DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

PHOSPHORUS RECOVERY FROM SEWAGE SLUDGE

by

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October, 2007

İZMİR

PHOSPHORUS RECOVERY FROM SEWAGE SLUDGE

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by
Nazlı BALDAN PAKDİL

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İZMİR

Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"PHOSPHORUS RECOVERY FROM SEWAGE SLUDGE "** completed by **NAZLI BALDAN PAKDİL** 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 Doctor of Philosophy.

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PHOSPHORUS RECOVERY FROM SEWAGE SLUDGE

ABSTRACT

In recent years, new phosphorus recovery technologies have been developed to decrease the cost of sludge disposal and to recovery of phosphorus in content of sewage sludge as useful product. Phosphorus can be recovered from sewage sludge, wastewaters, and concentrated process waters. This research has utilized knowledge of phosphorus recovery as struvite from synthetic solutions and P-rich liquid which extracted from sludge, parameters affecting phosphorus recovery process like temperature, pH, pumice amount, and the applicability of pumice stone at struvite precipitation. Experimental results were evaluated by using Box-Wilson Experimental Design and Box-Behnken Experimental Design.

It was detected that nitric acids is significantly efficient on phosphorus release by using acids at experimental results which were evaluated by using Box-Wilson Experimental Design. Box-Benhken Experimental Design was used to determine effects of base concentration, mixing time and temperature on phosphorus release with base. It was observed that sodium hydroxide (NaOH) has efficiency than potassium hydroxide (KOH) on phosphorus release. Temperature and base concentration on phosphorus release is the principal effect. However, mixing time slightly affected.

Box-Benhken Experimental Design was used to determine effects of pH, pumice amount and temperature on PO_4-P, NH_4-N, Mg removals in the model reactor. According to experimental results, temperature and pH in model reactor are the most important parameters on phosphorus, ammonium and magnesium removal. The amount of pumice slightly affected phosphorus, ammonium, and magnesium removal. Good phosphorus removal could be achieved by pumice stone as crystal seeding. It was observed that struvite crystals were precipitated on pumice stone.

It was observed that phosphate and ammonium precipitated significantly as struvite and calcium phosphate compounds on pumice stone and concentrations of heavy metals like cadmium, chromium, and nickel showed exchange with time, but copper concentration increased during reaction times at studies of struvite precipitation with P-rich liquid in model reactor.

Keywords: Phosphorus recovery, pumice stone, sewage sludge, struvite

ARITMA ÇAMURLARINDAN FOSFOR GERİ KAZANIMI

ÖZ

Son yıllarda çamur bertaraf maliyetini azaltmak ve yararlı bir ürün olarak arıtma çamurun içeriğindeki fosforu geri kazanmak amacıyla yeni fosfor geri kazanım teknolojileri geliştirilmektedir. Fosfor arıtma çamurlarından, atıksulardan ve konsantre kirliliğe sahip proses sularından geri kazanılabilmektedir. Bu çalışmada sentetik çözeltiler ve çamurdan ekstrakte edilmiş fosforca zengin sular kullanılarak struvite olarak fosfor geri kazanımı, struvite çökeltilmesinde pomza taşının kullanılabilirliği ve pomza taşı miktarı, pH, sıcaklık gibi geri kazanımı etkileyen parametreler araştırılmıştır. Deneysel sonuçlar Box-Wilson Deneysel Dizayn ve Box-Behken Deneysel Dizayn kullanılarak değerlendirilmiştir.

Box-Wilson Deneysel Dizaynı kullanılarak yapılan deneysel çalışma sonuçlarının değerlendirilmesinde, çamurdan fosfor salınmasında nitrik asidin en etkili asit olduğu belirlenmiştir. Baz kullanılarak yapılan fosfor salınması deneysel sonuçları Box-Behnken Deneysel Dizayn kullanılarak, ayrıca fosfor salınmasını etkileyen baz konsantrasyonu, karıştırma süresi ve sıcaklık gibi parametreler de değerlendirilmiştir. Fosfor salınmasında sodyum hidroksitin (NaOH), potasyum hidroksitten (KOH) daha etkili olduğu gözlenmiştir. Ayrıca fosfor salınması üzerinde baz konsantrasyonu ve sıcaklığın önemli bir etkiye sahip olduğu ancak karıştırma süresinin etkisinin daha zayıf olduğu belirlenmiştir.

Model reaktörde yapılan çalışmalarda PO_4-P, NH_4-N, Mg gideriminde pH'ın, pomza miktarının ve sıcaklığın etkisi incelenmiş ve sonuçlar Box-Behken Deneysel Dizaynı kullanılarak değerlendirilmiştir. Sonuçlara göre model reaktörde sıcaklık ve pH'ın en etkili parametreler olduğu belirlenmiştir. Pomza taşı miktarının çökelmeyi önemli ölçüde etkilemediği görülmüş; pomza taşının kristal çekirdeği olarak fosfor gideriminde iyi bir materyal olduğu ve struvit kristallerinin pomza taşı üzerine çökeldiği tespit edilmiştir.

Nitrik asit ile hazırlanan fosforca zengin su kullanılarak model reaktörde yapılan çalışmalarda ise reaksiyon süresince fosfat ve amonyumun struvit ve kalsiyum

bileşikleri olarak çökeldiği ve kadmiyum, krom, nikel gibi ağır metallerin konsantrasyonlarının değiştiği, bakır konsatrasyonunun ise sürekli arttığı gözlenmiştir.

Anahtar Sözcükler: Fosfor geri kazanımı, pomza taşı, arıtma çamuru, struvit

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CHAPTER ONE
INTRODUCTION

1.1 Introduction

Municipal wastewaters may contain from 4 to 15 mg/L of phosphorus as P. The usual forms of phosphorus found in aqueous solutions include the orthophosphate, polyphosphate, and organic phosphate (Metcalf & Eddy, 1991). Wastewater discharges of nitrogen and phosphorus to the environment are undesirable because these nutrients accelerate eutrophication (Lee et al., 2003). Therefore, various phosphorus removal technologies have been developed like chemical precipitation, biological phosphorus removal, ion exchange (Morse et al., 1998). During the wastewater treatment 40 - 95 % of the incoming phosphorus load is transferred into the sewage sludge depending on the technology applied (Berg et al., 2005). Phosphorus balance for a typical wastewater treatment plant (WWTP) and phosphorus removal efficiencies of the processes can be shown as in Figure 1.1. Approximately 11% of the phosphorus is separated by the primary sludge (PS) and 28 % by the secondary (surplus) sludge (SS) 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).

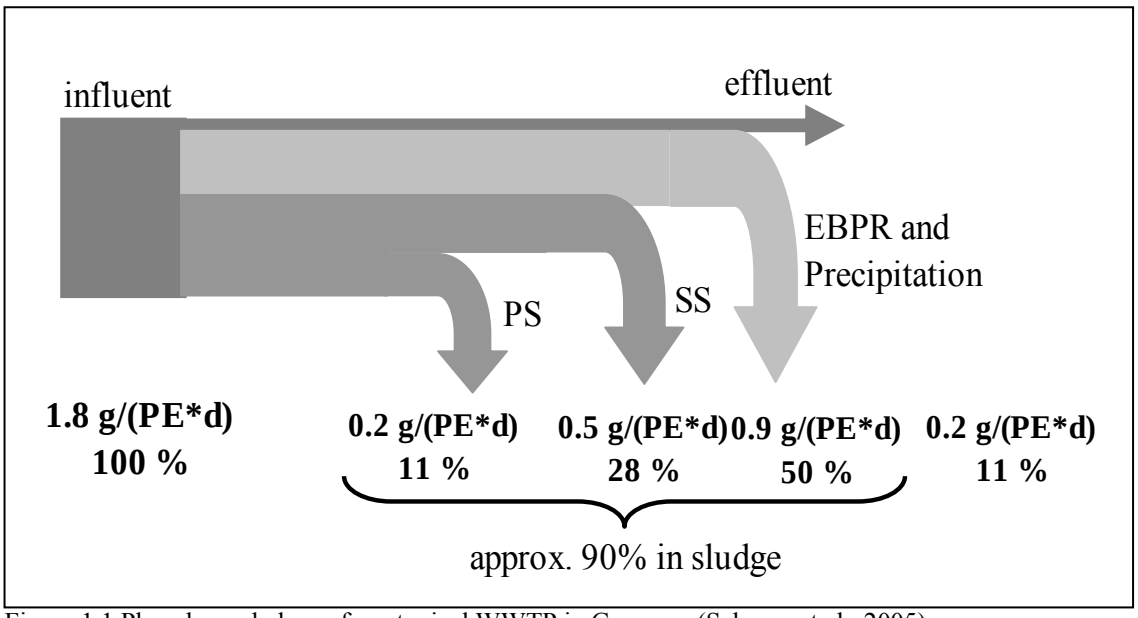


Figure 1.1 Phosphorus balance for a typical WWTP in Germany (Schaum et al., 2005)
(PS: Primary Sludge; SS: Secondary Sludge (surplus sludge); PE: Population Equivalent; EBPR: Enhanced Biological Phosphorus Removal)

Highest phosphorus reserve nations have West Sahara, Senegal, Morocco, America, Russia, and Christmas Island in the world (Arakane et al., 2007). Increasingly, the processing of the mineral and the manufacture of phosphoric acid and basic fertilizers are carried out at, close to, the phosphate mine from hence they are exported. Historically, fertilizers have been relatively inexpensive (or even subsidized in some countries) and have been applied liberally to farmland in order to ensure an adequate supply of nutrient to crops. In a number of countries the rate of fertilizer addition has far exceeded the level needed for adequate crop nutrition and in many regions the net result has been an increase in soil phosphate levels and high concentrations of nitrates in water. The migration of these nutrients to water can either be through loses direct from the soil (erosion, dissolution during storm events), from animal wastes or (via the food chain, industry and consumer products) from sewage and effluent treatment plants (Brett et al., 1997). Steen (1998) has pointed out that the annual global production of phosphate is around some 40 million tonnes of P_2O_5, derived from roughly 140 million tons of rock concentrate by the year 1998. It was reported that the mineral fertilizers account for approximately 80% of phosphates used worldwide with the balance divided between detergents (12%), animal feeds (5%) and speciality applications (3%), for example, food grade, metal treatment etc. World fertilizer use would reach 60-70 million t/a of phosphates by

2050 (Figure 1.2). It is concluded that global phosphate resources extend, for all intents and purposes, well into the future, but that depletion of current economically exploitable reserves can be estimated at somewhere from 60 to 130 years. The study have remarked that the phosphate reserves would last for at least 100+ years using the median reserves estimates and under reasonable predictions (Steen, 1998).

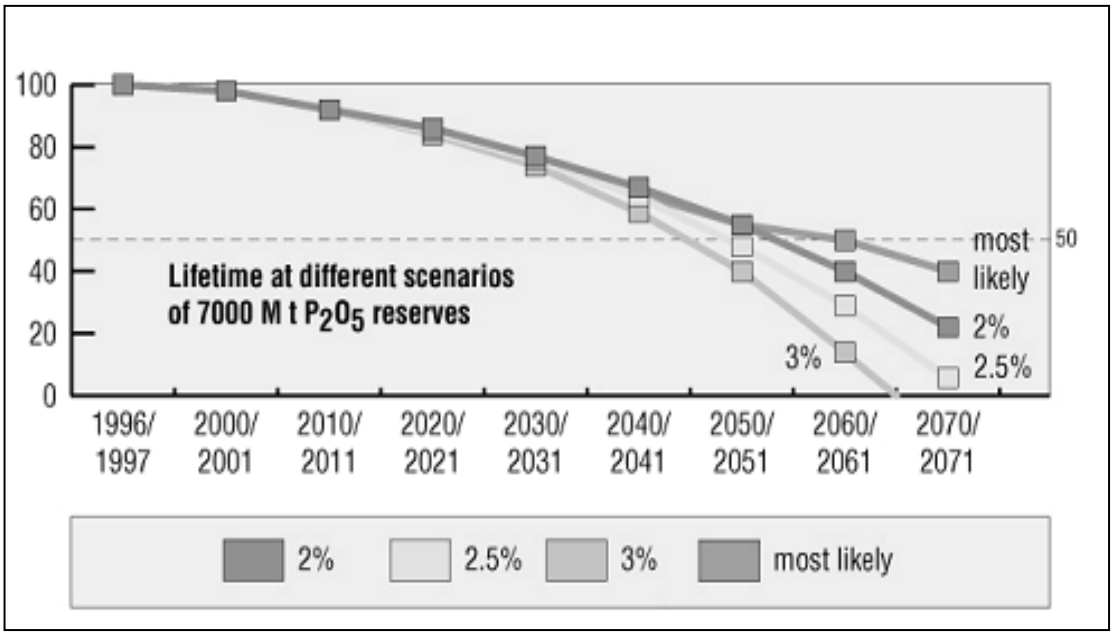


Figure 1.2 Estimated lifetimes of reserves (Steen, 1998)

Therefore phosphate should be recovered various source such as wastewaters, sludge, sludge ash. To disposal of excess sludge produced in wastewater treatment plant and find new sources of the limited phosphorus deposits is the enormously high cost (Takashi et al., 2001, Saktaywin et al.,2005). Phosphorus can be recovered various forms as struvite, calcium phosphate types in different phosphorus recovery systems.

Advantages of P-recovery systems can be listed in the following to (Jeanmaire, 2001);

1. to avoid P-rich flows returning to the head of WWTP
2. to limit the problems generated by the unexpected precipitation of struvites

3. to manage more easily the agricultural reuse, since phosphorus represents the factor that determines the surface area of spreading
4. to limit the incidence of phosphorus in the framework of sludge incineration in the cement works
5. last and to a lesser extent, to reduce the total sludge production
6. to reduce ash volumes going to landfill where sludge is incinerated

In addition, incentive for consciously forming struvite is its impact on sludge disposal as the recovery of phosphorus can reduce the volume of sludge generated by 49 %. Another sludge disposal issue involves reducing the nitrogen and phosphorus concentrations of sludge via controlled struvite precipitation allowing a greater volume of sludge to be speared per hectare of land (Doyle et al., 2002).

1.2 Scope and Research Objectives of the Thesis

In this thesis, it was studied on parameters effecting struvite precipitation/crystallization and recovery of phosphorus as struvite from sewage sludge. The research objectives of the thesis were therefore:

- Determination of parameters (pH change, pumice amount and size, optimum mixing speed and magnesium amount) affecting struvite precipitation by using synthetic solution and pumice stone as seeding material at laboratory scale.

- Determination of the effect of various acid types (Sulphuric acid, nitric acid and hydrochloric acid, oxalic acid, citric acid) on phosphorus release from sewage sludge.

- Investigation of the effect of concentration, temperature and mixing time on phosphorus release by using Box–Wilson Statistical Experiment Design. Nitric acid, oxalic acid and magnesium hydroxide was used for phosphorus release from sludge

- Investigation of the effect of base concentration, temperature and mixing time on phosphorus release by using Box Behnken Experiment Design when sodium hydroxide and potassium hydroxide was used for phosphorus release from sludge

- Detection of optimum conditions which affected PO_4-P, NH_4-N, and Mg removals and observation of the applicability of pumice stone as seeding material for struvite crystallization at model reactor.

- Struvite crystallization from extracted P-rich liquid from sewage sludge by using nitric acid. Pumice Stone which was using as seeding material has been used to plant growth as medium at agriculture sector, in addition struvite can be used as fertilizer for plant growth. So, it was aimed that formation of useful product to be used at plant growth.

CHAPTER TWO
PHOSPHORUS RECOVERY TECHNOLOGIES

2.1 Phosphorus Release from Sludges

Phosphorus can be recovered from sewage sludge, sewage sludge ashes, and concentrated process waters. All processes for a recovery of phosphorus include a chemical or a chemical/thermal treatment, respectively, whereby phosphorus (and the contaminants) is re-transferred into an aqueous phase prior to the separation of phosphorus from the pollutants (Berg et al.,2005).

It is usually used three steps phosphorus recovery systems from sludge. The recovery of phosphorus from (digested) sludge generally consists of the following steps (Weidelener et al., 2005):

- Dissolution of the sludge using acids, bases, heat, pressure or a combination of them all
- Separation of the phosphorus-enriched liquid phase from the remaining solid phase
- Precipitation of the phosphorus in the liquid phase (p.e. as MAP) and separation of the precipitation.

It was discovered that water temperature affected the leaching of phosphorus from ash. The higher the temperature; the higher the rate of leaching (Brett et al., 1997).

Stark (2006) pointed that leaching with acid gives a higher release of phosphorus than leaching with base. When leaching with base the calcium content in the sludge binds phosphorus as calcium phosphate, decreasing the degree of phosphorus release. However leaching with acid gives a higher metal contamination of the leachate than leaching with base. Leaching with base will preferentially dissolve phosphorus and the metal contamination of the phosphorus can be decreased (Stark et al., 2006).

Phosphorus can be recovered technically by precipitation or crystallization when fulfilling the following conditions (Jeanmaire, 2001):

- Liquid stream with a minimal P content
- Liquid stream with low SS contents
- Adapt the molar ratios necessary for the formation of the researched compounds
- Create an increase in the pH value
- Reactor or settler enabling recovery

The commonly used phosphorus recovery methods from sewage sludge are briefly summarized below.

2.2 Phosphorus Recovery

The possibility to fix phosphate in sludge handling liquors supplied from a carbon-nitrogen wastewater treatment plant thorough the crystallization of struvite was investigated by Battistoni. The anaerobic supernatant used for the experiments was obtained from the dewatering unit (belt-press) of an 85000 equivalent inhabitant's civil wastewater treatment plant, with a combined carbon oxidation and nitrogen-denitrification and anaerobic digestion of sludge. The experimental results showed that a natural aging with phosphate precipitation can be observed in a few days with a different percentage of struvite and hydroxyapatite in relation to the liquor composition; moreover supersaturation curves play a major role in the interprepation of the process. Finally, the fluidized bed reactor (FBR) plant managed in batch mode assures a good phosphate removal through crystallization on quartz sand in about 100 min (Battistoni et al., 2000). In other study conducting by Battistoni, the phosphorus removal form a real anaerobic supernatant through the crystallization of struvite and or hydroxyapatite was investigated. A comparison between experimental results on phosphorus crystallization carried out in a fluidized bed reactor (FBR) on a bench-scale and on a half-scale plant is presented, together with a double saturational model able to describe all experimental results, independent of the different geometry of the reactors, the distinct contact times and the unlike products obtained.

Experimental results show that removal efficiencies are very satisfactory, and the maximum phosphorus removal is of 80 % (Battistoni et al., 2001). In study conducting by Stratful, struvite could be precipitated out of solution at pH 10 and increasing the ion concentration stoichiometrically could increase crystal yield. Increasing the NH_4^+ concentration increased purity of the precipitate. As reaction time was increased from 1 to 180 min, crystal size was found to increase from 0.1 to 3 mm (Strantful et al., 2001).

Jang and Kang examined on phosphorus removal using cow bone in hydroxyapatite crystallization. According to Jang and Kang, seed crystal used for the experiments was prepared by the calcinations of cow bone. The experimental results showed that a good phosphorus removal could be achieved by cow bone crystal seeding (Jang and Kang, 2002).

Münch and Barr studied on controlled struvite crystallization for removing phosphorus from anaerobic digester sidestreams. The pilot scale reactor was an air agitated column reactor with a reaction and a settling zone, based on the Phonix process of Unitika Ltd., Japan. The pilot scale process achieved an ortho-P removal ratio of 94 % from an average influent ortho-P concentration of 61 mg/L. The dry MAP product had cadmium, lead and mercury concentrations well below the legal limits for fertilizers in Queensland Australia and can be reused as a valuable slow-release fertilizer (Münch et al., 2001).

2.3. Processes for Phosphorus Recovery from Sewage Sludge

2.3.1 The Krepro and Cambi/Krepro Process

The Krepro Process developed by Kemira Kemwater, Alpha Laval, and the operator of the Helsingborg's WWTP (Sweden) allows a separation of sewage sludge into four fractions: iron phosphate, highly calorific organic sludge, precipitation chemicals, and a carbon-rich centrate. Phosphorus is recovered as iron phosphate. In the first step, as shown in Figure 2.1, the sludge is passed on to a hydrolysis reactor,

where it remains for 0.5 to 1.0 h at a pH of 1.5, a temperature of up to 150°C, and a pressure of 4 bar. Under these conditions, about 40 – 60 % of the organic substance (Recktenwald, 2002) and, depending on the precipitant used, about 75 % of the phosphorus is dissolved (Recktenwald, 2002, Cornel and Schaum, 2004, Berg et al., 2005).

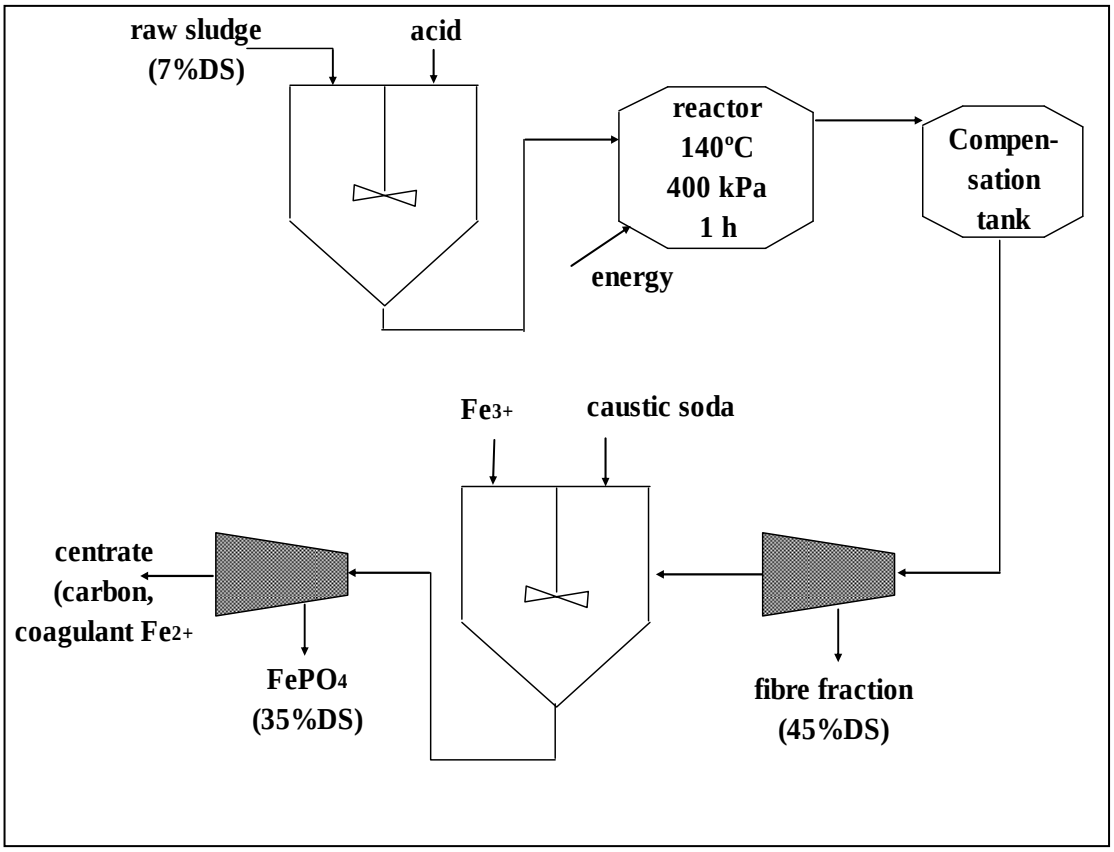


Figure 2.1 Simplified flowchart of the Krepro process (Berg et al., 2005)

The Cambi/Krepro process (Figure 2.2) is a combination of earlier developed systems by Cambi and Kemira/Alfa Laval, respectively. The idea of Cambi was to use steam as a heat source directly into pre-dewatered sludge and then digest it. The full scale process was commissioned in 1996 in Hamar, Norway (Hultman et al., 2007).

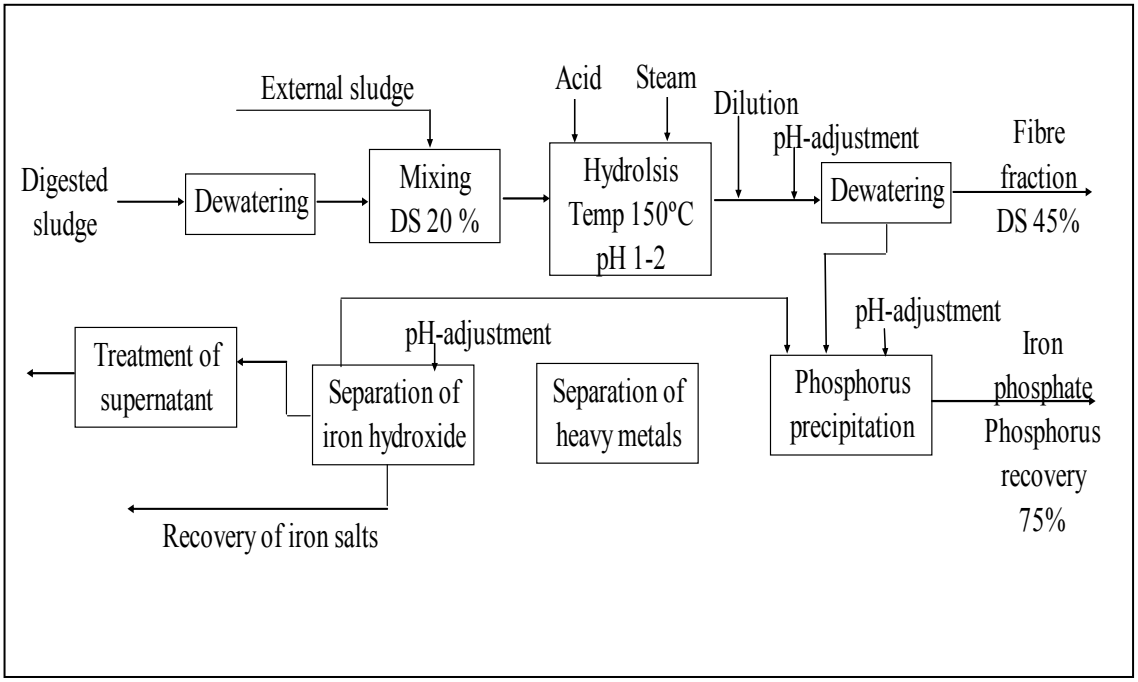


Figure 2.2 Cambi/Krepro process (Hultman et al., 2007)

2.3.2 Kemicond Process

The Kemicond process is a new method for conditioning and dewatering of digested or undigested sludge. It operates at relatively low pH values and consists of several steps as shown in Figure 2.3. In the first step sulphuric acid is added until pH value around 4 is achieved. Then a release of gases, mainly carbon dioxide (CO_2) and some hydrogen sulphide (H_2S) occurs. Furthermore, gel-like water-holding inorganic matter is dissolved and chemically bounded water that cannot be removed with only mechanical dewatering is released, i.e. the iron- or aluminium- based coagulants, hydroxides and phosphates are dissolved at this pH, and most of them remain in solution. Part of the organic matter is also dissolved (Nikolic et al., 2004).

