Yogesh Chapagain

Methods and Possibility for Recycling of Phosphorus from Sludge

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This thesis presents a review of the phosphorus cycle, environmental effect of excess phosphorus on environment, different methods approach taken to recover phosphorus compound from waste sludge, and possible uses for recovered phosphorus.

Phosphorus is a critical nutrient for the agricultural production and living organism survival. The use of phosphorus in fertilizer secures future food demand but threatens water resources. The uncontrolled use of agricultural phosphorus and commercial products are leading to contamination and environmental degradation in water bodies nearby agricultural land. The inefficient use of phosphorus creates uncertainties in supply and demand of this nonrenewable resource for future demand. The amount of phosphorus has a directly impact on the agricultural production which affects the food industry.

Sludge produced from sewage and water treatment plant are enriched with nutrients. This thesis focused on methods for recovery of phosphorus from sludge with four different methods: microalgae and cyanobacteria(Bio-extraction), wet extraction process, thermochemical method, nanofiltration in diafiltration mode. Recovery methods performed by different researchers suggest the efficiency range from 50-90% depending on properties of sludge composition and sludge extraction process in sludge and water treatment plant. All the experiments methods were performed in laboratory condition.

The extraction of phosphorus from sludge has high potential for fulfilling growing demand of phosphorus for fertilizer, commercial products like detergent and phosphoric acid. The side products obtained from recovering phosphorus from sludge can be used as additives for cement manufacturing.

Keywords	phosphorus, recycling, leaching, fertilizer, filtration, sludge, sewage sludge ash, surface runoff treatment

Contents

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List of Figures

List of Tables

Abbreviations

DO	Dissolved Oxygen
DS	Digested Sludge
EBPR	Enhanced Biological Phosphorus Removal
EOC	Emerging Organic Contamination
HM	Heavy Metal
MOCA	Minnesota Pollution Control Agency
P	Phosphorus
PAO	Polyphosphate Accumulating organism
PSO	Phosphorus Solubilizing Organism
TP	Total Phosphorus
TN	Total Nitrogen
SR	Surface Runoff
SSA	Sewage Sludge Ash
SCWO	Super Critical Water Oxidation
VOC	Volatile Organic Compound
WEP	Water Extractable Phosphorus

1 Introduction

Phosphorus (P) is an important element for all life and is a prerequisite for sustained agricultural productivity. The earth's crust is made from 0.01% of phosphorus. Due to high reactive nature of phosphorus, it is not available naturally in its elemental form. Phosphorus is present in compound form, especially in mineral like phosphate rock ($Ca_3(PO_4)_2$. Mineral phosphate is a natural resource which can be measured, quantified and exploited in mining. Bones and all living tissue are partly composed of phosphorus (Cordell et al., 2011). The ocean floor is also the biggest source for phosphorus in earth. There is no artificial substitute for fulfilling the demand of phosphorus. Knowledge of recycling Phosphorus has become an important issue to meet the future demand for agriculture and human life.

In recent years, the researchers have reported on phosphorus release pathways to environment from sources like agriculture and sewage. These pathways raise the ionic phosphorus level in water body and lead to eutrophication. The quality of water and productivity of soil is degraded. Soil contamination leads to high bioaccumulation in food chain from plant to human. The potential of recycling phosphorus from sludge, waste has been studied extensively in recent years to prevent possible phosphorus release to environment. Many standard procedures for recycling phosphorus from waste and sludge has been studied and performed around the globe at research scale. Research data presented in the literature suggest many applicable ways of recycling as well as effect of recycling of phosphorus on global food security.

Phosphorus is limited resource; high percentage composition of phosphorus in sludge indicates the greatest potential for recovering phosphorus. Sludge is produced from industrial and municipal wastewater treatment plant. High percentage of nutrients excreted by human body in form of urine is processed from wastewater treatment plant. So recovering phosphorus from sludge has high prospective. A considerable amount of research has been done in the field of extraction of phosphorus from sludge but suitable extraction process varies from country to country. However, less attention has been paid to the recycling of phosphorus from sludge. The reuse of recycled phosphorus will certainly decrease the phosphorus footprint. Since, it is wise idea for preserving earth composed of 0.01% of phosphorus. Phosphorus recycling from wastewater and sludge is important to control the eutrophication of water bodies. Recycling of phosphorus can be performed by physical, chemical and biological methods. Sludge is processed from sewage treatment and water treatment plant. Sludge is removed from different phase of treatment plant i.e. primary clarifiers, secondary clarifiers. Presence of high nutrient contain in sludge makes it high value resource well worth the expense of capture infrastructure (Cordell et al., 2014 and Cordell et al., 2009).

This thesis presents a review of a competing sludge treatment processes with a focus on phosphorus recycling in terms of efficiency and cost.

2 Goal and Scope

The limited supply of phosphorus and its applicability to different sectors makes it more valuable. Phosphorus compounds are used for products like food, packing industry, personal care product, detergents. Collection of consumed phosphorus in sewage and treatment of sewage generate phosphorus rich sludge ending up in landfill, agriculture lands, mining, production of soil. Recycling of sludge before ending up in landfill or soil production could help to fulfill increasing demand of phosphorus in globe (Hideaki et al., 2015 and Jiechen wt al., 2015).

Excessive use of phosphorus in synthetic fertilizer results in runoff from agricultural land end up in water resources, which leads to eutrophication. This also effects the P cycle, triggering to major ecological effects and environmental damage. Treatment of sewage and waste enriches phosphorus and other nutrients. These nutrients may be captures and provide two benefits. The treated waste would reduce the risk associated with release of nutrients to the environment and the captured nutrients represents a continuous source for a valuable limited natural resource (Y.Liu and J.Chen 2014).

This thesis is a theoretical study, the purpose of which is to determine possible methods and technologies for recycling phosphorus from sludge. Also to understand the policy applied by different countries for recycling phosphorus from sludge and waste. Since this thesis is a literature review of papers published by different authors, there is no experimental component. Removal techniques researched in different countries for recycling of phosphorus from sludge are compared from a critical perspective. The countries from which the research papers are drawn range economically and geographically; they include Japan, India, Australia, Sweden, Switzerland, USA and China. This thesis compares the different possible methods for recycling phosphorus for sludge. The outcome of this thesis might be fascinating to reads with different backgrounds as well as waste and water treatment plants for determining the efficient way of recycling phosphorus.

3 Literature Review

This chapter includes general overview about the phosphorus presence in earth and methodology for sludge production from waste and water treatment plant. It also describes the ways in which phosphorus is consumed as well as released to the environment and atmosphere. In addition, the chapter describes the composition of nutrients in sludge and the use of sludge for different purposes like landfill, anaerobic digester for energy production and soil manufacture. Basically the information about phosphorus and sludge cycle is explained in this section.

3.1 Phosphorus

Phosphorus is an essential chemical element, which cannot be produced in laboratory but are consumed and found in food by all living beings (Daniel et al., 2011). There are several forms of phosphorus called white, red and black phosphorous. Although with properties of spontaneously flammable and toxic, phosphorus is an essential element for the survival of organism (Lenntech, 2015). Phosphorus is highly reactive; therefore, it is used in the form of compound for extraction. Phosphate rock is major source of P. The most important source for phosphorus mineral is apatite, $Ca_{10}F_2(PO_4)_6$ (Daniel et al., 2011, Patyk et al., 1997)

3.1.1 Phosphorus Presence in Earth

Phosphorus is the 11th most abundant element in the earth's crust, amounting tentatively to four quadrillion tons (Cordell et al., 2011). A non-renewable phosphate rock take 10 -15 millions of years for its formation are mined globally (Cordell et al., 2009). Mining for phosphorus production is increasing annually and ongoing mining operations have many negative environmental impacts. Agriculture is the largest user of phosphorus and the primary source is mineral phosphate from mines (Shiroyama et al., 2015). Due to depleting reserve and decline quality, the value of mineral phosphate is increasing leading to increase the cost for the fertilizer affecting the global food cost (Genevieve et al., 2015). With the current extraction of phosphate rock, and 2.3 % increase in demand per annum, it is expected to completely use within 50-100 years. Morocco has around 85 % of 0.007% of the total phosphorus on earth crust followed by China with 6% and USA by 3% (Cordell et al., 2009; Adhya et al. 2015; Shiroyama et al., 2015). Figure 1. Shows physical, chemical and social factors limiting the availability for agriculture.

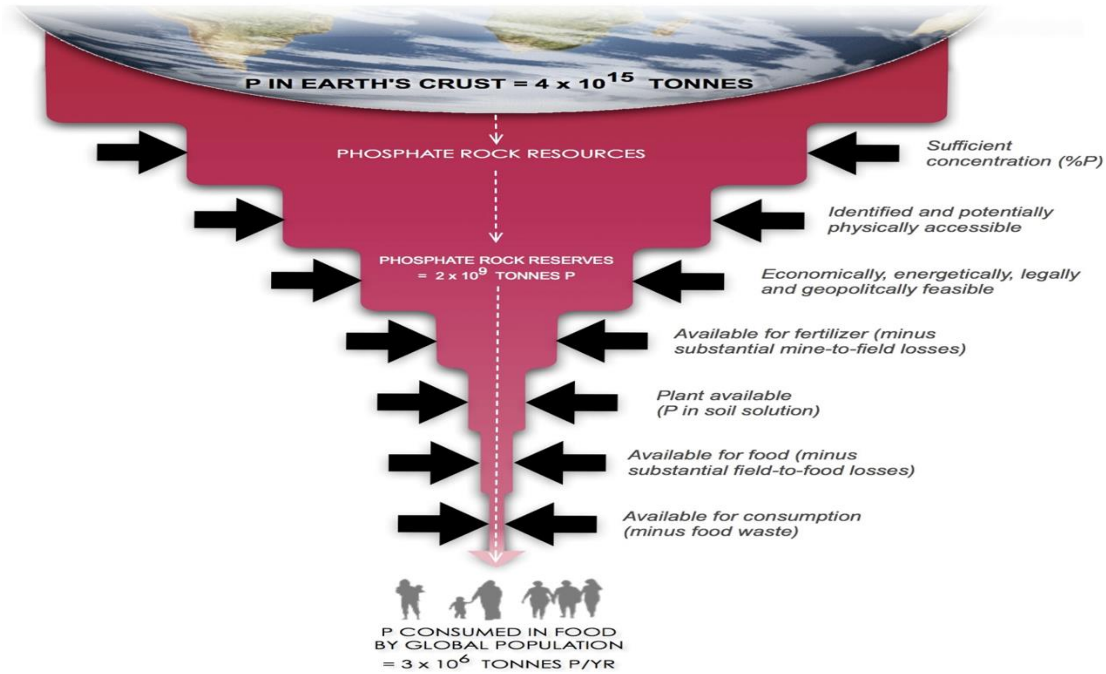

Figure 1. Phosphorus Bottlenecks: Physical, economic, social and ecological factors limiting the availability of phosphorus for productive use by humans for fertilizer and hence food production. (Cordell et Al., 2011)

3.1.2 Sources of Phosphorus

Natural source for phosphorus are mineral phosphate sequestered in the earth crust and phosphorus in compound from cycling through environment. Phosphorus is present in regular diet of all living things. Agricultural diversion from the cycle through the use of enriched fertilizers has been responsible for the so called green revolution. The phosphorus nutrient used by plants and passes to higher organism. Bioaccumulation process, products like meat, milk, beans; nuts are secondary source of phosphorus. Living cells rely on phosphorus compound as fundamental component of DNA and tissue is linked by phosphorus compounds. The main source for human for phosphorus is via grains, meat and vegetable. Industrial uses of phosphorus include manufacturing products like paper packaging, textile products, detergent, personal care product as well as newspapers (Jiwchen Wu et. al., 2015). Phosphorus is emitted from vehicles in traffic areas, are transported by wind and deposited to water sources or soil through rainfall (Jonathan et. al., 1990).

