REUSE OF ALUM SLUDGE FOR PHOSPHORUS REMOVAL FROM MUNICIPAL WASTEWATER

By

Nida Maqbool

(2010-NUST-MS PhD-Env E-02)

Institute of Environmental Sciences and Engineering (IESE)
School of Civil and Environmental Engineering (SCEE)
National University of Sciences and Technology (NUST)

Islamabad, Pakistan
(2012)

REUSE OF ALUM SLUDGE FOR PHOSPHORUS REMOVAL FROM MUNICIPAL WASTEWATER

By

Nida Maqbool

2010-NUST-MS PhD-Env E-02

A thesis submitted in partial fulfillment of
the requirements for the degree of

Master of Science

In

Environmental Engineering

Institute of Environmental Sciences and Engineering (IESE)
School of Civil and Environmental Engineering (SCEE)
National University of Sciences and Technology (NUST)

Islamabad, Pakistan
(2012)

It is certified that the contents and form of the thesis entitled

"REUSE OF ALUM SLUDGE FOR PHOSPHORUS REMOVAL FROM MUNICIPAL WASTEWATER"

Submitted by

Nida Maqbool

has been found satisfactory for the requirement of the degree of

Master of Science in Environmental Engineering

Supervisor: ______________
Dr. Zahiruddin Khan
Associate Professor
IESE, SCEE, NUST

Member: ________________
Dr. Sher Jamal Khan
Assistant Professor
IESE, SCEE, NUST

Member: ________________
Dr. Muhammad Ali Awan
Assistant Professor
IESE, SCEE, NUST

External Examiner: ________________
Dr. Muhammad Zubair
Professor
GCU, Faisalabad

DEDICATION

This thesis is dedicated to my Father **Maqbool Ahmad Ch.** He did not only raise and nurture me but also taxed himself dearly over the years for my education and intellectual development. He has been a source of motivation and strength during moments of despair and discouragement. He has always taught me that diligence and perseverance are the keys to success.

DECLARATION

I hereby declare that I (Nida Maqbool) am the sole author of this thesis and that this work has not been published anywhere else before. This is a true copy of the thesis, including any final revisions, as accepted by my examiners.

Nida Maqbool

MSEE-15

ACKNOWLEDGEMENTS

I thank the Great Allah for blessing me with courage to accomplish my task of research work and thesis writing. It is all because of Holy Prophet (PBUH) who showed us the path of learning.

I feel great pleasure in expressing my sincere gratitude to my respected supervisor **Dr. Zahiruddin Khan** (Associate Professor, IESE, SCEE, NUST). By his continuous assistance, support and valuable suggestions for my research work I am able to complete my thesis. I am highly indebted to my GEC members **Dr. Muhammad Ali Awan** (Assistant Professor, IESE) and **Dr. Sher Jamal Khan** (Assistant Professor, IESE) for their support throughout this research work. I am also grateful to my external examiner **Dr. Muhammad Zuber** (Professor, GCU Faisalabad).

Last but not least, my deepest gratitude goes to my beloved parents; **Maqbool Ahmad Ch.**, **Mrs. Yasmeen Maqbool** and also to my Brother **Jahanzeb Ahmad Maqbool** and **Sisters** for their endless love, prayers and encouragement. To those who indirectly contributed in this research, your kindness means a lot to me. Thank you very much.

Nida Maqbool

Table of Contents

APPENDICES

LIST OF ABBREVATIONS

ASTM	American Society for Testing Materials
ATP	Adenosine Triphosphate
BOD	Biological Oxygen Demand
BPR	Biological Phosphorus Removal
CP	Condensed Phosphorus
DNA	Deoxyribo Nucleic Acid
EBPR	Enhanced Biological Phosphorus Removal
GAOs	Glycogen Accumulating Organisms
MBR	Membrane Bioreactor
MGD	Million Gallon per Day
MWW	Municipal Wastewater
MWWTF	Municipal Wastewater Treatment Facility
OP	Ortho Phosphorus
PAOs	Phosphorus Accumulating Organisms
PHA	Phyto Hem Agglutinin
RAS	Rawal Alum Sludge
RNA	Ribo Nucleic Acid
RO	Reverse Osmosis
SAS	Simli Alum Sludge
SHMP	Sodium Hexa Meta Phosphate
SRT	Sludge Retention Time
VFA	Volatile Fatty Acids
WWT	Wastewater Treatment

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Municipal wastewater (MWW) is mostly rich in nutrients such as phosphorus (P), nitrites (NO_2^-), nitrates (NO_3^{2-}) and ammonium (NH_4^+) etc. When discharged into water bodies, MWW cause algal growth resulting into eutrophication leading to taste and odor problems in drinking water supplies. P can be removed by chemical and biological processes but such processes are either costly or time consuming. Potable water supply facilities use alum for turbidity removal. The settled and dewatered alum sludge from water treatment facilities can effectively be used to remove P from MWW. In this study Orthophosphorus (OP) and Condensed phosphorus (CP) are taken as model pollutants as they were commonly found in MWW.

Mojor objective of this work was to evaluate the effectiveness of waste alum sludge from various sources to remove P from MWW at optimum dose, mixing time and pH. Alum sludge was collected from two water treatment plants namely Rawal water treatment plant and Simli water treatment plant. Batch experiments were performed to determine P removal under equilibrium conditions i.e. sludge mass, contact time, pH and initial concentration. The maximum adsorption capacity (Q_o) for Simli sludge was found to be 4.5 mg/g at 12g/L dose and 90 min contact time at 25 ± 2^{o}C. For Rawal sludge Q_o was 1.53 mg/g at 30g/L dose and 80 contact time at 25 ± 2^{o}C. Experimental data were fitted on two adsorption isotherms models i.e. Langmuir and Freundlich adsorption isotherm to evaluate the P removal phenomenon by alum sludge. Langmuir adsorption isotherm was best fit (R^2=0.99) while experimental data were less favorably fitted to Freundlich isotherm model. Results showed that pH significantly affect adsorption capacity and better removal is achieved in acidic range (pH 4.0-5.5). This study concluded that P removal was achieved by waste alum sludge through this cost effective and resource reuse method. Thus, reducing environmental hazards and burden of large quantities of waste alum sludge.

Nida Maqbool

Chapter 1

INTRODUCTION

Water is the basic necessity for all types of lives existing on the earth. It is evident from the history that human being always settled near the water sources. Water is under assault by numerous types of pollution from centuries since the evolution of mankind. Industrial development from engineering to medicine in the post World War II era drastically increased water pollution. Industrial, commercial and household wastewater often finds level found their way to water bodies. In 1960's the water pollution due to phosphorus bearing detergents was given due attention and the use of such detergents was banned.

In the nineteenth century the general awareness of wastewater treatment and disposal came under consideration due to the tremendous growth in population and industrial revolution. In Britain, the principle employed was dilution is the solution to pollution. So, the wastewater was conveyed and discharged into water bodies untreated resulting in catastrophic situation of the water reservoirs. Thus water treatment was considered the only solution. In 1925 the concept of BOD was initially introduced and method of determination was given for the wastewaters. These methods were then followed in most of the countries around the world and are considered as the pioneer in wastewater (Streeter and Phelps, 1925).

The practice of removing heavy particles from wastewater is not new. Since centuries, pits and sedimentation basins are being used for this purpose until secondary treatment was regulated by clean water act in 1972. Secondary treatment removed organic compounds by the utilization of already present micro organisms. Attached growth and suspended growth are the most common mechanisms for secondary wastewater treatment (Metcalf and Eddy, 2003). With the greater understanding of impacts of wastewater on all living creature, environment and water bodies, the standards of wastewater were made more and more stringent. In addition to organics, nutrients such as N and P required removal to meet treated wastewater standards.

Thus, advanced biological and physico-chemical treatment came into being for excessive nutrients removal from wastewater before they are sent to water reservoirs. Particular attention was given to phosphorus (P) and nitrogen (N) present in wastewater.

P is the second most abundant element on earth. It is found naturally in soil and rocks. P is an essential nutrient for the growth of plants, animals and humans as it is the key to energy. In soils deficient of phosphorus it is provided in the form of fertilizers for enhancing the growth plants. Phosphorus was used as binder in the synthetic detergents.

With the extensive uses of the above mentioned products, the runoff and municipal wastewater had a very heavy amount of phosphorus in them. When such water enters the fresh water bodies, phytoplankton consumes more phosphorus and plants grow rapidly particularly on the surface i.e., algal bloom sets in. So, the plants beneath the surface die. These dead plants are consumed by bacteria. Large fraction of oxygen in the water is taken up by the bacteria and this result in decreased population of more aquatic animals like fish. Due to fish mortality and increased bacteria, the water quality is decreased resulting in unpleasant taste and odor problems in potable waters. This makes water body look aesthetically unpleasant, restrict recreation and promote eutrophication.

Phosphorus removal can be achieved through a variety of process that includes chemical as well as biological phosphorus removal. In case of biological phosphorus removal phosphorus accumulating organisms (PAOs) accumulate phosphorus and use it as source of energy and during cell synthesis. As a result up to 30% of initial phosphorus removal can be accomplished. In biological phosphorus removal less amount of sludge is produced but more capital cost is involved. The process of phosphorus removal by organisms is too complex and the achievement up to real low levels is not in every case (Helness and Odegaard, 2001).

1.1 Phosphorus Removal Strategies

Phosphorus removal by addition of chemicals includes coagulation and precipitation through metal salts of iron and aluminum. This process assures removal up to lowest levels but the foremost drawback is the cost of chemical involved in addition to large quantity of the sludge produced that is difficult to handle (Metcalf and Eddy, 2003). On the basis of the pros and cons observed in the above mentioned processes, new techniques are to be established to address the problems associated. Adsorption has been identified as the appropriate solution to the problem by various researchers (Bubba, *et al.*, 2003; Bashan, *et al.*, 2004; Georganatas, *et al.*, 2005; Xiaohong, 2005; Mortula, *et al.*, 2007; Babatunde, *et al.*, 2009; Mohammad and Rashid, 2012)

Adsorption is the process by which pollutant from liquid or gaseous phase gets deposited either physically or chemically on the surface of another material that is in contact with the pollutant in liquid or solid phase. In this process the material which is being deposited is called adsorbate and the responding material, on which the pollutant is accumulated, is called Adsorbent. Adsorption is the widely known as vital option for the removal of nutrients from wastewater. For this purpose various materials have been tested like fly ash; red mud; slag; iron oxide tailing, activated alumina and various synthetic ion exchange resin etc. (Yang *et al*., 2006). The successful removal of the phosphorus is highly dependant on the properties of the adsorbent (Mohammad and Rashid, 2012).

Withdraw of phosphorus also depends upon the charge present on the adsorbent used. Divalent and trivalent cationic adsorbents are considered as excellent materials for P removal. Therefore, aluminum-based residuals (i.e., alum sludge) are a viable option for being an effective phosphorus removal material. Alum is typically effective in phosphorus removal in chemical precipitation process (Aguilar *et al.*, 2002). Therefore, use of alum sludge can be effective for phosphorus removal as well. Air-dried alum sludge has also been attempted in limited manner by some researchers with success (Kim *et al*., 2003). However, the use of waste material (alum sludge) not only provides low-cost appropriate technological alternative for small-scale applications but also reduce hazard and cost related to the disposal of large amount of alum sludge.

1.2 Objectives

The main objective of this research work was to use alum sludge from various drinking water treatment plants as low cost adsorbent to remove phosphorus from municipal wastewater. To achieve the goals bench scale experiments were carried out. The specific objectives of the study were:

1. To determine of the efficiency of dewatered and oven dried alum sludge for removing phosphorus from municipal wastewater.
2. To study of the effects of various conditions like dose, contact time, pH and initial concentration on the percentage removal of P
3. To characterize sludges from various sources and determine their elemental composition.

1.3 Significance of the study

a) Cost effectiveness

Phosphorus (P) is most commonly removed by the use of chemicals all over the world. The problem can be resolved easily by the use of alum sludge which is considered as waste.

b) Two sided benefits

Accomplishment of OP removal is amicable by this cost effective and resource reuse method. Thus reducing environmental hazards and handling related issues of huge amount of alum sludge.

Chapter 02

LITERATURE REVIEW

2.1 Phosphorus in Wastewater

Wastewater or contaminated water is a big environmental challenge all over the world. Municipal wastewater comprises of sewage coming out of residential areas, small enterprises and sometimes storm water runoff. It contains a number of contaminants coming from washing, flushing and other manufacturing processes. Heavy amount of nutrients like nitrite, nitrate and phosphates are contained by wastewater. These elements are necessary for plants growth in the receiving waters. Micro organisms utilize such nutrients found in wastewater for biological treatment but their required quantity is very less as compared to that found in wastewater. So, these excessive amounts of nutrients should be removed through proper treatment.

Phosphorus is a macro-nutrient that is necessary to all living cells. It is a limiting nutrient with regard to growth of algae and plants in lakes. Due to the unique chemical properties of phosphates and its importance in cell structure it is an essential part of Adenosine Triphosphate (ATP), Phospholipids and Nucleic acids like DNA and RNA. Phosphorus act as energy transfer medium in cells so it is the fundamental element distinguishing between living and non living parts of the biosphere. Phosphate also serves as an intermediary in metabolism. Under natural conditions concentration of phosphorus in aquatic systems is well balanced because accessible mass of this constituent is close to the requirements of the ecological system (Mohammed and Rashid, 2012).

Phosphorus can exist in various phosphate species, which are classified as orthophosphates, condensed phosphates, and organic phosphates. Phosphorus in the natural water environment occurs almost solely in the ortho- phosphate form. Orthophosphate is of significant concern because it is not only the most abundant form of P in water and wastewater, but also is the form that can be immediately utilized by organisms (APHA 2005). Micro organisms like bacteria utilize phosphorus in the form of orthophosphate for the generation of solid phase structures like organic phosphates.

2.2 Phosphate Cycle

Phosphorus (in the form of phosphate) is an essential nutrient and energy carrier on many different levels of life, and a key element in mediating between living and non living parts of the biosphere as shown in Fig 2.1.

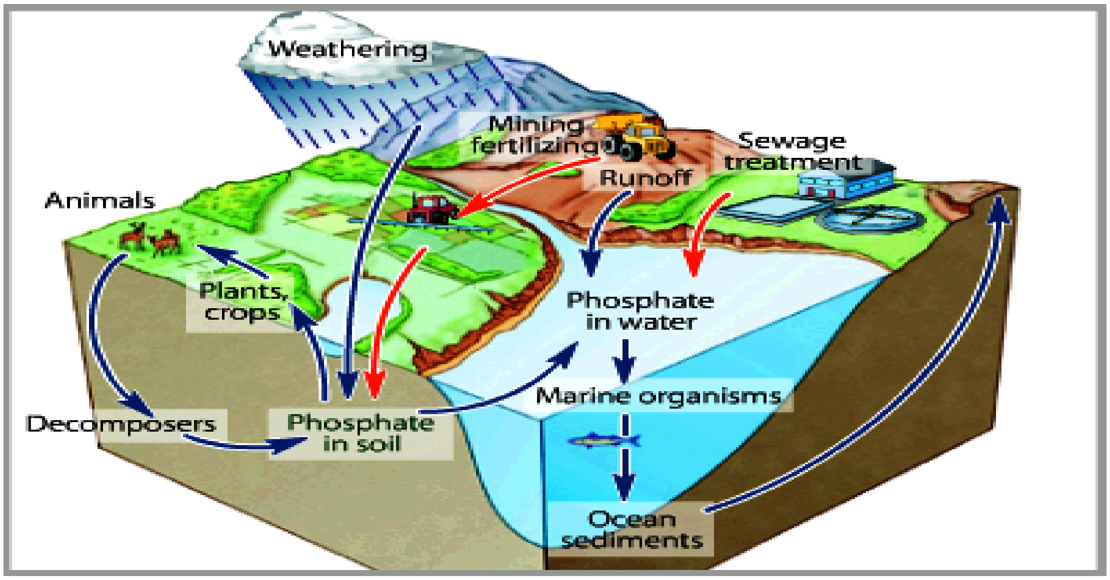


Figure 2.1 Phosphate Cycle

(http:// sumanasinc.com/webcontent/animations/content/phosphorouscycle.html)

Phosphorus enters naturally into our environment through weathering of igneous and sedimentary rocks. Volcanism especially in association with the formation of apatite-bearing carbonatites constitutes l-2% globally and locally up to 20-30% of P_2O_5. In such areas where this weathering affects, phosphorus is stored in soil profile as impermanent resource. This phosphorus becomes available to the plants and is utilized and finally converted and stored in organic phosphorus from (Fdlmi. 1996).

When Phosphorus is taken away from rocks and soils through the natural processes like weathering and leaching, it is transferred through running water to water bodies like oceans, rivers and lakes Phosphate is not transferred through atmosphere; instead it has a sedimentary cycle. So, lakes are important phosphate sinks. Phosphate cycle is interrupted by human activities like mining and fertilizing. These activities add extra phosphates to the environment which is finally added to lakes and rivers and upsetting the natural cycle (Fdlmi. 1996).

2.3 Phosphate Sources

The phosphorus load to surface waters is mainly due to discharge of wastewater and fertilization of the soil. The share of nitrogen and phosphorus is not equal, i.e., 1 kg of phosphorus contributes as much as 10 kg of nitrogen. According to a study 23% phosphate originates from human, 11% from detergents, 32% from livestock, 17% from fertilizers, 7% from industry and 10% from background sources (Morse *et al*., 1993).

Sewage contains phosphates from human sources, about 2 g P/capita/day, detergents, food waste, food additives and other products. Phosphorus excreted by human being has been estimated at 0.5-2.7 g P/capita/day, with the yearly mean comes out to be 1.6 g P/capita/day. A study was conducted on the contribution of soap and detergents toward phosphate concentration in sewage wastewater and it had been determined to be 0.3 g P/ person /day (Reddy, 1998).

2.4 Impacts of Phosphate

In natural conditions the nutrients concentration in water is balanced, i.e., the accessible mass of this constituent is close to the requirements of the ecological system. Under natural systems, fresh water bodies have low level of nutrients and they are called as oligrograhic, while old one having high amount of nutrients present are named as eutrophic. Mesotrophic is the term used in which water body is in transition state between oligotrophic and eutrophic. Naturally eutrophication takes place in thousand of years and is irreversible process. Human development, land required for residence and agriculture enforced men to cut down trees to clear areas increased eutrophication drastically. Due to higher input of nutrients (Carbon, Nitrogen and Phosphorus) plants grow excessively reducing the water body's quality. Eutrophication was given attention in late 1940's and 1950's by science sector (Harper. 1991).

Eutrophication can be defined as —"*the enrichment of waters by nutrients and the consequent deterioration of quality due to the luxuriant growth of plant life, and its repercussions on the ecological balance of the waters affected*" (Yeoman *et al*., 1988).

When eutrophication takes place, the high concentrations of nutrients in water bodies promote the growth of algae and aquatic plants. Eutrophication is basically the excessive growth of plants due to photosynthesis. The reaction is as follows:

$$CO_2 + \text{Nitrogen} + \text{Phosphorus} + H_2O \xrightarrow[\text{Photosynthesis}]{\text{Sunlight}} \text{Algae} + O_2 \qquad \ldots\ldots\ldots\ldots 2.1$$

Eutrophication can be reduced only by limiting the above reaction. CO_2 and water cannot be limited so the way to control the process is to lower the nutrients (nitrogen and phosphorus) concentration (Porcella. 1974).

It is made clear by studies conducted earlier that Blue green algae termed as Cynobacteria are the organisms that fixes nitrogen from air found in molecular form thus they don’t need nitrogen from water bodies coming in the form of ammonium and nitrate. Hence, lowering phosphate is the most possible objective to achieve for the reduction of eutrophication (Lee *et al*., 1978).

The consequential bloom of algae and aquatic plants can eliminate the dissolved oxygen from the water body to create hypoxia (DO level < 2 mg/L). It often results as water quality degradation, death of aquatic life, odor and taste problems, and poison effects generated by algae to fish and even livestock (Yeoman *et al*., 1988). The enormous damage to ecological, health and economic values due to eutrophication of various water bodies has become a serious issue in recent decades.

2.5 Forms of Phosphate in Wastewater

Phosphorus is present in water and wastewater solely as phosphates. Different forms of phosphorus are classified according to their chemical composition (organic versus inorganic) or physical properties (soluble versus insoluble) (Arceivaa and Asolekar, 2007) such as

- Organic phosphorus is the form of phosphorus found in living organisms, attached with detritus particles.
- Inorganic phosphorus is the mineral form of phosphorus found in rocks and soils.
- Soluble phosphorus is all type of phosphorus including colloidal that can pass out of 0.45 µm pore size filter.
- Insoluble phosphorus is that colloidal form phosphorus that cannot pass through 0.45 µm filter.