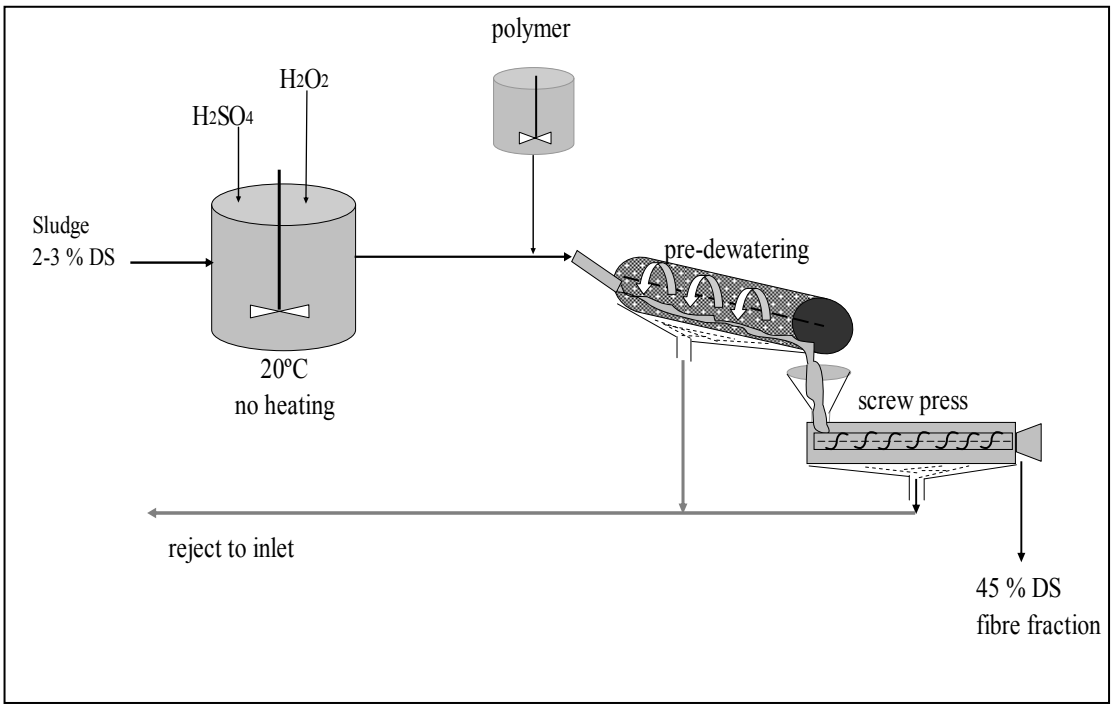


Figure 2.3 Flow diagram of the Kemicond process (Nikolic et al., 2004)

2.3.3 The Aqua Reci Process

The Aqua Reci process is a wet oxidation process for sewage sludge, which is run in the supercritical range of water (p > 221 bar, T > 374°C) (Figure 2.4). Under these conditions, pure oxygen is added for a complete oxidation of all sludge constituents to take place within a residence time of 60 seconds in the reactor. The heat generated during oxidation allows for an autothermal mode of operation, such that thermal energy is required for the start-up of the process exclusively. The accrued sludge is considerably depleted in organic compounds. From the remaining inorganic sludge, phosphorus may be separated by the addition of base in terms of calcium phosphate (Berg et al., 2005).

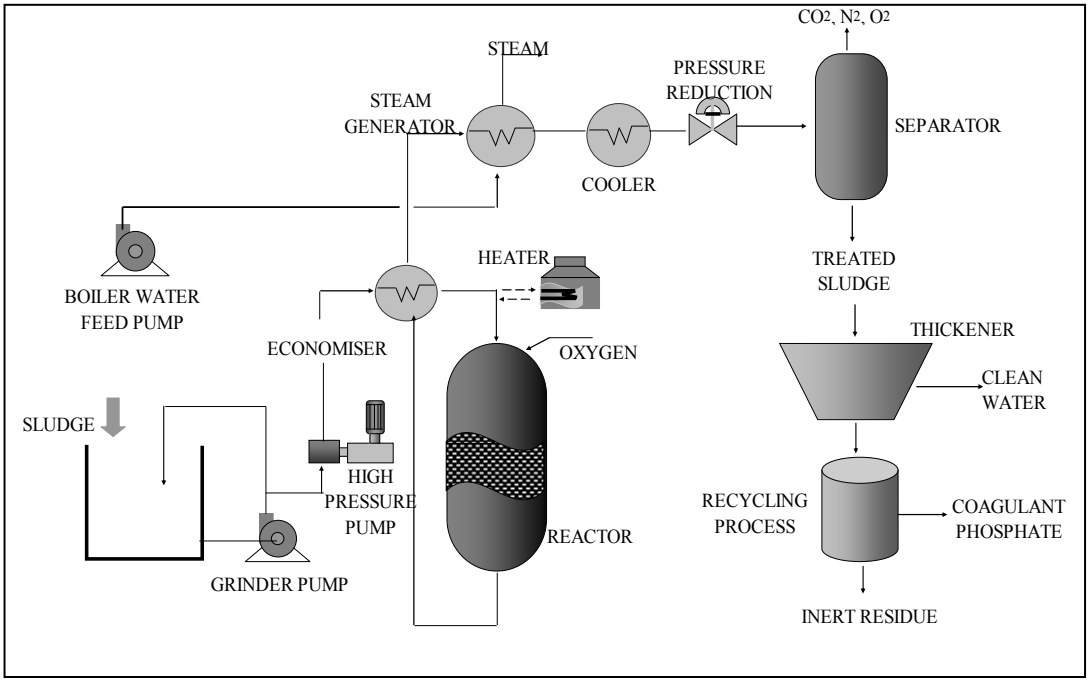


Figure 2.4 Simplified flowchart of the Aqua Reci process (Stendahl et al., 2003)

2.4 Processes for Phosphorus Recovery from Sewage Sludge Ashes

2.4.1 The BioCon Process

Bio-Con is a Danish company that has developed a system for heat drying of sludge and incineration (Figure 2.5). As a third part of the BioCon sludge handling a system has been developed to recover resources from ashes by leaching with sulphuric acid and recovery of resources by ion exchange. The two developed systems are in the stage to be implemented in full scale but there is still a need for a careful evaluation of the function of the systems under different conditions (Hultman, 2001).

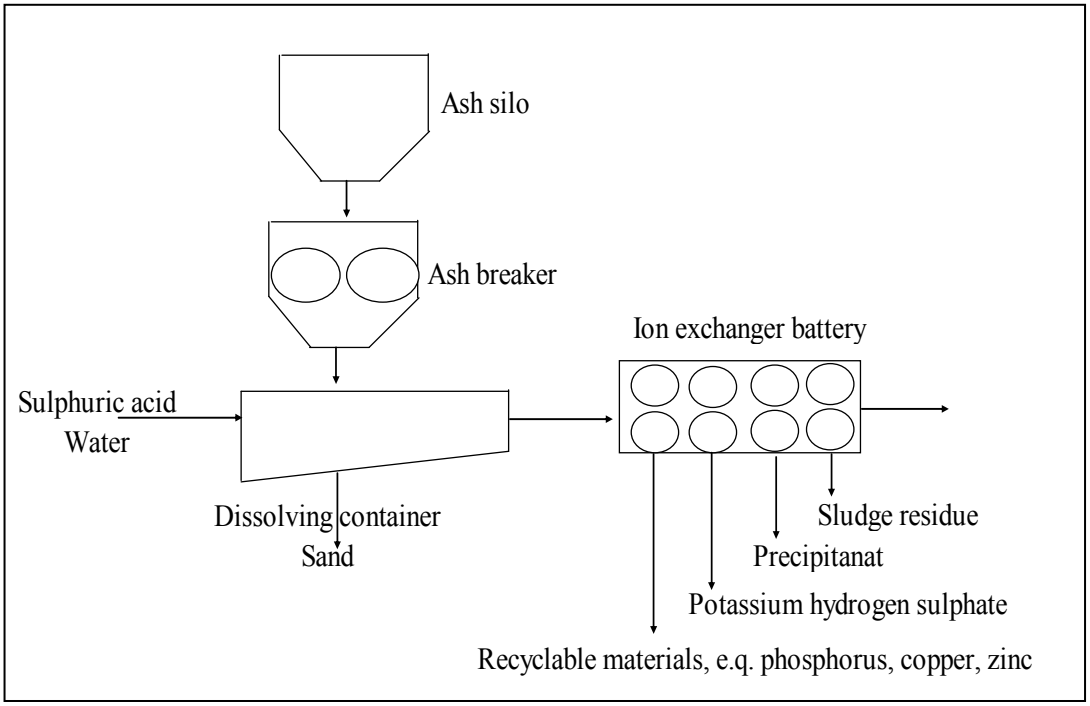


Figure 2.5 Biocon process (Hultman, 2001)

2.4.2 The SEPHOS Process

The SEPHOS (sequential precipitation of phosphorus) process is under development by the Institut *WAR* of the TU Darmstadt and the Ruhrverband (Germany). In this process, sludge ash is treated with sulphuric acid (pH < 1.5), the residual solids (mostly sand) are separated (Figure 2.6). In the filtrate, the pH value is then stepwise increased with caustic soda to pH 3.5 to separate phosphorus and heavy metals (Schaum et al., 2004). The precipitant product is an aluminum phosphate, which can be used as raw material in the electrochemical phosphate industry. It is also feasible to produce calcium phosphate, which could be reused as a fertilizer by inserting a further process, step: The amphoteric elements, especially aluminum and phosphorus of the aluminum phosphate are dissolved by an elution with a base (pH 12 – 14); the insoluble residuals (heavy metals) are separated. The dissolved phosphorus can then be precipitated as calcium phosphate by the addition of calcium ions, potentially also by crystallization. The dissolved aluminum can be recycled as coagulant for the wastewater treatment (advanced SEPHOS process) (Berg et al., 2005).

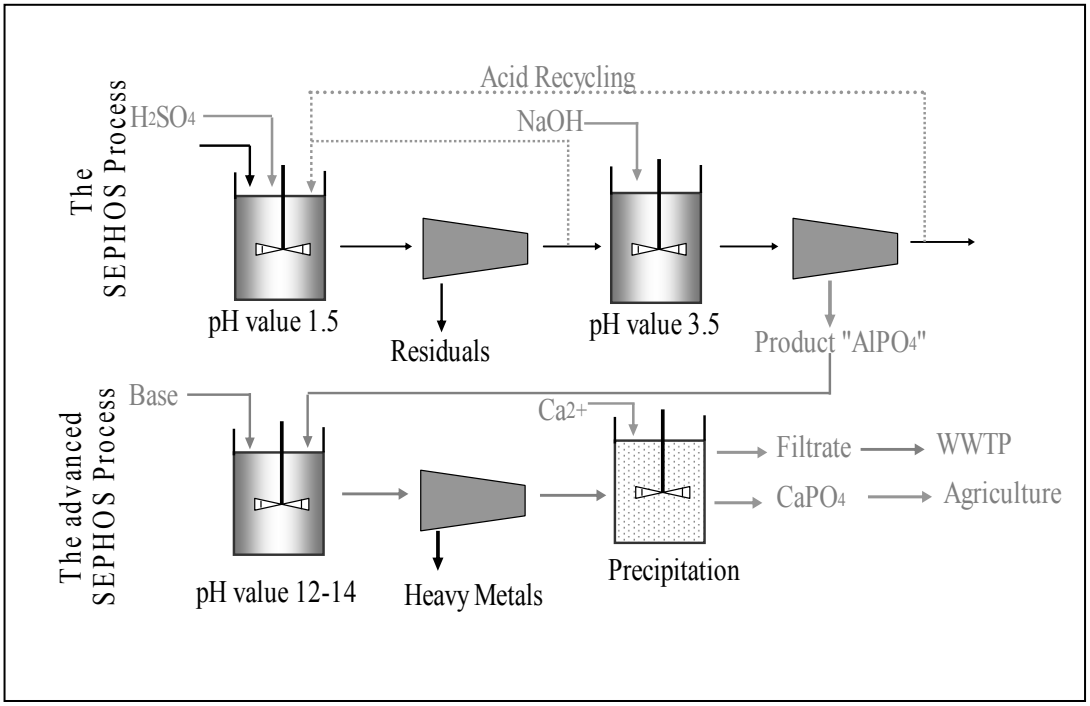


Figure 2.6 Simplified flowchart of the SEPHOS process (Berg et al., 2005)

2.5 Phosphate Crystallization Processes

2.5.1 The DHV Crystalactor™ Pelletiser

The Crystalactor™ process is based on the crystallization of calcium phosphate in a granular form using a fluidized bed (Figure 2.7). It treats the effluent form existing works, or a works modified to produce a phosphorus enriched sidestream. The major advantage is that phosphorus removal produces no additional sludge, only a quantity of water-free pellets that can be re-used in the phosphate processing industry (Brett et al., 1997). The development of crystallization technology started in the 1970s, in response to more stringent phosphorus removal requirements combined with the desire to produce a more marketable end-product. Although there have been a number of initiatives, the leaders in this technology are DHV Consulting Engineers (Morse et al., 1998).

The process is based on a fluidized reactor in which calcium phosphate crystallizes on a seeding grain, typically sand. The process conditions are adjusted by adding either caustic soda (NaOH) or milk of lime ($Ca(OH)_2$). During operation the pellets

increase in diameter and on reaching the desired size, are removed and replaced by smaller diameter seed grains. To ensure low phosphate concentrations in the final effluent, the reactor carry-over may be removed by dual-media (anthracite/sand) filtration or recycled to the start of the works (Brett et al., 1997).

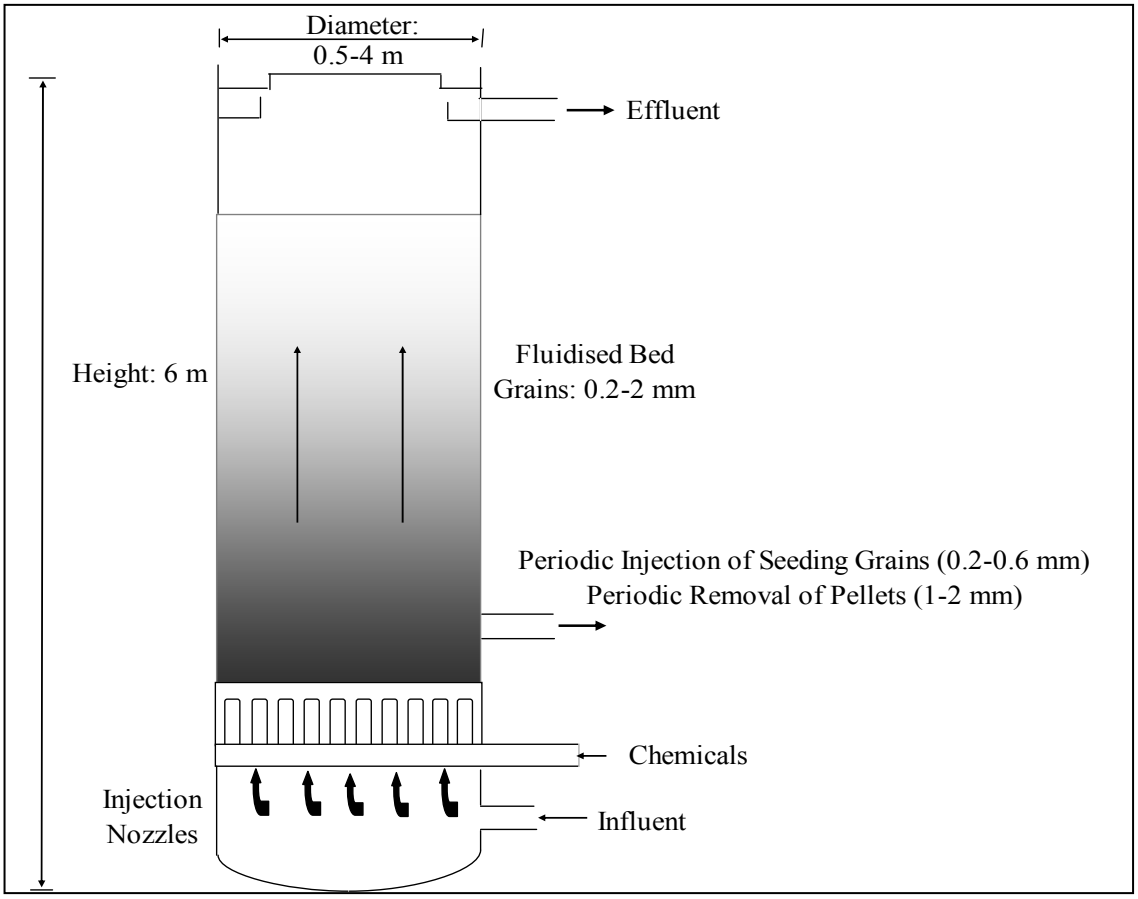


Figure 2.7 The DHV Crystalactor™ Pelletiser (Brett et al., 1997)

2.5.2 The CSIR Fluidized Bed Crystallization Column

The CSIR Fluidized Bed Crystallization Column is a laboratory scale process using crystal nucleation and growth chemistry that is similar to the DHV Crystalactor™ and Kurita Fixed Bed Column. It is designed to remove phosphorus from a variety of influent, whilst producing a granular hydroxyapatite(HAP) product with minimal sludge production. The crystallization can be categorized into two processes, nucleation (generation of crystals from solution) and growth (ion transportation onto the crystal surface and into the lattice). Work on HAP crystallization has been done

using a variety of seed materials including phosphate rock, bone charcoal, magnesia clinker, zirconium hydroxide, pumice stone and sand. It is shown following to CSIR Reactor in Figure 2.8 (Brett et al., 1997).

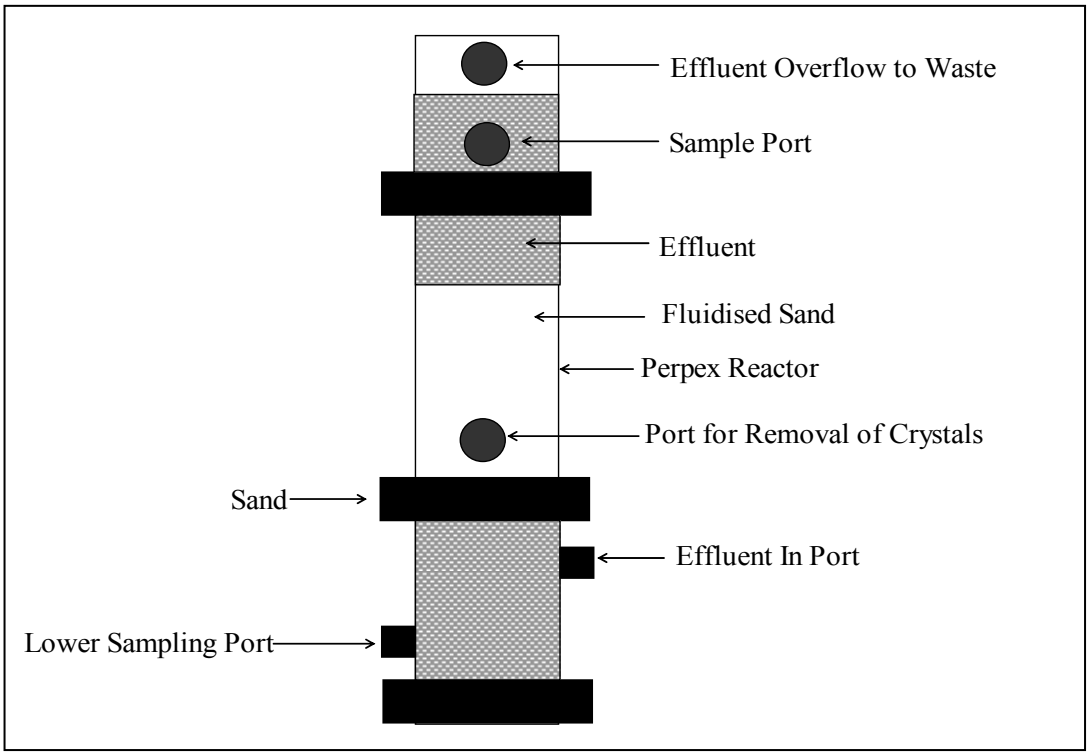


Figure 2.8 CSIR Reactor (Brett et al., 1997)

2.5.3 The Kurita Fixed Bed Crystallization Column

The Kurita Fixed Bed Crystallization Column is based on similar chemistry to the DHV Crystalactor^{TM}. It is designed to remove phosphate from the secondary effluent by use of phosphate rock seeding grains, without the production of sludge. Calcium phosphate is produced. The process is based on a fixed bed column reactor, packed with phosphate rock seeding with a diameter of 0.5 – 1.0 mm. It is illustrated in Figure 2.9 (Brett et al., 1997).

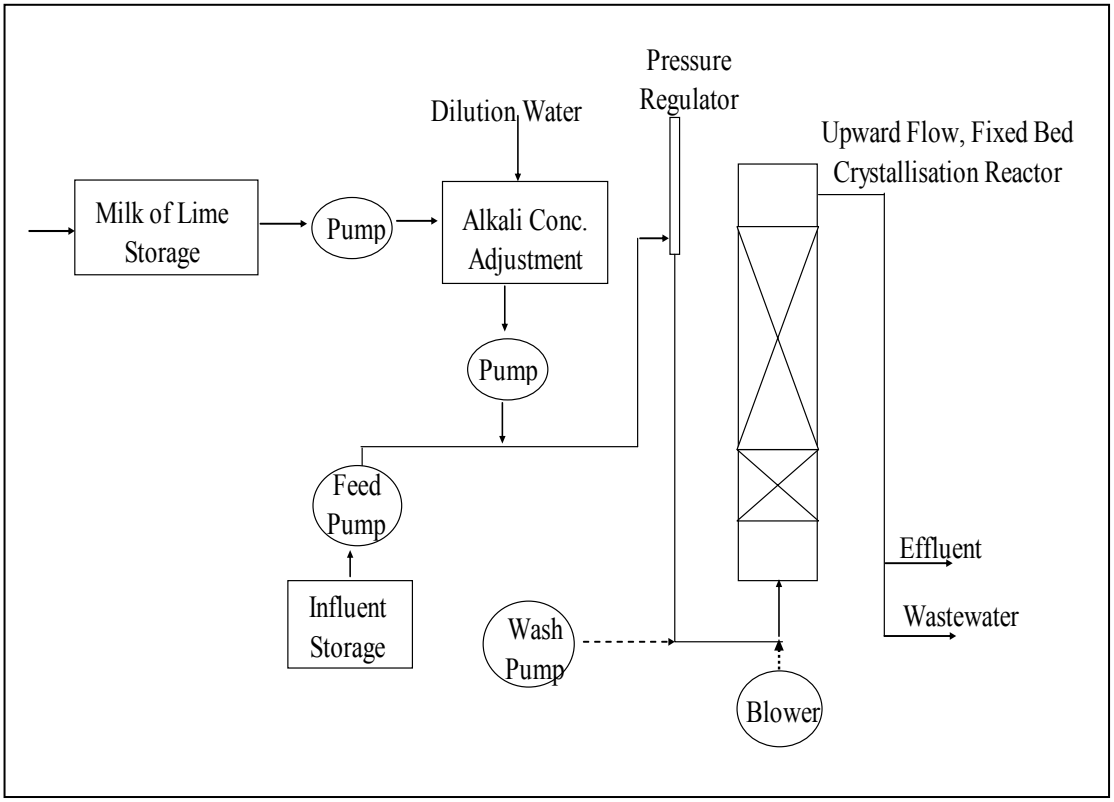


Figure 2.9 The Kurita Process (Brett et al., 1997)

2.5.4 Anaerobic Digestion of the Organic Fraction of Municipal Solid Waste (OFMSW) and Biological Nutrient Removal (BNR)

This is a three stage process design to integrate anaerobic digestion of the organic fraction of municipal solid waste (OFMSW), biological nutrient removal and phosphate crystallization (Figure 2.10). It produces struvite fertilizer MAP and a three stage, integrated process comprising anaerobic fermentation, biological nutrient removal and a struvite crystallization. The recovered product is either HAP or struvite, depending on operating conditions such as pH and calcium, magnesium, phosphate and ammonium concentrations (Brett et al., 1997).

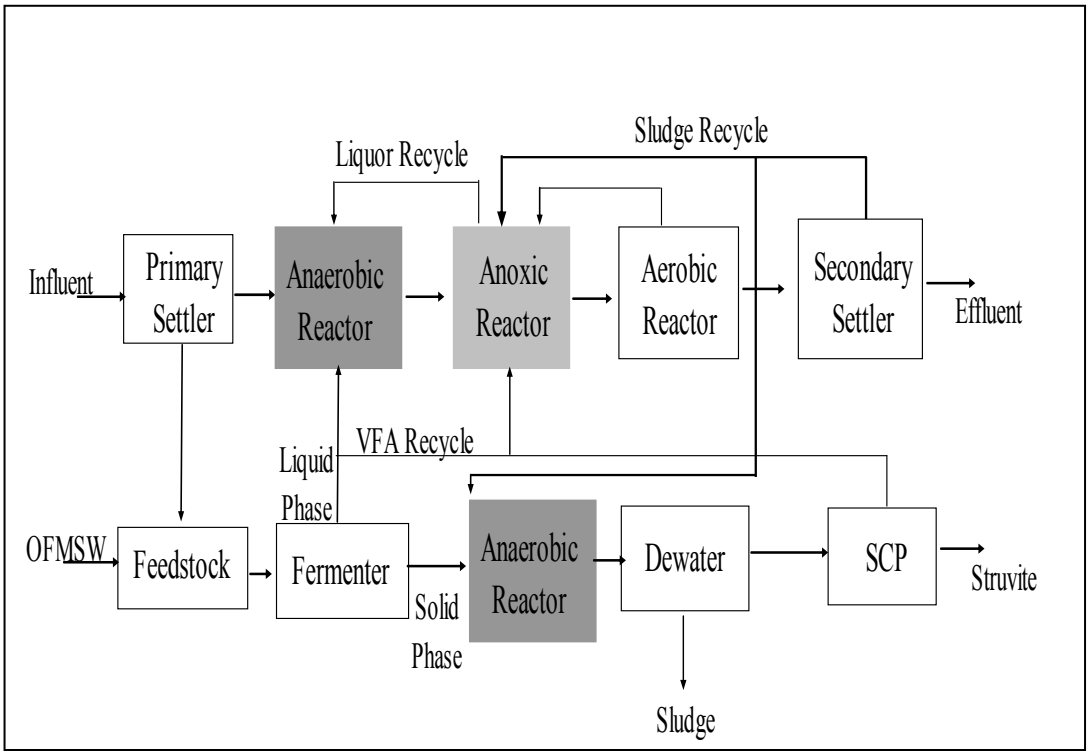


Figure 2.10 OFMSW and BNR flow sheet (Brett et al., 1997)

2.5.5 The RIM-NUT Ion Exchange Process

The RIM-NUT ion exchange-precipitation process removes ammonia and phosphate ions from tertiary wastewater. It produces a struvite ($MgNH_4PO_4$), which can be used as a slow-release fertilizer, and no additional sludge. The RIM-NUT process consists of three stages. Process consists of two columns of cationic resin, two columns of ionic resin and the nutrient precipitation. A dual column system is adopted for each resin to allow regeneration at the same time as removal of the nutrients, without disturbing the process or risking a nutrient discharge. Secondary effluent enters the process where the pH and temperature are measured and the flow controlled using a rotameter. It enters one of the cationic resin columns which contain 0.45 m^3 of the natural zeolite, clinoplolite. This selectively removes the ammonium ions. It then enters the anionic column which contains 0.43 m^3 of a strongly basic resin (*unnamed*) (Brett et al., 1997).

2.5.6 The Unitika Phosnix Process

The Unitika Phonix Process is a tertiary phosphorus removal system based on the crystallization of struvite from an enriched phosphate stream (Figure 2.11). It was developed by Unitika Ltd. in Japan, the motivation being environmental protection legislation and the desire to create a process which is cheaper than conventional phosphorus removal systems. It produces no additional chemical sludge. The Phonix process is based on air agitated column reactor, with ancillary chemical dosing equipment. The Phonix process is classified as sidestream, and treats phosphorus enriched wastewater (Brett et al., 1997).