Phosphorus is released to water and soil from industrial wastewater treatment plant, farmlands, and runoff due to rainfall from landfill. Agriculture fertilizers runoff is the biggest source of phosphorus in water bodies as well as municipal sewage treatment plant is another big contributor for phosphorus into environment. Production of soil from sludge is another source of phosphorus to environment. Runoff and leachate generated from the sludge soil directly increases the amount of phosphorus in environment. Nutrient used for agriculture is not totally used by plants, which are carried by runoff or disaster like soil erosion and landslide. Disasters contributing to high level of phosphorus to another location leading for adverse effect like eutrophication or over nutrient.

3.1.3 Phosphorus Cycle

Phosphorus is part of DNA-molecules, molecules that stores energy and fats of cell membrane. Animal and human body depends upon the phosphorus for growth of certain part. Phosphorus is present in agriculture, soil, water, sediments and river catchment (Daniel et at., 2015). The Phosphorus cycle spans the phases and has stages with geological time frames and is therefore the slowest matter cycle on the planet (Lenntech, 2015).

Inorganic phosphorus ionic compounds are obtained from phosphate salts in rock formation and ocean sediment. Due to high polarity nature phosphate rock dissolve in water, soil water and is absorbed by plants for photosynthesis and their growth. Since phosphorus is a limiting agent for plant growth, fertilizers with high phosphorus content can result in high yield in farmland which is deficient in phosphorus. Bioaccumulation is medium in which the phosphorus cycle directly affects animals and plants. Consumed phosphorus will be utilized and discharge as solid and liquid waste which supports the microbial communities in the soil or is flushed via continental aquatic systems to the ocean floor. The phosphorus rich sediment from the periodical flush of seasonal rainfall leads for formation of sedimentary rock beneath the mass of eons of trapped material (Y.Liu and J.Chen 2014, ; Lenntech, 2015). Figure 2 illustrates A schematic representation of the phosphorus cycle presents sources, consumption, collection, treatment and end of life with natural process of time consuming recycling for phosphorus.

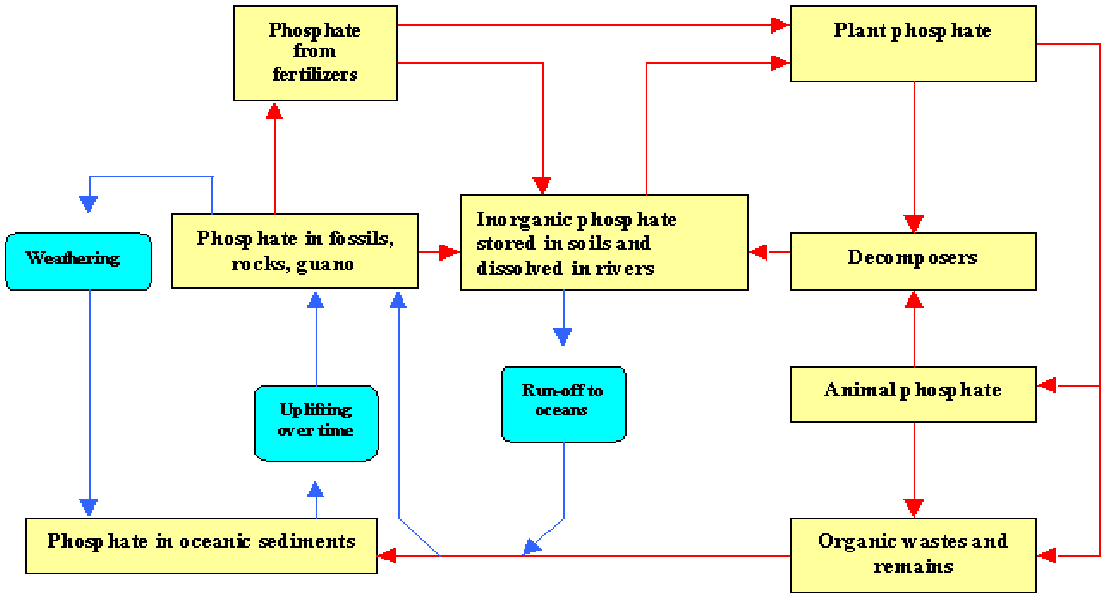

Figure 2. Schematic Representation of the Phosphorus Cycle (Lenntech, 2015)

3.2 Possible ways of Releasing of Phosphorus to Environment

This chapter covers possible ways of release of phosphorus to environment due to directly and indirect human activities. The theoretical background of this chapter is based on literature published on the internet and other research papers. The basic human activities for releasing the phosphorus to environment are explained below.

3.2.1 Crop Production

Phosphorus is released and absorbed during the process of crops production. Nitrogen and phosphorus are fertilizer used in agriculture. The impact of phosphorus from agriculture use depends on the specific crops uptake and removal parameters, and the land characteristics such as runoff, erosion and leach ability (Andrew et, al., 1994).

During uptake and removal of crops, phosphorus concentrations from plants tissues are recovered in range of 0.1 to 0.5% in dry mass. Crops absorb phosphorus from soil phosphorus and from fertilizers containing phosphorus. Phosphorus concentrations from fertilizers are more dynamic than those of natural soil sources. Concentration of fertilizer phosphorus constantly changed in soil because of rainfall and weathering. Rainfall infiltration and percolation can remove phosphorus from soil. Rainfall transport leads to increase the concentration of bioavailable phosphorus in surface water. Rainfall and weathering can cause phosphorous to leach, which have an adverse effect on phosphorus deficient soil. The losses of phosphorus from agriculture land also affected by site-specific soil and types of cropping and tillage system (Gregory Mullins, Virginia Tech). Figure 3. Presents the leaching of soil and effect of rainfall, weathering, and soil erosion for phosphorus loss from top soil to nearby water resources.

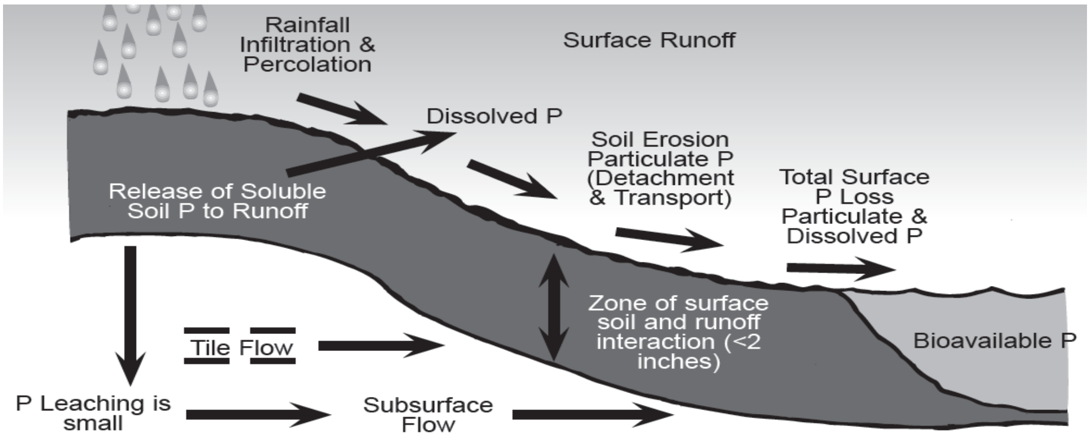

Figure 3. Transport of Phosphorus from Agricultural Land to Surface Water (Gregory Mullins, Virginia Tech).

3.2.2 Livestock Rearing

Phosphorus is essential for livestock growth especially bones and teeth. It plays a role in the proper growth of all living creature. Rumens and other plant eating stocks get their dietary phosphorus from plant based feed. The manure produced from livestock is significant source of emission of Phosphorus to environment (Gregory Mullins, Virginia Tech). Manure fertilizer is very rich in phosphorus, typically having phosphorus concentration 1.4 times those necessary for healthy plant growth (Hochschule et, al., 1995). The use of Water - Extractable Phosphorus (WEP) in manure used in agriculture in some countries correlated well to runoff from soil. Optimal use of manure by farmer due to the logistical and nutritional benefits, can offset and supplement the use of artificial fertilizers. with environmental loss of nutrients. Surface runoff and leachate production from stacking center are the main source for release of nutrient to environment. Livestock manure can be defined on basis of WEP (Peter et al. 2004 and Jian et al. 2014).

3.2.3 Meat Processing

Animal's bone and meat are great source for phosphorus. Phosphorous content in bone and meat is 9-11% in mass percentage. Animal waste from meat processing is source of 1.1 % of phosphorus. Bone and waste meat are not consumed for other animal feed as well as fertilizer. It is left for biomass formation because of health risk and hygienic reasons. Disposal of meat and bone in incineration plant, phosphorus ended in waste likes ashes that made difficult for recovery. Use of the ashes for manufacturing cement removes phosphorus from natural cycle. The biomass or manure with high nutrient value ended up in farmland which leaches runs off to affect local water resources (Daniel et al. 2011).

3.2.4 Sewage and Waste Management

Sewage and industrial effluents are considered are the major sources for phosphorus input to water bodies. Phosphorus is transported in form of dissolved and particulate phosphorus (Helen and Paul, 2006). Artificial products, personal care products, bulky goods and packing cardboard are source for phosphorus in sewage and waste (Jiechen and Maria, 2015).

Sewage effluents from treatment plant, septic tanks are released to environment, which reacts with soils microbes, and enrich the soil with phosphorus compound. During the flood, soil erosions, surface runoff the nutrient contents are released to water bodies.

Waste treatment facilities are big source of phosphorus to environment. Landfill and incineration convert phosphorus from one state to another. Leachate generated from landfill are the big contributor for metals ions and as well as nutrient. Surface Runoff (SR) and rainfall can make flow of nutrients to water bodies nearby and affect the aquatic environment (Kouassi et al. 2016 and Manimaran et al 1997). Waste incinerated converts waste to ashes that need to be disposed to landfill or chemical treatment facilities. The disposed ashes consist of same percentage of phosphorus, which can be released to environment through SR and storm water with high potential of recovery (Daniel et al, 2011).

3.3 Effect of Phosphorus on Environment

Eutrophication is a consequence of naturally high levels of nutrient in freshwater and coastal marine systems. Algae plumes flourish in nutrient rich environments negatively affecting water quality and leading to oxygen deletion and impaired aquatic ecosystem services and economic damage. Nutrient levels in water are driving elements for Eutrophication (Chen and Graedel, 2016).

Nutrients are transported from agricultural land through SR, agricultural runoff. The decomposition of phosphorus leads to an unnatural ecosystem within the contaminated sediment. The sedimentation is source for the nuisance phytoplankton as well as algae (Helen et al., 2005).