There are three main classifications of phosphates based on the chemical composition:

a) Orthophosphates: PO_4^{3-} , HPO_4^{2-} ,H_2PO^{4-} ,H_3PO_4
b) Polyphosphates: complex molecules with multiple phosphorus atoms
c) Organic phosphates

Total phosphorus is the measure of phosphorus in all its forms. The most commonly found inorganic form of P is orthophosphate. Other forms of dissolved inorganic phosphorus include condensed phosphates such as pyro-, meta- and polyphosphates.

Organic phosphate must be converted back to an inorganic form via mineralization in order to be usable by higher plants. Humus and organic matter will decompose to release

HPO_4^{2-} or $H_2PO_4^-$, depending on pH (Stumm and Morgan. 1981). In solution, the principle inorganic species are related by the pH-dependent dissociation series:

$H_3PO_4 \leftrightarrow H_2PO_4^- + H^+$ Ka = $10^{-2.2}$ ………… 2.2

$H_2PO_4 \leftrightarrow HPO_4^{2-} + H^+$ Ka = $10^{-7.2}$ …………. 2.3

$H_2PO_4 \leftrightarrow PO_4^{3-} + H^+$ Ka = $10^{-12.3}$ …………. 2.4

When pH is in between 5.5 and 7.4 $H_2PO_4^-$ and HPO_4^{2-} are the anions that are present significantly. $H_2PO_4^-$ decreases as pH increases as it exist in acidic environment while HPO_4^{2-} is more dominant in slightly basic conditions as demonstrated by Figure 2.2.

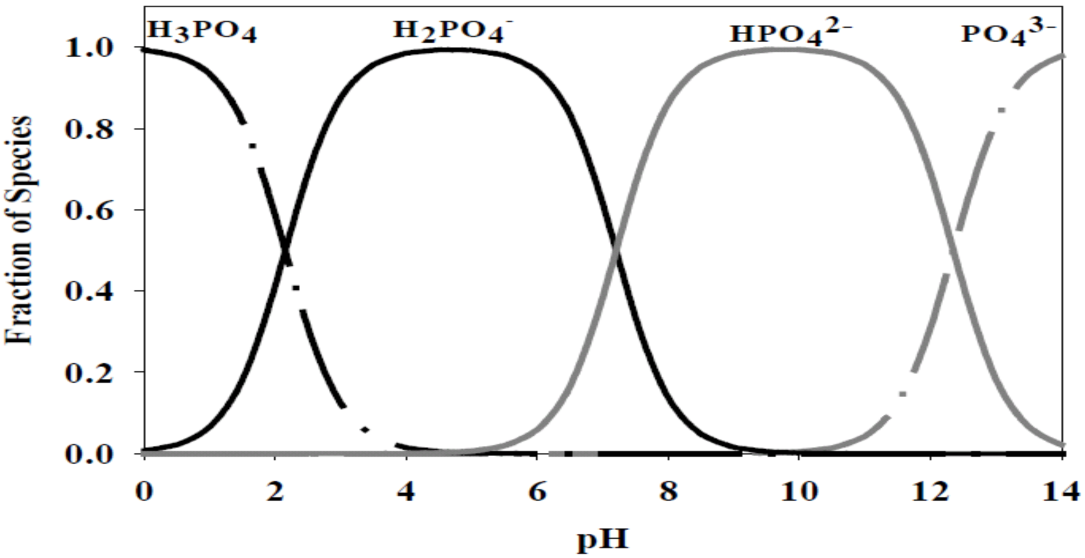


Figure 2.2 Phosphate Forms at various pH

2.6 Regulations on Phosphate Reduction

One of the major issue from decades regarding water quality is eutrophication of water bodies. It is caused by excessive nutrients loading due to anthropogenic sources created by human (Conley *et al.*, 2009). According to World Resources Institute there are 415 coastal zones in the world where oxygen level is too low to be required by existing aquatic life in the water bodies. In fresh water bodies this condition is alarming as 54% of lakes in Asia, 53% in Europe, 48% in North America, 41% in South America and 30% in Africa being identified as eutrophic (World Resource Institute, 2012).

There is dire need of lowering phosphorus found in water bodies, so relative regulatory framework is required for setting up some standard for phosphorus. Phosphorus standards differ from place to place (Conley *et al.*, 2009; Jiang *et al.*, 2005). Standard of phosphorus for MWW is only made by some developed countries and rarely in developing countries. Moreover, the current phosphorus removal methods (either chemical or biological) used in MWWTF are complex, extremely expensive, consume large amounts of energy and generate large volumes of sludge that then must be appropriately disposed off (Jiang *et al.*, 2005).

Phosphorus discharge criteria for other point and nonpoint pollution sources (agricultural, industrial, or residential onsite wastewater treatment systems and septic systems) are not included in the current wastewater regulations. This situation is extremely alarming given the exponential growth of population, livestock and food production. For example, 30-40% of the population in developed countries relies on septic systems consisting of a septic tank and a drain field. A hundred years ago, soil drain fields were considered natural adsorbing materials for phosphorus. However, the phosphorus retention capacity of any adsorbing material is finite and once it’s reached, the material needs to be replaced. The situation is much more disturbing in developing countries, where semi urban settlements are not approved by the local and national governments. As a result, many rivers in third world cities are being used as large open sewers (Westholm *et al*., 2011).

Since 1970 removal of phosphorus is becoming increasingly important. Although phosphorus is present in is present in low concentrations but its release to the water bodies is of environmental significance (Georgantas and Grigoropouou, 2005). Significant removal of phosphorus from wastewater is mandatory but it is not followed by many countries (Bashan and Bashan, 2004). In Pakistan's regulatory framework phosphorus is not given worthy importance yet to have its own standard for municipal and liquid industrial effluent.

The absence of authentic legal structure diminishes funding and the aspiration for scientific advancements for phosphorus removal technologies. Phosphorus removal using sorbents is of great interests now days. Such treatment can be used in onsite WWTP (Westholm *et al*., 2011).

2.7 Phosphorus Removal Technologies

Since gaseous forms of phosphorus are limited, phosphorus must be converted to a particulate (solid) form and removed as such from the wastewater (nitrogen components can be removed as N_2). Orthophosphate, the most abundant phosphorus species, is a reactive species in chemical reactions and can be consumed in biological growth. Organic phosphorus can be converted to both orthophosphate and polyphosphate (Reddy, 1998).

This literature review briefly explains that phosphorus can be removed from wastewater using a lot of processes like natural, physical, biological and chemical. The main list of the processes is as under:

- 2.7.1 Natural processes
- 2.7.2 Physical processes
    - i. Filtration for particulate phosphorus
    - ii. Membrane technologies
- 2.7.3 Biological Processes
    - i. Biological phosphorus removal (BPR)
    - ii. Enhanced biological phosphorus removal (EBPR)
- 2.7.4 Wetlands
- 2.7.5 Chemical Processes
- 2.7.5.1 Precipitation of Metal Salts
    - i. Iron Phosphorus Precipitation
    - ii. Alum Phosphorus Precipitation
    - iii. Calcium Phosphorus Precipitation
    - iv. Magnesium Phosphorus Precipitation
- 2.7.5.2 Adsorption
    - i. Cement clinker
    - ii. Slag

iii. Zeolite

iv. Alum Sludge

2.7.1. Natural process

Primary treatment of wastewaters removes 5-15% of the phosphorus which is associated with particulate matter. Conventional biological treatment removes up to 10-25% of phosphorus (Bitton G., 2005). Stoichiometric composition of micro-organisms and the composition of the wastewater is such that 20 to 30% of inlet phosphorus is removed by normal assimilation, i.e. stoichiometric coupling to microbial growth (Riding *et al.*, 1979). Phosphorus removal in sludge may also be the result of natural simultaneous precipitation, if cations such as Ca, Fe, Al, Mg and Zn are present.

Advantages

- Natural processes are cheapest
- No need of treatment and supervision

Disadvantages

- Reduces only limited amount of phosphates in wastewater
- Need of further treatment

2.7.2 Physical processes

1. *Filtration for particulate-P*

Solid particles found in wastewater have phosphorus attached to them. In biological treatment plants P content is higher. Thus, sand and gravel filtration and some other separating techniques like membrane and chemical precipitation helps reducing phosphorus. But, this method don’t reduces P up to the required concentration for reducing eutrophication (Storm. 2006).

2. *Membrane Technologies*

Membrane technologies for WWT are of increasing trend in general and for P recently. In addition to removing the P in the TSS, membranes also can remove dissolved phosphorus. Membrane bioreactors (MBRs), which incorporate membrane technology in a suspended growth secondary treatment process), tertiary membrane filtration (after secondary treatment), and reverse osmosis (RO) systems have all been used in full-scale plants with good results. According to a study on phosphorus removal through MBR reported that several plants are achieving <0.1 mg/L TP in their effluent, and suggested the current reliable limits of technology are 0.04 mg/L for MBRs and tertiary membrane filtration, and 0.008 mg/L for RO (Storm. 2006).

Advantages

- Highest level of phosphates removal is achieved.
- Most reliable method of phosphate treatment.

Disadvantages

- High capital, operational and repairing cost.
- Strict supervision needed.

2.7.3 Biological processes

1. *Biological Phosphorus Removal (BPR)*

For the biological removal of P in wastewater certain types of micro organisms exists like phosphorus accumulating organisms (PAOs) that preferentially uptake phosphorus present in soluble form in water. The mixed liquor is sent to anaerobic and then to the aerobic reactor. PAOs uptake/assimilate VFA (Volatile Fatty Acids) resulted in the fermentation occurring in the anaerobic digester. PAOs use the assimilated VFA as energy source in the aerobic reactor and assimilate Phosphorus thus reducing the amount of phosphorus in wastewater. In BPR systems, phosphorus accumulates in the biomass and is removed in the form of waste-activated sludge (Thomas. 2008).

2. *Enhanced Biological Phosphorus Removal (EBPR)*

EBPR is a wastewater treatment based on the selective enrichment of bacteria accumulating inorganic polyphosphate as an ingredient of their cells. It involves microbial metabolic cycling via several microbial-accumulated biopolymers (polyphosphate, PHA, and glycogen) (Bashan and Bashan. 2004). This metabolic cycling is induced in microorganisms by alternating the incubation conditions of the wastewater by:

- Initially carbon-rich, strictly anaerobic incubation (no oxygen or nitrate are present)
- Followed by carbon-poor, aerobic incubation.

EBPR activated sludge has a reputation of variable performance due to the competition between the growth of PAOs (Phosphorus accumulating organisms) and GAOs (Glycogen accumulating organisms). The key factor in the competitive growth is specific type of VFA found in influent of the bio reactor. The PAOs use Propionate more eagerly for their growth while the GAOs are more consented toward the presence of acetate. So, the secret to achieve reliable EBPR is to ensure the adequate supply of Propionate or an alternative substrate such as molasses that can readily fermented to Propionate (Thomas. 2008).

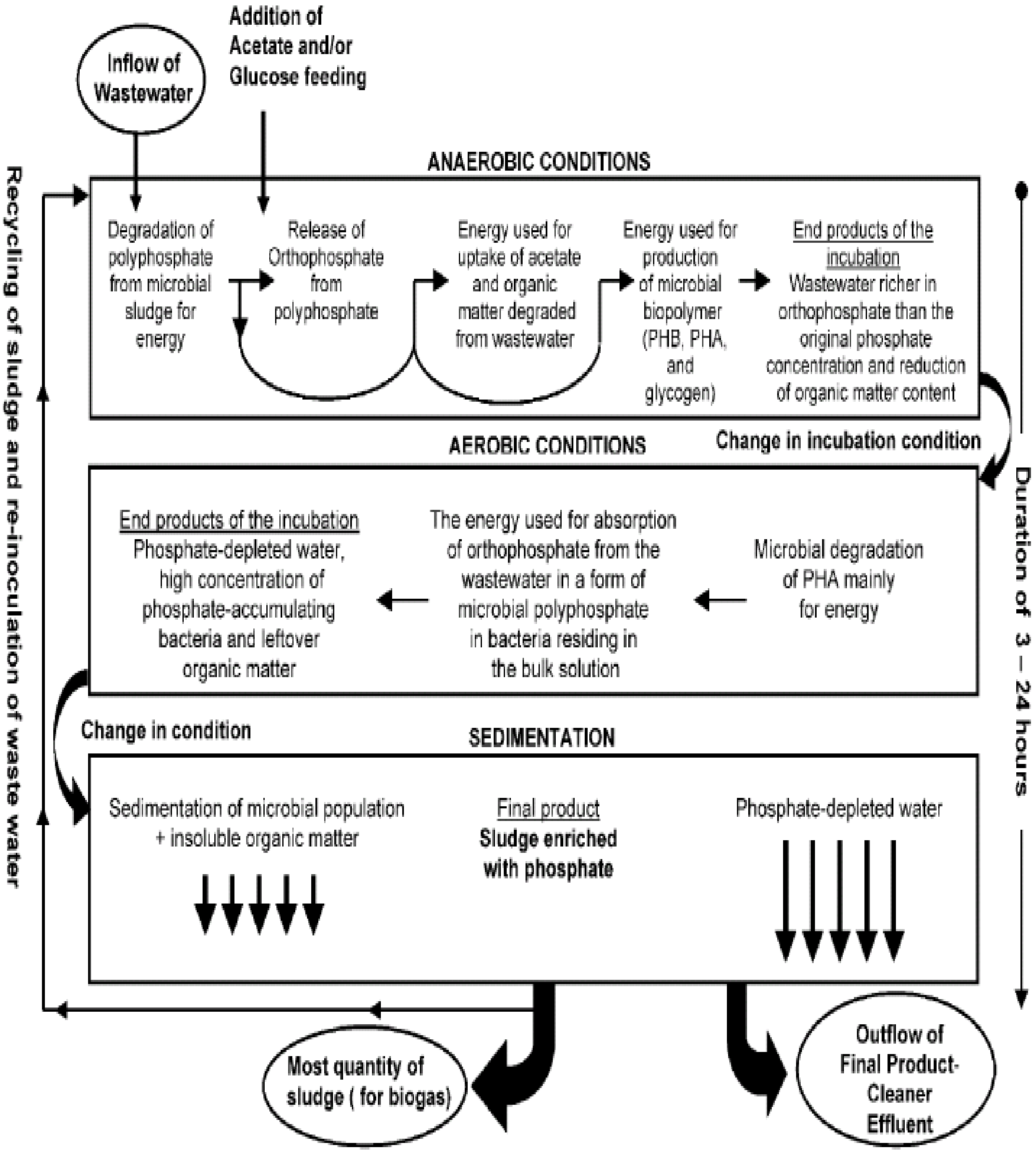


Figure 2.3 Conceptual Model of EBPR (Bashan and Bashan. 2004).

Factors affecting performance in EBPR are

pH: Findings from activated sludge of many WWTPs shows that there is increase of 50 143% in level of orthophosphates uptake when pH is reduced to 5.5 rather than 7.5 (Sham *et al*., 2008).

Retention Time: Adequate retention time is required for the enrichment of PAOs. So the initial anaerobic period should not be shortened during the start up of EBPR. Otherwise facultative bacteria start competing with the PAOs (Bashan and Bashan, 2004).

Sludge Retention Time (SRT): For complete P removal no less than 15 days SRT is needed (Merzouk *et al*., 2001).

Temperature: Efficiency of EBPR improved as temperature decreases and EBPR performed better at colder temperature (5^{o}C). Better performance of the system was ascribed to reduced competition for substrate in the non-oxic zones, which resulted in an increased PAO population (Erdal *et al*., 2003).

3. Wetlands

An engineered wetland is a wetland that can be changed at will, according to the ever-changing conditions of both climate and the type of wastewater; the process conditions and operations can be modified, manipulated, and controlled by the facility management. Basically, it is a container (as small as a bucket or as big as a very large pond) planted with mainly aquatic, but sometimes with terrestrial plants. The roots of plants, especially aquatic macrophytes, both emergent and submerged, work as a giant biological filter that removes organic matter of all kinds (Bashan and Bashan. 2004). Performance of such wetlands in removing pollutants, including phosphorus, can be enhanced by using a reactive sorbent. The sorbent must have a high phosphorus sorption capacity and an adequate hydraulic conductivity. Aluminum based water treatment residual is also used as sorption media in engineered wetlands (Babatunde *et al*., 2009).

Advantages

1. The operational and maintenance costs are minimum and affordable even in developing countries.
2. Improvements in plant selection, size and type of substrate, and especially combined with better design for the control of the wetland as an ‘‘engineered wetland’’, might make the wetland system the method of choice for wastewater treatment where land is available and resources are scarce.

Disadvantages

1. The wetlands are not usually to remove nutrients, such as phosphorus but they do so as these ions are nutrients for plants.
2. The design ions not flexible, once designed tough to change.
3. Plants often assimilate nutrients so the pollution transferred from one state to the other and the final disposal of such plants is also an issue as otherwise upon degradation the extract out all the nutrients stored within them.

2.7.4 Chemical processes

This process falls under the category of tertiary chemical phosphorus removal processes and is designed to achieve 95% removal efficiencies. Now days, the main commercial processes for removing phosphorus from wastewater effluents are chemical precipitation with iron, aluminum, calcium and magnesium salts.

2.7.4.1 Precipitation

Precipitation is the formation of insoluble products from the combination of soluble reactants. The removal of phosphorus is ultimately achieved through physical storage of the phosphorus precipitates within the substrate media. Naturally occurring soluble iron, aluminum and calcium can result in significant removal of phosphorus by precipitation (Cooke. 1992; Sakadevan and Bavor. 1999; Ayoub *et al*., 2001; Bashan and Bashan. 2004). Aluminum chlorohydrate and Poly Aluminum Chloride (PAC) have also been investigated as possible precipitants. Polymers are used in conjunction with alum and lie as flocculant aids.

A. <u>Iron Phosphorus Precipitation</u>

Ferric chloride (FeCl2) and Ferric Sulfate ($Fe_2(SO_4)_3$) are most commonly used in conventional wastewater treatment facilities to precipitate phosphorus, with subsequent physical removal from the system by co-settling with the organic suspended solids. The simplified chemical reactions for ferric sulfate, ferric chloride and alum are as under (Lind. 1998; Ayoub *et al*; 2001).

Ferric Sulfate

$$Fe_2(SO_4)_3 + 3Ca(HCO_3)_2 \rightarrow 2Fe(OH)_3 + 3CaSO_4 + 6CO_2 \quad \text{……….. 2.5}$$

Ferric Chloride

$$2FeCl_3 + 3Ca(HCO_3)_2 \rightarrow 2Fe(OH)_3 + 3CaCl_2 + 6CO_2 \quad \text{………... 2.6}$$

$$Fe(OH)_3 + PO_4^{3-} \rightarrow FePO_4 \downarrow + 3(OH)^- \quad \text{…………2.7}$$

B. Aluminum Phosphorus Precipitation

Aluminum hydroxide, Al(OH)$_3$, is a strong adsorption agent for orthophosphate and condensed phosphate Most organic and inorganic forms of phosphorus are readily removed by precipitation with the use of alum. Adsorption by aluminum sulfate can be enhanced by adding organic polyelectrolytes, like tannin, synthetic anionic polyelectrolyte, and clay (Ozacar and Sengil. 2003).

Alum (Aluminium Sulfate):

$\mathrm{Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \rightarrow 2Al(OH)_3 + 3CaSO_4 + 6CO_2}$ …………2.8

$\mathrm{Al(OH)_3 + PO_4^{3-} \rightarrow Al(PO)_4 \downarrow + 3(OH)^-}$ …………..2.9

C. Calcium Phosphorus Precipitation

Phosphorus removal efficiencies in this process ranged from 75% to 85%. Finally, lime was also suggested as a pre-treatment of municipal wastewater before the biological process (Moriyama *et al*., 2001; Marani *et al*., 1997).

$\mathrm{Ca(OH)_2 \leftrightarrow Ca^{2+}\ 2OH}$ ………… 2.10

$\mathrm{5Ca^{2+} + 3PO_4^{3-} + OH^- \rightarrow Ca_5(PO_4)_3(OH) \downarrow}$ …………. 2.11

Lime, which previously was one of the main chemicals used for phosphorus removal is nowadays less frequently used because of increased production of sludge as well as the operational and maintenance problems associated with its use (Metcalf and Eddy. 2003). For cost-effective operation, a thermal lime regeneration unit is required.

D. Magnesium Phosphorus Precipitation

Applying $Mg(OH)_2$ to an anaerobic sludge digester resulted in a larger reduction in suspended solids and COD, a higher biogas production rate, and a lower level of phosphate and ammonia concentrations. The required reaction time depends on the initial phosphorus concentration and the dose of $Mg(OH)_2$ (Wu *et al.*, 2001).

