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Removal of Phosphorus from Municipal Wastewater

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DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

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ABSTRACT

Removal of Phosphorus from Municipal Wastewater

Removal of phosphorus from municipal wastewater is essential to minimise eutrophication in receiving water bodies. A variety of methods for the removal of phosphorus from wastewater, based on either chemical or biological processes, have been developed over past decades. The performance of the many techniques available for the phosphorus removal is still unsatisfactory when compared with the effluent quality and with the cost. This study focused on evaluation of the performance of phosphorus removal with chemical coagulation using alum and developed recommendations to improve the phosphorous removal from wastewater to meet the permissible effluent discharge limits. It entailed determination of the best parameters for this process through bench scale studies using jar test apparatus.

The aim of the present study was to improve the effectiveness of phosphorus removal from wastewater using alum (aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$)). The effect of various parameters including the initial pH of the solutions, different alum dosing regimes (incremental or single alum dosing with and without incremental pH correcting), the effect of dissolved organic carbon (DOC) and the effect of alum dose on phosphorus removal in municipal wastewaters was evaluated. Jar test experiments were conducted using both synthetic wastewater and real wastewater obtained from a conventional activated sludge wastewater treatment plant in Perth, Western Australia. Synthetic wastewater allowed the study of processes under controlled conditions and findings from these experiments were validated using real wastewater. The results of this study with changing initial pH of the solutions showed that the maximum phosphorus removal occurred at pH 6.5 which was in agreement with previously published studies. The effect of varying the alum dosing regime was trialled: specifically, alum was dosed in a single dose and also incrementally over periods up to 40 minutes and also while continuously controlling the pH. Controlling the pH of the synthetic wastewater with incremental alum dosing removed more phosphorus compared to real wastewater. Overall, the phosphorus removal with the incremental alum addition without pH control was higher than the single alum addition with or

without controlling the pH of the solutions (about 9%). The optimum phosphorus removal in wastewater was achieved with 40 - 80 mg/L of alum dosage (around 1 mg/L of residual phosphate concentration). An increase in the DOC removal was observed with the increase in aluminium ion dosage in synthetic wastewater and, consistent with this, the phosphorus removal efficiency was hindered by the increase of DOC concentration in real wastewater. Studies were conducted to determine the mechanism of removal of phosphorus from wastewater. These showed that removal of phosphorus occurred via phosphate precipitation with aluminium sulphate (presumably as aluminium phosphate) and the adsorption of phosphate by aluminium hydroxide which was formed during the chemical coagulation process (i.e. hydrolysis of alum upon reaction with water). As the nature of aluminium hydroxide changed with ageing, its phosphorus removal capability was decreased.

The findings of this thesis, especially the optimum pH value and the optimum alum dosage for improved coagulation would be beneficial for wastewater treatment plant operations, for optimisation of operating conditions. Further studies regarding the alum dosing regime (i.e dosing alum incrementally) would be worthwhile as there is little discussion on this topic in the current literature.

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LIST OF ABBREVIATIONS

BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DOC	Dissolved Organic Carbon
EBPR	Enhanced Biological Phosphorus Removal
PST	Primary Sedimentation Tank
SS	Suspended Solids
SST	Secondary Sedimentation Tank
TN	Total Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorus
TSS	Total Suspended Solids
WWTP	Waste Water Treatment Plant

CHAPTER 1

Introduction

1.1 Introduction

Phosphorus is a limiting nutrient in the world and it helps for the growth of algae and other aquatic weeds when it associates with fresh water. Extreme quantities of phosphorus entering into fresh water bodies like lakes and streams cause eutrophication and its related issues, which creates detrimental effects for the aquatic life and the environment. Hence, minimising phosphorus levels in wastewater (WW) is necessary before it is discharged to the environment.

Phosphorus is released to the environment by various human activities which include industrial, agricultural and other activities. Although many countries have established strict effluent discharge limits for phosphorus due to increasing concerns about the eutrophication, phosphorus pollution is still increasing. Typically a residual of 1 mg/L as P is required in effluents discharged to natural water bodies. This value may vary depending on how much the receiving water bodies are ecologically fragile. Phosphorus in wastewater can be present as orthophosphate, polyphosphate or organic phosphorus compounds. Chemical, biological or physical processes have been deployed for the removal of phosphorus in wastewater. The most economical way to remove phosphorus from wastewater is chemical precipitation. Many metal salts are being used to remove phosphorus by precipitating as phosphoric complexes which are insoluble. The addition of chemical coagulants at different locations to remove excess amounts of phosphate to achieve the permissible limits is done many wastewater treatment plants. Phosphorus removal has previously been carried out using substances such as aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$), ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and calcium hydroxide ($\text{Ca}(\text{OH})_2$) in the chemical phosphorus removal process. Among all these substances, the use of aluminium sulphate gives the lowest theoretical weight ratio for the removal of phosphorus with the optimum pH of 6 to 6.5 which is close to the pH of domestic wastewater. In a wastewater treatment plant, many parameters affect the performance of the process and achievable levels of residual phosphorus in the effluent. The chemical composition of the phosphorus

compounds present in the wastewater, pH, and suspended solids, dissolved organic matter, type and dose of chemical coagulant, mixing conditions and the configuration of the process are among those parameters which affect for the final quality of the effluent.

The main objective of this study was to enhance the phosphorus removal efficiency of a wastewater treatment process by understanding the role of operating parameters and impact of wastewater components. Based on this main aim, the study aimed to find the effect of pH, dosage of chemical coagulant, mixing regime, role of dissolved organic carbon (DOC) and the effect of aluminium hydroxide on the phosphorus removal in municipal wastewater. Tests were conducted using both synthetic wastewater and real wastewater. Synthetic wastewater allowed studies of processes under controlled conditions and findings from these experiments were validated using real wastewater.

1.2 Aims and Objectives

The main objective of this research was to enhance the phosphorus removal efficiency by understanding the role of operating parameters and impact of wastewater components, especially DOC, when wastewater is treated with alum. To achieve this main objective, the following broad tasks were pursued.

- Investigate the role of operating parameters such as pH and mixing regime (mixing speed and multiple/single dosing) to enhance the efficiency of alum in removing phosphorus from synthetic wastewater
- Understand the role of DOC, both in terms of concentration and the type of DOC (chemical functionality) in hindering phosphorus removal efficiency of wastewater while using alum
- Investigate the effect of aluminium dose for the removal of phosphate
- Verify the outcomes from synthetic wastewater using real wastewater obtained from various locations within a local wastewater treatment plant
- Determine the molar ratio of total phosphorus removed to the chemical coagulant added to meet the permissible effluent phosphorus discharge standards

1.3 Significance of the Study

In a wastewater treatment plant, many parameters affect the performance of the process and it is necessary to achieve a permissible level of phosphorus residuals in the effluent. The chemical composition of the phosphorus compounds present in the wastewater, pH, suspended solid, dissolved organic matter, type and dose of chemical coagulant, mixing conditions and the configuration of the process are among those parameters which affect for the final quality of the effluent. Hence, the study of removal of phosphorus from municipal wastewater plays an important role in the process of wastewater treatment to enhance the effectiveness of the process and to minimise unnecessary costs involved with the process. The goal of the study is designed to investigate the effect of different parameters mentioned above for the efficient removal of phosphorus from municipal wastewater. Although there are large number of studies done on different parameters related to the phosphorus removal in wastewater, there are very few studies done on the effect of alum dosing regime. Improved understanding of optimal conditions of these parameters for alum addition can assist water utilities in reducing costs and their environmental footprint (e.g. sludge disposal costs and volume; chemical costs). This is only a small contribution for the studies associated with this topic. The greater demand for the effective and low cost phosphorus removal methods justifies the need for more researches on this area of study. Thus, the relevant authorities of the wastewater treatment plants will be benefited from the results of this study as they may use optimum conditions in the operation of their plants. For the researchers, the findings of this study will help them to uncover some of the areas which were not studied by past researchers.

The following chapters elucidate the effect of each parameter in detail.

1.4 Organization of Thesis

Seven chapters are included in the overall thesis. Chapter 1 offers an introduction to the study and for the thesis. Chapter 1 consists of introduction, aims and objectives of the study, significance of the study and the organisation of the thesis. The introduction provides a short description about the importance of controlling phosphorus in wastewater, the chemical coagulants use in a typical wastewater treatment plants, the parameters affecting for the performance of a wastewater treatment plant and a brief

description about the wastewater used during the course of this study. The aims, objectives and the significance of this study have also been given in this chapter.

Chapter 2 is a literature review related to the research in the field of study to date. Topics discussed include wastewater composition, wastewater quality parameters, and categories of wastewater treatment processes, phosphorus control in municipal wastewater and the chemical characteristics of aluminium coagulant. Australian Guidelines for Sewerage Systems – Effluent Management have also been reviewed in this chapter.

Chapter 3 describes the findings of the studies on the effect of initial pH on removal of phosphorus in municipal wastewater. Chapter 4 includes the findings from the experiment of varying alum dosage in wastewater. Chapter 5 discusses the results of studies to find the effect of alum dosing regime. Chapter 6 presents the results of experiment to find the effect of dissolved organic carbon (DOC) on phosphorus removal by alum and Chapter 7 describes the results of phosphorus removal by pre-formed aluminium hydroxide. Each of these chapters from Chapter 3 to Chapter 7 comprises of a brief introduction to each chapter, the objective of each experiment, the materials and methods used in the experiments and the results and conclusion sections. Chapter 8 discusses the conclusions of the studies and provides recommendations for future research.

CHAPTER 2

Literature Review

2.1 Introduction

Phosphorus moves through various parts of the environment including rocks, soil, water and sediments, either in the form of particulate bound phosphorus or as a solute in the aquatic environment.

The following figure depicts the phosphorus cycle which shows the movement of phosphorus in nature.

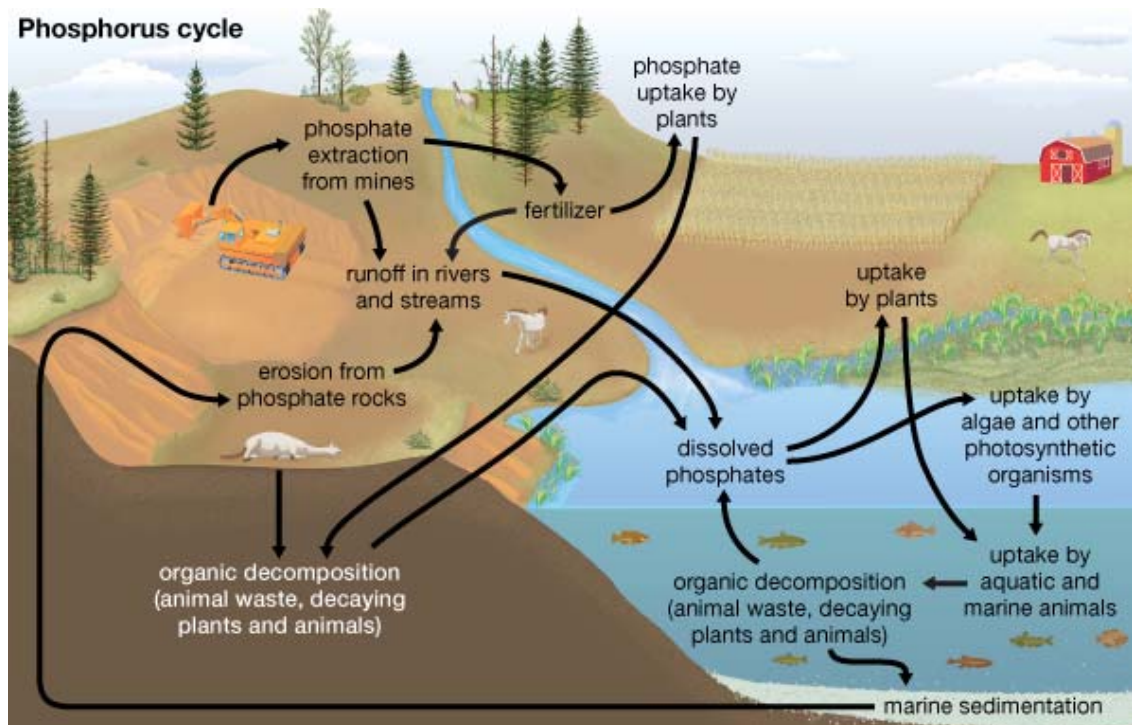


Fig. C2.1: Phosphorus Cycle (Encyclopaedia Britannica 2010)

In the past few decades, the phosphorus removal from wastewater has been identified as a key requirement for municipal wastewater treatment plants to control the input of phosphorus to water bodies (Morse, Brett et al. 1998, Loganathan, Vigneswaran et al. 2013). Discharge of wastewater into lakes and streams renders the water unsuitable for use by creating conditions that promote algae blooms (De Haas, Wentzel et al. 2000, Banu, Do et al. 2008, Chong and Thai 2015, Park, Ampunan et al. 2016). This leads

to eutrophication (Correll 1998, Kwak and Lee 2015, Park, Ampunan et al. 2016). Human excreta, detergents (Guan, Liu et al. 2005), food additives, corrosion inhibitors and industrial wastes are the main sources of phosphorus in wastewater.

Phosphorus in natural water or wastewater is normally present in the form of phosphate (PO_4^{3-}) and according to Mezenner and Bensmaili (2009) municipal wastewater typically contains 4 – 15 mg/L of phosphorus as $\text{PO}_4\text{-P}$. Synthetic detergents contribute to more than half of this amount and maximum standards for the phosphate content of detergents exist in some countries (Jenkins, Ferguson et al. 1971). This phosphorus in wastewater may be in the form of orthophosphate (dissolved form), polyphosphate (inorganic form) or organically bound phosphate (Mezenner and Bensmaili 2009, Loganathan, Vigneswaran et al. 2013). The main compound of phosphorus in wastewater is orthophosphate (reactive phosphorus) and it is the most basic form which is used to measure the amount of phosphorus that is present to react with the chemical coagulants or the biological process. Orthophosphate is also important because it is the most bioavailable form. The concentration of orthophosphate can be measured before or after the addition of chemical coagulants or after the biological adsorption and settling.

Phosphorus removal can be carried out either physically, chemically or biologically (Francisco 1976, Yeoman, Stephenson et al. 1988, Fytianos, Voudrias et al. 1996, Shanshool and Sawsan 2009). Filtration for particulate phosphorus and membrane technologies are used in physical phosphorus removal processes. In the chemical phosphorus removal process, either precipitation by chemical coagulants or physical-chemical adsorption method is used. Chemical coagulation is the most common method used in many wastewater treatment plants to remove phosphorus. Chemical coagulants are added to react with wastewater to convert soluble phosphorus into particulate phosphorus which then can be removed by settling (Kwak and Lee 2015). In the biological treatment process, assimilation or Enhanced Biological Phosphorus Removal (EBPR) methods are used. All these methods include the removal of precipitated insoluble phosphates which are formed (Morse, Brett et al. 1998) and the formation of these phosphate solids can be either biological solids or chemical precipitant (de-Bashan and Bashan 2004).

The chemical phosphorus removal process using alum is a complex process with mechanisms that are poorly understood and which may be largely dependent on the

conditions of reaction. The process is thought to include coagulation and flocculation, in which chemical precipitates are produced by transferring dissolved phosphates into particulate phosphates. Particulate phosphates may include (a) aluminium phosphate precipitates (AlPO_4), (b) phosphate adsorbed to or co-precipitated with $\text{Al}(\text{OH})_3$ and (c) phosphate entrained and/or adsorbed within floc formed during alum coagulation and flocculation. During the solids separation process in the wastewater treatment plant, the precipitates are removed. As stated by Aguilar et al. (2002), the following reactions take place between alum and phosphate

- Phosphate ions are incorporated into the solids in the suspension of the wastewater
- After the addition of alum in wastewater, hydrolysis products are formed and phosphate ions are directly adsorbed on it
- Insoluble phosphate precipitates are formed with the added alum

(Aguilar, Sáez et al. 2002)

Addition of alum to treat wastewater is widely being used in the wastewater treatment plants (WWTP) (Ratnaweera, Odegaard et al. 1992, Boisvert, To et al. 1997, De Haas, Wentzel et al. 2000, Wang, Han et al. 2005, Georgantas and Grigoropoulou 2007, Ramasahayam, Guzman et al. 2014). There are several reasons for the usage of alum as the chemical coagulant in WWTP as it can be used to obtain more or less any required residual phosphate-P concentrations and it is cheaper compared to other chemical coagulants to get lower phosphorus residuals (Ferguson and King 1977).

A previous study by Hsu (1975) with the use of iron salts has mentioned that when evaluating the effectiveness of the phosphorus removal, two factors should be taken into consideration. Those two factors are the concentration of the residual phosphate and the amount of phosphate removed per mole of iron. A much larger dose of chemical coagulant than the amount of phosphate present is required to remove phosphate completely from the solution. If phosphate presents in large excess, one mole of phosphate is removed by one mole of iron (III) at maximum. Hence, those two factors are not compatible.