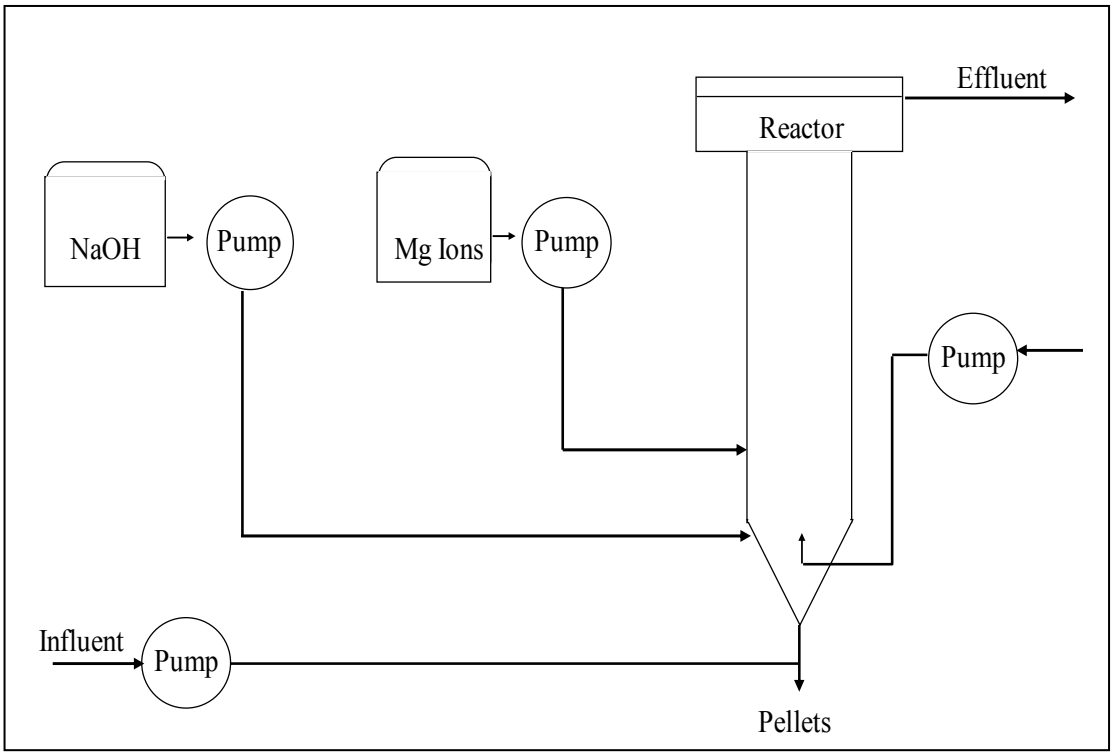


Figure 2.11 The Unitika Phonix Process (Brett et al., 1997)

CHAPTER THREE
PHOSPHORUS RECOVERY PRODUCTS

It is used usually crystallization/precipitation process at composing phosphorus recovery products. Crystallization refers to the formation of solid crystals from a homogeneous solution. Crystals are grown in many shapes, which are dependent upon downstream processing or final product requirements. Crystal shapes can include cubic, tetragonal, orthorhombic, hexagonal, monoclinic, triclinic, and trigonal. In order for crystallization to take place a solution must be "supersaturated". Supersaturation refers to a state in which the liquid (solvent) contains more dissolved solids (solute) than can ordinarily be accommodated at that temperature (Chemical Engineering, 2005).

Phosphorus recovery products are formed by using crystallization/precipitation process. These are primarily struvite (MAP-$MgNH_4PO_4 \cdot 6H_2O$), hydroxyapatite (HAP-$(Ca_3(PO_4)_3OH)$, tricalcium phosphate (TCP-$Ca_3(PO_4)_2$), octacalcium phosphate (OCP-$Ca_4(PO_4)_3.3H_2O$), dicalcium phosphate dihydrate (DCPD-$CaH(PO_4).2H_2O$), Amorphous Calcium Phosphate (ACP) (Karapinar et al., 2006, Brett et al., 1997, Van der Houwen et al.,2001, Regy et al., 2001). Struvite is used at agriculture sectors as fertilizer and the calcium phosphate recovered are used in the phosphorus industry (Regy et al, 2001).

3.1 Struvite (MAP)

Struvite was found in anaerobic digestion sludge from animal farming liquid wastes. Struvite is named after the Russian diplomat H.G. von Struve (1772-1851). It has a white color and an orthorhombic pyramidal crystal system (Wu et al., 2002). Struvite in the wastewater treatment plants was identified in 1939 because of deposits in the pipes. The blockage of pipes leads to an increase in pumping costs (maintenance, workforce, etc.) (Regy et al., 2001). The formation of struvite ($MgNH_4PO_4 \cdot 6H_2O$) during wastewater treatment causes scaling on the inner surface of pumps, pipes and other equipments of wastewater treatment plants (Loewenthal, 1994).

Struvite which crystallizes as a white orthorhombic crystalline structure (it was illustrated in Figure 3.1) is composed of magnesium, ammonium and phosphate in equal molar (1:1:1) concentrations as well as six water of hydration (Regy et al., 2001 and Lee et al., 2003, Smith, 2001, Montag et al., 2007, Rahaman et al., 2007). The specific gravity is 1.7 (Qingzhong, 2002, Regy et al., 2001). The struvite formation reaction is shown below (3.1):

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4(H_2O)_6 \quad \text{.....(3.1)}$$

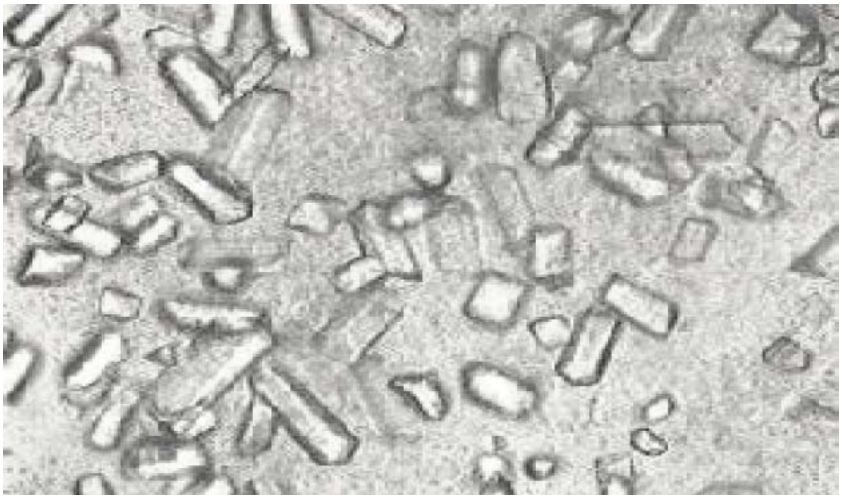


Figure 3.1 Denotes the characteristic shape of struvite crystals (Smith, 2001)

In addition, struvite can be composed with potassium (K^+) instead of ammonium (NH_4^+) and it is called as K-struvite ($MgKPO_4.6H_2O$) which is valuable fertilizers (Yi et al., 2005).

In Figure 3.2, it was illustrated formation of struvite by adding $MgCl_2$ (as magnesium source) and NaOH (for pH adjustment) (Arakane et al., 2007).

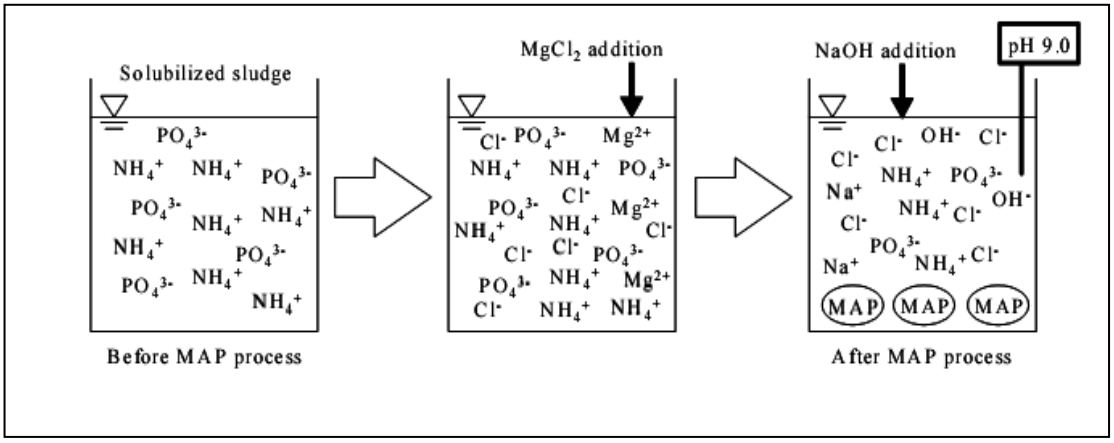


Figure 3.2 The flowchart of MAP process (Arakane et al., 2007)

The traditional solubility product of magnesium ammonium phosphate, struvite ($MgNH_4PO_{4(s)}$) illustrates a situation where more than one of the dissolving species is affected by solution pH. These species are the ammonium ion (NH_4^+) and phosphate ion (PO_4^{-3}). Because an increase in pH will decrease the ammonium ion concentration and increase the phosphate ion concentration, it follows that there should be a pH value where the solubility of $MgNH_4PO_{4(s)}$ is a minimum, that is, the pH where the product $[Mg^{2+}][NH_4^+][PO_4^{-3}]$ is a minimum [Snoeyink, 1980]. On the other word, the struvite is highly soluble at acidic pH and highly insoluble at alkaline pH in wastewater. When the pH increases the orthophosphate concentration increases whereas the magnesium and ammonium concentration decrease. So, it exists an optimum pH to precipitate struvite, the pH range is between 7 and 11. The minimum solubility in the waste water is around pH = 9. The minimum solubility implies a maximum potential for struvite formation. The turbulence influences the struvite formation. Increased turbulence leads to CO_2 liberation, so an increase in pH and hence in struvite precipitation (Regy et al., 2001, Snoeyink et al., 1980, Qingzhong, 2002)

Precipitation kinetics can be separated into two phases, nucleation and growth. Nucleation occurs when ions combine to form crystal embryos that can act as the foundation for growth into detectable crystals. Several mechanisms are possible, depending on the supersaturation level of the crystallizer. Homogeneous primary nucleation corresponds to nuclei apparition directly in the supersatured solution.

Heterogeneous primary nucleation takes place on foreing surfaces which can be dust in suspension or parts of the crystallizer itself. Secondary nucleation correspond to the nuclei formation on the surface these particles. The new born surface nuclei are then detached by the shear exerted by the fluid or by shocks undergone by the particles. Types of nucleation as summary were presented in Figure 3.3. Growth results from the assimilation of ions into the lattice structure established by the crystal embryo foundation (Ohlinger, 1999).

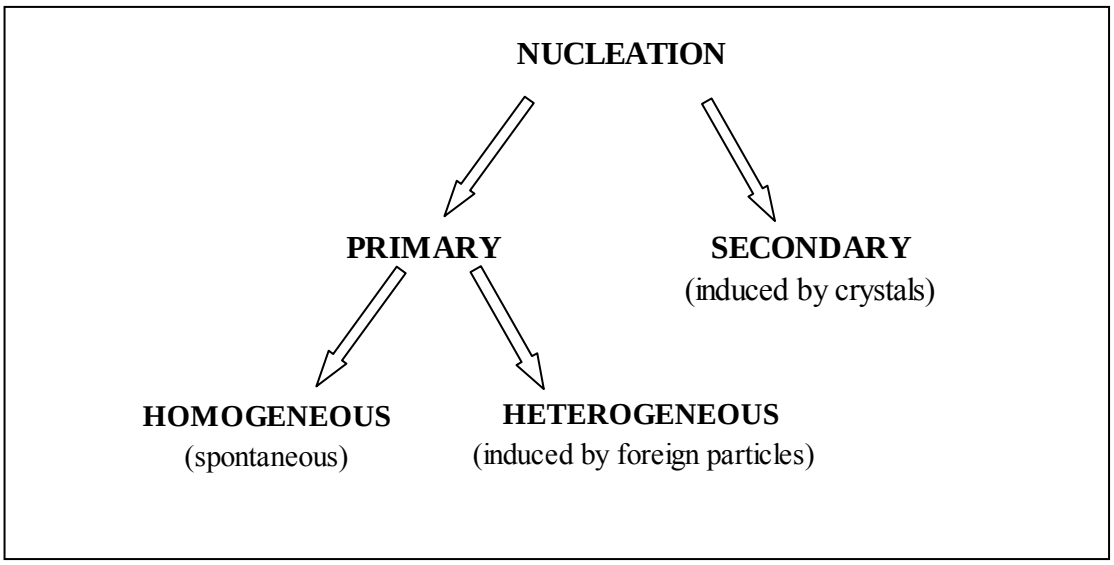


Figure 3.3 Types of nucleation (Wu, 2002)

A pH and temperature increase leads to reduce the induction time. At pH<8, the struvite precipitation is very slow and it can take several days. The induction time is significantly influenced by the supersaturation, and is also influenced, to a much lesser degree, by mixing energy (Ohlinger, 1999). This is not surprising since up to now, nothing could explain any influence of mixing on primary nucleation (Regy et al., 2001).

As mentioned previously, the success of the MAP process depends on two main factors: the molar ratio of Mg:N:P and the pH value in the reactor (Munch et al., 2001). In most cases, magnesium deficiency in wastewater allows it to be added to remove all available nutrients such as phosphorus and/or ammonium-nitrogen in water phase. Two types of magnesium, $Mg(OH)_2$ and $MgCl_2$, are generally used in

the MAP process. Compared to $Mg(OH)_2$, $MgCl_2$ is more widely used because it dissociates faster than $Mg(OH)_2$ and results in shorter reaction time. If the MAP process is applied to remove ammonium-nitrogen only, phosphate forms of H_3PO_4 or $NaHPO_4$ are usually needed (Siegrist, 1996; Schulze-Rettmer, 1991).

Magnesium oxide (MgO) is a slightly soluble solid material but due to its alkali character, it increases the pH-value in the solution, which promotes precipitation. An alternative could be highly soluble magnesium chloride ($MgCl_2$), however due to its slightly acidic character; it has no positive effect on the pH value. MgO can be found as an industrial by-product and it is therefore readily available at low prices. The experiments have shown that the impurities of the by-product were present in negligible amounts. By the addition of MgO instead of $MgCl_2$, the costs (Mg-source) can be reduced by 6, additional to the savings produced by reducing of NaOH required for the pH-adjustment. Results showed that an overdosing of MgO in the ratio $Mg: NH_4^+ :PO_4$ =1.5:1:1 improved the process, as this helped the higher dissolution of the MgO (Antakyalı et al., 2005).

Celen has pointed that $MgCl_2$ is a better Mg source than MgO. However less caustic is used for pH adjustment when MgO is used (Celen et al., 2001).

To achieve the reaction condition of MAP process, several methods can be applied such as:

1. Adding of MgCl and adjusting pH 9.0 by using NaOH (Demeestere et al. 2001, Shin and Lee, 1997),
2. Adding of Mg (OH) to form MAP precipitation and adjusting pH 9.0 (Arakane et al. 2006),
3. Adding MgCl and adjusting pH 9.0 by aeration (Battistoni et al., 1997).

According to Stratful studies, examination of the precipitate with a light microscope revealed that maximum crystal size increased with time. Crystals of up to 0.1mm were precipitated at 1 min (Figure 3.4a). At 60 min maximum crystal size had

increased, with some reaching lengths of 0.8mm (Figure 3.4b) and at 180 min crystals 3mm in length were observed (Figure 3.4c) (Stranful et al., 2001).

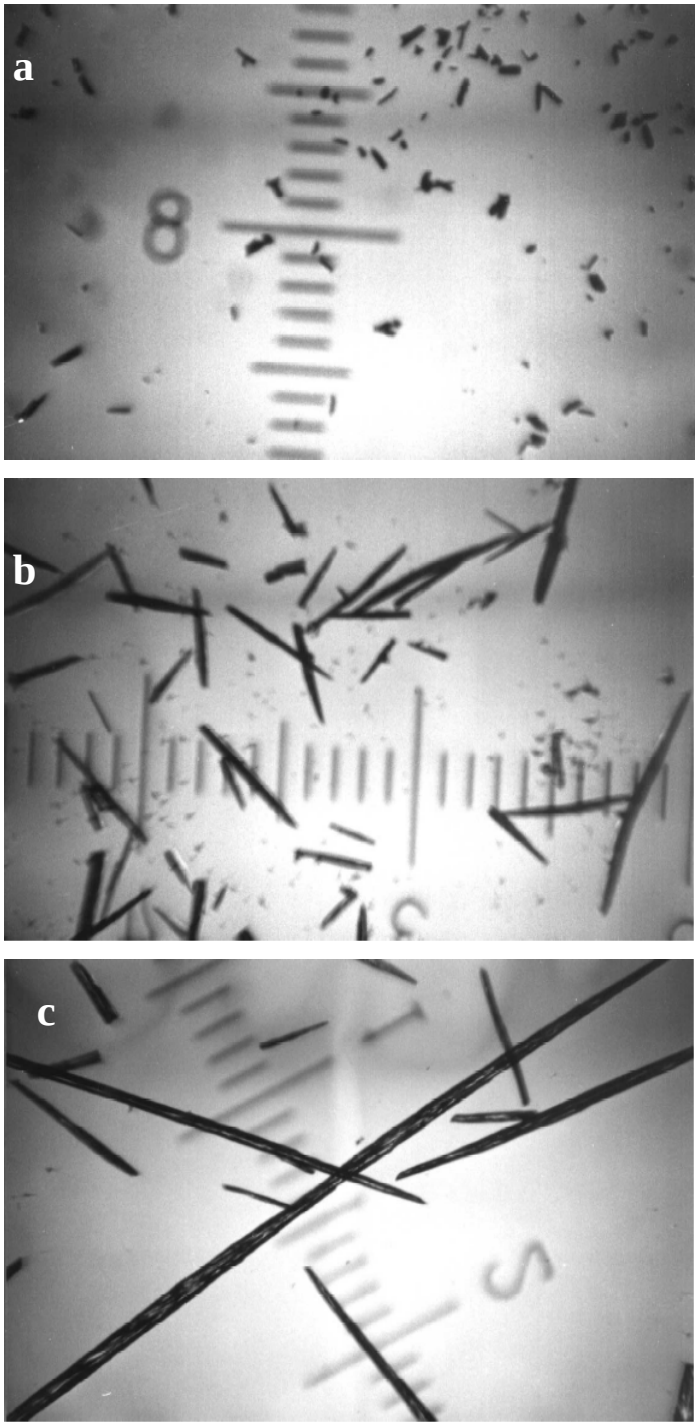


Figure 3.4 Variation crystal size with time (Stranful et al.,2001)
a) Crystals precipitated at 1 min b) Crystals precipitated at 60 min
c) Crystals precipitated at 180 min

The recent investigations have proved that this mineral is a high quality fertilizer due to its composition and low solubility (Goto, 2001). Struvite can use as fertilizer for plant growth. The advantages of struvite as a fertilizer are: (Munch et al., 2001).

- Because nutrients are released at a slower rate throughout the season compared to soluble fertilisers, plants can take up most of the nutrients without waste by leaching.
- Less frequent application is required.
- Fertiliser burn is not a problem even at high application rates.

Grains of seeding material assist nucleation of the crystals and recovered phosphorus precipitate on the seeding material. It has been used sand as seeding material in most of phosphorus recovery processes. It is illustrated various seeding material which are used in different phosphorus recovery processes in Table 3.1 (Brett et al., 1997).

Table 3.1 Seed materials using at various phosphate crystallisation processes

Phosphate Crystallisation Processes	**Seed Material**
The DHV Crystalactor™ Pelletiser	Sand
The CSIR Fluidised Bed Crystallisation Column	Quartz Sand
The Kurita Fixed Bed Crystallisation Column	Phosphates Rock or Sand
The Unitika Phonix process	Struvite or Sand
The Sydney Water Board Reactor	Magnesia Particles

To optimize the size of the recovered struvite crystals, researches have often tested crystallization onto seed materials such as sand (Battistoni et al., 2002) or performed struvite crystals (Shimamura et al., 2003).

3.2 Hydroxyapatite (HAP)

The reaction to produce hydroxyapatite (HAP-$Ca_3(PO_4)_3OH$) can be described as (3.2):

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \rightarrow Ca_{10}(OH)_2(PO_4)_6 \quad \text{.....(3.2)}$$

Equation 2 indicates that the efficiency of crystallization is influenced by the seeding material, phosphate concentration, calcium ion concentration and pH (Brett et al., 1997, Kim et al., 2006). It is claimed that HAP would be suitable as a fertilizer/soil conditioner, assuming that heavy metal concentrations do not exceed safe limits, although this seems unlikely without additional processing since HAP is very insoluble (Brett et al., 1997).

In HAP crystallizations, it has been used various seed materials as sand, phosphate rock, bone charcoal, magnesia clinker (Kim et al., 2006, Brett et al., 1997). Alkalinity and the presence of ionic magnesium, fluoride, and iron were found to affect phosphorus removal by HAP crystallization using converter slag as seed crystals (Kim et al., 2006).

Primary nucleation or spontaneous nucleation may not involve the formation of the most thermodynamically stable phase but normally the formation of a “precursor phase” with a higher solubility than the stable phase. Then, eventually, this precursor phase recrystallizes as HAP, the most thermodynamically stable phase. Depending on the conditions, precursors phases are: DCPD, OCP, TCP, ACP. At a pH range of 7-9, the transformation is the following: ACP-OCP-HAP, the conversion rate depends on the temperature and pH. At pH>9 ACP transforms directly in HAP (Regy et al., 2001).

CHAPTER FOUR
MATERIAL-METHOD

4.1 Materials

4.1.1 Solutions

Ammonia/phosphate solution which was used in experimental studies were prepared by using KH_2PO_4 (Merck); NH_4Cl (Merck). Magnesium chloride ($MgCl_2.H_2O$) was used as sources of magnesium ions. 0.5 M NaOH solution was prepared for pH adjustment. Dried sludge samples were leached with potassium hydroxide (KOH) and sodium hydroxide (NaOH).

4.1.2 Sludges

Sludge samples to be used at phosphorus release studies were taken from belt press stages of a municipal wastewater treatment plant. Sludge samples were dried at 103^0C in oven and afterwards they were crushed. The samples were sieved using a 30-mesh ASTM (600 μm) sieve. Leaching of dried samples was performed with the dried sludge which have sizes up to 600 μm.

4.1.3 Devices

- Jar test apparatus was used struvite precipitation with synthetic solutions.
- Magnetic stirrer/hot plate (Heidolph- MR 3001 K) and electronic temperature controller with stainless steel temperature sensor (Heidolph-EKT-3001) were used for the leaching process.
- Residues taken from reactor bottom have been dried in oven at 103^0C.

4.1.4 Pumice Stone

Pumice is a kind of volcanic rock. It has a glassy shape. As a result of volcanic activities; two kinds of pumice produced; acidic pumice, basalt pumice. (Scoria, basaltic pumice) The color of basalt pumice is dark and its specific weight rather more according to acidic pumice (1.2 - 2 gr/cm^3). Acidic pumice is the most widespread and it is used a lot in the world. The color of this pumice is light grey color / dark white because of its own features as silisium, potassium and sodium. During the formation, because of sudden cold and sudden gas abandon of structure, it got rather pore shape. Nearly all the pores don't have connections each other. Its density is changed between 0.5-1 gr/cm^3. Because of much pore of pumice; its permeability is very low against to voice and heat. Hardness of pumice is about 5.5 – 6 according to mohs scale and the its SiO_2 ratio which formed its structure is between 60% - 75%. As a result of this ratio; pumice can even abrade the steel. Pumice doesn't contain crystal water. Pumice stone is ineffective as chemical (Tekcanlar Ltd. Şti, 2007). In this study, pumice stone was used as seeding material. Chemical and physical properties of pumice stone samples used in experimental studies are given in Table 4.1 and 4.2.

Table 4.1 Chemical characteristics of pumice stone samples

Constituent	**Percentage present**
SiO_2	71-73
Al_2O_3	12-14
Fe_2O_3	0.5-1.25
FeO	0.61-1.25
CaO	0.71-0.96
MgO	0.03-0.10
K_2O	4.20-4.37
Na_2O	3.50-3.65
TiO_2	0.1
P_2O_5	0.002
SO_2	0.08

Table 4.2 Physical characteristics of pumice stone samples

Constituent	**Percentage present**
pH	5,5-6,0
Specific Gravity	2,327

Two types of pumice stone powder samples were used and they are called as NMP2 and NMP3 in this study. Pumice stone samples were supplied by Soylu Company (İzmir). The sieve size values of NMP2 and NMP3 pumice stone samples are given in the Figure 4.1. It was illustrated pumice stone samples in Figure 4.2.

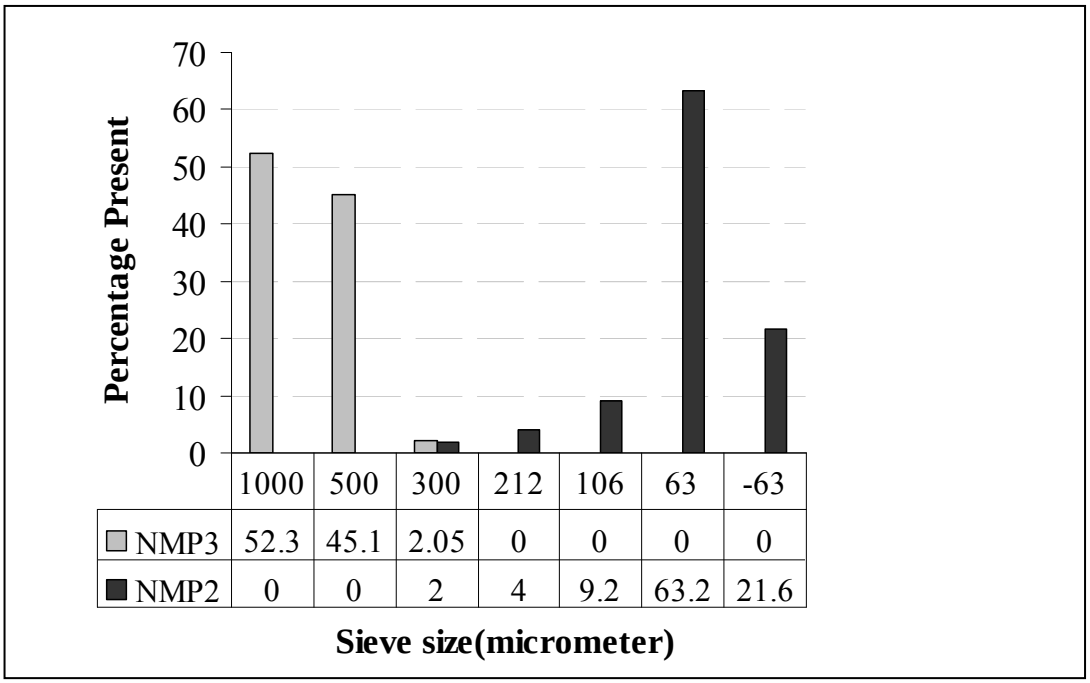


Figure 4.1 Sieve size values of NMP2 and NMP3 pumice stone samples

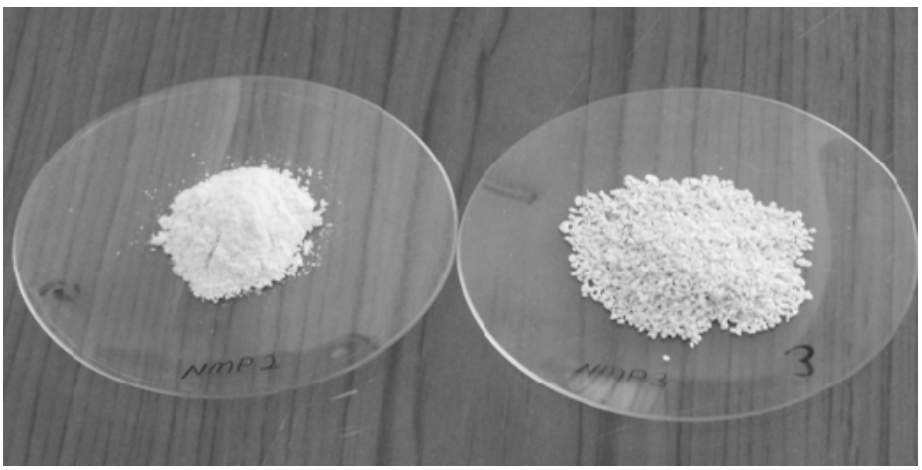


Figure 4.2 NMP2 and NMP3 (pumice stone samples)

4.2 Methods

4.2.1 Analytical Methods

- The concentration of phosphate and ammonium was respectively analyzed using Stannous Chloride Method; 4500-P D and Ammonia-selective electrode method; 4500-NH_3 D according to standard methods (APHA, 2005).
- Metals concentrations like Mg, Ca, Al, Fe, Cd, Cr, Ni, and Cu was measured by using ICP-OES (Perkin Elmer-Optima 2100 DV).
- Chemical composition of dried sludge and pumice stone was determined using X-ray diffraction analysis (XRD-Rigaku) at Department of Metallurgical and Materials Engineering, Dokuz Eylul University.
- The microphotographs of pumice stone and dried sludges and phosphates precipitates were taken by Scanning Electron Microscope (SEM-Jeol 6060).

4.2.2 Statistical Methods

4.2.2.1 Box-Wilson Experimental Design

The number of runs required by Box-Behnken Design is given in Table 4.3. The experiments consisted of six axial (A), eight factorial (F) and one centre (C) points at Box-Wilson Experimental Design. The centre point was repeated three times. The amount of phosphorus release was described by the following response function:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \ldots.(4.1)$$

Where; Y is the predicted response function (phosphorus release), b_0 is the constant, 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.