Phosphorus is considered as main contributor for eutrophication of surface water according to European Union (EU) Water Frame- work Directive (WFD). Growth of algae is supported by high water temperature, water resident time and abundant light level during growth season from spring to early autumn (Helen et al., 2005). Human activities and industrial revolution, mostly from agricultural sources has steadily increased the demand of phosphorus. SR, leaching, other waste handling process phosphorus reaches the surface water affects the ecosystem which responds by sequestering the nutrients in sediment layers. The sediment and unnatural ecosystem supports represents a self- renewing contamination sources that spoils aquatic resources and require long periods of time to remediate (Cordell et al., 2009; Adhya et al. 2015; Shiroyama et al., 2015).

3.3.1 Eutrophication Process

According to United States Geological Survey (USGS), "the process by which a body of water acquires a high concentration of nutrients, especially phosphates and nitrates. These typically promote excessive growth of algae. As the algae die and decompose, high levels of organic matter and the decomposing organisms deplete the water of available oxygen, causing the death of other organisms, such as fish. Eutrophication is a natural, slow-aging process for a water body, but human activity greatly speeds up the process." - Art, 1993 [Online Available on: http://toxics.usgs.gov/definitions/eutrophication.html] Figure 4. Graphical flowchart for eutrophication process.

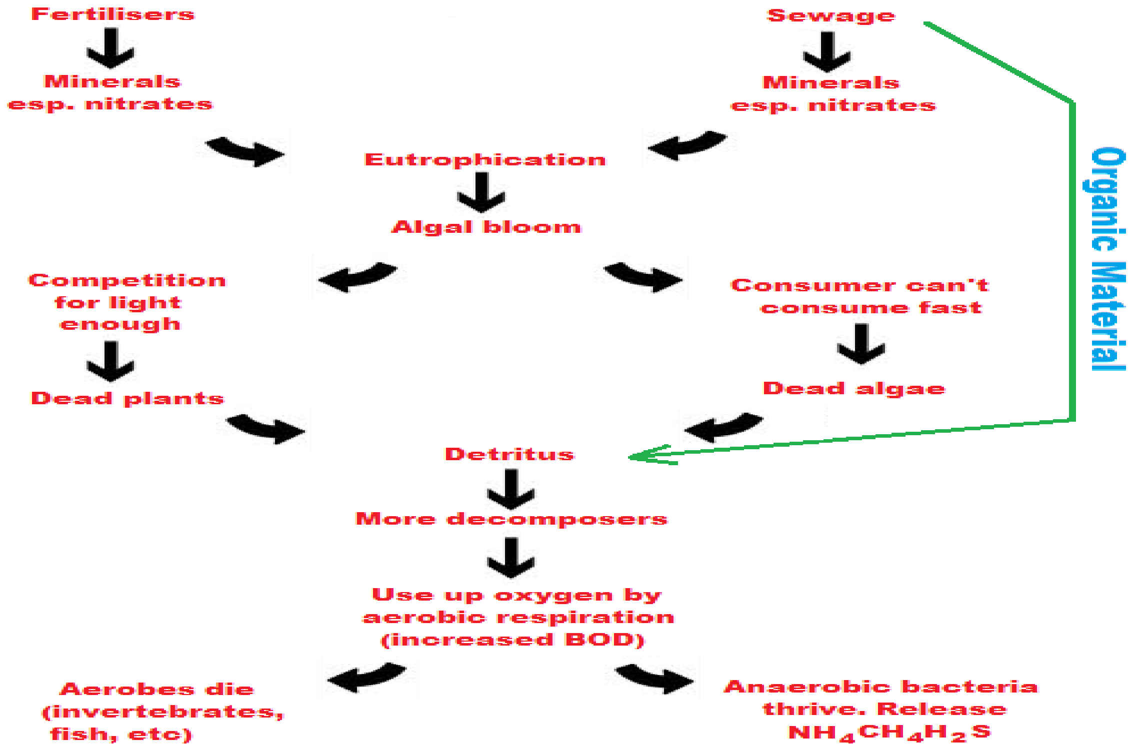

Figure 4. Process of Eutrophication. (TutorVista, N. D.)
Online [http://chemistry.tutorvista.com/biochemistry/eutrophication.html]

Due to human and agricultural activities, nutrient levels are increasing in topsoil. SR and discharge of effluent from sewage, levels of nutrient at water bodies is increasing. The high concentration of nutrient levels leads to unnaturally large algae plumes in affected bodies of water. Rapid growth of algae leads to high respiration of dissolved oxygen (DO). Algae bloom causes releases to toxic compound and noxious gases such as hydrogen sulfide, ammonia. These affects water quality and turbidity. Additional SR, the more favorable condition is generated for algae growth. The growth of Algae decreases the sunlight penetration to surface of water as a result it affects the aquatic vegetation. Death of vegetation leads to increase of organic load. Increase of organic load positively affects microbial respiration of DO which when consumed results in a dead zone in higher life form (Akpor et al., 2015).

3.3.2 Effect of Eutrophication

The water surface is considered as eutrophic if the total phosphorus (TP) concentration is high than 0.02mg/L and total nitrogen (TN) level above 0.5 mg/L (Hua-peng et al., 2013). As the limit value for TN and TP increases the eutrophic effect is observed on water bodies. As an effect, the thick algae bloom is observed that causes more organic mass. Level of DO concentration is decreased. Main effects observed from eutrophication are increased biomass, depletion of DO, odor and color of water, decrease in water transparency and decreased the aquatic biodiversity.

3.3.3 Effect on Bioaccumulation

Fisheries and aquaculture are an important sources of protein in many populations. Eutrophication has a negative effect on the quality and quantity of fish and aquatic products. The high levels of nutrient in aquatic animal subject to eutrophic waters can be toxic if consumed by human beings (Chhatra, 2015). Reduced quality of fishery product and seafood is a consequence of bioaccumulation and the presence of algal toxins present in eutrophic water bodies.

Algae secrete organic metabolites with trace of toxic elements. Lakes and surface water are also considered as drinking water source in many countries. Direct consumption of eutrophic water or fisheries product from lakes and river can affect the health of people. And the presence of eutrophic condition is harmful to the established aquatic environment. The potential for human and animals to be exposed to toxins in water requires regular monitoring and enforcement of quality standards (Piotr and Barbar, 2014).

3.3.4 Health Risk of Eutrophication

Nutrient and organic pollutant flow to water sources through SR. Physical, chemical and biological aspect of water is changed due to organic load. Physical and chemical characteristics make the suitable condition for biological growth of coliforms, pathogens, and virus adding with high level of nutrient level in water (Kouassi et al., 2015). The water consumed form eutrophic water source can cause the water bone diseases in human health and loss of aquatic vegetation. Figure 4 shows; the invertebrates don't have suitable environment for survival. The eutrophic poisons also may affect people through bioaccumulation of small invertebrate fish and filter feeding fishes to bigger predatory fish and finally the consumption of those fish by humans. (Piotr and Barbar, 2014).

Intake of phosphorus in different form has adverse impacts on cardiovascular and bone health on human begins. Consumption level of Phosphorus varies according to age group of people for growth of tissue and bone. Although phosphorus is important nutrient for human tissue and bone, excess consumption for long period of time phosphorus could be connected to tissue damage. The increase consumption of industrial products adding up eutrophic water source could lead to health issue like cardiovascular diseases as well as impacting kidney function (Calvo and Uribarri, 2013). Calvo and Uribarri (2013) studied regular direct and indirect consumption of phosphorus can induce secondary hyperparathyroidism and bone loss.

4 Phosphorus Treatment Technologies

This chapter covers the physical, chemical and biological treatment method for phosphorus from municipal and industrial wastewater. This chapter aims to provide the general overview of phosphorus removal process.

4.1 Physical

4.1.1 Filtration for Particulate Phosphorus

The organic solids consist of 2-3 % of P (Strom, 2006). Filtrations process with granular media is used in water and wastewater treatment technology is used for removal of total suspended solid particles (Storm, 2006 & Tchobanoglous et al., 2003). Contact filtration process followed by chemicals for coagulation is highly efficient in removing the suspended solid particle, nutrients and stabilize the algae growth (Micheal et al., 1977).

4.1.2 Membrane Technology

Membrane bioreactor and reverse osmosis are suggested the current reliable membrane technology for removing phosphorus from total suspended solid. According to Strom (2006) the membrane technology also can remove the dissolved phosphorus from influent. Physical method of treatment is much more expensive than chemical and biological methods although the efficiency of removal of dissolved phosphorus is high (Jayawardana et al., 2015).

4.2 Chemical

Chemical treatment methodology for removal of phosphorus from water and wastewater treatment facilities has developed over a long period of time. The process involves the addition of compounds of calcium, aluminum and iron. Chemical are added on feed to primary clarifier and sedimentation clarifier (Minnesota Pollution Control Agency (MPCA), 2006). Sludge production increases by 40% and 26% in the primary treatment process and activated sludge plants respectively using the chemical treatment (Strom 2006, MPCA, 2006).

According to MPCA report, a dose of 1.0 mole of aluminum compound is sufficient per mole of phosphorus. The pH value plays another important role in removal for P using the aluminum or other salt compound. pH range from 5 to 7 and 6.5 to 7.5 for aluminum and ferric salt respectively is important to maintain of solution to stop precipitates to dissolve into solution. Aluminum compound makes it highly useable due to its less corrosive nature than ferric chloride.

Chemical treatment technique is mostly study method for and effective for removable of suspended and dissolved solid particles. However, the cost of chemical and sludge handling is expensive. The process is complex and the effluent quality is 0.05 mg/L of TSS particle (Storm, 2006 & Tchobanoglous et al., 2003).

Another chemical technique, Gas Concrete, was used to remove the phosphate from aqueous solution. The advantage of this process was its functioning capability at low pH and with the potential to recycle the recovered phosphate (Oguz et al., 2003).

4.3 Biological

Phosphorus removal from wastewater is obtained with natural biological process. Natural system uses phosphorus from wastewater back to natural cycle in environment. Natural systems are practiced in small wastewater production community and local system. Use of activated algae, growing of algae in small wastewater treatment plant helps to obtain 95 % of removal phosphorus from wastewater (Stanislaw, 1998). Constructions of artificial and natural wetland are practiced method for removal of phosphorus from wastewater. The advantage of this system is no additional sludge, low maintenance and cost. Wetland organism accumulates phosphorus and removal of phosphorus is low from wastewater. It is suggested to treatment before and after the water is passed through wetland for efficient removal of phosphorus (Levin et al 1965 and Stainslaw, 1998).

Enhanced Biological Phosphorus Removal (EBPR) process to activate the sludge system for removal of phosphorus with the effect of polyphosphate accumulating organism (PAO). The process is implement and efficient in anaerobic rather than aerobic digester (Metcalf & Eddy, 2003). This process has high potential of achieving 0.1mg/L of P level in effluent at modest cost and minimum sludge. The phosphate concentration in sludge produced from EBPR is 5-3% more than non-EBPR sludge (Storm, 2006 & Tchobanoglous et al., 2003). The Phosphate is accumulated within the cells of microbes. The biomass is separated from the digester, later the phosphorus accumulating microbes are processed and phosphorus is recovered. The cyanobacteria and microalgae shows dual role of bioremediations and recovery of phosphorus. Another effective effect of microbes is also identified having high bioremediation capabilities (Krishna, 2016). The wastewater sludge produced in EBPR is bulky and mostly contaminated with heavy metals, harmful pathogens and toxic substance which interferes with crops growth so, it is not recommended to use directly as agricultural fertilizer (Sartorius et al., 2012, and Yuan et al., 2012).

