DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

PHOSPHORUS RECOVERY AS A STRUVITE FROM SEWAGE SLUDGE APPLYING BOX - BEHNKEN EXPERIMENTAL DESIGN METHOD

by
Yaprak AVCI

July, 2015
İZMİR

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Yaprak AVCI

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M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"PHOSPHORUS RECOVERY AS A STRUVITE FROM SEWAGE SLUDGE APPLYING BOX-BEHNKEN EXPERIMENTAL DESIGN METHOD"** completed by **YAPRAK AVCI** under supervision of **PROF.DR. AYŞE FİLİBELİ** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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PHOSPHORUS RECOVERY AS A STRUVITE FROM SEWAGE SLUDGE APPLYING BOX-BEHNKEN EXPERIMENTAL DESIGN METHOD

ABSTRACT

Phosphorus (P) is one of the fundamental element for all living organisms. Phosphorus recovery technologies are developing day by day because of the realizing the importance of phosphorus. While recovering the phosphorus, pipeline's clogging problem which is one of the most important problem in wastewater treatment facilities is minimized and sludge storage problem decrease.

In this study, phosphorus recovery potential of sludge filtrate which obtained by electro dewatering process was investigated. In this process, recycled sludge of secondary settling tank of Bolu Municipal Wastewater Treatment Plant was used. Phosphorus was recovered as a struvite which consists of magnesium, ammonium and phosphorus. Parameters, affecting the phosphorus recovery such as temperature, mixing time and concentration of the added magnesiumhydroxide are searched for determining the optimum conditions for the phosphorus recovery. Pumice stone was used for struvite crystals. Experimental results were evaluated by using the Box Behnken Design and Minitab 17 statistical software method.

At the continuation of the experiments, determined three independent variables and three values for each independent were applied to the filtrate samples of sewage sludge . Determined ranges are 24-80 ^{0}C for temperature, 30-60 minutes for mixing time and 0.1-2.0 M for magnesiumhydroxide concentration.

According to the comparison results between predicted and observed phosphorus recovery values R squared was found 0.91. The maximum phosphorus recovery condition was found at 80^{0}C sample temperature, 2.0 M magnesiumhydroxide concentration and 45 minutes mixing time and the maximum value for phosphorus recovery was found as 15.8125 mg PO4-P /L. According to our experimental and statistical studies' results phosphorus recovery percent is reached 37 percent as a

maximum value. Temperature of the sample and magnesiumhydroxide concentration are the most important factors which affect the phosphorus recovery.

Keywords: Phosphorus recovery from sewage sludge, struvite, wastewater treatment plant problems, MAP

BOX-BEHNKEN DENEYSEL TASARIM YÖNTEMİ UYGULANARAK ARITMA ÇAMURLARINDAN STRUVİT OLARAK FOSFOR GERİ KAZANIMI

ÖZ

Fosfor bütün yaşayan organizmalar için esas elementlerden biridir. Fosforun öneminin anlaşılması sayesinde fosfor geri kazanım teknolojileri günden güne gelişmektedir. Fosfor geri kazanılırken arıtma tesislerindeki en önemli problemlerden biri olan iletim borularındaki tıkanma problemi azaltılır ve çamur depolama sorunu azalır.

Bu çalışmada, son çökeltim havuzu çamurundan elektro susuzlaştırma ile elde edilen filtratın fosfor geri kazanım potansiyeli araştırılmıştır. Elektro susuzlaştırma çalışmaları için çamur örnekleri Bolu Kentsel Atıksu Arıtma Tesisi son çökeltim havuzu geri devir hattından temin edilmiştir. Fosfor, magnezyum, amonyum ve fosfat içeren sütrivit olarak geri kazanılmıştır. Fosfor geri kazanımında optimum koşulları belirlemek için sıcaklık, karıştırma süresi ve eklenen magnezyumhidroksit konsantrasyonu gibi fosfor geri kazanımını etkileyen parametreler araştırılmıştır. Strüvit kristalleşmesi için çekirdek materyali olarak toz halinde ponza taşı kullanılmıştır. Deney sonuçları Box Behnken tasarım metodu ve Minitab 17 istatiksel programı kullanılarak değerlendirilmiştir.

Çalışmanın devamında, önceden karar verilen üç bağımsız ve her bir değişken için üç ayrı değer çamur filtrat örneklerine uygulanmıştır. Belirlenen aralıklar sıcaklık için 24-80 ^{0}C, karıştırma süresi için 30-60 dakika ve magnezyumhidroksit konsantrasyonu için 0.1-2.0 M'dır.

Tahmini ve gözlenen fosfor geri kazanım değerleri arasındaki karşılaştırma sonuçlarına göre R^2 değeri 0.91 olarak bulunmuştur. Maksimum fosfor geri kazanımı 80^0C sıcaklık, 2.0 M magnezyumhidroksit konsantrasyonu ve 45 dakikalık karıştırma süresi koşulunda sağlanmıştır ve fosfor geri kazanımı için maximum değer 15,81 mg

PO_4-P/L olarak bulunmuştur. Deneysel ve istatistiksel çalışmaların sonuçlarına göre maksimum fosfor geri kazanım yüzdesi, yüzde 37 'ye ulaşmıştır. Örnek sıcaklığı ve magnezyumhidroksit konsantrasyonu fosfor geri kazanımını ekileyen en önemli parametreler olarak belirlenmiştir.

Anahtar kelimeler: Arıtma çamurundan fosfor geri kazanımı, sütrivit, atıksu arıtma tesisi problemleri, MAP

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CHAPTER ONE
INTRODUCTION

1.1 Overview

Over the years importance of the phosphorus has better understood but the source of the phosphorus is depleting day by day. The current depletion of phosphorus has led to the development of various phosphorus recovery techniques and finding new phosphorus sources. One of these source is phosphate rocks but there are 11,000 million tons of phosphate rocks that cannot be processed economically at present (Shu et al., 2005). Even if these reserves could be processed economically in the future, they are not a renewable resource. Most important use of phosphate rock is fertilizer. Up to 90% of all mined phosphate rock is used to produce mineral fertilizers (Cisse and Mrabet, 2004). The other option for the phosphorus source is phosphorus that can be recovered from wastewater or sewage sludge. Phosphorus cycle from source to the its usage for modern societities is illustrated in Figure 1.1.

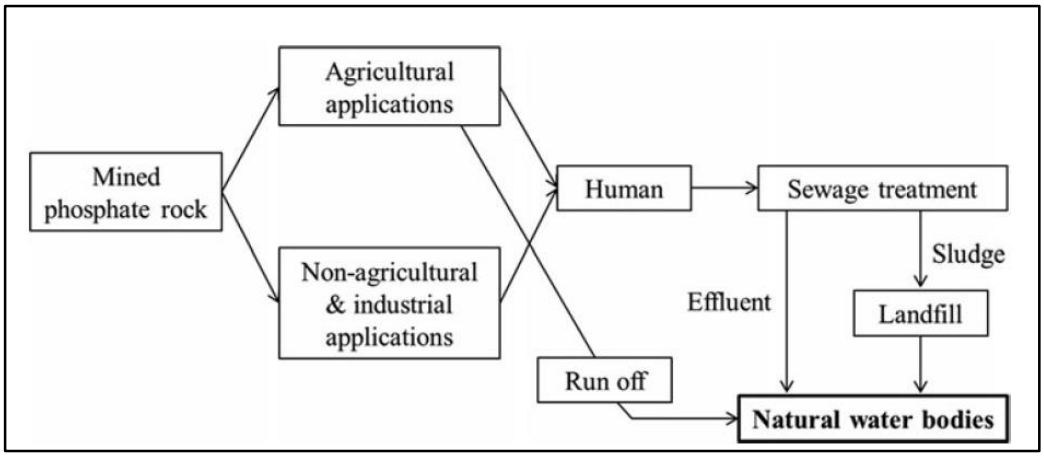


Figure 1.1 Open phosphorus cycle in modern society (modified from Centre European d'Etudes des Polyphosphates, 2012a)

Phosphorus can be found in various forms in nature such as orthophosphate, polyphosphate and organic phosphorus. Municipal wastewaters may contain from 5 to 20 mg/L of total phosphorous, of which 1-5 mg/L is organic and the rest in inorganic form. During the wastewater treatment 40 - 95 % of the incoming phosphorus load is transferred into the sewage sludge depending on the technology applied (Berg and

Schaum, 2005). In a typical wastewater treatment plant, phosphorus balance can be seen in Figure 1.2.

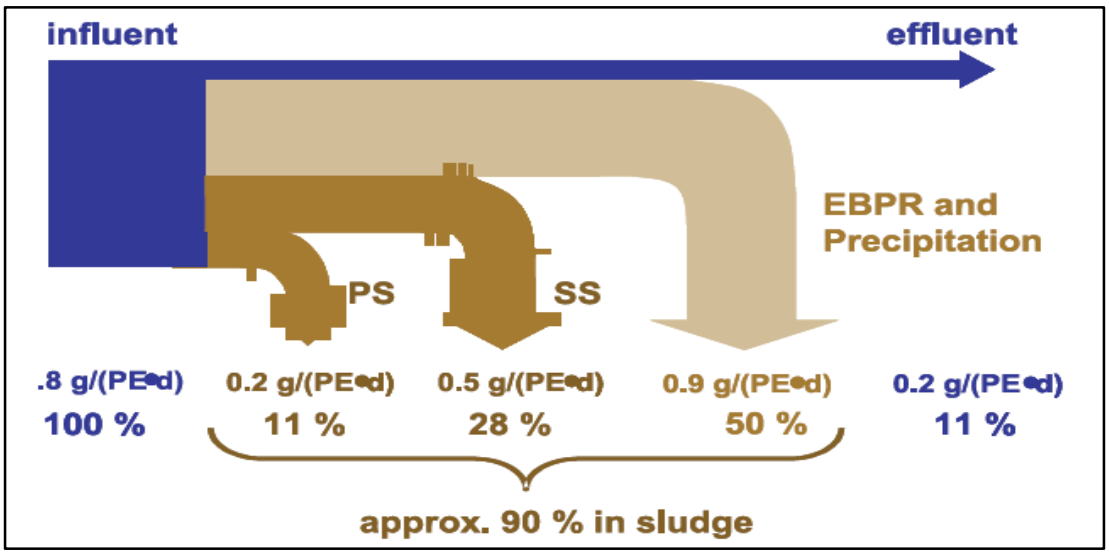


Figure 1.2 Phosphorus balance for a typical WWTP in Germany (PS: Primary Sludge; SS: Secondary Sludge (surplus sludge); PE: Population Equivalent; EBPR: Enhanced Biological Phosphorus Removal), (Schaum et al., 2007)

Approximately 11 % of the phosphorus is separated by the primary sludge (PS) and 28% by the secondary sludge without any specific phosphorus removal. Thus, approximately 50% of the phosphorus has to be eliminated by means of enhanced biological phosphorus removal (EBPR), precipitation, or other phosphorus-removal techniques. With the generally applied EBPR and/or precipitation techniques, 90% of the incoming phosphorus ends in the sewage sludge (Schaum et al., 2007). Concentration of the phosphorus in wastewater depends on many things. People's lifestyle, industrialization are just some of them. The most important and the biggest sources of the phosphorus are waste matter discharged from the body and detergents - especially phosphate detergents for industrial usage - in municipal wastewater treatment system. If the phosphorus concentration is higher than it can be assimilated by living organisms in water, it causes eutrophication. For these reasons, several phosphorus removal technologies are developed. At the present time phosphorus removal technologies are biological, chemical, or combined biological and chemical processes.

A modern wastewater treatment process removes phosphorus from sewage using an activated sludge process or a chemical precipitation process, transferring over 90% of the incoming phosphorus to the sludge fraction (Cornel and Schaum, 2009). Many technologies has been developed for recovering the phosphorus from the municipal sewage sludge and at the end of these operations phosphorus are converted into the usable form.

1.2 Aim and Scope of the Thesis

In this thesis, investigation of phosphorus recovery potential from sludge filtrate and parameter's effects were aimed. For this purpose, filtrate of sludge samples which were obtained by electro-dewatering process and transported from Bolu was used. Sewage sludge samples were taken from secondary settling tank's recycled line of Bolu Municipal Wastewater Treatment Plant. Different parameters such as temperature, mixing time and $Mg(OH)_2$ was applied at different levels. Box-Behnken Experimental Design was applied in this study and the result was evaluated with Minitab 17 Statistical Software.