Table 4.3 Coded forms of independents variables for Box-Wilson statistical experiment design

	X1	**X2**	**X3**
A1	+1	0	0
A2	-1	0	0
A3	0	+1	0
A4	0	-1	0
A5	0	0	+1
A6	0	0	-1
F1	+k	+k	+k
F2	+k	+k	–k
F3	+k	–k	+k
F4	+k	–k	–k
F5	–k	+k	+k
F6	–k	–k	+k
F7	–k	+k	–k
F8	–k	–k	–k
C	0	0	0

Axial Points (A1, A2, A3, A4, A5, A6), Factorial Points (F1, F2, F3, F4, F5, F6, F7, F8), Center Point (C)

4.2.2.2 Box-Behnken Experimental Design

Box-Behnken designs are experimental designs for response surface methodology, devised by George E. P. Box and Donald Behnken in 1960 (Wikipedia, 2007).The Box-Behnken design is an independent quadratic design in that it does not contain an embedded factorial or fractional factorial design. In this design the treatment combinations are at the midpoints of edges of the process space and at the center. These designs are rotatable (or near rotatable) and require 3 levels of each factor. The designs have limited capability for orthogonal blocking compared to the central composite designs. Figure 4.3 illustrates a Box-Behnken design for three factors. The

geometry of this design suggests a sphere within the process space such that the surface of the sphere protrudes through each face with the surface of the sphere tangential to the midpoint of each edge of the space (NIST, 2007)

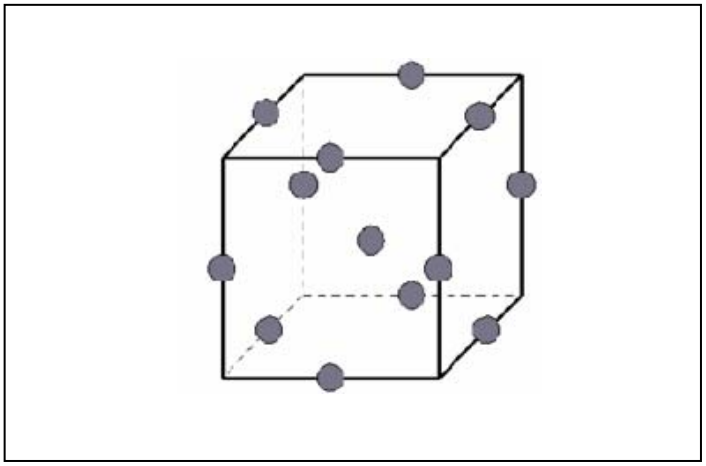


Figure 4.3 A Box-Behnken Design for three factors (NIST, 2007)

The efficiencies of Box-Behnken designs are shown in the following plot. The I-efficiencies of Box-Behnken designs for full-second-degree model functions and $3 \leq k \leq 10$ are in the range 30–98% (Figure 4.4). Note: There is no Box-Behnken design with 8 factors (Design of experiments, 2007).

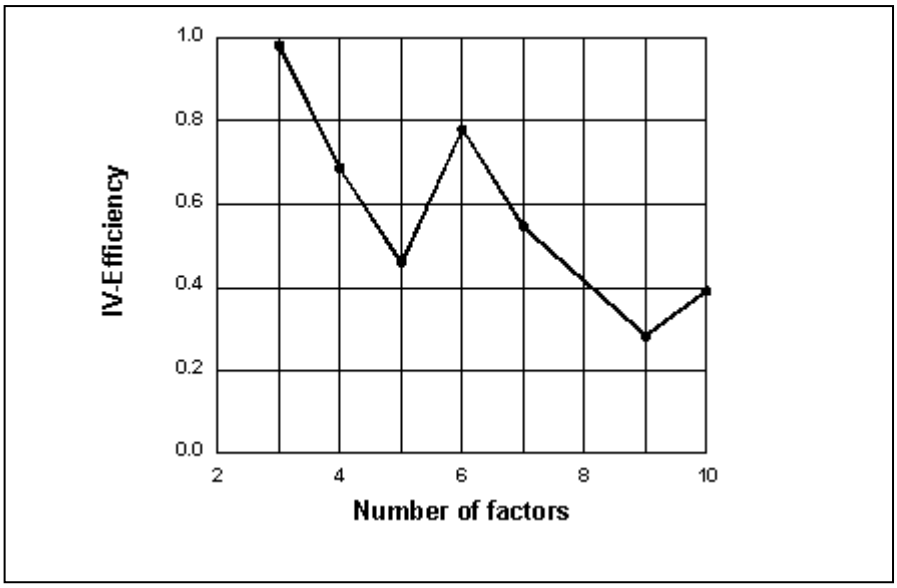


Figure 4.4 The efficiencies of Box-Behnken designs (Design of experiments, 2007)

It illustrated Box-Behnken design with three factors (coded form) in Table 4.4 where + 1 is the high value, –1 is the low value and 0 is the center value. Designs exist for

other numbers of factors. The number of runs required by Box-Behnken Design is given in Table 4.5.

Table 4.4 Box-Behnken design with three factors

Run	**X1**	**X2**	**X3**
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
13	0	0	0
14	0	0	0
15	0	0	0

Note: X1, X2, X3 independent variables

Table 4.5 Number of Runs Required by Box-Behnken Designs (NIST, 2007)

Number of Factors	Number of Experiment (with 3 replicates at center)
3	15
4	27
5	46
6	54

4.3 Model Reactor

Figure 4.5 depicts a schematic view of model reactor made from stainless steel and has volume of 30 liter. The model reactor is composed of two parts to avoid having fines in the effluent. The outward of the model reactor is settling zone and the inward part of model reactor is reaction and mixing zone. The experimental device is composed of the model reactor, three injection tubes (feeding solution, $MgCl_2$ solution, and NaOH solution), a pH-probe, a temperature sensor, and two stirrers for the model reactor and feeding tank (Figure 4.6). Outside of reactor was covered with oil blanket to supply temperature control. Temperature degree in of reactor by measuring with temperature sensor was kept at desired temperature on ±2 accuracy. Addition, pH value was continuously measured and maintained with dosing NaOH at desired pH value. It was mixed influent tank which volume has 30 liter during process to not settle pumice stone and to supply homogeneous mixture (pumice stone + feeding solution).

It has used ammonium-phosphate solution which prepare with $NH_4H_2PO_4$ (Merck), concentrated NaOH (Merck) solution which utilized pH adjustment, and $MgCl_2.6H_2O$ (Merck) solution as magnesium source. The model reactor is used batch system. Feeding solution was added 8.13 L/h with flow rate, and $MgCl_2$ solution was added 5.22 L/h with flow rate. It was feed both feeding solution and pumice stone which has 150-200 μm size at the same time to reactor.

The phosphate and ammonium concentration in the solution before and after process were analyzed according to standard methods (APHA, 2005). It was controlled progressively effluent PO_4 and NH_4 concentrations, pH values at the reaction time inside reactor, Mg concentrations. Effluent solution was analyzed to determine the concentration of PO_4^{-3} and NH_4. Residues taken from reactor bottom composed of struvite forms and pumice stone.

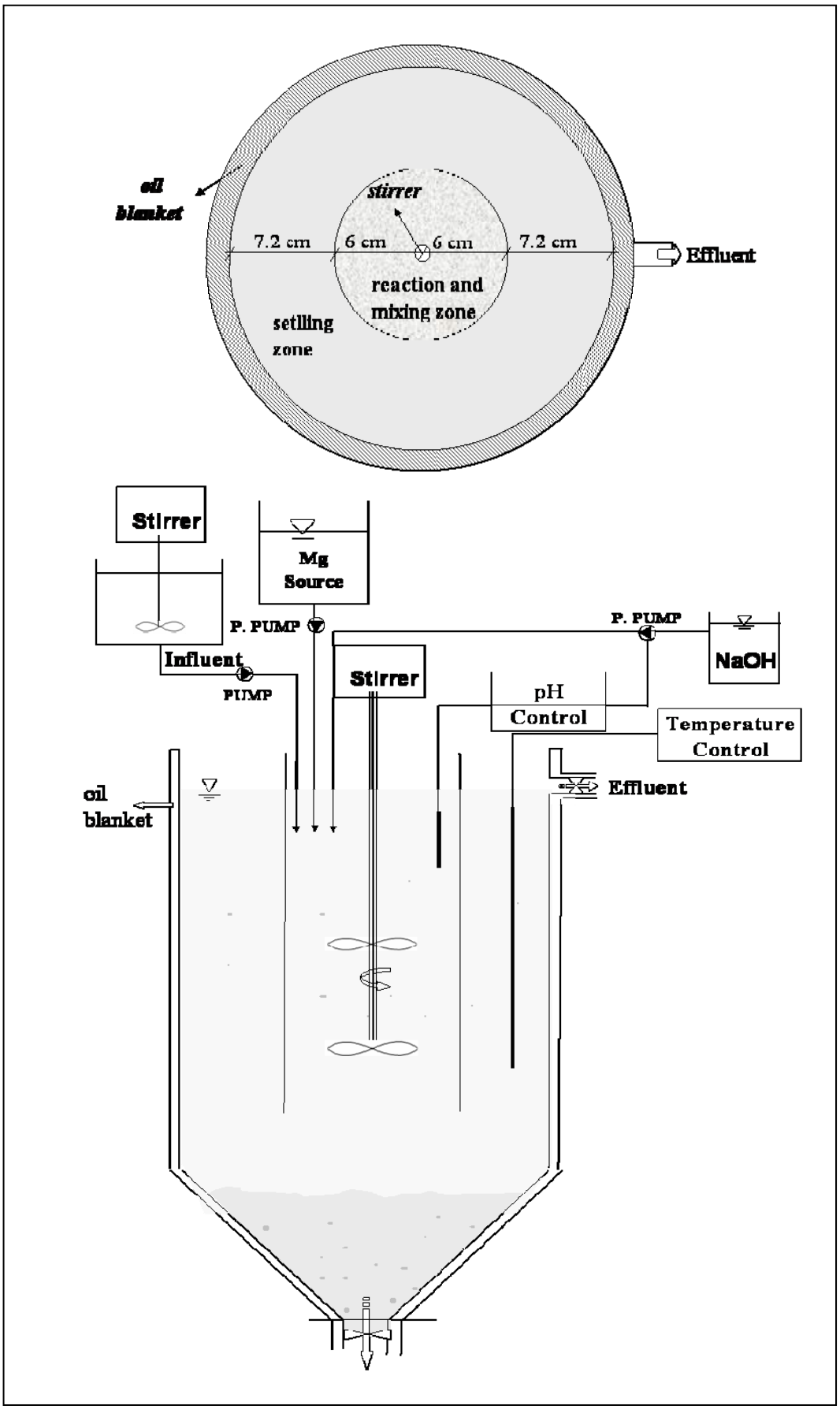


Figure 4.5 Schematic view and plan of model reactor





Figure 4.6 View of model reactor

CHAPTER FIVE
STRUVITE PRECIPITATION WITH SYNTHETIC SOLUTION

In this chapter, it is given the results of initial experimental studies done to research the applicability of pumice stone as a seed material in struvite crystallization. The effects of pH, pumice amount and size, magnesium chloride amount (as magnesium source) on struvite formation by using jar test apparatus were examined for prepared synthetic solution by batch experiments in lab scale.

5.1 Sample Preparation

Samples (ammonia/phosphate solution) which will be used in experimental studies were prepared by using KH_2PO_4; NH_4Cl. Samples have 40 mg/L phosphate concentration (estimated phosphate concentration of supernatant of the anaerobically digested sludge). Magnesium chloride ($MgCl_2.H_2O$) was used as sources of magnesium ions. Magnesium chloride solution was prepared by adding to deionized water at 1000 mg/L concentration. 0.5 M NaOH solution was prepared for pH adjustment.

Experiments were carried out using a jar test apparatus. Jars were filled to a volume of 300 ml with samples. The initial pH was adjusted and, 10 ml of MgCl solution was added to each jar during mixing. Samples were withdrawn after mixing times of 1, 10, 20, 30, 60, 90, 120, 150, and 180 min and immediately filtered through 0.45 μm pore size membrane filters. It was illustrated struvite precipitation with time in Figure 5.1.

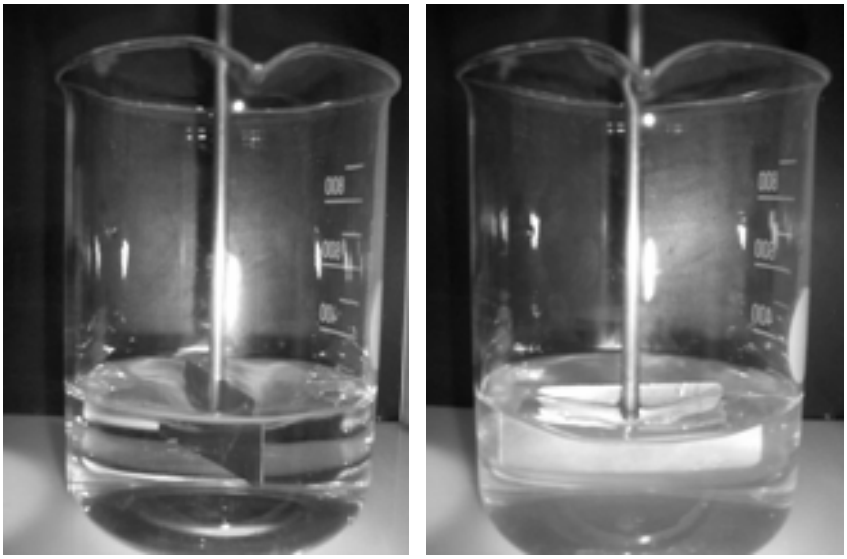


Figure5.1 Struvite precipitations with time

5.2 Results

5.2.1 Determination of pH Effect

The effect of pH was first investigated. As reaction time increased there was 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 (Stranful et al., 2001). Experiments were carried out at time period among 1-180 minutes. Two types of pumice stone powder called as NMP2 and NMP3 were used. pH was adjusted to 7,8,9,10,11,12 for each stage and it was used 1 g NMP2 (pumice stone powder sample I) for each trial. Initial phosphate concentration was 40 mg/L and mixing speed was 140 rev/min (Lee et al., 2003). The change of phosphate concentrations at different pH values are compared in Figure 5.2. The best phosphate removals were obtained between pH 9-10. On the contrary, phosphate removal was decreased at pH 7 and 8. In comparison, Lee et al. found an optimum pH 9.6, whereas Stranful et al. reported as pH 8.5 (Lee et al., 2003, Stranful et al., 2001)

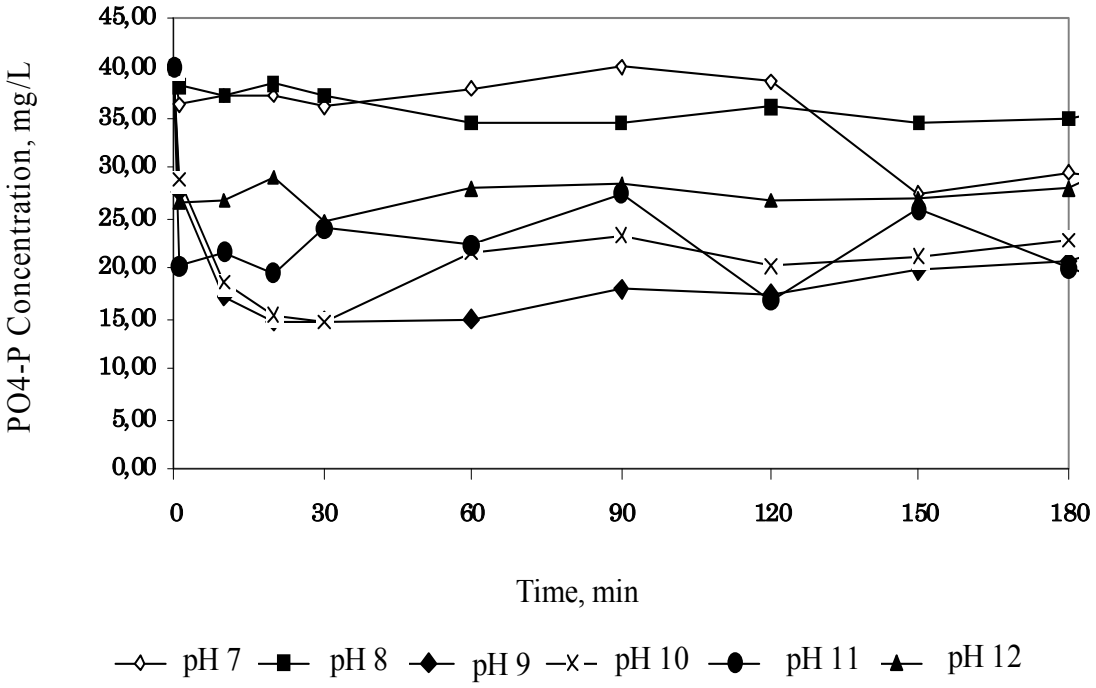


Figure 5.2 Change of phosphate concentration with time at different pH value

5.2.2 Determination of pH Change

Initial phosphate concentration was 40 mg/L and mixing speed was 140 rev/min. Initial pH was adjusted to 9 and it was used 1 g NMP2 (pumice stone powder sample I) for each trial. The change of phosphate concentration with time at pH 9.0 is shown in Figure 5.3.

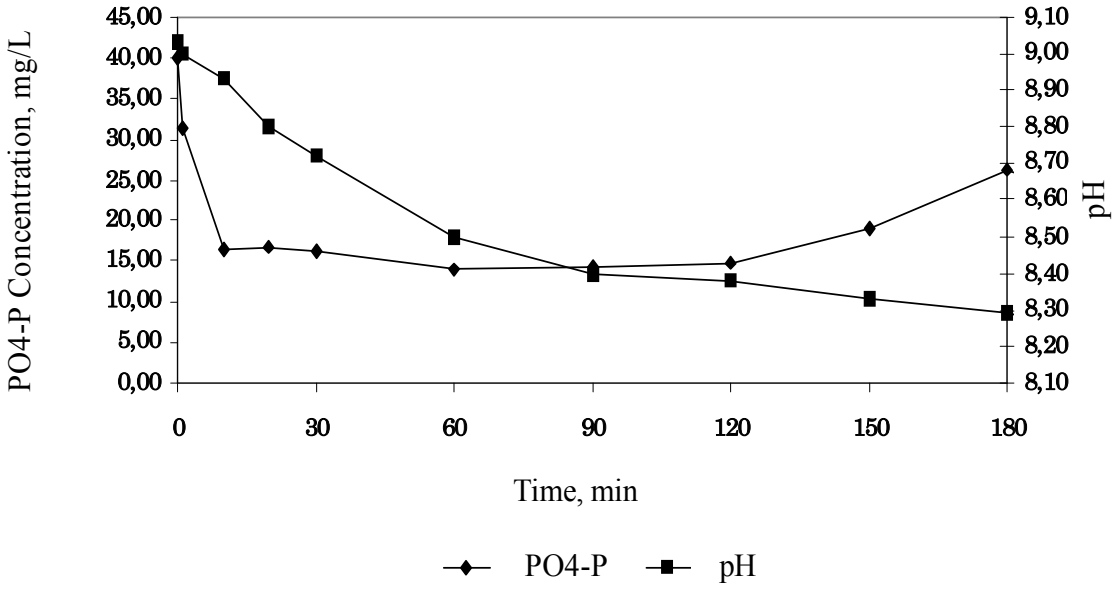


Figure 5.3 Change of phosphate concentration with time at pH 9.0

pH value decreased in time from 9 to 8.2. Because the minimum phosphate concentration (13 mg/L) was found in pH 8.5, second trial was carried out in maintaining constant pH 8.5. The change of phosphate concentration with time at maintaining constant pH 8.5 is shown in Figure 5.4. As a result of this trial, the minimum phosphate concentration (12 mg/L) was achieved in pH 8.42 at 90 minute.

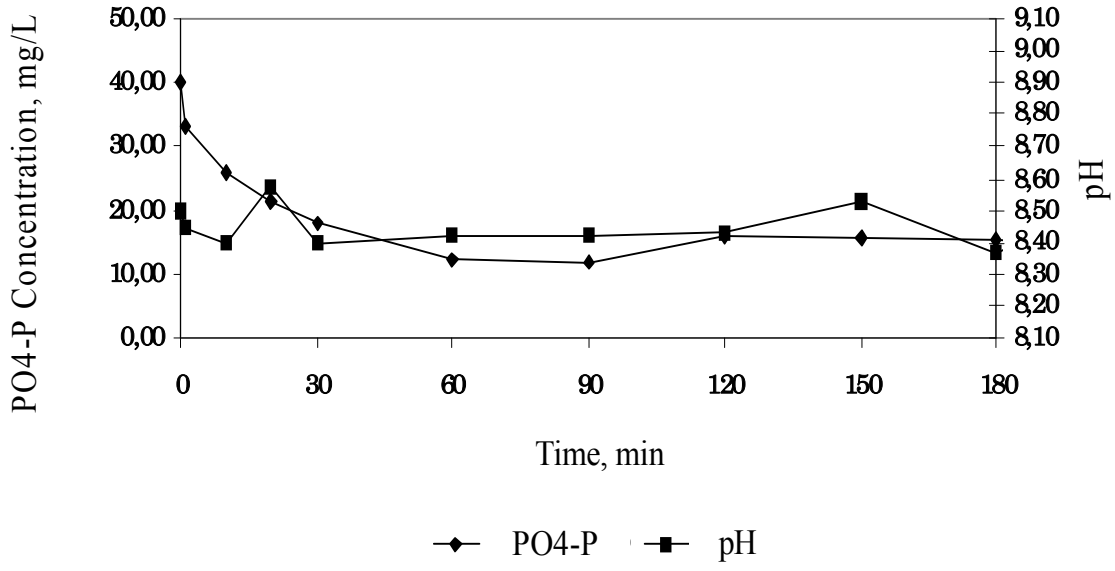


Figure 5.4 Change of phosphate concentration with time at maintaining constant pH 8.5

5.2.3 Determination of Pumice Powder Amount

In the second trial, the effect of pumice powder amount was investigated. Experiments were carried out at time period among 1-180 minutes pH was adjusted to 8.5 and it was used different amount of pumice stone powder (0.3, 1.5, 3.0 g) NMP2 for each trial. Each of 300 ml samples was respectively added to 0.3, 1.5, 3.0 g pumice stone powder to obtain 1000, 5000, 10000 mg pumice powder/L samples. Initial phosphate concentration was 40 mg/L and mixing speed was 140 rev/min. Phosphate concentration change at different pumice stone powder amount is shown in Figure 5.5. Minimum phosphate concentration was obtained 1.5 g pumice powder NMP2 (5000 mg pumice powder/L samples).

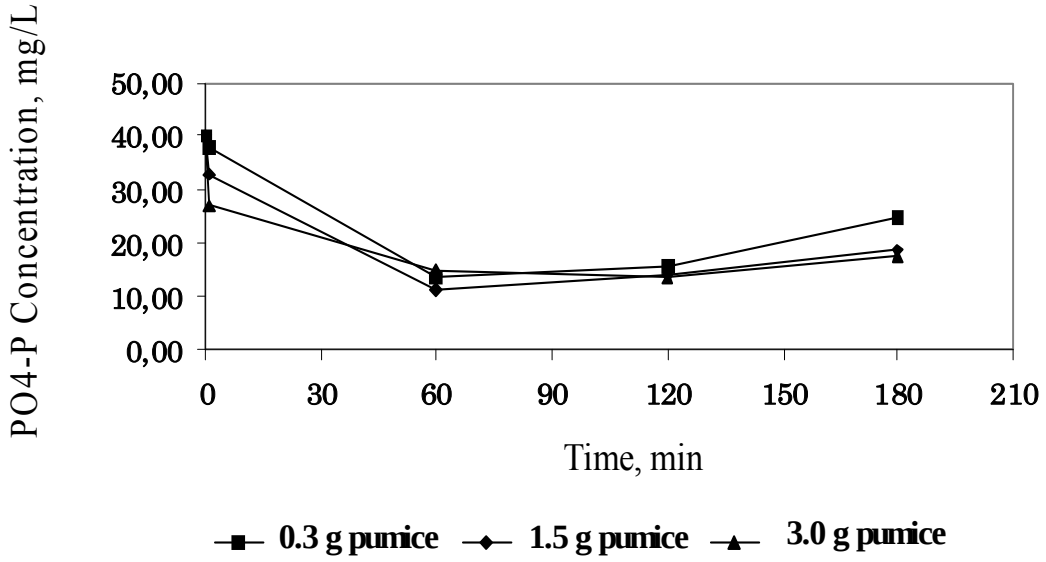


Figure 5.5 Phosphate concentration change at different pumice stone powder amount

5.2.4 Determination of Magnesium Amount

In the third trial, the effect of magnesium amount was investigated. Experiments were carried out at time period among 1-180 minutes. pH was adjusted to 8.5 and it was used pumice stone powder 1.5 gr NMP2 for each trial. 5, 10, 20, 40, 60, 80 ml $MgCl_2$ solution (1000 mg/L) to each of 300 ml samples were added respectively. Initial phosphate concentration was 40 mg/L and mixing speed was 140 rev/min.

Phosphate concentration changes at different magnesium amounts are shown in Figure 5.6. Minimum phosphate concentration in samples was obtained using 40 ml $MgCl_2$ solution (1000 mg/L).

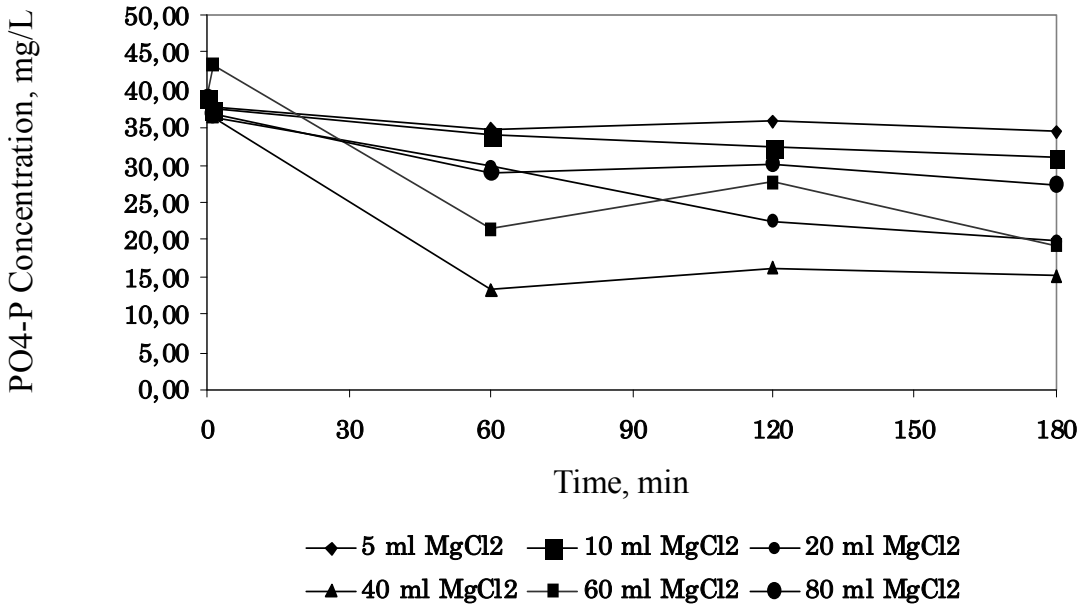


Figure 5.6 Phosphate concentration change at different magnesium amount

5.2.5 Comparison of Different Size Pumice

Experiments were carried out at time period among 1-180 minutes. pH was adjusted to 11 and 1.0 g NMP2 and NMP3 pumice stone powder samples were used . 10 ml $MgCl_2$ solution (1000 mg/L) was added to each of 300 ml samples. Initial phosphate concentration was 39 mg/L and mixing speed is 140 rev/min. NMP3 and NMP2 performances are respectively shown in Figure 5.7. It was obtained a stable phosphorus recovery in using of NMP2, with respect to NMP3 pumice stone powder sample.