5 Sludge

This chapter includes the background information about the sludge production and composition. Sludge extraction process from waste and water treatment facilities and discuss the possibility use for sludge to fulfill future need demand of nutrients and artificial soil formation.

5.1 Sludge Source

United Nations Environment Programme (UNEP) indicates wastewater treatment facilities are the biggest source for sludge production. Increasing demand of water and production of high wastewater are main source for sludge production. Yan Wu et al., (2016) reported sewage sludge containing of 90% of water is increasing. Treatment facilities remove the solids particles from inflow wastewater to system. Sludge is produced in each step of water treatment facilities. Management of sludge in treatment facilities is one of the biggest issues in industrial and municipal water treatment plant. Human excreta, industrial waste are main solid component present in wastewater responsible for high organic and nutrients value in Sludge (Yan Wu et al., 2016). Present study shows that the sludge is produced also from treatment of storm water, which is less organic in compared to wastewater sludge (UNEP).

5.2 Sludge Composition

Sludge composition varies according to waste–water treatment plants according to different geographical location and treatment methodology. Protein, carbohydrate, lipid are organic component and inorganic compound like heavy metals are present in Sludge. Sludge is composed for 50-70% of volatile organic compound (VOC). Different nutrients are linked with protein and lipid chain. Sewage sludge can emit greenhouse gases if they are not properly treated (Meiyan et al., 2015). Vasiliki et al., (2016) reported 99 emerging organic contaminants (EOC) are present in sludge. After the chemical analysis for pharmaceuticals, it is observed contaminates like synthetic phenolic compounds, siloxanes, caffeine, per fluorinated compounds and toxic hydrocarbon. Presence of different organic component can alter the soil's microbial community and functioning. Presence of inorganic compound in sludge makes it favorable for fertilization (Eva et al., 2016).

Phosphorus is concentrated in dried sewage sludge is approximately 4 % of total mass and after the incineration of the sludge the percentage increases to 10 (EU, P-REX Policy). Hence, recovering the phosphorus from sludge has high potential.

5.3 Sludge Extraction Process

Municipal wastewater is mixture of human waste, debris, suspended solid particles and chemical waste from industries like paper and pulp, paints (Kouassi et al., 2016). Figure 5 describes the graphical representation on sludge extraction process in municipal wastewater and water treatment plant.

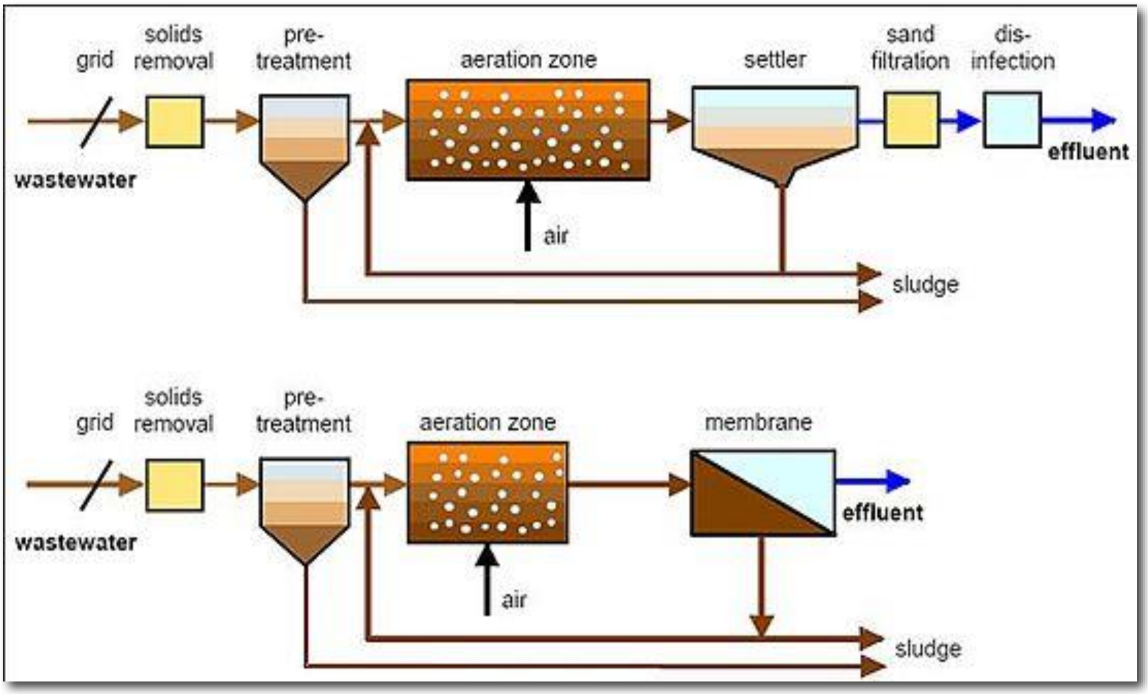

Figure 5. Flow diagram for sludge extraction process from Municipal Water Treatment Plant via activated sludge process and external membrane bioreactor. (A. Drew et al., 2005)

According to European Statistic the dry sludge produced per capita is 90gm (Meiyan et al., 2014). The composition of organic compound percentage is different in different stage. The volatile organic compound concentration in primary sludge (PS) is higher that digested sludge (DS) from anaerobic digester (Meiyan et al., 2014, Eva et al., 2016 and A. Drew et al., 2005).

5.4 Sludge Treatment

Sewage sludge undergoes the biological, chemical or thermal treatment to decrease effects of toxins, VOCs, other chemical release to environment. Sludge is treated using as nutrients in agricultural land to minimize the health hazard and bioaccumulation in food chain (FAO). Table 1 presents the effective sludge treatment processes in the United Kingdom (UK) before the sludge is used in agricultural field.

Table 1. Effective sludge treatment processes (Water Research Centre, 1989). It published on Second Edition of a 'Manual of good Practice on Soil Injection of Sewage Sludge'

Table 1. EFFECTIVE SLUDGE TREATMENT PROCESSES

Process	**Descriptions**
Sludge Pasteurization	Minimum of 30 minutes at 70°C or minimum of 4 hours at 55° C (or appropriate intermediate conditions), followed in all cases by primary mesophilic anaerobic digestion
Mesophilic Anaerobic Digestion	Mean retention period of at least 12 days primary digestion in temperature range 35°C +/- 3°C or of at least 20 days primary digestion in temperature range 25°C + /- 3°C followed in each case by a secondary stage which provides a mean retention period of at least 14 days
Thermophilic Aerobic Digestion	Mean retention period of at least 7 days' digestion. All sludge to be subject to a minimum of 55°C for a period of at least 4 hours
Composting (Windrows or Aerated Piles)	The compost must be maintained at 40°C for at least 5 days and for 4 hours during this period at a minimum of 55°C within the body of the pile followed by a period of maturation adequate to ensure that the compost reaction is substantially complete
Lime Stabilization of Liquid Sludge	Addition of lime to raise pH to greater than 12.0 and sufficient to ensure that the pH is not less than 12 for a minimum period of 2 hours. The sludge can then be used directly
Liquid Storage	Storage of untreated liquid sludge for a minimum period of 3 months
Dewatering and Storage	Conditioning of untreated sludge with lime or other coagulants followed by dewatering and storage of the cake for a minimum period of 3 months if sludge has been subject to primary mesophilic anaerobic digestion, storage to be for a minimum period of 14 days

5.5 Uses of Sludge

Different composition of organic and inorganic compound in sludge makes it valuable. The sludge from treatment plant is used as a nutrients fertilizer on soil for agricultural soil. Tiago et al., (2009) explained sludge deposition in agriculture land is less expensive method and also helps to improve the soil nutrient level. Levels of nutrient, organic compound and microbial activities have higher hazardous impact than benefit to soil with nutrients level (Vasiliki et al., 2016 and Tiago et al., 2009). The toxic elements level is observed before sludge is used for making agricultural soil according to standard of Council of the European Communities 196 directive No. 86/278/EEC. This directive prohibits the sludge disposal in agricultural land unless required level of different toxic, nutrient level is maintained (FAO, Agricultural Use of sewage sludge).

The reuse of sludge rather than depositing it to landfill reduces the negative impact on environment (Mohanned et al., 2016 and Meiyan et al., 2014). Meiyan et al (2014) reported dried sewage sludge is used as alternative feedstock for power generation via incineration. Hence this could be used for energy mitigation although there is the lack of knowledge for combustion value for dried sludge. The sludge is used for construction of road material and brink manufacturing (Mohanned et al., 2016). The presence of high organic matter in dried sewage makes high calorific value in sludge, which is used in incineration plant. The fly ash and industrial blast- furnace slags can contribute to cement manufacturing with reducing the CO_2 emission. The cement composition can be changed 10% of treated sludge, 85 % clinker and 5 % gypsum (Mohanned et al., 2016 and Raifu et al., 2012).

6 Methods and Possibilities for Recycling of Phosphorus from Sludge

This Chapter includes the possible method for recycling the phosphorus from sludge. The chapter is based literature review from research work around the globe. The data and methodology are based on the research papers that give overall view for the experimental procedure. The potential of recovering 15% phosphorus from Municipal sewage sludge was reported by Van Dijk et al N.D.

6.1 Polyphosphate Accumulating Microalgae and Cyanobacteria (Bio extraction)

Microalgae species like Chlorella sp., Scenedesmus Microalgae and Cyanobacteria species like Aphanothece sp., Spirulina sp., Arthrospira sp., and Phormidium sp, are used in removing the nutrients from the wastewater. Cyanobacteria are microorganism that grow and uptake inorganic phosphorus and store it within their cells as poly -P granules. Cyanobacteria and algae can cope with unfavorable conditions like salt stress, osmotic stress, UV-radiation and fluctuations of pH and temperature in the environment (Achbergerova and Nahalka, 2011; Ray et al., 2013). According to Ray et al., (2013), microalgae and cyanobacteria not only are used for P removal from wastewater but phosphorus in poly - P in their cell can be used the release the phosphorus to the soil as bio-fertilizer. Bio-fertilizer, releases of phosphorus depend upon the phosphorus- solubilizing organism (PSO) present in soil. PSO makes this process slow and steady making supply of phosphorus for crops reducing the excess supply of P and also reduced the loss because of the soil run-off.

According to the experiment performed by Krishna Ray 2016, West Bengal University, microalgae and cyanobacteria were used for soluble phosphorus in parboiled rice effluent and its remediation. 5 g biomass of 25 days old culture of cyanobacteria was cultured in 15-liter ml of effluents and incubated for 24 days at 28 °C under 12:12h light: dark condition. Poly-p was extracted and quantified from equal dry weight of cyanobacteria and microalgae cell after 24 days. The soluble phosphorus level was observed and recorded on interval of 3 days for 21 days. Data obtained was used for calculating the percentage removal of phosphorus from the effluent using confocal microscope and fluoresce to indicate the presence of polyphosphate. After 21 days, the microalgae and cyanobacteria was harvested and dried.

