a supersaturated solution. The most important factors affecting of struvite are pH, molar ratios of Mg^{2+}, NH_4^+ and PO_4^{-3}, temperature and the presence of foreign ions. Normally, the phosphorus rich side stream is fed into a reactor together with seed material for crytal growth, magnesium source and the pH is controlled either by NaOH or with CO_2 stripping. For the formation of struvite that given in the Figure 2.9, a molar ratio of 1:1:1 of Mg^{2+}: NH_4^+: PO_4^{-3} is needed. However, magnesium is usually not present in sufficient quantities in the wastewater and needs to be added. Many researches have been indicated that on finding an optimal ratio Mg^{2+}: PO_4^{-3} and a ratio of 1.1 – 1.6:1.0 is often reported (Liu et al. 2013). However, an optimal molar ratio of the constituents is dependent on the characteristics on the raw wastewater. In addition, if the molar concentration of the Mg^{2+} falls below the molar concentration of PO_4^{-3}, the system is not optimal with respect to the removal of phosphorus. Struvite can be precipitated in a range of pH values 7,0 – 11,5 and the solubility of struvite is at a minimum at near pH is 10,3 (Rahman et al., 2013).

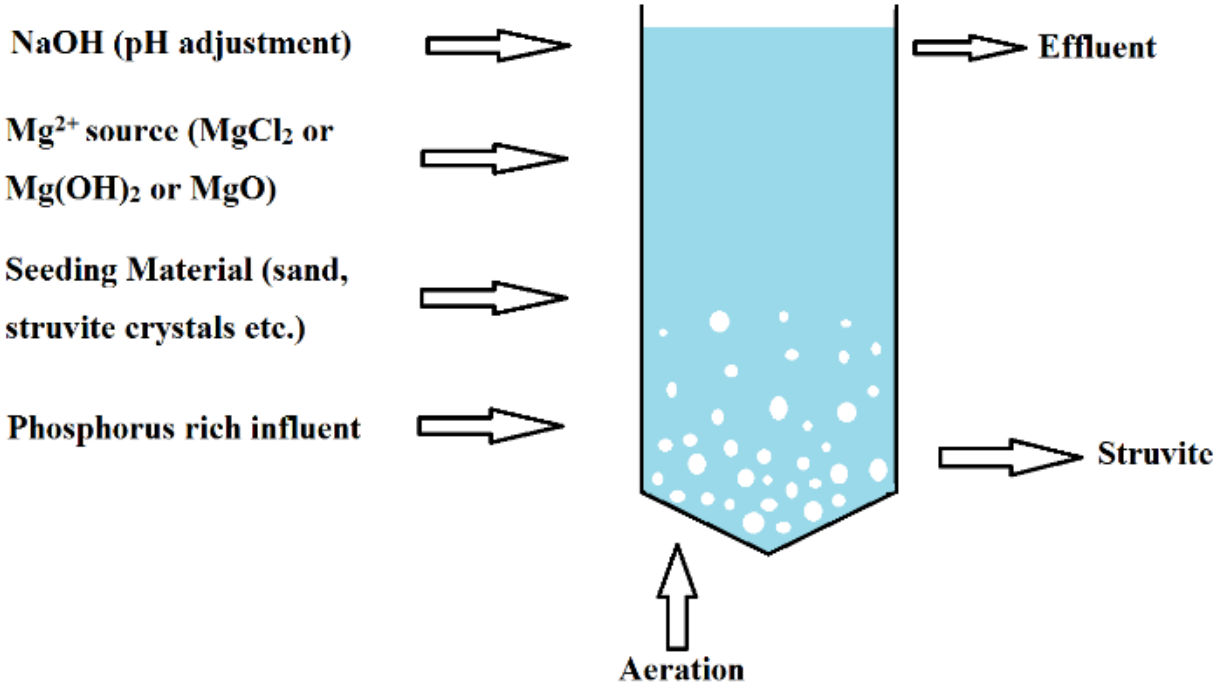

Figure 2.9 : General principle of struvite recovery from wastewater.

Different optimal pH values for struvite recovery have been suggested by various authors, and based on a review of different studies, Liu et al., (2013), suggested an optimal pH value between 8,5 – 9,0 for wastewater. However, typically struvite recovery reactors is operated in the range of 8,0 – 8,8 to minimize the addition of chemicals and minimize the formation of other products such as calcium phosphate. In contraty to these results, Hao et al., (2008), found that highly pure (99,7%) struvite was found to formed at pH:7,0 – 7,5. To evaluate the quality of the struvite crytals, a quantitive assestment is needed.

pH is normally controlled through the removal of CO_2 by aeration or by the addition of NaOH and the choice of method depends among others on the characteristics of the influent, the preference of the designer/operator and availibilty of chemicals.

The other important point of crystallization is seed material which affects the crystallization process and to ensure the good crystal growth. This helps from good crystals that have an improved settleability and improve the struvite reaction rate. Different seed materials have been used in practice, such as sand, silica, granite, quartz and recycled struvite (Wang et al., 2006).

The temperature has an effect on the solubility of struvite and on the crystal growth. The rate of crystal growth often increase with temperature, affect the shape, and size (Le Corre et al., 2009). The solubility has been found to generally increase up to limit around 60ºC where the solubility drops significiantly.

Phosphorus recovery as struvite precipitation studies that from diverse sourceses and different operation conditions are summarized at Table 2.5.

The crystallization technology that was developed use the mainstream in the sludge treatment as a phosphorus source is also available. At the technology uses the sludge as a phosphorus source. The products are then crystallized within the sludge. The major advantages with this methos are struvite scaling on sludge treatment equipment can be avoided and dewaterability is increased.

Table 2.5 : Struvite precipitation for various source and operation conditions.

Waste Streams	**pH**	**Molar Ratio Mg:N:P**	**Magnesium Source**	**Observations**	**Struvite Recovery**	**References**
Anarobic Swine lagoon effluent	8,9 – 9,25	1:1:1 to 1,6:1:1	$MgCl_2.6H_2O$	pH was adjusted with 0,1 M NaOH	96%	Nelson et al. (2003)
Liquor stream	9,0	1,05:1:1	$MgCl_2.6H_2O$	Annula yields of struvite were calculated to be 42 – 100 tons a year	97%	Jaffer et al. (2002)
Landfill leachate	8,5 – 9,0	1:1:1	$MgCl_2.6H_2O$ + $NaHPO_4.12H_2O$	NH_4-N content quickly reduced from 5618 to 112 mg/l within 15 min.	92%	Li et al. (1999)
Synthetic swine wastewater	9,5 – 10,5	1,4:1:1	$MgCl_2.6H_2O$	CO_3^{2-} can effect the P removal efficiency	>97 %	Song et al. (2007b)
Sewage sludge anaerobic digester effluent	8,0 – 9,0	1,5:1:1	$MgCl_2.6H_2O$ + 85% H_3PO_4	pH was adjusted with 20% NaOH	95%	Uysal et al. (2010)

Table 2.5 (continued) : Struvite precipitation for various source and operation conditions.

Waste Streams	pH	Molar Ratio Mg:N:P	Magnesium Source	Observations	Struvite Recovery	References
Fertilizer industry wastewater	8,5 – 10,0	1,2:1:1	$MgCl_2.6H_2O + NH_4Cl$	pH of wastewater was 3,8	85%	Hutnik et al. (2013)
Poultry manure digester effluent	8,5 – 9,5	1,5:1:1	$MgCl_2.6H_2O$ + 75% H_3PO_4	External P source was necessary for the recovery of NH_4-N along with the PO_4-P	97,4 (NH_4-N)	Yilmazel and Demirer (2011)
Cola beverage waste	9,5	1:1:1	$MgCl_2.6H_2O + NH_4Cl$	Recovered solids at pH 9,5 presented a pure and crystalline phase	97%	Foletto et al. (2013)
Anaerobically digested dairy maure	8,5		$MgCl_2.6H_2O + Mg(OH)_2$	Initial pH adjustment to 8,50 using NaOH did not resulted in any significiant increase in the removal	>95 % (NH_4-N) recovery	Uludag-Demirer et al. (2005)
Fertilizer industrial wastewater	9,6	1,6:0,6:1	Bittern	Bittern is a source of Mg^{2+} ions is effective on struvite precipitation	47,52 g/l	El Diwani et al. (2007)
Swine wastewater	8 – 8,5	0,81:16, 4:1	Aeration, $MgCl_2$	Recovered struvite is approximately 95% pure	171 g/m^3	Suzuki et al. (2007)
Anaerobically digested cattle manure	9,0	1,5:1:1,25	$MgCO_3$, $Mg(OH)_2$, MgO, $MgSO_4$	Potassium also removed from wastewater	>56 %	Zeng and Li (2006)
Anaerobically digested dairy maure	8,5		$MgCl_2.6H_2O + Mg(OH)_2$	Initial pH adjustment to 8,50 using NaOH did not resulted in any significiant increase in the rem.	>95 % (NH_4-N) recovery	Uludag-Demirer et al. (2005)

There are mainly two technologies have been developed for recovering phosphorus from sewage sludge which are Air Prex and Fix – Phos. Their details are given at Table 2.6

Table 2.6 : Commercial technologies for P recovery from wastewater around the world.

Name	Organization	Recovered Product	Chemicals Used	P recovered of influent	Scale	Reference
Air Prex	Berliner Wasserbetriebe Germany	Struvite	$MgCl_2$	~80%	Semi industrial	Heinzmann et al. (2003)
Fix - Phos	TU Darmstadt Germany	Calcium Phosphate	CSH (Calcium Silicate Hydrate)	21 – 31%	Pilot	Petzet et al. (2012)

These systems are developed to be used together with EBPR systems, and therefore are not usable together with chemical phosphorus removal. At the same time, there are various commercial technologies for phosphorus removal from municipal wastewater with phosphorus recovery as an end product. Some of these technologies are given in detail in Table 2.7.