The thesis is mainly composed of 6 chapters. In Chapter One, importance of phosphorus, phosphorus source in wastewater treatment plants and the aspect of this thesis are explained. Phosphorus recovery methods, previous studies and today's technology for recovery are given in Chapter Two. Phosphorus recovery products and their usage potential are explained in Chapter Three. In Chapter Four, processes, operational conditions, used equipments and applied experimental analyzes are introduced. Also, used statistical method is briefly explained. In Chapter Five, obtained results are given and discussed. In the last chapter, all thesis is concluded and some recommendations are given for future projects.

CHAPTER TWO
LITERATURE REVIEW

2.1 Phosphorus Recovery

Phosphorus is not renewable source that is crucial for the development of life and agricultural production. The main sedimentary phosphate producers are China, USA, Morocco, and Tunisia (Scholz and Wellmer, 2013). The World phosphate rock reserves can be seen in Figure 2.1. Approximately 95% of the remaining reserves are controlled by five countries, including Morocco, China, USA, South Africa and Jordan (Cordell and White, 2011). Taking into account the scarcity of this source, phosphorus recovery from wastewater, sewage sludge and sewage sludge ash is becoming necessary for sustainable development.

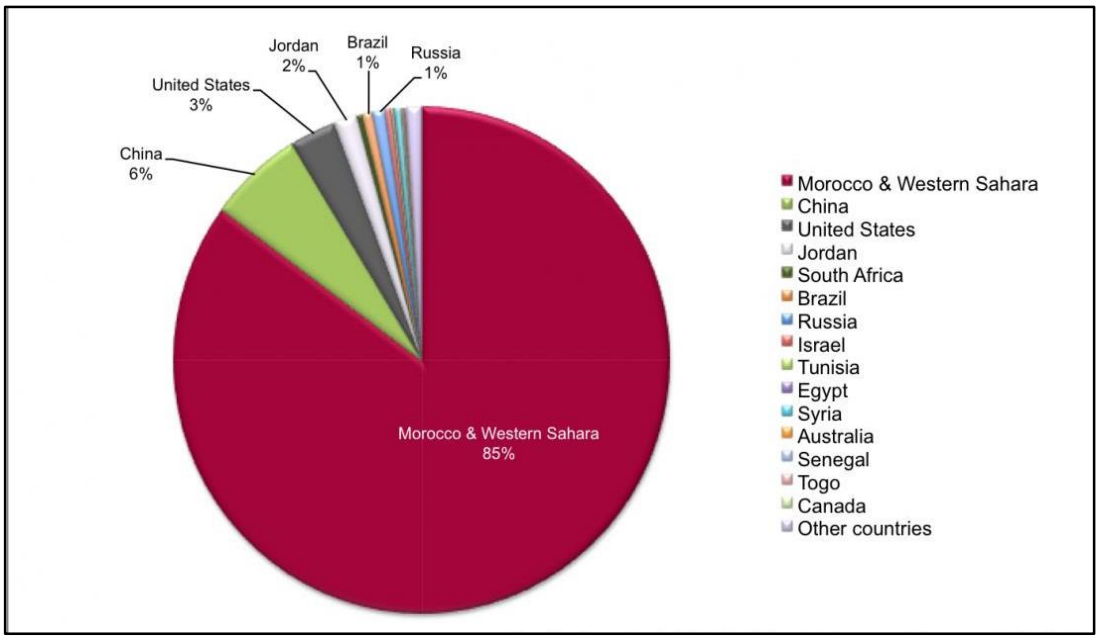


Figure 2.1 World phosphate rock reserves (Cordell and White, 2011)

Global phosphorus scenario for phosphorus recovery and phosphorus demand can be seen in Figure 2.2.

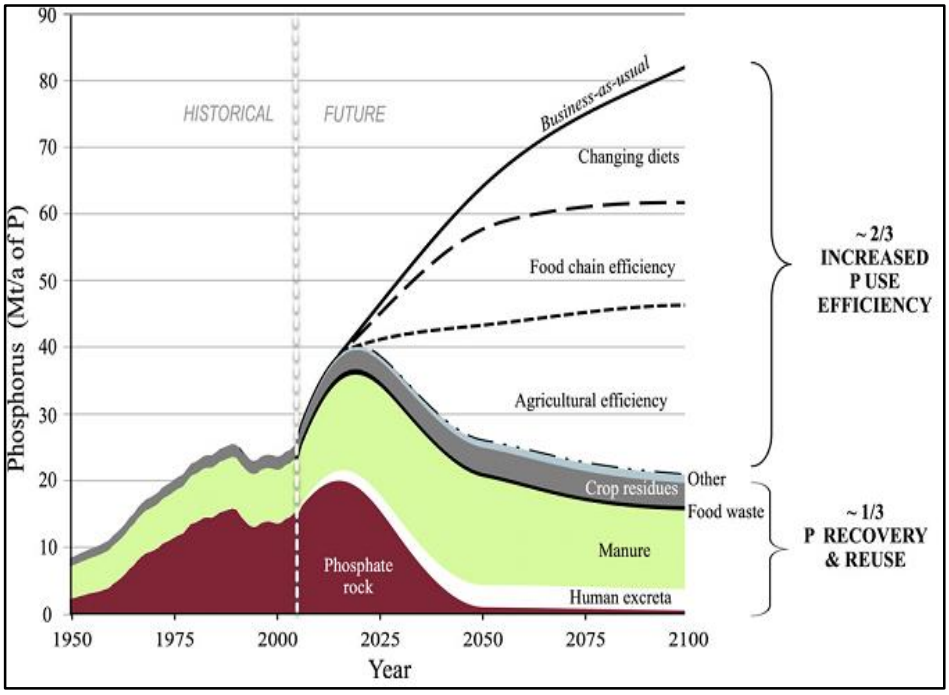


Figure 2.2 A scenario for phosphorus recovery and phosphorus demand (Cordell et al., 2011)

Phosphate recovery techniques developed for industrial or municipal wastewater treatment can be applied at various points in the treatment process. Possible locations for phosphorus recovery are shown in Figure 2.3.

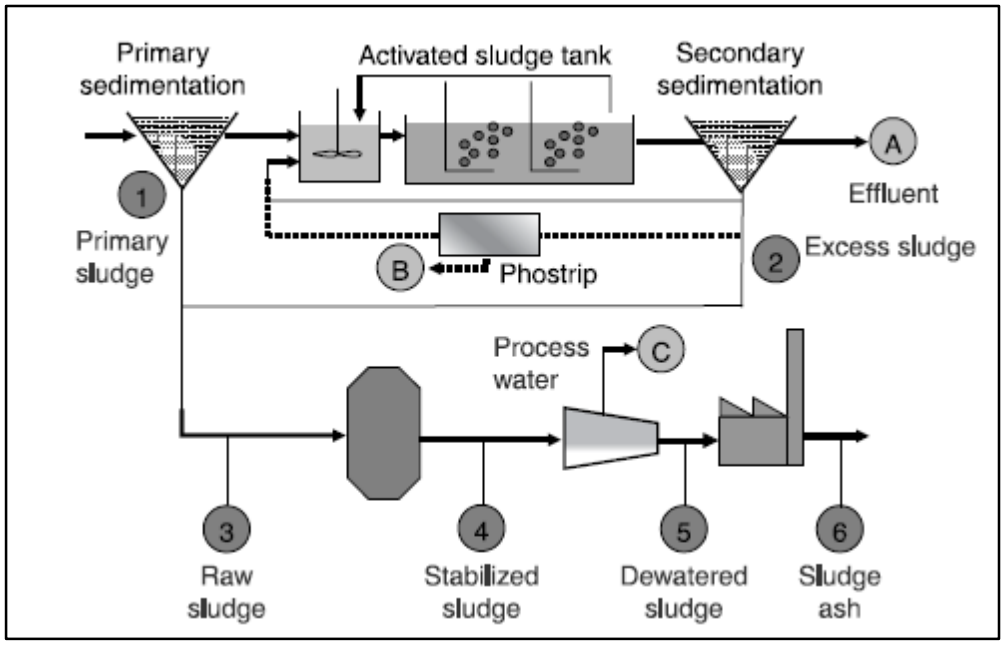


Figure 2.3 Illustration of different places of installation of phosphorus recovery units (Cornel et al., 2009)

A, B, C are the possible locations for phosphorus recovery units from the liquid phase. Point A is the effluent of the wastewater treatment plant. B is the supernatant liquor and C is the sludge liquor. Recovery degree for liquid phase is less than 50-60 % in treatment plants which is used activated sludge process.

Numbers (1 – 6) indicate the points for phosphorus recovery from sewage sludge: (1) Primary sludge, (2) excess sludge, (3) raw sludge, (4) stabilized sludge, (5) dewatered sludge, (6) sludge ash.

2.1.1 Phosphorus Recovery From Sewage Sludge Ash

A research about phosphorus for the EU27, Japan and Sweden municipality, showed that solid waste's incineration ashes contain as much phosphorus as sludge on an annual (Matsubae–Yokoyama et al., 2009 ; Ott and Rechberger, 2012). The today's inclination is sewage sludge incineration rather than direct usage of the sludge for landfill or agricultural purposes (Blöcher et al., 2012). Volume of the sewage sludge are decreased by incineration. At the end of the incineration process sludge ash containing nutrients occurs. When organic contaminants are destroyed, 60–70 % phosphorus is concentrated in the sewage sludge ash (Li et al., 2015). There are two methods for phosphorus recovery from sludge ash: a dry thermal process and a wet chemical process (Kaikake et al., 2009). In the dry thermal process, ashes are melt for phosphorus recovery. In the wet chemical process, by using acid and solvent phosphorus is extracted and recovered from the solution.

For sewage sludge ash (SSA), the required chemical amount is less than sewage sludge on the other hand direct usage of the sewage sludge ashes are limited because of the heavy metal content. An additional treatment step is necessary for removing heavy metals and thermochemical treatment is mostly used for this purpose. Adam et al. (2009) have reported that operating temperature is about 1000^{o}C in this treatment process. And this thermochemical process reduces the volume of the sewage sludge about 80-90% (Atienza-Martinez et al., 2014). In Figure 2.4 sewage sludge ash's treatment steps which start with sewage sludge and end up with occurance of fertilizer can be seen.

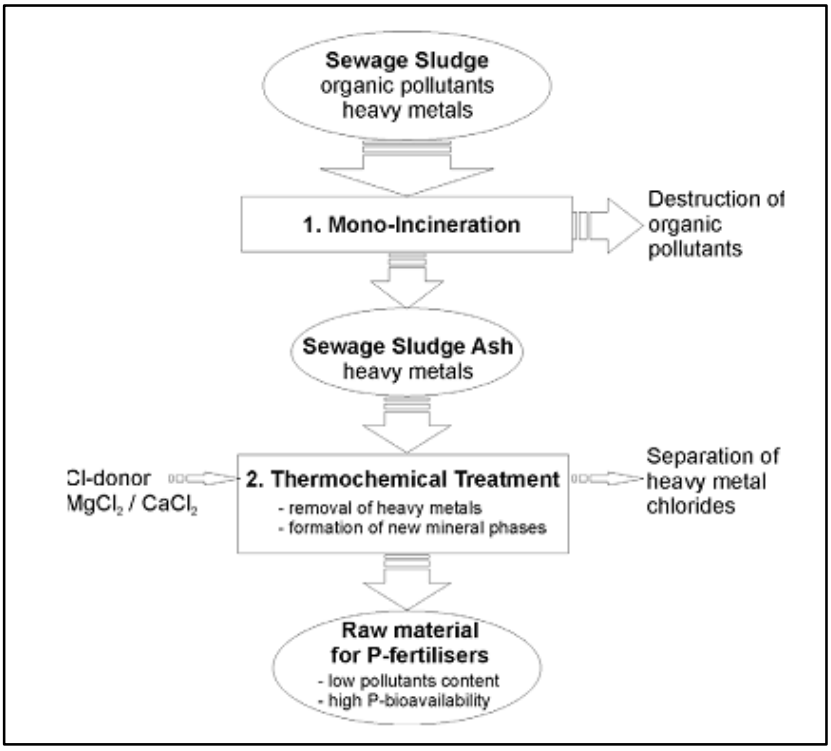


Figure 2.4 Treatment steps for heavy metal of the sewage sludge ash (Adam et al., 2009)

In all over the World many projects have been carried out for searching the phosphorus recovery potential from sewage sludge ash and one of them is SUSAN Project. The European SUSAN (Sustainable and Safe Re-use of Municipal Sewage Sludge for Nutrient Recovery) project's aim is to find a way for nutrient recovery from the sewage sludge by using thermal methods and this way must be sustainable. In this Project many types of sewage sludges were used for incineration and their ashes were obtained in a furnace at the laboratory. At the end of the SUSAN Project many articles were published. According to the project, sewage sludge ashes (SSA) which occur at the end of the incineration process contain 15-25 % P_2O_5 as a phosphorus (Sustainable and safe re-use of municipal sewage sludge for nutrient recovery final activity report (2009). May, 2015. http://www.susan.bam.de/).