Similarly, in the case of alum, the initial ratio of phosphate to aluminium present in the solution impacts on many factors including the optimum pH range for phosphorus

removal, the minimum concentration of the phosphate residual in the solution and the maximum amount of phosphate precipitated per mole of aluminium. When the pH of the solution is low, it is more difficult for Al^{3+} ions to release H^+ ions from H_2PO_4^- . And if the pH of the solution is high, there is a strong competition between OH^- ions and PO_4^{3-} ions for Al^{3+} ions. Both scenarios have to be taken into consideration in the formation of AlPO_4 (Hsu 1975).

A study by Chunjuan (2009) states that the phosphorus removal is affected by many factors including alkalinity, pH, dose of coagulant and method of mixing. An adequate amount of mixing allows a better contact with various particles in the solution including the colloids which are freshly formed and soluble phosphorus or suspended or colloidal particles to be combined which can be removed from wastewater. However unnecessary mixing can disintegrate the already formed flocs and this may cause the re-release of adsorbed phosphorus. The optimum pH value for phosphorus removal is around 6. Within this pH range, the precipitated aluminium phosphate has the lowest solubility. If the pH drop after the addition of alum is lower than 5.5, then the precipitated aluminium phosphate becomes soluble. Near neutral pH, highly charged large polymerizations are formed by hydrolysing the aluminium ions. These polymerised particles have a higher phosphorus adsorbent quality and an improved phosphorus removal by adsorption occurs. When the solution pH is further increased from the neutral value, AlO_2^- is formed and this reduces phosphorus adsorption. Therefore, phosphorus removal from wastewater is a combination of precipitating as aluminium phosphate and adsorbing phosphate on aluminium hydroxide. The increase of the coagulant dose also increases the phosphorus removal by precipitation. Although a relatively large dosage of alum is required to achieve the permissible discharge limits, the chemical cost and the amount of sludge produced have to be considered when applying those doses (Chunjuan D. 2009).

The definition of eutrophication as given in the Wikipedia is “*the ecosystem’s response to the addition of artificial or natural substances, mainly phosphates, through detergents, fertilisers or sewage to an aquatic system*”. Algal blooms or the excessive increase of phytoplankton in a water body due to the increased levels of nutrients is of one example. Hypoxia (the depletion of oxygen in the water) is one of the negative environmental effects of eutrophication which may cause death to aquatic animals (Wikipedia).

Phosphorus is a limiting nutrient in the world (Omoike 1999, Omoike and vanLoon 1999, Bai, Zhu et al. 2010) and it helps for the growth of algae and other aquatic weeds when it associates with fresh water which causes for the eutrophication. Since this eutrophication has been drawn as a significant environmental concern (Yeoman, Stephenson et al. 1988, Carpenter, Caraco et al. 1998, Omoike 1999, Mezenner and Bensmaili 2009), strict effluent discharge limits for nutrients discharge into ecologically fragile areas has been imposed by many countries to minimise the harmful effects of eutrophication (Omoike 1999, Qualls, Sherwood et al. 2009, Loganathan, Vigneswaran et al. 2013, Desmidt, Ghyselbrecht et al. 2014) and typically a residual of 1 mg/L as P is required in effluents discharged to natural water bodies (Council 1997). This value may vary depending on how much the receiving water bodies are ecologically fragile (Omoike 1999).

In wastewater treatment plants, phosphorus is readily removed using various methods and techniques. Phosphorus has been removed in wastewater treatment plants using various chemicals including calcium, aluminium and iron salts precipitants. These precipitants can be added at various locations. Phosphorus removal using aluminium sulphate is a quite cheaper method compared to other chemicals and with this more than 90 % removal of phosphorus can be achieved. This level of phosphorus removal is required to control the eutrophication. A previous study done by Francisco et. al. (1976) has shown that the optimum pH for the phosphorus precipitation using aluminium sulphate occurred at a pH of 6. Above pH 6, phosphate is removed by adsorption of an aluminium complex or by adsorption on aluminium hydroxide floc. If hydroxyl ions are not competing with phosphate ions for aluminium ions, then the phosphorus removal would be according to the stoichiometry. Stoichiometric removal can be seen if the initial phosphorus to aluminium ratio is low (Francisco, Strauss et al. 1976).

2.2 Wastewater Composition

Wastewater is a complex mixture of organic matter, solids, nutrients and pathogens and should be treated as it is important to remove constituents or contaminants that could harm the environment. There are different categories of wastewater namely municipal wastewater, industrial wastewater, infiltration wastewater and inflow wastewater (Omoike 1999). In this study, only the municipal wastewater was

considered. Municipal wastewater originates from households and various activities related to commercial and institutional facilities (Nedjah, Hamdaoui et al. 2015). Typical municipal wastewater contains various wastes including liquid (about 99.94 %) and solids (0.06 %) (Omoike 1999).

In Australia, about 70,000 litres of wastewater is produced per person per year only with the usage of domestic water (Council 1997). In addition to this, industrial and commercial wastewater is also added to the total wastewater volume. The wastewater plant from which samples were taken for this study treats up to 61.4 million litres a day which comes from a population of 350,000 people. The discharged water from household kitchens, bathrooms, toilets and laundries count for this wastewater. More than 99% of this wastewater comprises of water (www.watercorporation.com.au 2015).

2.3 Municipal Wastewater Quality Parameters

A number of wastewater quality parameters are typically measured to characterise wastewater physically, chemically and biologically and these parameters are useful in the design of a wastewater treatment plant. Colour, odour, suspended solids (SS) and temperature of wastewater are measured as physical quality parameters. For potential health hazards and aesthetics, it is necessary to remove components which produce colour and odour. Also, it is necessary to reduce the amount of suspended solids which enters into the natural water bodies as it may impact the amount of light which the aquatic life receives. The temperature of the effluent should be in a desirable range as high temperatures may have negative effects on receiving water bodies.

The chemical characteristics of wastewater include chemical oxygen demand (COD), biological oxygen demand (BOD), nitrate, phosphate, sulphate, ammonia-nitrogen and total Kjeldahl nitrogen. The presence of excessive amounts of these parameters causes adverse effects on natural water bodies. Nutrients such as organic carbon, nitrogen and phosphorus in wastewater exacerbate eutrophication.

Microorganisms in wastewater comprise the biological characteristics of wastewater and some of these are disease-causing pathogens which must be reduced prior to discharge to the environment.

Correct pH adjustment of the wastewater is important during the treatment for an optimised chemical coagulation and biological activity (Omoike 1999, Omoike and vanLoon 1999).

2.4 The Composition of Municipal Wastewater

Wastewater composition may vary from region to region, season to season, but a typical composition of municipal raw wastewater is shown in the following table.

Table C2.1: Typical Composition of Municipal Raw Wastewater

Parameter	Range
Biochemical Oxygen Demand (BOD) (mg/L)	150 - 500
Total Suspended Solids (TSS) (mg/L)	150 - 450
Total Nitrogen (TN) (mg/L)	35 - 60
Total Phosphorus (TP) (mg/L)	6 - 16
E Coli Org / 100 ml	$10^7 - 10^8$
Anionic Surfactants (mg/L)	5 - 10
Oil & Grease (mg/L)	50 - 100

Source: Australian Guidelines for Sewerage Systems – Effluent Management

2.5 Wastewater Treatment Processes

There are four commonly used treatment processes in a wastewater treatment plant to remove undesirable components in wastewater namely preliminary treatment, primary treatment, secondary or biological treatment and advanced or tertiary treatment (Shon, Vigneswaran et al. 2006). The characteristics of the wastewater, guidelines for quality of the discharged effluent, the capital and operating cost for the treatment system and site availability are among many factors which affect for the choice of the treatment process. The following figure illustrates a schematic diagram of a typical wastewater plant. The chemicals used in the chemical coagulation process (aluminium sulphate, ferric sulphate, etc.) are added in the chemical addition stage of this treatment process.

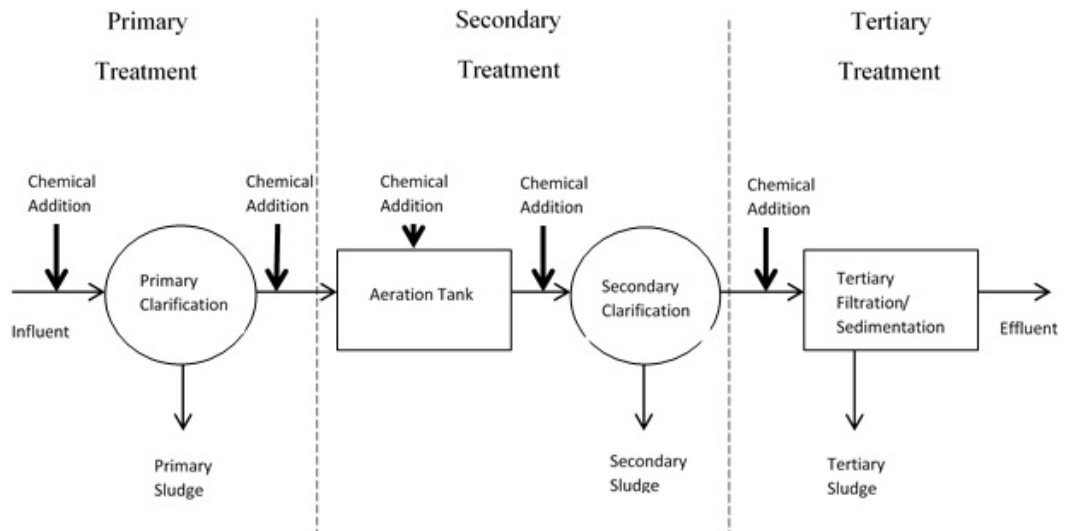


Fig. C2.2: Schematic Diagram of a Typical Wastewater Treatment Plant

2.5.1 Preliminary Treatment Process

In the preliminary treatment process, large materials including gross solids, coarse suspended solids and floating matter which include oil and grease are removed. These may create mechanical and functional problems after clogging. Screens and grit chambers are used in this process (Omoike 1999, Shon, Vigneswaran et al. 2006).

2.5.2 Primary Treatment Process

In the primary treatment process, suspended solids which are not removed by the preliminary treatment are removed by sedimentation in the sedimentation tanks as sludge. Any floating layer is removed simultaneously. If no further treatment is required, the effluent is disinfected and discharged. Chemical coagulants (aluminium or iron based chemical coagulants) are used in some of the old wastewater treatment plants to improve the primary treatment (Omoike 1999, Shon, Vigneswaran et al. 2006).

2.5.3 Secondary or Biological Treatment Process

The most commonly used process in the secondary treatment process is the activated sludge process (Omoike 1999). Either biological aerobic processes or chemical coagulation processes are normally deployed in the secondary treatment process. In this process, most of the remaining contaminants from the previous processes including fine suspended solids, colloidal and dissolved organic matter are removed (Shon, Vigneswaran et al. 2006).

In the secondary wastewater treatment process, a number of biological processes have been established and the activated sludge process is one of those commonly used secondary treatment methods. In this process, organic matters are broken down with the use of sludge which contains mixed populations of degradative, aerobic, heterotrophic microorganisms. The primary treated wastewater is passed into an aeration tank after mixing with the return activate sludge. This aeration tank is fixed with bubble diffusers or surface aerators for the sufficient supply of dissolved oxygen which is necessary for the functioning of microbial activities. This helps the sludge to keep in suspension to assist interaction with the microorganisms and the biodegradable organic matter in wastewater. A part of the suspended and dissolved organic matter are reacted with the microorganisms in the mixture and converted into carbon dioxide and the rest is assimilated into new microbial cells. This mixed liquor is then transferred into a final sedimentation tank or clarifier. With calm conditions, this sludge which contains living microorganisms settles to the bottom of the sedimentation tank. This settled sludge is then removed (Omoike 1999).

2.5.4 Advanced or Tertiary Treatment Process

Advanced or tertiary treatment process is used to remove dissolved materials after the secondary treatment and residual suspended solids. A range of physical, chemical and biological processes have been used to remove nutrients and other contaminants to obtain the permissible effluent discharge limits (Omoike 1999). Advanced wastewater treatment is generally applied to obtain a better quality of the effluent if the discharged wastewater receiving water body is highly sensitive. Sand filtration, ion exchange and

microfiltration are some of the processes used in advanced wastewater treatment process which gives a good quality effluent with admissible discharge limits.

Nutrient removal is done to reduce the nitrogen and phosphorus levels to an acceptable limit and disinfection is done to reduce the levels of pathogens in the effluent to a permissible limit for either reuse or discharge of the treated wastewater (Council 1997).

The different treatment process categories deployed in a typical wastewater treatment plant, the parameters removed in each process category and the examples of treatment processes used in each treatment process category are summarised in the following table.

Table C2.2: Treatment Process Categories with Examples with the Parameters Removed in Each Category

Treatment Process Category	Parameters to be Removed	Examples of Treatment Process
Pre - Treatment	Gross Solids (for fine screens, some readily settleable solids)	Screening
Primary Treatment	Gross Solids plus readily settleable solids	Primary Sedimentation
Secondary Treatment	Most Solids and BOD	Biological Treatment, Chemically Assisted Treatment, Lagoons
Nutrient Removal	Nutrients after removal of solids	Biological, Chemical Precipitation
Disinfection	Bacteria and Viruses	Lagooning, Ultraviolet, Chlorination
Advanced Wastewater Treatment	Treatment to further reduce selected parameters	Sand Filtration, Microfiltration

Source: Australian Guidelines for Sewerage Systems – Effluent Management

According to the Australian guidelines, certain effluent quality levels should be achieved after a various levels of treatment in a typical wastewater treatment plant, as shown in Table 2.3.

Table C2.3: Typical Effluent Quality following Various Levels of Treatment

Treatment	BOD (mg/L)	Total Suspended Solids (TS) (mg/L)	Total Nitrogen (TN) (mg/L)	Total Phosphorus (TP) (mg/L)	E Coli Org / 100 ml	Anionic Surfactants (mg/L)	Oil & Grease (mg/L)
Raw Wastewater	150 - 500	150 - 450	35 - 60	6 - 16	10^7 - 10^8	5 - 10	50 - 100
Pre Treatment	140 - 350	140 - 350					
Primary Treatment	120 - 250	80 - 200	30 - 55	6 - 14	10^6 - 10^7		30 - 70
Secondary Treatment	20 - 30	25 - 40	20 - 50	6 - 12	10^5 - 10^6	< 5	< 10
Nutrient Removal	5 - 20	5 - 20	10 - 20	< 2			< 5
Disinfection					< 10^3		
Advanced Wastewater Treatment	2 - 5	2 - 5	< 10	< 1	< 10^2		< 5

Source: Australian Guidelines for Sewerage Systems – Effluent Management

2.5.5 Coagulation and Flocculation

The coagulation flocculation process is a key phase in the wastewater treatment process (Bratby 2006, Tzoupanos and Zouboulis 2008). This is widely used because of its simplicity and the low cost. General application of this process is to remove or separate colloids and suspended particles, natural organic matter and metal ions. In the wastewater treatment process, toxic metals, anions such as phosphates, color and odor

are removed additionally. This is normally done either as a pre or post treatment stage irrespective of the type of the water sample. The wastewater treatment process is highly affected by the efficiency of the coagulation flocculation process. Therefore, a high efficiency of the coagulation process is a main factor for the efficient treatment process of wastewater. This coagulation/flocculation process can be divided into two separate procedures, namely coagulation and flocculation, which can be applied successively. In this coagulation process, dispersed colloids are destabilised and aggregated for the particles to be removed by sedimentation and for the filtration. In the flocculation process, suspended solids and organic materials are eliminated (Amuda and Alade 2006). In this coagulation process, proper chemical coagulants are used, typically aluminium or iron salts (Westerhoff 1968, Bratby 2006, Tzoupanos and Zouboulis 2008, Manamperuma, Ratnaweera et al. 2016). In the flocculation process, the destabilised particles come together to form large agglomerates or flocs, which then can be separated easily through the settling by gravity. Polyelectrolytes are used in the flocculation process for the development of particles accumulation. Coagulation occurs within a very short period of time, usually about 10 seconds and flocculation takes place over a long period compared to coagulation, normally about 20 - 45 minutes. There are two types of flocculation namely micro flocculation (or perikinetic flocculation) and macro flocculation (or orthokinetic flocculation). In micro flocculation, the particles are aggregated by the thermal motion of fluid molecules whereas in macro flocculation, the particles are aggregated by inducing velocity gradients and mixing in the suspension (Mazille F.). The most widely used metal coagulants are based on aluminium and iron. Aluminium sulphate (alum) is extensively used in the wastewater treatment plants (Tzoupanos and Zouboulis 2008).