2.5.2 Wet chemical technologies

Wet chemical technologies are defined as technologies that apply a strong acid – base to relase the phosphorus that is bound in sludge (digested or dewatered sludge) or sewage sludge ash. The phosphorus can also be released by heating the sludge, applying pressure and a combination of these. Sulfuric acid (H2SO4) or hydrochloric acid (HCl) is used for dosing typically. When the phosphorus is dissolved by using chemicals, heavy metals are dissolved too. For that reason, removal of heavy metals is needed from the water before phosphorus can be recovered. After metals are removed the phosphorus can be recovered in different ways such as ion exchange, crystallization, nanofiltration etc. However, it is typically combined with crystallization of struvite or calcium phosphates.

Wet chemical technologies are considered significiantly more complex than the crystallization technologies due to the high amount of chemical and processing steps**.**

2.5.3 Thermochemical technologies

The thermochemical technologies are based on treating the sewage sludge ashes that come from incineration of the sludge. The main objective of the reatment is to remove heavy metals and increase the bioavailability of the sludge.

A major advantage with this method is that most types of sewage sludge ashes can be treasted

Table 2.7 : Phosphorus removal from municipal wastewater technologies with phosphorus recovery as end product in around the world.

Technology	Country	Observation	References
DVC Crystalactor	The Netherlands	A fluid bed type of crystallizer in which phosphate is removed and recovered from the wastewater while phosphate pellets with a typical diameter of 1 mm are produced	Piekema and Giesen (2001)
The Pearl Process	Canada	Controlled chemical precipitation in a fluidized bed reactor that recovers struvite in the form of highly pure crystalline pellets	Ostara Nutrient Recovery Technologies (2013), http://www.ostara.com/
The Kurita Fixed bed crystallization column	Japan	Phosphate is removed from secondary effluent of sewage treatment work by use of phosphate rock seed. Calcium phosphate is produced without production of sludge	Joko (1985)
OFMSW&BNR	Italy, Spain	A three-stage system which combines anaerobic digestion, biological nutrient removal, and phosphate crystallization as struvite	Cecchi et al. (1994)
Phosnix	Japan	Spontaneous nucleation of P in an air agitation column and recovery as struvite	Unitika Ltd (2013), http://www.unitika.co.jp/e/csr/envproducts.html
RIM-NUT Process	Italy	A process using ion exchange followed by struvite precipitation	Liberti et al. (1986)
Terra Blue Inc.	USA	Simultaneous P removal from raw swine wastewater via a multistep treatment system using solideliquid separation, nitrification/denitrification, and P recovery as calcium phosphate	Vanotti et al. (2010)
Renewable Nutrients LLC	USA	Removal of P as calcium phosphate from biosolid side streams in municipal wastewater treatment plants	Szogi et al. (2014)

and therefore is less dependent on the characteristics of the sewage sludge ash compared with wet chemical technologies (Petzet et al., 2013). It is also a favorable method if chemical phosphorus removal is used in the WWTP.

The main thermochemical technology were developed in on European project called SUSAN (Sustainable and safe re – use of municipal sewage sludge for nutrient recovery). The basic principle of the system is that the ashes are fed into a furnace together with chloride. Under high temperature (850 - 1000ºC), the chlorides will react with the heavy metals and form heavy metal chlorides and these will vaporize thereby the heavy metals are removed. Due to chemical transformations of the phosphorus during the treatment from mainly aluminum and new types of calcium phosphates (Adam et al., 2009).

2.6 Phosphorus Recovery Products

Phosphorus can be recovered as various products from WWTP. Most methods are based on recovering the phosphorus in a way so it can be used as a fertilizer at the agriculture.

There are 3 main different phosphorus recovery products which are struvite, hydroxyapatite and sewage sludge ash that is recovered with improved fertilizer qualities.

2.6.1 Struvite

Magnesium ammonium phosphate hexahyrate, is displayed in Figure 2.10, also known as struvite has the chemical formula; $MgNH_4PO_4{:}6H_2O$, which is normally recovered from EBPR plants as the sludge, contains high amount of phosphorus without metal bound (Liu et al., 2013).

Struvite forms when molar ratio of magnesium, ammonium and phosphorus are theoretical 1:1:1 and normally under slightly alkaline pH values. At the same time as described at the Crystallization part, molar ratio could be different amount for the best precitipation. In practice, the molar ratios are slightly higher with the respect to magnesium ion. For example, $Mg{:}NH_4{:}PO_4$ molar ratio of 1,5:1:1, the P recovery rate was 90-95% (Uysal et al., 2010), also molar ratio of 1,7:1:3,4 the P recovery rate was 98% at pH 9,8 (Gadekar and Pullammanappallil, 2010).

Struvite forms according to the general reaction shown in Equation 2.1:

Figure 2.10 : Different particle sizes of produces struvite fertilizer from Ostara.

$$Mg^{2+} + NH_4^+ + PO_4^{2-} + 6H_2O \leftrightarrow MgNH_4PO_4 * 6H_2O \quad \textbf{(2.1)}$$

This chemical equation is a simplification of the chemistry involved in the struvite precipitation which has been accepted some side reactions are related to struvite formation that given at serial equations from 2.2 to 2.10 (Doyle, 2002).

$$MgOH^+ \leftrightarrow Mg^{2+} + OH^- \quad \textbf{(2.2)}$$

$$NH_4{}^+ \leftrightarrow H^+ + NH_3 \quad \textbf{(2.3)}$$

$$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^- \quad \textbf{(2.4)}$$

$$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-} \quad \textbf{(2.5)}$$

$$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-} \quad \textbf{(2.6)}$$

$$MgH_2PO_4^+ \leftrightarrow Mg^{2+} + H_2PO_4^- \quad \textbf{(2.7)}$$

$$MgHPO_4 \leftrightarrow Mg^{2+} + HPO_4^{2-} \quad \textbf{(2.8)}$$

$$MgPO_4 \leftrightarrow Mg^{2+} + PO_4^{3-} \quad \textbf{(2.9)}$$

$$H_2O \leftrightarrow H^+ + OH^- \quad \textbf{(2.10)}$$

Not only molar ratios but also other factors affect to struvite precipitation. One of them is solubility product, which becomes a key issue in the performance of the phosphorus recovery process. The solubility of struvite can be described by the thermodynamic solubility product, defined as K_{sp} that represents the product of the activities of the precise species involved in the equilibrium of struvite.

If the effective concentrations of magnesium, ammonium and phosphate in solution exceed the equilibrium solubility of struvite, the struvite will be formed. If those concentrations are lower than the equilibrium solubility, then the struvite in the solution will dissolve. The solubility of the struvite is affected by some factors which are temperature, pH and ions impurity.

2.6.1.1 pH

Struvite solubility depends heaviliy on pH cause of that the decrease in apparent struvite solubility in an alkaline medium is a consequence of side reactions accompanying with the solubility equilibrium. Side reactions and speciation of the components caused are pH dependent and respectively affect the struvite solubility in different pH ranges (Buchanan et al., 1994). Therefore, the net effect of these side reactions causes the struvite solubility to decrease with the increasing pH value.

According to the recent studies, the minimum struvite solubility occurred at pH:10,3 (Ohlinger et al., 1998) But Buchanan et al., reported the inimum solubility point of 9,0 (Buchanan et al., 1994). The reported pH with the minimum struvite solubility ranges from 8,0 to 10,7. The

difference in struvite solubility among these works results from the selection of different K_{sp} values (Ohlinger et al., 1998).

2.6.1.2 Temperature

Struvite solubility is influenced by temperature through thermodynamics. The effect of temperature on solubility shows a steady increase with increasing temperature initially, followed by a steady decline in solubility over the range of between 10 – 65ºC (Doyle, 2002).

It was also,reported that, the struvite solubility increased to a maximum at 20ºC (Durrant et al., 1999) However some study was conducted by Aegre et al(1995)., and they found that maximum solubility was at 50ºC. The reason of that is the struvite formation in solution is on endothermic reaction.

2.6.1.3 Ions impurity

Another factor is impurty of ions. Magnesium, ammonium and phosphate ions would form complexes with each other or with other species present in the solution, tending to increase solubility (Booram et al., 1975). At the same time, the presence of impurity ions will affect the ionic strength of a solution, which will affect solubility cause of the electrostatic interactions of ions in solution to reduce their activities or effective concentrations.

As a concequence, the net effect of pH, temperature, imputriy ions and any unknown factors will change the struvite solubility. Among these factors, the influence of pH is dominant, so that in the anaerobic digestion process that normally performs under a high pH, the suppression of struvite solubility will occur easily leading to struvite precipitation (Borgerding, 1972).

2.6.1.4 Struvite as a fertilizer

Due to containig of high amount nitrogen and phosphorus, struvite has been used to be an effective slow – relase fertilizer. In addition, a low water solubility (0,018g/100ml, at 25ºC) of struvite, the nutrients are made less mobile compared to highly soluable fertilizers.

A slow relase rate is beneficial cause of that:

1) The plants are able to use more of the nutrients in the fertilizer.
2) A less frequent application rate can be used.

3) Decrease the loss of nutrients due to surface runoff or leaching into the groundwater (Münch et al., 2001).

In adddition, the struvite can be recovered from digested sludge or anaerobic digesters in WWTPs usually have low or no heavy metal content (Liu et al., 2013).

Struvite can be used as a fertilizer for various purposes such as turfs, tree seedling, ornamentals, vegatables and flower boards. Several studies have also investigated the fertilizing properties of struvite recovered from various soruces; landfill leachate (Liu et al., 2013), swine wastewater (Liu et al., 2011), poultry wastewater (Yetilmezsoy et al., 2009), industrial wastewater (El Diwani et al., 2007).

As a result, all studies demonstrated that struvite has great fertilizing properties. Moreover, Shu et al. (2006) evaluated the potential amount of struvite that can be recovered from wastewater. They found that, approximately 1 kg of struvite can be crystallised from 100 m^3 wastewater. Thus, according to the data of amount of treated wastewater at the WWTP at Turkey in 2012; approximately 3257 ton struvite per year would be gain (Turkish Statistical Institue Wastewater Statistics, 2012).