There is another research for phosphorus recovery from sewage sludge ashes and it's name is Recophos Project. In this project phosphorus can be recovered with thermo-reductive processes. Wöhler Process is used for basic process. In a furnace phosphate react with carbon and silicon dioxide, and at the end of reaction its

phosphate content is reduced to phosphorus. Carbonmonoxide (CO) is used as a main agent for reducing the phosphorus. Coke beds are heated and sewage sludge ashes form a thin film on coke particles. Reduced phosphorus can easily evaporate from coke particles as a form of white phosphorus or phosphoric acid. Phosphorus recovery is about 90% from the slag (Recovery of phosphorus (2015). May, 2015. http://www.recophos.org/).

2.1.2 Phosphorus Recovery From Wastewater

Phosphorus is a valuable source in wastewater treatment facilities due to it's reuse as a fertilizer (Khiewwijit et al., 2015). Recovery of phosphorus has become one of the most important issue in wastewater treatment plants. Phosphorus contents of the wastewater vary by type of wastewater. For instance, while in domestic wastewater phosphorus content is about several milligrams per liter, in industrial wastewater is about tens of thousands milligram per liter (Ping et al., 2015).

Many appropriate recovery technologies have been developed but they have not been adapted to full scale wastewater treatment plants. Some of these technologies are not cost effective so some new methods are developed such as electrochemical phosphorus recovery (EPR) (Kappel et al., 2013) and reversible adsorption of phosphate on iron oxides (Martin et al., 2009).

Kappel et al. (2013), use membrane concentrates for recovery of P. A membrane bioreactor (MBR) and nanofiltration membrane (NF) concentrates are pumped to the EPR system. The EPR comprise of a platinum anode and a steel cathode. Both anode and cathode parts are fed separately with the same NF concentrate. In a continuous process, the NF concentrate could first pass the anode to strip the carbonates and then pass the cathode to recover phosphate. Phosphorus can precipitate as amorphous calcium phosphate (ACP), monetite, brushite or hydroxyapatite (HAP). Phosphorus recovery by using EPR process can be seen in Figure 2.5.

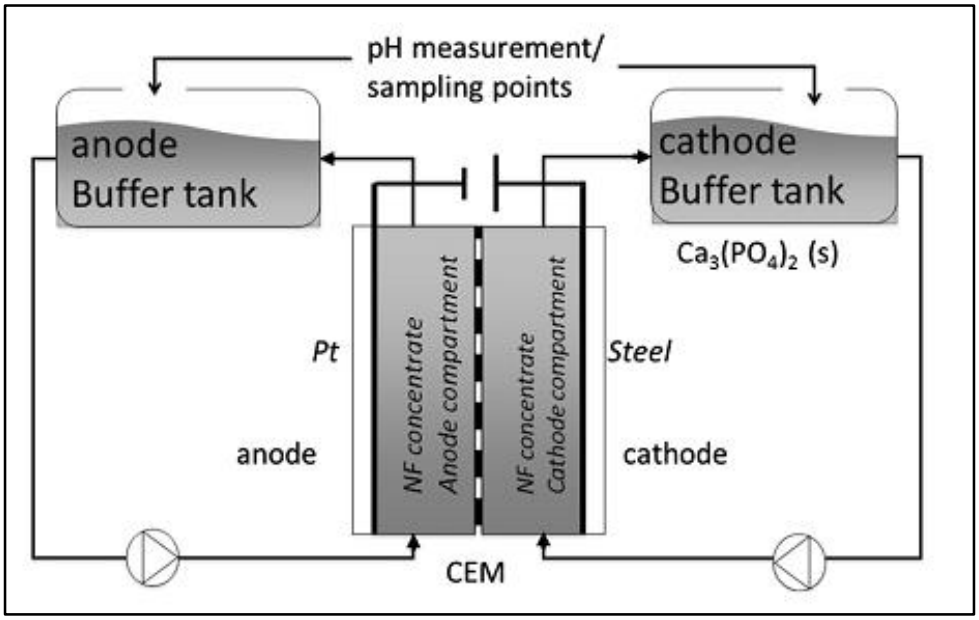


Figure 2.5 EPR system in phosphorus recovery (Kappel et al., 2013)

Several pHs were applied to concentrates and the most effective pHs were 10.0 and 11.0. Both of these pHs gave 96% phosphorus recovery. According to the results, when pH increases phosphorus recovery percent increases.

Martin et al. (2009) used ion exchange media in their studies and this media is highly selective for phosphate. The media consists of hydrated iron oxide nanoparticles. The media was trialled in fixed bed mini column experiments. Final effluent from two UK sewage treatment plant was used in their experiments. Wastewater passed through the system and then regenerative process was applied by using solution which contains 4% NaOH and 2% NaCl. Results have shown that 80% of the phosphorus was eluted in the first bed volume.

Concentration of Mg^{2+}, NH_4^+ and $PO4^{3-}$ ions, pH and temperature are the most important parameters for P recovery from wastewater. Acelas et al. (2015), researched the effect of Ca^{2+} and Al^{3+} concentration on struvite precipitation. They applied three different molar ratio of Mg^{2+} : Ca^{2+} and Mg^{2+} : Al^{3+}. According to their studies, they found that precipitation of struvite calcium is an effective only if it is in equal or greater than magnesium as a molar and even if aluminum is in lower concentration than the magnesium, it can inhibit the struvite precipitation.

2.1.3 Phosphorus Recovery from Sewage Sludge

Phosphorus recovery efficiency changes liquid phase to sewage sludge. Phosphorus can be recovered from sewage sludge by a wet chemical or a thermal technology. Table 2.1 and Table 2.2 give an overview of the full scale recovery processes.

Table 2.1 Overview (developers, influent type, chemicals, locations, and market) of the full-scale phosphate recovery processes for municipal and industrial wastewater

Full-scale process	**NuReSys** (Bergmans, 2011; European Sustainable Phosphorus Platform, 2015)	**Airprex** (Bergmans, 2011)	**Seaborne** (Müller et al., 2007; Bergmans, 2011)
Developer	Akwadok bvba	Berliner Wasserbetriebe	Seaborne Environmental Research Laboratory
Influent type	Anaerobic digestion effluent/Digested sludge	Digested sludge/sludge liquor	Digested sludge
Chemicals	$MgCl_2$, NaOH	$MgCl_2$, flocculent	H_2SO_4, Na_2S, NaOH, MgO, flocculent
Location(s) - Country (number of installations)	Germany (1) Belgium (2)	Germany (2) The Netherlands (1)	Germany (1)
Market	Exported to wine grower in France, mixed with Compost	Fertilizer industry	Reused as fertilizer in agriculture

Table 2.2 Overview of the flow for the full scale phosphate recovery from the sewage sludge processes for municipal and industrial wastewater

Full-scale process	**NuReSys** (Bergmans, 2011; European Sustainable Phosphorus Platform, 2015)	**Airprex** (Bergmans, 2011)	**Seaborne** (Müller et al., 2007; Bergmans, B., 2011)
Used technology and reactor type	P recovery from wastewater/sludge in a CSTR	P recovery from sewage sludge in a CSTR	Wet chemical P recovery from sewage sludge in a CSTR
Input flow (m^3/day)	1920–2880	1680–2000	110
Influent P concentration (mg/L)	60–150	150–250	600
Final product	Struvite- Biostuvite	Struvite	Struvite
Production (tons of final product.day^{-1})	1.43–1.58	1–2.5	0.58
Removal Efficiency (wt %)	85	80–90	~90

2.1.3.1 AirPrex

The AirPrex technology has been developed by the 'Berliner Wasserbetriebe'. This system does not only recover struvite as a fertilizer but also optimizes sludge dewatering performance and decreases the plant's all operating cost. In this technology air and magnesium chloride ($MgCl_2$) is added to the sludge. The resulting struvite (MAP) can be taken from the bottom of the reactor.

Air is added to tank for two reasons. First one is air increases the pH through the CO_2 content. Struvite solubility decreases while pH increases. Second one is cycle from the air supplying allows the struvite to grow. In the second tank, small struvite crystals settle down. Figure 2.6 shows AirPrex reactors (Bergmans, 2011).

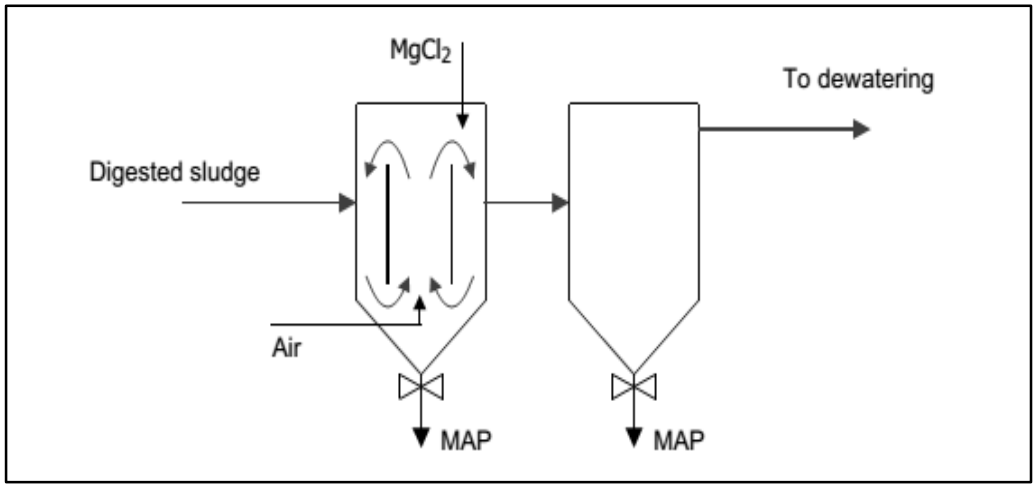


Figure 2.6 AirPrex technology (Bergmans, 2011)

2.1.3.2 Seaborne Process

The Seaborne process was developed by the Seaborne Environmental Research Laboratory. Seaborne Technology can be shown in Figure 2.7.

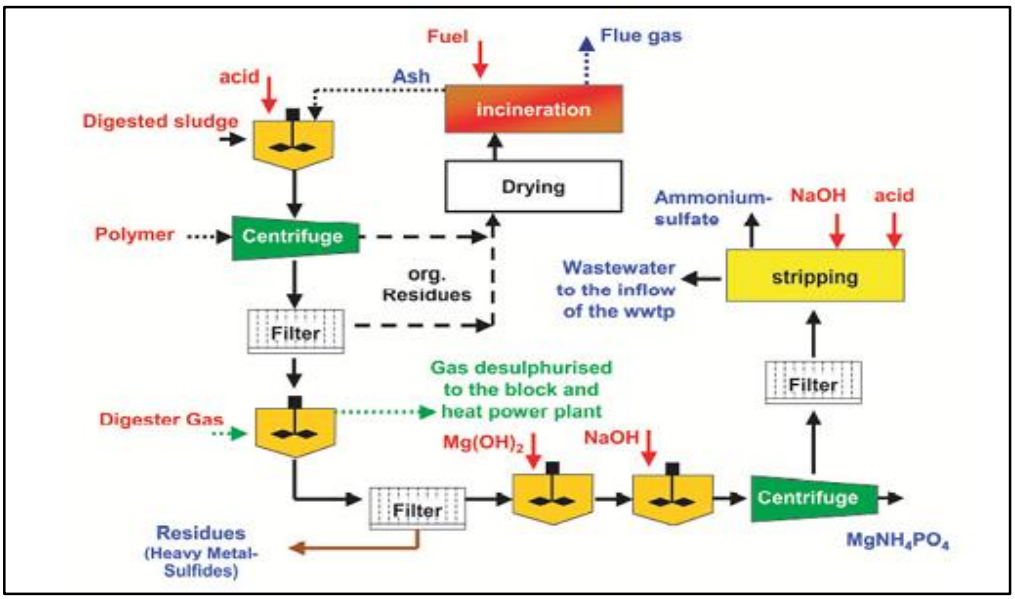


Figure 2.7 Process flow sheet of the Seaborne process at the WWTP Gifhorn (Müller et al., 2007)

In Seaborne Technology phosphorus separate from sludge and effectuate fertilizer. Produced fertilizer does not contain any heavy metals. Firstly, sulfuric acid is added to the sludge for acidification (Müller et al., 2007). During acidification, solids are dissolved. Centrifuge and filter are used for separating solids. These residue solids are dried and directly sent to the incineration process. Digester gas is used for removing the heavy metals from the liquor. The next process is struvite precipitation by using $Mg(OH)_2$ and NaOH. NaOH is used for adjusting pH of the system. At the final step, nitrogen is recovered by air stripping.