2.6 Phosphorus in Municipal Wastewater

2.6.1 Phosphorus Forms

Generally, phosphorus in wastewater originates from the wastes of humans and animals, discharge from food processing plants, fertilisers, runoff from agricultural activities, industrial wastewater and the detergents use in households (Loganathan, Vigneswaran et al. 2013).

Phosphorus is present in wastewater in dissolved or soluble form and solid form. They may be in the form of orthophosphate, condensed or polyphosphate and organic phosphate (Mezenner and Bensmaili 2009, Loganathan, Vigneswaran et al. 2013). Around 30 % of phosphorus in wastewater comes from fecal and waste materials and industrial and commercial uses. The biggest fraction of the phosphorus in wastewater comes from synthetic detergents and cleaning products (Yeoman, Stephenson et al. 1988). The amount of phosphorus presents in wastewater normally varies. An estimation of various forms of phosphorus presents in wastewater has been given by Jenkins et.al. in 1971. According to their estimation, typical wastewater contains about 5 mg/L of P as orthophosphate, 3 mg/L of P as tripolyphosphate, 1 mg/L of P as pyrophosphate and 1 mg/L of P as organic phosphate (Jenkins, Ferguson et al. 1971). According to Fytianos et.al. (1996) wastewater contains 3 - 4 mg/L of P as orthophosphate, 2 - 3 mg/L of P as condensed phosphate (e.g., pyro-, tri-, meta-phosphate) and 1 mg/L of P as organic phosphorus (Fytianos, Voudrias et al. 1996). In 2008, Mezenner et al. published a paper in which they have mentioned that the municipal wastewater contains about 4 – 15 mg/L of phosphorus as PO_4^{3-} (Mezenner and Bensmaili 2009).

2.6.2 Mechanism of Phosphorus Removal

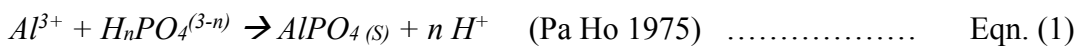
The mechanism of phosphorus removal with the formation of phosphate precipitate is quite complicated because of the formation of complexes between phosphate ions and metal ions, and between metal ions and other various particles in the wastewater. The formation of hydroxide precipitates with the alkalinity of wastewater is an example of side reactions that occur during coagulation with metal ions such as alum.

Phosphorus in wastewater is removed as aluminium phosphate precipitate, a complex of aluminium hydroxy phosphate or it is adsorbed into the hydrous aluminium oxide which is precipitated newly just after the addition of aluminium sulphate to the wastewater (Omoike 1999).

When alum is added to wastewater, it rapidly dissociates and forms Al^{3+} ions (Omoike and vanLoon 1999). Not only phosphate ions but also many other components in wastewater compete for these Al^{3+} ions to form different complexes. Suspended solids, colloidal substances and organic matters are some of these other competitive components for the Al^{3+} ions with phosphate ions. These components react with the

aluminium ions and form different complexes of aluminium species (Omoike 1999). Because of this reason, stoichiometric removal of phosphorus (i.e. 1:1 Al:P removal) cannot be achieved in a real situation. Hence, more alum has to be added to obtain a better phosphorus removal. Generally, 95% of phosphorus removal in a municipal wastewater treatment plant can be achieved with 2.1:1 and 2.3:1 of aluminium to total phosphorus molar ratio (Omoike 1999).

The following equation illustrates the precipitation of phosphorus with alum to form $AlPO_4$ during the wastewater treatment process.



Pa Ho (1975) stated that the initial ratio of phosphate to aluminium present in the solution has a great impact on various factors including the optimum pH for better phosphorus removal, the minimum phosphate residual present in the solution after coagulation and the maximum amount of phosphate removed per mole of aluminium. If the initial concentration of phosphate present in the solution is high, then the amount of phosphate removed from the solution is also high (Pa Ho 1975).

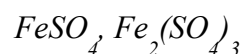
As stated by Yeoman et. al. (1988), if the phosphate concentration is low (<10 mg/L of P), then the formation of hydroxides prevents the stoichiometric removal of metal to phosphate because of the competition between hydroxyl groups and phosphates for the metal ions (Yeoman, Stephenson et al. 1988).

A previous study done by Hsu (1975) has suggested an alternative mechanism for precipitation of phosphate from solution using aluminium salts. According to this study, instead of precipitating separately as aluminium hydroxide $[Al(OH)_3]$ or aluminium phosphate $[Al(PO)_4]$, the precipitation of phosphate occurs by the incorporation of Al-OH-Al and Al- PO_4 -Al bonds (Hsu 1975).

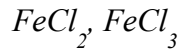
2.6.3 Phosphorus Removal Adsorbents

Several types of chemical coagulants are used in the chemical precipitation process.

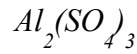
- Ferrous (+2) and Ferric (+3) Sulphate



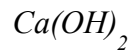
- Ferrous (+2) and Ferric (+3) Chloride



- Alum (Al^{3+})



- Lime (Ca^{2+})

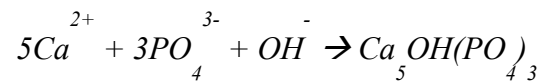


The following equations show the chemical reactions of each coagulant with phosphate.

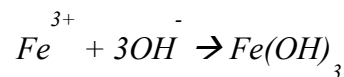
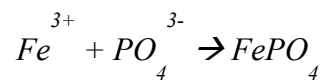
- Alum



- Lime



- Ferric Chloride



When alum is added to wastewater, aluminium hydroxides $[Al(OH)_3]$ and different forms of aluminium phosphate species $[Al_2(PO_4)(OH)_3^0, Al_2PO_4(OH)_2^+, AlPO_4(OH)^-]$ are formed (Omoike and vanLoon 1999).

Among all of the coagulants mentioned above which have been used for the phosphorus removal in wastewater treatment plants, the use of aluminium sulphate gives a better effluent quality and it is economically worthwhile.

2.6.4 Phosphorus Control in Wastewater

Various methods and techniques have been used to control the phosphorus in wastewater before it is discharged into the natural environment. Chemical coagulant

assisted phosphorus removal and biological phosphorus removal has been used extensively in wastewater treatment plants all around the world to meet the imposed standard discharge limits. Chemical phosphorus removal methods involving the addition of chemical coagulants are more efficient compared to the biological phosphorus removal methods. Also, there are some other benefits of using chemical coagulants. It reduces the concentration of suspended substances and organic matter as well as the improvement of settleability of microbial flocs. For these reasons, chemical coagulant assisted phosphorus removal has been used widely in many wastewater treatment plants for decades (Omoike 1999).

As shown in Table C2.2, typical raw municipal wastewater contains about 6 – 16 mg/L of total phosphorus and the extent of removal of phosphorus in the primary treatment and the secondary treatment processes is negligible. However, after the nutrient removal process, the total phosphorus level decreased to less than 2 mg/L and in the advanced treatment process, this level has been further reduced to less than 1 mg/L. This is the acceptable total phosphorus limit for the discharge of effluent to natural water environment and this value may vary according to the fragility of the receiving water body.

The application of the chemical coagulant can be done in various locations.

- Pre precipitation in the Primary Treatment process
- Simultaneous precipitation in the Secondary Treatment process
- Post precipitation in the Tertiary Treatment process

(Yeoman, Stephenson et al. 1988)

The chemical dose requirement for the phosphorus removal depends on many factors including wastewater characteristics (pH, alkalinity, amount of organic carbon present in wastewater, temperature, hardness and especially the phosphorus concentration), the desired percentage of phosphorus removal, wastewater flow rate, hydraulic loading, type of chemical using for the treatment, chemical application point and mode and the dose adjustment frequency (Jenkins, Ferguson et al. 1971).

The addition of chemical coagulant can be done at various points as shown in the Figure C2.1 in an activated sludge wastewater treatment process. These points include immediately upstream of the primary clarifier, immediately downstream of the primary clarifier before the aeration tank, in the aeration tank, after the aeration tank

and before the secondary clarifier, after the secondary clarifier and at more than one point simultaneously (Bai, Zhu et al. 2010, Desmidt, Ghyselbrecht et al. 2014).

There are some advantages and disadvantages of each of these locations. Some of the components in wastewater specially some organic compounds competes with phosphate ions for aluminium ions and the effect of these organic compounds has to be considered when determining the point of addition of chemical coagulant as the organic compounds hinder the phosphorus removal efficiency (Omoike and vanLoon 1999).

When phosphorus is present in larger quantities, the amount of phosphate adsorbed into chemical coagulant is also high, so the effectiveness of alum should be greater per mole at locations where the phosphate concentration is highest.

Struvite precipitation is one of the methods of nutrient removal in wastewater. Phosphorus and nitrogen can be removed with this method. This is done by means of simultaneous precipitation of soluble orthophosphate and ammonium nitrogen with the use of magnesium salt (Ren, Zhou et al. 2016). This method is of interest as the precipitated phosphorus and nitrogen can be recovered. Struvite is a composition of magnesium ammonium phosphate hexahydrate. Since it has nitrogen, phosphorus and magnesium, struvite can also be used as a fertiliser (Chong and Thai 2015). Another method of phosphorus removal from wastewater is the use of seeding materials. In this method, calcium phosphate is precipitated directly (crystallization) by calcite which acts as the seeding material (Donnert and Salecker 1999). Activated alumina is also used for the removal of phosphorus which shows a favour for the phosphate anions even with the presence of high concentrations of sulphate and chloride ions. Phosphorus is adsorbed on to granular or powdered material in this method. This method has several advantages including the production of small quantity of sludge, ability to obtain low effluent concentrations of P such as 0.1 mg/L, ability to recover phosphorus as calcium phosphate and no increase of the concentrations of sulphate or chloride (Donnert and Salecker 1999).

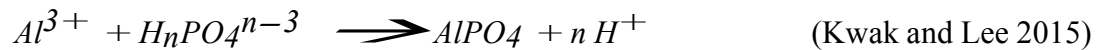
2.7 Chemical Characteristics of Aluminium Coagulant

A series of complex chemical reactions occur between phosphate ions and aluminium ions when aluminium sulphate (alum) is added to wastewater, which leads to a great aluminium requirement than the required amount from the stoichiometric removal (Fytianos, Voudrias et al. 1996).

When alum is added to wastewater in the wastewater treatment process, it forms aluminium ions (Al^{3+}) after rapidly dissociating which is immediately hydrated as aluminium hydroxide [$Al(OH)_3$] (Cooke, Welch et al. 1993). After this formation, the pH of the solution is decreased. This aluminium hydroxide is a colloidal, amorphous floc with a crystalline structure. This is formed over a number of rapid hydrolysis reactions and it is insoluble in the range of pH 6 - 8. These aluminium hydroxide flocs have high coagulation and phosphorus adsorption properties (Cooke, Welch et al. 1993). It aids for the removal phosphorus by adsorption and physical entrapment (Galarneau and Gehr 1997).

Above pH 6, various aluminium hydroxide or complicated hydroxyl aluminium phosphate products are precipitated.

The following equation shows the theoretical molar ratio of Al:P for the chemical phosphorus removal.



Chemical coagulants convert soluble phosphorus in to particulate phosphorus which then can be removed from wastewater so as to remove phosphorus.

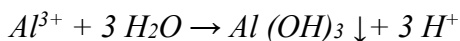
CHAPTER 3

Effect of Initial pH on Removal of Phosphorus in Municipal Wastewater

3.1 Introduction

The pH of the solution is one of the main factors affecting the performance of alum in the process of removing phosphorus from wastewater. Numerous studies have been done in the past to identify the effect of the pH for the phosphorus removal in wastewater (Clark & Stephenson, 1999; Ebeling, Sibrell, Ogden, & Summerfelt, 2003; Shanshool & Sawsan, 2009).

As stated by Georgantas et al. (2007), to obtain an effective coagulation, coagulation process has to be done in the optimum pH zone which is favourable for maximum phosphorus removal. The approximate pH of commercially available alum is 2.4 (Beecroft, Koether, & vanLoon, 1995). When alum is added to wastewater, the alkalinity of wastewater gets neutralised and carbon dioxide releases to the wastewater. These two processes cause for a reduction of pH in wastewater. After the addition of alum to the wastewater, the pH of the solution decreases because of the formation of aluminium hydroxide and the release of H^+ ions to the solution (Shanshool & Sawsan, 2009). The reaction is as follows.



Usually municipal wastewaters have the natural buffering capacity and thus the drop of pH after adding alum usually will be in the range of 5 - 7 (Georgantas & Grigoropoulou, 2007; Kabayama, Kawasaki, Nakamura, & Tanada, 2005). The alkalinity of wastewater has a great impact on the amount of this pH reduction. If the alkalinity of the wastewater is high, then the pH reduction after the addition of a particular alum dose is low. But most wastewaters have adequate alkalinity which prevents a large pH reduction below about 6.0 to 6.5 even for a higher alum dose (Özacar & Şengil, 2003).

Most studies in the literature agree that a pH around 6 is optimal for phosphorus removal using alum. Several reports have shown that the optimum phosphorus removal occurred within pH 5 - 7 (Ferguson & King, 1977; Francisco, Strauss, & Dempsey, 1976; Shanshool & Sawsan, 2009). It has been suggested that a pH of 6.5 is more effective with low Al:P mole ratios for an optimum coagulation than the higher pH values (Francisco et al., 1976). Trinh and Kang (2013) have also stated that the maximum phosphorus removal occurs in pH 5.0 – 6.0 range (Trinh & Kang, 2013). A previous study done by Wang et. al. (2005) shows that the maximum phosphorus removal efficiency was achieved at a pH of 6.3 and with the dose ratio of aluminium sulphate to phosphate of 4.13:1 (Al:P) (Wang, Han, Xu, Bao, & Zhu, 2005).

The pH adjustment of the wastewater is quite important during the treatment for an optimised chemical coagulation and for biological activity (A.I. Omoike, 1999; A. I. Omoike & vanLoon, 1999). And also pH is one of the wastewater characteristics which determines the chemical dose requirement for the phosphorus removal (Jenkins, Ferguson, & Menar, 1971).

If the pH of the solution is below 6 or above 8, then the precipitation of phosphorus as aluminium phosphate is not possible as aluminium ions are soluble in these pH ranges. Hence, the coagulation efficiency of alum decreased (Georgantas, Matsis, & Grigoropoulou, 2006a, 2006b).

The present study was designed to determine the effect of the initial pH of the solutions for the removal of phosphorus in municipal wastewater. The experiments were carried out using both synthetic wastewater and real wastewater obtained from a Wastewater Treatment Plant (WWTP) in Perth. The effect of initial pH was investigated by maintaining a constant aluminium and phosphate dosage, but adding acid or base to vary the initial pH.

The phenomenon of optimum pH value has been described by Bratby in 1980 in his work. As stated by him, for a certain pH value, in any specific time, a certain quantity of phosphorus is associated with the added metal coagulant. The optimum pH value for a certain coagulant is the pH value where the biggest portion of the phosphorus precipitates with that added chemical coagulant. If the dosage of the added chemical coagulant exceeds the required stoichiometric quantity, then the phosphorus removal will occur over a wider pH range. But after a certain maximum value of pH, though

the coagulant dose is increased, no more removal of phosphorus can be achieved. Bratby found that the maximum phosphorus removal occurred with the aluminium coagulants in the optimum pH range of 5.5 to 6.1. These minor variances in these optimum pH values may be possibly because of the use of different wastewater and the differences in the wastewater components (Bratby, 1980).

According to Pa Ho (1975), the initial ratio of phosphate to aluminium presents in the solution has a great impact on various factors including the optimum pH range for the phosphate precipitation, the minimum residual phosphate concentration in the solution and the maximum amount of phosphate precipitated per mole of aluminium (Hsu, 1975).

3.2 Objective of the Study

Series of experiments were conducted to find the optimum pH for the maximum phosphorus removal in municipal wastewater with aluminium sulphate $[Al_2(SO_4)_3]$.

3.3 Materials and Methods

3.3.1 Apparatus and Experimental Procedure

Jar test experiments were carried out at ambient temperature using a six paddle jar test apparatus (VELPSCIENTIFICA – JLT6 flocculator). Synthetic and real wastewater samples (500 ml) were used in each test and pre-weighed potassium dihydrogen phosphate (KH_2PO_4) was dissolved in deionised water to prepare the standard phosphate solutions. Analytical grade chemicals were used for all the experiments.

Acid (H_2SO_4) or base (NaOH) was used to adjust the initial pH of each solution to the required value before adding the coagulant.

For the determination of the optimum pH value for the phosphorus removal in wastewater, synthetic wastewater samples prepared in the laboratory were firstly added to a series of beakers and the pH values of each beaker were adjusted to 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0 and 9.5 respectively.