2.6.2 Hydroxyapatite

Phosphorus can be recovered as hydroxyapatite (HAP) is called calcium phosphate also. It has four different forms which are listed in Table 2.8;

Table 2.8 : Possible calcium phosphates that are formed.

Name	Chemical Formula	Solubility Product
Tricalcium phopshate	$Ca_3(PO_4)_2$	Variable
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	$4{,}7x10^{-59}$
Dicalciumphosphate dihyrate	$CaHPO_4{\cdot}2H_2O$	$2{,}49x10^{-7}$
Octacalcium phosphate	$Ca_4H(PO_4)3{\cdot}2{,}5H_2O$	$1{,}25x10^{-47}$

Calcium is normally added as line $Ca(OH)_2$ and formation of hydroxyapatite follow this chemical reaction in Equation 2.11 (Tchobanoglus et al., 2004).

$$\mathbf{10}Ca^{2+} + \mathbf{6}PO_4^{3-} + \mathbf{2}OH^- \leftrightarrow Ca_{10}(PO_4)_6(OH)_2 \qquad \textbf{(2.11)}$$

Calcium phosphates normally form in calcium and phosphorus rich water and with a high pH in the range of 8,0 – 9,0 in terms of pH. High oversaturation is needed for spontaneous precipitation of calcium phosphates.

Calcium phosphate has become a less favorable as a product of phosphorus recovery due to the high chemical usage and proposed low fertilizr qualitie compared to struvite (Tchobanoglous et al., 2014).

2.6.2.1 Hydroxyapatite as a fertilizer

To use calcium phosphates as a direct substitute in industrial production of fertilizer is possible. At the same time, to mix together with other nutrients or apply it directly as a slow release fertilizer is possible too.

2.6.3 Sewage sludge ash

The phosphorus could be recovered also from sewage sludge ash by using thermochemical technologies. However, sewage sludge ash normally contains high levels of heavy metal due to it is produced by incineration of sludge from WWTP. In addition of this limitation, the sewage slude is often co-incinerated together wih other wastes which contain low amount of phosphorus. For these reasons, ashes are typically unattractive for phosphorus recovery (Adam, 2008). Therefore, only mono-incinerated sludge is considered for phosphorus recovery.

The ash could be used in fertilizer production or applied directly as a fertilizer. Mono – incinerated sewage sludge ashes can have high phosphorus content in the range of 15 – 25 % P_2O_5 and it is comparable to low grade phosphate rock (Adam et al., 2009).

2.7 Phosphorus Recovery Applications

There are many phosphorus recovery studies, which are in the research or development stage and few have been implemented on a full scale basis. A number of different processes for recovering phosphorus as either struvite (MAP) or calcium phosphate (HAP).

One of the most successful companies in terms of commercialization of phosphorus recovery from WWTPs at industrial scale can be said Ostara Pearl Reactor Process (Canada). The process is based on the crystallization of struvite in a fluidized bed reactor.

The influent is normally taken from the dewatering side stream. Magnesium is added as $MgCl_2$ and pH is adjusted if necessary with NaOH. This process can be recover phosphorus at 80-90 % from influent to crystallization reactor. Th product is slow release fertilizer in form of struvite, marketed as Crystal Green. The process is also installed in full scale at various locations in North America and Europe (Ostara, 2013).

Another well-known process is Unitika Phosnix has many similarities with the Ostara Pearl Reactor process. They use $Mg(OH)_2$ for a magnesium source and NaOH for pH adjustment like Ostara. The phosphorus recovery rate of this process is 80 – 90% from influent to crystallization reactor and the end product can be use as a slow fertilizer in the struvite form. Also for improving crystallization of struvite, small struvite crystals are recycled back to the reactor and acts as a seeding material. The reactor is operated with a pH ranging from 8,2 – 8,8 (Ueno et al., 2001).

There are not only crystallization technologies but also thermochemical process for recovering the phosphorus. The ASH – DEC is a thermochemical treatment which is reduction of heavy metals and improved bioavailability of phosphorus was developed as a part of European Research Project SUSAN. A pilot plant was constructed in Leoben, Austria in 2008. It is treating 7 tons of sewage sludge ash per day. The efficiency of the system that main advantage of this technology has the highest possible phosphorus recovery rate (>90% incoming phosphorus in WWTP). But the limit of the system is that end product need mixed with other nutrients (NH_4NO_3, K_2SO_4, KCl) to create multi nutrient fertilizers with nitrogen, phosphorus and potassium.

Not only these technologies but also various technologies have been installed for phosphorus recovery. Generally, the performanceof pilot or full – scale struvite crystallization processes used by different studies are quite satisfactory in terms of phosphorus removal ratio.

In Japan, several full – scale MAP processes have been installed and operated since 1995. The MAP process in Fukuoka City achieves 80% of phosphate removal efficiency even with high phosphate concentraions (245mg/l phosphate in the influent).

Another full – scale MAP process, with a capacity of $500m^3/d$ was operated in the Shimane Prefecture Lake Shinji East Clean Center in 1998. The minimum removal rate of phosphate

reached 90% and the total phosphorus in the effluent ranged between 0,3 – 0,6 mg/L phosphorus (Ueno and Fujii 2001)

In Italy, the pilot scale MAP crystallization process was set up by Battistoni et al(2000). Their results showed that in the low range of phosphate concentration between 30 to 60 mg/l phosphorus, 81% of phosphate removal could be achieved. (Battistoni et al., 2000).

The phosphate removal at the anaerobic digeter sidestream with the phosphate concentration of 61mg/l phosphate was achived 94% by Munch and Barr (Munch and Barr 2001).

2.8 Economical Analysis for Phosphorus Recovery

Through the development of various phosphorus recovery technologies, the economical feasibility of recovering phosphorus from wastewater is still unclear. Due to the many technologies have not reached industrial scale and the recovered products have yet to be fully accepted by the agriculture organization and government it cannot be evaluated exactly (Shu et al., 2006). Moreover, prediction of operational cost technologies is difficult. However, there are various studies about economical analysis for phosphorus recovery from wastewater. One of them was conducted by Petzet et al (2013). They evaluated the cost of various phosphorus recovery technologies based on lab – scale and pilot – scale projects by the German Water Association and were presented in Table 1.4. (Petzet et al., 2013)

Table 2.9 : Cost of Phosphorus Recovery for Different Technologies.

Source	Cost (€/kg P)
Liquid Phase	9 – 15
Sewage Sludge	2 – 25
Sewage Sludge Ash	2,6 – 7,5

However these costs that are given in Table 1.6, do not take into account savings in the operational costs in the WWTP or sludge handling. Also, Balmer (2003) calculated cost of about 3600€/Mg.P for a phosphorus recovery from wastewater in combination with a phosphorus elimination. So, phosphorus recovery from sewage sludge was calculated about 8800€/Mg.P by Balmer at the same time. However, these costs cannot bedirectly compared as phosphate rock has to be processed before use and the recovered phosphorus is off different quality.

In addition, mining of phosphate rock price is changeable for instance, 1 ton phosphate rock was approximately 400 dollar in 2008, it is 115 dollar in 2015 (Url - 4). Consequently, present phosphorus recovery technologies cannot compete with phosphate rock as a source for phosphorus in terms of priceses (Petzet et al., 2013).

2.9 Anaerobic Digestion

Anaerobic digestion is a process to convert organic material into biogas and carried out by a consortium of microorganisms in the absence of air transforming through a series of metabolic phases (Henze, 2008).

Using biogas that could evolve from decaying organic matter as an energy source to start with Jan Baptita Van Helmont at 17th century although which was used for heating bath water in Assyria during the 10th century B.C. and Persia during 16th century (Abbasi et al., 2012). Following this, Volta resolved that there was a direct connection between organic material used and gas produced in 1776. Vairous materials were used as raw material for biogas production. Therefore, Sir Humphry Davy determined that methane was present in the gases produced during anaerobic digestion of cattle manure in 1808 (Tietjen, 1975).

As a result of these developments, the first digestion plant was built at a leper colony in Bombay, India in 1859 (Meynell, 1976). Used to fuel street lambs in Exeter, when anaerobic digestion reached England, at that case biogas was recovered from a "carefully designed" sewage treatment facility in 1895 (McCabe and Eckenfelder, 1957). During the following centuries, biogas has been developed to diverse purposes. By virtue of short supplying and expensive cost for energy, anaerobic digestion has a far greater relevance at developing countries than developed countries. Especially India and China meet the energy needs with the anaerobic digestion technologies (Abbasi et al., 2012). However, Turkey has few biogas plants though which is a developing country.

In Turkey, first biogas application had started at 1957 however it was cancelled suddenly (T.C. Environment and Urban Ministry, 2011). After that, a lot of biogas plants and biogas projects have been conducted with increasing of energy demand. Although number of potential biogas plants which can feed with just manure, is 2000, Turkey has got 36 biogas plants in operation and 49 biogas plants in planning stage according to Turkish – German Biogas Project in 2011.

The anaerobic process has involve four main stages for convertion, hydrolysis, acidogenesis, acetogenesis and methanogenesis, which are demonstrated in the Figure 1.5. In the first step namely hydrolysis, complex particulate matter such as lipids, proteins and carbohydrates is converted into dissolved compounds with a lower molecular weights such as short sugars, fatty acids and amino acids. Hydrolytic or fermentative bacteria that release extracellular enzymes facilitate this process. Proteins are degraded via polypeptides to amino acids, carbonhydrates are transformed into soluable sugars (mono- and disaccharides) and lipids are converted to long chain fatty acids and glycerine. In practice, the hydrolysis rate can be limiting for the overall rate of anaerobic digestion (Haandel and Lettinga, 1994).