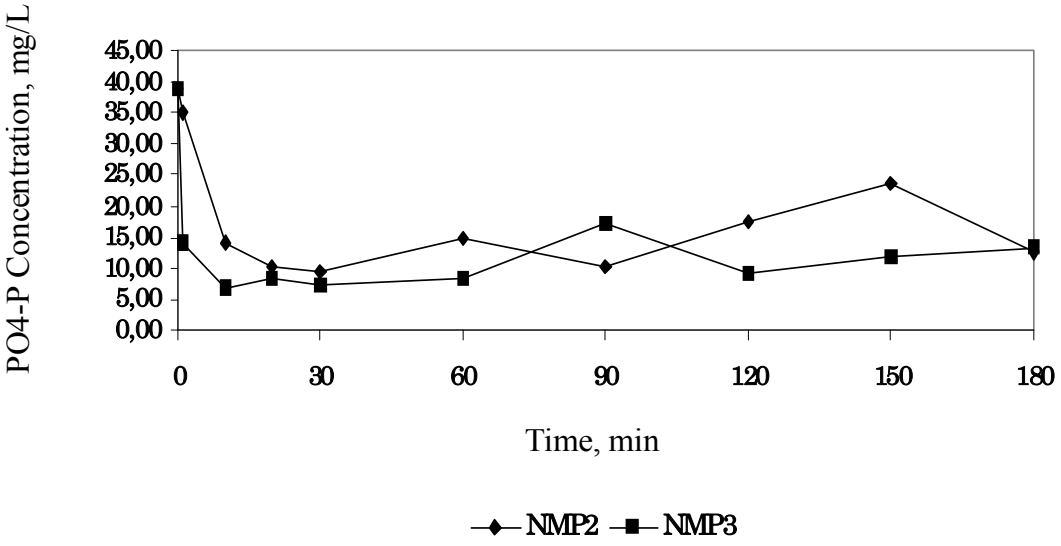


Figure5.7 Effect of NMP3 pumice stone powder sample on phosphate concentration

5.2.5 Zeta Potential

Zeta Potential was measured at prepared sample by using 1.5 gr pumice stone and 40 mg/L $MgCl_2$ for 300 ml sample volume. Struvite crystallization was performed using at different pH values. It was observed that zeta potential has higher value (-24.3 mV) at pH 9 (Figure 5.8).

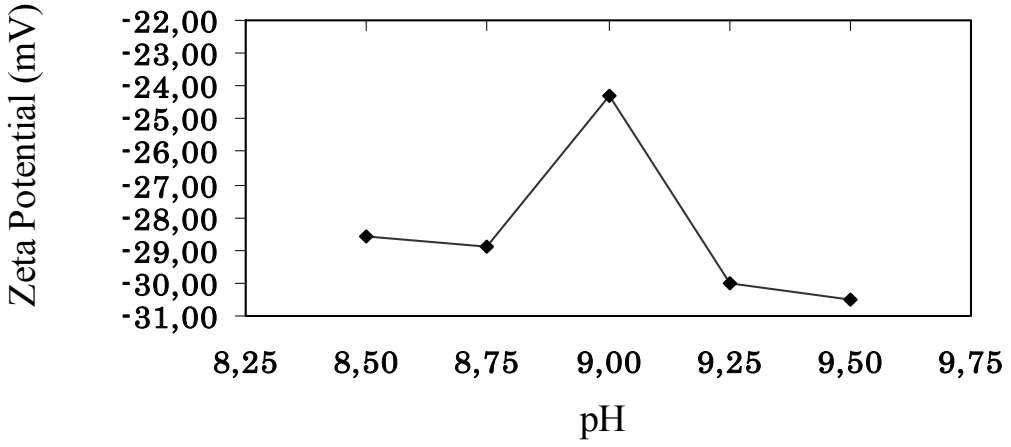


Figure 5.8 Zeta potential of samples

CHAPTER SIX
PHOSPHORUS RELEASE BY USING ACIDS AND A BASE

In this chapter, in order to release the phosphorus fixed in the sewage sludge, various chemicals (sulphuric acid, hydrochloric acid, nitric acid, oxalic acid, and magnesium hydroxide) has been utilized. The effects of parameters which determine the efficiency of mixture temperature, mixing time and concentration on the phosphorus release are investigated. For the analysis of the results, Box-Wilson Experimental Design Method has been used. The analysis results have shown that nitric acid is more efficient as compared to oxalic acid and magnesium hydroxide. In experiments carried out with nitric acid, it has been observed that the increase in nitric acid concentration and mixing time do not significantly affect phosphorus release, while an increase in mixing temperature effects considerably. Experiments conducted using oxalic acid have shown that mixing temperature increases phosphorus release, whereas concentration increase and mixing time have no significant effect. No high phosphorus release value has been obtained with magnesium hydroxide; while mixing temperature has a positive effect on phosphorus release value.

6.1 Comparison of Sulphuric Acid, Nitric Acid and Hydrochloric Acid

6.1.1 Sample Preparation

Sludge samples were taken from three different stages of a municipal wastewater treatment plant. These stages are final sedimentation tank (sludge effluent), thickening, and belt press. It was determined moisture and dry solids content of sludges. The water and dry solids content of the sludges is reported in the Table 6.1.

Table 6.1 Dry solids values and water values of samples

	Dry solids	**Water**
Final Sedimentation Tank (sludge effluent)	**%5.08**	**%94.92**
Thickening	**%5.75**	**%94.25**
Belt Press	**%27.92**	**%72.08**

Heavy metal composition of belt press sludge was determined using extraction ($HClO_4$+HF) procedure given in standard methods (APHA, 2005). 100 ml samples were prepared.

The extractants used are concentrated HCl, HNO_3, H_2SO_4. 10 ml concentrated HCl (%37) HNO_3 (%65), H_2SO_4 (%98) was added to each 100 ml sludge samples (Acid/Sludge: 1/10). Sludges were keeping at room temperature during 12 hours. Samples were withdrawn after times of 1, 3, 6, 12 hours and centrifuged at 5000 rpm during 15 min. Then, the liquid phase was immediately decanted and filtered through 0.45 μm pore size membranes filters. It was adjusted pH values of samples to neutral. The filtrates were analyzed to determine of phosphate concentration.

Different acid concentrations were used for phosphorus extraction at second trial such as 0.1, 1.0, 10.0, 0.5, and 5 M. Acid solutions were prepared at different concentration for each acid. 3.5 ml HCl (4 g) (at different concentrations) were added to 40 ml (~40 gr) dewatering unit sludge samples (Acid/Sludge: 1/10 as weight). Sludges were shaked using rotator at high speed during 3 hours. It were withdrawn from liquid phase of samples times of 1, 2, 3 hours and centrifuged at 5000 rpm during 15 min. Then, the liquid phase was immediately decanted and filtered through 0.45 μm pore size membranes filters (Schleicher and Schuell Membrane Filters 0.45 μm Ø 47 mm). It was adjusted pH values of samples to neutral. The filtrates were analyzed to determine of phosphate concentration.

6.1.2 Results

Sludges coming from belt press unit were exposed to acid solution ($HClO_4$+HF) at high temperature. Prepared solution after extraction process was analyzed by ICP. Phosphate value of sample is 51 mg/L. The results of heavy metals analysis are presented in Figure 6.1.

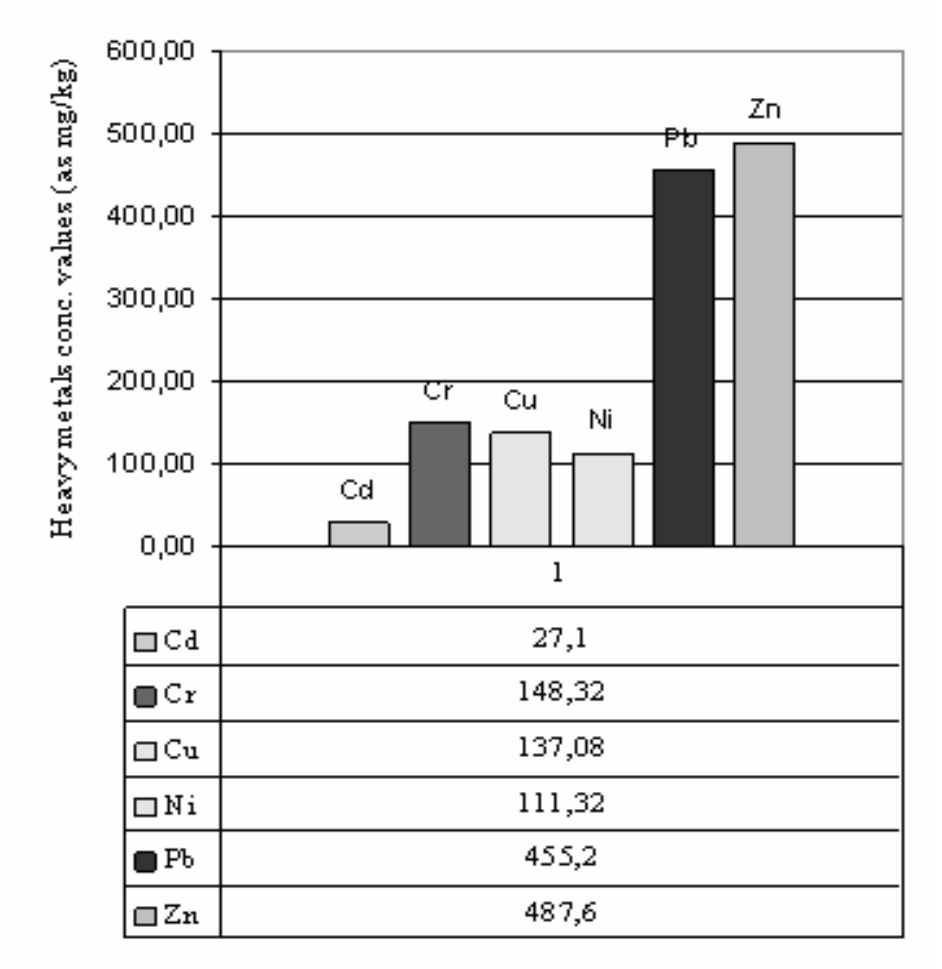


Figure 6.1 Results of heavy metal analysis for belt press sludges (as mg/kg)

The extractions results indicate that belt press sludge have slightly heavy metals concentration. The average percentage quantity of heavy metal in solution increases in the order Cd < Ni < Cu < Cr< Pb < Zn. The concentration of extracted Cd is very low due to concentration of extracted Zn.

Concentrated HCl, HNO_3, H_2SO_4 are used for phosphate release from final sedimantation sludge and dewatering sludge. 10 ml amount from each acid type was added to 100 ml each sludge samples (Acid/Sludge: 1/10). Sludges were keeping at room temperature during 12 hours. The results are presented in Figure 6.2.

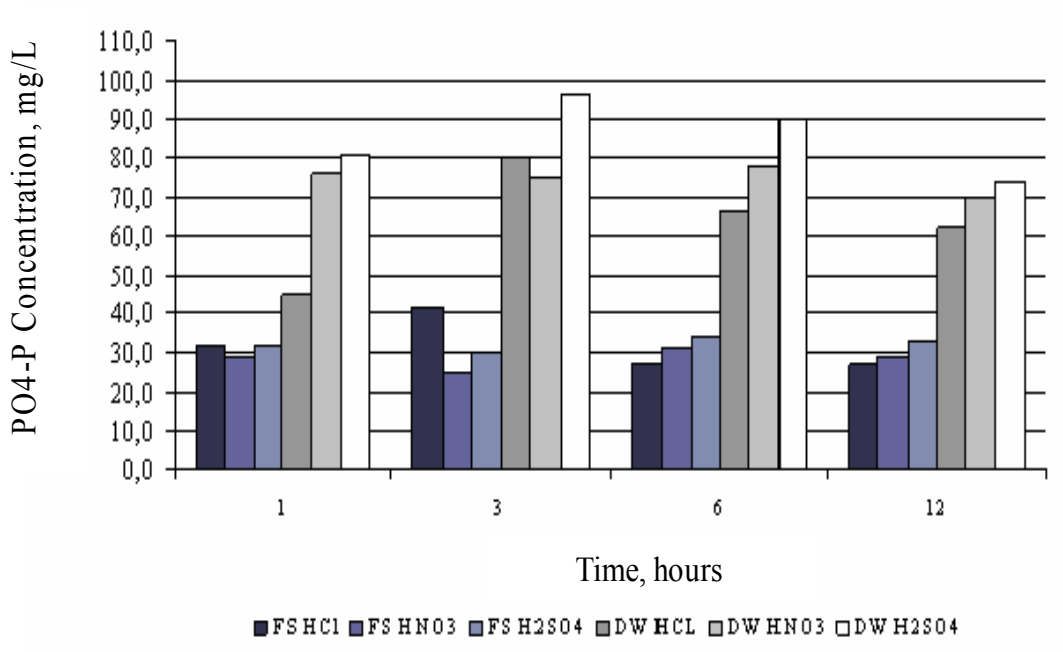


Figure 6.2 Released phosphate concentrations using by concentrated acids
(FS: Final sedimentation sludge, DW: Dewatering sudge)

Phosphate release results indicate that phosphate concentration which has dewatering sludge is high double times due to phosphate concentration which has final sedimentation tank sludge. It is observed maximum phosphate release for every sludge in third hour and that H_2SO_4 is effective than other acids (HCl and NHO_3) in phosphate release from sludge.

Different acid concentrations (0.1, 1.0, 10.0, 0.5, and 5 M) were used for phosphorus extraction of thickening sludge. It were withdrawn from liquid phase of samples times of 1, 2, 3 hours. Released phosphate concentration results with HCl extraction of thickening sludge are shown in Figure 6.3

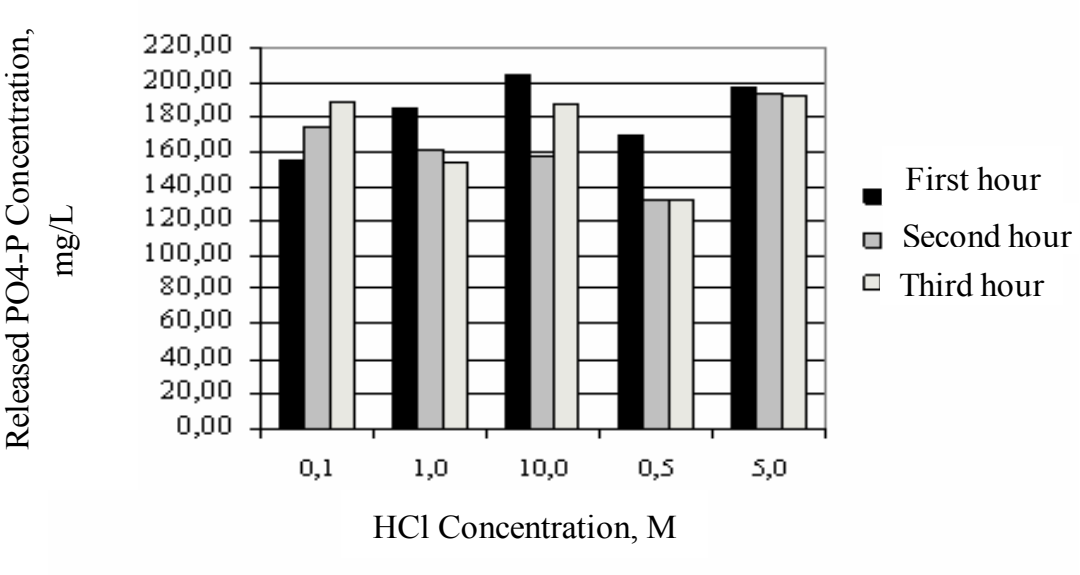


Figure 6.3 Release phosphate concentration results with HCl extraction of thickening sludges

Different acid concentrations were used for phosphorus extraction such as 0.1, 1.0, 10.0, 0.5, and 5 M. It was not observed very different changes at released phosphate concentrations for each acid concentration value. Maximum released phosphate concentration at first hour was achieved using 10 M HCl acid.

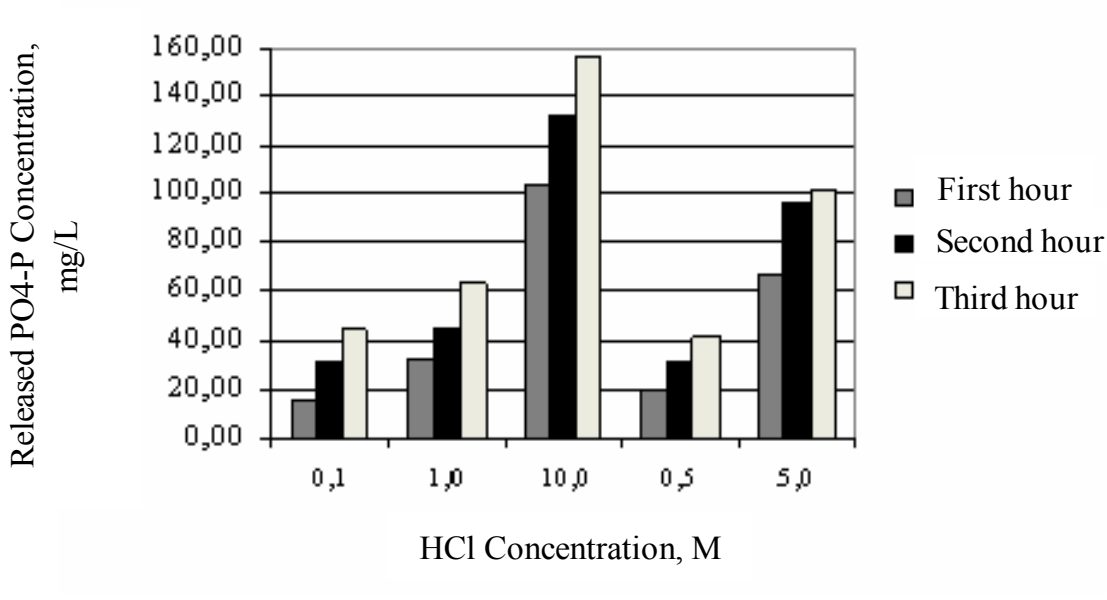


Figure 6.4 Release phosphate concentration results with HCl extraction of belt press sludges

Released phosphate concentrations with HCl extraction of belt press sludges are shown in Figure 6.4. The average percentage quantity of phosphate concentration in solution increase in the order 0.1 M < 0.5 M < 1 M < 5 M< 10 M. Maximum released phosphate concentration was observed at third hour by using 10 M HCl.

6.2 Comparison of Nitric Acid, Oxalic Acid and Magnesium Hydroxide

6.2.1 Sample Preparation

Sludge samples were taken from belt press stages of a municipal wastewater treatment plant. Chemical composition of dried sludge coming from belt press unit was presented in Figure 6.5.

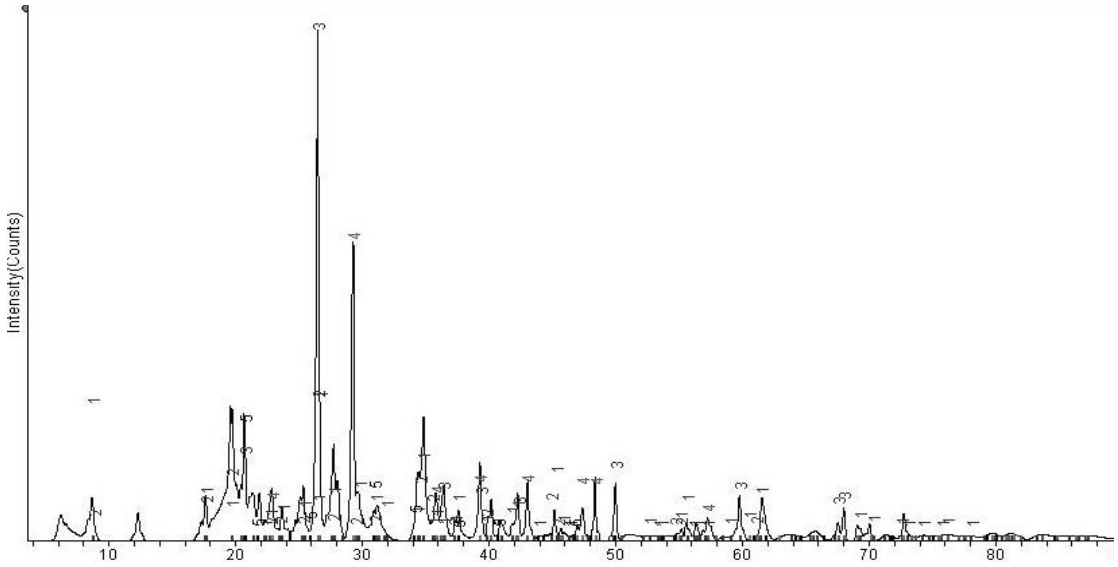


Figure 6.5 Chemical composition of dried sludge

(1) Muscovite-2M1-KAl2(Si3Al)O10(OH,F)2 ,
(2) Potassium Mica KAl3Si3O11,
(3) Quartz SiO2,
(4) Calcite CaCO3
(5) Phosphorus Oxide P2O5

Dried sludge samples were leached with inorganic acid (nitric acid), organic acid (oxalic acid), and base (magnesium hydroxide) by applying different concentrations, various mixture temperatures, and various mixing times which were adjusted to desired levels specified by the Box–Wilson Experimental Design Method. Ratio of dried sludge (g)/ solution volume (ml) was chosen as 1/50. All leaching stages are repeated twice for each experimental step.

6.2.2 Box–Wilson Statistical Experimental Design

Box–Wilson Statistical Experiment Design Method was used to determine the effects of parameters, such as mixture temperature (X_1) solution concentration (X_2) and mixing time (X_3) on phosphorus release from dried sludge. Solution concentration was varied between 0.1- 4 M for nitric acid and 0.1-2 M for oxalic acid and magnesium hydroxide. In addition mixing time was between 15-180 min and mixture temperature was in the range at 20^0C and 100^0C. Temperature control was achieved by using electronic temperature controller at a temperature accuracy of $\pm 2^0$C. Points of independent variables for Box–Wilson statistical design for nitric acid, oxalic acid, and magnesium hydroxide are shown in Table 6.2.

Table 6.2 Points of independents variables for Box-Wilson statistical experiment design

	Temperature (^{0}C)	**Concentration(M)** *for nitric acid*	**Concentration(M)** *for oxalic acid and magnesium hydroxide*	**Time (min)**
A1	100	2.05	1.05	97.5
A2	20	2.05	1.05	97.5
A3	60	4	2	97.5
A4	60	0.1	0.1	97.5
A5	60	2.05	1.05	180
A6	60	2.05	1.05	15
F1	83	3.2	1.6	145
F2	83	3.2	1.6	50
F3	83	0.9	0.5	145
F4	83	0.9	0.5	50
F5	37	3.2	1.6	145
F6	37	0.9	0.5	145
F7	37	3.2	1.6	50
F8	37	0.9	0.5	50
C	60	2.05	1.05	97.5

Axial Points (A1, A2, A3, A4, A5, A6), Factorial Points (F1, F2, F3, F4, F5, F6, F7, F8), Center Point (C)

The experiments consisted of six axial (A), eight factorial (F) and one centre (C) points. The centre point was repeated three times. The amount of phosphorus release was described by the following response function:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \ldots.(4.1)$$

Where; Y is the predicted response function (phosphorus release), b_0 is the constant, 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 . Statistica 5.0 software program was used to determine, the response function coefficients which are presented in Table 6.3.

Table 6.3 Coefficients of the response functions for nitric acid, oxalic acid and magnesium hydroxide

Coefficients of the response functions	**$Y_{P\ Release}$** *Nitric Acid*	**$Y_{P\ Release}$** *Oxalic Acid*	**$Y_{P\ Release}$** *Magnesium Hydroxide*
b_0	-1.723081	7.698404	1.604698
b_1	-0.027996	-0.212260	-0.040161
b_2	2.463290	-4.478831	0.205064
b_3	0.096032	0.014818	0.000502
b_{12}	0.000591	0.037549	-0.005435
b_{13}	-0.000106	0.000589	0.000034
b_{23}	-0.011270	-0.008612	-0.001435
b_{11}	0.001389	0.001602	0.000407
b_{22}	-0.128437	1.755940	0.040166
b_{33}	-0.000237	-0.000188	-0.000002

The response functions with the detected coefficients were used in calculating the predicted phosphorus release values for nitric acid, oxalic acid and magnesium hydroxide. Observed (in experimental studies) and predicted (by calculating in software program) phosphorus release values for nitric acid, oxalic acid and magnesium hydroxide as mgPO_4-P/g Dried Solid are given in Table 6.4.

Table 6.4 Observed and predicted phosphorus release values for nitric acid, oxalic acid and magnesium hydroxide

Nitric Acid		Oxalic Acid		Magnesium Hydroxide	
$Y_{P\ Release}$ (mg PO_4-P/g DS) *Observed*	$Y_{P\ Release}$ (mg PO_4-P/g DS) *Predicted*	$Y_{P\ Release}$ (mg PO_4-P/g DS) *Observed*	$Y_{P\ Release}$ (mg PO_4-P/g DS) *Predicted*	$Y_{P\ Release}$ (mg PO_4-P/g DS) *Observed*	$Y_{P\ Release}$ (mg PO_4-P/g DS) *Predicted*
19.23	17.82	11.03	8.20	1.88	1.56
6.95	7.45	1.65	2.04	1.02	1.06
12.72	11.63	3.95	4.73	0.57	0.53
8.07	8.22	6.80	3.55	1.10	0.87
12.02	10.47	3.10	1.66	0.75	0.71
6.48	7.13	1.90	0.91	0.82	0.59
12.38	14.68	6.32	6.73	0.88	0.90
14.47	14.21	4.38	5.46	0.58	0.83
13.70	13.87	2.52	5.55	1.05	1.30
10.13	10.94	1.42	3.38	0.90	1.09
9.05	8.92	1.08	0.96	0.65	0.67
7.23	8.17	0.92	1.67	0.85	0.80
7.48	7.99	3.45	2.26	0.80	0.75
6.40	4.78	0.65	2.08	0.55	0.74
10.27	10.39	2.56	2.56	0.57	0.66

The predicted values of phosphorus release amount were in accordance with the observed values. It was found that R-squared values are respectively 0.995, 0.853, and 0.790 for nitric acid, oxalic acid, and magnesium hydroxide.

6.2.3 Results

Results were evaluated in terms of the effects of concentration -mixing time, temperature-mixing time, and concentration - temperature on phosphorus release from the sludge.

6.2.3.1 Effects of concentration and mixing time on phosphorus release

Phosphorus release has increased with the increase in nitric acid concentration and mixing time at 60^0C constant temperature (Figure2). However, it has decreased by progressive stages after 120 minute. Best phosphorus release (12 mg P / g DS) was detected at 90 min mixing time and 4 M nitric acid concentration as shown in Figure 6.6.

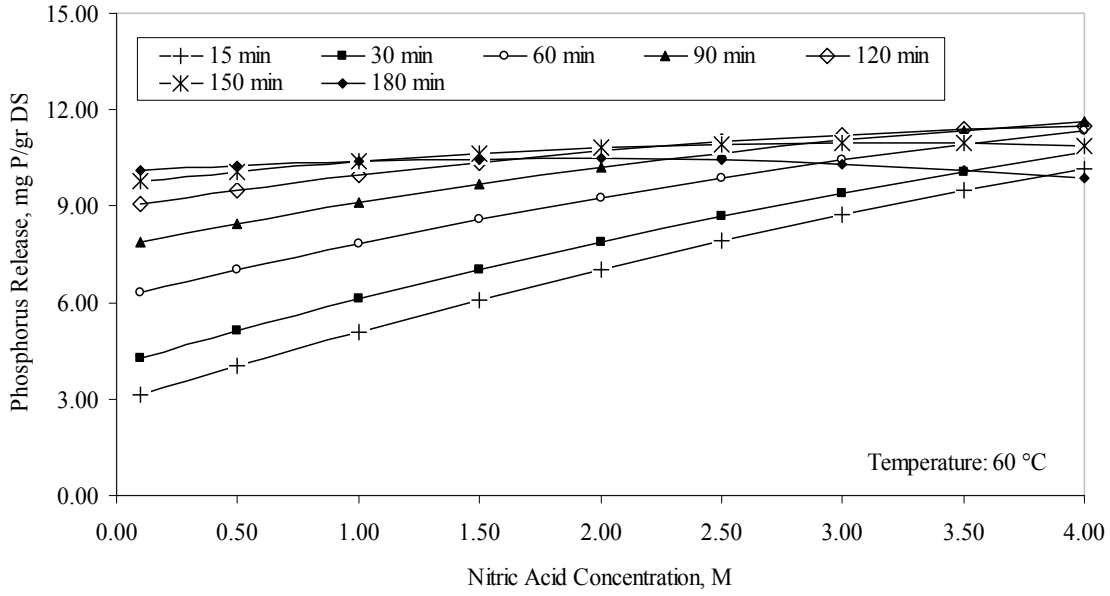


Figure 6.6 Variation of phosphorus release with nitric acid concentration at different mixing times

The variation of phosphorus release with oxalic acid at different mixing time for 60^0C mixing temperature is illustrated in Figure 6.7. No constant relationship was observed between the oxalic acid concentration and mixing time. Phosphorus release is 1-3 mg P/gr DS at low mixing times (up to 60 min). Up to 1 M oxalic acid concentration the phosphorus release shows a decreasing tendency, while after 1 M it has an increasing tendency.