Initially, the experiments were done with synthetic wastewater and later municipal wastewater obtained from the different locations in the WWTP namely primary

sedimentation tank inlet (PST inlet), primary sedimentation tank outlet (PST outlet), secondary sedimentation tank inlet (SST inlet) and secondary sedimentation tank outlet (SST outlet) were used for validating the results

The initial phosphorus concentration and the Aluminium (III) concentration of all the samples were set to 10 mg/L of PO₄-P and 10 mg/L of Al³⁺ respectively. All the sample solutions were stirred 1 minute with 200 RPM followed by 30 minutes continuous stirring with 45 rpm. Solutions were allowed to settle for 15 minutes and sub samples were taken and were filtered through 0.45 µm Millipore Millex HP Hydrophilic PES membrane filters for residual phosphate analysis.

3.3.2 Preparation of Synthetic Wastewater

Synthetic wastewater was prepared by adding different concentrations of cations and anions as shown in Table 1 to deionized water. Calcium chloride, magnesium sulphate and sodium bicarbonate were used to get the relevant anions and cations. Samples with different phosphate concentrations were prepared by adding predetermined amounts of KH₂PO₄ to prepared synthetic wastewater. The ionic concentrations of the synthetic wastewater used to mimic the real wastewater is presented in Table 1. The pH of the synthetic wastewater samples was adjusted using H₂SO₄ (0.2 M) or NaOH (1 M).

Table C3.1: The Ionic Concentrations of the Synthetic Wastewater

Cations	Concentrations (mg/L)	Anions	Concentrations (mg/L)
Ca ²⁺	41.60	Cl ⁻	72.65
Mg ²⁺	6.72	SO ₄ ²⁻	26.56
Na ⁺	47.40	HCO ₃ ⁻	125.73
pH : 7.9			

3.3.3 Preparation of Municipal Wastewater Samples

Wastewater samples from four different locations in a wastewater treatment plant in Perth [namely Primary Sedimentation Tank inlet (PST inlet), Primary Sedimentation Tank outlet (PST outlet), Secondary Sedimentation Tank inlet (SST inlet) and

Secondary Sedimentation Tank outlet (SST outlet)] were used for the experiments. The effluent characteristics of the wastewater differ from location to location in the wastewater treatment plant. These characteristics have been measured during the experiments and summarised in Table C3.2.

Table C3.2 Characteristics of Wastewater Samples

Characteristics	Location			
	PST Inlet	PST Outlet	Secondary Inlet	Secondary Outlet
DOC	88.3	79.1	180.2	11.9
SS	57.5	102.5	554.2	1.7
pH	7.13	6.94	6.68	7.0
PO ₄ -P	12.3	13.1	22.1	6.7

3.3.4 Analytical Procedure

A Labmedics Aquakem 200 Konelab analyser was used for the analysis of the residual phosphorus based on molybdenum blue colorimetric method. This spectrophotometer analyses the reactive phosphorus at wavelength 880 nm (or 660 nm). A Hach HQ30d pH probe with a glass electrode was used for pH measurements.

3.4 Results and Discussion

It is considered to be essential to use the synthetic wastewater for the studies of various characteristics of wastewater because of its simplicity. The real wastewater then can be used for the verification of the results obtained with the synthetic wastewater. The simplicity of the synthetic wastewater helps for understanding the complicated mechanisms involving in real wastewater.

The residual phosphorus concentration varied with the change of the initial pH of the wastewater. The results for the varying initial pH with synthetic wastewater is plotted in Figure C3.1 in terms of residual phosphorus concentration against the initial pH.

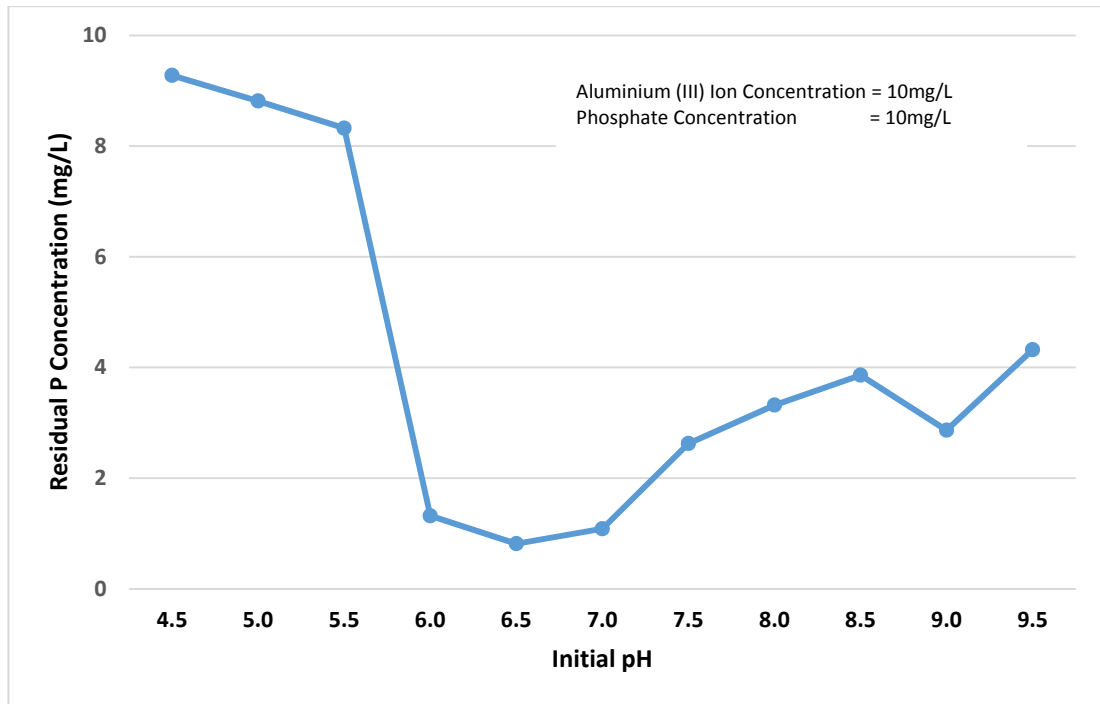


Fig. C3.1: Effect of Initial pH on the Removal of Phosphate from Synthetic Wastewater Sample using Alum

As shown in the above figure, the residual phosphorus amount shows an increasing then decreasing trend with the increase of initial pH. From this graph, showing that the residual phosphorus amount decreased with the increase of pH up to pH 6.5 and beyond that the residual phosphorus increased with the increase of pH up to pH 8.5. Further increase of pH led to a decrease of residual phosphorus amount and the greatest phosphorus removal (lowest concentration of residual phosphorus) occurred at an initial pH of 6.5. The maximum phosphorus removal efficiency was 91.9 % with the residual phosphorus concentration of 0.8 mg/L which is below the allowable maximum phosphorus discharge limit of 1 mg/L.

The same experiment was done with the municipal wastewater and as with the synthetic wastewater, the residual phosphorus concentration was varied with the varying with the initial pH of the municipal wastewater. PST inlet, PST outlet and SST outlet wastewater samples were used for the experiments. The wastewater samples from all these three locations were used for the comparison of results in each location and to find an optimum pH value for the phosphorus removal in municipal wastewater. The investigation of the effect of the initial pH of the solutions on the phosphorus removal process in municipal wastewater is presented graphically in Fig C3.2.

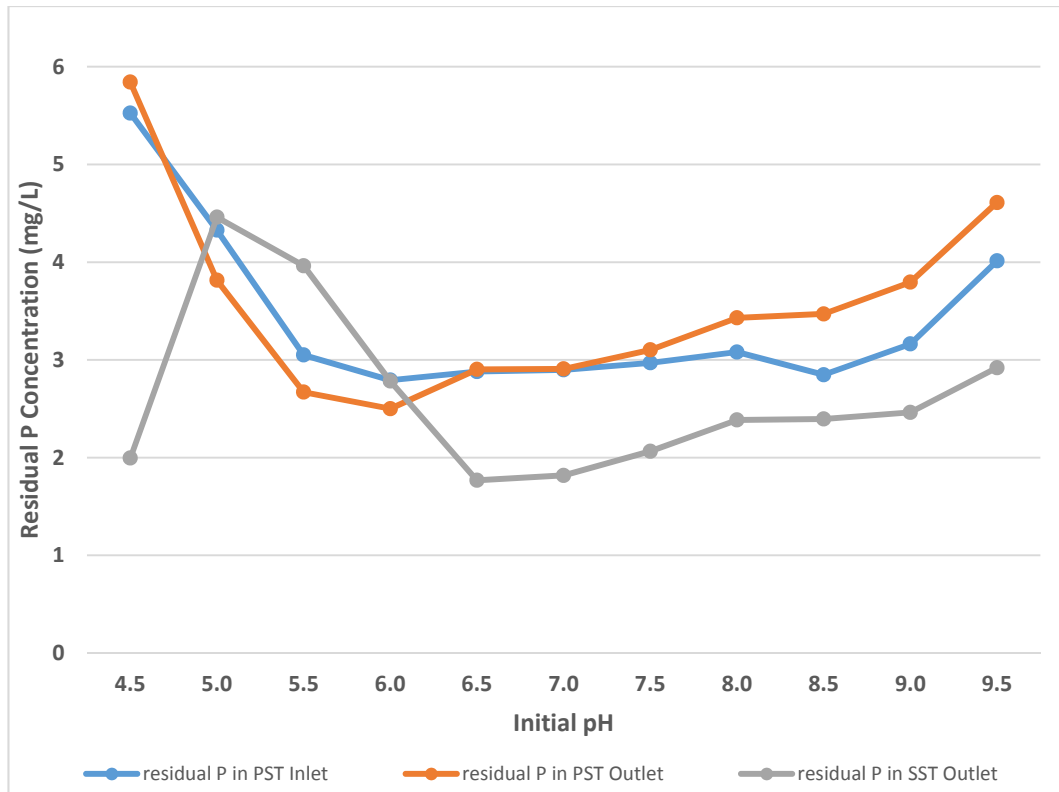


Fig. C3.2: Effect of Initial pH on the Removal of Phosphate from PST Inlet, PST Outlet and SST Outlet Wastewater Samples using Alum

Figure C3.2 shows that the residual phosphorus amount decreases with the increase of initial pH of the solutions up to 6 in PST inlet and PST outlet wastewater samples (2.8 and 2.5) and up to 6.5 in SST outlet wastewater sample (1.8). Beyond those two pH values, the amount of residual phosphorus tends to increase with the increasing initial pH of the solutions in all three samples. The maximum phosphorus removal occurred in the range of pH 6 – 6.5 in all three municipal wastewater samples. The literature survey also reveals that the maximum phosphorus removal occurs at pH values of 5 - 7 (Ferguson & King, 1977). Hence, these results are in line with those of previous studies. A previous study done by Francisco et al. (1976) has shown that the optimum pH for the phosphorus precipitation using aluminium sulphate occurred at a pH of 6. In 2007, Georgantas et al. published a paper in which they described that if the solution pH is below 6 or above 8, the precipitated $AlPO_4$ is soluble (Georgantas & Grigoropoulou, 2007).

Fig. C3.3 presents the results obtained for the varying initial pH of the SST inlet wastewater sample experiment. No significant pH value for an optimum phosphorus removal can be seen with the SST inlet wastewater sample since the residual phosphorus concentration decreased or remained constant with increasing initial pH.

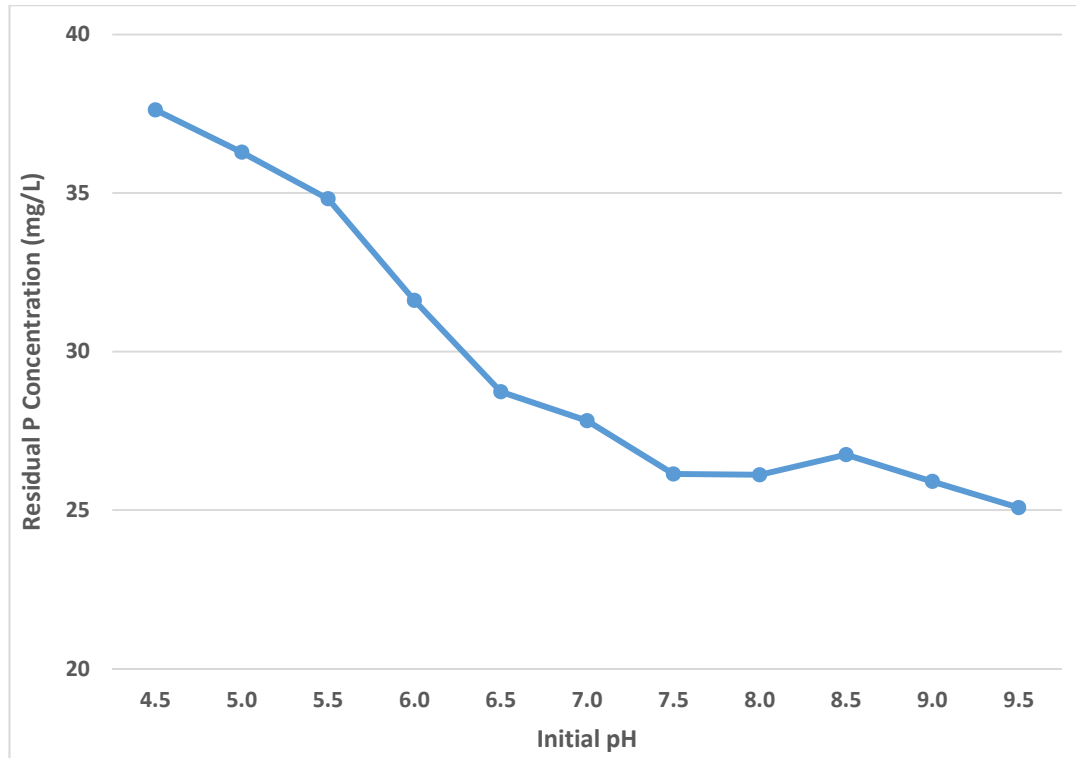


Fig. C3.3: Effect of Initial pH on the Removal of Phosphate from SST Inlet Wastewater Samples using Alum

According to Georgantas et al. (2007), above pH 8 the most prevalent aluminium species is $\text{Al}(\text{OH})_4^-$ and the main phosphorus species is PO_3^- . As both species are negatively charged, they repel each other preventing an interaction and hence the efficiency of the coagulation process is decreased (Georgantas & Grigoropoulou, 2007).

The residual soluble aluminium in the samples of secondary sedimentation tank outlet wastewater was measured and most of the aluminium had precipitated at pH 6.5 and above which confirms above result. The results are shown in the figure below.

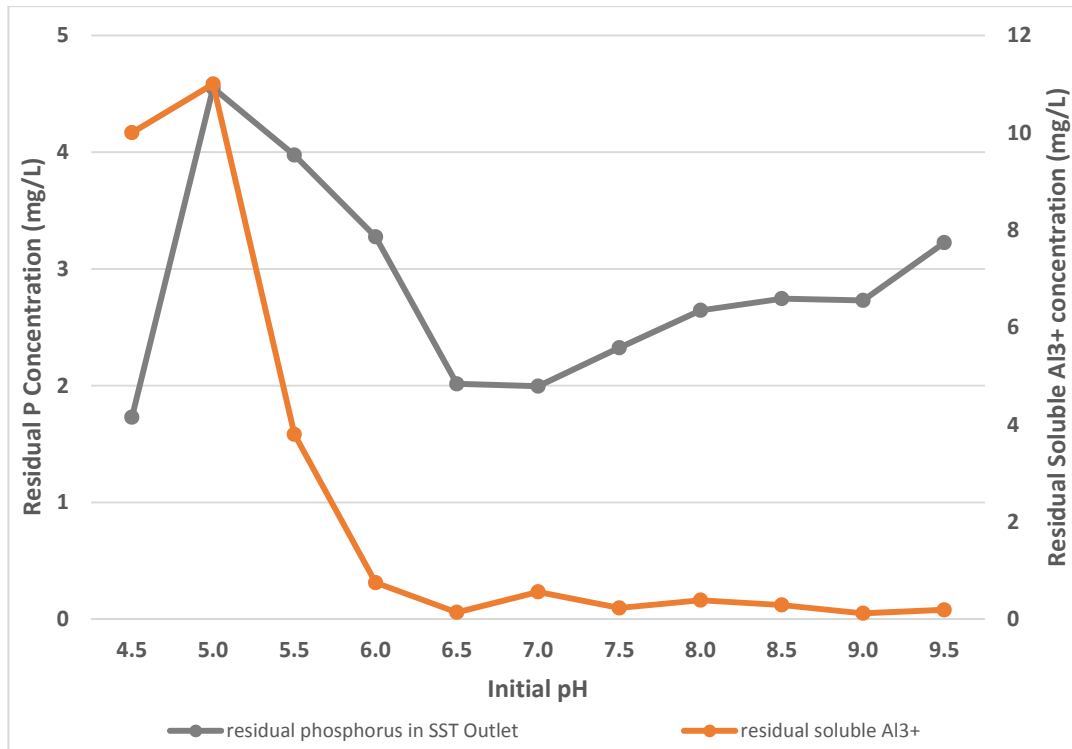


Fig. C3.4: Residual Soluble Aluminium (Al³⁺) and Residual Phosphate Concentrations in SST Outlet Wastewater Sample with Varying Initial pH

The minimum residual of phosphorus (2 mg/L) can be seen in the pH range of 6.5 – 7.0. Also, the occurrence of minimum residual soluble aluminium ions started from pH 6.5. The further increase of the initial pH had very little effect on the residual soluble aluminium levels after pH 7. Since of the higher OH⁻ concentration at pH 6.0 to 9.5, the formation of aluminium hydroxides takes preference over the formation of AlPO₄. Hence, in this pH range, the residual phosphorus is higher as it does not get precipitated as AlPO₄ and the soluble aluminium is in negligible amount as aluminium is bound to OH⁻ ions as aluminium hydroxides.