At the acidogenesis stage which is called fermentation and acidification, fermentative bacteria transform dissolved compounds; sugars and other monomeric organic products from hydrolysis into simple organic compounds such as volatile fatty acids, alcohols, lactic acid and mineral compounds such as carbon dioxide, hydrogen, ammonia and hydrogen sulphide gas. Acidogenic fermentation is carried out by a diverse group of bacteria, most of which are obligate anaerobes. However, some of them is facultative and can also metabolise organic matter via the oxidative pathway. This issue is important cause of that in anaerobic sewage treatment, as dissolved oxygen might otherwise become toxic to obligate anaerobic organisms such as the methanogens (Haandel and Lettinga, 1994).

At the following stage is acetogenesis, alcohols and volatile fatty acids (VFAs) are anaerobically oxidized by hydrogen-producing acetogenic bacteria into acetate, hydrogen and carbon dioxide. To produce acetic acid, acetogenic bacteria need oxygen and carbon. For this reason, they use the dissolved oxygen in the solution or bounded-oxygen. Hereby, the acid-producing bacteria create an anaerobic condition, which is essential for the methane producing microorganisms responsible for the next step. Consequently, the conversation of the influent organic matter into acetic acid is accompanied by the formation of hydrogen.

In the final stage, methanogenic bacteria, methanogens, which are strictly anaerobic, transform the acetic acid, carbon dioxide and hydrogen into a mixture of methane, carbon dioxide and varying quantities of nitrogen, hydrogen sulfide and other components which mixture is called biogas. Particularly, methane is produced acetate or from the reduction of carbon dioxide by hydrogen using acetotrophic and hydrogenotrophic bacterias respectively.

The bacteria producing methane from hydrogen and carbon dioxide grow faster than utilizing acetate, so that the acetotrophic methanogens are usually rate limiting with respect to the transformation of complex macromolecules in biomass to biogas (Pipoli, 2005; GTZ, 2009; Maghanaki et al., 2013; Khanal, 2008; Schink, 1997; Westermann, 1996; Surendra, 2014; Ileleji, 2008).

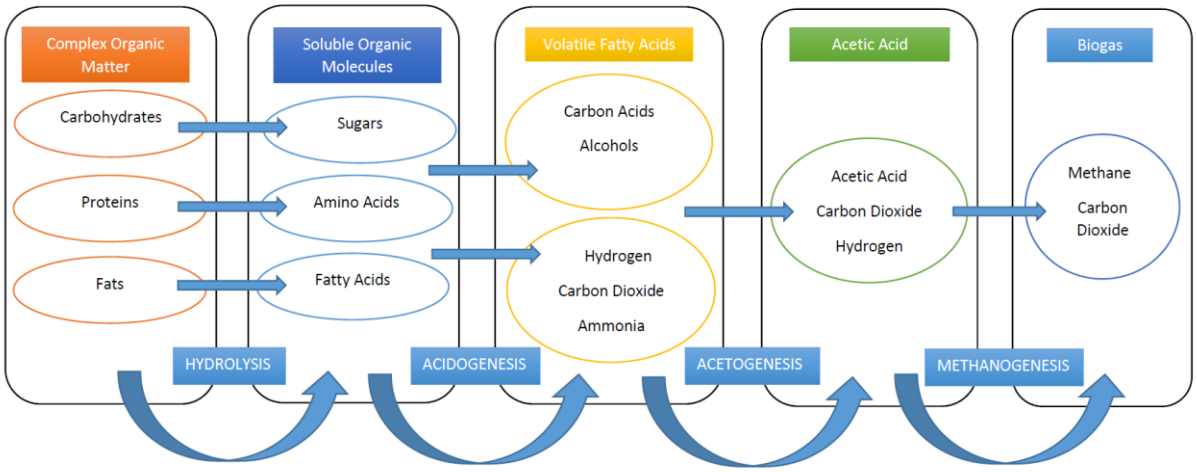

Figure 2.11 : Major biochemical steps of anaerobic digestion process.

2.9.1 Environmental Factors

Anaerobic digestion is affected by environmental factors that temperature, pH, the presence of essential nutrients and the absence of excessive concentrations of toxic compounds in the influent. Anaerobic digestion, like other biological processes, strongly depends on temperature. With respect to the conversion rate of digestion processes, there are three temperature zones can be distinguished for which bacterial populations are effective. Lower than 20°C temperature zone for psychrophilic, between 25 and 35°C temperature zone for mesophilic and above 45°C temperature zone for thermophilic microorganisms. Increasing the operating temperature of an anaerobic digestion installation is one method of adapting it to increase the substrate treated (Anjum, 2012). The system work to efficiently pH is an important factor besides temperature. The value and stability of the pH in an anaerobic reactor is extremely significant because methanogenesis only proceeds at a high rate when the pH is maintained in the neutral range.

At pH values lower than 6,3 or higher than 7,8 the rate of methanogenesis decreases.

Acidogenic populations are significiantly less sensitive to low or high pH values, and the hence acid fermentation will prevail over methanogenic fermentation.

Apart from the hydrogen ion concentration, severeal other compounds affect the rate of anaerobic digestion, even at very low concentrations such as heavy metals and chloro-organic compounds. At the same time, there are some operation conditions, which are bacteria population, mixtures of substrates or co-digestion, carbon/nitrogen (C/N) ratio, and organic loading rate effects the process efficiency significiantly (Henzen and Harremoes, 1983)

There are advantages and disadvantages about biogas from manure and other organic waste, some of them are [10, 14, 15];

- Removal a huge amount of organic waste also recovering energy from it,
- Animal manure would be utilized as fertilizer in agriculture after anaerobic digestion,
- National independence about energy demand,
- Solution for the odor problems resulting from manure,
- Economic and social development in rural areas,
- Offer an employment opportunity
- Anaerobic digestion reduced pathogens associated with manure discharges

However, it has also some disadvantages,

- Less suitable in cold and droughty regions,
- High investment cost for large scale plants,
- It should be monitored for operation and maintenance

Nevertheless, the use of biogas as an energy source has many unique qualities that provide environmental benefits. Due to the composition of biogas include methane and carbon dioxide which are greenhouse gasses, using of biogas can help mitigate climate change. Also, it can reduce acid rain cause of that biogas has no sulfate content which primarily caused acid rain. At the same time, soil erosion, water pollution and pressure on landfills, provide wildlife habitat and help maintain forest health though better management (Sabonnadiere, 2009).

2.10 Phosphorus Recovery from Anaerobic Digester Supernatat

Due to the anaerobic digestion process does not remove any nutrients during the transformation process, the digested effluent still has a high P concentration (Sung and Santha, 2003; Zhang et al., 2000). Thus, the excess phosphorus in the effluent could be recovered before the discharge where supernatant or sewage sludge. Moreover, phosphorus recovery from anaerobic digestion enables not only phosphorus recovery but also maximum bioenergy recovery (Yuan et al, 2012).

Phosphorus enriched EBPR sludge contains 5-7% phosphorus in contrast with normal activated sludges that contains 1-2% phosphorus dry weigth (Tchobanoglous, 2003), as mention about phosphorus removal part, usisng combination of anaerobic digester and EBPR process is favourable. Almost all studies about phosphorus recovery is combined with the anaerobic digestion (Britton et al, 2005; Battistoni et al, 2002; Zhao et al, 2010; Yilmazel and Demirer, 2013; Rahaman et al, 2008).

Britton et al. (2005) was conducted a pilot – scale plant for struvite recovery from anaerobic digester supernatant at an EBPR wastewater treatment plant. They fed the reactor with primariy and secondary sludge at 4-month period.

Anaerobic digestion supernatant stream through the addition of magnesium chloride and pH adjustment was recovered phosphate in the form of struvite with 90% efficiency (Britton et al, 2005).

3. MATERIAL AND METHODS

This is a case study to investigate disposal of different wastes via anaerobic digestion. and recover phosphorus from anaerobic digester supernatant. The anaerobic digestion is introduced with sewage sludge, municipal organic waste and leachate. Sewage sludge is taken from anaerobic sludge digester output of Samsun Doğu Advanced Biological WWTP. In Samsun WWTP, sludge is dewatered for easy transportation to anaerobic digestion plant. Municipal organic waste and leachate are taken from Samsun Avdan Energy landfill power plant. In real case implementation, these wastes are digested anaerobically and then solid output is sent tocompost plant and the another part that liquid form output of 67% is recycled to anaerobic digestion, the 33% of liquid output is sent to the leachate treatment plant. Schematic representation of the Samsun case study implementation where the sludge used in this study is also taken is given in Figure 3.1.

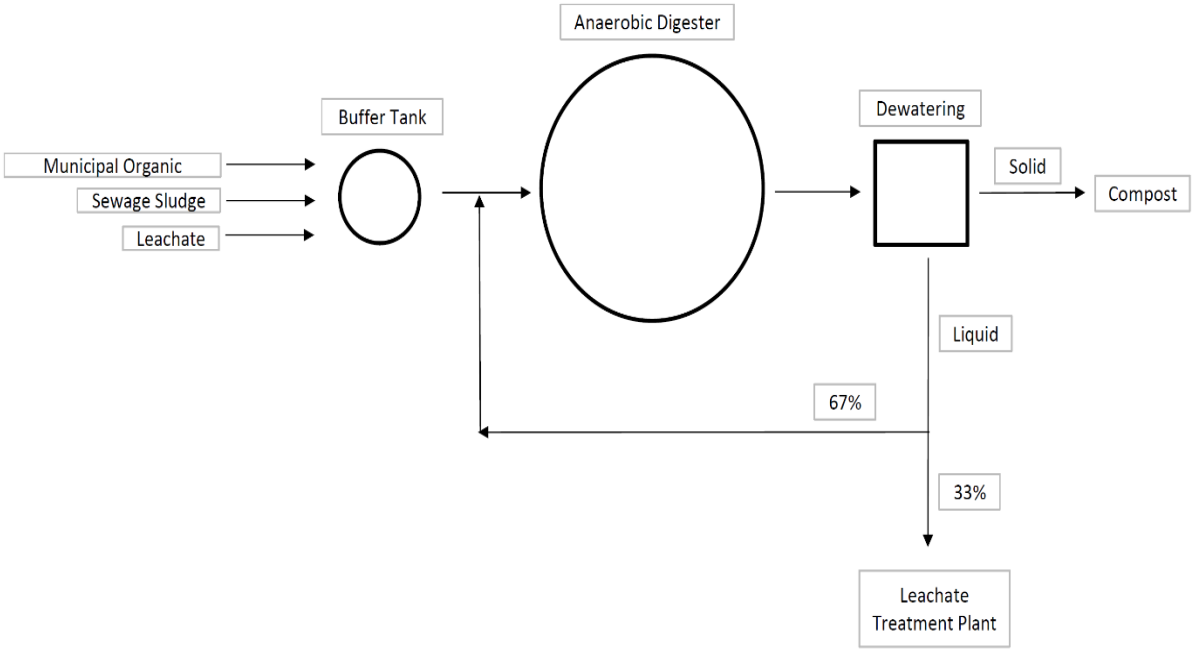

Figure 3.1 : Schematic representation of Samsun Case Study

3.1 Samsun Doğu Advanced Biological Wastewater Treatment Plant

Samsun Doğu Advanced Biological Wastewater Treatment Plant treats almost 105,000 m^3 daily wastewater. The plant is one of the biggest wastewater treatment plant of Black Sea Region that is displayed in Figure 3.2.