Magnesium chloride ($MgCl_2$) can be used as a Mg source for phosphate and ammonium removal in municipal wastewater. Phosphate can be precipitated by producing magnesium-ammonium-phosphate (struvite). Magnesium hydroxide ($Mg(OH)_2$) can be used instead of magnesium chloride. Magnesium chloride can also be used in combination with calcium hydroxide ($Ca(OH)_2$) in non-sulfate containing waste streams. By adding magnesium chloride and calcium chloride, magnesium hydroxide is formed in situ, whereby contaminants (metals or organics) co precipitate, enabling the re-use of process water.

Disadvantages of precipitation

- Large amount of sludge is produced
- High cost of salts required for precipitation
- Negative ecological effect of the concentration of aluminum and iron salts in the effluent

2.7.4.2 Adsorption

Adsorption phenomena were already exploited by the Egyptians and Sumerians, who used charcoal 3750 B.C. for reducing copper, zinc, and tin levels during bronze manufacturing. Following this, the Egyptians and later Hippocrates used charcoal for first medical purposes before the first application for potable water treatment was described by the Phoenicians (Kammerer *et al*., 2011).

Adsorption is defined as

“Adsorption a physical and/or chemical process in which a substance (the contaminant- hereinafter called adsorbate) is accumulated at an interface between solid and liquid phases.” Adsorbate is the substance or contaminant to be removed from the liquid or gas at the solid interface e.g., phenols from refinery wastewater. Adsorbent is the solid phase onto which the accumulation of adsorbate or contaminant occurs (Reynold and Richard, 1985).

Pollutant (adsorbate) is transported from bulk (air/ liquid) to adsorbent via following processes (Refer Fig. 2.4)

- First of all pollutant is moved from bulk to the liquid film or to the boundary layer.
- Solute is diffused through the liquid film.
- The diffusion of solute through the capillaries or pores within the adsorbent solid
- The adsorption of solute onto the capillary walls or particle surface.

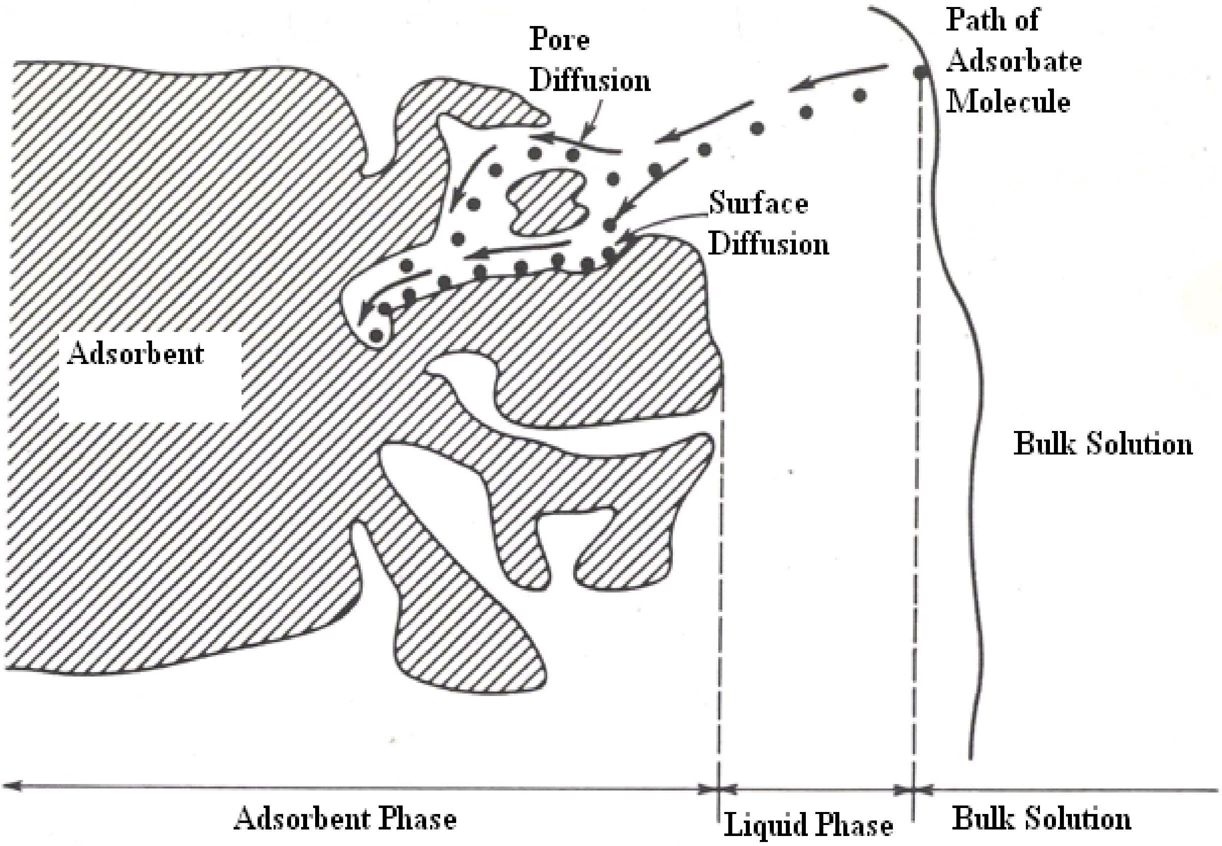


Figure 2.4 Mass Transfer Mechanism in Adsorption (Reynold and Richard,1985)

Adsorption process is of various types depending upon the contact between adsorbent and adsorbate.

- Physical adsorption is a reversible mechanism in which adsorbate is accumulated on the surface of adsorbent through van der Waals forces, dipole forces, dipole-dipole forces and dispersion forces.
- Chemical adsorption is a type of adsorption whereby accumulation of adsorbate onto adsorbent occurs through chemical bonding.

- Ionosorption is a type in which adsorption occurs due to ion transfer. It is site and charge specific chemisorption. The greater the charge on the adosrbate ion, greater adsorption or removal.

Adsorption Isotherms

"*An adsorption isotherm is a quantitative relationship describing the equilibrium between the concentration of adsorbate in solution (in mg/L) and its sorbed concentration (in mg of adsorbate/ gm of adsorbent) at a given temperature*" (Montgomery.; Reynold and Richard). Mostly used adsorption isotherms are Langmuir and Freundlich (Zhao *et al*., 2007; Zheng *et al*., 2009).

- Freundlich isotherm is an empirical equation to describe heterogeneous adsorption systems; it is the earliest known relationship describing the adsorption equation.
- Langmuir isotherm is most widely used for the sorption of a pollutant from a liquid solution. The model assumes that the sorption takes place at specific homogenous sites within the adsorbent, i.e., once a sorbate molecule occupies a site, further adsorption at this site is impossible.

Adsorption mechanism of phosphorus

Ligand exchange of phosphate ions and metal hydroxides on media surfaces is believed to be the predominant mechanism for the sorption of phosphorus (Yang *et al*., 2006). The uptake of phosphorus by this adsorption is known as exchange adsorption. When contacting with aqueous solutions, the metal (hydr) oxides on the surface of the sorbent material become hydrated or hydroxylated, serving as the binding sites. Phosphate anions can be exchanged with the hydroxyl ions on the solid surface to form surface complexes, thus being immobilized (Guan and Xiaohong. 2005). The proposed equation for the uptake of phosphorus is as follows (Yang *et al.*, 2006):

$$M(OH)_3 + HPO_4^{2-} \rightarrow MPO_4 + H_2O + 2OH^- \qquad \ldots\ldots\ldots\ldots\ldots\ldots 2.12$$

$$M(OH)_3 + H_2PO_4^{2-} \rightarrow MPO_4 + 2H_2O + OH^- \qquad \ldots\ldots\ldots\ldots\ldots\ldots 2.13$$

Adsorbents for phosphorus removal

Cement Clinker

Cement clinker is produced in the cement factory during the production of cement. The constituents of clinker are aluminum and iron oxide. Its surface is porous in nature. Cement clinkers are found to be good adsorbent for phosphorus removal even when phosphorus concentrations were very high. But clinker increased the pH of the effluent (Calder *et al.*, 2006).

Steel Slag

Steel slag is a byproduct produced in large amounts in the steel-making process. It is an important resource that can be effectively utilized. Slag from different sources may be chemically different and will have varying sorption capacities. Slag treated with water produces a lightweight porous medium having good hydraulic conductivity and numerous sites for sorption. Steel slag was found to be very effective in adsorbing phosphorus at 7.5g/L, the contact time 2h, and the pH value was equivalent to 6.5, over 99% of phosphorus removal was achieved (Lan *et al.*, 2006). Steel slag showed a good performance that decreased with time, adsorption appearing to be the dominant mechanism for P removal. When steel slag was mixed with lime, it didn’t decrease the performance (Drizo *et al.*, 2006). Steel slag filters are also used for the removal of phosphorus from water. It removed 77% of TP (Total Phosphorus) (Shilton *et al.*, 2005).

Zeolite

Zeolite is material produced naturally by volcanic eruption but it can also be produced artificially. Zeolite has negative charge and high surface area so surfactants can be used to change the negative charge to a positive charge thus enabling the sorption of phosphate anions. Natural Zeolite was used which gave more than 70% of phosphorus removal. The study reveals that phosphorus adsorption was increased with decreasing pH however, in alkaline conditions phosphate decreases due to precipitation with calcium and barium (Wanchun *et al.*, 2011).

In a study adsorption capacity of synthetic Zeolite was enhanced by incorporating aluminum sulfate in it. Efficiency of phosphate removal by the zeolites was reduced with an increase in solution pH and a decrease in sorbent mass. Ions such as nitrates, sulfates, and chlorides that form outer-sphere complexes with binding sites improved slightly the phosphate removal efficiency while fluoride ions, which form inner-sphere complexes with binding sites, reduced the phosphate capacity of the active sites. Zeolites have shown to be potential sorbents for the removal of phosphate ions from water (Onyango *et al.*, 2007).

Alum Sludge

Recycling of alum for phosphorus removal in domestic wastewater is not a new technique. It was used at first time in 1977 to remove phosphorus rather recovering aluminum from it. Study concluded that by using alum sludge cost of aluminum phosphate sludge handling was significantly reduced. The process should be equally applicable to large and small treatment plants (Cornwell and Zoltek. 2000).

Air dried alum residuals were used to reduce phosphorus from wastewater. The adsorption capacity of spent alum was found to be approximately 0.30-0.33 mg/g of sludge (Haung and Chiswell. 1977). Water treatment residuals are side products of drinking water treatment plants and have the capacity to adsorb large amounts of P. P-loaded WTR was mixed for 1 to 211 days. The initial and final analysis of elements present i.e. Ca, Al and P was done by ICP-MS. Results indicated that when pH increased from 7.5 to 8.5, adsorption of P was decreased (Ippolito *et al*., 2003).

Konstantinos investigated the P sorption mechanisms that could affect the long-term stability of sorbed P by WTRs. Phosphorus sorption kinetics by the WTRs exhibited a slow phase that followed an initial rapid phase, as typically occurs with metal hydroxides. The fast reaction is ascribed to low-energy external surface sites, where ligand exchange is believed to be the main adsorption mechanism. The slow reaction between P and metals with metal hydroxides proceeds for days or months and has been attributed to surface precipitation reactions or intraparticle diffusion into micropores (Konstantinos *et al*., 2004).

A comparison of alum sludge and pure alum was made to evaluate the efficiency to remove P from synthetic wastewater. Pure alum demonstrated much better results being 5 times better than alum sludge. With increase of sludge age, its efficiency was dropped due to polymerization of $Al(OH)_3$. Although pure alum is much efficient but the low cost and high availability it is much wise to use alum sludge (Georgantas and Grigoropouou, 2005).

Adsorption behaviors were investigated as a function of amount and particle size of alum sludge, pH, and contact time. Many factors may affect the adsorption rate and adsorption capacity. The results have shown that pH plays a major role not only in the adsorption process but also in the adsorption capacity. Alum sludge has a higher phosphate adsorption capacity in acid pH region than in alkaline pH region. Amount and particle size of alum sludge have the important effects on adsorption behavior. Large quantity and fine grain of sludge increased adsorption process for phosphorus removal (Yang *et al.*, 2006).

The adsorption characteristics of phosphate adsorption on the dewatered alum sludge were identified as a function of pH and ion strengths in solution. Results show that the adsorption capacity decreased from 3.5 to 0.7 mg P/g sludge when the solution pH was increased from 4.3 to 9.0. The results of the competitive adsorption between phosphate and typical anions found in wastewater, such as SO_4^{2-} and Cl^-, onto alum sludge reveal that alum sludge can selectively adsorb phosphate ions. The insignificant effect of SO_4^{2-} and Cl^- on P-adsorption capacity indicates that phosphate adsorption is through a kind of inner-sphere complex reaction (Yang *et al.*, 2006).

The adsorption process is highly dependant on the pH of the suspension and is good at low pH with adsorption capacities in the order of orthophosphate > polyphosphate > organic phosphate. At pH 4.0, the adsorption capacity for orthophosphate was 10.2 mg-PO_4^{3-}/g DWTS (Drinking Water Treatment Residual), polyphosphate was 7.4 mg-$PO_4^{3-/}$g DWTS and organic phosphate was 4.8 mg-PO43−/g DWTS (Drinking Water Treatment Sludge) (Razali *et al.*, 2007).

Effectiveness of alum residuals for Aquaculture process waters was determined because such water is often scrutinized for loading phosphorus discharges into surface water. Alum residuals were dried using an oven at 105^{o}C for 24 h. Experimental results observed phosphorus removal of 94–99% using an alum residuals concentration of 4–16 g/L. Oven dried alum residuals were a better adsorbent for orthophosphate phosphorus than total phosphorus. There was aluminum leaching from oven dried alum residuals, however, not high enough to cause toxicity for aquatic species if disposed in surface water (Mortula and Gagnon. 2006).

The adsorption equilibrium of a wide range of phosphorus species by aluminum-based water treatment sludge was examined in this study. Four kinds of adsorption-isotherm models, namely Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich, were used to fit the adsorption equilibrium data. This study reveals that the Freundlich isotherm appears to be the best model to fit the experimental equilibrium data. Langmuir and Temkin isotherms are also good models in current experimental conditions while the Dubinin-Radushkevich isotherm poorly described the adsorption behavior (Zhao *et al.*, 2007).

The capacity of alum sludge was determined for condensed phosphorus only as a lot of work was already been performed on orthophosphorus. Continuous and batch study was made to determine sludge's efficiency. A maximum adsorption capacity of 4.52 mg-P/g of water treatment residual was obtained at a pH of 4.0. P removal efficiency decreased from 90 to 30% when loading was increased from 3.9 to 16.5 g-P/m^2 day in continuous system (Babatunde *et al*., 2008).

Two strategies for P removal from reject water using alum sludge were made. One strategy is the use of the alum sludge in liquid form for co-conditioning and dewatering with the anaerobically digested activated sludge in MWWTP (Municipal Wastewater Treatment Plant) while other strategy involves the use of the dewatered alum sludge cakes in a fixed bed for P immobilization from the reject water (Yang *et al*., 2009).

Li and Zhao assessed the potential reuse of aluminum coagulated drinking water treatment sludge as a main substrate in constructed wetland to replace soil for the treatment of P-enriched wastewater. The maximum P adsorption capacity of the sludge and the soil was 39.4 mg P g^{-1} (which is more than four times greater than the value on soil) and 9.5 mg P g^{-1}, respectively, at conditions of pH of 4.0 and temperature of 23°C (Li and Zhao. 2010).

Zhao and Yang accessed the change of alum sludge characteristics and its P-adsorption capacity over the location of the alum sludge produced and the raw water being treated. There is no significant change on maximum P-adsorption capacity (14.3mg P/g sludge for Ballymore- Eustace sludge and 13.1 mg P/g sludge for Leixlip sludge at pH 7.0). The study supports that the raw water quality will affect the sludge characteristics and therefore influences its adsorption ability (Zhao and Yang. 2010).

Tie *et al.*, used oven dried and activated alum sludge for P removal. Sludge was activated at 300, 500 and 900^{o}C respectively. Results indicated that adsorption was best carried out by the sludge activated at 300^{o}C. Lower pH and higher temperature are favorable for P adsorption (Tie *et al*., 2011).

Oven-dried alum sludge was effective in adsorbing phosphorus from deionized water. In batch experiment the percent removal of phosphorus increases (85%) with increasing in the oven-dried alum sludge dose (i.e., 50 g/L at deferent pH). Batch kinetics experiments showed that equilibrium time was about 6 days without mechanical mixing (Mohammed and Rashid. 2012).

Chapter 03

MATERIALS AND METHODS

This chapter describes the materials and equipment used and methodology adopted for the research work.

3.1 Alum Sludge Generation

Drinking water is supplied to the residents of Islamabad and Rawalpindi by Rawal and Simli water filtration plants. Water comes into these dams by the melting of snow, storm water runoff and municipal wastewater mixed with fresh river water. Raw water coming from these sources exhibits medium to high turbidity levels. This turbidity is then removed by the addition of alum in the water treatment plants adjacent to the water reservoirs.

Two types of alum sludge was used in this study namely

- Rawal water treatment plant sludge
- Simli water treatment plant sludge

3.2 Sludge Collection and Processing

Rawal alum sludge was collected from Rawal water treatment plant in October 2011. Sludge was collected from the drainage pipe coming out of sludge removal pump. Sludge was brown in color and viscous in nature. Sludge was collected in ice box to bring it from treatment facility to IESE labs. The dose of alum (Aluminum Sulfate Octadecahydrate, $Al_2SO_4^{3-}.18H_2O$) at the time of sludge collection was 20 mg/L.

Simli alum sludge was obtained from Simli water treatment plant in January and February 2012. Simli dam is located at a distance of 42Km from NUST. Sludge was gathered from the bottom of the secondary sedimentation basin via outlet. Turbidity was reduced by the addition of 50 Bags / 35 MGD (9.0 mg/L Aluminum Sulfate Octadecahydrate, $Al_2SO_4^{3-}.18H_2O$). Less amount of alum was added to the water because in winter season turbidity is low.

Figure 3.1 Sludge Collection

Figure 3.2 Collected sludge

3.2.1 Air drying

The sludges collected were allowed to air dry. Rawal sludge was in semi solid state so it was spread on plastic sheets in the environmental chemistry lab at room temperature. Simli sludge was in the form of viscous liquid so was air dried first in the ice box.

3.2.2 Oven drying

Both the sludges were allowed to dry in the electric oven (WTE Bindertuttlingen, Germany) at 103^{o}C for 24 hours. Then sludge was allowed to cool down at room temperature. The dried sludges were placed into desiccators so that they may not capture any moisture.

3.2.3 Grinding, sieving and storing

Dewatered alum sludges were grinded manually with the help of pestle and mortar to bring the particle size of the sludges in the desired range. The crushed sludge was then screened out using ASTM mesh number 10 to bring the particle size of the sludge less than 2mm. The grinded sludges were stored in air tight plastic containers.

3.3 Synthetic Wastewater Preparation

3.3.1 Orthophosphate (OP)

Orthophosphate (OP) enriched wastewater was prepared by diluting stock solution of Potassium Di Hydrogen Phosphate (KH_2PO_4) to the desired Orthophosphate concentration. The concentration of the stock solution came out to be 250 mg/L. Chemical name, concentration and manufacturing date was properly labeled on the bottle. Stock solution was prepared by dissolving 0.37g of Potassium Di Hydrogen Phosphate

(KH_2PO_4) in 1000 mL of distilled water in room temperature. Orthophosphate solution was prepared by diluting 50mL of the stock solution in 1000 mL tap water. The concentration of the resulted wastewater was obtained to be 25 mg/L which was based on the concentration found typically in municipal wastewater.

3.3.2 Condensed Phosphate (CP)

Stock solution for the condensed phosphate (CP) was prepared by mixing 1.61 g of Sodium Hexa Meta phosphate (SHMP) ($Na_2P_3O_5$. H_2O) in 1000 mL of distilled water and was placed at room temperature. The stock solution had a concentration of 250mg/L. Stock solution was preserved in Pyrex (1L) and was properly labeled. Stock solution was taken in the amount of 12 mL and was diluted to the same 1000mL distilled water made above to bring down the concentration to 15 mg/L of CP in the wastewater containing 25mg/L of OP.

3.4 Reagents Preparation

The protocol of preparation of Vendate-Molybdate Reagent is as described below.

2.5g ammonium molybdate $(NH_4)_6Mo_7O_{24}.4H_2O$ was dissolved in 30mL distilled water as solution 1. 0.125g of ammonium metavendate (NH_4VO_3) was dissolved in 30mL of boiling distilled water (Solution 2). Solution 2 was allowed to cool and after cooling, mixed in 30mL of concentrated hydrochloric acid (HCl, 37% pure). The solution was cooled down and after cooling solution 1 was added in solution 2. The volume of reagent was made up to 100mL by adding distilled water. Stored in clean pyrex bottle (100mL).