After the addition of aluminium sulphate to wastewater, it dissociates producing trivalent Al³⁺ ions which undergo a series of hydrolysis reactions producing various species including aluminium hydroxide [Al(OH)₃]. Depending on the pH of the wastewater, these hydrolysis products may be negatively or positively charged. They are negatively charged at high pH values and positively charged at low pH values. The colloidal particles in the wastewater are negatively charged and hence the positively charged hydrolysis species are adsorbed onto the surface of these colloidal particles causing a charge neutralisation and forming flocs. With high coagulant dosages,

aluminium hydroxide precipitate is formed. This precipitate has the ability to remove the colloidal particles in the suspension of wastewater. This is called sweep floc coagulation. These previously formed flocs have the ability to entrap the adjacent particles and the phosphorus in wastewater could be removed by this process. Many studies have been proved that alum is more effective in reducing total phosphorus in wastewater. But according to Bai et.al. (2010), maximum effectiveness of alum can be achieved over a very limited pH range which is of 6.5 - 7.5 (Bai, Zhu, Zhang, Zhang, & Gong, 2010).

The coagulation performance of aluminium sulphate is affected by the pH of the solution which relates to the coagulation mechanism of alum. At low pH values, Al^{3+} is the main species of alum in wastewater. The adsorption/ bridge formation process is highly influenced by the higher charges and lower polymeric species. This finally causes for a poor coagulation performance. But with neutral or slightly alkali environments, polymeric complexes are formed and phosphorus could be removed with the adsorption or bridge mechanism. At higher pH values, AlO_2^- is formed causing a poor coagulation performance. This formation has a negative impact on the adsorption formation mechanism (Bai et al., 2010).

When aluminium sulphate is added to wastewater which contains phosphorus, it forms aluminium phosphate ($AlPO_4$). This is insoluble between pH 5 and 7. Hence, pH is an important parameter for the phosphorus removal by means of $AlPO_4$ precipitation. The Al^{3+} ions readily react with phosphate ions and also with hydroxyl ions. Thus, a greater amount of aluminium ions than the stoichiometric amount (i.e. 1:1 Al:P) need to be added for efficient phosphorus removal (Balamane-Zizi & Ait-Amar, 2009).

The pH of the solution has a great impact on hydrolysis reactions and this gives an aluminium hydroxide precipitate in the range of pH 6 – 8.

3.5 Conclusion

The experimental results with synthetic wastewater showed that the maximum phosphorus removal was achieved with an optimum initial pH of 6.5. This result was verified with the experiments done using municipal wastewater. The optimum pH for the maximum phosphorus removal was within the range of pH 6 – 6.5 in PST inlet,

PST outlet and SST outlet municipal wastewater samples. These values generally agree with values published in the literature. No significant pH value for an optimum phosphate removal could be seen with the SST inlet wastewater sample. For this sample it may be necessary to use higher doses of alum since the initial phosphate concentration was significantly higher than in the other wastewater samples (37 mg/L in SST inlet versus < 10 mg/L in the other samples).

CHAPTER 4

Effect of Alum Dosage on Removal of Phosphorus in Municipal Wastewater

4.1 Introduction

The suitability of use of aluminium sulphate as a coagulant and its dosage depends on several factors of the wastewater. This includes the pH of the wastewater, alkalinity of the wastewater and the concentration of colloids present in the wastewater. A series of jar test experiments was done in order to identify the optimal dosage of alum for phosphorus removal. Jar test experiments and the zeta potential test are the most commonly used tests for the identification of optimum coagulant dosage and optimum pH. In this study, jar test experiments were done in all cases. One of the advantages of the use of alum to remove phosphorus from wastewater is it can attain any phosphorus residual within the range of 0.05 mg/L to 2 mg/L of P as phosphate. Also, it is cheaper compared to other chemicals used for phosphorus removal. Moreover, also it creates fewer problems with contaminants in sludge (e.g iron salts often contain heavy metal contaminants) and very little pH adjustment of the wastewater is required (Ferguson & King, 1977).

Although the use of alum salts for phosphorus removal from wastewater is very common, the mechanism of phosphorus removal by this coagulant is not yet well understood. As being the strongest competitor, the presence of hydroxyl ions hinders the phosphorus removal process. The phosphorus removal efficiency of alum is low if the alum dosage is low (Diamadopoulos & Benedek, 1984).

According to Kwak et. al. (2015), more than the stoichiometric ratio of Al:P (i.e. 1:1 ratio of Al:P) is required to remove phosphorus in wastewater as aluminium phosphate precipitate. According to them, 2:1 or higher ratio of Al:P is required to remove phosphorus completely (Kwak & Lee, 2015). The variation of the stoichiometry with decreasing P concentration Al:P ratio shows that there is a precipitate of aluminium hydroxide phosphate. Phosphate ions are adsorbed onto or ion exchanged with the aluminium hydroxide in addition to the precipitation as aluminium phosphate (Kwak & Lee, 2015).

In the range of pH 6 – 8, aluminium hydroxide is insoluble. Some other soluble aluminium forms are present within pH 4 – 6 and soluble aluminium ions (Al^{3+}) present below pH 4. Some of the phosphorus present in the solution adsorbs onto the formed aluminium hydroxides and with high pH levels which are greater than pH 8, this adsorbed phosphorus is released from the floc. This is unfavourable for effective phosphorus removal. Cooke et. al. (1993) have studied the effectiveness of aluminium salts for controlling the internal phosphorus loading in lakes and they have found that aluminium hydroxide can adsorb a considerable amount of inorganic phosphorus and that it is less effective for adsorbing or removing dissolved organic phosphorus. And also with lower pH values than 8, this phosphorus does not release back to the solution (Cooke et al., 1993).

In this study, different concentrations of alum were applied to solutions at an initial pH of 6.5 without controlling the pH (i.e. pH was only adjusted at the beginning of the experiments but not during or after the addition of alum) and the phosphorus remaining in the solutions after precipitation was measured.

4.2 Objective of the Study

A set of experiments was conducted to find the effect of alum dosage for phosphorus removal in municipal wastewater with aluminium sulphate [$\text{Al}_2(\text{SO}_4)_3$] and to determine the molar ratio of total phosphorus removed to the chemical coagulant added to meet the permissible effluent phosphorus discharge standards.

4.3 Materials and Methods

4.3.1 Apparatus and Experimental Procedure

The effect of alum dose for the phosphorus removal efficiency was studied on a laboratory scale. Jar test experiments were carried out at ambient temperature using a six paddle jar test apparatus (VELPSCIENTIFICA – JLT6 flocculator) in order to determine the effect of aluminium ion dosage and aluminium sulphate dosage for phosphorus removal in wastewater. Both synthetic wastewater and real wastewater were used for all experiments. Standard phosphate solutions were prepared by

dissolving pre-weighed potassium dihydrogen phosphate (KH_2PO_4) in deionised water. Analytical grade chemicals were used for all the experiments. Equal amounts of samples (500 mL each) were poured in to jars and different amounts of chemical coagulant (aluminium sulphate) were added to each jar under stirring. The pH of the solutions was adjusted using H_2SO_4 or NaOH to 6.5.

One set of experiments which was done to find the effect of aluminium ion concentration: the initial phosphorus concentration of all the samples were set to 10 mg/L of $\text{PO}_4\text{-P}$. This experiment was done with the synthetic wastewater and the initial pH of all the sample solutions was set to 6.5. For the other set of experiments, both synthetic wastewater and real wastewater samples were used and this was done to find the effect of aluminium sulphate (alum) dosage. In this experiment, the initial phosphorus concentration and the initial pH of the solutions were set to 10 mg/L $\text{PO}_4\text{-P}$ and 6.5 respectively. The final pH of each sample was recorded at the end of each experiment.

All the sample solutions were stirred for 1 minute at 200 rpm followed by 30 minutes continuous stirring with 45 rpm. Solutions were allowed to settle for 15 minutes and sub samples were taken. These were filtered through a 0.45 μm Millipore Millex HP Hydrophilic PES membrane filter prior to residual phosphorus analysis.

The same method as in Section 3.3.2 and Section 3.3.3 in Chapter 3 (test for initial pH) was followed to prepare synthetic wastewater and municipal wastewater samples. Also, the same analytical procedure as in Section 3.3.4 in Chapter 3 was followed for these sets of experiments.

4.4 Results and Discussion

4.4.1 Effect of Aluminium Ion (Al^{3+}) Dosage on Phosphorus Removal

The effect of Al^{3+} dosage on phosphorus removal in synthetic wastewater having 10 mg/L of PO_4^{3-}P by chemical precipitation was studied. The final pH level was also monitored. The Al^{3+} dosage was changed as follows: 0.5 mg/L, 1 mg/L, 2 mg/L, 3 mg/L, 5 mg/L and 10 mg/L. Residual phosphorus concentration for each sample was measured and the results are shown below in Figure C4.1.

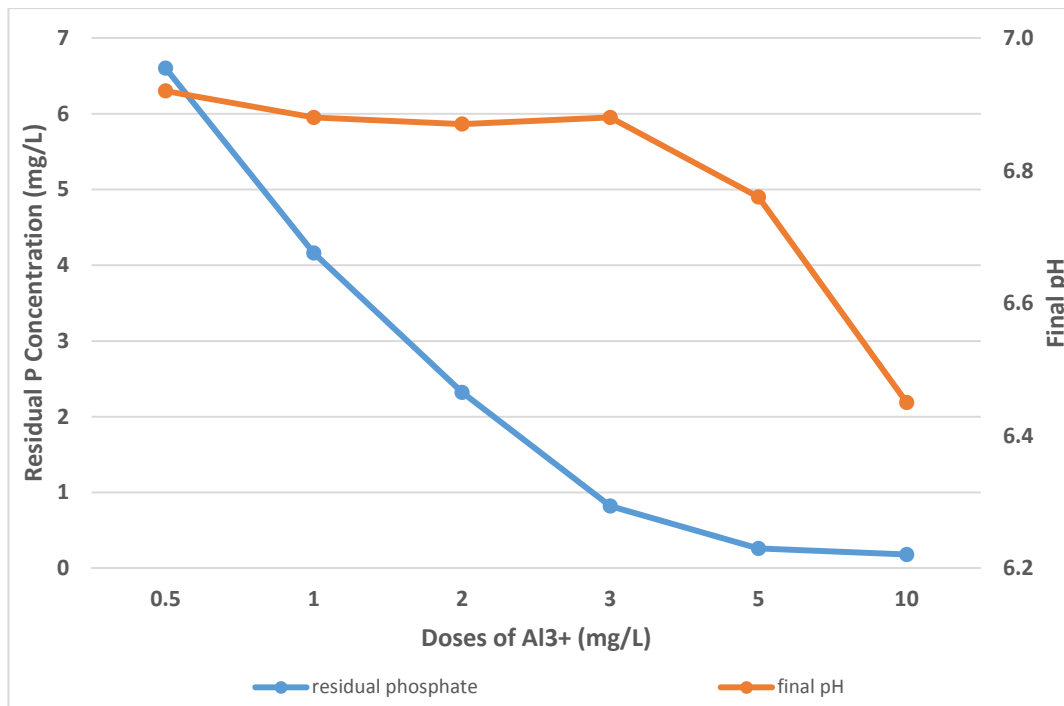


Fig. C4.1: Effect of Al³⁺ Dose on Phosphorus Removal and Final pH with Synthetic Wastewater (initial pH 6.5)

Figure C4.1 shows that there is a clear trend of decreasing the residual phosphorus amount with the increase dosages of Al³⁺. The final pH of the solutions with up to 3 mg/L of aluminium ion dosage remained nearly the same and it was higher than the initial pH value. The final pH of the solution with 5 mg/L of aluminium ion dosage was bit less than the final pHs of solutions with lower Al³⁺ doses and it was still higher than its initial pH. However, with 10 mg/L of aluminium ion dosage (63.4 mg/L of aluminium sulphate), the final pH of the solution was quite similar to its original pH value. What is interesting in this data is that this aluminium ion dosage is a bit higher than the required alum dosage for a stoichiometric removal (1:1 Al:P mole ratio) of phosphorus and its final pH was not much altered from its original pH by this dosage.

4.4.2 Effect of Alum Dosage on Phosphorus Removal

The impact of the aluminium sulphate (alum) dosage on phosphorus removal was studied by varying the alum dosage in synthetic wastewater first, prior to verification of these results in real wastewater samples. The alum dosage was varied as follows: 5 mg/L, 10 mg/L, 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L, 100 mg/L, 120 mg/L and 140 mg/L. The results obtained from the experiments are shown in Figures C4.2 and C4.3.

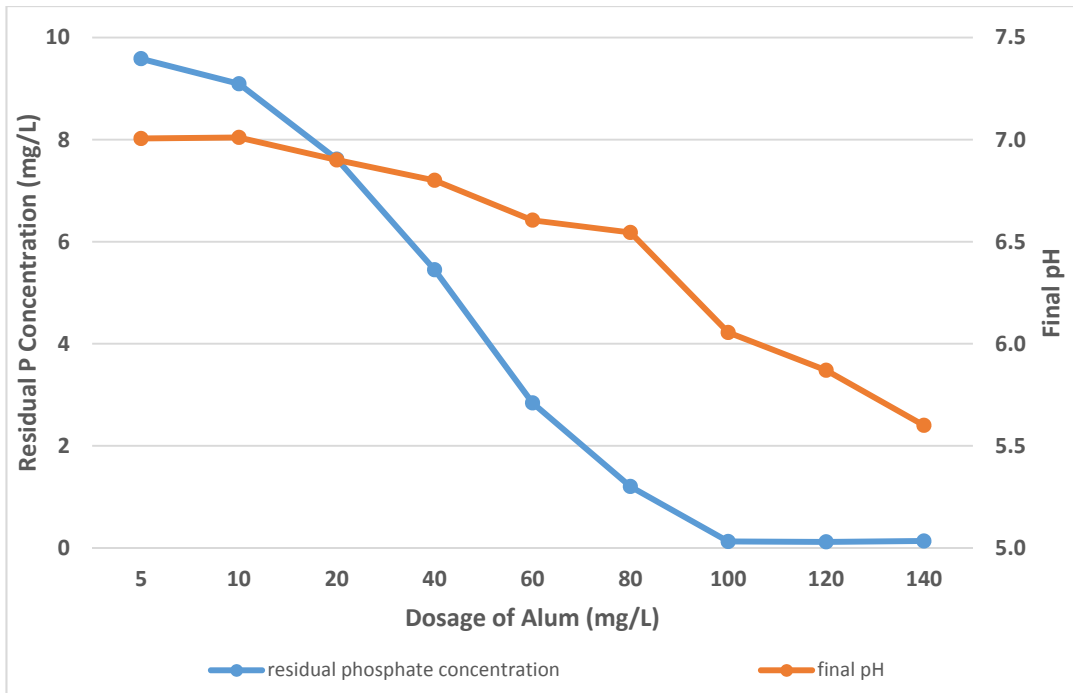


Fig. C4.2: Effect of Alum Dosage on Phosphorus Removal in Synthetic Wastewater

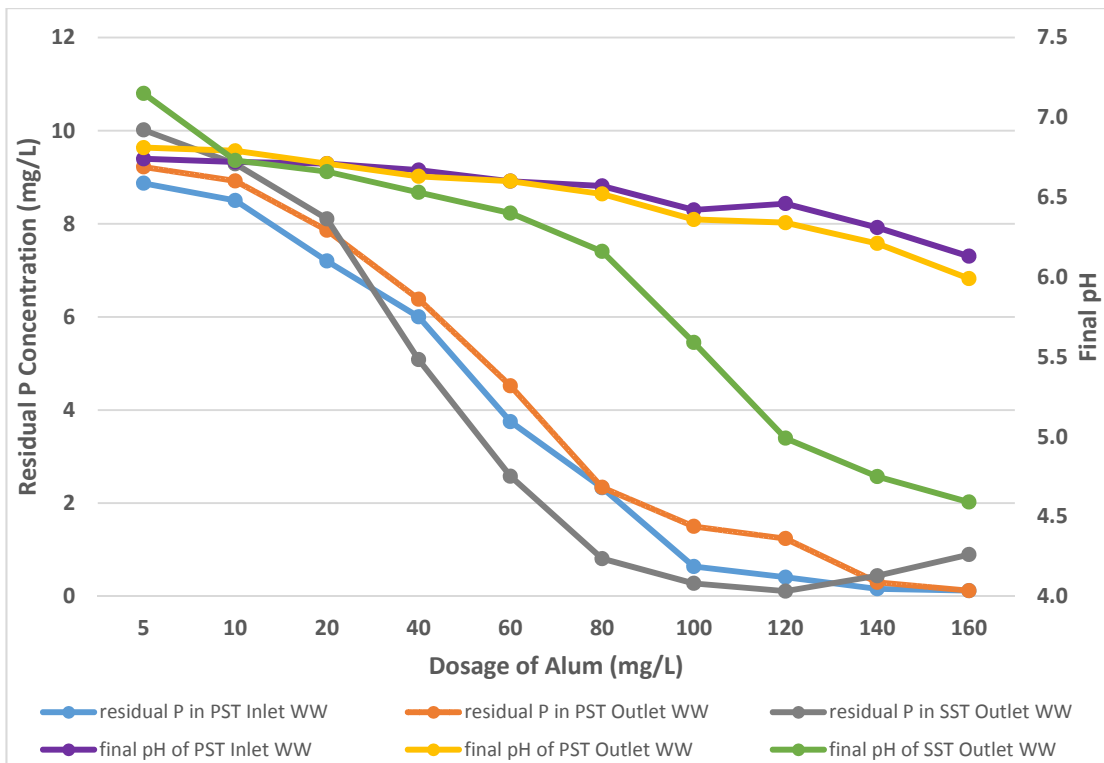


Fig. C4.3: Effect of Alum Dosage on Phosphorus Removal in PST Inlet, PST Outlet and SST Outlet Wastewater Samples