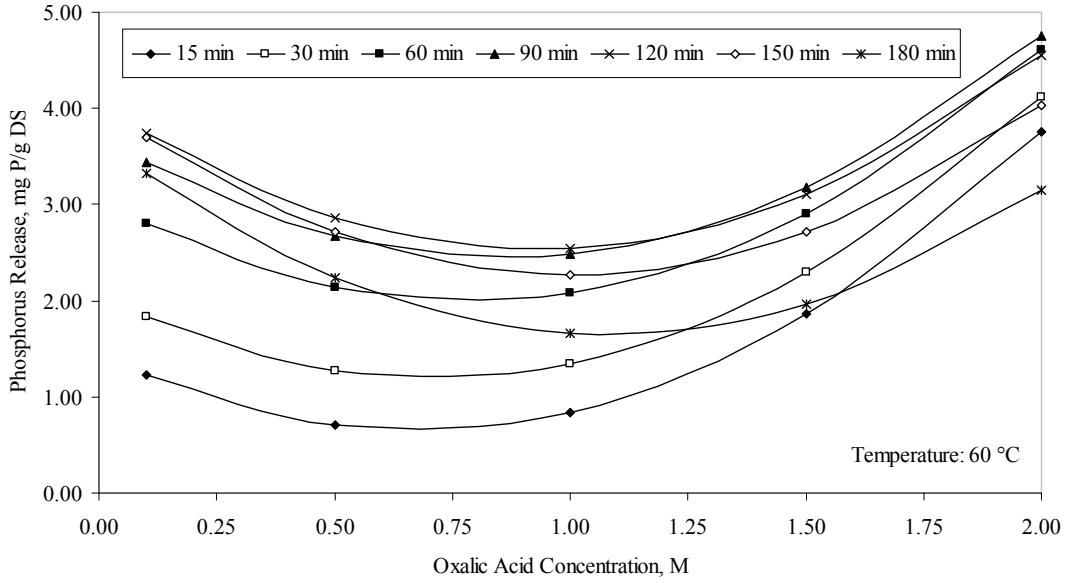


Figure 6.7 Variation of phosphorus release with oxalic acid concentration at different mixing times

Figure 6.8 shows the relationship between the phosphorus release and magnesium hydroxide ($MgOH_2$) concentration at different mixing times. It is found that phosphorus release increased with mixing time when concentration of magnesium hydroxide increases approximately up to 1.6 M. Best phosphorus release (1 mg P/gr DS) was detected at 180 min mixing time and 0.1 M magnesium hydroxide concentration.

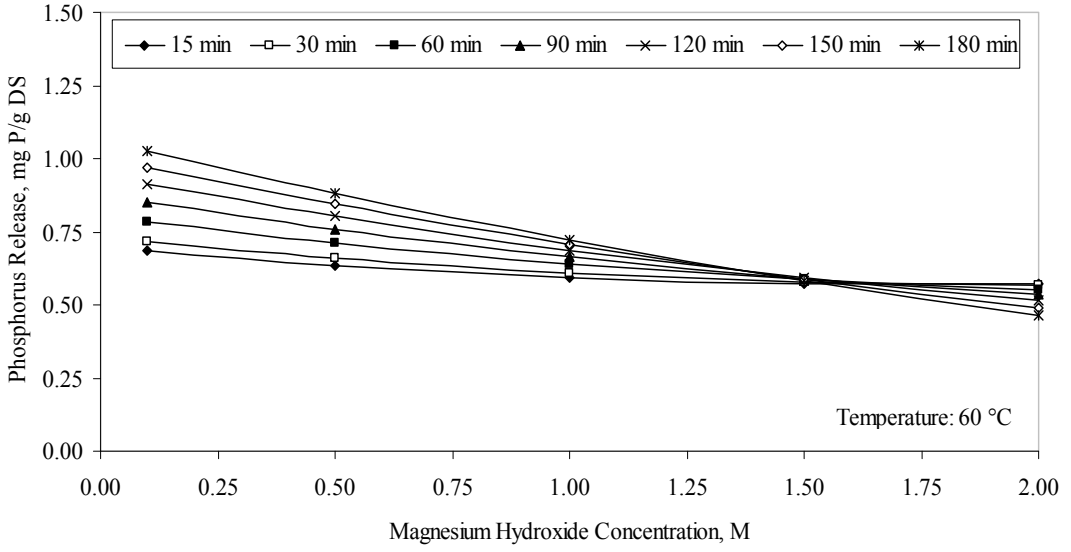


Figure 6.8 Phosphorus release with magnesium hydroxide concentration at different mixing times

6.2.3.2 Effects of temperature and mixing time on phosphorus release

Phosphorus release did not change significantly by the increase of mixing time; however it has increased, when the temperature of mixture was increased. High amount phosphorus release, 18 mg P/g DS, was accomplished at 90 min mixing time and 100^0C mixture temperature (Figure 6.9).

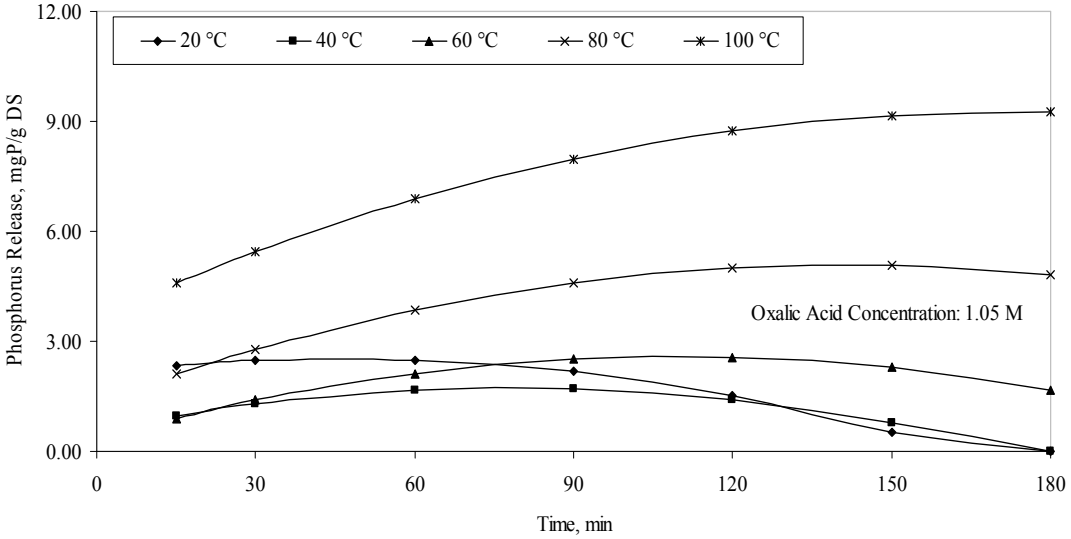


Figure 6.9 Phosphorus release variations for nitric acid with the mixing time at different temperatures

In experiments carried out by using oxalic acid, phosphorus release has increased by increasing of the mixing time and mixture temperature (Figure 6.10).

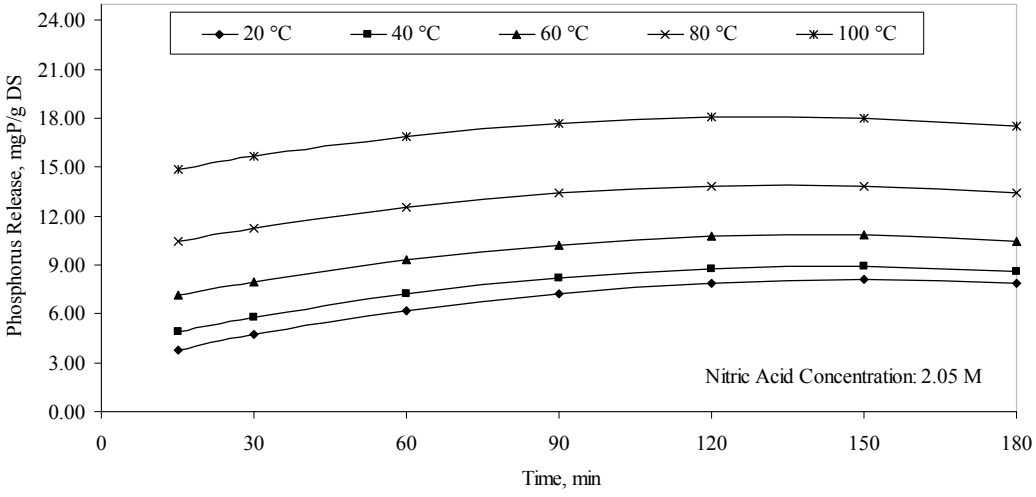


Figure 6.10 Phosphorus release for oxalic acid with the mixing time at different temperatures

As can be seen in Figure 6.11, the phosphorus release was not affected significantly by the increase in temperature of mixture.

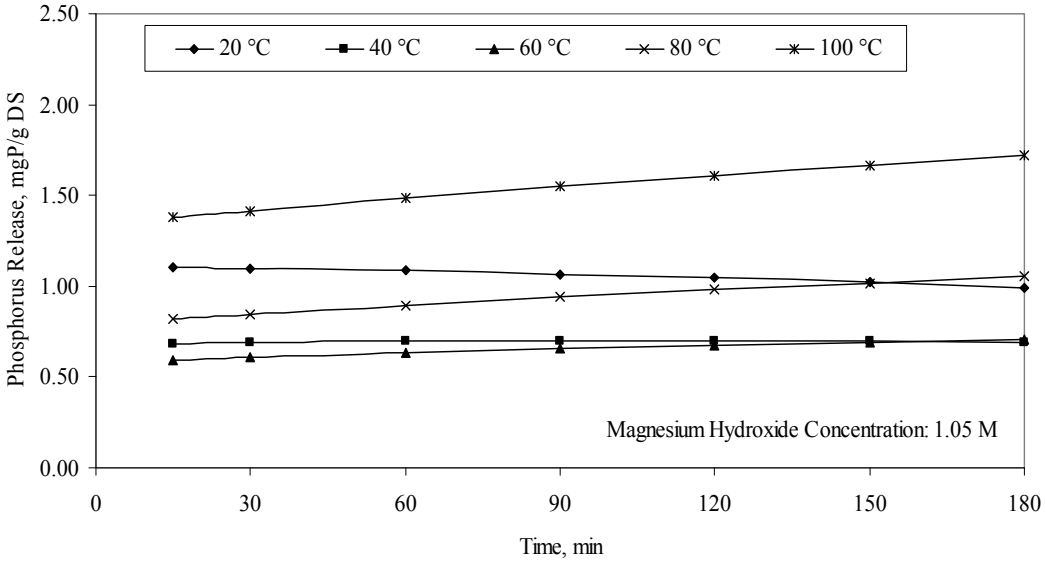


Figure 6.11 Phosphorus release variations for magnesium hydroxide with the mixing time at different temperatures

6.2.3.3 Effects of temperature and acid concentration on phosphorus release

It was determined that the amount of phosphorus release increases with the increase in nitric acid concentration and temperature of mixture at constant mixing time. It can be seen that for each 20^0C temperature increase level the phosphorus release amount has increased progressively. In addition, it has been observed that 4 mg of phosphorus release difference has occurred between approximately 0.1 M and 4 M nitric acid concentration (Figure 6.12).

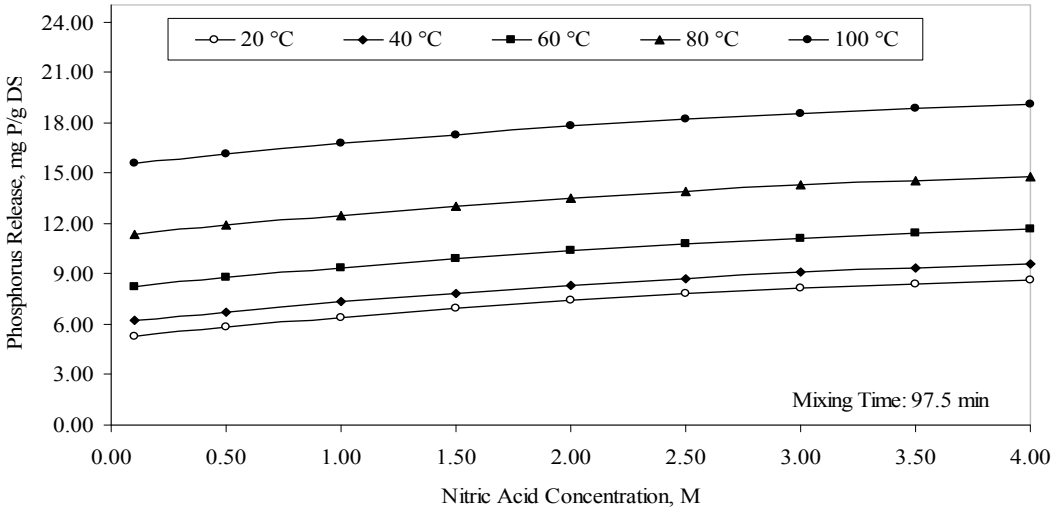


Figure 6.12 Variation of phosphorus release with nitric acid concentrations at different temperatures

In Figure 6.13, it is illustrated that phosphorus release increases with increasing mixture temperature in. However, increase in oxalic acid concentration does not significantly affect phosphorus release. For example, when the phosphorus release value is 7.8 mg P / g DS at 100^0C mixing temperature and 0.1 M concentration, it has increased to 11.8 mg P / g DS at 2 M concentration.

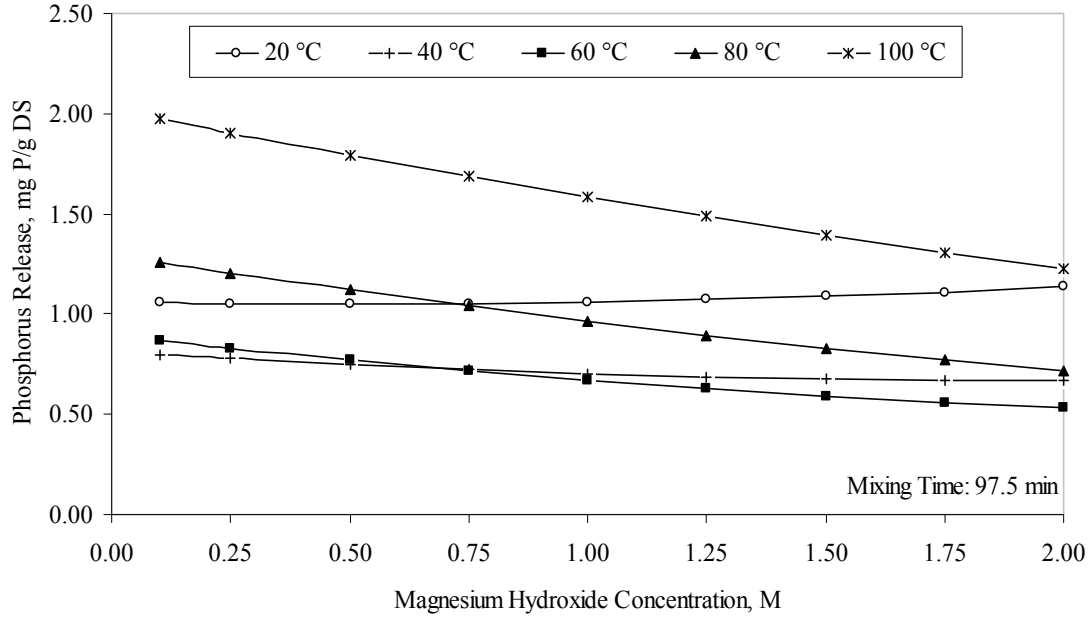


Figure 6.13 Variation of phosphorus release with oxalic acid concentrations at different temperatures

Figure 6.14 shows that phosphorus release doesn't significantly change with base concentration at different mixing times. Further increases in magnesium hydroxide concentration caused very little decreases in phosphorus release amounts. Therefore it has been concluded that in phosphorus release studies carried out with magnesium hydroxide, it is possible to release phosphorus by using high temperature and low concentration values.

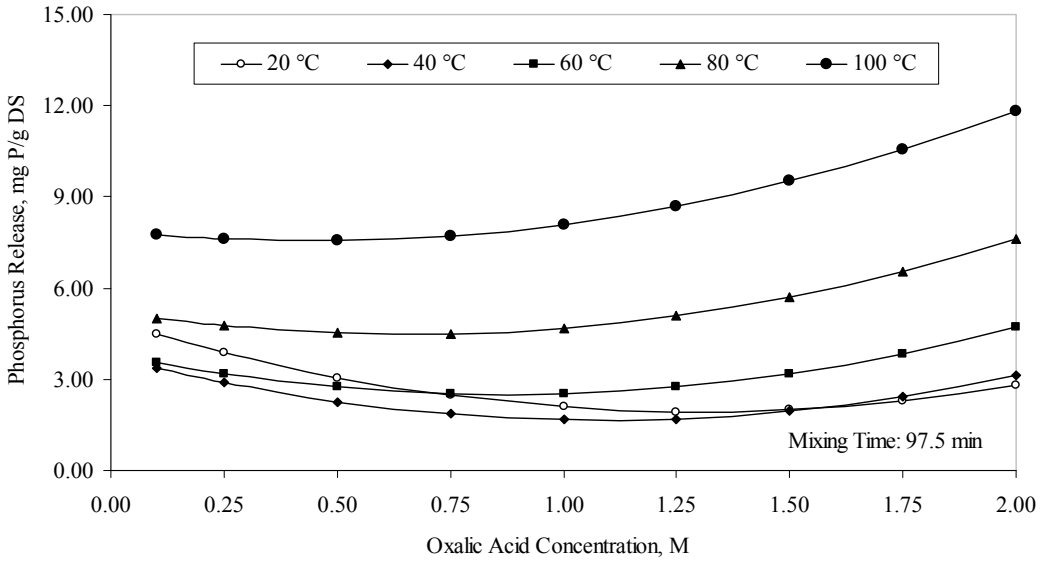


Figure 6.14 Variation of phosphorus release with magnesium hydroxide concentrations at different temperatures

CHAPTER SEVEN
PHOSPHORUS RELEASE BY USING BASE

In this chapter, it was investigated the phosphorus release with NaOH (Sodium Hydroxide) and KOH (Potassium Hydroxide) and factors which affected to like temperature, base concentration and mixing time. Box-Benhken Experimental Design Method was used to determine the effects of these factors.

7.1 Experiment Design

Box-Benhken Experimental Design was used to determine effects of base concentration, mixing time and mixture temperature on phosphorus release with various bases. It was given coded and actual values of independent variables; base concentration (X1), mixing time (X2), mixture temperature (X3) used for experimental design in Table 7.1.

Table 7.1 Coded and actual values of independent variables (X1, X2, and X3)

Independent Variables	**Coded Symbols**	**Levels**		
		-1	**0**	**1**
Base Concentration (M)	X1	0.1	0.55	1
Mixing Time (min)	X2	10	65	120
Mixture Temperature (^{0}C)	X3	10	55	100

Response functions defining variations of dependent variables with the independent variables can be described as Equation (7.1)

$$Y = B_0 + \sum_{i=1}^{k} B_i X_j + \sum_{i=1}^{k} B_{ii} X^2 + \sum_{i\rangle 1}^{k} B_{ij} X_i X_j \quad \text{.....(7.1)}$$

Where, Y is predicted response, B_0 is a constant; B_i and B_{ij} are cross product and quadratic coefficient respectively (i, j =1, 2, 3). The design matrix composes 17 runs including five replicates of the center point (level 0).

7.2 Results

The response function coefficients were determined by using the experimental data the Stat-Ease Design Expert 7.1.3 (Trial version) software program (Table 7.2).

Table 7.2 Coefficients of the response functions for phosphorus release with NaOH and KOH

	Phosphorus release with NaOH R-Squared = 0.9221	Phosphorus release with KOH R-Squared= 0.9298
BO	-2.36511	-0.58611
B1	-0.97699	0.009079
B2	0.20051	0.15434
B3	-0.00159091	-0.017684
B12	-0.04798	0.025253
B13	-0.040123	-0.030864
B23	0.00007575	0.000101
B11	10.40123	3.45185
B22	-0.001039	0.0009259
B33	0.000978	0.0009624

The predicted values determined by using the estimated coefficients are compared with the observed results in Table 7.3. Predicted values of dependent variables were in good agreement with the observed values.

Table 7.3 Predicted and observed phosphorus release values of dependent variables

Observed values of dependent variables		**Predicted values of dependent variables**	
Phosphorus release (NaOH)	Phosphorus release (KOH)	Phosphorus release (NaOH)	Phosphorus release (KOH)
10.75	9.25	12.31	10.31
9.25	9.87	9.10	8.85
7	8.75	6.12	7.19
12.25	11.5	11.56	12.00
12.25	13.75	14.50	14.69
9.5	9.89	9.10	8.85
8	9	9.10	8.85
1.5	3.25	2.19	2.75
10	7.25	9.31	7.37
8.5	6.75	9.37	8.31
9	8	9.10	8.85
4	2.75	1.75	1.81
9.75	7.5	9.10	8.85
8.5	5	9.19	4.88
17.25	15	15.69	13.94
20.25	17.5	18.69	16.06
4.5	4.25	6.06	5.69

P- Value<0.05 or 0.01 was evaluated as significant. The ANOVA regression analysis of phosphorus release indicated that the suggested quadratic model was adequate lowest standard deviation, the highest R-Squared and the lowest press value (Table 7.4).

Table 7.4 ANOVA regression analysis for phosphorus release using NaOH and KOH*

Phosphorus release with NaOH

Source	**Sum of squares**	**df**	**Mean Square**	**F value**	**p-value Prob>F**	
Means vs Total	1548.53	1	1548.53	8.76	0.0019	*Suggested*
Linear vs Mean	215.91	3	71.97	0.29	0.8348	
2FI vs Linear	8.42	3	2.81	6.79	0.0176	*Suggested*
Quadratic vs 2FI	73.19	3	24.40	17.03	0.0096	*Aliased*
Cubic vs Quadratic	23.31	3	7.77			
Residual	1.82	4	0.46			
Total	1871.19	17	110.07			
Lack of Fit Tests						
Linear	104.92	9	11.96	25.55	0.0035	*Suggested*
2FI	96.50	6	16.08	35.25	0.002	
Quadratic	23.31	3	7.77	17.03	0.0096	*Suggested*
Cubic	0.000	0				*Aliased*
Pure Error	1.83	4	0.46			
Model Summary Statistics	**Std. Dev.**	**R-Squared**	**Adj. R-Squared**		**PRESS**	
Linear	2.87	0.6692	0.5928		220.74	*Suggested*
2FI	3.14	0.6953	0.5124		493.91	
Quadratic	1.90	0.9221	0.8219		375.85	*Suggested*
Cubic	*0.68*	*0.9943*	*0.9774*		+	*Aliased*

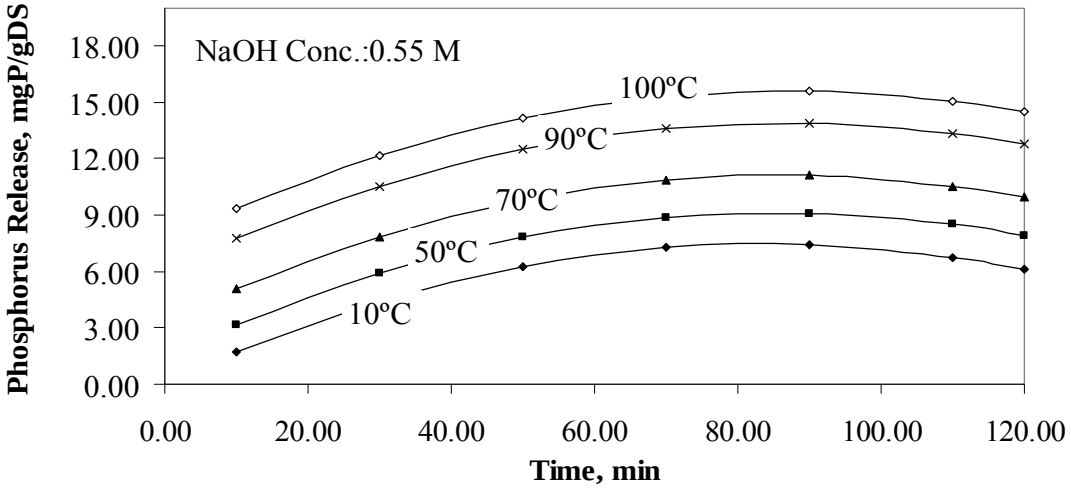
Phosphorus release with KOH

Source	**Sum of squares**	**df**	**Mean Square**	**F value**	**p-value Prob>F**	
Means vs Total	1310.5	1	1310.5	11.72	0.0005	*Suggested*
Linear vs Mean	189.81	3	63.27	0.17	0.9152	
2FI vs Linear	3.38	3	1.13	6.20	0.0220	*Suggested*
Quadratic vs 2FI	48.54	3	16.18	3.86	0.1126	
Cubic vs Quadratic	13.56	3	4.52			
Residual	4.69	4	1.17			
Total	1510.48	17	92.38			
Lack of Fit Tests						
Linear	65.47	9	7.27	6.21	0.0472	*Suggested*
2FI	62.10	6	10.35	8.83	0.0269	
Quadratic	13.56	3	4.52	3.86	0.1126	*Suggested*
Cubic	0.000	0				
Pure Error	4.69	4	1.17			
Model Summary Statistics	**Std. Dev.**	**R-Squared**	**Adj. R-Squared**		**PRESS**	
Linear	2.32	0.7301	0.6678		142.32	*Suggested*
2FI	2.58	0.7431	0.5890		324.24	
Quadratic	1.61	0.9298	0.8395		224.33	*Suggested*
Cubic	*1.08*	*0.9820*	*0.9278*		+	

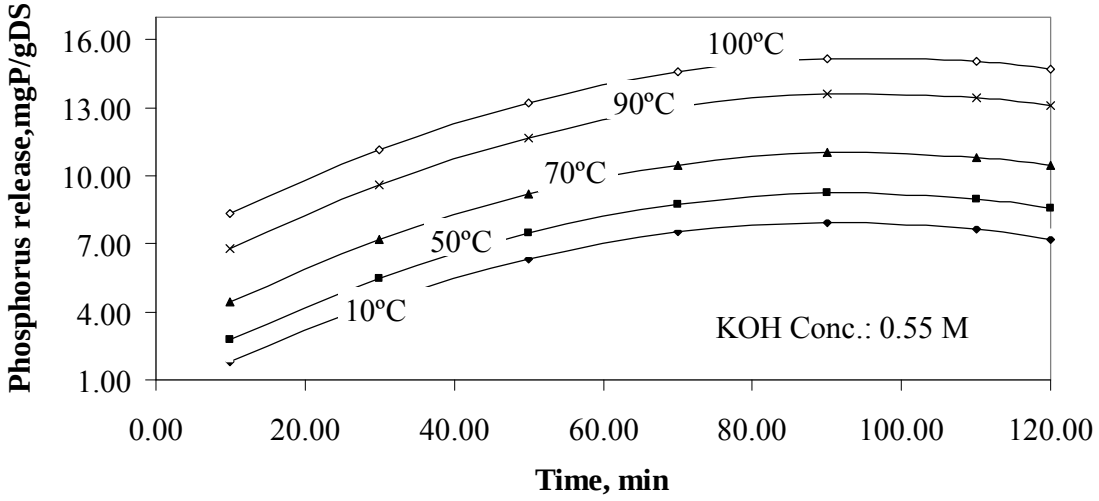
(*) ANOVA Outputs are given in Appendix 1

7.2.1 Effects of temperature and mixing time on phosphorus release at constant base concentration

It was observed that NaOH has efficiency than KOH on phosphorus release at constant base concentration (0.55 M). In experiments carried out by using KOH and NaOH, phosphorus release has increased by increasing of the mixing time and mixture temperature (Figure 7.1).