Strong acid solution was prepared for the acid hydrolysis of the wastewater. Solution was made by adding 30mL of concentrated sulfuric acid (H_2SO_4 98% pure) to 60mL of distilled water. Added 0.4mL of nitric acid (HNO_3) in the solution and diluted the volume of the solution to 100mL. Sodium hydroxide, NaOH, 6N was prepared by adding 24 g of sodium hydroxide pellets to 100mL of distilled water. Stored in clean pyrex reagent bottle (100mL).

3.5 Adsorption Experiment

The whole study was carried out in routine manner by the batch experiments. The study was conducted using jar testing apparatus (Phipps and Bird PB-700^{TM}-Virginia-USA). A known amount of the sludge was weighed by the electronic balance (Schimadzu-Japan) and was added to the 1000mL solution containing OP (25mg/L) and CP (15 mg/L). The samples were then stirred at 200 rpm for the specific time. After mixing, samples were taken out of jar testing apparatus and were allowed to settle for one hour. On the completion of experiment, settled samples were filtered through 0.45µm cellulose filter to separate out sludge from the wastewater. The effluent obtained at the end was analyzed by HACH 2400 Spectrophotometer. The experiments were performed at room temperature. Phosphorus concentration decrease from the solution was understood to be adsorbed on dewatered alum sludge. The remaining phosphate concentration was determined with the help of Hach 2400 spectrophotometer. Each experiment was carried out in triplicate to find out the consistent behavior of sludge.

Figure 3.3 Jar testing apparatus (Phipps and Bird PB-700^{TM}-Virginia-USA)

To pursue the effectiveness of dewatered alum sludge and to gather equilibrium data experiments were conducted in the following sequence.

3.5.1 Effect of sludge mass

Effect of dewatered alum sludge mass was conducted by series of experiments. Varying amount of dewatered alum sludge from Rawal water treatment plant i.e., 1mg/L-36mg/L was introduced to the synthetic wastewater of known characteristics. Similarly, different dose of Simli dewatered alum sludge ranging from 1mg/L to 20 mg/L was mixed with synthetic wastewater until equilibrium state. This mixture of sludge and wastewater was allowed to mix thoroughly on the jar testing apparatus at 200rpm for a pre defined time period.

3.5.2 Contact time

To determine the time required for the maximum phosphate species removal, the composite samples were agitated from 30 min (0.5 hour) to 360 minutes (6 hours). Mechanical agitation on jar testing apparatus was carried out at 200rpm.

3.5.3 Effect of pH

To determine the effect of pH on the phosphate removal by dewatered alum sludge tests were performed within a pH range of 3 to 9 using 0.1MNaoH and $0.01MH_2SO_4$.

3.5.4 Isotherm experiments

Series of batch adsorption experimental investigations were conducted on P adsorption behavior coupled with the adsorption capacity of the dewatered alum sludge. The initial concentration was varied from 10 to 55 mg/L.

3.5.5 Adsorption isotherm

Adsorption isotherms are the graphs which are used to study adsorption. It depicts the effect of initial concentration of the adsorbate as function of adsorbent mass with the temperature kept constant. In this study Freundlich and Langmuir isotherms were used.

3.5.5.1 Freundlich isotherm

In 1909, an isotherm equation was developed by Freundlich to study the behavior of pollutant i.e. adsorbate on the concentration of the adsorbent. This equation is world widely known as Freundlich Isotherm equation. This isotherm models describes the heterogeneous behavior of the adsorbent. The Freundlich isotherm equation is:

$$q_{e=}\ K_F C_s^{\frac{1}{n}} \qquad \text{…………….3.1}$$

The linear form of the Freundlich equation is:

$$\log q_e = \log K_F + \frac{1}{n}\log C_s \qquad \text{………………..3.2}$$

Where,

q_e= mass of P adsorbed on adsorbent at equilibrium (mg/g)

C_s= equilibrium concentration of P solution (mg/L)

K_F = Adsorption affinity (1/g)

n = deviation from linearity of the adsorption

The feasibility of the data on the basis of n value is as given in the table 3.1

Table 3.1: Favorability of Freundlich isotherm

Value of n	**Type of Isotherm**
=1	Linear
<1	Adsorption is chemical
>1	Favorable physical adsorption

3.5.5.2 Langmuir isotherm

In 1916, Langmuir proposed an adsorption model in which he described that sorption rather being heterogeneous, is homogenous within specific sites of the adsorbent. The adsorption is truly monolayer and once the surface of adsorbent is occupied it is not viable for the adsorbate to attach further on that same site. The Langmuir adsorption isotherm equation is:

$$q_e = \frac{Q_o\, b\, C_s}{1 + bC_s} \qquad \text{…………..3.3}$$

The linear form of the Langmuir isotherm equation is:

$$\frac{C_s}{q_e} = \frac{C_s}{Q_o} + \frac{1}{b\, Q_o} \qquad \text{…………..3.4}$$

Where, q_e= mass of P adsorbed on adsorbent at equilibrium (mg/g)

C_s= equilibrium concentration of P solution (mg/L)

Q_o = Adsorption capacity of monolayer

b = Langmuir constant (l/mg) attraction of the adsorbate for the adsorbent (Affinity)

The plot of C_e/q_e versus C_e gives a straight line from which the isotherm parameters can be determined. The Langmuir dimensionless constant called the equilibrium parameter R_L indicates the type of isotherm.

$$R_L = \frac{1}{1 + bC_i} \qquad \text{……………3.5}$$

Where, C_i = initial phosphate concentration

Table 3.2: Feasibility of Langmuir Isotherm

Value of R_L	**Type of Isotherm**
>1	Unfavorable
= 1	Linear
0-1	Favorable

3.6 Total Analysis of Wastewater

3.6.1 Spectrophotometric analysis:

Figure 3.4Hach 2400 Spectrophotometer

In an orthophosphate solution, ammonium molybdate reacts to form molybdophosphoric acid. In presence of vanadium, vanadomolybdophosphoricacid $[PO_4.VO_3.16MoO_3]^{4-}$ (yellow in color) is produced. The intensity of the yellow color is relative to the phosphate concentration. Test results are measured at 430 nm. Entered stored program 480 for reactive phosphorous (orthophosphates) in Hatch DR/2400 Portable data logging spectrophotometer and adjusted the wavelength to 430nnm. Added 1 ml of molybdovendate reagent in 25mL of distilled water (as blank, for zeroing) as well as in 25mL of sample to be tested, left them for 3 minutes. Placed blank in holder, adjusted zero, placed sample cell in holder, pressed read and noted down the results in P (which will be orthophosphorus) in sample.

3.6.2 Preliminary acid hydrolysis

Condensed phosphorus is not readily available as reactive phosphorus. Sample is needed to be acid hydrolyze to convert it into orthophosphorus form. 100 mL of sample was taken in the Duran beakers(1L). 50µL of phenolphthalein indicator was added to each 100mL sample. If red color was developed, strong acid solution was poured drop-wise to just discharge the color. Added 1mL H_2SO_4 solution and solution boiled for 90 minutes on hot plate. The volume of the wastewater was allowed to remain in between 25 to 50mL. After boiling the sample was cooled to room temperature and titrated against 6N NaOH and 0.1N H_2SO_4 until faint pink color achieved. The volume was then maintained to 100mL. 25 mL of the sample was taken and analyzed as stated above.

3.6.3 pH and turbidity

pH of the treated sample was measured with the help of Hach pH meter. The probe of the pH meter was gently shaken in water until reading was locked. Turbidity of the treated wastewater was measured by putting 25mL of sample in turbidity cells.

3.7 Alum Sludge Characterization

Inductively coupled plasma optical emission spectroscopy (ICP-OES)

ICP-OES is an analytical technique used for the detection of metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample. The instrument is capable of determining the concentration of 40-70 elements to very low detection limits (ppm-ppb).

3.7.1 Working principle

The analytical principle used in the ICP-OES is Optical Emission Spectroscopy. A liquid is nebulized and then evaporated within the Argon plasma. Atoms and ions contained in the plasma vapor are excited into a state of radiated light (proton) emission. The radiation emitted can be passed to the spectrometer optics, where it is dispersed into its spectral components. From the specific wavelength emitted by each element, the most suitable lime for the application is measured by the means of charge coupled device.

3.7.2 Analysis

Quantitative analysis of the sludge was performed at food toxicology labs, NIAB Faisalabad on payment. The samples were at first digested in a microwave accelerated reaction system (CEM Corp, Matthews, USA), and then the concentration of Al, Fe, Caand Mg in the digested solution was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Vista-Pro Axial, Varian Pty Ltd, Mulgrave, Australia).

3.8 Experimentation on Real Wastewater

Real municipal wastewater was collected from the main drain of NUST which contains the institutional as well as municipal wastewater. Batch tests were operated for this municipal wastewater on the optimized condition to get the actual picture of efficiency of alum sludge to remove phosphates.

Chapter # 04

RESULTS AND DISCUSSION

As described in chapter 3, laboratory scale experiments were conducted to determine the effectiveness of sludge in removing phosphorus from wastewater. This chapter describes the results obtained from those experiments in the following order:

1. Determination of the alum sludge efficacy for P removal from synthetic WW a)Sludge Dose, b) Contact time and c) pH
2. Application of isotherm models to identify the most appropriate isotherm.
3. Evaluation of the results obtained in (1) for the real wastewater.

4.1 Characterization of Wastewater

Wastewater was synthesized artificially in the water and wastewater lab using chemicals as mentioned in previous section. The characteristics of the wastewater as related to this study are given in table 4.1 below

Table 4.1Characteristics of synthetic wastewater

Parameter	**Value**
OP (Orthophosphorus)	25 mg/L
CP (Condensed Phosphorus)	25 mg/L
pH	7.0-7.5
Turbidity	<1 NTU

4.2 Sludge Characteristics

Alum sludge from both sources was characterized using Inductively coupled plasma optical emission spectroscopy (ICP-OES, Vista-Pro Axial, Varian Pty Ltd, Mulgrave, Australia). At first qualitative analysis of the Rawal Alum Sludge (RAS) and Simli Alum Sludge (SAS) was performed to determine the constituents of sludges by using X-Ray Fluorescence (XRF Jeol JSX-3202 Element Analyzer Na-U). Four metals were found in high concentrations in both sludges namely Al (Aluminum), Ca (Calcium), Mg (Magnesium) and Fe (Iron). Later on, the quantitative analysis was carried out by ICP-OES to determine the exact concentrations of the metals present in alum sludge. The results of ICP-OES are given in table 4.2.

Table 4.2 Elemental Composition of Alum Sludge from Rawal and Simli Treatment Plant

	Al (mg/g)	**Ca (mg/g)**	**Mg (mg/g)**	**Fe (mg/g)**
RAS	108.00	240.00	44.05	14.70
SAS	174.60	214.00	48.90	17.31

4.3 Optimization of Dependant Variables

Series of batch experiments were performed to evaluate alum sludge capacity for adsorption of phosphorus from the wastewater. Residual phosphorus depicted good performance before and at equilibrium stage.

4.3.1 Optimization of sludge dose

Pre determined quantities of fully processed Simli and Rawal alum sludge were added to synthetic wastewater and mixed for 4 hours at 200 rpm to determine the optimum sludge dose for maximum phosphorus removal. These quantities of alum sludge selected were based upon the preliminary experiments conducted to check wether phosphorus is removed by alum sludge or not. Results obtained from Simli Alum Sludge (SAS) are shown in Figure 4.1 while Figure 4.2 shows the results of Rawal Alum Sludge (RAS). Figure 4.1 (a, b, c) and Figure 4.2 (a, b, c) show the relationship between Alum Sludge dose and effluent phosphorus concentration, %age removal and adsorption capacity respectively.

The results indicate that:

- Effluent Orthophosphorus and Condensed phosphorus concentration is decreased by increasing the dose of alum sludge (Figure 4.1 a, 4.2 a).
- pH and turbidity are not affected (Figure 4.1 a, 4.2 a).
- Percentage removal is increased as the amount of sludge increased (Figure 4.1 b, 4.2 b).
- It is also observed that as sludge dose is enhanced, the adsorption capacity of alum sludge is reduced (Figure 4.1 c, 4.2 c).

These facts reveal that phosphorus is removed by Rawal Alum Sludge as well as Simli Alum Sludge. On initially low dose of sludge, it is observed that Condensed phosphorus (CP) is decreasing gradually, but as the amount of sludge is increased the performance of the sludge increases.

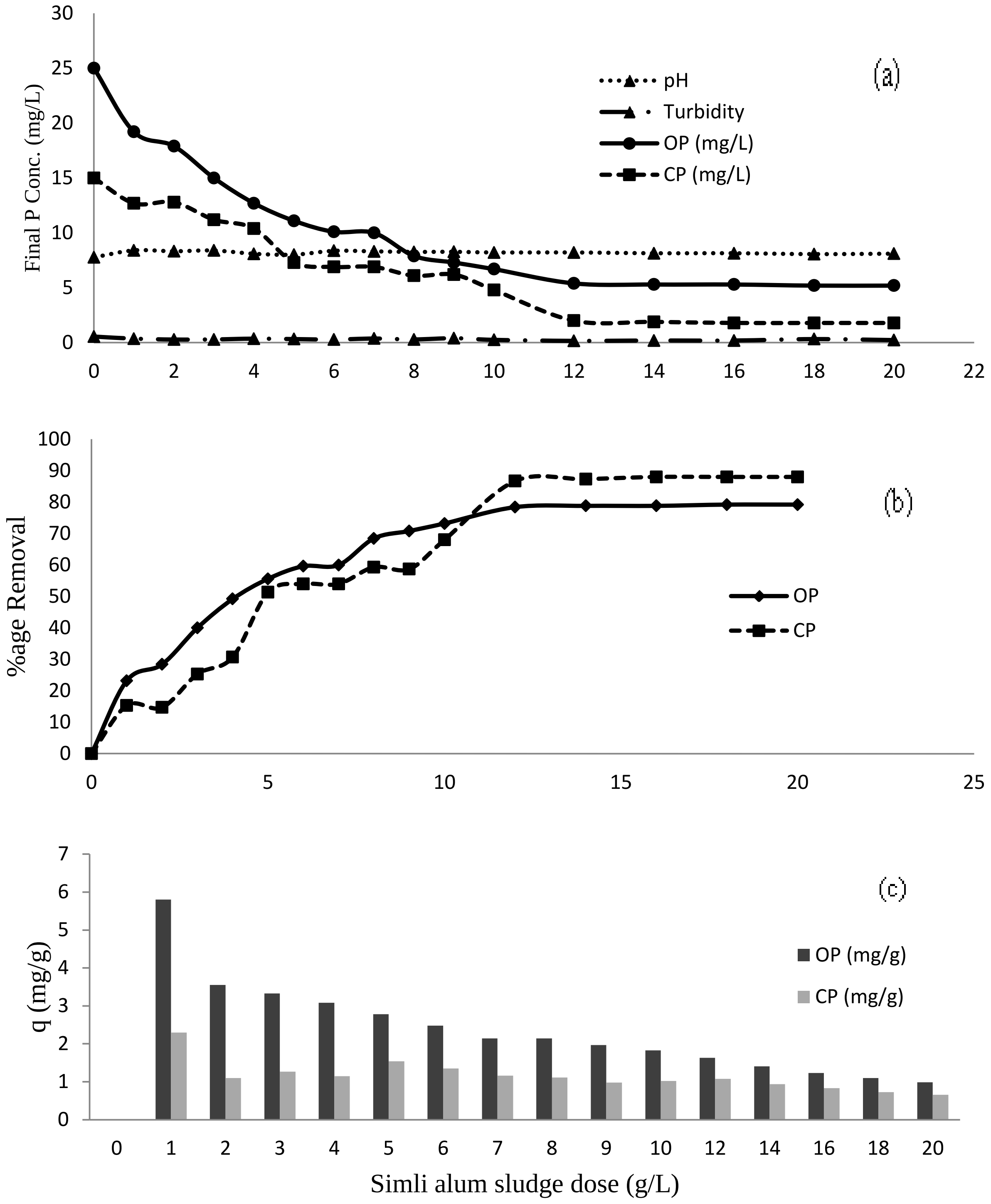


Figure 4.1: Effect of variable Simli Alum Sludge dose on the Effluent Phosohorus concentration (a), %age Removal (b) and Adsorption Capacity (c)

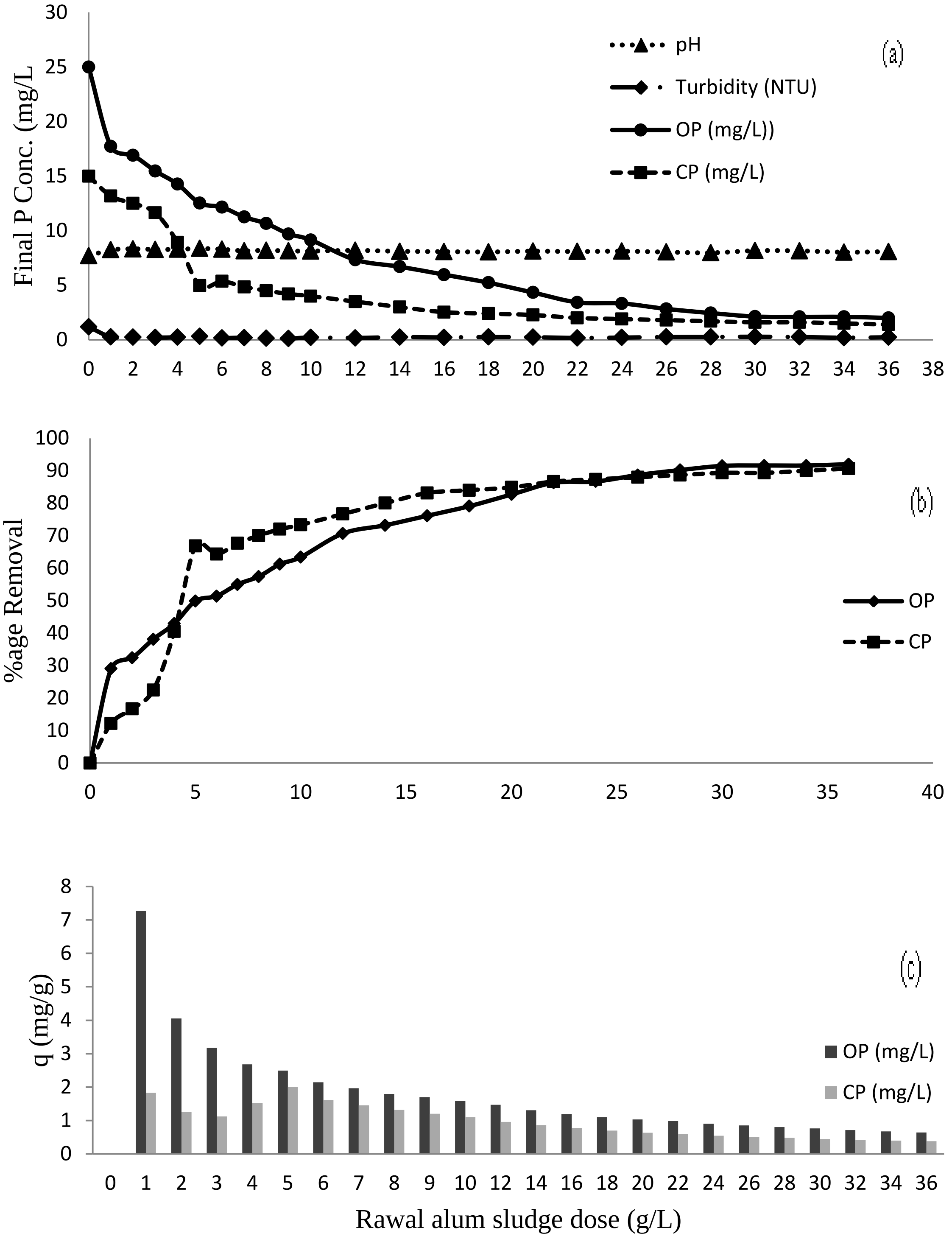


Figure 4.2: Effect of variable Rawal Alum Sludge dose on the effluent phosphorus concentration (a), %age Removal (b) and Adsorption Capacity (c)

These trends describe that the more alum sludge dose, more is the percent removal of OP and CP but lower the adsorption capacity. Figure 4.1 (c) and 4.2 (c) shows adsorption capacity graphs which disclose that at minimum dose of alum sludge, most of the phosphate is attached on the sludge surface. The reason behind is that at lower dose of sludge abundant phosphate species were present in solution. At that time, there was competition between phosphate species to be adsorbed on sludge. Adsorption of phosphorus species was limited as fewer free sites were available due to smaller quantity of alum sludge. On adding more sludge abundant adsorption sites were available that decreased concentration of phosphates. This addition was continued until no subsequent removal was observed. At that point the dose obtained was termed as optimized dose.