The biomass was weight from 5 g to 50 g after the bioremediation of effluent. 84mg of poly-p out of initial 175 mg of soluble phosphorus was obtained by average microalgae and cyanobacteria. Algae and cyanobacteria were observed under confocal microscope. The presence of polyphosphate was indicated by yellowish green fluorescence where as cell without poly -p emitted blue fluorescence. The percentage of recovery was 48 % and worth valve of €24 million in West Bengal only.

The biomass obtained from cyanobacteria and microalgae were mixed with 5 kg of non-sterile soil maintain pH of 7.13 in separate pots. Soil was also mixed with 575 mg of superphosphate and NPK (20:20:13). Soil decomposers degrade the biomass added to non-sterile soil and its poly-p reservoir is exposed. PSOs release the organic acid and phosphatases from poly - p reservoir, slow but steady increases of soluble P content in soil over 45 days. Figure 1 in Appendix 1 shows that the P is released from biomass from initial 10 days. The entire process is also depending on available of soil microbe to decay the microalgae and cyanobacteria (Ray, 2016).

The advantage of this technique can be applied to the wastewater produced after dewatering of sludge. Dewatering process is source of soluble phosphorus, organic compounds and toxic elements. Microalgae and cyanobacteria uptake poly - p granules under unfavorable conditions like acidic pH, temperature from wastewater. The biomass produced after harvesting microbes can be directly used in agriculture as bio fertilizer for crop growth.

6.2 Recovery Method of Phosphorus from Sewage Sludge Ash (SSA)

Sewage Sludge Ash is the form of slag and dust produced from thermal utilization (incineration) of sewage produced from municipal waste and water treatment plant. (KAtarzyna et al., 2016). The sludge- waste having phosphorus compounds present in form of insoluble phosphate have potential to be recovered and substitute for natural ore by thermal processing. Only in EU, 0.6 million tons of sewage sludge ash per year is produced which in counts 10-21% of whole sludge amount (Nowak et al., 2012). Different parameters of sludge must be taken into consideration while extracting the phosphorus and also is important to use appropriate method for recovery since, the chemical composition depends upon treatment method used in the water treatment plant. Coagulation agent changes the chemical composition used for phosphorus compound precipitation. The important parameter focused during the recovery methods is the presence of heavy metals (HM) (Gorazada et al., 2012 and Nowak et al., 2012).

The composition of SSA is dependent on the type of the thermal utilization used. The best available technology for incinerating sludge to recover phosphorus is in a fluidized bed technology and grate furnace technology. Gorazada et al., (2012) reported the disadvantage of incineration in fluidized bed is low temperature of 850 °C used that is high enough to eliminate the pathogen, organic compounds and stabilize the waste but iron present in sludge forms a calcium –iron phosphate, which make it recovery and handling process difficult. But at 950°C, iron contained in ash is converted into a hematite form that is insoluble in mineral acid (Gorazada et al., 2012). The methods of phosphorus recovery from SSA can be achieved from wet extraction and thermochemical methods.

6.2.1 Wet Extraction for Sewage Sludge Ash

Wet extraction method involves the leaching of SSA with acids and bases. The parameter to be considered during extraction process are type and concentration of acids and bases, pH values, detention time, and temperature on incineration temperature.

- ➔ Acidic leaching is performed with sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, critic and oxalic acid (Biswas et al., 2009 and Gorazda et al., 2012).
- ➔ Basic Leaching is done with Sodium Hydroxide (Biswas et al., 2009).
- ➔ Supercritical fluid extraction of ashes from supercritical water oxidation (Stark et al., 2006)

- ➔ Acid and Basic Leaching for SSA

Katartyna et al., (2016), reported the phosphorus recovery process with wet extraction method for acid take place within 2 h using of 2.7 mol dm^{-3}(HNO_3). Experiment was carried out in laboratory scale from samples obtained from incineration plant. Samples were continuously mixed in the reactor with constant velocity and continuous pH, temperature and phosphorus was determined. After 2 hours of extraction process the solutions and sediments were analyzed for metals and phosphorus using X-ray power diffraction. Phosphorus was determined using the spectrophotometric method and metal were determined atomic absorption spectrometry.

Result from Katartyna et al., (2016) suggest the phosphorus concentration was leached from ash to the solution during nitric acid extraction. Recovery phosphorus for different samples were obtained maximum with in 30 minutes of leaching. The factor affecting the leaching of calcium phosphate is concentration of nitric acid used or leaching and presence of iron and aluminum during coagulating in primary and secondary basin. The leaching is also affect by the sludge ash from different waste and sludge from different sources incinerated. The efficiency for extraction using SSA for fluidized bed technology was 3 times more efficient that grate furnace technology. 90% of phosphorus was recovered for some samples using nitric acid extraction. The greatest advantage of this technology is extracts can be used for fertilizer is crops production, the extracts contain high micronutrients and the level of heavy metals like mercury, arsenic, lead and cadmium were limited. Phosphorus extraction was varied depending upon the extraction acid and base and also dependent upon the SSA production from incinerated plant. The removal of phosphorus from SSA must take in account the method of waste and water treatment plants during chemical and biological treatment with iron and aluminum salt.

Table 2 compares the recovery method of phosphorus from sewage sludge ash using wet extraction methods using sulfuric acid, nitric acid, hydrochloric acid, potassium hydroxide, sodium hydroxide, calcium oxide and presents obtained product in form phosphorus compound.

Table 2. A comparison of Phosphorus Recovery from Sewage Sludge Ash with wet extraction method.

Methods (Chemical Used)		Principle	Obtained Product	Reference
Wet Extraction Methods	H_2SO_4 (Lab) (Pilot)	SSA leaches with Sulfuric acid that make extracted solution pH value of 1.5. Sodium hydroxide is used to neutralize the solution and the precipitation is formed of aluminum phosphate. Advanced method is used to separate the heavy metals by dissolution of $AlPO_4$ with NaOH. Extracts can also be treat-ed on ion exchange columns.	$AlPO_4$ $Ca_3(PO_4)_2$ H_3PO_4	Schaum et al. 2013 Donatello et al., 2010
	HNO_3, Phosphoric Acid	SSA is treated with nitric acid and phosphoric acid and leachate produced is treated with calcium oxide to produce calcium phosphate.	Calcium Phosphate	Calcium Phosphate
	HCL (Pilot)	8% Hydrochloric acid is used for leaching the SSA. Liquid- Liquid extraction using tri-n-butyl phosphate was used to obtained high phosphorus against iron recovery. Phosphorus precipitation was obtained form extraction solution.	Magnesium or calcium phosphate	Dittrich et al., 2009
	Acid Leaching (Lab)	Acidic leaching leads to phosphorus transformation of Aluminum - Phosphorus form. Treating the precipitate with basic extractant. Phosphorus compound is formed after basic treatment.	Calcium Phosphate	Petzet et al., 2012
	Basic Leaching (KOH and NaOH)	Treating SSA with basic (KOH and NaOH) Intermediate liquid fertilizer is obtained and final step the precipitation is treated with milk lime to produce liquid Potassium Phosphate and calcium phosphate.	Potassium Phosphate and calcium phosphate.	Spirit 21, 2007

Products produced from the wet exaction process are high phosphorus compound and solid residues. Solid waste recovered from the process can be used for construction material like cement factory due to presence of Gypsum. Gypsum sums 20% of composition for cement manufacturing. Solids residual after processing could be used for aggregates, micro-filers, special blends (Mohanned et al., 2016). The obtained phosphorus product from wet extraction are classified as solution fertilizer. This solution fertilizer can be used for agricultural purpose of crops growth and leaf sprays after neutralization process to pH 7. (Gorazda et al., 2016).

Factors affecting the efficiency of recovery depends upon source of the sludge, temperature for incinerating, residence time and temperature in the furnace effect the quartz structure of SSA. Heating the sludge for long time in high temperature leads to formation of quartz appearance which creates more resistant on the extraction because of lower surface area for contact with acid and base. As a result, the phosphorus remains in solid residue (Dittrich et al., 2009 and Gorazda et al., 2016).

The best and most popular extractant for wet extraction process are sulfuric acid and hydrochloric acid. Because of it low cost and high efficiency of removal of phosphate in leachate up to 99%, it is the most popular method (Biswas et al., 2009). The presence of heavy metal in SSA needs an additional treatment step which can be removed by methods like metal remover in form of sulphides via precipitation method, liquid-liquid extraction and as well as ion exchange. Using of acid for wet extraction process, by products like gypsum (Calcium chloride) is produced. Biswas et al., (2009) and Gorazda et al., (2012) reported the leaching efficiency is reduced by 30% if the extractant is used base. High dissolved phosphorus compound were obtained from extraction of acid and base, where as the solid residue was rich in hematite, quartz, magnesioferrite, Berlinite (Gorazda et al., 2012).

- ➔ Supercritical fluid extraction of ashes from supercritical water oxidation followed by Acid and base extraction

Acid and base extraction process is also applied on the residual produced from the Super Critical Water Oxidation to recover the phosphorus. Sludge incinerated by supercritical water oxidation produce the ash and residual with different property than normal incinerated Ash (Ginder et al, 2000). The Supercritical Water Oxidation reactions is performed at pressure of 275 bars and temperature between 400 and 600 °C. The advantage of incineration of sludge using super critical water oxidation method leads to loss of high percentage of organic material from sludge (Stark et al.,2006).

Experiment carried by Stark et al., (2006), SCWO residual was leached with acid, hydrochloric acid and base, sodium hydroxide. Experimental result suggests leaching with acid dissolves metals and phosphorus to form homogenous solution. Using the base extraction method, dissolves phosphorus product with low concentration of metal.

So the extraction of phosphorus could be achieved with high efficiency. The experiment was carried out from the ash and residual received from 4 different incinerating plant from Sweden. The Figures 6. presents the recover percentage of phosphorus from incinerated and SCWO residuals and Figure 7. Presents percentage of phosphorus leaching from SCWO residue using sodium hydroxide base.