Figure 3.2 : Samsun Doğu Advanced Biological Wastewater Treatment Plant.

The treatment plant is designed as to treat the wastewater by removing carbon, nitrogen and phosphorus. From existing design criteria, the main requirement of the treatment plant is to reduce biochemical oxygen demand (BOD_5) from 300 mg/l to 20 mg/l, nitrogen load from 60 mg/l to 10 mg/l, phosphorus load from 8 mg/l to 2 mg/l and the suspended solid matter from 500 mg/l to 35 mg/l. Moreover, the phosphorus amount suppressed in the treatment plant is 630 kg/day, BOD_5 amount 29,400 kg/day and nitrogen amount 5,250 kg/day.

The plant includes primary (mechanical) and secondary (biological) treatment processes. Primary treatment aim is to remove particles, sediments, fat, natural organic matter and colour

from the sewer water. The process consists grit separation, grase and sand removal with aeration and primary clarifier.

Secondary treatment is carried out using activated sludge process. The process is based on removal of carbon, nitrogen and phosphorus biologically. Wastewater flows through aerobicanoxic tanks subsequently, where carbon removal, nitrification and denitrification is performed. Activated sludge is supplied to the anaerobic reactor by sludge recycle. Activated sludge wastewater mixture leaving the biological phosphorus unit enters the denitrification tanks at the first section. Phosphorus, nitrogen and carbon are removed through biological unit.

In the activated sludge tank, 56% of wastewater is fed continuously into an aerated tank where microorganisms break down organics and mixes with return sludge and then, the mixture enters the biological phosphorus tanks. The resulting microbial floc is settled under quiescent conditions in a final clarifier and returned to an aeration tank.

Wastewater conveyed from activated sludge tank arrive at a distribution unit and enter the final sedimentation tanks, which are equipped with semi-rotary bridge scrapers. After final sedimentation tanks, sludge goes sludge thickners and sludge storage tanks respectively. Treatment plant processes are displayed schematically in Figure 3.3.

Treated water overflowed from the outlet weirs of the final sedimentation tanks is conveyed to the discharge unit by means of the deep-sea discharge.

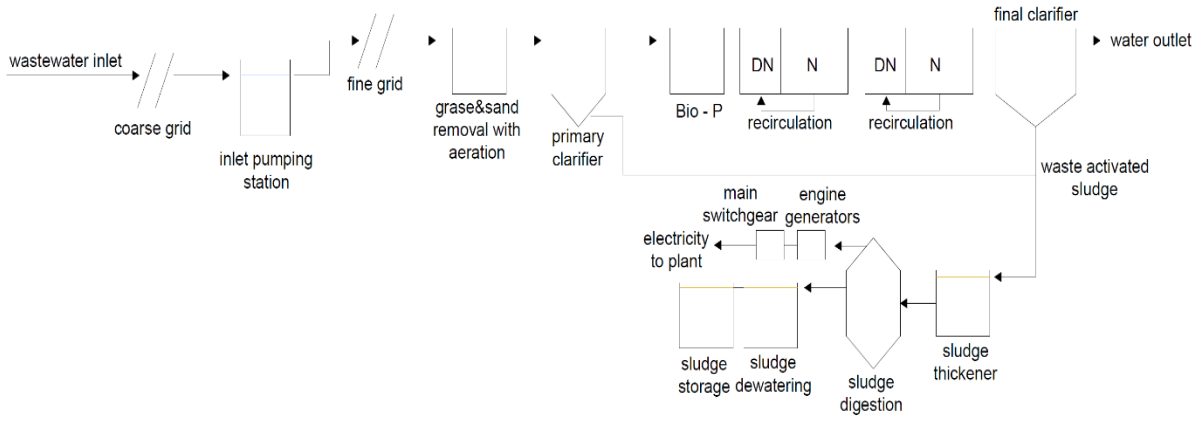

Figure 3.3 : Wastewater treatment processes of Samsun Doğu Advanced WWTP.

3.2 Samsun Avdan Energy Landfill Power Plant

Samsun Avdan Energy Landfill Power Plant is the waste disposal plant of Karadeniz Region, Turkey, providing not only the disposal of wastes but also benefits to the country economy by generating electrical energy via producing biogas. The plant produces 3,6 MW electrical energy daily by using municipal organic wastes that are taken from Samsun and nearby cities. The plant is displayed in Figure 3.4.

Figure 3.4 : Samsun Avdan Energy Landfill Power Plant.

Experimental analysis is conducted at two stages mainly. First one is set – up anaerobic digestion reactor by using various wastes which has different characterizations. Following that, the second part constitute from phosphorus recovery at this reactor's supernatant via struvite precipitation.

Since the main purpose of this study is anaerobic digestion of sewage sludge and phosphorus recovery from the supernatant of this anaerobic digester, the sewage sludge is taken from raw sludge tank of Samsun Doğu Advanced Biological Wastewater Treatment Plant. Raw sludge

tank includes both primary and secondary settling tank sludge 23% and 77% respectively. However, the low phosphorus and nitrogen contents and high total solids concentration at sewage sludge is observed with characterization analysis results. Supplement materials having high nutrient content are added to enable sufficient phosphorus and nitrogen content.

Therefore, leachate is used both to dilute the total solid contents and to increase nitrogen concentration of anaerobic digester. Leachate is one of the waste generated in municipal landfill and it contains large amounts organic and inorganic contaminants. In particular, leachate is a great source of nitrogen. Thus, , Leachate taken from Samsun Avdan Energy landfill power plant is used to balance nitrogen and total solid concentrations of anaerobic digester.

Beside the insufficient nitrogen concentration, there is lack of phosphorus content too. In order to overcome phosphorus deficiency, municipal organic waste that contains high amount of phosphorus is used. The municipal organic waste is taken from Samsun Avdan Energy landfill power plant. Not only to increase phosphorus concentration of digester but also to redound biogas efficiency of the anaerobic digestion with increasing organic material content of reactor, is aimed via adding municipal organic waste externally.

Consequently, disposal of sewage sludge, municipal organic waste and leachate is a major problem nowadays from the point of their treatment. To sum up, four major purposes are aimed while setting up anaerobic digestion reactor by using these wastes;

- To evaluate the efficiency of phosphorus recovery from anaerobic digester supernatant.
- To enable the suitable conditions for proper struvite precipitaion in terms of molar ratio by adding high nitrogen content waste (leachate) and high phosphorus content waste (municipal organic waste).
- To increase amount production of biogas from anaerobic digestion with adding organic wastes
- To dispose wastes (sewage sludge, leachate and municipal organic waste) difficult to treat otherwise (requiring high chemical addition and/or operating cost requirement for treatment) together through anaerobic digestion.

Sampling, methods of analysis, experimental set – up and calculations are discussed in this part respectively.

3.3 Anaerobic Digestion

Municipal organic waste, leachate and inoculum are used in different ratios to adjust total and volatile solid contents, phosphorus and nitrogen concentrations for efficient anaerobic digestion of sewage sludge. Inoculum is taken from the anaerobic digester tank of Samsun Doğu Advanced Biological Wastewater Treatment Plant.

Anaerobic digester is generally consised of 67% inoculum and 33% substrates (Öztürk, 2007). According to this rule, percentage of each waste is calculated and the ratios of substrates and inoculum are given in Figure 3.1 in detail. Hereby, the bottles include 11% sewage sludge, 11% municipal organic waste, 11% leachate and 67% inoculum. Also, total phosphorus, ortho – phosphate, total kjeldahl nitrogen and ammonia nitrogen are calculated therotically by using this rate.