It can be seen from the results shown in Figure C4.2 that the phosphorus removal in synthetic wastewater was increased with the increase of alum dosage up to 100 mg/L of alum and remained constant with the increase of alum dosage after that. Further increase in alum dosage greater than 100 mg/L did not make any difference to the phosphorus removal.

With higher alum doses, though a higher phosphorus removal efficiency could be achieved, the rate of removal was quite small with the increase of alum dosage.

As shown in Figure C4.3, with the SST outlet wastewater sample, the phosphorus removal was increased with the increase of alum dosage up to 120 mg/L of alum and afterwards the residual phosphorus concentration was begun to increase. This is more likely to be due to the lower pH. Phosphorus would be released or not adsorbed at all (depending on the mechanism of phosphate removal) as the pH decreased and the final pH was much higher. With the other two wastewater samples (PST inlet and PST outlet), the residual phosphorus amounts decreased with the increase of alum dosage. In all cases, the phosphorus removal was less with the low alum dosages up to 20 mg/L.

The first half of the experiment up to 80 mg/L of alum dosage is in agreement with the results obtained by Shanshool and Sawsan (2009), but the second half is in contrast with the study. Shanshool and Sawsan showed that at greater than 80 mg/L of alum, the phosphorus removal efficiency decreased with increasing alum dosage (Shanshool & Sawsan, 2009) which in this study happens after 120 mg/L of alum dosage only in SST outlet wastewater sample. A possible explanation for this might be that with higher alum dosages, the pH of the solutions may be shifted from the optimum pH range which creates an unfavourable situation for a phosphorus removal. Therefore, there is no point in adding more alum to remove phosphorus as it may only cost more and cause the reduction of coagulant performance.

The initial pH of all wastewater samples was set to 6.5. The final pHs of the PST inlet and PST outlet wastewater samples with the alum dosages up to 60 mg/L were a bit higher than their initial pH values and with 80 mg/L of alum dosage, the final pH of the solutions were quite similar to their initial value. With the increase of the alum dosage after 100 mg/L, the final pH of the wastewater samples was decreased. A similar final pH value to the original value was observed with 40 mg/L of alum dosage in SST outlet wastewater sample. Afterwards, a decrease in the final pH was observed

with the increase of alum dosage. The highest pH reduction can be seen with the SST outlet wastewater sample (pH 4.59 with 160 mg/L of alum). All these pH values depend on the buffering capacity of the wastewater.

Several factors affect the final pH of the wastewater solution including the concentration of the weak acids and bases present in the wastewater, the initial pH, addition of any acid or base to the solution, reactions occurring when precipitation takes place and passage of carbon dioxide while mixing to or from the solution (Ferguson & King, 1977).

The mole ratio of aluminium added to phosphorus removed from the solution (Al:P ratio) was calculated for each case and the Table C4.1 below presents a sample calculation for the PST inlet wastewater sample and Table C4.2 presents the summary of the calculated values for all locations and for synthetic wastewater.

Table C4.1: Sample Calculations for the Mole Ratio Al:P in PST Inlet Wastewater Sample

Alum Conc. (mg/L)	Alum Vol. (uL)	Alum Weight (g)	Al ³⁺ Moles (in 500mL of Solution)	Residual P in PST Inlet (mg/L)	Residual P in PST Inlet (mg/500mL)	Precipitated P as AlPO ₄ (mg)	P Moles	Al:P
5	7.7	3.9E-05	6.1E-06	8.9	4.44	0.57	1.4E-04	0.0
10	15.4	1.5E-04	2.4E-05	8.5	4.25	0.75	1.9E-04	0.1
20	30.8	6.2E-04	9.7E-05	7.2	3.60	1.40	3.6E-04	0.3
40	61.6	2.5E-03	3.9E-04	6.0	3.00	2.00	5.1E-04	0.8
60	92.3	5.5E-03	8.7E-04	3.8	1.88	3.13	7.9E-04	1.1
80	123.1	9.8E-03	1.6E-03	2.3	1.17	3.84	9.7E-04	1.6
100	153.9	1.5E-02	2.4E-03	0.6	0.32	4.68	1.2E-03	2.0
120	184.7	2.2E-02	3.5E-03	0.4	0.21	4.80	1.2E-03	2.9
140	215.5	3.0E-02	4.8E-03	0.2	0.08	4.92	1.3E-03	3.8
160	246.3	3.9E-02	6.2E-03	0.1	0.06	4.94	1.3E-03	5.0

Table C4.2: Calculated Values of Mole Ratio Al:P

Alum Conc. (mg/L)	Al:P Ratio			
	PST Inlet WW	PST Outlet WW	SST Outlet WW	Synthetic WW
5	0.0	0.1	0.2	0.1
10	0.1	0.2	0.3	0.2
20	0.3	0.4	0.5	0.3
40	0.8	0.8	0.6	0.7
60	1.1	1.3	0.9	1.0
80	1.6	1.6	1.3	1.4
100	2.0	2.2	2.0	1.9
120	2.9	3.1	2.8	2.8
140	3.8	3.9	3.9	3.8
160	5.0	5.0	5.4	-

The initial mole ratio of aluminium added to phosphorus removed is less than 0.2:1 with 5 mg/L of alum concentration for all samples obtained from PST inlet, PST outlet and SST outlet locations and for the synthetic wastewater. As alum dose increased up to 160 mg/L, the mole ratio also increased around 5:1. This indicates inefficient use of high doses of alum for phosphorus removal. Nearly stoichiometric removal (0.8 – 1.3) can be seen with 40 – 80 mg/L of alum concentration in all municipal wastewater samples.

For a 10 mg/L of P as phosphate, the 60 mg/L of alum dosage is about the stoichiometric ratio of 1:1. However, in all three wastewater samples, this amount of alum was insufficient to remove the phosphorus in wastewater to achieve the allowable discharge limits. With 60 mg/L of alum dosage, the residual phosphorus amounts in PST inlet, PST outlet and SST outlet wastewater samples were 3.8, 4.5 and 2.6 respectively which is less than 75% removal. Up to 80 mg/L of alum, only a small difference can be seen in the phosphorus residual amounts in PST inlet and PST outlet wastewater samples and with 80 mg/L of alum dosage, the residual phosphorus amount was almost same. Then for the other two alum dosages (100 mg/L and 120 mg/L), this

difference was quite high. Again there was almost no difference in the residual phosphorus limits with 140 mg/L and 160 mg/L of alum dosages.

The following figure shows the calculated mole ratio of Al:P against the alum dosage for all wastewater samples.

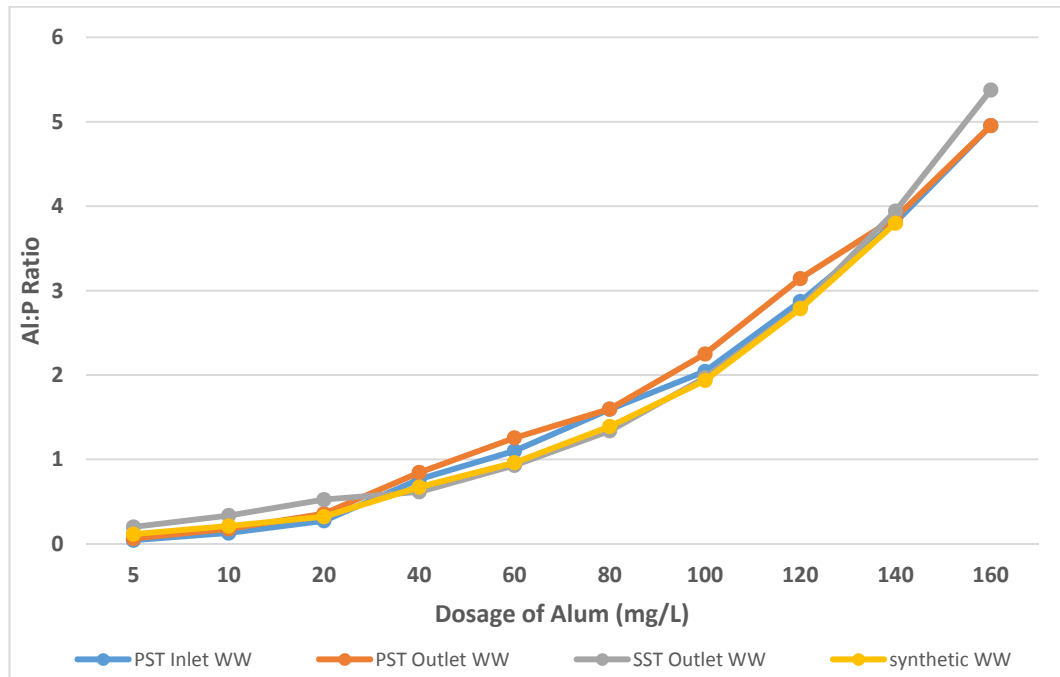


Fig. C4.4: Al:P Removal in Synthetic and Municipal Wastewater Samples

As illustrated in the above figure, the Al:P ratio increases with the increase of alum dosage in all four cases. The mole ratio of Al:P in SST outlet and synthetic wastewater samples are similar for all alum dosages.

Formation of aluminium hydroxide may be a cause for the higher Al:P ratios. The SST outlet wastewater sample gave less Al:P ratio compared to the other two municipal wastewater samples. All most all the studies done in the past relating to the aluminium phosphate precipitation shows that the Al:P ratio is greater than the stoichiometric removal of 1:1 (Balamane-Zizi & Ait-Amar, 2009; Chunjuan D. , 2009; Ferguson & King, 1977; Francisco, Strauss, & Dempsey, 1976). These values are in the range of 1.4 to 3.

Theoretically, a 1:1 Al:P molar ratio is required for phosphorus removal and in a real situation, this could not be achieved. A higher alum dosage is required for a higher phosphorus removal efficiency and in a previous study done by Balamane-Zizi and

Ait-Amar (2009) have found that an Al:P molar ratio of 3 would be required to obtain a 60 – 80 % removal of phosphorus from municipal wastewater. The pH of the solution has a great impact on the hydrolysis reactions (Balamane-Zizi & Ait-Amar, 2009).

In 1980, Bratby reported that the Al:P molar ratios for phosphorus removal vary from 1.4 to 3.4. The cause for this different Al:P ratios is that the use of different wastewater samples with different constituents or the different methods used for the solid liquid separation. An additional amount of chemical coagulant than the theoretical value is needed for a higher phosphorus removal. Adding more coagulants widens the pH range which is favourable for the phosphorus removal. (Bratby, 1980)

The presence of various aluminium phosphate complexes accounts for a high phosphorus residuals.

According to Ferguson et. al. (1977), the addition of chemical should be done uniformly in order to avoid the loss of the effectiveness of cations. Even if there are slight changes in the flow of the addition of chemicals may cause for a loss of the effectiveness of cations. This lower cation efficiency causes a decrease in phosphorus removal efficiency. Intense mixing has to be done at the point of alum addition, which helps the cations to disperse evenly in the solution and they have more chance to react with the phosphate ions rather than the hydroxyl ions present in wastewater. Typical wastewater solutions do not need a pH adjustment as most of them are within the stoichiometric removal zone of pH (Ferguson & King, 1977).

The following table shows the solubility products of aluminium hydroxide and aluminium phosphate.

Table C4.3: Solubility Products

Compound	Formula	K_{sp} (25 °C)
Aluminium Hydroxide	$Al(OH)_3$	3×10^{-34}
Aluminium Phosphate	$AlPO_4$	6.3×10^{-19}

(Wikipedia)

It has been suggested that aluminium hydroxide precipitates prior to aluminium phosphate from wastewater solutions (Ferguson & King, 1977) and this should be the case when considering the solubility products of each compound as shown in Table

C4.4. Aluminium hydroxide has the low solubility product value compared to an aluminium phosphate at room temperature, and hence it should be precipitated first in the wastewater solution. Due to the competitive reactions between phosphate and hydroxide more alum than the stoichiometric equivalent is required for phosphate removal under some conditions.

The above results are in agreement with numerous other studies published in the literature which found similar removal of phosphate from wastewater when using alum (Balamane-Zizi & Ait-Amar, 2009; Ferguson & King, 1977; Francisco et al., 1976). The minor differences may be caused by the use of different wastewaters, use of different jar test procedures, different filtering procedures and the difficulties of measuring the low phosphate concentrations.

4.5 Conclusion

The purpose of this set of experiments was to determine the effect of alum dosage for the phosphorus removal in municipal wastewater.

The results of this experiments show that more than 100 mg/L of alum dosage has to be applied to PST inlet or PST outlet to achieve a phosphorus residual of less than 1 mg/L. This is quite a high dose, but, in SST outlet, around 92 % of phosphorus removal efficiency was achieved with an 80 mg/L of alum dosage and the residual phosphorus concentration was 0.8 mg/L which is less than the allowable discharge limit of 1 mg/L. Overall, this study strengthens the idea that the phosphorus removal in wastewater is highly influenced by the alum dosage and a correct dosage and dosing location has to be identified to minimise the coagulant costs and to obtain an admissible discharge limit.

CHAPTER 5

Effect of Alum Dosing Regime on Removal of Phosphorus in Municipal Wastewater

5.1 Introduction

In the past few decades, the removal of phosphorus from wastewater has been identified as a key requirement for municipal wastewater treatment plants in order to control the input of phosphorus to water bodies (Morse, Brett et al. 1998). Discharge of wastewater into lakes and streams renders the water unsuitable for use by creating conditions that promote algae blooms (De Haas, Wentzel et al. 2000, Banu, Do et al. 2008).

Phosphorus in natural water or wastewater is normally present in the form of phosphate (PO_4^{3-}) and according to Mezenner and Bensmaili (2009), municipal wastewater typically contains 4 – 15 mg/L of phosphorus as $\text{PO}_4\text{-P}$. This phosphorus in wastewater exists in the forms of orthophosphate (dissolved form), polyphosphate (inorganic form) and organically bound forms (Mezenner and Bensmaili 2009). The main compound of phosphorus in wastewater is orthophosphate (reactive phosphorus) and it is the most basic form that is used to measure the amount of phosphorus that is present to react with the chemical coagulants or the biological process.

Alum has been widely used to remove phosphorus and to aid sedimentation in wastewater treatment plants (WWTP) (Ratnaweera, Odegaard et al. 1992, Boisvert, To et al. 1997, Omoike and vanLoon 1999, De Haas, Wentzel et al. 2000, Georgantas and Grigoropoulou 2007, Ramasahayam, Guzman et al. 2014).