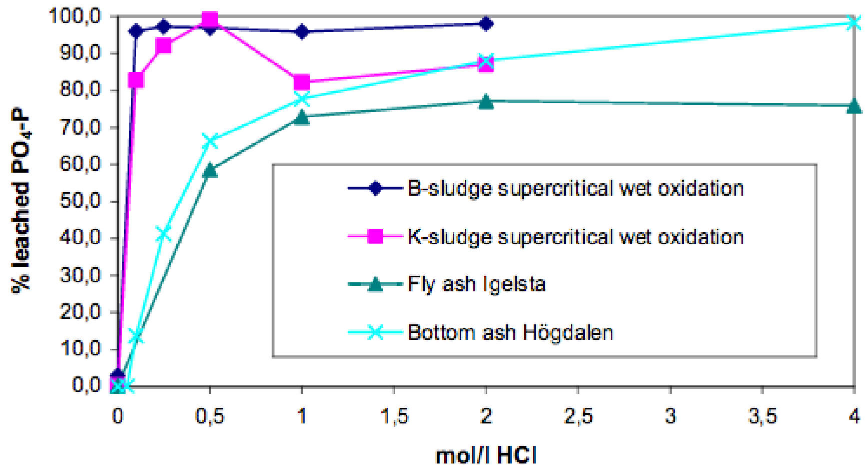

Figure 6. Recovered percentage of Phosphate from leaching ash and supercritical water oxidation residuals with HCL (Stark et al. 2006)

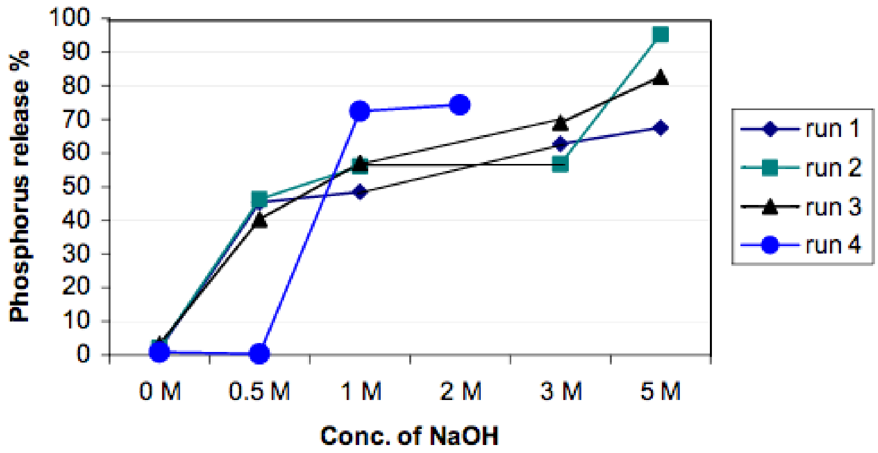

Figure 7. Recovery of Phosphorus from SCWO residual using NaOH (Stark and Hultman, 2003)

From figure 7. The sludge samples were taken from two different wastewater treatment plant. Run 1-3 was from Karlskoga and run 4 from Bromma Water treatment plant.

SCWO residual samples were leached with concentrated NaOH. Run 1-3 the optimum recovery was observed at 5 M and run 4 sample was observed at 2 M. The recovery percentage form figure 7 presents the relation between sludge type and revovery percentage.

The final recovery of phosphorus from leachate is precipitated with calcium addition. Stark and Hultman (2003) reported (figure 1 in Appendix 2) the increasing concentration of NaOH for precipitation can cause calcium iron or calcium aluminum and different species other than calcium phosphate. The best appropriate concentration for recovery of phosphorus is between 0.5 M and 1 M NaOH (Stark and Hultman, 2003).

Leaching percentage of Phosphorus is higher with acid than base as seen in the figures 6 and 7. The advantage of using the base in stead of acid is the low production of metal contamination of leaching and using base, the calcium binding capacity for phosphorus is higher and obtained product is in form of calcium phosphate, which can be used as fertilizer directly after neutralizing. The disadvantage of using the base is decrease phosphorus recovery from leachate with increasing concentration of base.

6.2.2 Thermo Chemical Methods for Phosphorus recovery from Ash

Thermo chemical method involve use of SSA mixed with chlorine and water. The mixture is presses to form pellets. Pellets are heated to melting point temperature of ash in reactor. The temperature of mixture is maintained 900-1050 °C that results for formation of volatile metal chloride and bioavailable form of phosphorus compound in ash. All the organic residuals are destroyed due to high temperature. All metal chloride formed due reaction of chlorine donor compound and heavy metals evaporates and makes the ash decontaminated (Nowak et al. 2010, Jingyong et al., 2015).

Nowak et al., (2010) reported 92% Cadmium, 83% Cupper and 22% Zinc was eliminated from the contaminated sewage sludge ash using calcium chloride. The disadvantage of this system is recovery of heavy metals from gas cleaning system. The experiment performed by Nowak et al., (2010) suggests factor affecting the removal of heavy metal from SSA are temperature, longer resident time, concentration of chlorine and high gas velocity. Amount of additional chlorinating agent increases the removal rate of heavy metals and removal depends upon the type of chlorinating agent. Magnesium chloride and calcium chloride have high chlorinating capacity for volatilization of heavy metal than sodium chloride (Jingyong et al., 2015).

The obtained product from this method are ash with high concentration of calcium and phosphorus concentration. Obtained ash can be used as a raw phosphate rock substitute since phosphorus compound is in bioavailable form. After removal of heavy metal from the sludge, can be used directly to agricultural. The removal of organic due to high temperature makes ash composition with high phosphorus percentage. Mixing of ash and natural phosphorus mixture highly feasible for manufacturing phosphoric acid (Hideaki and Masaru 2015, Nowak et al., 2012).

6.3 Nanofiltration

6.3.1 Nanofiltration in Diafilration Mode

Phosphorus recovery during nanofiltration process is performed from pretreated sewage sludge. Heavy metals are removed from the solution using nanofilters and phosphorus was recovered from the permeate solution. The process is totally depending upon the type of sludge, pH of pretreated sludge and pressured applied for filtration. Therese et al., (2015) reported diaflitration system would increase the yield of phosphorus. The experiment performed by Therese et al., was a laboratory scale.

This is an experimental procedure for recovering the Phosphorus according to Therese et al., (2015).

Initially, sewage sludge was pretreated to dissolve the phosphorus and heavy mental present in sludge suitable for nanofiltration. Sludge was diluted with 33% of deionized water per 100 ml sludge. Sulphuric acid is added 1.5ml per 100 mL of sludge to maintain pH of 1.5. Acidic condition was maintained to dissolve phosphorus into solution and this also result for dissolving of heavy metals. The leachate produced from addition of acid was separated and coarse filtration followed by ultrafiltration was performed to remove the solid particles. The leachate and solution obtained after coarse filtration was used for nanofiltration experiment. The composition of permeate was determined by triplicating analysis with coupled plasma optical emission spectrometry. The permeate had 820 mg/L of phosphorus concentration.

The experiment was carried out to compare the different nanofiltation membrane. The cross flow velocity was set to 1.6m/s, temperature to 20 °C and pressure was change from 5 -15 bar to identify the effect on separation. All the parameters for the experiment were controlled. After the single phase filtration, permeate was collected until the retentate volume was reached to 120 ml, 50% from Initial volume. The retentate volume was diluted to initial volume of feed, pH was maintained using sulfuric acid to 1.5. the process was repeated 3 times and permeate was collected and analyzed. The membranes were dried at 105 °C for a day and analyzed using scanning electron microscope for phosphorus concentration and heavy metals. Plasma optical emission spectroscopy was used for determining the concentration of phosphorus in permeate.

Therese et al., (2015) reported nanofiltration in difafilration achieved up to 85% of phosphorus recovery. Metal retention valve in membrane increase with lower pH than 1.5, decreasing the phosphorus recovery. The method of recovery for phosphorus have high investment cost and expenses for chemicals.

6.3.2 Low Pressure Wet Oxidation and Nanofiltration

The recovery of phosphorus is done through sludge samples from WWTP. Phosphorus is recovered from sludge with wet oxidation extraction process and nanofiltration. Insoluble phosphorus is dissolved by wet oxidation process using acid and nanofiltration system was used for separation.

The procedure for recovering of phosphorus was experimented by Christoph et al., (2012).

Sludge samples were allowed to settle for 24 hours for achieving certain thickening to determine the concentration of solids. Experiment was performed in titanium lined batch reactors of 10 L volume of gas injection stirrers. Reaction time was set to 1-4 hours, 4-6 L sludge was used and 160-200 °C was maintained. Sulphuric acid was used for maintain pH of 2. The sludge was heated in the reactor.

The effluent from reactor was passed through the cooling line dropping effluent temperature to 30 °C, suspended solid particles were separated using ceramic ultra filtration with transmembrane pressure difference of 2.1 bar, cross flow velocity of 4m/s. Permeate was used for nanofiltration for recovery of phosphorus.

Analysis of phosphorus concentration was performed using spectroscopic method. The recovery percentage from this method as reported by Christoph et al. (2012) is 54% in average.

6.4 Comparison of recovery methods

The main purpose of this thesis was to identify and determine the possiable technique for recycling of phosphorus from sludge. The recycling of phosphorus is done through different process such as bio extraction, wet extraction, SCWO and nanofiltration. Table 3. Illustrates a comparison of all methods presented in this thesis in terms of efficiency, time, limiting agents as well as advantage and disadvantages of methods.

Table 3. Comparison of Phosphorus recovery methods.

Method	**Agents**	**Samples**	**Phosphorus recovery (%)**	**Limiting Factors**
Bio - Extraction	Algae and Cyanobacteria	Water from Dewatering of Sludge	45-50 48(Average)	Level of inorganic P in Solution
Wet Extraction process	Acid	Incinerated sludge (SSA)	80 - 90*	Concentration of acid and based followed by calcium oxide for precipitating phosphorus in form on calcium phosphate, Metal /phosphorus ratio in SSA
	Base		50 - 70*	
	Acid	SCWO residual (SSA)	80- 95* 90♣(Calcium Precipitation)	
	Base		50 – 90* 98♣ (Calcium Precipitation)	

* Percentage of released phosphate from Leaching Ash
♣ Percentage recovery of P using calcium precipitation from leachates solution

♣ Percentage recovery of P using calcium precipitation from leachates solution

Nanofiltration	Diafilration Mode	Pretreated Sludge	78 -90♥ 84(Average)	pH of solution, percentage of water in sludge and type of membrane used for filtration.
	Low pressure wet oxidation	Sludge	54♥	

In order to select the appropriate method for recovering the phosphorus from sludge it is also important to understand the cost and timing required for different experiment.

Table 4 presents the advantage and disadvantages of experimental processes presented in this thesis.

Table 4. Advantage and disadvantage of method for recycling phosphorus from sludge.

Method	Advantage	Disadvantage
Bio- extraction	Algae and Cyanobacteria Combat unfavorable condition like salt stress, osmotic stress, UV radiation, pH. Method is Inexpensive.	The recovery time is long and totally depends upon micro organism. The PAO are important for discharging to soil.
Wet Extraction	Phosphorus recovery time from leachate is low. Incinerating waste with sludge reduces waste for landfill and recovery percentage of phosphorus is high.	The recovered phosphorus compound needs further treatment before utilization for agricultural purpose or commercial purpose. The method is expensive since heavy metals are also needed to be treated.
Thermochemical Process	High percentage removal, low recovery time of 2 hours, zero waste produc-	Necessary of flue gas cleaning system for heavy metal. Expensive method

♥ Phosphorus recovered in soluble form in permeate

	tion.	to implement system and chemicals requirement.
Nanofiltration	Recovered phosphorus of high purity, low retention time.	Expensive method for recovering, Membrane fouling, Separate handling of rejected flow for heavy metals.

7 Possible Uses for Recycles Phosphorus and the Side Products

This chapter includes the possible use areas for recycled phosphorus from sludge. Phosphors recovered from extraction process are mainly used for agricultural and personal products like detergent, manufacturing of phosphoric acid. The chapter also focused on the uses of side products generated, which is raw material for industrial process like construction industry.

7.1 Agricultural Fertilizer

Krishna (2016) reported use of polyphosphate granule accumulation by microalgae and cyanobacteria can directly used in agricultural field as source of phosphorus for crops production. The role of PSOs plays an important role for utilization recovered phosphorus from dried microalgae and cyanobacteria. In addition to fertilizer, microalgae and cyanobacteria play a role for bioremediation and recovery of phosphorus which was wasted due to uncontrolled use of artificial phosphorus fertilizer. Biomass produced can be used as bio-fertilizer for crop growth. The advantage of using poly-p biomass obtained from sludge is slow release of phosphorus at constant rate to the commercial fertilizer that discharge phosphorus rapidly after used in agriculture land.