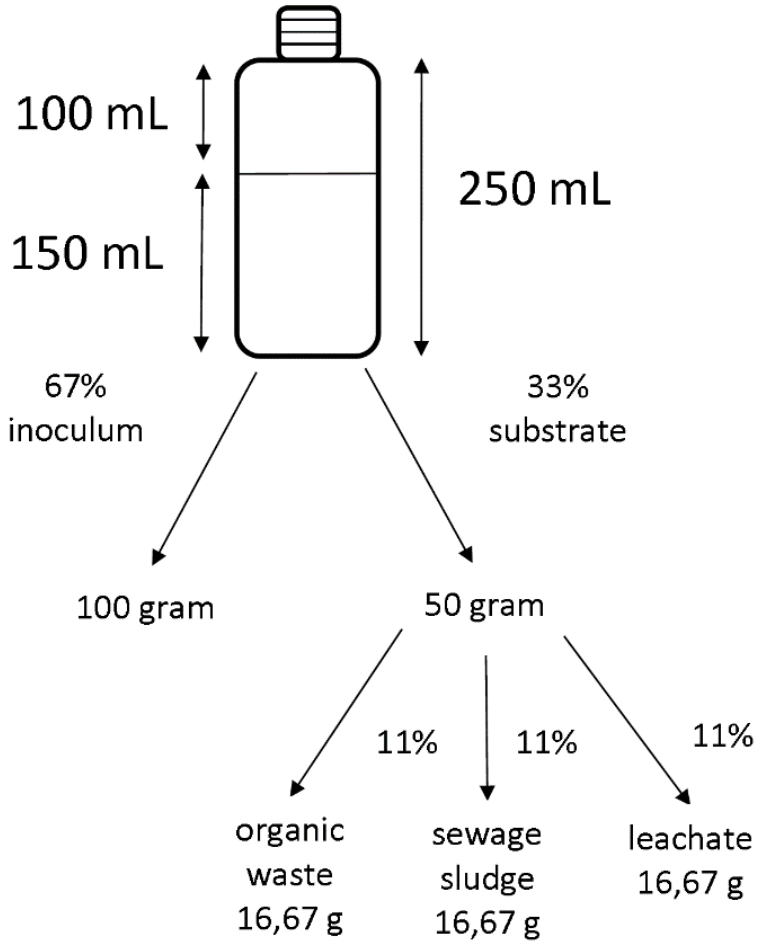

Figure 3.5 : Rate of substrates and inoculum in anaerobic digestion bottle.

Three bottles having the same contents (sewage sludge 11%, municipal organic waste %11, leachate 11% and inoculum 67%) are set up to control and check the anaerobic digestion process efficiency. In addition, two bottles are also set up by using only inoculum (100%) to observe the anaerobic digestion of inoculum. Their contents are given at Table 3.1.

Table 3.1: Anaerobic digester bottles and their contents.

Number of bottle	Contents
1	67 % inoculum, 11% sewage sludge, 11% organic waste, 11% leachate
2	67 % inoculum, 11% sewage sludge, 11% organic waste, 11% leachate
3	67 % inoculum, 11% sewage sludge, 11% organic waste, 11% leachate
4	100 % inoculum
5	100 % inoculum

The bottles are pressure tight and glass, also rubber closure and metal fixing mechanism as a cap, which enables the measurement of pressure inside the bottle without any leak. The bottles are located in the warm room with temperature 37ºC at solid waste laboratory. All bottle pressures are measured daily by using Letro PM-9107 manometer to evaluate the amount of biogas production, that is showed at the Figure 3.2. The bottles are displayed at the Figure 3.3. Amount of biogas production is calculated according to the ideal gas law by using daily gas pressures.

Figure 3.6 : Letro PM-9107 manometer.

Figure 3.7 : Anaerobic digestion bottles.

Experimental analysis for characterization of waste is conducted before and after anaerobic digestion.

The parameters analyzed for the characterization are: Total Solids (TS), Volatile Solids (VS), pH, Total Nitrogen Kjeldahl (TKN), Ammonia Nitrogen (NH_4-N), Total Phosphorus (TP) and Ortho – phosphate (PO_4-P-P). All analytical determinations were performed according to "Standard Methods" (APHA, 1989).

3.4. Phosphorus Recovery

Bottles are opened after fifty days when the gas production is reached to steady state. Conversion of total solids and amount of nutrients (phosphorus and nitrogen) characterization analyses is conducted at anaerobic digester bottles to find out the digestion efficiency. After characterization, 100 mL sample is taken from the digester for centrifugation. Samples are centrifuged during 20 minutes at 4500 rpm and then 50 mL samples are filtered out by using

syringe tip with 0,45 µm for separating total solids. This procedure is repeated for 3 times for preparing 3 samples for struvite precipitation. In addition, total phosphate, orthophosphate, ammonia nitrogen and total kjeldalh nitrogen are analyzed from this filtrate that is called also supernatant.

Samples are stirred continuously on magnetic stirrer and pH is controlled with pH meter. The starting pH is 7,6 for all bottles. 0,1 M NaOH is used for adjusting the pH. The pH is increased at first sample to 8,8 and at second one to 9,8 and at last one to 10,8. Samples are mixed for 60 minutes by using magnetic stirrer at 1400 rpm. Precipitation is conducted with only pH adjustment without any chemical addition. The precipitates are filtered with AP40 filter and then weighed. Precipitates that remaining on the filter are dried for 30 minutes in stove at 105 ºC. Then, the precipitates are dissolved by using acidic solution to pH 7,5. After that, total phosphate, orthophosphate, ammonia nitrogen and total kjeldalh nitrogen are analyzed at this solute for checking the struvite precipitation results.

For struvite precipitation, first, second and third bottles supernatants, which contain sewage sludge, leachate, municipal organic waste and inoculum, are used. Without any chemical addition, just pH adjustment with 0,1 M NaOH, at pH 8,8; 9,8; 10,8 struvite precitipation was enabled. Then, these solutions are filtered with 0,45 µm glass filter. Total phosphorus, ortho – phosphate, total kjeldahl nitrogen and ammonia nitrogen were measured for evaluating the struvite precipitation efficiency. Precipitated part was also dried and dissolved at acidic solution for phosphorus and ammonia nitrogen analysis in terms of cheking the struvite efficiency.

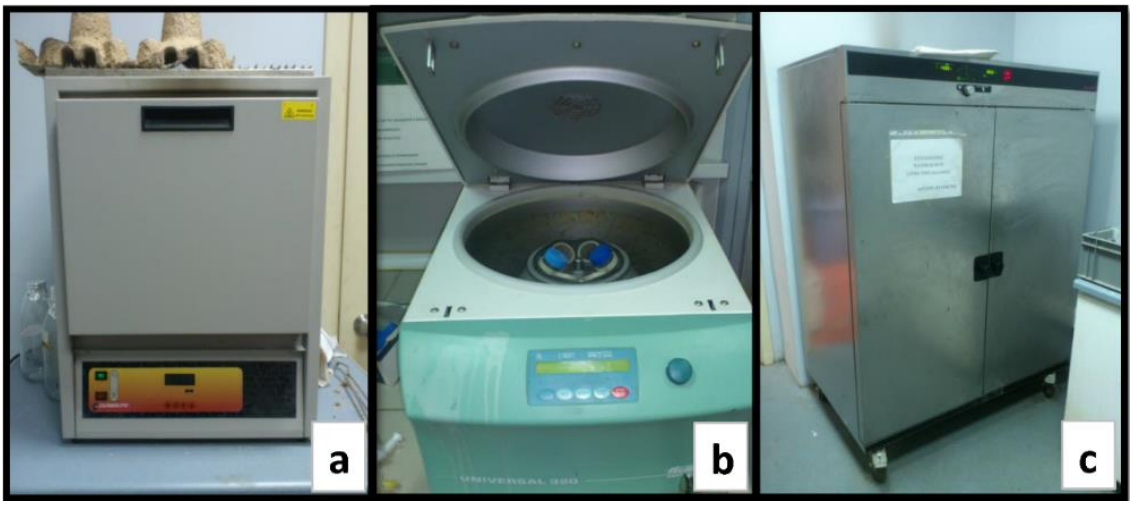

Figure 3.8 : The devices uses in experiments; a) oven, b) centrifuge, c) stove.

4. RESULTS AND DISCUSSION

Despite of the main aim of this study is to evaluate the phosphorus recovery efficiency from anaerobic digester supernatant, the another aim is to investigate anaerobic digestion of wastes, which have different characteristics, in together.

Sewage sludge, leachate and municipal organic waste are anaerobically digested and analyzed in this study. In addition, contribute to full scale applications for anaerobic digestion of these wastes is also aimed.

Results and discussion part constitues of three main parts which are results of characterization analysis at the beginning and end of the anaerobic digestion, monitoring the biogas production and struvite precipitation.

4.1 Characterization Analysis

In order to find appropriate rates of organic materials and nutrients from substrates for efficient anaerobic digestion, all substrates and inoculum was characterized. The characterization parameters and the beginning results of analysis for substrates are given at Table 4.1.

Table 4.1 : Characterization Results Wastes.

	TS %	**VS %**	**TKN mg/L**	**TP mg/L**	**Orth-P mg/L**
Sewage Sludge	24,18	13,84	840	*	6,94
Municipal organic Waste	41,27	22,18	1200	327	110,4
Leachate	1,6	0,55	2600	0,82	0,21
Inoculum	5,2	3,7	3147	63,2	27,03

Municipal organic waste has high total solid content due to it consists both organic and inorganic materials such as glass. At the same time, the organic portion of the waste includes generally household wastes. For that reason, it contains high nutrient concentrations. Because of low total and volatile solid contents of leachate, it is used to provide dilution for the anaerobic digester total solid concentration. However, leachate contains both organic and inorganic pollutans generally, and they may adversely affect the anaerobic digestion process. So, it should

be analysed in detail before using in biological systems. In particular, high ammonia concentratration can cause of the inhibition or toxic effects in terms of free ammonia.

4.2 Biogas Production

The second aim of this study is biogas production via anaerobic digestion by using different wastes. The anaerobic digestion efficiency are evaluated according to both amount of biogas production that is calculated by using daily gas pressures and rate of organic material digestion which is calculated by conversation of volatile solids at first and fiftieth days of anaerobic digestion.

Before set – up the anaerobic digester, characterization of wastes by analyzing of their total and volatile solid contents, total and ortho – phosphate, ammonia and total kjeldahl nitrogen concentrations is determined.