For Simli alum sludge it is evident from the figures 4.1 (a, b, c) that up to certain limit, there is potential decrease in orthophosphorus as well as condensed phosphorus. After 12 g/L further reduction in phosphorus in comparatively negligible. So, the maximum removal is achieved i.e. 79% for orthophosphorus (OP) and 86 for condensed phosphorus (CP) by Simli alum sludge using 12g/L.

Rawal alum sludge (Figure 4.2 (a, b, c) demonstrates good % removal for OP and Condensed phosphorus (CP) with adequate dose and no subsequent effect on pH and turbidity. When the adsorbent dose reached to 30g/L, 92% of orthophosphorus (OP) and 89% of condensed phosphorus (CP) removal was achieved with equilibrium concentrations of about 2.0 mg/L of orthophosphorus (OP) and 1.6 mg/ for CP.

Wadood and Rashid (2007) used oven dried alum sludge and concluded that percent removal of phosphorus depends upon the availability of adsorption sites. They used sludge dose ranging from 5-50 g/L and achieved 85% removal of phosphorus at 50g/L (Wadood and Rashid. 2012).Yang *et al*, (2006) also confirmed the results that the quantity of sludge has important effect on the efficacy of adsorption potential. Higher amount results in larger percent removal. They obtained maximum removal at 5.0 g/L.

The reason behind too much diversity of the results is based on the composition of the alum sludge. Physical and chemical properties of the alum sludge depend upon raw water and the coagulant used in drinking water treatment facility. So, the characteristics of alum sludge are variable from plant to plant and alum to alum. This difference leads to various phosphorus adsorption potential.

4.3.2 Equilibrium Time Determination

To determine the time required for the adsorption process to reach an equilibrium stage, the adsorption of phosphorus species by sludge was made as a function of contact time. Figure 4.3 (a,b) shows the profile of remaining phosphorus in the wastewater after reaction of optimized alum sludge dosages with various mixing times.

Results of these experiments revealed that:

- Quantity of phosphorus in wastewater is decreasing which indicates that phosphorus can be removed by both RAS and SAS as a function of time.

- At initial stage, there is rapid reduction in phosphorus concentration approaching toward equilibrium stage where further contact of sludge with wastewater has no influence.
- After 80 minutes of contact time, highest efficiency of RAS and SAS was achieved as described in Table 4.3

Table 4.3 Removal Percentages

Sludge	OP		CP	
	Concentration (mg/L)	Removal %age	Concentration (mg/L)	Removal %age
SAS	7.0	70	3.5	86
RAS	2.0	83	0.5	97

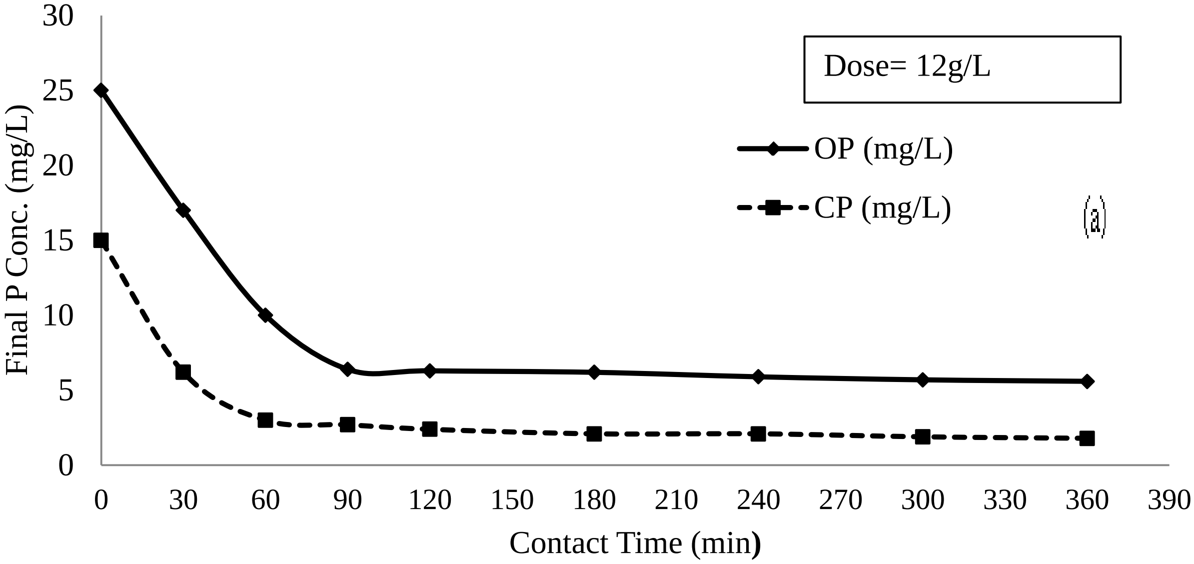


Figure 4.3 (a): Contact time (min) vs effluent phosphorus concentration (mg/L) for Simli Alum Sludge (SAS).

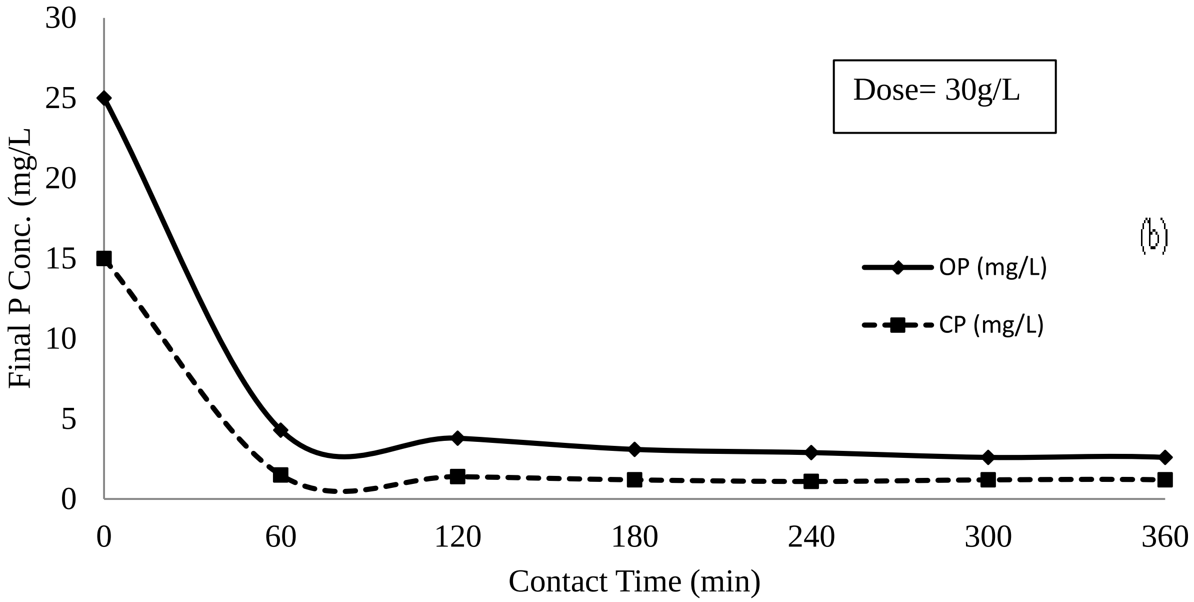


Figure 4.3 (b): Contact time (min) vs effluent phosphorus concentration (mg/L) for Rawal Alum Sludge (RAS).

It is evident from the graphs that, after 90 minutes for SAS and 801 min for RAS, there is no subsequent effect on percent removal. So the time optimized for further experiments is 90 minutes for SAS and 80 minutes for RAS. These results are in correspondence to that obtained by Yang where P concentration decreases significantly for first 2 hours (Yang *et al*., 2006). Georgants and Grigoropoulou used fresh alum sludge for experimentation and achieved equilibrium very rapidly in 30 minutes of contact time using only Orthophosphorus (OP) as P specie and obtained 90% removal (Georgantas and Grigoropoluou. 2005).

Razali and his co workers achieved equilibrium finally between 2 to 24 hours of contact time. This variation was due to different phosphorus species present in the wastewater (Razali *et al*., 2007). Zhao and his research fellows used dewatered aluminum based water treatment residual for phosphorus reduction from wastewater. They used contact time ranging from 17 hours to 80 days and concluded that 24 hours is the best time for obtaining the maximum removal (Zhao *et al*., 2007).

The time affects performance of sludge toward the removal of phosphates in two manners. At first the fast reaction in which the phosphate gets adsorbed to the external surface of the adsorbent and the phenomenon is of physical adsorption. While in the slow process, equilibrium is not achieved even in long period of time and this reaction is featured to precipitation (Konstantinos *et al*., 2004). Hence it is concluded from the discussion that phosphorus is being adsorbed by alum sludge as the reaction time equilibrated is 80 minutes.

4.3.3 Effect of pH

Phosphorus is present in wastewater in the form of anionic phosphate species. Divalent and trivalent cations are used to remove phosphorus species from wastewater. Alum sludge has high concentration of aluminum which is a trivalent cation Al^{3+}. Alum sludge consists of variety Al-OH molecules which are able to adsorb phosphorus.

Reaction between the phosphate and sludge is highly dependant upon the pH of the wastewater (Yang *et al.*, 2006). The graphs (Figure 4.4 a,b) depict the behavior that more phosphate species removal is accomplished in acidic range i.e. at lower pH. In case of SAS, removal of OP and CP is almost same from pH range of 4.0 to 6.0. In case of RAS, removal of OP and CP varies from 98% to 94% when pH is varied from 4.0 to 6.0.

Exchange of phosphates with OH^- ions is supported when Al-OH bond is weak enough. When the pH of the solution is low OH^- ions are weakly attached to the Al atoms. At this stage phosphate competes with the OH^- ions and replaces them leaving OH^- ions in the solution.

Phosphorus is removed by alum sludge due to the ion exchange process between phosphate (PO_4^{3-}) and hydroxyl ions (OH^-). As OH^- ions are not solely found in the form of AL-OH but the chemistry of alum sludge is more complex and they are in the form of some functional groups attached to them, hence the adsorption of phosphate on alum sludge is not ion exchange rather ligand exchange. So, the uptake of phosphates is due to release of hydroxyl ions (OH^-) as the pH of the wastewater increases after the completion of the reaction (Georgantas and Grigoropoluou. 2005).

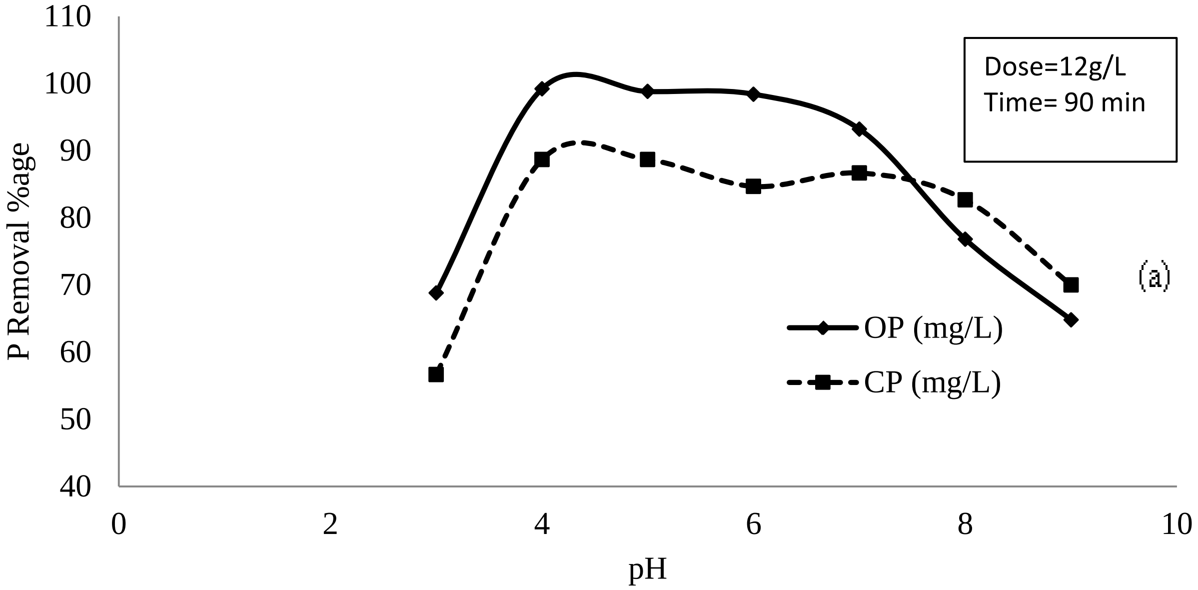


Figure 4.4(a): pH vs % removal of phosphorus using Simli Alum Sludge (SAS).

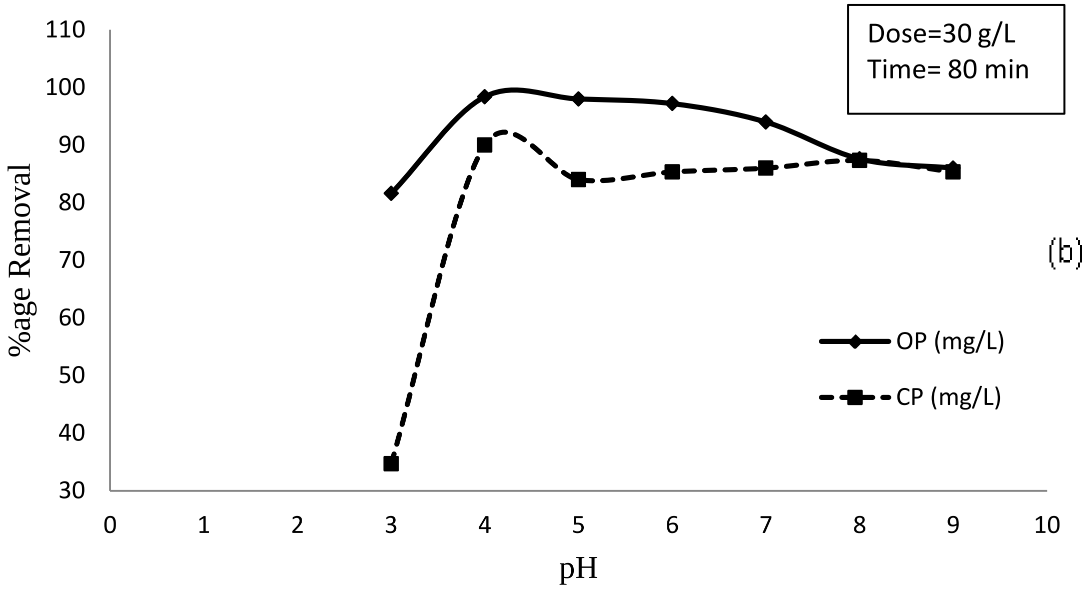


Figure 4.4(b): pH vs % removal of phosphorus using Rawal Alum Sludge (RAS).

Higher removal of OP and CP is achieved when pH of the solution is in acidic range i.e. 4.0-6.0 (Figure 4.4 a,b). When the pH of the wastewater is dropped below 4.0, $AlPO_4$ is formed. This AlPO4 molecule becomes soluble below pH 4.0 due to its chemical characteristics (Georgantas and Grigoropoluou. 2005). Now, due to the dissolution of $AlPO_4$ into the solution matrix, adsorbed PO_4^{3-} is re dissolved to the solution, thus reducing percentage removal of phosphates.

As the pH is increased, OH^- ions are found to be abundant in solution. These abundant OH ions surround Aluminum ion and repel phosphate ions. With the increment of the pH, the net surface charge on the alum sludge shifts from positive (+ve) to negative (–ve) (Pierzynski *et al.*, 2005). This net negative charge on the surface of alum sludge also repels the phosphates ions present in the solution thus phosphate ions don’t get adsorbed on alum sludge surface.

These results are in the coordination of the results obtained by other researchers (Yang *et al.,* 2006; Razali *et al*., 2007) who claimed that acidic environment is favorable for the adsorption of OP and CP on alum sludge and adsorption of OP and CP on alum sludge is maximum at pH=4.0.

4.3.4 Effect of Initial Concentration

The effect of increasing concentration of Orthophosphorus and Condensed phosphorus on the adsorption capacity(q) of Simli Alum Sludge and Rawal Alum Sludge is shown in Figure 4.5 (a,b) and Figure 4.6 (a,b). The results obtained describe that adsorption capacity of alum sludges increases up to a specific level until equilibrium is reached. After achieving equilibrium, further addition of initial concentration of OP and CP did not varied results considerably. The maximum adsorption capacity of SAS for OP is 3.58mg/g and for CP is 2.83 mg/g at initial concentration of 55mg/L. The maximum adsorption capacity of RAS for OP is 1.36 mg/g and 1.27 mg/g at initial concentration of 55mg/L.

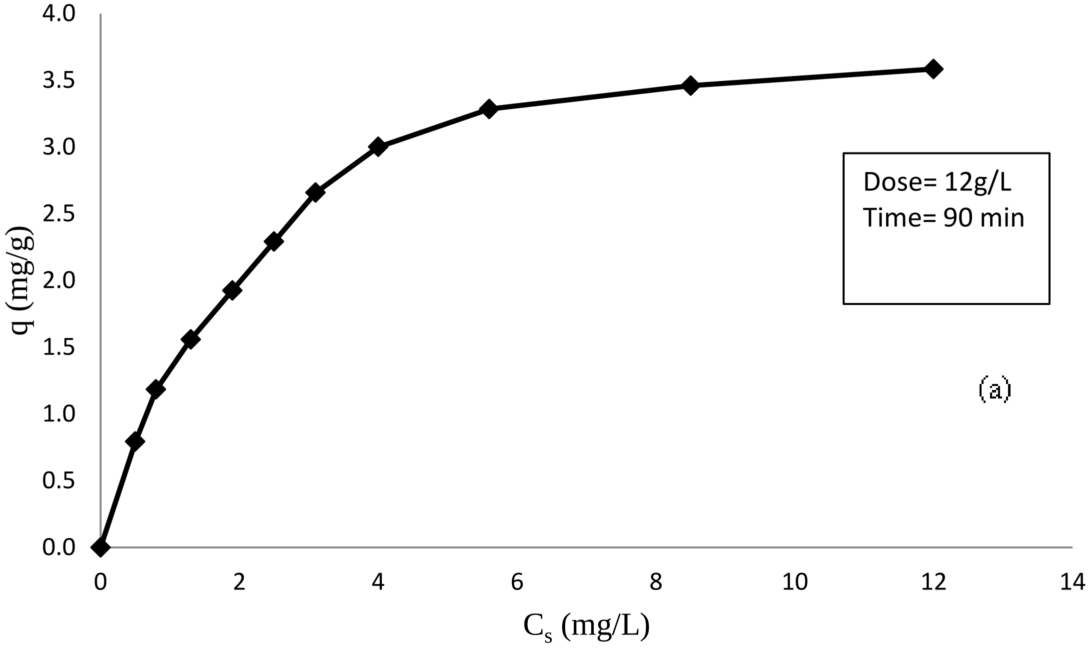


Figure 4.5(a): Final concentration (Cs) vs adsorption capacity (q) of OP for SAS.

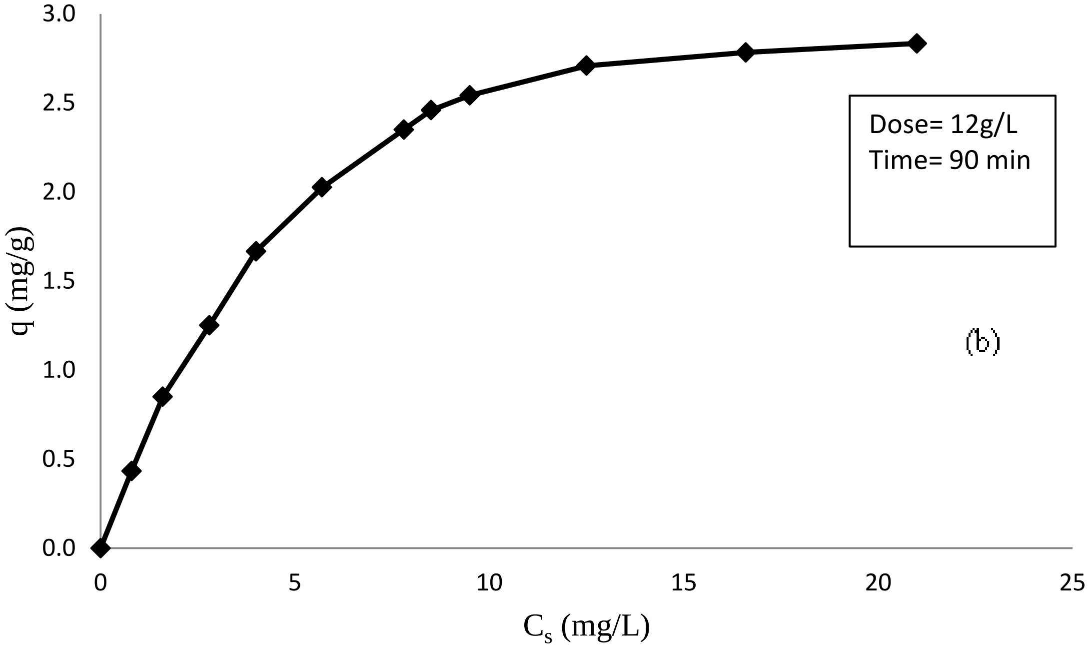


Figure 4.5(b): Final concentration (Cs) vs adsorption capacity (q) of CP for SAS.