(a)

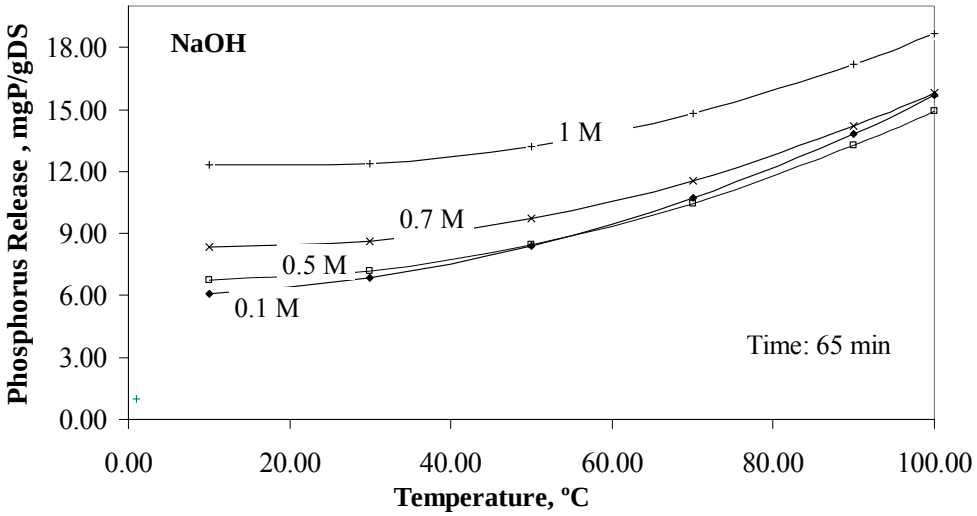


(b)

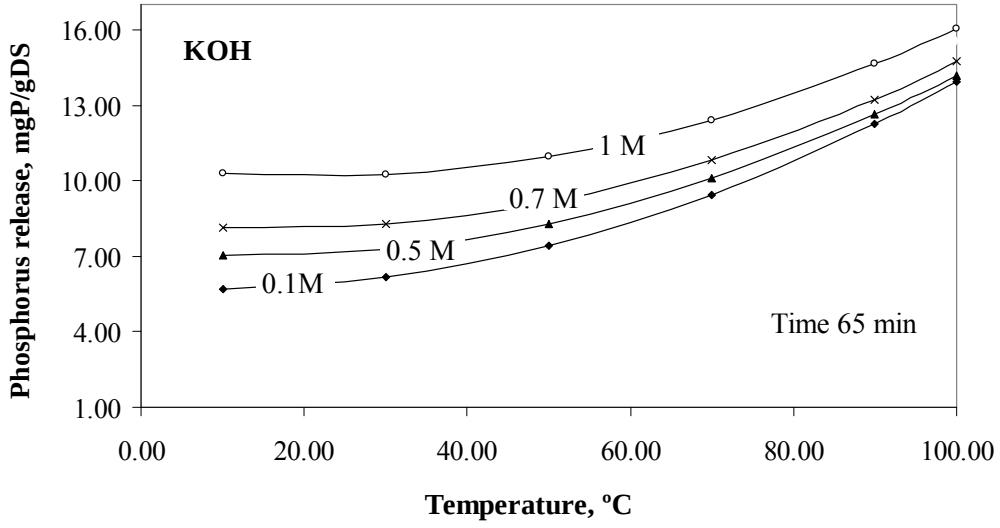
Figure 7.1Phosphorus release for NaOH (a) and KOH (b) with the mixing time at different temperatures

7.2.2 Effects of temperature and base concentration on phosphorus release

It was determined that the amount of phosphorus release increases with the increase in NaOH concentration and temperature of mixture at constant mixing time (Figure 7.2a). In Figure 7.2b, it is illustrated that phosphorus release increases with increasing mixture temperature. However, increase in KOH concentration significantly affects phosphorus release.



(a)

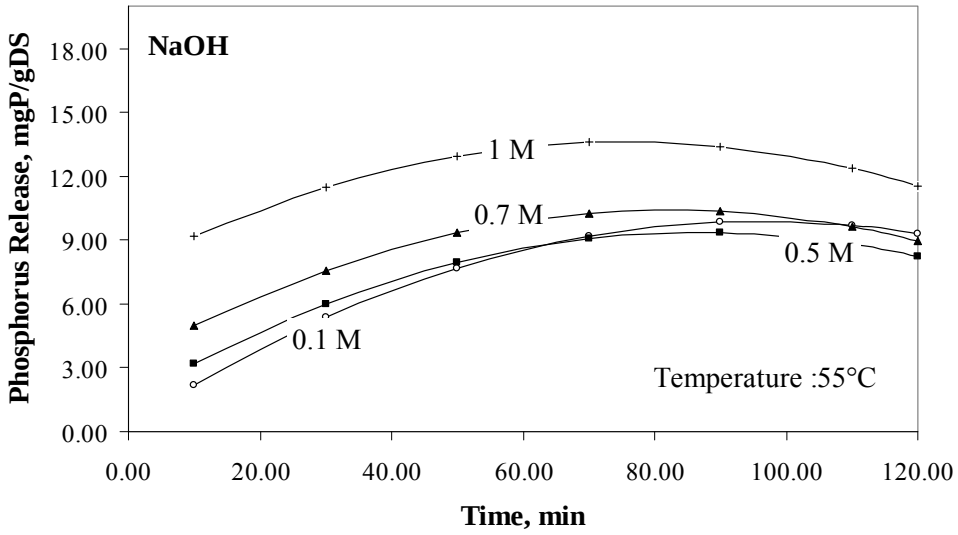


(b)

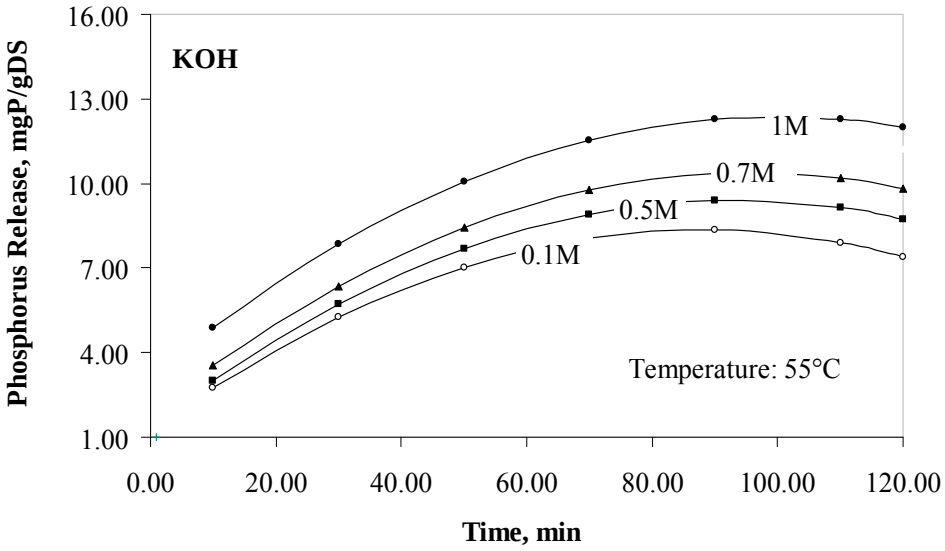
Figure 7.2 Phosphorus release with NaOH(a) and KOH(b)concentrations at different temperatures

7.2.3 Effects of base concentration and mixing time on phosphorus release

Phosphorus release has increased with the increase in NaOH concentration and mixing time at 55^0C constant temperature. Best phosphorus release (12 mgP /gDS) was detected at 60 min mixing time and 1 M NaOH as shown in Figure 7.3a. It was showed the relationship between the phosphorus release and KOH concentration at different mixing times in Figure 7.3bb. Best phosphorus release (12 mg P/gr DS) was detected at 60 min mixing time and 1 M KOH concentration.



(a)



(b)

Figure 7.3 Phosphorus release with NaOH (a) and KOH (b) concentration at different mixing times

CHAPTER EIGHT
STRUVITE CRYSTALLISATION IN MODEL REACTOR

In this chapter, it was investigated the using of pumice stone as a seed material and factors which affected to precipitation at recovery of phosphorus as struvite in model reactor. Struvite is formed as phosphorus, ammonium and magnesium elements. Box-Benhken Experimental Design was used to determine effects of pH, pumice amount and temperature on PO_4-P, NH_4-N, and Mg removals in the model reactor. The Model reactor which was given in detailed Chapter Four was used in experimental studies. It has been used ammonium-phosphate solution and magnesium solution for precipitation.

8.1 Method

The model reactor is used as batch system. Feeding solution was added 8.13 L/h with flow rate, and $MgCl_2$ solution was added 5.22 L/h with flow rate. It was feed both feeding solution and pumice stone which has 150-200 μm size at the same time to reactor. The molar ratio of Mg: PO_4^{-3}: NH_4^{+} was adjusted as 1.5:1:1.

8.2 Experiment Design

Box-Benhken Experimental Design (Box and Behnken, 1960) based on Response Surface Method was used to determine effects of pH, pumice amount and temperature on PO_4-P, NH_4-N, Mg removals in the model reactor. It was given coded and actual values of independent variables; pH (X1), pumice amount (X2), temperature (X3) used for experimental design in Table 8.1. Ranges of pumice amount were chosen according to previously done laboratory studies (Pakdil and Filibeli, 2005).

Table 8.1 Coded and actual values of independent variables

Independent Variables	**Coded Symbols**	**Levels**		
		-1	**0**	**1**
pH (pH)	X1	7	9	11
Pumice Amount (g)	X2	1	10.5	20
Temperature (^{0}C)	X3	10	22.5	35

Response functions defining variations of dependent variables with the independent variables can be described as Equation 7.1

$$Y = B_0 + \sum_{i=1}^{k} B_i X_j + \sum_{i=1}^{k} B_{ii} X^2 + \sum_{i\rangle 1}^{k} B_{ij} X_i X_j \quad \text{.....(7.1)}$$

8. 3 Results

The response function coefficients were determined by using the experimental data the Stat-Ease Design Expert 7.1.3 (Trial version) software program (Table 8.2).

Table 8.2 Coefficients of the response functions for PO_4-P, NH_4-N, and Mg removals

	PO_4-P R-Squared = 0.9684	NH_4-N R-Squared= 0.9723	Mg R-Squared= 0.9668
BO	-947.52807	-459.36523	-219.00218
B1	172.67030	91.58039	40.15376
B2	9.57794	2.19009	-6.47311
B3	15.00791	5.54113	5.11228
B12	-0.33605	-0.33289	0.57974
B13	-0.94590	-0.16050	0.54890
B23	-0.00273684	0.064547	0.024758
B11	-7.80456	-4.9781	-2.60219
B22	-0.31929	-0.021205	0.025526
B33	-0.11221	-0.092264	-0.16127

The predicted values determined by using the estimated coefficients are compared with the observed results in Table 8.3. Predicted values of dependent variables were in good agreement with the observed values.

Table 8.3 Predicted and observed values of dependent variables

Observed values of dependent variables			**Predicted values of dependent variables**		
PO_4-P removal (%)	NH_4-N removal (%)	Mg removal (%)	PO_4-P removal (%)	NH_4-N removal (%)	Mg removal (%)
0	0	0	2,13	0,92	0,63
68,57	12,17	7,61	73,04	10,62	10,17
65,63	45,81	88,31	75	48	98,33
96,62	44,78	71,62	97	44,5	71,62
96,62	44,78	71,62	96,6	44,6	72
70,33	26,66	85,52	75,8	27,62	90,65
74,47	19,80	36,98	70	21,35	34,41
26,20	28,74	27,45	21,3	25	20
17,48	12,27	52,57	16,48	9,76	50
42,93	24,03	96,49	43,93	26,54	99,06
34,27	26,42	15,02	24,9	24,23	5
96,62	44,78	71,62	96,7	45	71,48
30,87	14,91	6,05	25,4	13,95	0,92
96,62	44,78	71,62	96,82	45,4	71,5
59,69	19,71	100	46,32	15	98,84
59,75	32,86	77,55	64,65	36,6	85
96,62	44,78	71,62	96	44,4	71,5

P- Value<0.05 or 0.01 was evaluated as significant. The ANOVA regression analysis of PO4-P, NH_4-N and Mg removal indicated that the suggested quadratic model was adequate lowest standard deviation, the highest R-Squared and the lowest press value (Table 8.4).

Table 8.4 ANOVA regression analysis for PO_4-P, NH_4-N and Mg removal efficiency*

* PO_4-P removal efficiency

Source	**Sum of squares**	**df**	**Mean Square**	**F value**	**p-value Prob>F**	
PO_4-P						
Means vs Total	61448.65	1	61448.65	1.45	0.274	
Linear vs Mean	4282.28	3	1427.43	0.77	0.5372	
2FI vs Linear	2400.31	3	800.10	42.57	<0.0001	*Suggested*
Quadratic vs 2FI	9865.05	3	3288.35	1251.43	<0.0001	
Cubic vs Quadratic	540.17	3	180.06			
Residual	0.58	4	0.14			
Total	78537.04	17				
Lack of Fit Tests						
Linear	12805.53	9	1422.84	9889.05	<0.0001	
2FI	10405.22	6	1734.20	12053.12	<0.0001	
Quadratic	540.17	3	180.06	1251.43	<0.0001	*Suggested*
Cubic	0.0000	0				
Pure Error	0.58	4	0.14			
Model Summary Statistics	**Std. Dev.**	**R-Squared**	**Adj. R-Squared**		**PRESS**	
Linear	31.39	0.2506	0.0777		20381.34	
2FI	32.26	0.3911	0.0257		26752.99	
Quadratic	8.79	0.9684	0.9277		8643.55	*Suggested*
Cubic	*0.38*	*1.0000*			+	

* NH_4-N removal efficiency

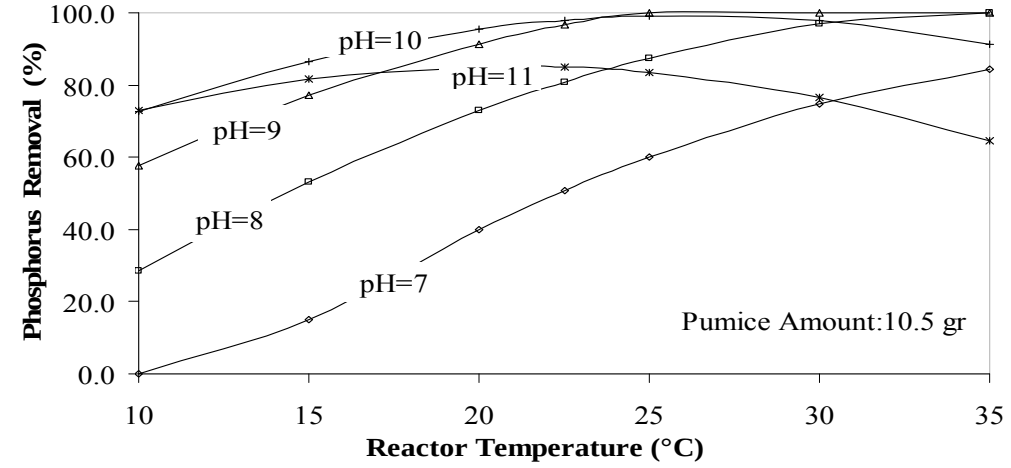
Source	**Sum of squares**	**df**	**Mean Square**	**F value**	**p-value Prob>F**	
NH_4-N						
Means vs Total	13750.74	1	13750.74			
Linear vs Mean	639.42	3	213.14	0.91	0.4628	
2FI vs Linear	459.43	3	153.14	0.59	0.6339	
Quadratic vs 2FI	2482.58	3	827.53	56.81	<0.0001	*Suggested*
Cubic vs Quadratic	101.28	3	33.76	196.28	<0.0001	
Residual	0.69	4	0.17			
Total	17434.13	17	1025.54			
Lack of Fit Tests						
Linear	3043.29	9	338.14	1965.95	<0.0001	
2FI	2583.86	6	430.64	2503.74	<0.0001	
Quadratic	101.28	3	33.76	196.28	<0.0001	*Suggested*
Cubic	0.000	0				
Pure Error	0.69	4	0.17			
Model Summary Statistics	**Std. Dev.**	**R-Squared**	**Adjusted R-Squared**	**Predicted R-Squared**	**PRESS**	
Linear	15.30	0.1736	-0.0171	-0.3802	5083.86	
2FI	16.08	0.2983	-0.1227	-1.1515	7924.68	
Quadratic	3.82	0.9723	0.9367	0.5598	1621.52	*Suggested*
Cubic	*0.41*	*0.9998*	*0.9993*		+	

Table 8.4 (continued)
* Mg removal efficiency

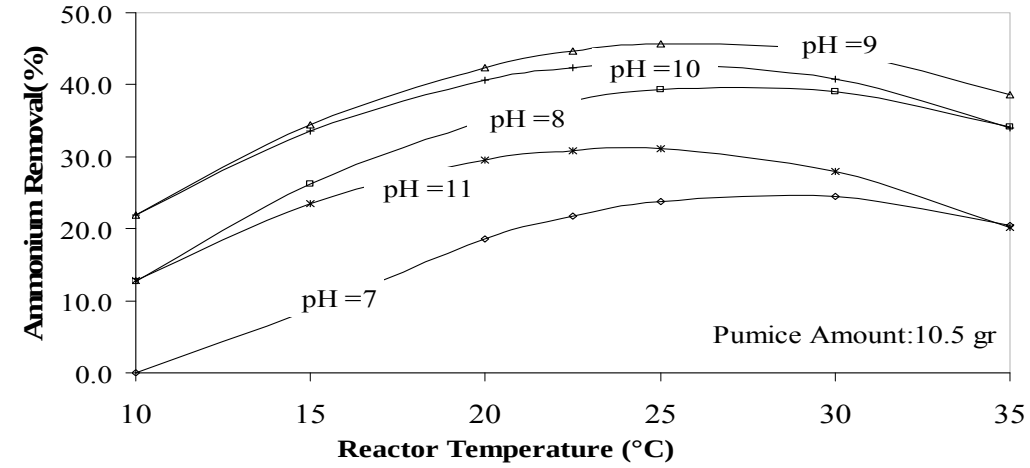
Source	**Sum of squares**	**df**	**Mean Square**	**F value**	**p-value Prob>F**	
Mg						
Means vs Total	53212.37	1	53212.37			*Suggested*
Linear vs Mean	16105.49	3	5368.50	0.0003		
2FI vs Linear	1273.12	3	424.37	0.4048		
Quadratic vs 2FI	3255.48	3	1085.16	0.0052		*Suggested*
Cubic vs Quadratic	707.82	3	235.94		<0.0001	
Residual	0.19	4	0.048	12071.06	<0.0001	*Suggested*
Total	74554.48	17	4385.56	13704.37	<0.0001	
Lack of Fit Tests				4895.05	<0.0001	*Suggested*
Linear	5236.43	9	581.83			
2FI	3963.3	6	660.55			
Quadratic	707.82	3	235.94			
Cubic	0	0				
Pure Error	0.19	4	0.048			
Model Summary Statistics	**Std. Dev.**	**R-Squared**	**Adjusted R-Squared**	**Predicted R-Squared**	**PRESS**	
Linear	20.07	0.7546	0.6980	0.5419	9777.06	*Suggested*
2FI	19.91	0.8143	0,7029	0.2766	15439.44	
Quadratic	10.06	0.9668	0.9242	0.4693	11325.48	*Suggested*
Cubic	*0.22*	*1.0000*	*1.0000*		+	

*ANOVA Outputs are given in Appendix 1.

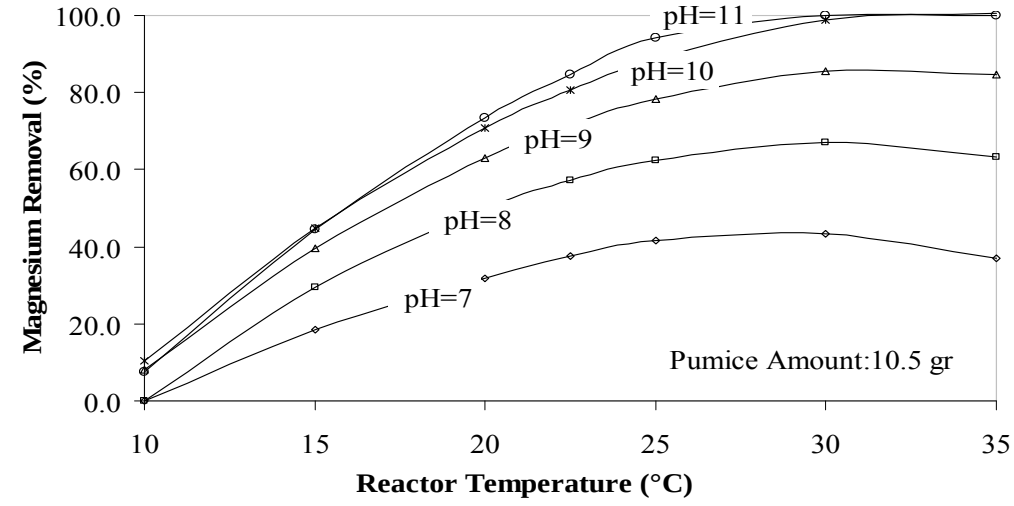
It was illustrated variation of phosphorus, ammonium, and magnesium removal with pH at different reactor temperature values at 10.5 g constant pumice amount in Figure 8.1. It was observed that temperature, pH and pumice amount have positively effect on phosphorus removal. pH value as significant model term was determined. Best phosphorus removal was detected at pH 9 and 10 values. It was obtained that phosphorus removal is increased with increasing temperature in model reactor and reached to 100% at 22.5 ^{0}C, pH 9-10 (Figure 8.1a). Variation of temperature and pH has significantly been affected ammonium removal like phosphorus removal at pumice amount 10.5 g (Figure 8.1b). It was obtained that ammonium removal is increased with increasing temperature in model reactor. While maximum ammonium removal was detected at pH 9, minimum ammonium removal was determined at pH 7. Temperature and pH is very effective, but pumice amount has negatively effect on magnesium removal (Figure 8.1c).



(a)



(b)

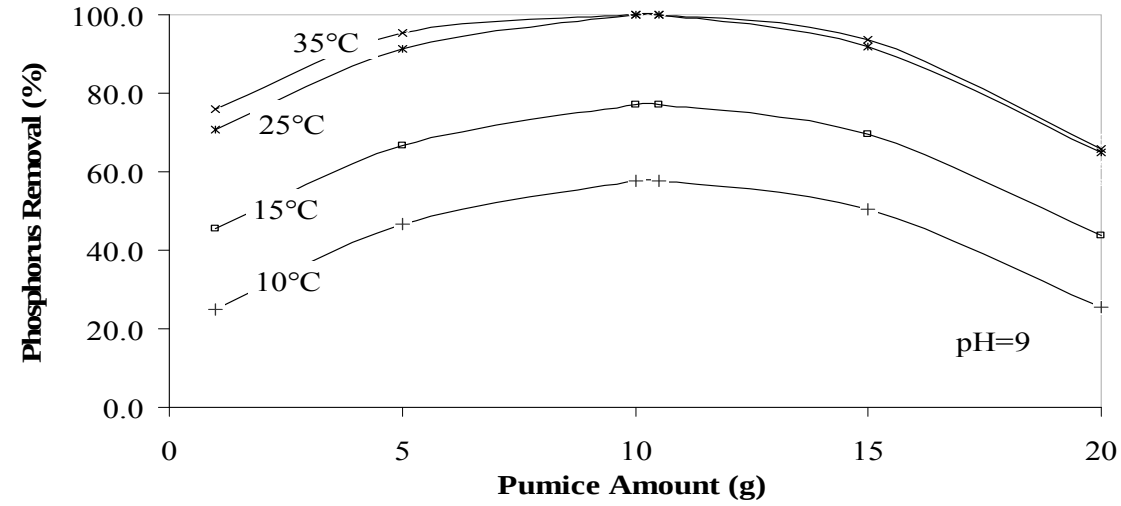


(c)

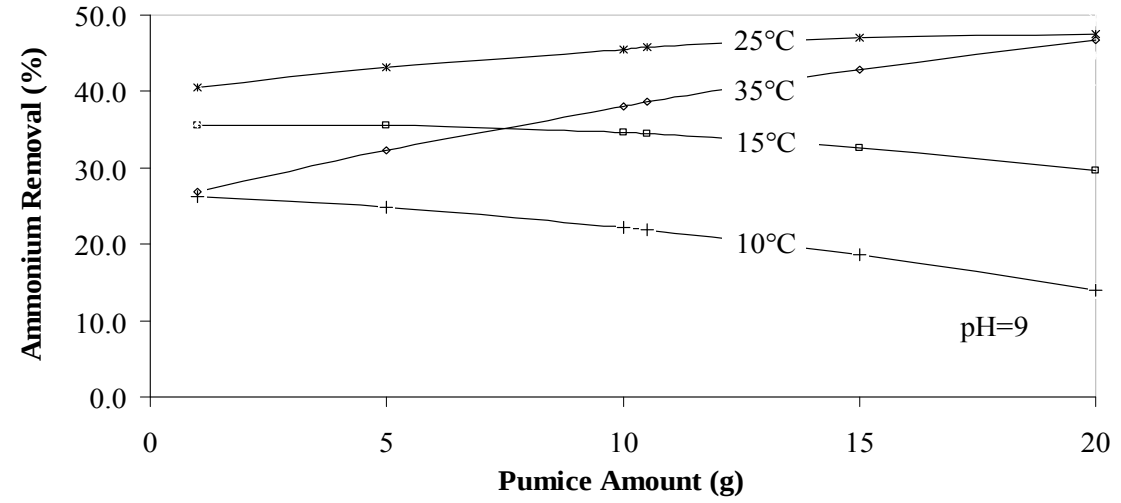
Figure 8.1 Changing of phosphorus (a), ammonium (b), and magnesium (c) removal with reactor temperature at different pH values

It was obtained that magnesium removal is rapidly increased with increasing temperature in model reactor and reached to 100% at 22.5 ^{0}C. Best magnesium removal was detected at pH 11 values on the contrary phosphorus and ammonium removal. It was concluded that it should be kept at pH 8.71 and 22.36^{0}C in model reactor, when 10.5 g pumice was added to model reactor to accomplish maximum removal efficiency for phosphorus, ammonium, and magnesium.

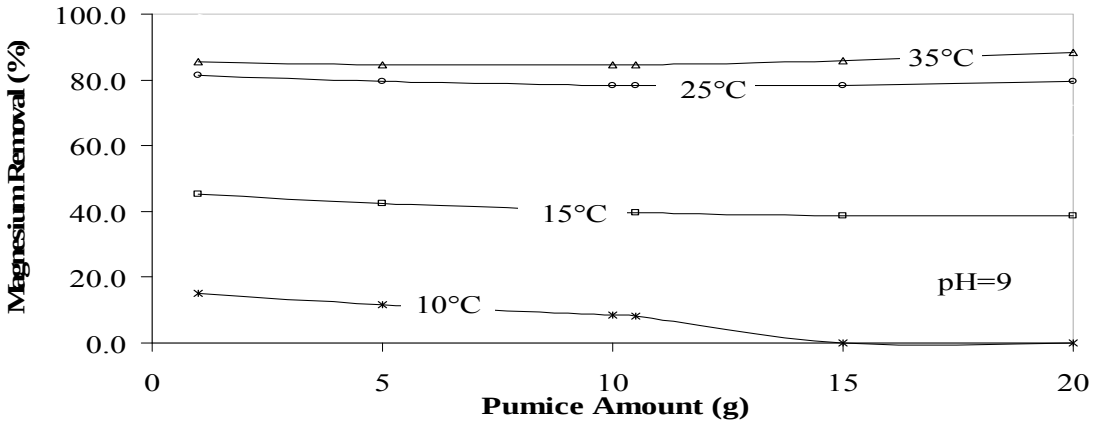
As can be seen in Figure 8.2a, the phosphorus removal was affected by progressive stages with increasing temperature at constant pH 9 and reached to 100% at greater than 25^{0}C. It was observed that pumice amount has slightly effect on phosphorus removal. The ammonium removal was affected significantly with increasing temperature at constant pH 9, but it was detected that it is not shown effectively chancing on ammonium removal after 25^{0}C temperature (Figure 8.2b). Ammonium removal was not significantly affected increase in pumice amount at 25^{0}C. Magnesium removal was significantly increased with increasing of temperature in model reactor, but decreased slightly with increasing of pumice stone (Figure 8.2c). In addition, magnesium removal was not reached to 100 % values like phosphorus and ammonium removal at pH 9. Maximum magnesium removal was accomplished at pH 11.



(a)



(b)



(c)

Figure 8.2 Variation of phosphorus (a), ammonium (b), and magnesium(c) removal with pumice amount at different reactor temperature

The microphotographs of pumice stone were illustrated in Figure 8.3. It was observed that surface of pumice is porous.