For proper anaerobic digestion, total solid concentration of digester is suggested to be between 8 – 15 % (Öztürk, 2007). For that reason, initial total solid content of digester is calculated by using these characterization results with mixing ratio of waste mass according to the Eq. 4.1. Total solid contents of each waste (TS_{SS}; TS_{MO}; TS_{LE}; TS_{IN} symbols are used to indicate the total solid contents of sewage sludge, municipal organic waste, leachate and inoculum respectively.) are compared according to the volume of bottle.

$$\boldsymbol{TS(mg * L^{-}) = \frac{(TS_{ss}\times 16{,}67)+(TS_{MO}\times 16{,}67)+(TS_{LE}\times 16{,}67)+(TS_{IN}\times 100)}{150}} \qquad \textbf{(4.1)}$$

Total solids and volatile solids concentreations are calculated both theoretically and experimentally. According to the Equation 4.1, by using total and volatile solid contents of each wastes , theoretical total and volatile solid contents for anaerobic digestion at first day is calculated. The average total solid concentration is 10,92 g/L and volatile solid concentration is 6,53 g/L in other words 11 % total solid contents and 6,5 % volatile solid concentration theoretically anaerobic digestion at first day for 1., 2., and 3. bottles. The experimental results of total solid concentrations are 10,98 %, 10,87% and 11,02% of first, second and third bottles respectively for 1. day of anaerobic digestion. The average of the experimental results of total solid concentration is 10,95 % for first three bottles. Thus, experimental and theoretical total

solid content results are same approximately in the first day of anaerobic digestion. After fifth days of anaerobic digestion, total and volatile solid concentrations are analyzed experimentally as well. According to the fiftieth days results of total solid concentrations which are 6,23 %, 6,76 % and 6,3 % in order of first three bottles, display the rate of total solid digestion. To sum up, avarage of total solid concentrations for three bottles which consists all wastes, while it was 10,95 % at first day, it is 6,43 % at fiftieth days. Results represents about 58,72 % of total solids is digested anaerobically. Total solid content decreases with anaerobic digestion of sewage sludge about 1 – 12 % depending on the type of waste and environmental conditions (Astals et al, 2012).

Furthermore, volatile solid concentrations are evaluated and compared with first and fiftieth days of anaerobic digestion, too. The experimental results of volatile solid concentrations, which are 6,49 %, 6,54 % and 6,52% for first three bottles, and theoretical results that is 6,5 % the average of three bottles, at first day of anaerobic digestion. After fiftieth days of anaerobic digestion, volatile solid concentrations are analyzed experimentally and its results are 2,97 %, 2,82 % and 2,81 % for first three bottles.

The average of the first and fiftieth days anaerobic digestion of experimental results volatile solid concentrations are 6,51 % and 2,86 % respectively. As a result of that calculation, 43,93 % volatile solid contents are digested anaerobically during the fifty days. The volatile solid conversation rate is 40 – 80 % with anaerobic digestion in literature (Öztürk, 2007). The total and volatile solid concentrations are given at Table 4.2 for each bottles.

Table 4.2 : Total solids and volatiles solids concentrations at the first and fiftieth days of anaerobic digestion.

	1. day		**50. days**	
Number of bottle	**TS (%)**	**VS (%)**	**TS (%)**	**VS (%)**
1	10,98	6,49	6,23	2,97
2	10,87	6,54	6,76	2,82
3	11,02	6,52	6,3	2,81
4	5,74	3,88	5,68	2,18
5	5,69	3,92	5,69	2,25

After the bottles were set up, their gas production is measured daily by using manometer. Production of gas is observed when it became stable. Figure 4.1 displays the daily biogas production in terms of volume for three bottles that consists wastes and inoculum. 1, 2 and 3

solid lines indicates the number of bottles and forth one which is dotted line is the average of three of them in Figure 4.1 and 4.2. Also, cumulative biogas volume is shown in Figure 4.2. Production of biogas is measured as a daily pressure in terms of millibars. Pressure is converted to mole of gas by using ideal gas law (P; measured pressure, V; volume of gas part in bottle, n; mole of gas; R; ideal gas constant and T; temperature in terms of Kelvin) that is given at Eq. 4.2. The mole of gas (n) is calculated by using these values.

$$\boldsymbol{P \times V = n \times R \times T} \qquad \textbf{(4.2)}$$

In the Equation 4.2, the daily measured biogas pressure is converted from milibar to atm, the gas volume of bottle is taken 100 ml, ideal gas constant (R) is taken 0,0821 liter·atm/mol·K and temperature is 37℃ that converted to 310 Kelvin (37+273).

By using Eq. 4.1, daily and cumulated biogas production volume is calculated. Fig. 4.1 and 4.2 display the biogas production daily and cumulative respectively. Although, there are some fluctuations about biogas production, each bottle has the same biogas production rate. Biogas production in the begining of anaerobic digestion is increasing to twentieth day and after that it is decreasing to the getting stable. Moreover, measurement of biogas production is continued until the fiftieth day to ensure anaerobic digestion is nearly completed.

Although, there are many anaerobic co – digestion studies which are including different combination of wastes, sewage sludge, municipal organic waste and leachate have never been used together for anaerobic digestion at the literature. For that reason, biogas production efficiency can not be compared with literature studies.

2.1 Phosphorus Recovery

The main goal of this study is phosphorus recovery from anaerobic digester supernatant via struvite precipitation. For evaluating P recovery efficiency; total phosphorus, orto – phosphate,

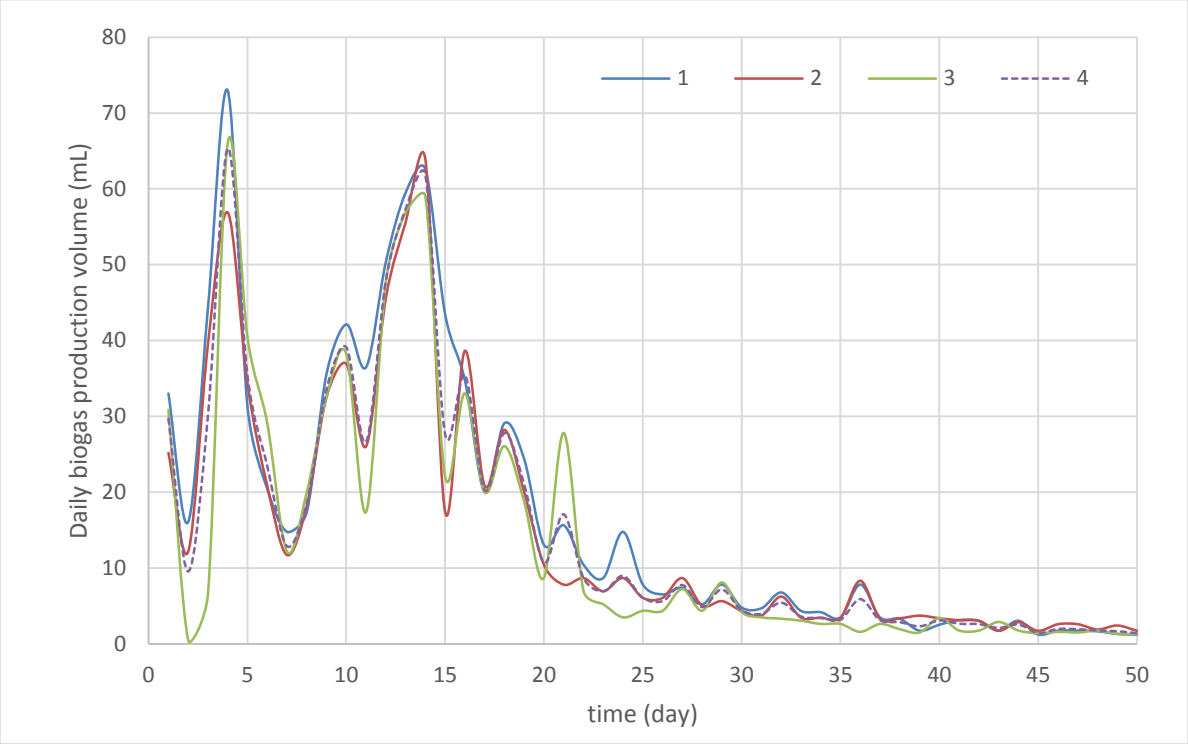

Figure 4.1 : Daily biogas production volume (mL).

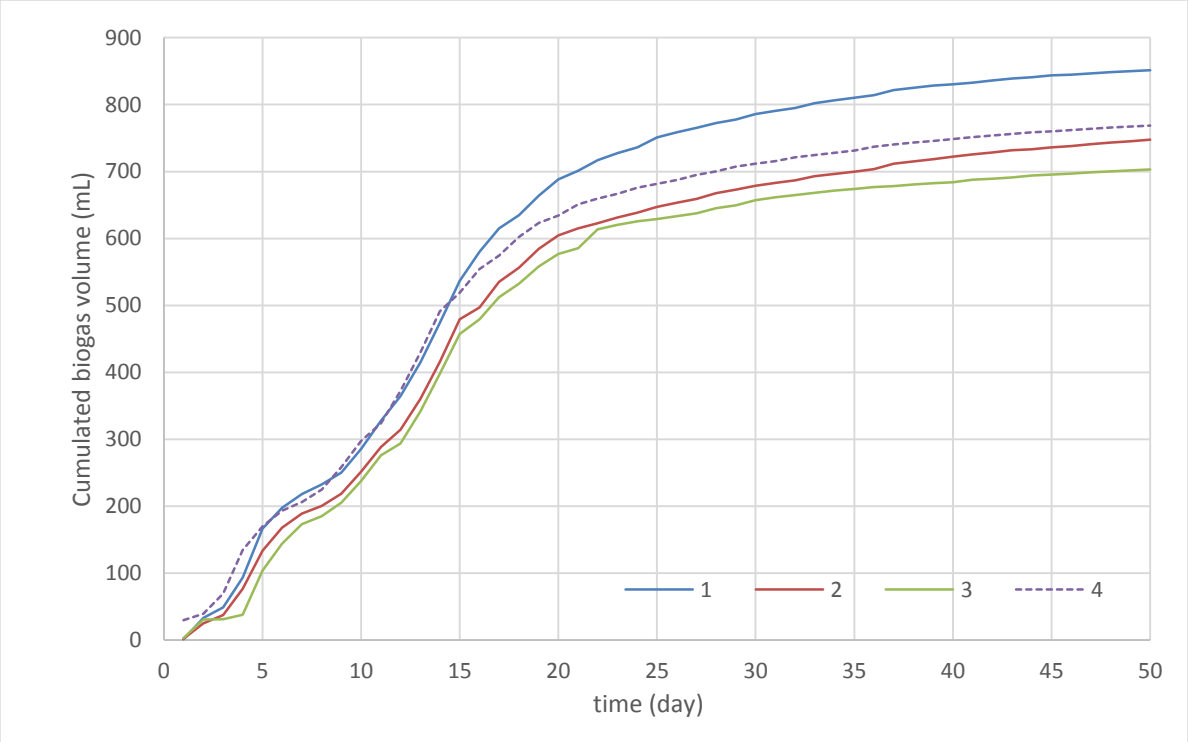

Figure 4.2 : Cumulated biogas production volume (mL).