The precipitation obtained from wet extraction of sludge can be used for crops growth after neutralization. Liquid calcium phosphate obtained form basic wet extraction of SSA is good fertilizer with ability to neutralize the acidic soil (Biswas et al., 2009). Ash produced after thermochemical method is a source for high calcium and phosphorus concentration that is suitable to substitute for raw phosphate (Nowak et al., 2012). The phosphorus obtained from nanofiltration can be used directly for as solution fertilizer (Christoph et al., (2012).

7.2 Construction and Industrial Applications

SSA is composed of oxides, metals, and quartz structure. Silicon oxide, Aluminum oxide, calcium oxide, ferrous oxide, magnesium oxide and phosphorus pent oxide are main component of SSA. Clinker, Limestone and gypsum are three main components for composition of cements. Dried sludge ash from incinerating of sludge is used for manufacturing of mortar, Gypsum component like silicon oxide, calcium oxide present in SSA makes it favorable for cement manufacturing and brick industry. Gypsum from SSA can contribute to 20% of raw material for cement industry (Mohanned et al., 2016). The advantage of using the SSA for cement and concrete include reduction of waste disposal costs, conservation of environment limiting to landfill.

The mixture of dried biomass of algae and cyanobacteria with non-sterile soil can be used reclaim infertile soil for construction of parks and agricultural fields. Phosphate rock and recycled phosphorus from sludge are used for producing phosphoric acid.

Phosphorus is important element for detergent industry. Detergent with phosphorus shows better performance in removing stain from cloths as well as region where hard-water is as main source of water. Hardwater minerals interfere with the cleaning capacity. Phosphorus allows the cleaning agent in detergent to perform better as catalyst. Recycled phosphorus used in detergent industry reduce load of dependency on phosphate rock and also contribute for combat he eutrophication (Bryan, 2010).

8 Discussion

The wet extraction and SCWO method for recovering phosphorus from SSA is efficient with high percentage recovery compared other methods. The electrochemical method of recovery has a different procedure of removal of heavy particles without affecting the concentration of phosphorus in ash. The factors effecting electrochemical methods are controlled temperature above 900 °C for incinerating sludge ash and chlorine compounds. Nanofiltration method has high efficiency of producing pure phosphorus. Although the experiments were conducted in from different researches in controlled environments, the percentage of phosphorus recovery showed a large amount of variation. This variation was observed due to different sources of sludge used for experimental procedure. It is important to consider the sludge production method from waste and water treatment facilities to determine the recovery of phosphorus from sludge.

The availability of only few costly methods for recycling of phosphorus does not encourage for many countries to adopt them although this method may show high potential for fertilizer production. Another important issue to be considered is the cost of the process, which depends upon material, labor and transport expenses.

9 Conclusion

On the basis of results shown in Table 3, it can be concluded that wet extraction form incinerated and SWCO residues and nanofiltration in diafilration can be effective methods for recovering P from sludge. The methods of incinerating and pretreating sludge have a high impact on the recovery percentage of P from different methods. It can be concluded from published results that the wet extraction process is affected by the metal/phosphorus ratio and the concentration of acid and base applied as the extractant. Although the leaching rate of phosphors increases with a higher concentration of acid and base, treating with calcium oxide to precipitate calcium phosphate decreases because of the formation of an iron calcium phosphate compound that has a low value in market and needs further treatment to recover the phosphate compound.

The general aim of nanofltration and thermochemical process is to separate phosphorus from heavy metals, to recover phosphorus for other applications. Recycled phosphorus from nanofiltration methods has high purity and can be used directly into agriculture and production of consumer products like detergent, packaging. This makes nanofiltration methods highly reliable for recycling to fulfil the future demand. Heavy-metal-, pathogens- and organic-hydrocarbon-free ash from thermochemical method is directly useable for growing crops without further treatment.

Use of recycled phosphorus reduces the dependency on raw phosphate rocks, ensures food security, decreasing the adverse effect on health and environment because of eutrophication. Recycling of phosphorus is possible only with sustainable development and policy regarding the use of phosphate-rich waste management. Use of recycled phosphorus decreases the dependency upon the natural limited nutrient. By-products from sludge have an impact on industrial development. Recycling of phosphorus reduces the eutrophic condition of the aquatic environment, which leads to limiting bioaccumulation in aquaculture and fishery. In addition, recycling phosphorus decrease dependency on countries like Morocco, China and USA for phosphorus, which are main producer country for phosphate rock.

References

Achbergerova, L., and Nahalja, J., 2011, Pilyphophate: an ancient energy source and active metabolic regulator, Microb cell Fact, 10: 63

Akpor O.B., Kayode- O.I and Banbalola O.O., 2015, Effect of Carbonated Dead Biomass of a non- Edible Mushroom on Nutrient Adsorption from Wastewater and Aqueous Solution, International Journal of Basis And applied Chemical Scieces Vol 5(3): 79-91.

A. Dews, H. Evenblij, S.Rosenberger., 2005, Potential and drwbacks of microbiolody-membrane interaction in membrane bioreactors, Environemtnal Progress 24(4): 426-433

Andrew N. Sharpley, S.c. Chapra, R. Wedepohl, J.T Sims, T.C Daniel and K.T. Reddy., 1994 Managing Agricultural Phosphorus for Protection of Surface Waters: Issues and Options, Journal of Environmental Quality, Vol.23 No. 3, 437- 451.

B. Manimaram, V. Ramadhas, R. Santhanam., 1997, Role of sewage phosphorus in coastal water energy production, Indian Journal of Geo-Marine Sciences 29(4):1326 - 1329.

Biswas BK, Inoue K, Harada H, Ohto K Kawakita H., 2009, Leaching of phosphorus from incinerated sludge ash by means of acid extraction followed by adsorption on orange waste gel, Journal of Environmental sciences 21: 1753-1760

Bryan Walsh., 2010, Water, raking the phosphate out of detergent leaves a cleaner planet- but are the Dishes dirtier Ecocentric. Online Available on [http://science.time.com/2010/10/27/water-taking-the-phosphates-out-of-detergent-leaves-a-cleaner-planet%E2%80%94but-are-the-dishes-dirtier/]

Christoph Blöcher, Claudia Niewersch, Thomas Melin., 2012, Phosphorus recovery from sewage sludge with a hybrid process of low pressure wet oxidation and nanofiltration, Jouranal of Water Research, 46: 2009-2019.

Chhatra M Sharma., 2015, Can Bio-Manipulation Be related to fisheries and Aquaculture through Environmental Pollution Perspective?, Fisheries and Aquaculture, School of Science, Kathmandu University.

Cordell D., Jan-Olof D., Stuart W., 2009, The Story of Phosphorus: Global Food Security and Food for thought, Journal of Globat Environmental Change 19:292-305

Cordell D., White S., 2011, Peak Phosphorus; Clarifying the key issues of a vigorous debate about long term phosphorus security, University of Technology Sydney, Sustainability, 3(10), 2027-2049; doi 10.3390/su3102027 [http://www.mdpi.com/2071-1050/3/10/2027]

Cordell D. and Stuart Bruce White., 2014, Life's Bottleneck: Sustaining the World's Phosphorus for a Food Secure Future, Annual Review of Environment and Resources 39 (1): 161-188

Daniel J Lang, Claudia Binder, Danube W. Scholz., 2011, The trade-off between Phosphorus Recycling and Health Protection during the BSE Crisis in Switzerland. A "Disposal Dilemma".

Daniel M. Blackburn, Philip Haygarth., 2015, B53K-01: Opportunities for optimizing te Phosphorus Cycle in The Land- Water Continuum (Invited), Conference Paper, Lancaster University, San Francisco, USA.

Eva Loret, Jose A Pascual, Eoin L. Brodie, Nicholas J. Bouskill, Heribert Insam, Marina Fernandez-Delgado Juarez, Marta Goberna., 2016, Sewage Sludge addition modifies soil microbial communities and plant performance depending on the sludge stabilization process, Journal of Applied Soil Ecology 101:37-46.

Ginder A., Almemark M., Stenmark L. and Östengren Ö., 2000, Treatmemt of sewage sludge by supercritical water oxidation. IBC's 6th Annual Conference Paper, London UK, 16-17

Gorazda K, Kowalski Z, Wzorek Z., 2012, From sewage sludge ash to calcium phosphate fertilizers, J of Chemical technology 14: 54-58.
Grogory Mullins, Phosphorus, Agriculture & The Environment, Virginia Tech University, Virginia, USA.

H. M. C. M. Jayawardana, D. M. S. H. Dissanayaka, P. P. U. Kumarasinghe, M.I.M Mowjood., 2015, Phosphorus Removal from Wastewater using Soil as an Adsorbent, Conference; Water professionals' Day.

Helen P Jarvie, Paul Withers., 2006, Risk of River Eutrophication that Agricultural Phosphorus? , Journal of Science of the Total Environment, 360: 246-253

Hau-Peng Qin, Soom-Thiam Khu & Chang Li., 2014, Water exchange effect on eutrophication in landscape water body supplemented by treated wastewater, Urban water Journal, 11:2, 108-115.

Hochschule Vechta., 1990, Phosphorus Fractions in soils from an area with high density of livestock population, Journal of Plant Nutrition and soil sciences, 159(3): 251 -256.

Jian Liu, Peter J. A. Kleinman, Douglas B.Beegle, Jennifer L. Weld, Andrew N. Sharpley, Lou S. SAporito, John P. Schmidt., 2015, Phosphorus and nitrogen losses from poultry litter stacks and leaching through soils, Nutrient Cycling in Afroecosystems, Vol 103, Issue 1, 101-104.

Jingyong Liu, Jiacong Chen and Limao Huang., 2015, Heavy metal removal from MSS fly ash by thermal and Chlorination treatments. Scientific Reports 5, doi:10.1038/srep17270

Jonathan J. Cole, Nina F. Caraco, And Gene E.Likens., 1990, Shortrange Atmospheric transport: A significant Source of Phosphorus to an oligotrophic lake. Limnol Oceanogr, 35(6): 1230 - 1237.

Katarzyna Gorazda, Barbara Tarko, Z. bigniew W. Zorek, Anna K. Nowak, Joanna Kulczycka, Anna Henclik., 2012, Phosphorus cycle- Possibility for its rebuilding. Acta Biochimica Polonica.

Katarzyna Gorazda, Barbara Tarko, Zbigniew WZorek, Anna K. Nowak, Joanna Kulczycka, Anna Henclik., 2016, Characteristic of wet methods of Phosphorus recovery from polish sewage sludge Ash with, open Chem., 14: 37-45.

Kouassi Jullen Mornou, Chantal Akou-Koffi, Karim Sory Traore, Djako Sosthene Akre, Mireille Dosso., 2016, Effects of rainfalls variability and physical-chemical parameters on enterovirus in sewage and laggon in Yopougon, Cote d'Ivoire, Appl water Science

Krishna Raj., 2016, Phosphorus recycling from an Unexplored Sources by Polyphosphate Accumulating Microalgae and cyanobacteria- A step to Phosphorus Security in Agriculture, Frontiers in Microbiology.