Full scale plant was firstly built in Germany for 50,000 people in 2005. By using Seaborne Technology daily production of struvite are around 580 kg. (Centre Europeen d'Etudes des Polyphosphates, 2012b).

2.1.3.3 NuReSys Technology

NuReSys is a combined technology for removal of phosphorus and nitrogen. At the end of the process struvite (MAP), which is valuable product, is obtained. This end product can be used as a fertilizer. With an additional clearance steps struvite can be used for food industry too.

NuReSys technology uses two tank. In the first tank (stripping reactor) pH is adjusted with air stripping or NaOH addition and pH increases. In the second tank (crystallization tank) $MgCl_2$ is added, Mg reacts with the P and N and $MgNH_4PO_4.6H_2O$ is formed. In Figure 2.8 NuReSys Technology can be seen (European Sustainable Phosphorus Platform, 2015).

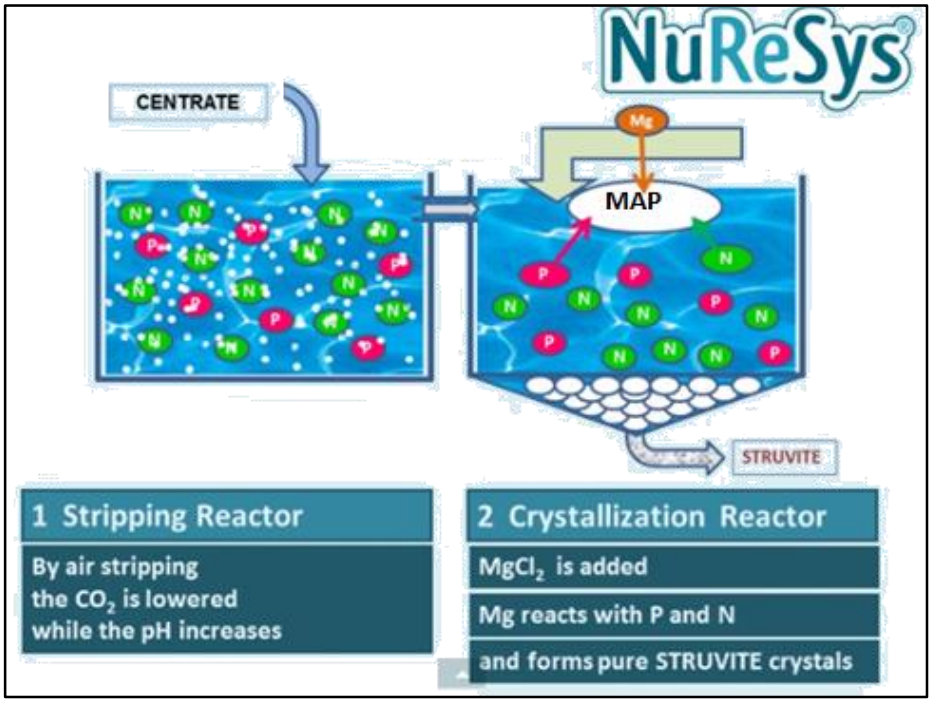


Figure 2.8 NuReSys Technology (European Sustainable Phosphorus Platform, 2015)

CHAPTER THREE
PHOSPHORUS RECOVERY PRODUCTS

Phosphate recovery from the sludge phase, which contains phosphorous in chemically and/or biologically bound form, includes recovery from the digester sludge before and after the dewatering unit (Desmidt et al., 2015). Most implementation cases in full scale are based on the largely researched technologies: the crystallization or precipitation of phosphorus as calcium phosphate (Giesen and Van der Molen, 1996; Berg et al., 2006a) or struvite (Ueno and Fuji, 2001).

3.1 Magnesium Ammonium Phosphate (MAP)

The municipal sewage sludge has a great concentration of phosphorus, nitrogen and magnesium. The combination of these ions found in sludge produced from nutrient removal, can result in the formation of a mineral called struvite. Struvite in wastewater treatment plants was identified as early as 1939 (Parsons et al., 2001). Rawn et al., (1939) identified struvite in the digested sludge supernatant lines. Problems with struvite formation were again highlighted in 1963 at the Hyperion Wastewater Treatment Plant where struvite crystal growth in a pipeline reduced the diameter of pipe from twelve to six inches (Borgerding, 1972). In Figure 3.1 scaling problem in pipes can be seen.



Figure 3.1 Scaling problems in pipes caused by struvite deposits (Bergmans, 2011)

Struvite is magnesium ammonium phosphate ($MgNH_4PO_4$) and forms a hard crystalline deposit when the molar ratio of $Mg:NH_4 : PO_4$ is greater than 1 : 1 : 1. Struvite forms according to the general reaction shown below;

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6\ H_2O \rightarrow MgNH_4PO_4\ 6\ (H_2O) \qquad (3.1)$$

Struvite has the following properties;

- Struvite is magnesium ammonium phosphate hexahydrate with the chemical formula of $MgNH_4PO_4.6H_2O$,
- White crystalline powder in its pure form but can also occur either as large single crystals, very small crystals, large curds or a gelatinous mass,
- Specific gravity is 1.7,
- Highly soluble at acidic pH and highly insoluble at alkaline pH,
- Struvite has a fertilizer potential and it leds scientists to study on recovering struvite.

Struvite crystals can be identified via X-ray diffraction (XRD) by matching the intensity and position of the peaks produced to a database for the crystal structure. Struvite crystal shape as in Figure 3.2 crystal has a orthorhombic shape.

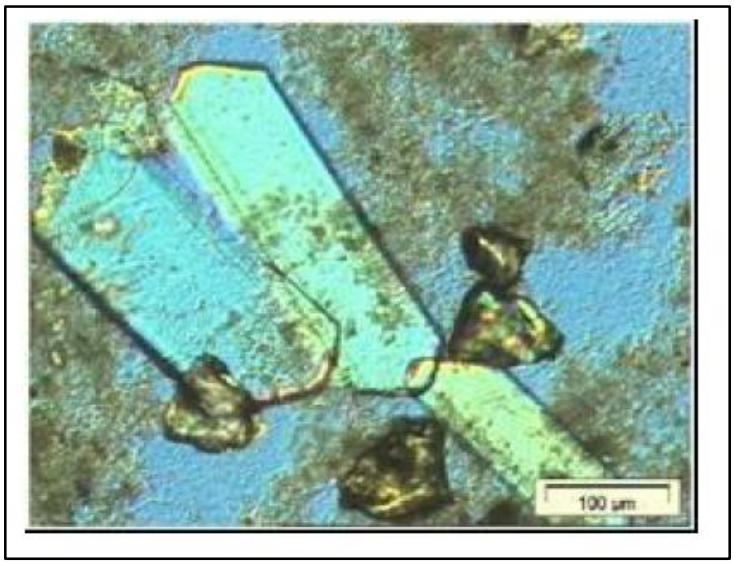


Figure 3.2 Struvite crystals (Heinzmann, 2009)

3.1.1 Sources of Struvite Components

1. Phosphorus: Phosphorus concentrations in urine can be used as an indicator of potential for recovery. Phosphorus in domestic sewage normally enters a wastewater treatment plant in the form of soluble, bioavailable, orthophosphates.

2. Ammonium: Sources of ammonium in wastewater are difficult to quantify as they are produced in situ during the degradation of nitrogenous material and are present due to urea in the wastewater.

3. Magnesium: Levels of magnesium in the flow to treatment can come from a number of sources. If the treatment plant is located in a hard water area, there will be an abundance of magnesium ions. Also, if the water treatment works is in a coastal area, seawater entering the works can be a source of magnesium

3.1.2 Struvite Precipitation

Because MAP crystallization process can simultaneously remove and recover N and P from wastewater, it has increasingly drawn more attention over the years (Doyle and Parsons, 2002; Suzuki et al., 2005). The by-product of combined removal of ammonium (NH_4^+), phosphate (PO_4^{3-}) and magnesium (Mg^{2+}) technology is magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4 \cdot 6H_2O$), which is commonly known as struvite. Struvite precipitates if the product of Mg^{2+}, NH^{4+}, $PO4^{3-}$ activities exceed the equilibrium ion activity product.

Struvite precipitation can be separated into two stages: nucleation and growth of crystal embryos into detectable crystals (Ohlinger et al., 1999). Nucleation occurs when constituent ions combine to form crystal embryos. Crystalization period is the time which is between starting of the supersaturation and the first physical change. After the crystallization period growth of crystal continues until equilibrium is reached.

The MAP (struvite) process depends on some operation parameters. Among the

ones known to be particularly important are pH, magnesium concentration, presence of foreign ions, retention time and presence of seed materials (Le Corre et al., 2005; Wang et al., 2006).

3.1.3 Significant Parameters on Struvite Precipitation

3.1.3.1 Effect of pH on Struvite Precipitation

While struvite occurs hydrogen becomes free and this reactions causes a decrease in pH. This reaction can be seen in equation 3.2 ;

$$HPO_4^{3-} + Mg^{2+} + NH^{4+} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O + H^+ \qquad (3.2)$$

pH is an important factor for struvite precipitation because it has a direct influence on the solubility of struvite. Marti et al. (2007) have reported that the struvite solubility decreases when the pH increases. Researches have revealed that the optimum pH range for struvite precipitation is 7.5 to 10. Burns and Finlayson's researches have shown that the minimum pH of the solution should be 7.0 for desirable struvite precipitation (Burns and Finlayson, 1982). According to the former researches about struvite precipitation, Yetilmezsoy et al. (2009) was reported optimum pH values were 8.5, 9 and between 9.5 and 10.5. In Figure 3.3 removal efficiency of the struvite against the pH is indicated.

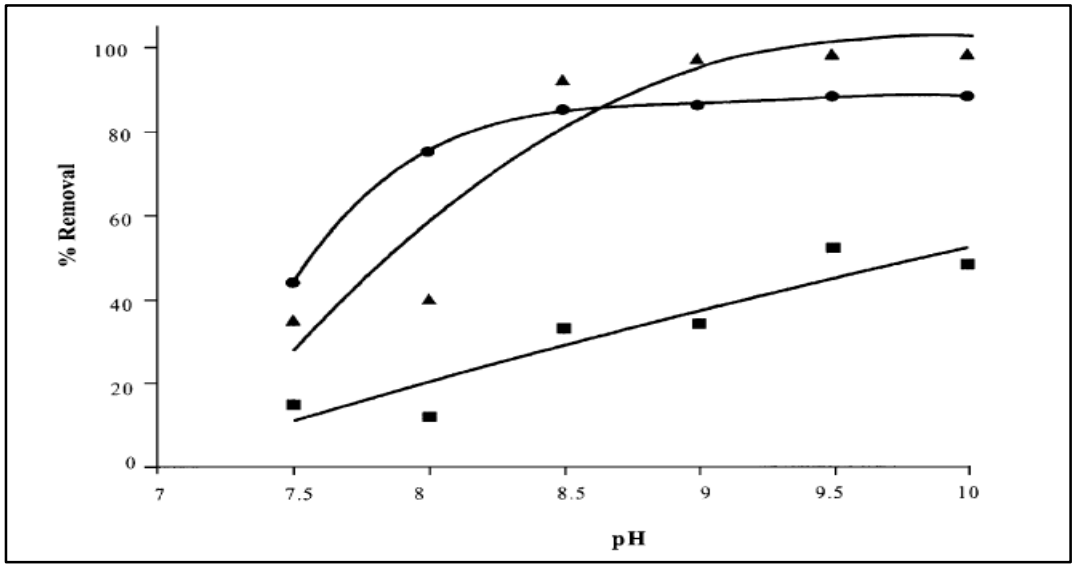


Figure 3.3 Percentage removal of struvite constituent ions against pH (▲) magnesium, (■) ammonium, (●) phosphate (Stratful et al., 2001)

3.1.3.2 Effect of Mg^{2+} on Struvite Precipitation

Two types of magnesium are mainly used for MAP process: Magnesium chloride ($MgCl_2$) and magnesium hydroxide ($Mg(OH)_2$). $MgCl_2$ separates faster comparing to $Mg(OH)_2$. On the other side, magnesium hyrdroxide is cheaper than $Mg(OH)_2$ and it also raises the pH.