total kjeldahl nitrogen and ammonia nitrogen are analyzed in mixed liquor, in supernatant at first day of anaerobic digestion, in supernatant at fiftieth day, after struvite precipitation, in precipitate that dissolved with acidic solution and in the filtrate which remained from the precipitation for Table 4.3 displays the result of the analysis. According to the experimental analysis results, total phosphorus concentration is 322 mg/l in mix liquor and 80,32 mg/l in supernatant at first day of anaerobic digestion. Due to the high total solid concentration of mix liquor, total phosphorus concentration has strictly different from mix liquor and supernatant. In a similar way, ortho – phosphate concentrations in mix liquor and supernatant at first day of anaerobic digestion have difference because of high total solid concentrations.

Table 4.3 : Characterization results at the first day and fiftieth day of anaerobic digestion.

Sample	**TP mg/L**	**Orth-P mg/L**	**TKN mg/L**	**NH_4 – N mg/L**
Mix liquor at 1. day	322,00	116,00		
Supernatant at 1. day	80,32	31,08	2370	*
Supernatant at 50. day	216,00	112,42	1502	1321
Struvite	163,54	87,30	1008	980
Filtrate	27,72	10,02	320	188

Moreover, owing to leachate has great amount of total kjeldahl nitrogen concentration, TKN is 2370 mg/l in the supernatant at first day of anaerobic digestion. In addition, theoretical TKN concentration in mix liquor is calculated by using each waste TKN concentrations. The theoretical TKN concentration in mix liquor at first day of anaerobic digestion is 2613 mg/L. This result is demonstrate that high total solid concentration is not affected the amount of TKN, unlike total phosphorus and ortho phosphate concentrations. Due to the low total solid concentration and high TKN concentration of leachate, these results could be found.

Total phosphorus concentration is 216 mg/l in supernatant after fifty days of anaerobic digestion. At the same time, this concentration is 163,54 mg/l and 27,72 mg/l in struvite precipitation and in filtrate respectively. This means that 33 % total phosphorus is converted from first day in the mix liquor to fiftieth day from supernatant. Also, 75,5 % total phosphorus

is removed via struvite precipitation from fiftieth days supernatant. To sum up, 50 % total phosphorus concentration is removed with struvite precipitation from first day in the mix liquor to fiftieth days in supernatant.

The phosphorus recovery rate could be calculated not only by using total phosphorus concentrations but also orto – phosphate concentrations could be used. The orto – phosphate concentration is 112,42 mg/l in supernatant in fiftieth days of anaerobic digestion. Additionally, this concentration is 87,30 mg/l in struvite and 10,02 mg/l in filtrate after struvite precipitation. So, approximately 3,5 % ortho – phosphate is converted from first day of anaerobic digestion to fiftieth day of anaerobic digestion. This conversion rate is lower than total phosphorus conversion owing to high total solid contents in the mix liquor. Furthermore, % 77 of orto – phosphate is removed with struvite precipitation from fiftieth days supernatant. Consequently, 75 % orto – phosphate concentration is removed with struvite precipitation from first day in the mix liquor to fiftieth days in supernatant.

Struvite precipitation is not only used to remove phosphorus but also nitrogen in wastewater cause of its chemical formula. For that reason, total kjeldahl nitrogen and ammonium nitrogen is analyzed experimentally from supernatant, mix liquor, struvite and filtrate. According to the total kjeldahl nitrogen concentration in supernatant at first day and fiftieth days of anaerobic digestion, which are 2970 mg/l and 1502 mg/l respectively, 49,5 % TKN is converted via anaerobic digestion. Also, 67 % TKN is removed with struvite precipitation from first day in supernatant to fiftieth days in supernatant. Moreover, 74 % of ammonium nitrogen is removed by struvite precipitation too.

Struvite precipitation is observed at three different pH (8,8; 9,8; 10,8) with just adding NaOH for adjusting pH. struvite precipitation is provided at different amounts without any chemical addition except pH adjusting, which can be seen at Table 4.4. The best results are found at pH 9,8 with 8,26 g struvite precipitation for 100 ml supernatant. For that reason, the characterization analysis is conducted at pH 9,8. Generally, struvite is precipitated 1 – 2 kg from 1 m^3 supernatant (Balmer, 2003; Cornel, and Schaum, 2009; Hao et al., 2008). However, in this study, struvite precipitation at supernatant is approximately 0,85 kg from 1 m^3 supernatant since the any chemical addition such as magnesium source, the molar ratio of struvite (Mg^{2+}: NH_4^+: PO_4^{-3}) is not provided efficiently.

Table 4.4 : Precipitation results.

pH	Struvite (g)
8,8	5,23
9,8	8,26
10,8	7,90

Another point of anaerobic digestion efficiency is related to total phosphorus relase Total phosphorus concentration in the mixed liquor is 322 mg/L in the beginning of anaerobic digestion and 216 mg/L is observed at the fiftieth day of anaerobic digestion corresponding to approximately 70% total phosphorus release through anaerobic digestion.

According to the Table 4.3, the ortophosphate concentration in supernatant at fiftieth day of anaerobic digestion is 112,42 mg/L and 87,30 mg/L of it is precipitated as struvite. Therefore, about 77% of ortophophate is removed via struvite precipitation. In literature, this rate is 85 – 99% generally (Le Corre et al., 2009; Munch and Barr, 2001; Petzet, et al., 2012; Sartorius et al., 2011). However, phosphorus recovery rate in terms of struvite precipitation depend on type of waste or wastewater, range of pH, molar ratio of phosphorus, nitrogen and magnesium in the sample and mixing time of precipitation. For example, Nelson et al. (2003), used anaerobic swine lagoon effluent at 8,9 pH with 1:1:1 molar ratio of Mg:N:P for struvite precipitation. Also, they used magnesium source externally and their struvite recovery rate is 96%. Similiarly, Uysal et al. (2010), used sewage sludge anaerobic digester effluent at pH 8, with 1,5:1:1 for molar ratio of Mg:N:P for struvite precipitation. Their phosphorus recovery rate is 95 % by using external magnesium. In addition, Song et al. (2007), used synthetic swine wastewater for struvite precipitation at 9,5 pH and molar ratio of Mg:N:P is 1,4:1:1. They used magnesium source externally too and their phosphoru recovery rate is 97 %. However, the phosphorus recovery rate not always high as much as these rates. For instance, Hutnik et al. (2013) used fertilizer industry wastewater with 1,2:1:1 molar ratio of Mg:N:P at pH 8,5 and 10,0. Although, they used magnesium source externally, their phosphorus recovery rate is 85 %. Interestingly, the another study is conducted by Zeng and Li (2006), for struvite precipitation. They used anaerobically digested cattle manure at 9,0 pH with 1,5:1:1,25 molar ratio of Mg:N:P by using external magnesium source. But their phosphorus recovery rate is 56 %. Additionally, El Diwani et al. (2007) are conducted a study for struvite precipitation at 9,6 pH. They used bittern

that is a source of Mg^{2+} ions and their molar ratio of Mg:N:P is 1,6:0,6:1. Consequently, they recovered 47,52 gram phosphorus per litre of fertilizer industrial wastewater.

The phoshorus recovery rate not only related to molar ratio of magnesium, nitrogen and phosphorus but also it is strictly depend on pH of sample. Jaffer et al. (2002), used wastewater liquor stream at 9,0 pH for struvite precipitation. Their phosphorus recovery rate is 97%. Likewise, Yilmazel and Demirer (2011) conducted a study to struvite precipitation in poultry manure digester effluent with pH 8,5. Their phosphorus recovery is higher than 97,4 %. In a similar way, Foletto et al. (2013), used cola beverage waste for struvite precipitation at 9,5 pH. They achieved 97 % phosphorus recovery rate. Additionally, Suzuki et al. (2007), are conducted a study for struvite precipitation by using swine wastewater, at pH 9,6. Their phosphorus recovery rate is 95 %.

In this study different wastes are used as substrate, some of them are insufficient in terms of nutrients also no chemical is used externally. Thus, the struvite precipition efficiency of this study is not much as in literature studies. Moreover, mixing time affects the precipitation efficiency.

3. CONCLUSIONS AND RECOMMENDATIONS

Phosphorus is an essential, yet limited resource which cannot be replaced by any other element. Therefore, it should be used sustainable and efficiently. For this reason, there are various technologies and studies are conducted for phosphorus recovery and reuse. The majorty of this technology relies on phosphorus recovery from the wastes. So, the main aim of this study is recovery of phosphorus from anaerobic digestion of different wastes.

With this study, following results are obtained;

- Sewage sludge, leachate and municipal organic waste which have different characterization and some troubles about treatment generally, not only digested anaerobically together but also biogas gained through this treatment. Anaerobic digestion became stable within about thirty days and maximum biogas production is 72 ml/day.
- Excess phosphorus and nitrogen recovered as struvite form that is a valuable fertlizer for agriculture. Moreover, organic load of treatment plant is reduced. Thus, treatment and disposal cost of excess sludge and chemical requirement decreased.

For further studies, waste streams from different industries (especially manure) could be combined to produce struvite efficiently. Also, new technologies for phosphorus recovery without chemical requirement for precipitation, can be improved.

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