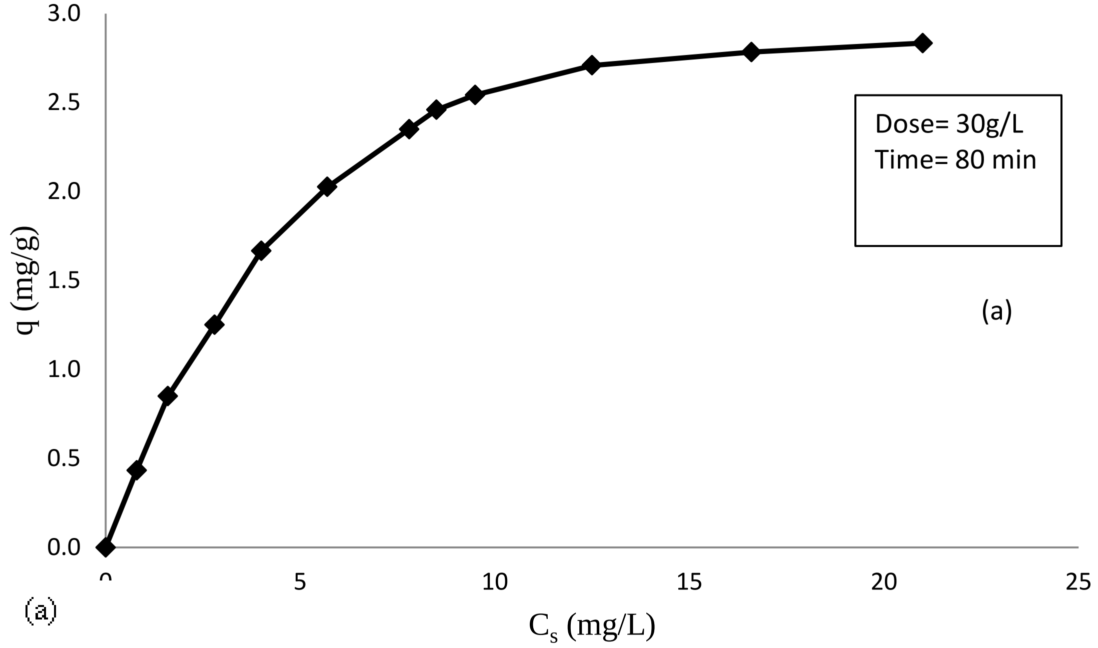


Figure 4.6(a): Final concentration (C_s) vs adsorption capacity (q) of OP for RAS.

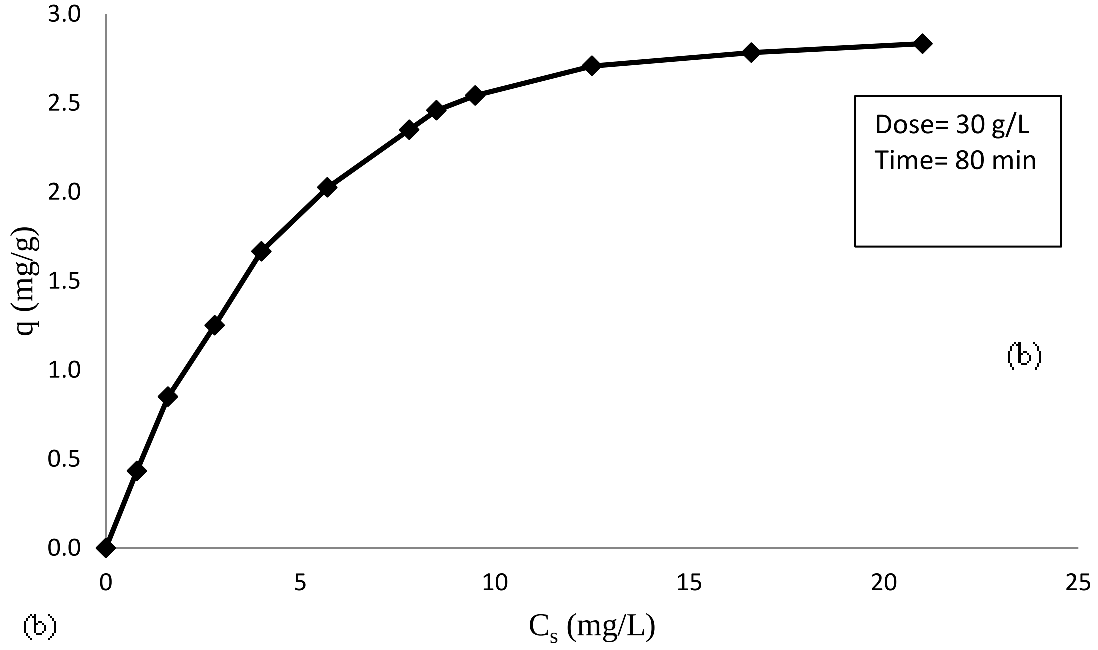


Figure 4.6(b): Final concentration (C_s) vs adsorption capacity (q) of OP for RAS.

4.3.5 Isotherm Study

Adsorption isotherms are the graphs which help predicting that the data is supported by what type of isotherm. In this study, three adsorption isotherms were used to determine the favorability of data with isotherms. Behavior of two compounds selected namely orthophosphorus and condensed phosphorus was under observation at same temperature i.e. 25±2°C.

4.3.5.1 Freundlich Isotherm

Freundlich isotherm describes the heterogeneity of the adsorbent. K_F and n are the factors affecting adsorption process (Adsorption affinity and non linearity). Higher K_F values show that higher is the adsorption capacity. n shows the deviation of data from linear position and decreases as the concentration of the pollutant (phosphate) increases in the solution. The values of constants (K_F, n and R^2) are in table 4.4.

Higher K_F values indicate higher binding energy. The value of K_F and n are higher for OP than CP in case of SAS. This indicates that sludge has higher adsorption affinity with OP as compared to CP. K_F value for OP is almost double of CP in SAS case. Thus it is recommended that aptitude of simli alum sludge to adsorb OP is higher. In case of RAS K_F values are higher for CP than OP but this difference is not significant.

In case of this study, n value lie in the permissible range as previously described in table 3.1 of material and methods. n values show that the adsorption is favorable . R^2 values also show that Freundlich isotherm favourable but less with reference to Langmuir. (Zhao *et al*., 2007). Hence, it can be said that Freundlich isotherm is also favorable to the data but less in comparison to Langmuir.

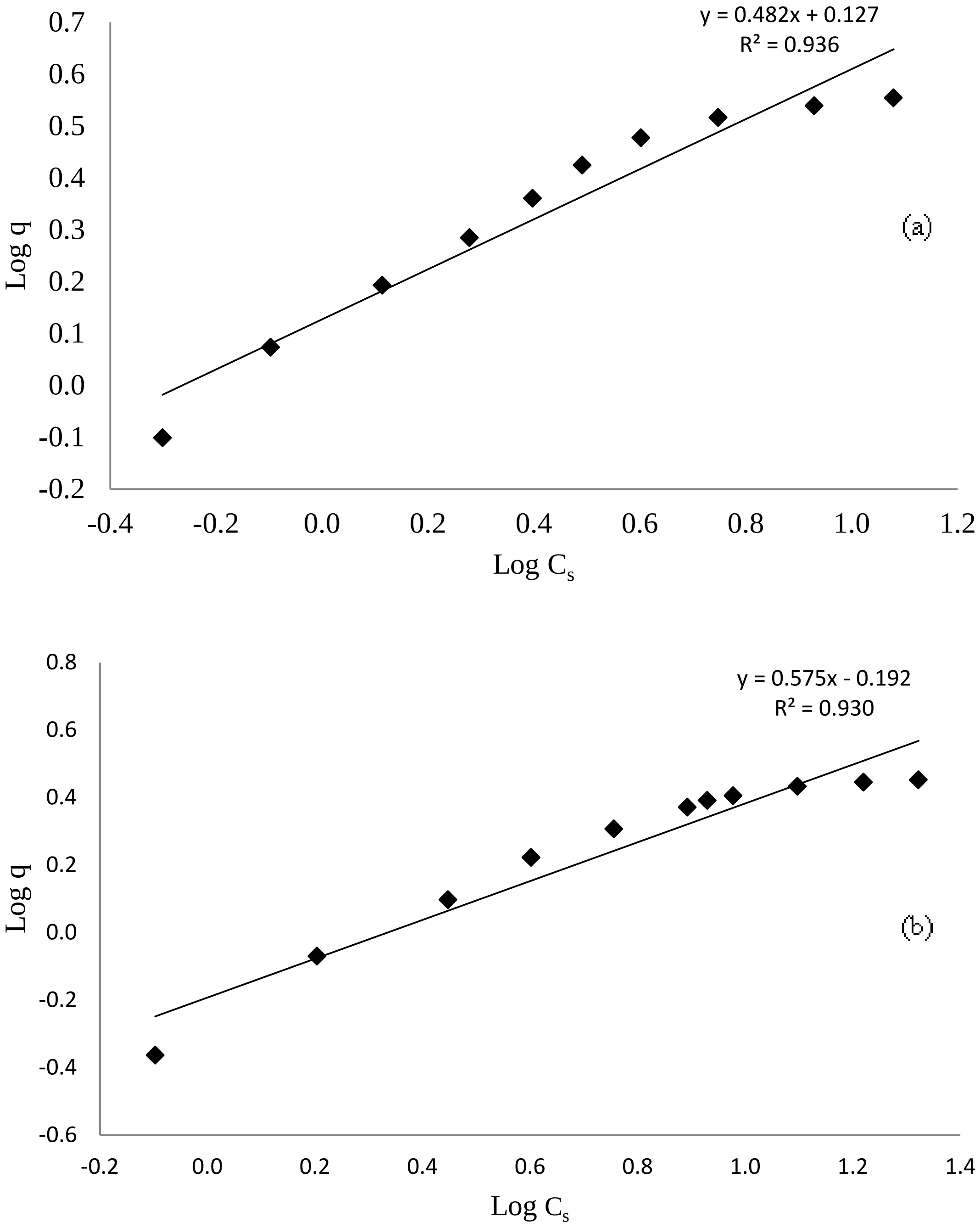
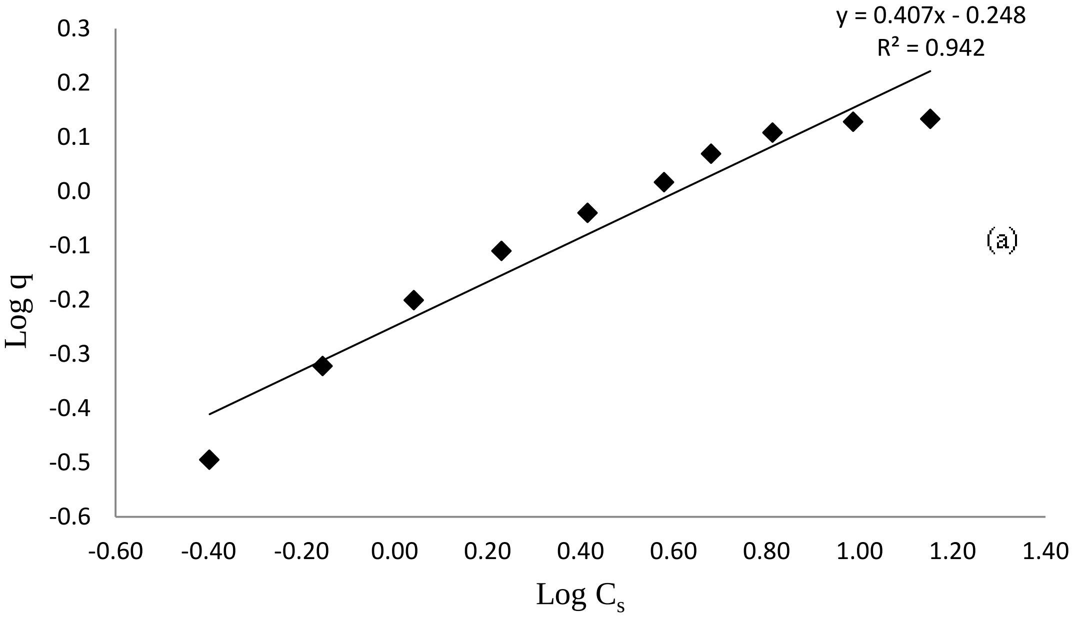


Figure 4.7 Freundlich Isotherm for OP (a) and CP (b) for SAS



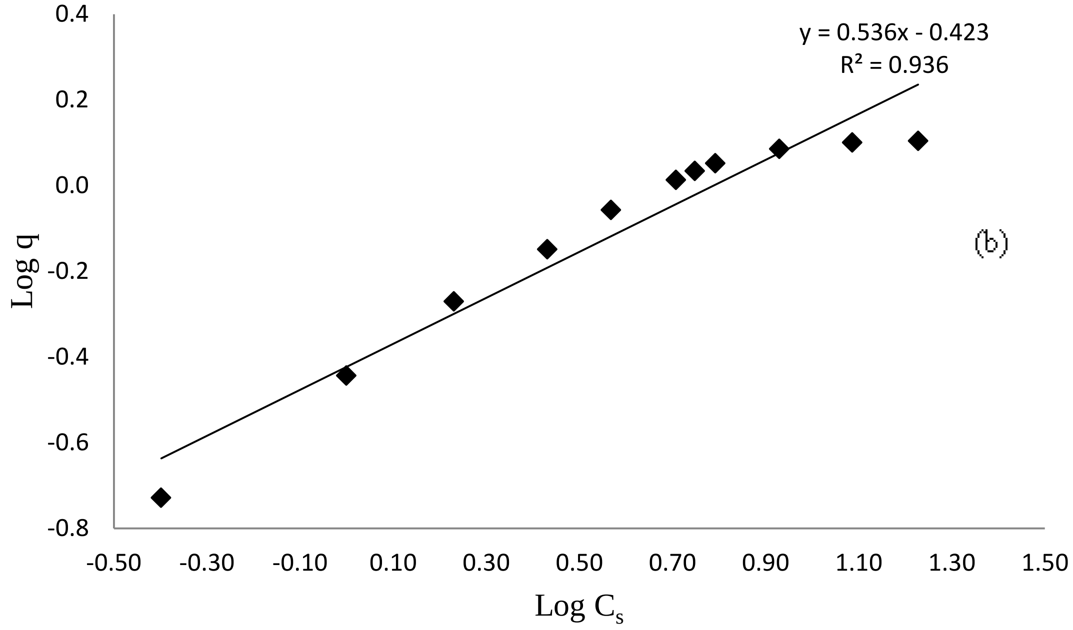


Figure 4.8 Freundlich Isotherm for OP (a) and CP (b) in case of RAS

Table 4.4 Constants of Freundlich Isotherm for RAS and SAS

Adsorbent	**Freundlich Constants**					
	OP			**CP**		
	K_f	n	R^2	K_f	n	R^2
SAS	1.34	2.07	0.936	0.64	1.74	0.930
RAS	0.56	2.45	0.942	0.67	1.86	0.936

4.3.5.2 Langmuir Isotherm

The Langmuir adsorption model is the most common model used to quantify the amount of adsorbate adsorbed on an adsorbent as a function of concentration at a given temperature. This isotherm describes that when sufficient adsorbent sites are occupied, further adsorption become impossible, thus adsorption is monolayer in nature. In Langmuir adsorption isotherm Q_o depicts the maximum adsorption capacity and b is the adsorption affinity describing that the material has attraction towards the compound. The values of constants (Q_o, b and R^2) obtained from trendlines are given in table 4.5.

The values of Q_o for SAS are 2-3 times higher for both OP and CP than that obtained by RAS. The highest adsorption capacity is 4.5 mg/g which is achieved for OP in SAS following CP in SAS. In case of RAS Qo for both OP and CP is same i.e. 1.53 mg/g.

The favorability of Langmuir isotherm depends upon R_L factor known as equilibrium parameter (Equation 3.5). The values of equilibrium parameter (R_L) are given in table 4.6. Langmuir isotherm fits the data fairly because the value of R_L should be within 0- 1 so that the data lies in the favorable mode (Table 3.2) (Babatunde *et al.*, 2008).

The coefficient of correlation (R^2) verifies that Langmuir isotherm is applicable on the data as the values are near to unity (0.992-0.998). Hence Langmuir isotherm is highly favorable for the adsorption of orthophosphorus (OP) and condensed phosphorus (CP) on RAS as well as SAS.

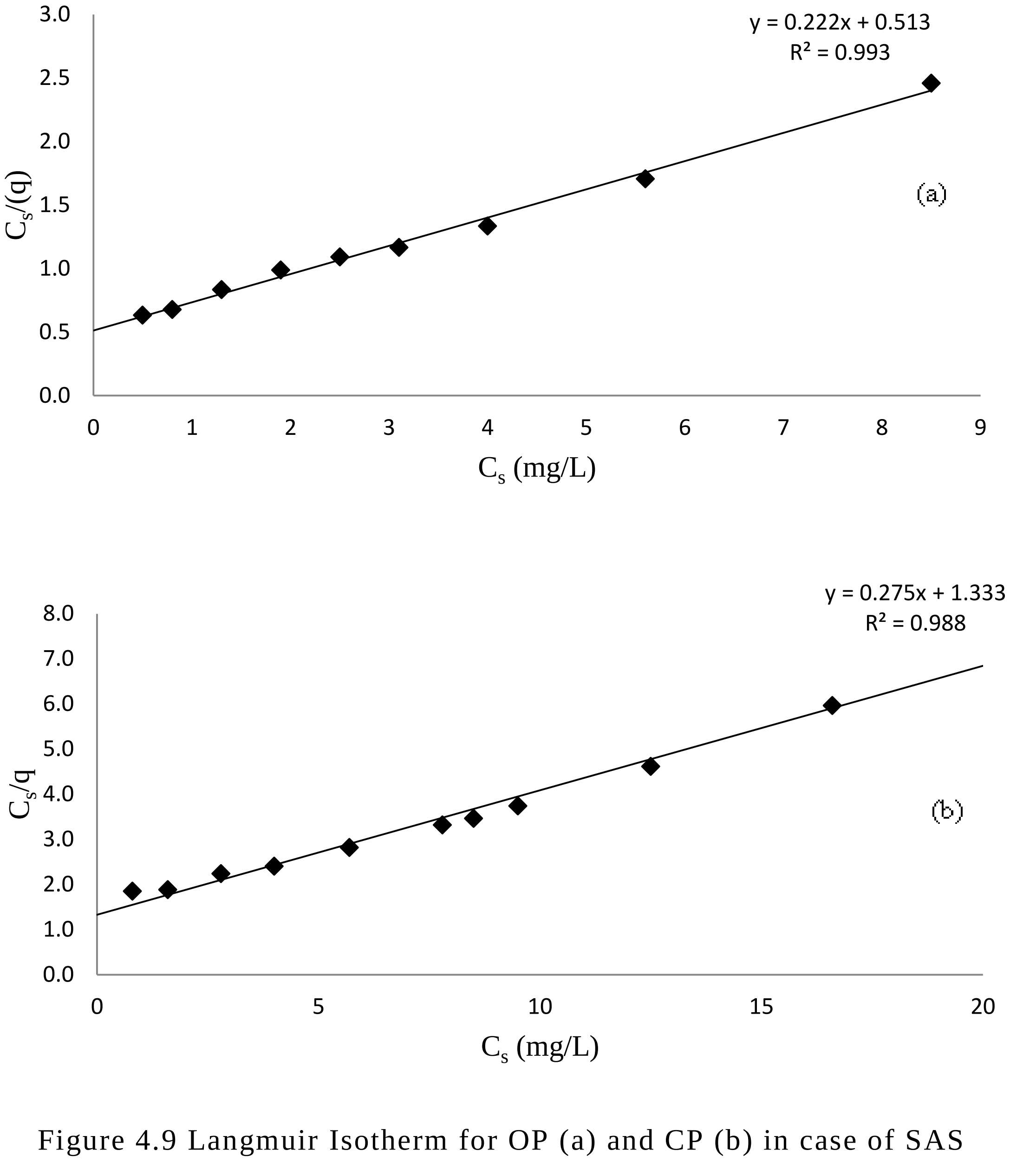
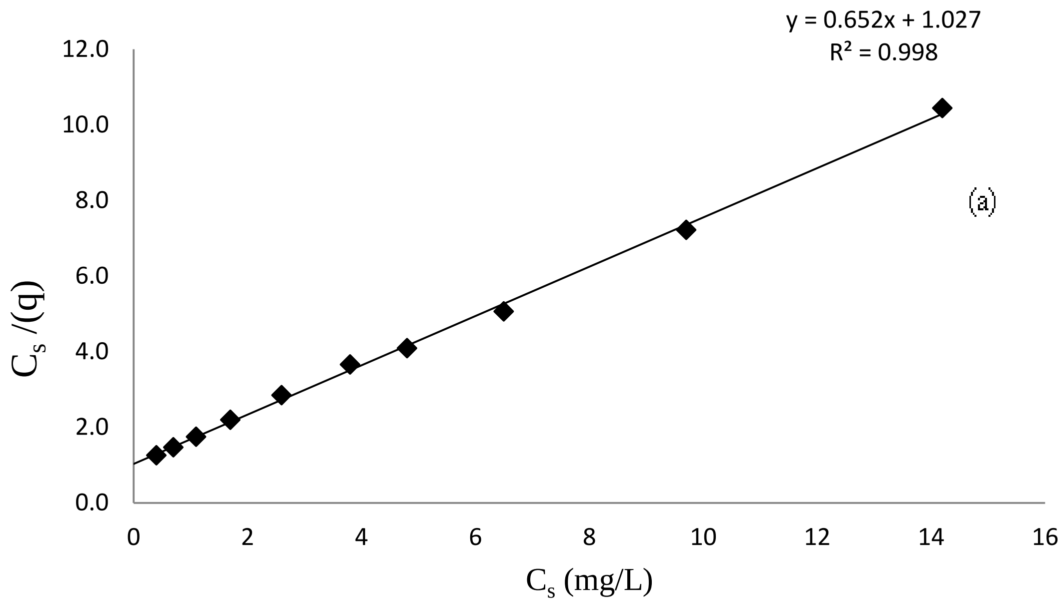