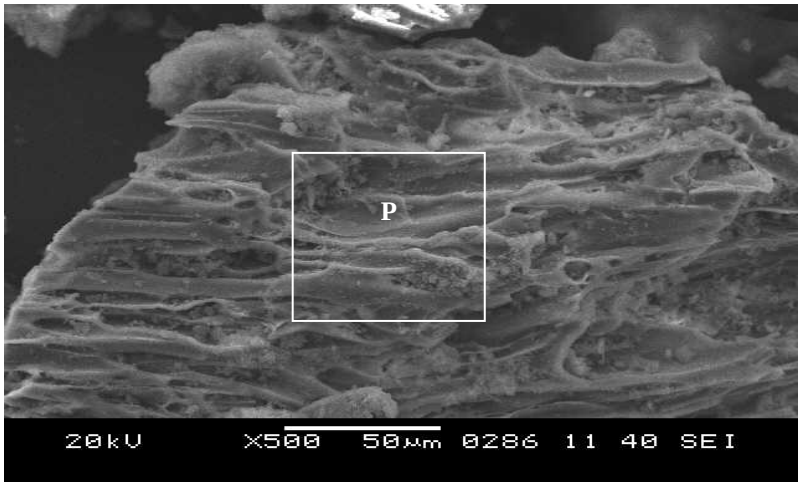


Figure8.3 Scanning electron micrograph of pumice stone (500X)

The chemical constituents of zone called as “p” in pumice stone sample are given in Table 8.5. It is found that major elements are silica, oxygen, potassium and aluminum, potassium in chemical composition of pumice stone. Precipitates consist of struvite particles were taken out reactor after studies. The photographs of dried precipitates were presented (Figure 8.4).

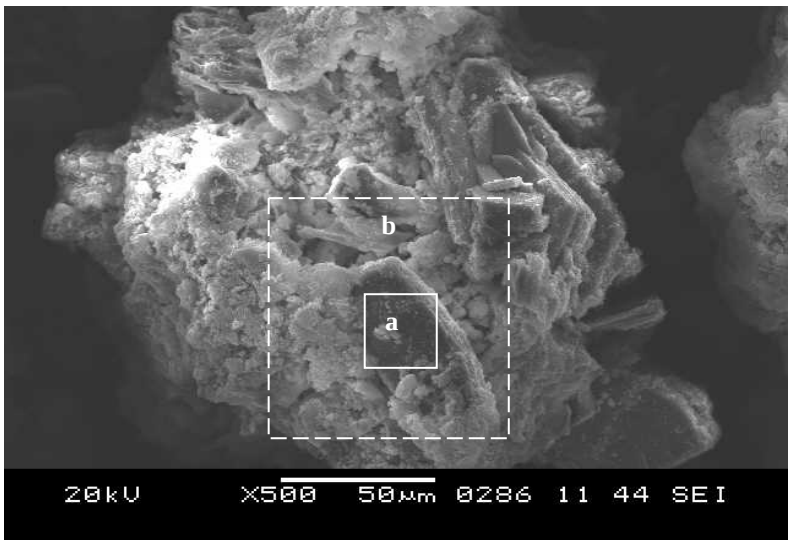


Figure 8.4 Scanning electron micrograph of dried precipitate (500X)

Table 8.5 Components of pumice stone taken at scanning electron micrograph

Element's Name	**Pumice Stone (%)**
O	42.831
Mg	2.747
Al	6.811
Si	34.313
P	2.744
Na	2.615
K	3.048
Ca	1.339
N	2.629
Cl	-
Fe	0.823

Table 8.6 Components of dried precipitates taken at scanning electron micrograph

Element's Name	**Chemical constituents of a zone (weight %)**	**Chemical constituents of b zone (weight %)**
O	46.189	45.148
Mg	21.291	11.675
Al	0.033	0.833
Si	-	4.618
P	27.346	12.309
Na	0.277	0.834
K	0.011	0.358
Ca	0.287	3.418
N	4.362	2.838
Cl	0.064	0.163
Fe	0.140	0.186

The chemical constituents of zone called as "a" and "b" was analyzed by using element analysis and given in Table 8.6. When SEM micrograph of dried

precipitates was look over, it can be seen rectangular precipitates on pumice. It is found that major elements of **a** zone are phosphorus, magnesium, nitrogen and oxygen, and major elements of **b** zone are phosphorus, magnesium, nitrogen, oxygen, silica and calcium in chemical composition of dried precipitates.

CHAPTER NINE
STRUVITE CRYSTALLISATON WITH EXTRACTED LIQUID FROM DRIED SLUDGE

In this chapter, process was applied two stages as phosphorus release and crystallization. It was used P-rich liquid which extracted from dried sludge for struvite crystallization.

9.1 Sample preparation

Experimental studies were carried out two stages as preparation of P-rich liquid by using nitric acid and crystallization process at model reactor. Pakdil and Filibeli was pointed that both inorganic acid and organic acids were effective at phosphorus release from dried municipal sludge and best phosphorus release can be accomplished by using nitric acid (Pakdil and Filibeli, 2007). Dried sludge samples were leached with 0.1 M nitric acid. Nitric acid solution was added to the dried sludge samples and was mixed for 30 minute time periods at 300 rpm by applying 100^0C temperatures according to ratio of dried sludge (g)/solution volume (ml) which was chosen as 1/50.

P-rich liquid was added 6.5 L/h with flow rate and $MgCl_2$ solution was added 5.22 L/h with flow rate during three hours after reactor was fulled. It was feed both P-rich liquid and pumice stone which has 150-200 μm size at the same time to reactor.

9.2 Results

Phosphate, ammonium and magnesium concentration in prepared P-rich liquid were analyzed. Phosphate, ammonium and magnesium concentration of P-rich liquid were respectively found as 46.00 mg/L, 53.10 mg/L, and 17 mg/L. It was added magnesium by using $MgCl_2$ solution and magnesium concentration increased to 75.04 mg/L in P-rich liquid. The molar ratio of P-rich liquid was determined as 2:2.5:1 after adding magnesium. Components of P-rich liquid feed to reactor were

illustrated in Table 9.1. Mg: PO_4^{-3}: NH_4^+ was continuously adjusted with $MgCl_2$ solution during all process times.

Table 9.1 Components of P-rich liquid feed to reactor

Components	**Concentration**
Phosphate (PO_4-P)	46.00 mg/L
Ammonium (NH_4-N)	53.10 mg/L
Magnesium (Mg)	75.04 mg/L
Calcium (Ca)	133.20 mg/L
Aluminum (Al)	1.30 mg/L
Iron (Fe)	12.57 mg/L
Cadmium (Cd)	19.97 µg/L
Chromium (Cr)	7.87 µg/L
Copper (Cu)	37.01 µg/L
Nickel (Ni)	45.24 µg/L

After it was feed both P-rich liquid and pumice stone, it was analyzed components of effluent given in Table 9.2.

Table 9.2 Components of model reactor effluent

Components	**Concentration**
Phosphate (PO_4-P)	10 mg/L
Ammonium (NH_4-N)	19.4 mg/L
Magnesium (Mg)	38.66 mg/L
Calcium (Ca)	66.16 mg/L
Aluminum (Al)	0.38 mg/L
Iron (Fe)	0.21 mg/L
Cadmium (Cd)	18.82 µg/L
Chromium (Cr)	41.11 µg/L
Copper (Cu)	91.68 µg/L
Nickel (Ni)	27.84 µg/L

Phosphate, ammonium, magnesium and calcium concentration in model reactor was observed at chosen times during three hours and illustarated in Figure 9.1. It was found that phosphate concentration decreased rapidly from 45 mg/L to 10 mg/L at first 30 minutes (phosphate removal efficiency: 77.8%) and it didn't change at other times. It was observed that ammonium concentration in model reactor decreased slowly during three hours (ammonium removal efficiency: 63.5%). Also, Magnesium

and calcium concentration diminished continuously. Therefore, it was concluded that phosphate at mixture was precipitated as struvite and calcium phosphate compounds.

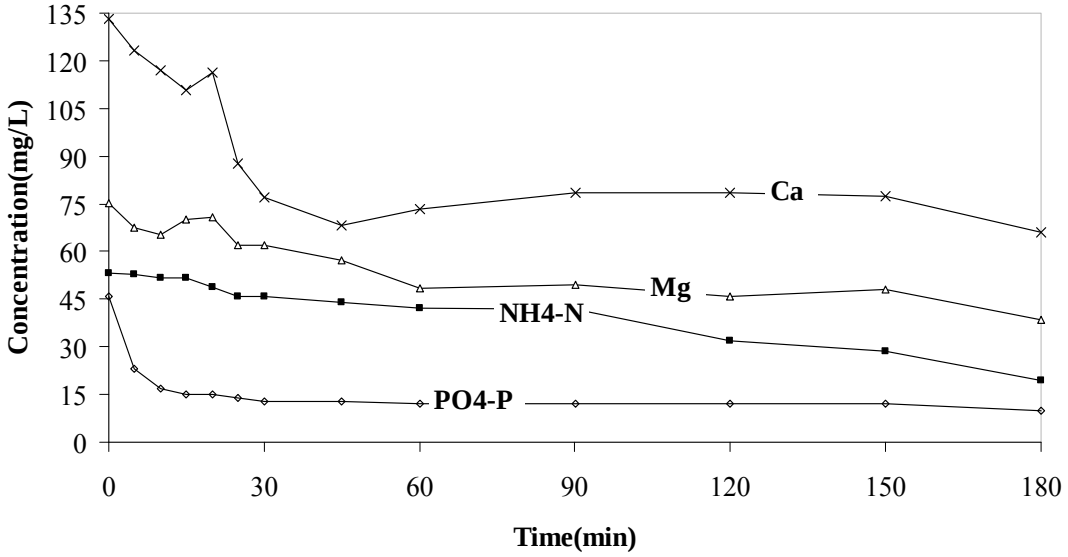


Figure 9.1 Variation of PO_4-P, HN_4-N, Mg, and Ca concentrations with time in model reactor

Variation of aluminum and iron concentration in model reactor was shown in Figure 9.2. It was found that 12 mg/L iron concentration lessened to 0.29 mg/L in ten minutes. Aluminum concentration doesn't significantly change at all reaction times.

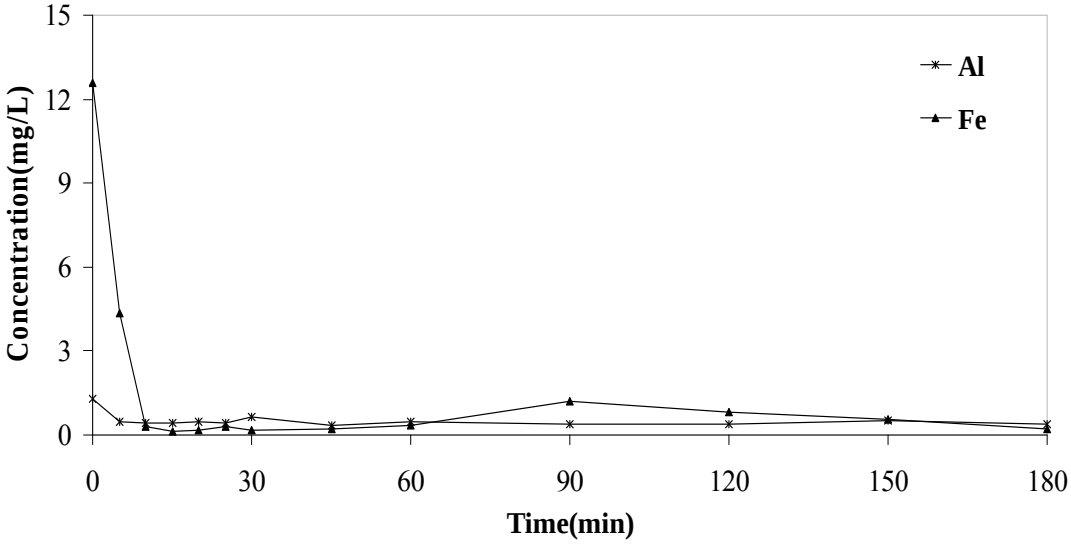


Figure 9.2 Variation of Al and Fe concentrations with time in model reactor

It was observed that concentrations of heavy metals like Cd, Cr, Ni and Cu changed with time. Cu concentration increased up to 91µg/L at the end of reaction times (Figure 9.3).

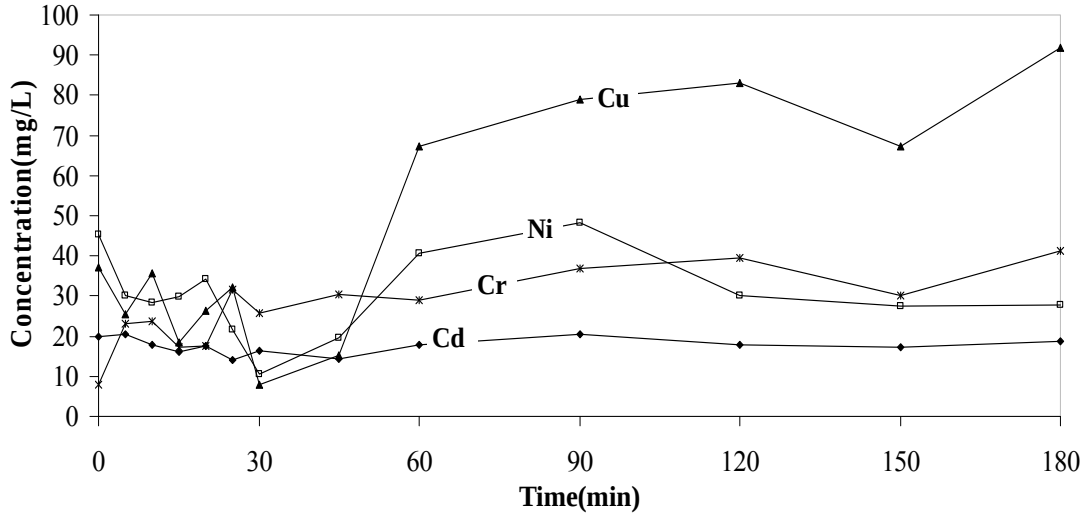


Figure 9.3 Variation of Cd, Cr, Ni and Cu concentrations with time in model reactor

Residues taken from reactor bottom composed of various phosphate precipitates and pumice stone was illustrated in Figure 9.4.

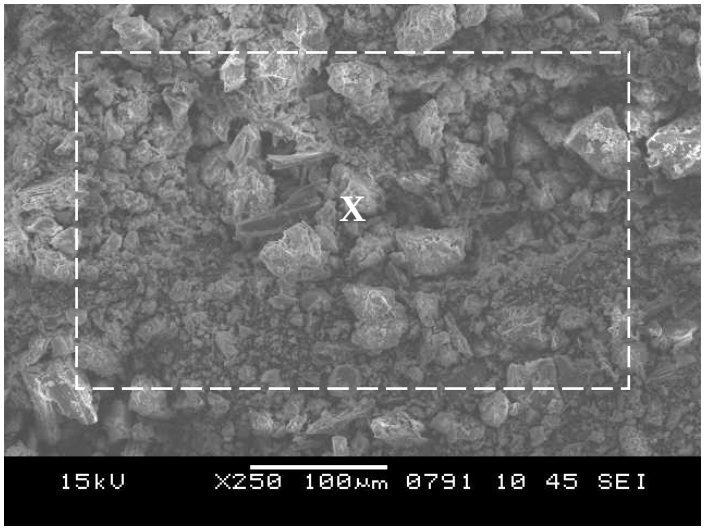


Figure 9.4 Dried residues taken from model reactor

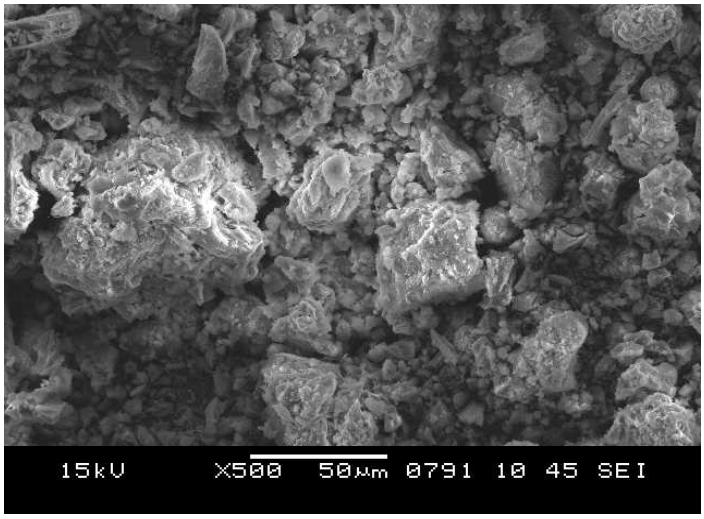
Precipitates consist of struvite particles were taken out reactor after studies. The microphotographs of dried precipitates were illustrated in Figure 9.5. The chemical constituents of zone called as “X” and “Y” were analyzed and given in Table 9.3. When components of dried precipitates was look over, it was detected that major elements of X zone are oxygen, silicium, calcium, magnesium, iron, phosphorus, sodium, aluminum, potassium and major elements of Y zone are oxygen, calcium, magnesium, phosphorus, iron, sodium, nitrogen, potassium.

Table 9.3 Components of dried precipitates taken at scanning electron micrograph

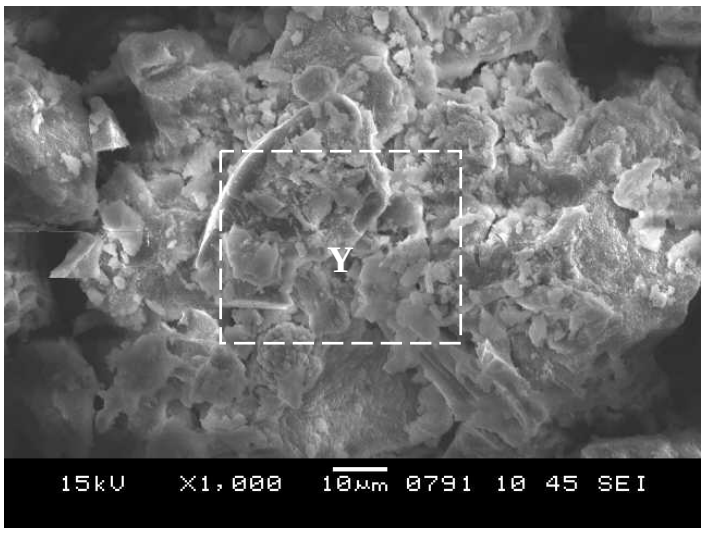
Element’s name	**Chemical constituents of X zone (weight %)**	**Chemical constituents of Y zone(weight %)**
Mg	5.083	8.749
Ca	11.797	16.347
P	4.263	6.891
N	0.139	1.419
O	40.594	43.029
Na	3.438	1.601
K	2.428	1.263
Fe	4.490	5.642
Ni	0.094	0.057
Cu	2.026	0.913
Cd	0.116	0.052
Cr	0.211	0.076
Al	3.355	-
Si	19.710	13.962
Cl	2.257	-



A



B



C

Figure 9.5 Scanning electron microphotographs of dried precipitates
A: 250X, B: 500X, C:1000X

CHAPTER TEN
CONCLUSIONS AND RECOMMENDATIONS

This research has utilized knowledge of phosphorus recovery as struvite from synthetic solutions and P-rich liquid which extracted from dried sludge, parameters affecting phosphorus recovery process like temperature, pH, pumice amount, and the applicability of pumice stone at struvite crystallization. This chapter presents the concluding remarks of this thesis and recommendations to develop the specific topics of the research study.

- struvite precipitation with synthetic solution at jar test apparatus

pH is an important parameter for phosphorus recovery using pumice stone powder. Optimum pH was determined,. 1.5 gr NMP2 pumice powder sample (5000 mg/L) was used to accomplish maximum phosphate removal rate. Maximum phosphate removal rate was obtained by adding 40 ml $MgCl_2$ (1000 mg/L) to 300 ml sample. It was obtained a stable phosphorus recovery using NMP2 pumice powder samples with compared to NMP3 samples. According to the experimental results, NMP2 pumice powder sample was more affective than NMP3 pumice powder sample to form nuclei; because of its small particle size. It was observed that a zeta potential value is -24.3 mV at pH 9.

- phosphorus release by using acids

Experimental results were evaluated by using Box-Wilson Experimental Design. The analysis of results has shown that nitric acid is more efficient compared to oxalic and magnesium hydroxide. The best phosphate release amounts are 16.8 mg P/g DS for nitric acid, 8.20 mg P/g DS for oxalic acid, and 1.56 mg P/g DS from magnesium hydroxide at 0.5 M concentration, 100^0C mixture temperature, and 97.5 min mixing time.

In experiments carried out with nitric acid, it has been observed that the increase in nitric acid concentration and mixing time does not significantly affect phosphorus release, while an increase in mixing temperature causes a great change. Experiments conducted using oxalic acid have shown that mixing temperature increases phosphorus release, whereas concentration increase and mixing time have very little effect. No high phosphorus releases values have been obtained with magnesium hydroxide; while mixture temperature has a positive effect on phosphorus release value. However, it was found that phosphorus release was fixed to 0.58 mg P/gr DS for 1.55 M magnesium hydroxide concentration at all mixing time values, at 60^0C mixture temperature.

- phosphorus release by using base

Box-Benhken Experimental Design was used to determine effects of base concentration, mixing time and temperature on phosphorus release using base. It was decided quadratic model from lowest standard deviation, the highest R-Squared and the lowest press value in evaluation of the ANOVA regression analysis of phosphorus release. According to experimental results, predicted values of dependent variables were in good agreement with the observed values at Box-Behnken Experimental Design. It was observed that NaOH was more effective than KOH on phosphorus release; temperature and base concentration on phosphorus release are the principal effect. However, mixing time was slightly affected phosphorus release.

- struvite precipitation with synthetic solution at model reactor

Box-Benhken Experimental Design was used to determine effects of pH, pumice amount and temperature on PO_4-P, NH_4-N, Mg removals in the model reactor. It was decided quadratic model from lowest standard deviation, the highest R-Squared and the lowest press value in evaluation of the ANOVA regression analysis of PO_4-P, NH_4-N and Mg removal.

It was observed that temperature, pH and pumice amount have positively effect on phosphorus removal. Best phosphorus removal was detected at pH 9 and 10 values. Variation of temperature and pH has significantly been affected ammonium removal like phosphorus removal. While maximum ammonium removal was detected at pH 9, minimum ammonium removal was determined at pH 7. Temperature and pH are very effective, but pumice amount has negatively effect on magnesium removal. Best magnesium removal was detected at pH 11 values on the contrary phosphorus and ammonium removal. It can be seen that temperature in model reactor is the principal effect on phosphorus, ammonium and magnesium removal. The phosphorus removal was affected by progressive stages with increasing temperature at constant pH 9 and reached to %100 at greater than 25^0C. It was observed that pumice amount has slightly effect on phosphorus removal. The ammonium removal was significantly affected with increasing temperature at constant pH 9, but it was detected that it is not shown effectively chancing on ammonium removal after 25^0C temperature. Ammonium removal was significantly not affected with pumice amount. Magnesium removal was significantly increased with increasing of temperature in model reactor, but decreased slightly with increasing of pumice amount. It was found that the independent variables for best combination which is maximized dependent variables are pH 9.52, pumice amount 12.84 g, and temperature 28.92^0C.

When SEM micrograph of dried precipitates was look over, it can be seen rectangular precipitates on pumice. Major element of these precipitates are magnesium, nitrogen and oxygen and major elements of all precipitates general composition are phosphorus, magnesium, nitrogen, oxygen, silica and calcium.

According to experimental results, predicted values of dependent variables were in good agreement with the observed values at Box-Behnken Experimental Design. It was observed that temperature and pH in model reactor is the principal effect on phosphorus, ammonium and magnesium removal. Pumice amount was slightly affected phosphorus, ammonium, and magnesium removal. Good phosphorus removal could be achieved by pumice stone as crystal seeding. It was observed that struvite crystals were precipitated on pumice stone.

- struvite precipitation with extracted liquid from dried sludge

Phosphate, ammonium, magnesium, calcium, aluminum, iron, cadmium, chromium, nickel, and copper concentration in model reactor were observed at chosen intervals during three hours operation period. It was found that phosphate and ammonium precipitated significantly as stuvite and calcium phosphate compounds. In addition, while iron concentration lessened, aluminum concentration doesn't significantly change at all reaction times. It was observed that concentrations of heavy metals like Cd, Cr, and Ni showed exchange with time, but Cu concentration increased during operation periods.

The liquid extracted from dried sludge using nitric acid and pumice were used in struvite precipitation studies at the model reactor. This process is beneficial for agricultural purpose. Especially, the precipitate with struvite particles can be used in plant growth. The struvite releases very slowly in soil media and beyond this, the pumice is plentiful and low-priced material in Turkey.

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APPENDIX 1

ANOVA Output;

Model: Terms estimating factors effects.

Sum of squares: Total of the sum of squares for the terms in model.

DF: Degrees of freedom for model. It is the number of model terms; including the intercept, minus one.

Mean Square: Estimate of model variance, calculated by the normal sum of squares divided by model degrees of freedom.

F value: Test for comparing model variance with residual (error) variance. If the variances are close to the same, the ratio will be close to one and it is less likely that any of the factors have a significant effect on the response. Calculated by model mean square divided by residual mean squares.

Prob> F: Probability of seeing the observed F value if the null hypothesis is true (there is no factor effect). Small probability values call for rejection of the null hypothesis. The probability equals the proportion of the area under the curve of the F-distribution that lies beyond the associated with the variances being compared.

Note: If the Prob> F value is very small (less than 0.05) then the terms in the model have a significant effect on the response.

Term: Each of the listed terms is currently in the model and individual statistics are calculated for them.

Sum of squares: For factorial terms the sum of squares equation reduces to: the number of factorial experiments divided by 4 times the squared factor effect.

DF: Degrees of freedom for the term. It is the number of levels for the term, minus one.

Mean Square: Estimate of the term variance, calculated by the term sum of squares divided by term degrees of freedom.

F value: Test for comparing term variance with residual (error) variance. If the variances are close to same, the ratio will be close to one and it is less likely that the term has a significant effect on the response. Calculated by term Mean Square divided by Residual Mean Square.

Prob> F: Probability of seeing the observed F value if the null hypothesis is true (there is no factor effect). Small probability values call for rejection of the null hypothesis. The probability equals the proportion of the area under the curve of the F-distribution that lies beyond the observed F value. The F distribution itself is determined by the degrees of freedom associated with the variances being compared.
Note: If the Prob> F value is very small (less than 0.05) then the individual terms in the model have a significant effect on the response.

Lack of Fit (LOF): This is variation of the data around the fitted model. If the model does not fit the data well, this will be significant.
Sum of Squares: residual sum of squares after removing the pure error sum of the squares.
DF: The amount of information available after accounting for blocking, model term, curvature, and pure error.
Mean Square: Estimate of lack of fit.
F value: Test for comparing lack of fit variance with pure error variance. If the variances are close to the same, the ratio will be close to one and it is less likely that lack of fit is significant.
Prob> F: Probability of seeing the observed F value if the null hypothesis is true. Small probability values call for rejection of the null hypothesis that lack of fit is not significant.
Note: If the Prob> F value is very small (less than 0.05) then lack of fit is significant. In other words the variation in the model points significantly differs from the variation in the replicated points. Consider adding more terms to this model. You want the Prob> F value for lack of fit to be greater then 0.10.

Pure Error: Amount of variation in the response in replicated design points.
Sum of Squares: Pure error sum of squares from replicated points.
DF: The amount of information available from replicated points.
Mean Square: Estimate of pure error variance.

Other Terms:

Std. Dev.: (Root MSE) Square root of the residual mean square. Consider this to be an estimate of the standard deviation associated with the experiment.

PRESS: Predicted Residual Error Sum of Squares- A measure of how the model fits each point in the design. The PRESS is computed by the first predicting where each point should be from a model that contains all other points except the one in question. The squared residuals (difference between actual and predicted values) are then summed.

R-squared: A measure of the amount of variation around the mean explained by the model.

The multiple correlation coefficients computed as

$1\text{-}SS_{residual}/ (SS_{model}+ SS_{residual})$

Use the Adjusted R-squared value fro designed experiments.

Adj R-Squared: A measure of the amount of variation arums the mean explained by the model, adjusted fro the number of terms in the model. The adjusted –Squared decreases as the number of terms in the model increases if those additional terms don't add value to the model.

Pred R-squared: A measure of the amount of variation in new data explained by the model.

The predicted R-squared and the adjusted R-squared should be within 0.2 of each other. Otherwise there may be a problem with either the data or the model. Look for outliers, consider transformations, or consider a different order polynomial.

Source: *Stat-Ease Design Expert 7.1.3 (Trial version) software program*