Song et al. (2007) investigated the Mg^{2+} effect and their studies have shown that phosphorus removal efficiency increases with the increase of Mg/P molar ratio at any pH value. Mg/P molar ratio's increase is very effective on MAP precipitation at lower pH value. For example at pH 8.0 when Mg/P molar ratio increase from 1.0 to 2.0 the phosphorus recovery increased by 20%.

Katsuura et al. (1998) investigated the effect of ammonium concentration, Mg:P ratio, and pH on the P removal performance. He reported that P removal ratio increases with an increase in Mg:P ratio. This increase was much more pronounced at low pH values (pH of 8.0) compared to high pH values (pH of 9.0).

There are two main types of crystal forms of MAP; distinctive orthorhombic structure (Parsons et al., 2001) and needlelike structure of different thickness and length (Stratful et al., 2001; Kofina and Koutsoukos, 2005). Struvite crystal structure is also effected by Mg/P molar ratio. Hirasawa et al., (1997) found that at Mg/P molar ratio of 2, the crystals agglomerate which result in large crystals. On the other hand, when the molar ratio is increased to 4, together with fine crystals, needlelike crystals are formed.

3.1.3.3 Effect of Reaction Time on Struvite Precipitation

As reaction time increases there is a negligible effect on the production of struvite with only 4% more Mg^{2+} and PO_4^{3-} ions being removed between 1 and 180 min of reaction time (Stratful et al., 2001). Researches have shown that size of the struvite crystals increases with the time. The stirring speed increases as the nucleation of struvite becomes rapid. As redundant mixing time may cause the breakdown of the struvite. As a result of the breaking down the settlealibilty of phosphorus can be decreased. Therefore, adjusting the optimum reaction time is so important.

3.1.3.4 Effect of Ca^{2+} on Struvite Precipitation

The presence of Ca^{2+} can effect the MAP crystallization, because of the occurrence of calcium phosphate precipitate. At low Ca/Mg molar ratio morphology of the crystals can be distinguished. The studies show that Ca^{2+} inhibit the formation of MAP. When Ca/Mg molar ratio increase, removal of Mg decreases but the removal of Ca increases (Song et al., 2007).

3.1.4 Struvite Usage as a Fertilizer

Struvite (MAP) is a precious fertilizer and it's usage as a fertilizer was discovered in the 1960s in Germany and the USA. A great quantity of phosphate fertilizers are applied to the soils every year. Phosphorus has no substitute in food production and in a world of 9 billion people by 2050, securing sufficient phosphorus will be critical for future food security (Cordell et al., 2011). Although required phosphate is mostly

acquired from the phosphate rocks, they are not renewable sources. Phosphate rock consumption is over one million tons yearly as fertilizer (Rahman et al., 2011). When struvite is compared with the specific fertilizers, there is no difference, struvite has a excellent fertilizer quality.

The advantages of struvite as a fertilizer are;

- It is slow release fertilizer,
- Nutrient which are in the fertilizer can be used more because nutrients are release slower than the other fertilizer types,
- Application rate is less frequent,
- Fertilizer is not burn even at high application rates,
- Heavy metal concentration of the product is lower than the other supplied fertilizers.

According to the researches 1 kg of struvite per day is enough to fertilize 2.6 ha of arable land at an application rate of 40 kg phosphorus as P_2O_5/ha/yr (European Fertilizer Manufacturers Association, 2000; Zheng et al., 2004).

3.2 Hydroxyapatite (HAP)

Magnesium ammonium phosphate (MAP) is not the only product of the phosphorus recovery. Phosphorus is also recovered as a calcium phosphates and it calls hydroxyapatite (HAP). The HAP crystallization on crystal seed can be described as given in reaction 3.3 ;

$$10\ Ca(OH)_2 + 6\ H_3PO_4 \rightarrow Ca_{10}(PO_4)_6\,(OH)_2 + 18\ H_2O \qquad (3.3)$$

The seed is needed for this reaction occurring and HAP growing. Many types of seeds crystals can be used for this purpose such as sands, calcite (Song et al., 2001) cow bone (Hoon and Kang, 2002), tobermorite (Moriyama et al., 2001) and apatite (Bellier et al., 2006).

pH effect on the phosphorus recovery as HAP is so important and complex. If the pH is higher than 9.0 phosphorus recovery decreases because bicarbonate ion is converted to carbonate ion and this conversion causes the decrease of free calcium ion.

Hydroxyapetite can be used production of the industrial fertilizer directly or can be mixed with other nutrients or used directly to the soil as a slow release fertilizer. There are several researches about calcium phosphate (HAP) usage as a fertilizer. Cabeza et al. (2011) indicated that calcium phosphate has potential as a fertilizer, however only in acidic pH. Bauer et al. (2007) demonstrated that it has a potential as a fertilizer but it’s effect is lower than commercial fertilizers.

CHAPTER FOUR
MATERIALS & METHODS

4.1 Materials

4.1.1 Sludge Sample

In this research phosphorus recovery potential of filtrate which obtained by electro dewatering process was investigated. Filtrate samples which were transported from Bolu have been obtained form recycled sludge of secondary settling tank of Bolu Municipal Wastewater Treatment Plant in Turkey.

4.1.1.1 Sludge Electro-Dewatering Process

Electro-dewatering is a process in which a low current (DC) is applied to the sludge to cause an electro-osmotic phenomenon (Tuan et al., 2012). Excess water in the sludge samples can be removed by electro-osmotic flow. Occurrence of electro kinetic phenomena can be seen in Figure 4.1.

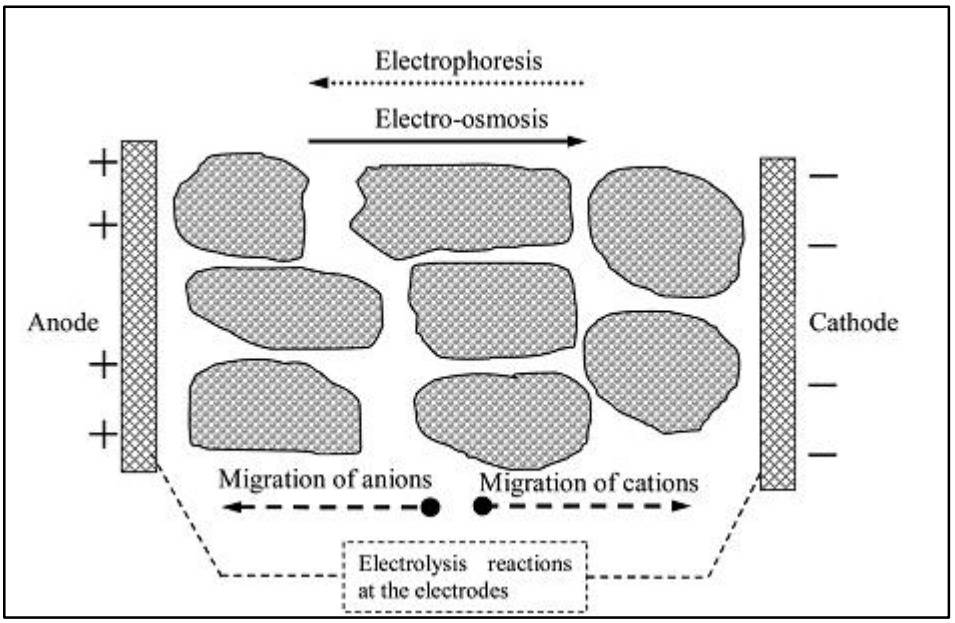


Figure 4.1 Electrokinetic phenomena occurring during electro-dewatering (Tuan et al., 2012)

The sludge particles are free to move in the fluid suspension. Particles tend to migrate toward at the anode due to the negative charge of the particles. When the solids content of the sludge increases, sludge particles are locked in position and unable to move.

In our study, electro-dewatering process was applied in Bolu. After electro-dewatering application, we got filtrate samples and these samples were transported from Bolu. All experimental studies have been carried out using these filtrate samples.

4.1.2 Devices

- Jar Test (VELP Scientifica FC6S) was used for stirring and precipitation of the struvite.
- Water bath (Clifton) was used for heating the samples which is added chemical solutions.
- Mercury thermometer was used for controlling the temperature of the samples.
- Ependorf centrifuge for soluble chemical oxygen demand (SCOD) analyzes.
- Nuve FN 400 oven was used for calculating the solid percent of the sludge samples.
- Nuve MF 120 muffle oven was used for the volatile solid percent of the sludge samples.
- pH measurements were done by using WTW 340i multi analyzer.
- Photo Lab S6 Photometer was used for PO_4-P and NH_4^+-N analyzes.

4.1.3 Chemical Solutions

EDTA (ethylenediaminetetraacetic acid) solution was used for magnesium analyzes. This solution was prepared at 0.01 M concentration. For solution, solid EDTA was weighed and brought the solution up to 1 L with distilled water and additionally this solution's pH was adjusted to about 10.5 with 1M NaOH solution before usage.

$Mg(OH)_2$ solutions with different molar concentration (0.1 M, 1.05 M, 2.0 M) was prepared by using MERCK magnesium hydroxide as a magnesium ion source and distilled water as a solvent.

0.5 M NaOH was prepared for pH setting by using MERCK sodium hydroxide pellet and distilled water. 20g sodium hydroxide pellets were weighed and solved in 1 liter distilled water.

4.1.4 Seeding Material

In this experiment pumice stone was used as a seeding material. Pumice stone (NMP2) was provided by Soylu Company. Pumice is a light, volcanic stone with a large surface area. Pumice has been widely tested and used in water treatment as an adsorbent, filter bed and support media (Onar and Ozturk, 1993; Akbal, 2005 ; Kitis et al., 2007).

The image of the original pumice can be seen in Figure 4.1. Pumice stone has many porous on its surface. In Figure 4.2 pumice stone samples can be seen.



Figure 4.2 Pumice stone sample

Pumice stone's general chemical properties have shown in Table 4.1 (Baldan Pakdil, 2007). The high level of SiO_2 gives this pumice it's white color. Pumice stone's specific weight is also much lower, at about 0.5-1 g /cm^3.

Table 4.1 General chemical characteristics of pumice stone (Baldan Pakdil, 2007)

Component	**Percentage (%)**
SiO_2	60-75
Al_2O_3	13-17
Fe_2O_3	1-3
CaO	1-2
Na_2O-K_2O	7-8
TiO_2	Trace
SO_3	Trace

4.2 Methods

4.2.1 Statistical Methods

4.2.1.1 Box-Behnken Method

The Box Behnken Design (BBD) coming under RSM, was devised by George E.P. Box and Donald Behnken in 1960. Box Behnken is an independent quadratic design. BBD does not contain fractional factorial desin. Combinations of the parameter are at the center.

Box-Behnken designs (BBD) are a class of rotatable design and this design requires 3 levels of each factor such as +1, 0 and -1. +1 is the maximum, 0 is the medium and -1 is the minimum level. Both number of design point and number of polynomial coefficients increase at the same rate by dint of Box Behnken design arrangement. Graphic for three factors Box Behnken design can be seen in Figure 4.3.

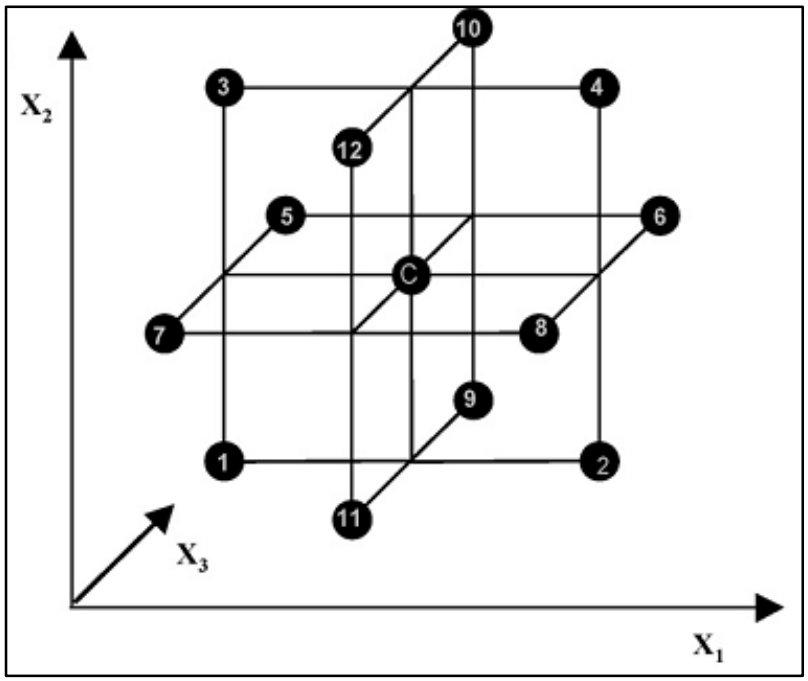


Figure 4.3 Graphical representation of three factor BBD (Ferreira et al., 2007)

The number of experiments (N) required for the development of Box Behnken design is defined as below Equation 4.1;

$$N=2k*(k-1)+C_0 \quad (4.1)$$

Where;

k: number of the factor,
C_0: number of central points.