The principle of chemical phosphate removal from wastewater using alum involves a combination of processes that convert dissolved phosphate to particulate form, allowing removal during sludge separation. As stated by Aguilar et al. (2002), the following reactions take place between alum and phosphate

- Incorporation of the phosphates with the solids in the suspension of the wastewater
- Direct adsorption of phosphate ions with the hydrolysis products formed by the addition of alum into wastewater
- Formation of insoluble phosphate precipitates with added alum

(Aguilar, Sáez et al. 2002)

Although extensive research has been carried out on phosphorus removal from wastewater to date, little evidence has been found to associate the effect of dosing regime on phosphorus removal. A previous study done by de Vicente et.al, 2008 suggests that the addition of alum in small aliquots is more effective than the addition of a single dose (de Vicente, Huang, Andersen, & Jensen, 2008).

Different dosing regimes of aluminium sulphate has impact on the process since it reacts as a coagulant in removing phosphate from municipal wastewater. This chapter explains the tests carried out to evaluate the effect of different alum dosing regimes (incremental or single alum dosing with and without incremental pH correcting) on phosphorus removal in municipal wastewater. Jar test experiments were conducted using both synthetic wastewater and real wastewater collected from various locations in a wastewater treatment plant in Perth. Synthetic wastewater allowed the study of processes under controlled conditions and findings from these experiments were validated using real wastewater.

A series of bench scale experiments were carried out to investigate the effect of a different alum dosing regime (as a single dose and as an incremental addition of an equal amount of aliquots) of removing phosphorus in municipal wastewater using aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$). The studies have been done with maintaining the Al: P ratio of 1:1. In this study, the jar testing consisted of alum addition (in some cases with the control of pH), 20 minutes rapid mixing with 200 rpm and 20 minutes continuous slow mixing with 20 rpm.

Two sets of experiments were done without controlling the pH and with a controlled pH at its original value of 6.5. This was done to determine if the results were comparable in both cases.

5.2 Objective of the Study

A series of experiments were carried out to find the effect of alum dosing regime for the phosphorus removal in municipal wastewater with aluminium sulphate [$\text{Al}_2(\text{SO}_4)_3$] (with the addition of required alum dosage as an incremental dosage and as a single dosage).

5.3 Materials and Methods

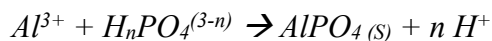
5.3.1 Apparatus and Experimental Procedure

Jar test experiments were carried out at ambient temperature using a six paddle jar test apparatus (VELPSCIENTIFICA - JLT6 flocculator). Synthetic and real wastewater samples (500 ml) were used in each test and standard phosphate solutions were prepared by dissolving pre-weighed potassium dihydrogen phosphate (KH_2PO_4) in deionised water. Analytical grade chemicals were used for all the experiments.

During rapid and slow mixing, sub-samples were taken for the analysis of residual phosphate after filtering through 0.45 μm Millipore Millex HP Hydrophilic PES membrane filters.

The same method as in Section 3.3.2 and Section 3.3.3 in Chapter 3 (test for initial pH) was followed to prepare synthetic wastewater and municipal wastewater samples. Also same analytical procedure mentioned in Section 3.3.4 in Chapter 3 was followed for these set of experiments.

The initial phosphorus ($\text{PO}_4\text{-P}$) concentration of the synthetic wastewater was set to 10 mg/L. According to the following equation, 55.2 mg/L of alum (as $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) is required to remove this phosphorus ($\text{PO}_4\text{-P}$) (the molecular weight of $\text{Al}_2(\text{SO}_4)_3$ is 342.15 g/mol). This required alum quantity was added as a single dose in the first case.



In the other set of experiments, the required quantity of alum for a stoichiometric removal was subdivided in to ten equal small aliquots which were dosed into the wastewater samples periodically. The mixing was done as illustrated in Fig. C5.1. In all cases, the rapid mixing was done for 20 minutes with 200 rpm and slow mixing was done continuously in 20 minutes with 20 rpm. In the rapid mixing phase, sub-samples were taken every 2 minutes and in the slow mixing phase, sub-samples were taken every 5 minutes.

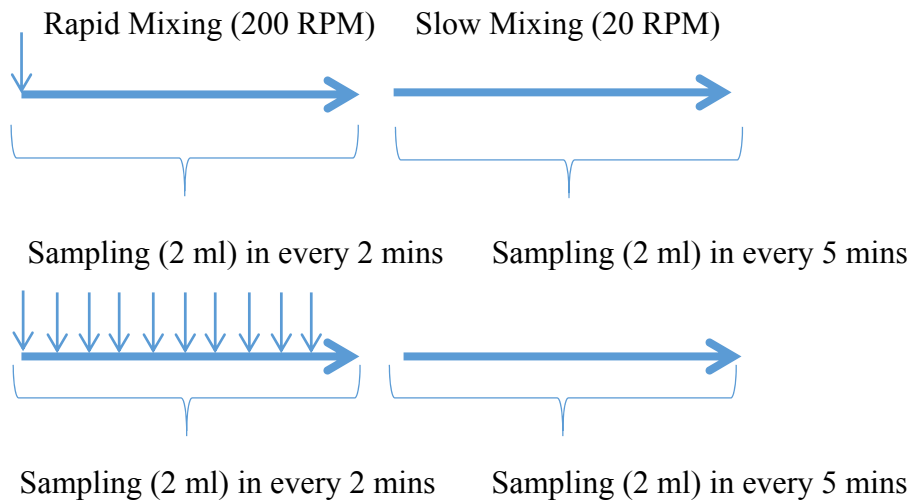


Fig. C5.1: Single and Incremental Alum Dosing and Sampling

In the previous set of experiments, optimum pH of 6.5 for maximum P removal was found after varying the initial pH of the solutions and this pH value was used for all later experiments. Initially, the experiments were done with initial pH of 6.5 without adjusting throughout and later by maintaining pH at its initial value of 6.5 to determine if there is any effect of pH on the phosphorus removal. The pH of the solutions was adjusted using either an acid (H_2SO_4) or base (NaOH).

5.4 Results and Discussion

Previous studies have shown that at most pH values and alkalinities, the initial phosphate removal follows the theoretical values with the addition of alum. As stated by Ferguson et al. (1977), the intense initial mixing and a constant chemical addition are two main factors to be considered for effective alum coagulation in the stoichiometric zone (Ferguson and King 1977).

5.4.1 Phosphorus Removal from Synthetic Wastewater

The amount of alum required for a stoichiometric phosphorus removal was dosed into synthetic wastewater as a single dose and incrementally. Figure C5.2 depicts the residual phosphorus in synthetic wastewater after single and incremental alum dosing without controlling the pH of the solutions.

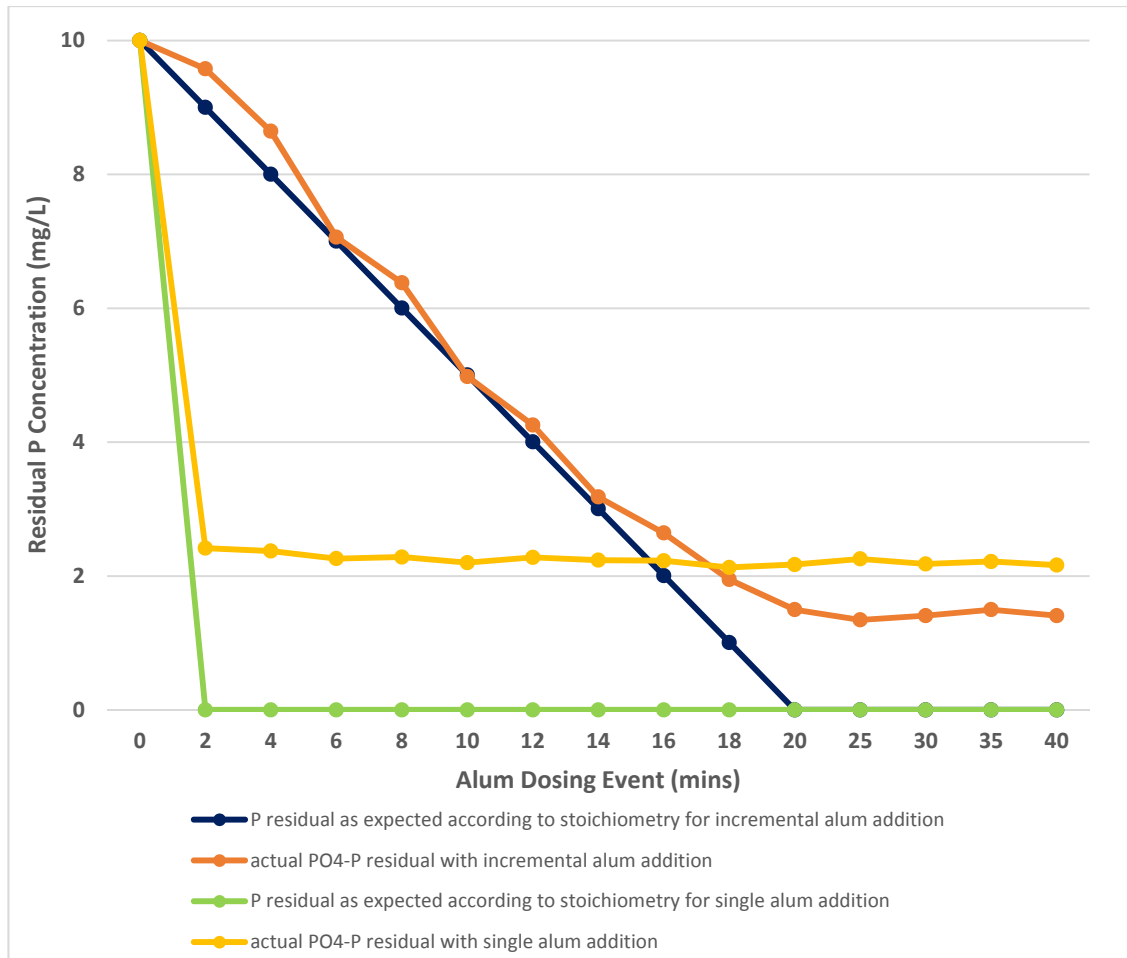


Fig.C5.2: Effect of Alum Dosing Regime in Synthetic Wastewater without pH Adjustment

The addition of alum incrementally in small doses (55.2 mg/L over 10 doses) was shown to improve the removal of phosphorus and the removal was closer to the expected removal according to stoichiometry when compared with a single alum dose (55.2 mg/L).

Further sets of experiments were carried out in order to find the effect of the alum dosing regime (single and incremental alum additions) with and without controlling the pH of the solutions. Figure C5.3 and Figure C5.4 show the effect of pH on the phosphorus removal with single and incremental alum additions.

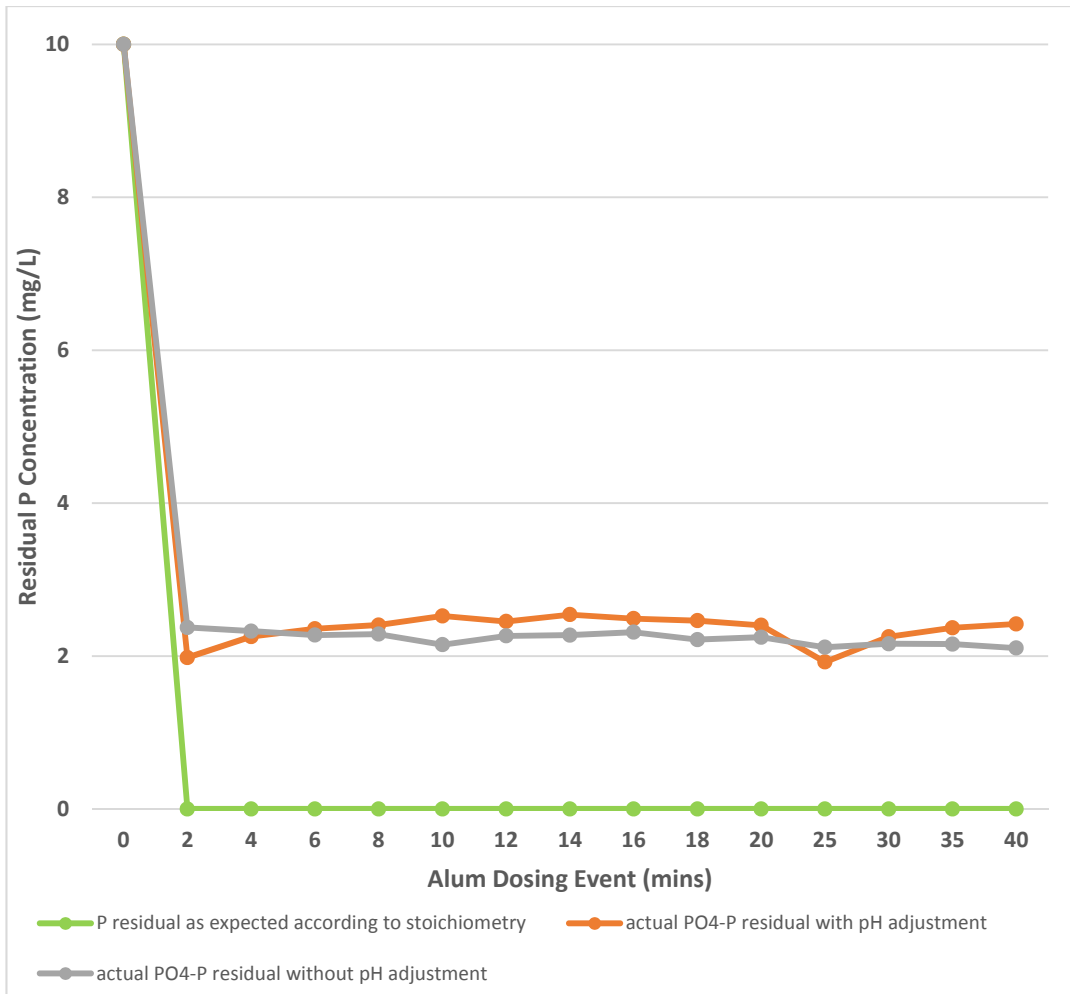


Fig. C5.3: Effect of Alum Dosing Regime in Synthetic Wastewater with Single Alum Addition (with and without pH Adjustment)

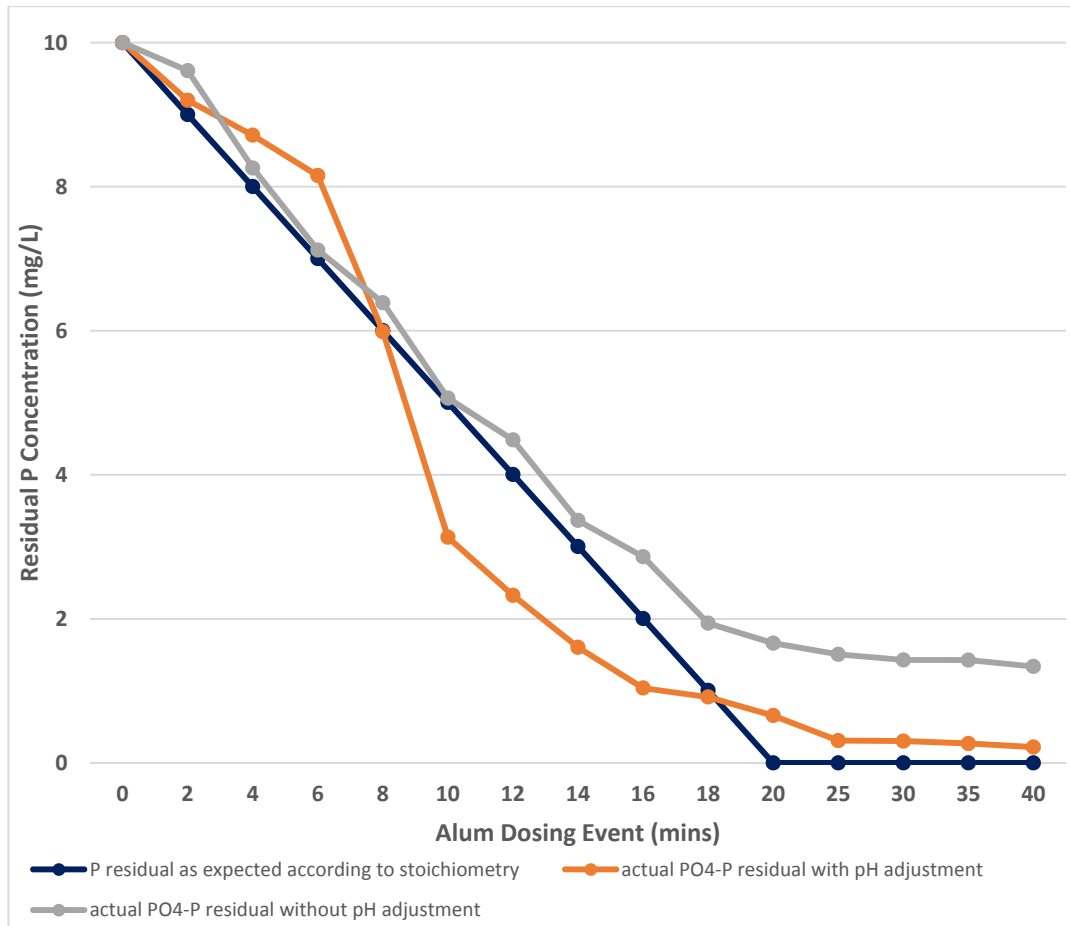


Fig. C5.4: Effect of Alum Dosing Regime in Synthetic Wastewater with Incremental Alum Addition (with and without pH Adjustment)

The initial pH of all samples was set to 6.5 and the final pH of the solutions with incremental alum addition and single alum addition without pH adjustment were 7.09 and 7.36 respectively.