Figure 4.9 Langmuir Isotherm for OP (a) and CP (b) in case of SAS



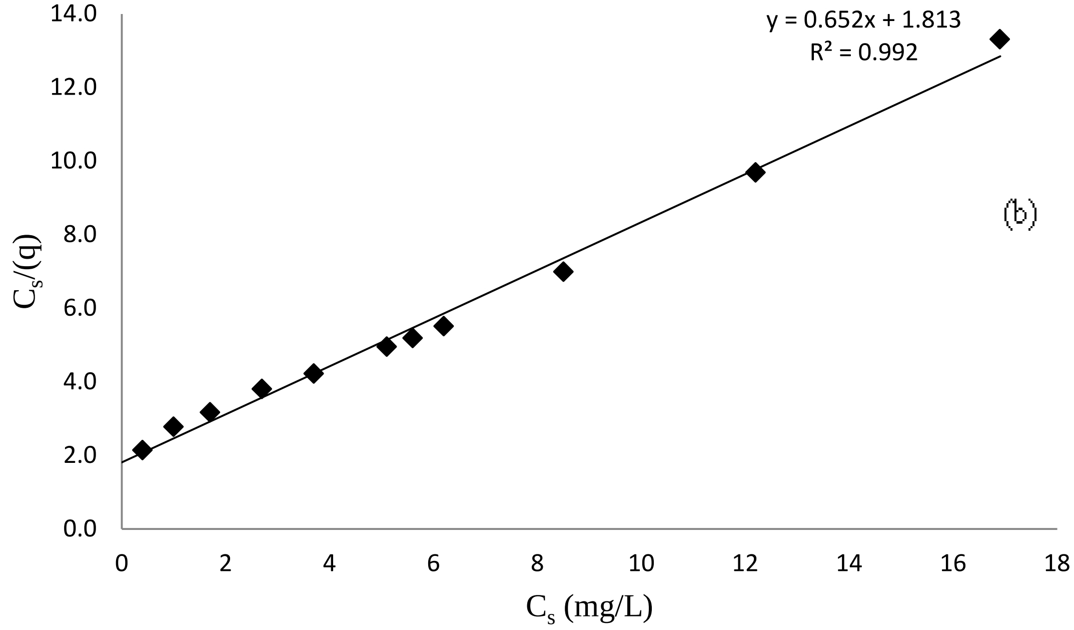


Figure 4.10 Langmuir Isotherm for OP (a) and CP (b) in case of RAS

Table 4.5 Constants of Langmuir Isotherm for RAS and SAS

Adsorbent	**Langmuir Constants**					
	OP			**CP**		
	b	Q_o (mg/g)	R^2	b	Q_o(mg/g)	R^2
SAS	0.43	4.5	0.993	0.21	3.64	0.988
RAS	0.64	1.53	0.998	0.36	1.53	0.992

Table 4.6 R_L values for Langmuir Isotherm

Ci (mg/L)	**R_L**		**Ci (mg/L)**	**R_L**	
	SAS	**RAS**		**SAS**	**RAS**
	OP	**OP**		**CP**	**CP**
10	0.190	0.135	6	0.44	0.32
15	0.130	0.094	12	0.29	0.19
20	0.104	0.072	18	0.21	0.13
25	0.085	0.060	24	0.17	0.10
30	0.072	0.049	30	0.14	0.08
35	0.062	0.043	36	0.12	0.07
40	0.055	0.037	38	0.11	0.07
45	0.050	0.034	40	0.11	0.06
50	0.044	0.030	45	0.10	0.06
55	0.040	0.028	50	0.09	0.05
			55	0.08	0.05

The results concluded from the isotherms are:

1. From Langmuir isotherm it is concluded that adsorption is favorably monolayer in nature and this model is most suitable to Orthophosphorus (OP) adsorption on RAS as well as SAS.
2. Freundlich isotherm states that adsorption is favorable.

Hence, finally wrapping up the fact with comment that adsorption is done on the sludges (adsorbent). It is noted from the literature that phosphorus was adsorbed successfully on 13 types of sand and Langmuir model highly supported the equilibrium data (Bubba *et al.*, 2006). In previous studies various isotherm models were used but Langmuir was found to be most suitable among them (Kim *et al*., 2002; Ippolito *et al*., 2003).

4.4 Real Wastewater Study:

Real wastewater samples were collected from NUST main drainage, where water from all schools and houses is dumped. Real municipal wastewater was collected and characterized. It contained 24.5 mg/L of OP (Orthophosphorus), 13.3 mg/L of Condensed phosphorus (CP) and 5.2 mg/L of Organic phosphates. This high concentration of phosphorus is due to excessive use of detergents, soaps and fecal and waste materials. Optimized dose and contact time for Simli Alum Sludge (SAS) and Rawal Alum Sludge (RAS) were employed on real wastewater samples. The removal trends are as shown in the figures below.

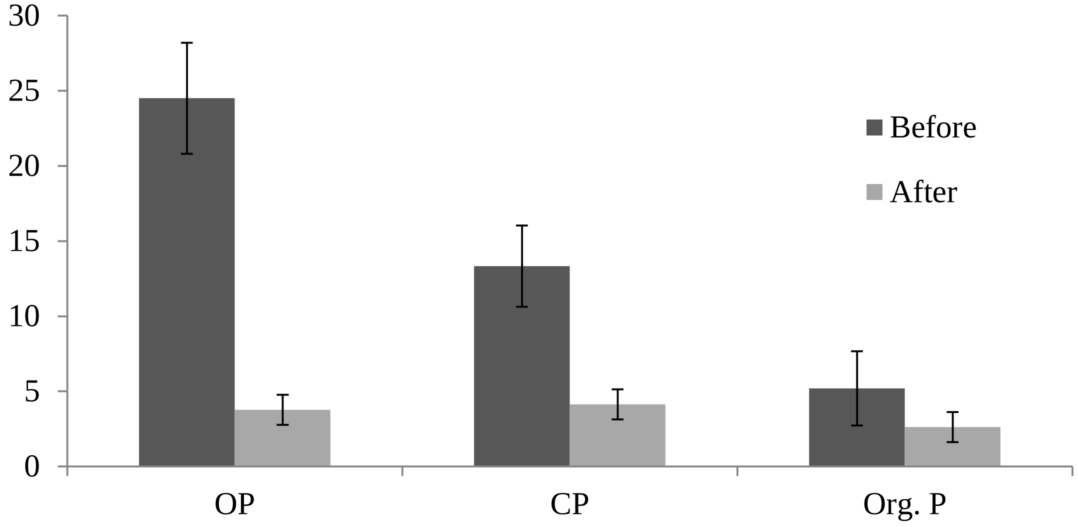


Figure 4.11 Phosphorus before and after treatment with SAS

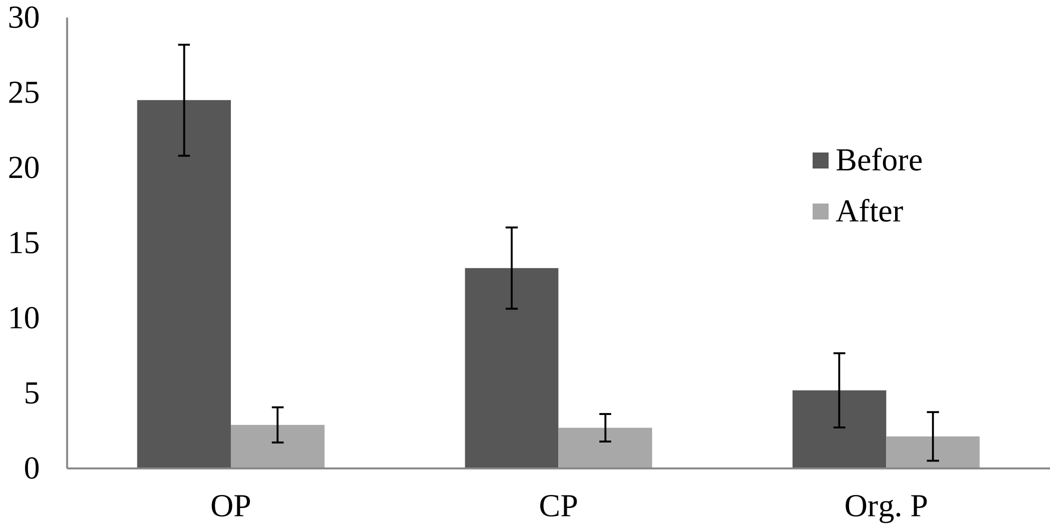


Figure 4.12 Phosphorus before and after treatment with RAS

85% of OP, 69% of CP and 50% of org. P was removed using 12g/L of Simli Alum Sludge (SAS). 88% of OP, 80% of CP and 60% of Org. P was achieved using 30g/L of Rawal alum sludge (RAS).

Chapter # 05

CONCLUSIONS AND RECOMMENDATIONS

5.1Conclusions

In this section, major conclusions from the results of this study are presented which are as follows

Alum Sludge Dose

Removal efficiency is directly proportional to the dose of alum sludge in case of Simli Alum Sludge (SAS) and Rawal Alum Sludge (RAS).

- For Simli alum sludge (SAS) equilibrium was achieved in removing OP and CP from wastewater using 12g/L which gave removal of 79% of orthophosphorus and 86% of condensed phosphorus. After optimized doses, no considerable change in % removal was observed on adding more and more dose.
- The highest removal of 92% of orthophosphorus and 89% of condensed phosphorus was achieved using 30g/L of Rawal Alum Sludge (RAS).

Contact Time

- Sharp drop of 75% for OP and 83% for CP was achieved at contact time of 90 minutes for SAS.
- For RAS 85% removal achieved for OP and 91% for CP in 80 minutes of mixing period.

pH

pH has no significant effect on the performance of sludges in wastewater. However, in acidic range both SAS and RAS performs better. Highest removal was achieved at 4.5 for SAS and 4.0 for RAS.

Adsorption Capacity

- Highest adsorption capacity of 3.58 mg/g and 2.8 mg/g of OP and CP for SAS was achieved at initial phosphorus concentration of 55mg/L.
- RAS gave highest adsorption capacity of 1.36 mg/g and 1.27 mg/g for OP and CP using 55mg/L of initial OP and CP concentrations.

Isotherm Models:

Freundlich and Langmuir adsorption isotherm models were applied for this adsorption study. Both proved to be favorable for SAS and RAS. However their favorability on the basis of R^2 is in the following order

Langmuir adsorption isotherm > Freundich adsorption isotherm

5.2 Recommendations

The following additional research is recommended to improve the understanding of this study and application of alum sludge for wastewater treatment:

- Further experiments to ascertain efficiency of alum sludges on fixed bed columns experiments should be carried out to study continuous wastewater treatment.
- Seasonal variation to be accomplished in this study as temperature has significant effect on production and removing phosphorus from wastewater.
- Alum sludge can be used to remove taste and odor problems in drinking water.

REFERENCES

Aguilar. M. I., J. Lloréns. S. M., Soler. A. and Ortuño. J. F. (2002). Nutrient removal and sludge production in the coagulation-flocculation process. Water Research., 36 (11): 2910–19.

Arceivaa S. and Asolekar S.R. (2007). Wastewater treatment for pollution control and reuse 3rd Ed., McGraw Hill Professionals, New York. pp.244-45.

Ayoub. G., Koopman. B. and Pandya. N. (2001). Iron and aluminum hydroxy(oxide) coated filter media for low-concentration phosphorus removal. Water Environment Research. 73: 478-85.

Babatunde. A.O., Zhao. Y.Q., Burke A.M., Morris M.A. and Hanrahan J.P. (2009). Characterization of aluminum-based water treatment residual for potential phosphorus removal in engineered wetlands. Environmental Pollution. 157(10):2830-36.

Babatunde. A.O., Zhao. Y.Q., Yang. Y. and Kearney. P. (2008). Reuse of dewatered aluminium-coagulated water treatment residual to immobilize phosphorus: Batch and column trials using a condensed phosphate. Chemical Engineering Journal**.** 136(2-3): 108-15.

Bajekal. S.S. and Dharmadhikari. N.S. (2008). Use of polyphosphate accumulating organisms (PAOs) for treatment of phosphate sludge. Conserving Lakes and Wetlands for Future. Proceedings of 12th World Lake conference, India. 918-22.

Bashan. Luz E. de. and Bashan Y. (2004). Recent advances in removing phosphorus from wastewater and its use as fertilizer. Water Research. 38(19): 4222-46.

Bitton G. (2005). Wastewater Microbiology 3rd Ed., Wiley Series in Ecological and Applied Microbiology. John Wiley, New York. 89p.

Bubba. D. M., Arias. C.A. and Brix. H. (2003). Phosphorus adsorption maximum of sands for use as media in subsurface constructed reed beds as measured by the Langmuir isotherm. Water Research. 37(14): 3390–3400.

Calder. N., Anderson. B.C. and Martin. D.G. (2006). Field investigation of advanced filtration for phosphorus removal from constructed treatment wetland effluents. Environmental Technology. 27(10):1063-71.

Conley. D.J., Paerl. H.W., Howarth. R.W., Boesch. D.F., Seitzinger. S.P., Havens. K.E., Lancelot. C. and Likens. G.E. (2009). Controlling eutrophication: Nitrogen and Phosphorus. Science. 323:1014-15

Cooke. J.G., (1992). Phosphorus removal in a wetland after a decade of receiving a sewage effluent. Journal of Environmental Quality. 21:733-39.

Cornwell, D. A., and Zoltek. J. (1977). Recycling of alum used for phosphorus removal in domestic wastewater treatment. Water Pollution Control Federation. 49(4): 600-12.

Drizo, A., Forget, C., Chapuis. R.P. and Comeau Y. (2006). Phosphorus removal by electric arc furnace steel slag and serpentinite. Water Research. 40(3): 1547-54.

Eaton, A.D., Clasceri. L.S., Rice. E.W. and Greenberg. A.E. (2005). Standard methods for the examination of water and wastewater 21st .Ed., American Public Health Association, Washington DC. pp. 4.146-4.152.

Erdal. U.G., Erdal. Z.K. and Randall. C.W. (2003). The competition between PAOs (phosphorus accumulating organisms) and GAOs (glycogen accumulating organisms) in EBPR (enhanced biological phosphorus removal) systems at different temperatures and the effects on system performance. Water Science and Technology. 47(11): 1-8.

Fdlmi. K.B. (1996). The phosphorus cycle, phosphogenesis and marine phosphate-rich deposits. Earth-Science Reviews. 40(1-2): 55-124 .

Georganatas, D.A. and Grigoropouou, H.P., (2005). Phosphorus removal from synthetic and municipal wastewater using spent alum sludge. Water Science and Technology. 52(10): 525-32.

Harper. D., (1991). Eutrophication of freshwaters. Chapman and Hall, London.

Helness. H. and Ødegaard. H. (2001). Biological phosphorus and nitrogen removal in a sequencing batch moving bed biofilm reactor. Water Science and Technology. 43(1): 233-40.

Huang. S.H. and Chiswell. B. (2000). Phosphate removal from wastewater using spent alum sludge. Water Science and Technology. 42(2-3): 295-300.

Ippolito. J.A., Barbarick. K.A., Heil. D.M., Chandler. J.P. and Redente. E.F. (2003). Phosphorus retention mechanisms of a water treatment residual. Journal of Environmental Quality. 32: 1857-64

Jiang. F., Beck. M.B., Cummings. R.G., Rowles. K. and Russell. D. (2005). Estimation of Costs of Phosphorus Removal in wastewater Treatment Facilities: Adaptation of Existing Facilities. Water Policy Working Paper #2005-011.

Johansson. W. L., Drizo. A. and Renman. G. (2011). The Use of Blast Furnace and Electric Arc Furnace Steel Slag in Water Pollution Control. Ferrous Slag - Resource Development for an Environmentally Sustainable World. EUROSLAG Publication No.5: 103-11.

Kammerer. J., Carle. R., Kammerer. D. R. (2011). Adsorption and Ion Exchange: Basic Principles and Their Application in Food Processing. Journal of agricultural and food chemistry, 59(1): 22-42.

Kim. J. G., Kim. J. H., Moon. H. S., Chon. C. M., Ahn. J. S. (2003). Removal capacity of water plant alum sludge for phosphorus in aqueous solutions. Chemical Speciation and Bioavailability. 14: 67–73.

Lan. Y.Z., Zhang. S., Wang. J.K. and Smith. R.W. (2006). Phosphorus Removal using steel slag. Acta Metallurgica Sinica (English Letters). 19(6): 449–454.

Lee. G.F., Rast. W. and Jones. R.A. (1978). Eutrophication of water bodies: Insight for an age-old problem. Environmental Science and Technology. 12: 900-08.

Li. W.C., Zhao. Y.Q. (2010). Phosphorus immobilisation in Aluminum drinking water treatment sludge (Al-DWTS) and soil under laboratory conditions. International Journal of Environmental Studies. 67(5): 747–762.

Lind. C. (1998). Typical reactions in the chemical removal of phosphorus. Water Engineering and Management. February: 18-21.

Makris. K.C., Harris. W. G., O'connor. G.A. and Obreza. T. A. (2004). Phosphorus immobilization in micropores of drinking-water treatment residuals: implications for long-term stability. Environmental Science and Technology. 38: 6590-6596.

Marani. D., Di Pinto. A.C., Ramadori. R. and Tomei. C. (1997). Phosphate removal from municipal wastewater with low lime dosage. Environmental Technology. 18: 225–230

Merzouki. M., Bernet. N., Delgenes. J. P., Moletta. R. and Benlemlih. M. (2001). Biological denitrifying phosphorus removal in SBR: effect of added nitrate concentration and sludge retention time. Water Science and Technology. 43(3):191–194

Metcalf and Eddy. (2003). Wastewater engineering: treatment and reuse. 4th Ed., McGraw Hill, New York. pp. 623-29.

Mohammed. W. T. and Rashid. S. A. (2012). Phosphorus Removal From Wastewater Using Oven Dried Alum Sludge. International Journal of Chemical Engineering Hindawi Publishing Corporation. Article ID 125296, 11 pages doi:10.1155/2012/125296.

Montgomery. J.M. (1985). Water Treatment Principle and Design. Wiley Inter Science, New York. pp. 174-91.