According to this equation experiment numbers which are necessary for Box Behnken design is illustrated in Table 4.2.

Table 4.2 Number of experiments according to number of the factors

Number of the Factor (k)	**Number of Experiment (with number of central points=3)**
2	7
3	15
4	27
5	46

Phosphorus recovery from the sludge by using Box Behnken experimental design was described as in Equation 4.2.

$$Y= b_o +b_1X_1 +b_2X_2 +b_2X_2 +b_3X_3 +b_{12}X_1X_2 +b_{13}X_1X_3 +b_{23}X_2X_3 +b_{11}X_1^2 +b_{22}X_2^2 +b_{33}X_3^2 \quad (4.2)$$

where;

Y: Phosphorus release,

b_0: constant,

b_1, b_2,b_3: linear terms,

b_{11}, b_{22}, b_{33}: quadratic terms,

b_{12}, b_{13}, $b2_3$: interaction terms.

Box Behnken design for three coded variables have shown in Table 4.3. According to the comparison between Box Behnken design and other surface design models (central composite, Doehlert matrix and three-level full factorial design) has shown that Box Behnken and Doehlert matrix are more efficient than the central composite design but much more efficient than the three-level full factorial design (Ferreira et al., 2007). In Table 4.4 comparison of efficiencies of these systems can be seen.

Table 4.3 Coded factor levels for a three level Box-Behnken design

Number of Experiment	**X_1**	**X_2**	**X_3**
1	-1	-1	0
2	1	-1	0
3	-1	1	0
4	1	1	0
5	-1	0	-1
6	1	0	-1
7	-1	0	1
8	1	0	1
9	0	-1	-1
10	0	1	-1
11	0	-1	1
12	0	1	1
C	0	0	0
C	0	0	0
C	0	0	0

Note: X_1, X_2, X_3 independent variabes

In Box Behnken experimantal design, there is no combination of all factors for minimum and maximum levels.

Table 4.4 Comparison of efficiency of central composite design (CCD), Box-Behnken design (BBD) and Doehlert design (DM)

Factors (k)	**Number of experiments**			**Efficiency (%)**		
	CCD	**DM**	**BBD**	**CCD**	**DM**	**BBD**
2	9	7	-	67	86	-
3	15	13	13	67	77	77
4	25	21	25	60	71	60
5	43	31	41	49	68	61
6	77	43	61	36	65	46
7	143	57	85	25	63	42
8	273	73	113	16	62	40

4.2.1.2 Sample Applications of Box-Behnken for Optimization

Aslan and Cebeci, (2007) used Box Behnken design for modeling of Turkish coals. In their study, the Box–Behnken experimental design was used for finding out the interactions between the response functions and independent variables for three different size fractions. Their variables were ball diameter, Bond work index and grinding time.

Kumar et al. (2008) investigated the acrylonitrile removal from wastewater and the parameters effect was analyzed with Box-Behnken surface statistical design. Researched parameters by authors were adsorbent dose, temperature and time of contact.

Raffin et al. (2011) research was about optimum conditions for integrated membrane system and consisting of microfiltration followed by reverse osmosis. They used Box–Behnken experimental design (BBD) for limiting the number of experiments required for optimization.

4.2.2 Analytical Methods

Filtrate characteristics were analyzed at the beginning of the experiment. These analyses included chemical oxygen demand (COD), soluble chemical oxygen demand (SCOD), total solids (TS), volatile solids (VS), suspended solids (SS), pH, ammonium nitrogen (NH_4-N) and phosphate phosphorus (PO_4-P).

In order to control the effect of the variable factors (mixing time, temperature, concentration of the solution) on precipitation of the MAP, ammonium nitrogen (NH_4-N), phosphate phosphorus (PO_4-P) and magnesium (Mg^{2+}) ion were analyzed.

All analyses were done according to Standard Methods (APHA, 2005). All measurement were done in triplicate.

4.2.2.1 COD and SCOD Analysis

COD and SCOD were analyzed with Open Reflux Method. For SCOD sample was diluted 1/20 with distilled water. Used COD system and centrifuge can be seen in Figure 4.4 and Figure 4.5.



Figure 4.4 COD system



Figure 4.5 Centrifuge

4.2.2.2 Total Solid (TS), Volatile Solid (VS) and Suspended Solid (SS) Analysis

Total Solid (TS) analysis was done according to Method 2540B (APHA, 2005), volatile solid (VS) analysis was done by using Method 2540E (APHA, 2005). Nuve MF 120 model muffle oven and Nuve FN 400 model oven were used for total solid and volatile solid measurements. For suspended solid measurement glass fiber filter was used according to Standard Methods. Nuve FN 400 oven and Nuve MF 120 muffle oven can be seen in Figure 4.6 and Figure 4.7.



Figure 4.6 Nuve FN 400 oven



Figure 4.7 Nuve MF 120 muffle oven

4.2.2.3 pH Measurement

pH of the samples were measured by WTW model 340i multi analyzer. Analyzer is shown in Figure 4.8.



Figure 4.8 WTW 340i multi analyzer

4.2.2.4 Magnesium and Calcium Analysis

In order to analysis of magnesium and calcium concentration of liquid phase sludge before and after precipitation measurements were done by using SM 2340 C method. Used testing apparatus are shown in Figure 4.9.



Figure 4.9 Magnesium and calcium testing apparatus

4.2.2.5 PO_4-P and NH_4-N Analysis

Measurement of the PO_4- P was done by using MERCK phosphate cell test. NH_4-N measurement was done by using MERCK ammonium test kits. After applied kits procedure, photo Lab S6 Photometer was used for measurement of the PO_4- P and NH_4- N. Photo Lab S6 Photometer is shown in Figure 4.10.



Figure 4.10 Photo Lab S6 Photometer

4.3 Struvite Precipitation

The purpose of the experiment is researching the effects of the mixing time, temperature and molar concentration of the solution. For researching these effects firstly the characterization studies were carried out. Characterization of filtrate samples which were got by electro dewatering method are shown in Table 4.5.

Table 4.5 Characteristics of the filtrate

Filtrate Sample Characteristics				
	N_1	**N_2**	**N_3**	**Average**
pH	5.0	5.12	5.22	5.12
Total Solids (mg/L)	2140	2170	2190	2167
Total Volatile Solids (mg/L)	1270	1330	1260	1287
Suspended Solids (mg/L)	300	240	300	280
COD (mg/L)	320	310	330	320
SCOD (mg/L)	240	230	250	240
PO_4-P (mg/L)	45	46	46	46

Three different concentrations of $Mg(OH)_2$ solutions were used for struving procuring. 0.1, 1.05, 2 M $Mg(OH)_2$ solutions were prepared by using distilled water. Three different mixing time period were applied to the jars for searching the mixing time effect. Jars were mixed during 30, 45 and 60 minutes. The last factor was temperature. Three different temperatures were applied to the samples which are 24^{o}C, 52^{o}C, 80^{o}C.

Jar test apparatus were used for the experiments. 300 mL sample which was procured from Bolu Wastewater treatment secondary settling tank's recycle line and samples were filled in the jars. Before starting the experiments samples were protected in ambient temperature. pH of the samples were measured and the initial pH were adjusted to 9 by using 0.5 M NaOH solution. During the all experiments pH level was

controlled in order to adjust the pH at 9.0. $Mg(OH)_2$ in different molar concentration was added to each jar. Filtrate samples which was added $Mg(OH)_2$ can be seen Figure 4.11.

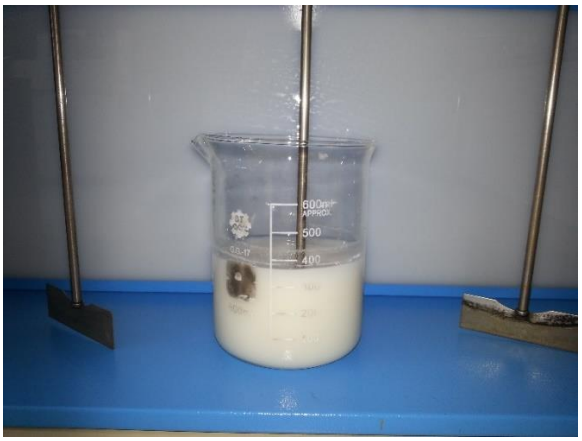


Figure 4.11 Sample with $Mg(OH)_2$

The other variable is temperature so samples were heated to desired degree with Clifton brand water bath. Water bath can be seen in Figure 4.12.

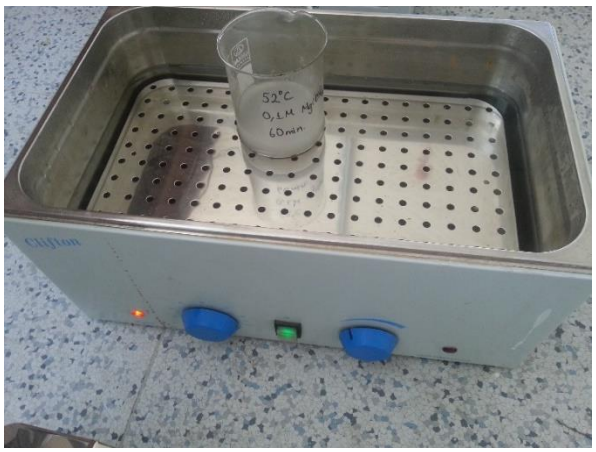


Figure 4.12 Clifton brand water bath

Apparatus were put into their place, all the jars mixing speed were set 120 rpm. VELP FC 6S flocculator was used for jar test. Flocculator is shown in Figure 4.13.



Figure 4.13 VELP flocculator

The samples were mixed during 30, 45, 60 minutes. After mixing time completed, waited some time to be precipitation of MAP. The samples after precipitation can be seen in Figure 4.14.

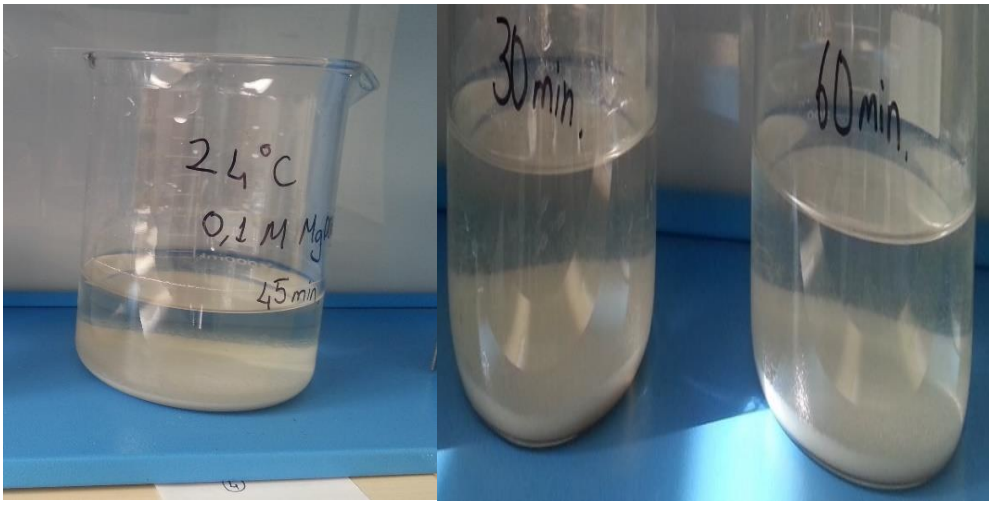


Figure 4.14 Samples after precipitation

Sample's supernatant liquids were taken and supernatant were analyzed for determining Mg^{2+}, NH_4^+, Ca^{2+} ion concentrations. Residuum at the bottom is called struvite it's characteristics depends on the variables.

CHAPTER FIVE
RESULTS AND DISCUSSION

5.1 Results

Results of the experiments are based on temperature, mixing time and concentration effect on phosphorus recovery from sewage sludge's filtrate. The results were achieved by laboratory scale experiments and statistical design experiments.