K. Ray, C. Mekherjee, A.N. Ghosh., 2013, A way to curb Phosphorus toxicity in the environment; use of polyphosphate reservoir of cyanobacteria and microalgae as a safe alternative phosphorus biofertilizer for Indian agriculture, Environmental Science Technology, 47: 11378-11379.

Levin G. V. Shapiro J., 1965, Metbolic uptake of phosphorus by wastewater organisms, Journal of Water Pollution Control Federation 37.

Micheal Kavanaugh, Jakob Eugster, Anton Weber and Markus Boller., 1977, Contact Filtration for Phosphorus Removal, J. Water pollution control federation, 49 (10): 2157-2171.

Meiyan Li, Benyo Xiao, Xu Wang, Junxin Liu., 2015, Consequences of sludge composition on combustion performance derived from thermogravimetry analysis, Waste Management 35: 141-147.

Minnesota Pollution Control Agency., 2006, Phosphorus Treatment and Removal Technologies, wq-wwtp9-02

Metcalf & Eddy., 2003, Wastewater Engineering: Treatment and reuse, Boston: Mcgraw - hill p.624

Nowak B., A. Pessl, P. Aschenbrenner, P. Szentannai, H, Mattenberger, H. Rechberger, L. Hermann, F. Winter., 2010, Heavy metal removal from Municipal solid waste fly ash by chlorination and thermal treatment, Journal of Hazardous Materials,

Nowak B., Rocha SF., Aschenbrenner H, Winter F., 2012, Heavy metal removal from MSW fly ash by means of chlorination and thermal treatment: Influence of the chloride type, Journal of Chemical Engineering, 179: 178 -185

Oguz, E., A. Gurses and N. Canpolat., 2003, Removal of Phosphate fro wastewaters, Cement & Concrete Research, 33: 1109-1113.

Peter J. A Keinman, Ann M. Wolf, Andrew N. Sharpley, Douglas B Beegle and Lou S. Saporito., 2004, Survey of Water- Extractable Phosphorus in Livestock Manures, Soil Sciences Society of America Journal, Vol. 69 no. 3, 701-708.

Peter F. Strom., 2006, Technologies to Remove Phosphorus from Wastewater, Professor of Environmental Sciences, Rutgers University.

Piotr Rzymski and Barbara Poniedzialek., 2015, Blue-green algae blooms: environmental and Health consequences, Causes, Economic Implications and Future Challenges, 155-182.

Rafiu Olasunkanmo Yusuf, Zainura Zainon Noor, Moh'd Fadhil Moh'd Din, Ahmad H. Abba., 2012, Use of sewage sludge ash (SSA) in the production of cement and concrete – A review, J of Global Environmental Issuses 12: 214 – 228

SPIRIT21., 2007, sewage technology development Project (Lotous Project), Zero Sludge Discharge technology, Technology Evaluation concerning Phosphorus Recovery from sewage sludge incinerator ash. Online Available on [nett21.gec.jp/rerss/reports/rp02.pdf]

Stainislaw. M. Rybicki., 1998, New Technologies of Phosphorus removal from wastewater. Online Available on [rymd.lwr.kth.se/forskningsprojekt/Polishproject/JPS3s121.pdf]

Stark K. and Hultman B., 2003, Phosphorus Recovery by one- or two step technology with use of acids and bases, Conference Paper Bio solid 2033 Wastewater sludge as a resource, 281-288.

Stark K, Plaza E, Hultman B., 2006, Phosphorus releases from ash, dried sludge and sludge residue from supercritical water oxidation by acid or base, Journal of Chemosphere 62: 827-832

S.B Sartious, J.V Horn, F. Tettenborn., 2012, Phophorus recovery from wastewater-Expert Survey on present Use and Future potential, Journal of Water Environment. 84: 313 - 322

Therese Scühtte, Claudia Niewersch, Thomas Wintgens, Suleyman Yüce., 2015, Phosphorus recovery from sewage sludge by Nanofiltration on diafiltration mode, J of Membrane Science, 480: 74-82

Tan Z, Lagerkvist A., 2011, Phosphorus recovery from biomass ash, Renew Sust Energy Rev 15:3588 -3602.

Tiago Natal-da-Luz, Serena Tidona, Bruno Jesus, Paula V. Morais, Jose P. Sousa., 2009, The Use of Sewage sludge as soil amendment. The need sore an Eco toxicological evaluation, J of Soil Sediment 9: 246 - 260

Tyagi VK, Lo SL., 2013, Sludge: A waste for renewable source for energy and resources recovery? Renew Sustain Energy 25: 708 – 728.

United Nations Environment Program, Bio-solid Management: An Environmentally sound Approach for Managing Sewage Treatment Plant Sludge, Freshwater Management Series No. 1 [Online Available on: http://www.unep.or.jp/ietc/publications/freshwater/fms1/2.asp]

Van Dijk, K. C., Lesschen, J. P and Oenema, O., N. P, Phosphorus flows and balanve of the European Union Member states.

Vasiliki S. Thomaidi, Athanasios S. Stasinakis, Viola L Borova, Nikolaos S. Thomaids., 2016, Assessing the risk associated with the presence of emerging organic contaminants in sludge- amended soil: A Country- Level Analysis, Sciences of total Environment 548-549; 280-288.

Yi liu and Jining Chen., 2004, Evalution of phosphorus flows in the Dianchi Watershed, southwest of China, Population and Environment 25(6): 637-653

Yan Wu, Panyue Zhang, Haibo Zhang, Guangming Zeng, Jianbo Liu, Jie Ye, Wei Fang, Xiying Gou., 2016, Possibility of sludge conditioning and dewatering with rice husk biochar modified by ferric chloride, Journal of Bio Resource Technology 205: 258-263.

Yuan Z, Pratt S, and Batstone D.J., 2012, Phosphorus recovery from wastewater through microbial Processes, Biotechnol, 23: 878-883

Apendix 1. Recycled polyphosphate as substitute to phosphorus fertilizer (Ray et al., 2016)

(A)

Source of P	Form of P present in the source	Accumulated polyphosphate present in mg per gm of dry cell biomass	Amount of P source added to the soil (mg kg^{-1})	Amount of different P form present in the P source added to the soil (mg kg^{-1})	Amount of P actually added to the soil (44% of P_2O_5) (mg kg^{-1})	Amount of maximum P release in the soil at Day 45 (mg kg^{-1})	
						Zone 1 (2- 4 cm depth)	Zone 2 (8- 10 cm depth)
Chlorella sp. isolate 10.2	Polyphosphate[b]	1.71	400[c]	0.9	-	18.25	32.31
Cyanobacterium sp. isolate Fardillapur	Polyphosphate[b]	3.05	400[c]	1.1	-	21.77	37.22
Lyngbya sp. isolate 2.1	Polyphosphate[b]	1.14	400[c]	0.5	-	25.28	38.07
Anabaena sp. isolate A2C2	Polyphosphate[b]	0.82	400[c]	0.22	-	13.05	18.96
Superphosphate[a]	P_2O_5	-	115	115.0	50.19	15.72	23.03
NPK (20-20-13)[a]	P_2O_5	-	115	23.0	10.04	17.41	36.10

[a] Chemical fertilizers added as per recommended dose to the soil.
[b] Polyphosphate is present in dry cell biomass of the organisms.
[c] P source represents the dry cell biomass of the organisms.
Data given here represents the average data of 10 replicate experiments.

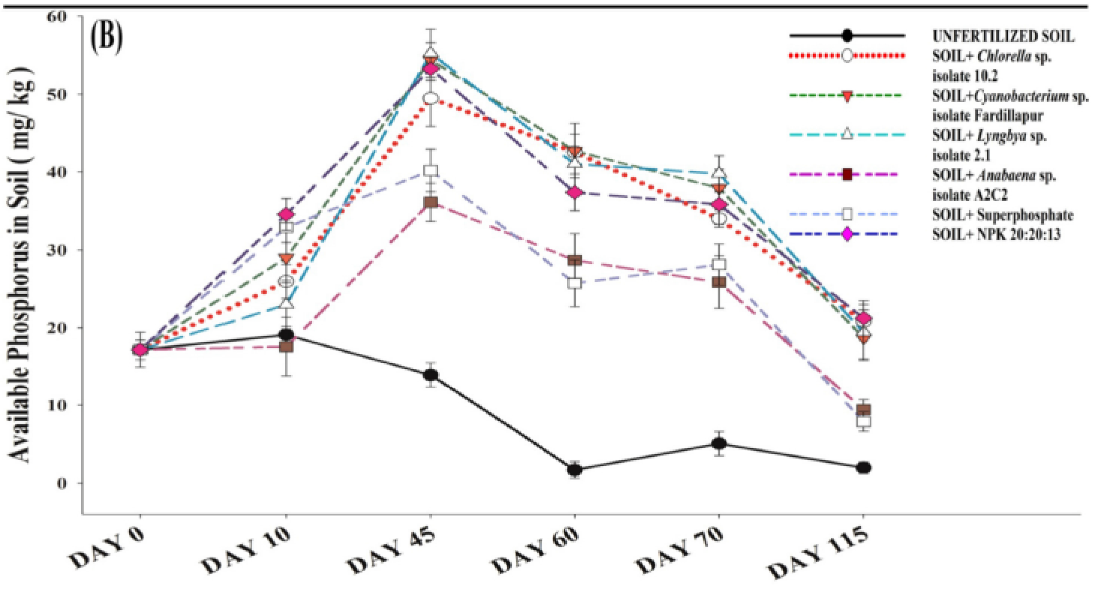

Figure 8 Recycled polyphosphate as substitute to phosphorus fertilizer. (A)Table showing the rate of conversion of polyphosphates accumulating by microalgae and cyano-bacteria into soluble phosphorus and comparison of its release to conventional chemical phosphorus fertilizer. (B)Polyphosphate releases soluble phosphorus at a comparison but slower rate with recommended dose of superphosphate and NPK. All the points of gragh represent the average data of 10 replicate.

Appendix 2. Wet Extraction for SWCO residual

Result of phosphorus recovery by precipitation from leachate with calcium under different concentratiosd of NaOH(Stark and Hultman, 2003)

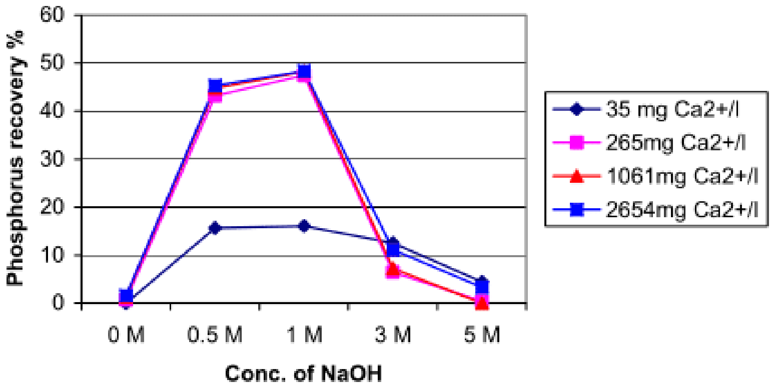

Figure 9. Recovery of phosphorus by precipitation from leachate with calcium under different concentration of NaOH