Moriyama. K., Kojima. T., Minawa. Y., Matsumoto. S. and Nakamachi. K. (2001). Development of artificial seed crystal for crystallization of calcium phosphate. Environmental Technology. 22: 1245–1252.

Morse. G.K., Lester. J.N. and Perry. R. (1993). The economic and environment impact of phosphorus removal from wastewater in the European Community. Selper Publications London.

Mortula. M.M. and Gagnon. G.A. (2007). Alum residuals as a low technology for phosphorus removal from aquaculture processing water. Aquacultural Engineering. 36: 233–238.

Onyango. M.S., Kuchar. D., Kubota. M. and Matsuda. H. (2007). Adsorptive Removal of Phosphate Ions from Aqueous Solution Using Synthetic Zeolite. Industrial & Engineering Chemistry Research. 46(3): 894-900.

Özacar. M. and Sengil. I.A. (2003). Enhancing phosphate removal from wastewater by using polyelectrolytes and clay injection. Journal of Hazardous Material. 100:131-146.

Pierzynski. G. M., Thomas. S.J. and George. F. V. (2005). Soils and environmental quality 3rd Ed., Taylor & Francis Group, LLC.

Porcella. D.B. (1974). Comprehensive Management of Phosphorus Water Pollution. *Socioeconomic Environmental Studies Series, Office of the Research and Development U.S. Environmental Protection Agency*

Razali. M., Zhao. Y.Q. and Bruen. M. (2007). Effectiveness of drinking water treatment sludge in removing different phosphorus species from aqueous solution. Separation and Purification Technology. 55: 300– 306.

Reddy. M. (1998). Biological and chemical systems for nutrient removal. *WEF, special publication.*

Reynold. T.D. and Richards. P.A. (1996). Unit Operations Processes in Environmental Engineering 2nd Ed., PWS Publiching Company, Boston. pp. 350-71.

Riding. J.T., Elliot. W.R. and Sherrard. J.H. (1979). Activated sludge phosphorus removal mechanism. Journal of Water Pollution Control Federation. 51(5): 1040-53.

Sakadevan. K. and Bavor. H.J. (1999). Nutrient removal mechanisms in constructed wetlands and sustainable water management. Water Science and Technology. 40(2): 121-128.

Shilton. A.N., Elmetri. I., Drizo. A., Pratt. S., Haverkamp. R.G. and Bilby. S.C. (2006). Phosphorus removal by an active slag filter-a decade of full scale experience. Water Research. 40(1):113-8.

Storm. P.F. (2006). Technologies to remove phosphorus from wastewater. Rutgers University.

Streeter. H.W. and Phelps. E.B. (1925). A study of the pollution and natural purification of the Ohio River III. Factors concerned in the phenomena of oxidation and reparation. Public Health Bull. pp.146-175.

Stumm. W. and Morgan. J.J. (1981). Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters 2nd Ed., John Wiley & Sons, New York.

Thomas. M.P. (2008). The secret of achieving reliable biological phosphorus removal. Water Science and Technology. 58(6): 1231-36.

Tie. J., Zhao. L. and Guo. H. (2011). Phosphorus Adsorption by Dewatered and Activated Alum Sludge. 2011 Fourth International Conference on Intelligent Computation Technology and Automation.

Wanchun. T., Qiuyun. W., Yunbo. W. and Zhengke. P. (2011). Third International Conference on Measuring Technology and Mechatronics Automation.

World Resources Institute. (2012). Eutrophication and Hypoxia: Nutrient Pollution in Coastal Waters.

Wu. Q., Bishop. P.L., Keener. T.C., Stallard. J. and Stile. L. (2001). Sludge digestion enhancement and nutrient removal from anaerobic supernatant by $Mg(OH)_2$ application. Water Science and Technology. 44: 161–66.

Xiaohong, G. (2005). Adsorption of phosphates and organic acids on Aluminum hydroxide in aquatic environment – mechanism and interactions. Ph.D dissertation. Hong Kong University of Science and Technology.

Yang. Y., Tomlinson. D., Kennedy. S. and Zhao. Y.Q. (2006). Dewatered alum sludge: A potential adsorbent for phosphorus removal. Water Science and Technology. 54(5): 207–213.

Yang. Y., Zhao. Y.Q., Babatunde. A.O. and Kearney. P. (2009). Two strategies for phosphorus removal from reject water of municipal wastewater treatment plant using alum sludge. *Water Science and Technology*. 60 (12): 3181-3188.

Yang. Y., Zhao. Y.Q., Babatunde. A.O., Wang. L., Ren. Y.X. and Han. Y. (2006). Characteristics and mechanisms of phosphate adsorption on dewatered alum sludge. Separation and Purification Technology. 51: 193– 200.

Yeoman. S., Stephenson. T., Lester. J. N. and Perry. R. (1988). The Removal of Phosphorus during Wastewater Treatment: A Review. Environmental Pollution. 49: 183-233.

Zhao. Y. Q., Yang. Y. (2010). Extending the use of dewatered alum sludge as a P-trapping material in effluent purification: Study on two separate water treatment sludges. Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering. 45(10): 1234-39.

Zhao. Y.Q., Razali. M., Babatunde. A.O., Yang. Y. and Bruen. M. (2007). Reuse of Aluminium-based water treatment sludge to immobilize a wide range of phosphorus contamination: Equilibrium study with different isotherm models. Separation Science and Technology. 42: 2705-21.

Zheng. H., Liu. D., Zheng. Y., Liang. S. and Liu. Z. (2009). Sorption isotherm and kinetic modeling of aniline on Cr-bentonite. Journal of Hazardous Materials. 167: 141–147.

APPENDICES

APPENDIX-A

Adsorption Study of Simli Alum Sludge (SAS)

1.1 Dose

Dose (g/L)	**pH**		**Turbidity (NTU)**		**OP (mg/L)**		**Removal (%age)**	**Adsorption Capacity q (mg/g)**	**CP (mg/L)**		**Removal (%age)**	**Adsorption Capacity q (mg/g)**
	Initial	Final	Initial	Final	C_i	C_o			C_i	C_o		
0	7.78	7.78	0.56	0.56	25	25.0	0	#DIV/0!	15	15.0	0.0	#DIV/0!
1	7.78	8.41	0.56	0.37	25	19.2	23.2	5.80	15	12.7	15.3	2.30
2	7.78	8.33	0.56	0.29	25	17.9	28.4	3.55	15	12.8	14.7	1.10
3	7.78	8.4	0.56	0.3	25	15.0	40	3.33	15	11.2	25.3	1.27
4	7.78	8.1	0.56	0.37	25	12.7	49.2	3.08	15	10.4	30.7	1.15
5	7.78	8.02	0.56	0.33	25	11.1	55.6	2.78	15	7.3	51.3	1.54
6	7.78	8.37	0.56	0.29	25	10.1	59.6	2.48	15	6.9	54.0	1.35
7	7.78	8.32	0.56	0.38	25	10.0	60	2.14	15	6.9	54.0	1.16
8	7.78	8.27	0.56	0.3	25	7.9	68.44	2.14	15	6.1	59.3	1.11
9	7.78	8.28	0.56	0.41	25	7.3	70.8	1.97	15	6.2	58.7	0.98
10	7.78	8.22	0.56	0.26	25	6.7	73.2	1.83	15	4.8	68.0	1.02
12	7.78	8.22	0.56	0.17	25	5.4	78.4	1.63	15	2.0	86.7	1.08
14	7.78	8.15	0.61	0.26	25	5.1	79.48	1.42	15	2.2	85.5	0.92
16	7.78	8.15	0.61	0.29	25	4.6	81.48	1.27	15	2.1	86.2	0.81
18	7.78	8.07	0.61	0.27	25	4.5	82.12	1.14	15	2.1	85.8	0.72
20	7.78	8.11	0.61	0.77	25	4.5	82.12	1.03	15	2.0	86.7	0.65

1.2 Contact Time

Time (min)	pH		Turbidity (NTU)		OP (mg/L)		Removal (%age)	CP (mg/L)		Removal (%age)
	Initial	Final	Initial	Final	C_i	C_o		C_i	C_o	
0	8		5.38		25	25	0	15	15	0
30	8	8.2	5.38	0.2	25	17	32	15	6.2	58.67
60	8	8.17	5.38	0.171	25	10	60.00	15	3	80.00
90	8	8.2	5.38	0.55	25	6.4	74.40	15	2.6	83.00
120	8	8.17	5.38	0.7	25	6.3	74.80	15	2.4	84.00
180	8	8.23	5.38	0.194	25	6.2	75.20	15	2.1	86.00
240	8	8.4	5.38	0.259	25	5.9	76.40	15	2.1	86.00
300	8	8.49	5.38	0.17	25	5.7	77.20	15	1.9	87.33
360	8	8.51	5.38	0.21	25	5.6	77.60	15	1.8	88.00

1.3 pH

pH	OP (mg/L)		Dose (g/L)	Adsorption Capacity q (mg/g)	Removal (%age)	CP (mg/L)		Adsorption Capacity q (mg/g)	Removal (%age)
	C_i	C_o				C_i	C_o		
3	25	7.8	12	1.43	68.8	15	6.5	0.71	56.7
4	25	0.2	12	2.07	99.2	15	1.70	1.11	88.7
5	25	0.3	12	2.06	98.8	15	1.70	1.11	88.7
6	25	0.4	12	2.05	98.4	15	2.30	1.06	84.7
7	25	1.7	12	1.94	93.2	15	2.00	1.08	86.7
8	25	5.8	12	1.60	76.8	15	2.60	1.03	82.7
9	25	8.8	12	1.35	64.8	15	4.50	0.88	70.0

1.4 Initial Concentration of Phosphorus Langmuir and Freundlich Isotherm

(a) OP

C_i (mg/L)	C_s (mg/L)	x=diff. (mg/L)	m=dose (g/L)	Adsorption Capacity q (mg/g)	$C_s/(q)$	Log C_s	Log q	Removal (%age)	ln C_s
0	0	0	12	0.00				-	-
10	0.5	9.5	12	0.79	0.63	-0.30	-0.10	95.00	-0.6931
15	0.8	14.2	12	1.18	0.68	-0.10	0.07	94.67	-0.2231
20	1.3	18.7	12	1.56	0.83	0.11	0.19	93.50	0.26236
25	1.9	23.1	12	1.93	0.99	0.28	0.28	92.40	0.64185
30	2.5	27.5	12	2.29	1.09	0.40	0.36	91.67	0.91629
35	3.1	31.9	12	2.66	1.17	0.49	0.42	91.14	1.1314
40	4	36	12	3.00	1.33	0.60	0.48	90.00	1.38629
45	5.6	39.4	12	3.28	1.71	0.75	0.52	87.56	1.72277
50	8.5	41.5	12	3.46	2.46	0.93	0.54	83.00	2.14007
55	12	43	12	3.58	3.35	1.08	0.55	78.18	2.48491

(b) CP

C_i (mg/L)	C_s (mg/L)	x=diff. (mg/L)	m=dose (g/L)	Adsorption Capacity q (mg/g)	$C_s/(q)$	Log C_s	Log q	Removal (%age)	ln C_s
0	0	0	12	0.00				-	-
6	0.8	5.2	12	0.43	1.85	-0.10	-0.36	86.67	-0.2231
12	1.6	10.2	12	0.85	1.88	0.20	-0.07	86.44	0.47
18	2.8	15	12	1.25	2.24	0.45	0.10	84.27	1.02962
24	4	20	12	1.67	2.40	0.60	0.22	83.33	1.38629
30	5.7	24.3	12	2.03	2.81	0.76	0.31	81.00	1.74047
36	7.8	28.2	12	2.35	3.32	0.89	0.37	78.33	2.05412
38	8.5	29.5	12	2.46	3.46	0.93	0.39	77.63	2.14007
40	9.5	30.5	12	2.54	3.74	0.98	0.41	76.25	2.25129
45	12.5	32.5	12	2.71	4.62	1.10	0.43	72.22	2.52573
50	16.6	33.4	12	2.78	5.96	1.22	0.44	66.80	2.8094
55	21	34	12	2.83	7.41	1.32	0.45	61.82	3.04452

1.5 Real wastewater study

				Mean	St. Dev				Mean	St. Dev
OP (mg/L)	28.3	24.3	20.9	24.5	3.70	5.2	3.5	2.6	3.8	1.32
CP(mg/L)	15.5	14.2	10.3	13.3	2.71	5.5	3.9	3	4.1	1.27
Org. P (mg/L)	7.5	5.5	2.6	5.2	2.46	3.1	2.6	2.2	2.6	0.45

APPENDIX-B

Adsorption Study of Rawal Alum Sludge (RAS)

2.1 Dose

Dose (g/L)	pH		Turbidity (NTU)		OP (mg/L)		Removal (%age)	Adsorption Capacity q (mg/g)	CP (mg/L)		Removal (%age)	Adsorption Capacity q (mg/g)
	Initial	Final	Initial	Final	C_i	C_o			C_i	C_o		
0	7.69	7.69	1.18	1.18	25	25.0	0.00	-	15	15.0	0.0	-
1	7.69	8.24	1.18	0.27	25	17.7	29.08	7.270	15	13.2	12.2	1.8
2	7.69	8.33	1.18	0.23	25	16.9	32.40	4.050	15	12.5	16.7	1.3
3	7.69	8.28	1.18	0.2	25	15.5	38.12	3.177	15	11.6	22.5	1.1
4	7.69	8.29	1.18	0.23	25	14.3	42.92	2.683	15	8.9	40.5	1.5
5	7.69	8.37	1.18	0.31	25	12.5	49.88	2.494	15	5.0	66.9	2.0
6	7.69	8.29	1.18	0.17	25	12.2	51.40	2.142	15	5.4	64.3	1.6
7	7.69	8.15	1.18	0.19	25	11.3	55.00	1.964	15	4.9	67.7	1.5
8	7.69	8.2	1.18	0.14	25	10.7	57.40	1.794	15	4.5	70.0	1.3
9	7.69	8.14	1.18	0.12	25	9.7	61.20	1.700	15	4.2	72.0	1.2
10	7.69	8.13	1.18	0.2	25	9.2	63.40	1.585	15	4.0	73.3	1.1
12	7.69	8.19	1.18	0.17	25	7.3	70.68	1.473	15	3.5	76.7	1.0
14	7.69	8.11	1.18	0.24	25	6.7	73.20	1.307	15	3.0	80.0	0.9
16	7.69	8.08	1.18	0.22	25	6.0	76.12	1.189	15	2.5	83.1	0.8
18	7.69	8.05	1.18	0.25	25	5.2	79.08	1.098	15	2.4	84.0	0.7
20	7.69	8.12	1.18	0.23	25	4.3	82.68	1.034	15	2.3	84.9	0.6
22	7.69	8.09	1.18	0.17	25	3.4	86.28	0.980	15	2.0	86.7	0.6
24	7.69	8.12	1.18	0.2	25	3.3	86.68	0.903	15	1.9	87.3	0.5
26	7.69	8.04	1.18	0.25	25	2.8	88.68	0.853	15	1.8	88.0	0.5
28	7.69	7.97	1.18	0.26	25	2.5	90.20	0.805	15	1.7	88.7	0.5
30	7.69	8.17	1.18	0.28	25	2.1	91.48	0.762	15	1.6	89.3	0.4

32	7.69	8.15	1.18	0.25	25	2.1	91.6	0.716	15	1.6	89.3	0.4
34	7.69	8.03	1.18	0.19	25	2.1	91.6	0.674	15	1.5	90.0	0.4
36	7.69	8.08	1.18	0.23	25	2.0	92.0	0.638	15	1.4	90.7	0.4

2.2 Contact Time:

Time (min)	**pH**		**Turbidity**		**OP (mg/L)**		**Removal (%age)**	**CP (mg/L)**		**Removal (%age)**
	Initial	**Final**	**Initial**	**Final**	**C_i**	**C_o**		**C_i**	**C_o**	
0	7.75		4		25	25	0	15	15	0
60	7.75	7.9	4	0.144	25	4.3	82.80	15	1.5	90.00
120	7.75	7.97	4	0.197	25	3.8	84.80	15	1.4	90.67
180	7.75	8.33	4	0.13	25	3.1	87.60	15	1.2	92.00
240	7.75	8.11	4	0.124	25	2.9	88.40	15	1.1	92.67
300	7.75	8.35	4	0.14	25	2.6	89.60	15	1.2	92.00
360	7.75	8.37	4	0.117	25	2.6	89.60	15	1.2	92.00
420	7.75	8.13	4	0.116	25	1.6	93.60	15	0.8	94.67
480	7.75	8.26	4	0.19	25	2	92.00	15	1.4	90.67
540	7.75	8.27	4	0.331	25	2.8	88.80	15	1	93.33
600	7.75	8.32	4	0.156	25	1.5	94.00	15	2.3	84.67
660	7.75	8.3	4	0.18	25	1.9	92.40	15	1.8	88.00
720	7.75	8.51	4	0.15	25	1.9	92.40	15	1.9	87.33

2.3 pH

pH	OP (mg/L)		Dose (g/L)	Adsorption Capacity q (mg/g)	Removal (%age)	CP (mg/L)		Adsorption Capacity q (mg/g)	Removal (%age)
	C_i	C_o				C_i	C_o		
3	25	4.6	30	0.68	81.6	15	9.8	0.17	34.7
4	25	0.4	30	0.82	98.4	15	1.50	0.45	90.0
5	25	0.5	30	0.82	98.0	15	2.40	0.42	84.0
6	25	0.7	30	0.81	97.2	15	2.20	0.43	85.3
7	25	1.5	30	0.78	94	15	2.10	0.43	86.0
8	25	3.1	30	0.73	87.6	15	1.90	0.44	87.3
9	25	3.5	30	0.72	86	15	2.20	0.43	85.3

2.4 Initial Concentration of Phosphorus Langmuir and Freundlich Isotherm

(a) OP

C_i (mg/L)	C_s (mg/L)	x=diff. (mg/L)	m=dose (g/L)	Adsorption Capacity q (mg/g)	$C_s/(q)$	Log C_s	Log q	Removal (%age)	ln C_s
0	0	0	30	0.00					
10	0.4	9.6	30	0.32	1.25	-0.40	-0.49	96.00	-0.916
15	0.7	14.3	30	0.48	1.47	-0.15	-0.32	95.33	-0.357
20	1.1	18.9	30	0.63	1.75	0.04	-0.20	94.50	0.095
25	1.7	23.3	30	0.78	2.19	0.23	-0.11	93.20	0.531
30	2.6	27.4	30	0.91	2.85	0.41	-0.04	91.33	0.956
35	3.8	31.2	30	1.04	3.65	0.58	0.02	89.14	1.335
40	4.8	35.2	30	1.17	4.09	0.68	0.07	88.00	1.569
45	6.5	38.5	30	1.28	5.06	0.81	0.11	85.56	1.872
50	9.7	40.3	30	1.34	7.22	0.99	0.13	80.60	2.272
55	14.2	40.8	30	1.36	10.44	1.15	0.13	74.18	2.653

(b) CP

C_i (mg/L)	C_s (mg/L)	x=diff. (mg/L)	m=dose (g/L)	Adsorption Capacity q (mg/g)	C_s/(q)	Log C_s	Log q	Removal (%age)	ln C_s
0	0	0	30	0.00				#DIV/0!	#NUM!
6	0.4	5.6	30	0.19	2.14	-0.40	-0.73	93.33	-0.9163
11.8	1	10.8	30	0.36	2.78	0.00	-0.44	91.53	0
17.8	1.7	16.1	30	0.54	3.17	0.23	-0.27	90.45	0.53063
24	2.7	21.3	30	0.71	3.80	0.43	-0.15	88.75	0.99325
30	3.7	26.3	30	0.88	4.22	0.57	-0.06	87.67	1.30833
36	5.1	30.9	30	1.03	4.95	0.71	0.01	85.83	1.62924
38	5.6	32.4	30	1.08	5.19	0.75	0.03	85.26	1.72277
40	6.2	33.8	30	1.13	5.50	0.79	0.05	84.50	1.82455
45	8.5	36.5	30	1.22	6.99	0.93	0.09	81.11	2.14007
50	12.2	37.8	30	1.26	9.68	1.09	0.10	75.60	2.50144
55	16.9	38.1	30	1.27	13.31	1.23	0.10	69.27	2.82731

2.5 Real Wastewater Study:

				Mean	St. Dev				Mean	St. Dev
OP (mg/L	28.3	24.3	20.9	24.5	3.70	3.9	3.2	1.6	2.9	1.18
CP (mg/L)	15.5	14.2	10.3	13.3	2.71	3.7	2.5	1.9	2.7	0.92
Org. P (mg/L)	7.5	5.5	2.6	5.2	2.46	4	1.3	1.1	2.1	1.62