5.1.1 Box Behnken Experimental Design Results

Box-Behnken experimental design was used for analyzing the effect of the variables which is included temperature, mixing time and concentration. These three variables were coded as X_1 (temperature), X_2 (concentration), and X_3 (mixing time). For these parameters maximum, minimum and average values were determined and they were coded as -1, 0, +1. These independent variables real values are represented in Table 5.1.

Table 5.1 Variables coded and actual levels

Variables	**Variable Codes**	**Levels**		
Temperature (^{0}C)	X_1	24.0	52.0	80.0
Concentraion (M)	X_2	0.1	1.05	2.0
Time (min.)	X_3	30	45	60

*Temperature accuracy $\pm 2^0$C.

+1 demonstrated maximum value, 0 demonstrated average value and -1 demonstrated minimum value. Mixing time of the experiment was between 30 – 60 minutes, temperature unit is Celsius and it was in the range at 24^0C - 80^0C, solution concentration was between 0.1 - 2 M. Box-Behnken statistical design independent variables and their values which is used for Box-Behnken Statistical Design are shown in Table 5.2.

Table 5.2 Independent variables of Box Behnken statistical design

Run Order	Temperature (^{0}C)	Concentration of Solution (M)	Mixing Time (min.)
1	24	1.05	30
2	24	1.05	60
3	80	1.05	30
4	80	1.05	60
5	52	0.1	30
6	52	0.1	60
7	52	2	30
8	52	2	60
9	24	0.1	45
10	80	0.1	45
11	24	2	45
12	80	2	45
C	52	1.05	45
C	52	1.05	45
C	52	1.05	45

C: Central point

Central point was repeated three times in this design. The recovered phosphorus amount was found by using Equation 4.2.

$$Y= b_o +b_1X_1 + b_2X_2 +b_3X_3 +b_{12}X_1X_2 +b_{13}X_1X_3 +b_{23}X_2X_3 + b_{11}X_1^2 +b_{22}X_2^2 +b_{33}X_3^2 \quad (4.2)$$

where; Y is the predicted amount of recovered phosphorus, b_0 is the constant and b_1, b_2, b_3 are linear terms, b_{12}, b_{23}, $b_{13}$are interaction terms, and b_{11}, b_{22}, b_{33} are quadratic terms. Minitab 17 statistical program was used for calculating the amount of phosphorus recovery. Coefficient of the responses are shown in below Table 5.3.

Table 5.3 Response function coefficients

Response function coefficient	Y (Phosphorus recovery)
b_0	4.0
b_1	2.6250
b_2	-1.0625
b_3	1.4375
b_{12}	2.75
b_{13}	-0.25
b_{23}	-1.625
b_{11}	2.9375
b_{22}	4.5625
b_{33}	-1.6250

These coefficient of responses were used for determining the predicted phosphorus recovery values. According to experiments which were done in laboratory, observed phosphorus recovery values were found. Observed and predicted P-recovery values are shown in Table 5.4.

After analyzing responses with Minitab 17 statistical software program, it was seen that predicted values and observed values for phosphorus recovery were similar to each other. R squared value is 0.91 for our design and it means that experiments result are successful.

Table 5.4 Observed and predicted P recovery values

Number of Experiment	**X_1**	**X_2**	**X_3**	**P Recovery (Predicted)**	**P Recovery (Observed)**
1	-1	0	-1	0.9375	3
2	-1	0	1	4.3125	5.5
3	1	0	-1	6.6875	5.5
4	1	0	1	9.0625	7
5	0	-1	-1	4.875	4
6	0	-1	1	11	11
7	0	1	-1	6	6
8	0	1	1	5.625	6.5
9	-1	-1	0	12.6875	11.5
10	1	-1	0	12.4375	14.5
11	-1	1	0	5.0625	3
12	1	1	0	15.8125	17
C	0	0	0	4.0	4
C	0	0	0	4.0	4
C	0	0	0	4.0	4

5.2 Comparison of the Results

Temperature effect and this effect's results were first researched parameter. Experiments have shown that recovery percent of phosphorus increases proportionally with the temperature. For example, at 24^0C P recovery value was about 5.0625 mg PO_4-P/ L however at 80^0C value become 15.8125 mg PO_4- P/ L.

Concentration was the second parameter and it's effects were analyzed. Results have shown that phosphorus recovery percent gone up with the concentration. To illustrate, when concentration was 0.1 M P recovery was about 4.875 mg PO_4-P/ L though at 2.0 M P recovery was 6.0 mg PO_4-P/ L.

When we investigate the effect of the mixing time, phosphorus recovery increases as mixing time increase. For 60 minutes mixing time P recovery was 9.0625 mg PO_4-P/ L but at 30 minutes this value becomes 6.6875 mg PO_4-P/ L.

In Minitab 17 statistical software, we can get contour and surface profiles. Contour profiles are two dimensional while surface plots are three dimensional. They were generated by using multiple nonlinear regression models. In Figure 5.1, Figure 5.2 and Figure 5.3 two dimensional surface plots can be seen. In surface plots, figures are between two variables and the third variables are kept zero.

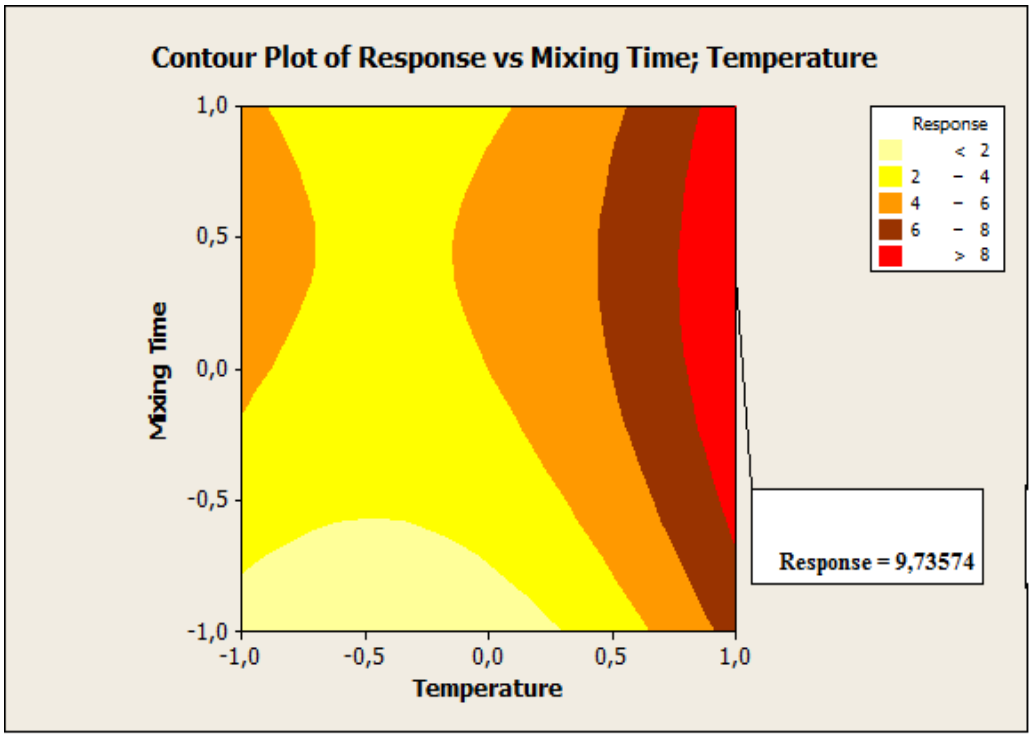


Figure 5.1 Contour plot of temperature vs time at constant level of concentration

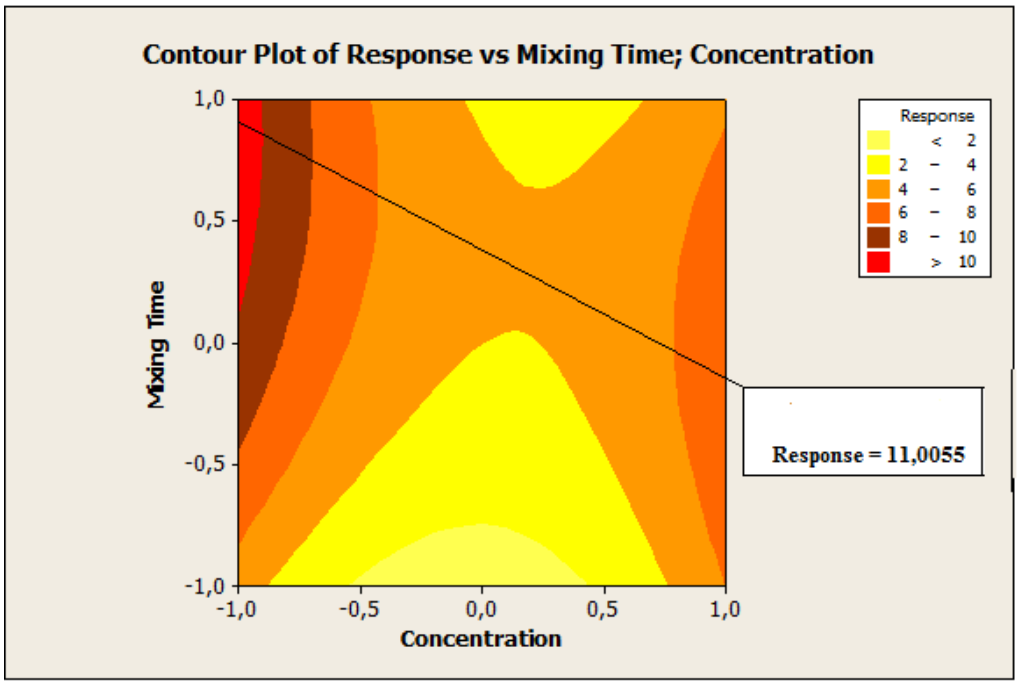


Figure 5.2 Contour plot of concentration vs time at constant level of temperature

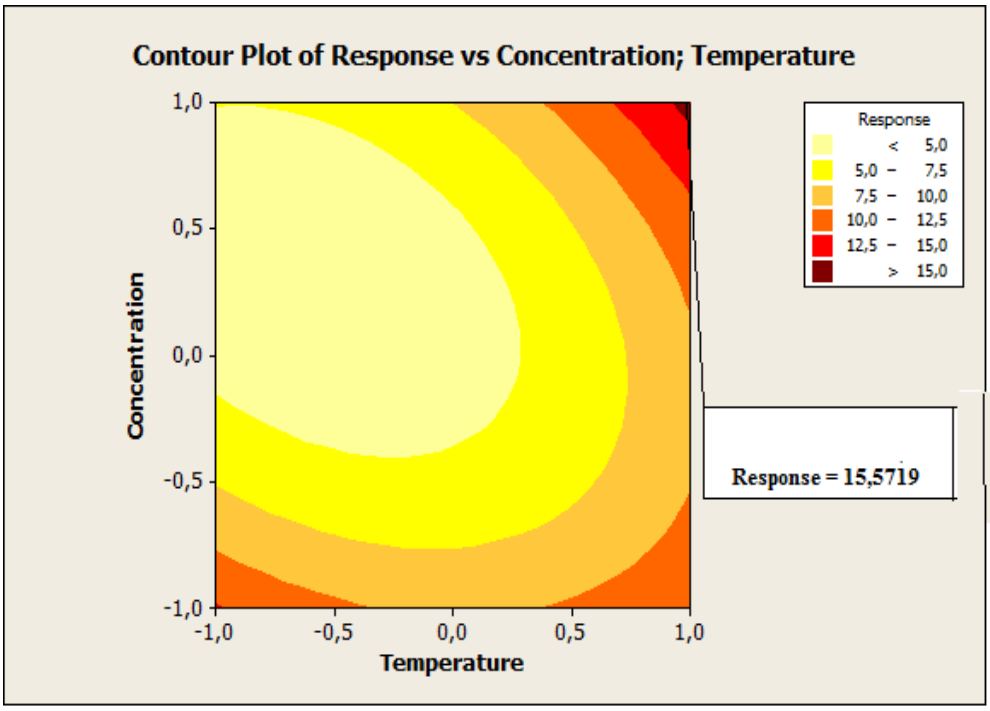


Figure 5.3 Contour plot of concentration vs temperature at constant level of time

According to contour plot of Minitab 17 for temperature vs time (Figure 5.1), high level of time and medium level of temperature give the optimum P recovery for the

constant level of concentration that can be seen from the flagged point and the region that is deep red.

As a result of Figure 5.2, low level of concentration and high level of mixing time give the optimum phosphorus recovery percent for the constant level of temperature and this part can be seen deep red.

In Figure 5.3, high level of temperature and high level of concentration give the optimum level for recovery of phosphorus. This region is deep as can be seen in figure.

Three dimensional response surface model based on two independent variables was drawn, while the third independent variable was kept at a constant level. 3D response surface models can be seen in Figure 5.4, Figure 5.5 and Figure 5.6.

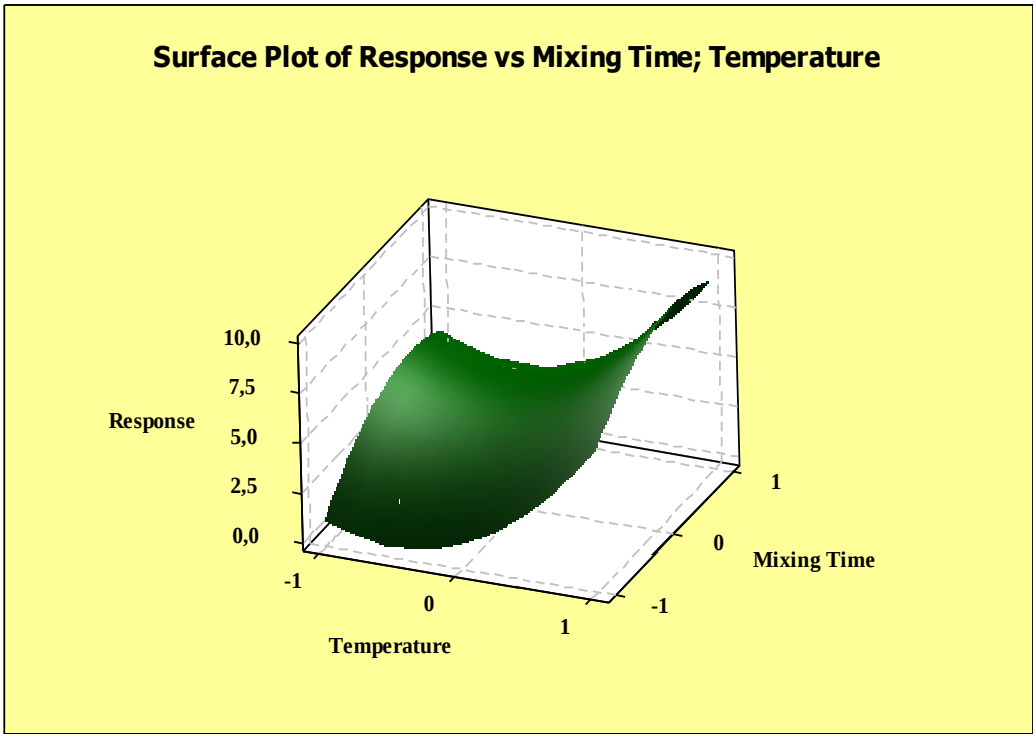


Figure 5.4 Response surface plot of temperature vs time at constant level of concentration

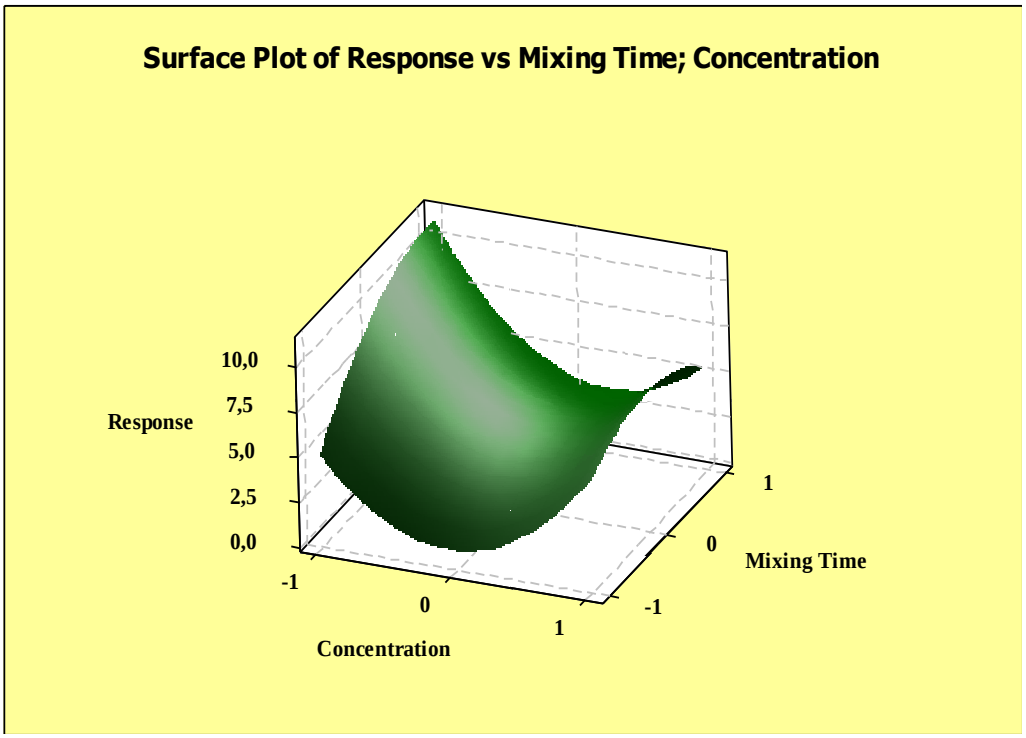


Figure 5.5 Response surface plot of concentration vs time at constant level of temperature

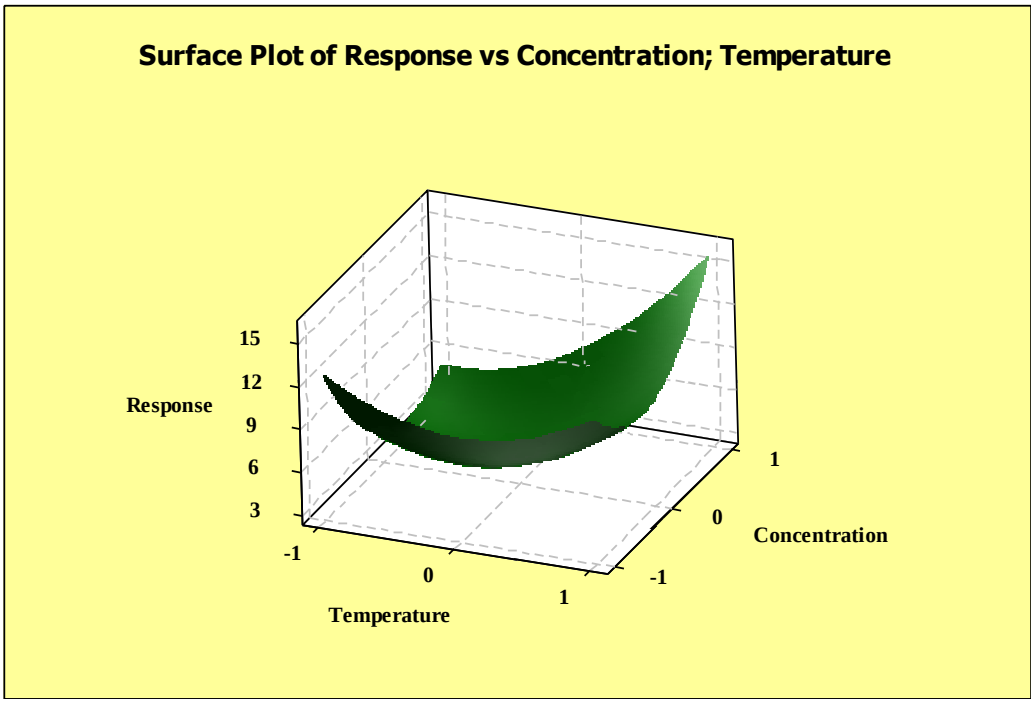


Figure 5.6 Response surface plot of temperature vs concentration at constant level of time

According to these three response surface plot figures, the optimum conditions for P recovery were determined. Time vs temperature surface plot shows us high level of time and medium level of temperature give optimum result. Figure 5.4 gives the same results with contour plot of time vs temperature. Optimum conditions are high level of time and low level of concentration. For the last figure of temperature vs concentration, high level temperature and high level of concentration give optimum condition.

CHAPTER SIX
CONCLUSIONS AND RECOMMENDATIONS

The effective parameters on P recovery such as temperature, mixing time and $Mg(OH)_2$ concentration were investigated in this thesis and investigations were done by lab-scale experiments. According to studies, most appropriate conditions were determined.

In phosphorus recovery studies, magnesium, calcium, ammonium and phosphorus were examined before and after processes. COD, SCOD, pH, SS, VSS were analyzed before carrying out the process. Temperature and pH were controlled during the whole experiments. All these analysis were done by using Standard Methods.

Firstly, used statistical design was determined as Box-Behnken Statistical Design and parameters to be investigated for P recovery was determined as mixing time, sample temperature and concentration. For these three independent variables, statistical design program gave us number of the necessary experiment by using an equation and the number of experiment is fifteen (with three central point).

Sewage sludge samples were provided from Bolu Wastewater Treatment Plant's secondary settling tank. Before starting the experiments electro dewatering process was applied and filtrate of the sludge was obtained. The samples were waited at room temperature about a day before starting the experiments. In these lab-scale studies, beakers were used as a reactor and jar test apparatus was used as mixing equipment.

Firstly, three different variables were applied to the filtrate samples, for each of them three value were determined. These values indicated minimum, average and maximum values. For temperature, these values are 24, 52, 80^0C, for mixing time 30, 45, 60 minutes and for $Mg(OH)_2$ concentration 0.1, 1.05, 2.0 M. Box-Behnken Experimental Design was used to designate effects of sample temperature, mixing time

and concentration on phosphorus recovery. Before this application all samples' pH were set at 9.0.

After experiments, same analyzes were carried out for calculating the recovery percent of phosphorus. The experimental results show that the maximum phosphorus recovery value were obtained at 80^0C sample temperature, 2.0 M $Mg(OH)_2$ concentration and 45 minutes mixing time and these value is 17.0 mg PO_4-P /L. This value was got by lab-scale experiments.

Experimental results and independent variables were used for finding response function coefficient values. By using these coefficients an equation was generated and predicted P recovery values was calculated with Minitab 17 Statistical Software. The design result gave the same result with lab-scale experiments and the maximum value were obtained at 80^0C sample temperature, 2.0 M $Mg(OH)_2$ concentration and 45 minutes mixing time. Maximum value is 15.8125 mg PO_4-P /L.

Design results and experimental results were compared with each other by using Minitab 17 Statistical Software. Response surface analyze was used for this comparison and correlation coefficient (R^2) was found as % 91.

Heinzmann et al. (2001) investigated the phosphorus recover from centrate of the digested sludge. They recovered 15 % of the influent P load. The other research on phosphorus recovery is phosphorus recovery from wastewater (Berg et al., 2005). They used P-RoC process (the phosphorus recovery straight from the aqueous phase by crystallization of calcium phosphate). According to their studies, generated crystallization products include at least 10-11% P-total. In the literature the recovery potential, based on the incoming load, is limited to approximately 10–40 % at the end of the various recovery technologies. In our study, maximum phosphorus recovery can reach 37 % by adding $Mg(OH)_2$ as a magnesium source, heating up to 80^oC and mixing about 45 minutes. Percentage of the phosphorus recovery is between the literature's ranges.

Response surface plots and contour plots for each variable were drawn by using Minitab. While these graphs were drawing, one of three variables was supposed at constant level. When concentration was assumed at constant, phosphorus recovery percent increased with increasing level of mixing time. When average value of the temperature and maximum level of mixing time come together P recovery percent reached the maximum levels. When temperature was fixed, concentration and mixing time must be at low levels for getting higher recovery percent. If we set the mixing time, high level for temperature and low level for concentration gave the maximum P recovery value.

In this thesis, phosphorus recovery potential from sludge filtrate and effective parameters on recovery percent was investigated. All findings points were analyzed with statistical software. For getting more detailed and conclusive results all studies should be done at full-scale.

Applied variable ranges can be changed or expanded for determining the more accurate optimum conditions. Different independent variables can be applied to the filtrate for phosphorus recovery such as different acids or bases at different concentrations.

In further studies, sewage sludge, sewage sludge filtrate, sewage sludge ashes and wastewater can be compared for determining the most effective method for phosphorus recovery. Not only their P recovery analyzes but also their cost analyzes can be done.

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