Figure C5.3 shows the actual phosphorus residual with and without the pH adjustment for single alum dosing in synthetic wastewater with the expected P residual according to the stoichiometry. In this single alum addition, the pH adjustment of the solution did not have an impact on the process of phosphorus removal as both solutions with and without pH adjustment gave more or less the similar amounts of phosphorus residuals.

However, in contrast to this, with the pH adjustment in incremental alum addition gave a different result compared to that of without pH adjustment as shown in Figure C5.4. In the rapid mixing zone of the pH adjusted solution, more phosphorus was removed

than the expected value and in the slow mixing zone; the phosphorus removal was almost same as the expected value.

5.4.2 Phosphorus Removal from Municipal Wastewater

The same set of experiments was done with real wastewater to validate the results obtained with synthetic wastewater and the results are shown in Figure C5.5 and Figure C5.6.

The experiments were done with PST inlet, PST outlet and SST outlet wastewater samples without controlling pH and with controlling pH to its original value.

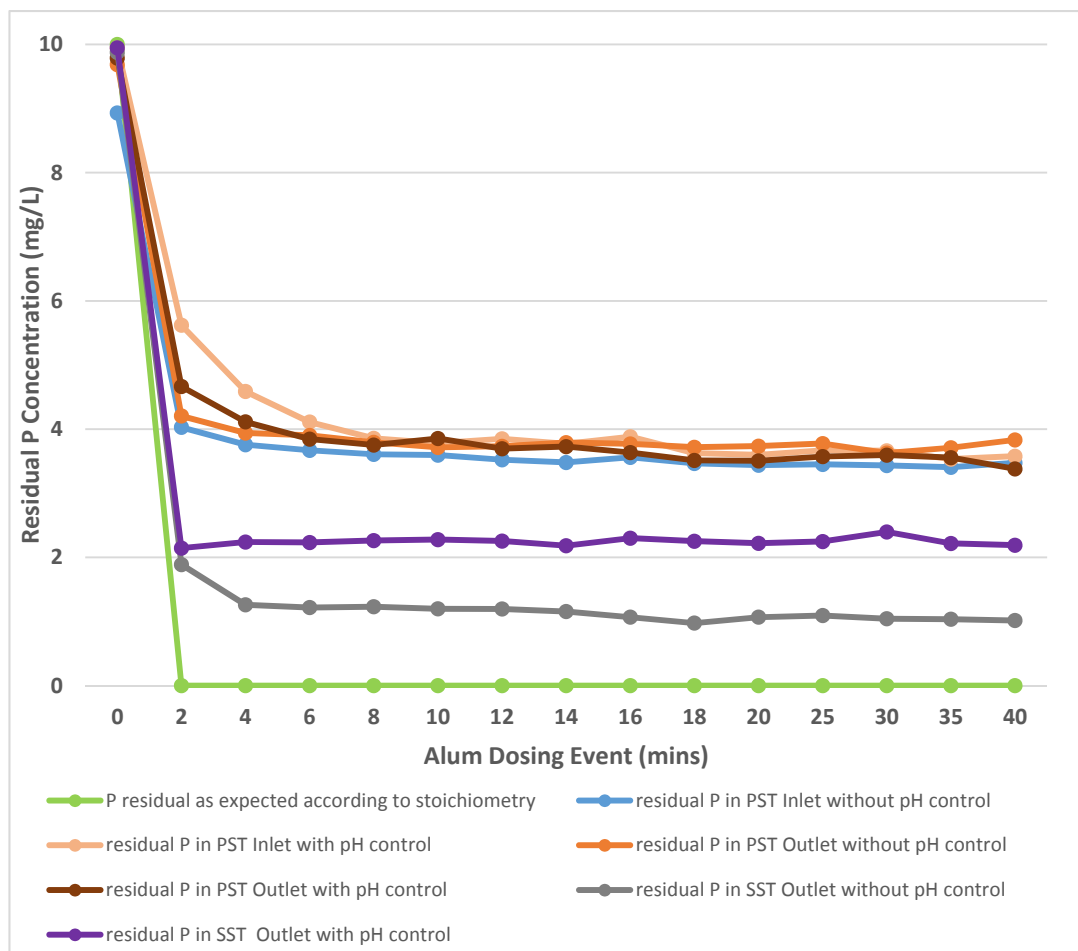


Fig. C5.5: Effect of Alum Dosing Regime in Real Wastewater with Single Alum Addition (with and without pH Adjustment)

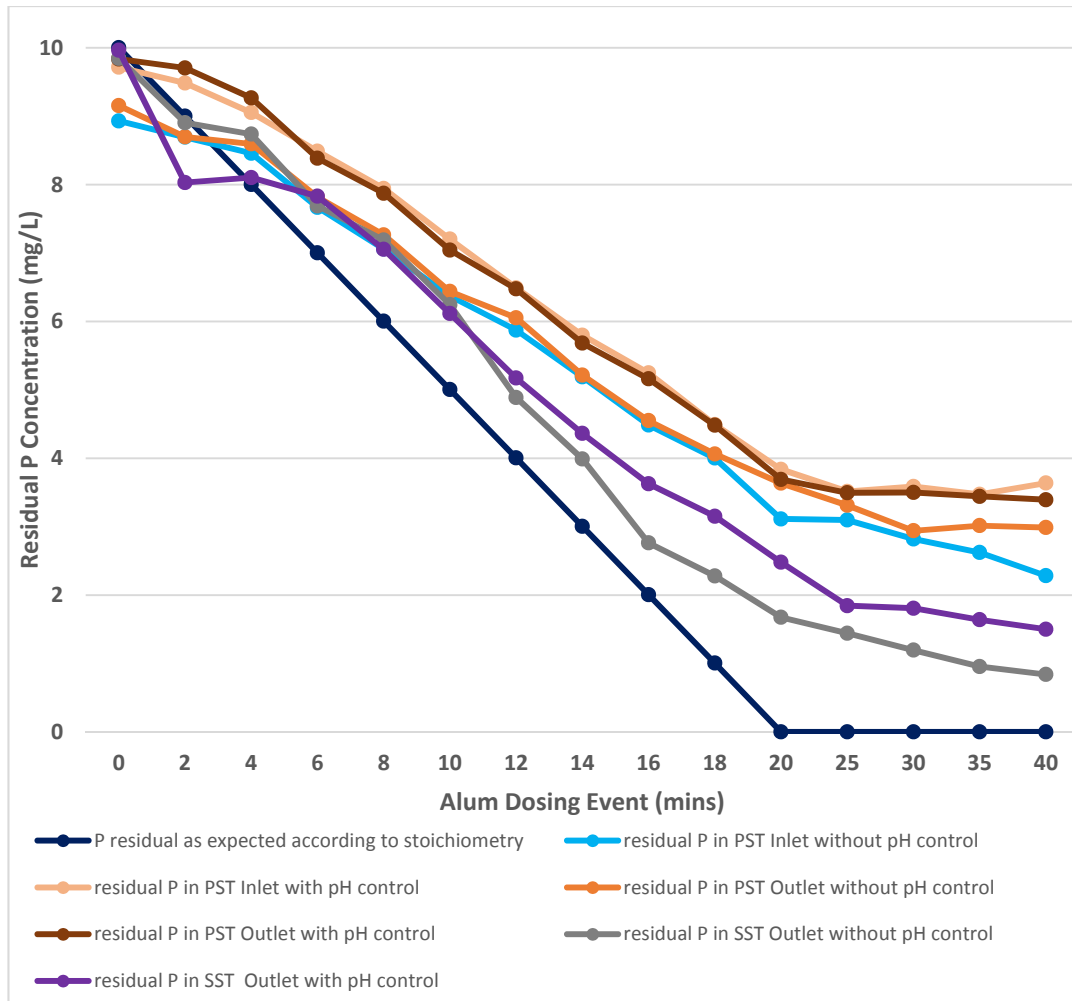


Fig. C5.6: Effect of Alum Dosing Regime in Real Wastewater with Incremental Alum Addition (with and without pH Adjustment)

The initial pH of all the solutions was 6.5 and the final pH of incrementally alum added solutions of PST inlet, PST outlet and secondary outlet without pH adjustment was 7.02, 6.89 and 6.98 respectively. The final pH of the solutions with single alum addition in PST inlet, PST outlet and secondary outlet without pH adjustment was 7.24, 6.89 and 7.28 respectively.

As shown in Fig. C5.5, with the single alum addition, the maximum phosphorus removal occurred in SST outlet wastewater sample without adjusting the pH of the sample and the minimum phosphorus removal occurred in PST outlet wastewater sample without pH adjustment. When considering phosphorus removal in all samples, the maximum phosphorus removal was observed with the SST outlet wastewater sample with and without the pH adjustment. In other wastewater samples (i.e. from PST inlet and PST outlet), the pH adjustment of the solutions did not show much effect

on the phosphorus removal. Both pH adjusted solutions and non pH adjusted solutions gave similar results in those two locations.

According to the results shown in Fig. C5.6, with the incremental dosing of alum, the maximum phosphorus removal was observed in SST outlet wastewater sample without adjusting the pH. The least phosphorus removal was observed in PST inlet wastewater sample with the pH adjustment of the solution. Controlling pH of the solutions did not show a significant difference in PST inlet and PST outlet wastewater samples.

The single most striking observation to emerge from the above data comparison was that the higher phosphorus removal with incremental alum addition compared to the single alum addition. This finding is aligned with observations in an earlier study by de Vicente et al. (de Vicente, Huang et al. 2008).

The pH of the solutions had less effect on the phosphorus removal except the single alum dosing in the PST outlet sample. Phosphorus removal without adjusting the pH was higher in all other experiments; in the PST outlet with single alum dosing, the phosphorus removal with controlled pH was slightly greater than that of uncontrolled pH.

However, according to Sawsan et al. 2009, removal of phosphorus using alum greatly depends on pH and the optimum pH lies within 5.7 - 6. With buffering at pH 6, better phosphorus removals can be achieved (Shanshool and Sawsan 2009). In this study, the solutions were adjusted to pH 6.5 using acid (H_2SO_4) or base (NaOH)

When dosing alum incrementally, the PO_4^{3-} ions may have a higher chance of bonding with Al^{3+} ions compared to single dosing as PO_4^{3-} ions have to compete with OH^- ions for Al^{3+} ions. This may be the reason for the higher phosphorus removal with the incremental alum addition. Possibly with the incremental alum addition, there is less opportunity for the creation of localised zones of higher concentration of alum, which could result in greater formation of $\text{Al}(\text{OH})_3$. This may be due to the dependence of the reaction kinetics on concentration. There is a preferential formation of $\text{Al}(\text{OH})_3$ at a relatively higher concentration of alum, while at a lower concentration, the preference is for the formation of AlPO_4 .

5.5 Conclusion

Two different Alum dosing regimes (single and incremental Alum dosing) were assessed to observe the differences in their performance for phosphorus removal. The pH was also varied according to the different regimes and tests were carried out with and without pH adjustments since adjustment of pH would add complexity for any real-world treatment applications. Even though the control of pH resulted in greater phosphorus removal in synthetic wastewater, this was not the case in the real wastewater samples. More phosphorus was removed without controlling the pH of the samples in all wastewater samples (PST inlet, PST outlet and secondary outlet). This may have been due to competing reactions occurring in real wastewater that did not occur in synthetic wastewater. For example, the real wastewater contained organic carbon and turbidity (e.g. colloidal material) not present in the synthetic samples, both of which can react with alum, e.g. to form floc. Phosphate may also be removed in this process due to co-precipitation or adsorption onto floc.

According to Bai et.al, alum is most effective over pH 6.5 - 7.5 (Bai, Zhu et al. 2010) as already shown in Chapter 3. When adding alum incrementally, the pH of the solutions remained within this range and with the single alum addition, the pH of the solutions reached near the upper limit of this range both in synthetic and real wastewater samples which reduced the phosphorus removal efficiency. However, since the reactions involved in alum treatment of water are extremely complex, with several competing processes, the optimal pH varies depending on water quality parameters. This is probably the major reason for the discrepancies between synthetic wastewater and real wastewater

The results of this study showed that controlling the pH of the synthetic wastewater with incremental alum dosing removed more phosphorus compared to real wastewater. Overall, phosphorus removal with incremental alum addition without incremental pH control was much greater than that of single alum addition.

Therefore, greater phosphorus removal can be achieved by dosing the required alum quantity incrementally in small doses rather than in a single alum dose. The addition of alum incrementally in small doses showed that the removal was closer to expected removal according to the expected stoichiometry, assuming that the major reaction was

the formation of AlPO_4 . Together, these results provide important insights into the effect of alum dosing regime and highlight the need for more studies in this area.

CHAPTER 6

Effect of Dissolved Organic Carbon (DOC) on Removal of Phosphorus in Municipal Wastewater

6.1 Introduction

The dissolved organic carbon (DOC) present in wastewater may have many adverse effects on phosphorus removal using aluminium and ferric salts (Qualls et al. (2008)). DOC consumes a large amount of these metal salts which would otherwise be available for the removal of phosphorus in wastewater. It competes with the phosphate ions for the binding sites of aluminium ions, while hindering the precipitation of phosphorus by hindering the crystallisation process. It also produces a considerable amount of low-density sludge which has an unfavourable effect on the effluent water quality (Qualls, Sherwood et al. 2009).

Dissolved organic carbon (DOC) is defined as the fraction of organic carbon that can pass through a 0.45 µm pore size membrane. DOC is an ill-defined complex material containing various substances including aquatic humic substances, hydrophobic bases, hydrophobic neutrals, hydrophilic acids, hydrophilic bases and hydrophilic neutrals. The quality of the DOC depends largely on the type of wastewater. A substantial part of DOC is not biodegradable and hence its quality affects the final outcome of a wastewater treatment plant. This poorly biodegradable DOC may be discharged to the natural environment with the wastewater effluent after treatment (Katsoyiannis and Samara 2007).

Just after the addition of alum to wastewater, rapid hydrolysing reactions occur in which the DOC present in wastewater is displaced. The organic matter in the wastewater is negatively charged and these negatively charged particles are bound by the aluminium ion with a positive charge and the resulting alum floc by charge neutralisation (Malecki-Brown, White et al. 2009). In essence, DOC and phosphate compete for alum via different mechanisms: if the DOC is present in high concentrations, it may hinder the phosphorus removal efficiency by alum. (Qualls, Sherwood et al. 2009). Presumably the consumption of alum by DOC results in less alum being available for reaction with phosphate to form AlPO_4 or other aluminium phosphate precipitates.

For this study, wastewater samples were collected from four locations in a wastewater treatment plant in Perth. The mean concentration levels of DOC in primary sedimentation tank inlet (PST inlet) and outlet (PST outlet) were quite similar (PST inlet – 88 mg/L and PST outlet – 79 mg/L). This means that the primary treatment resulted in negligible DOC removal from wastewater. DOC concentrations in the secondary sedimentation tank inlet (SST inlet) were higher (180 mg/L) because of the high level of biomass present in the wastewater in the SST inlet. However, the treated effluent in the secondary sedimentation tank outlet (SST outlet) was considerably lower (12 mg/L), demonstrating significant DOC removal by the process in the biological reactor. These results are in agreement with the findings of other workers (Katsoyiannis and Samara 2007).

In order to explain the influence of DOC on phosphorus removal by alum in wastewater, the amounts of phosphate adsorbed by alum at different DOC concentration were determined in this study.

6.2 Objective of the Study

A set of experiments was conducted to find the effect of dissolved organic carbon (DOC) concentration for the phosphorus removal process in municipal wastewater with aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$).

6.3 Materials and Methods

6.3.1 Apparatus and Experimental Procedure

A series of jar test experiments were carried out at laboratory temperature using a six paddle jar test apparatus constructed by VELPSCIENTIFICA (JLT6 flocculator). Synthetic wastewater samples and municipal wastewater samples collected from a WWTP in Perth (500 ml) were used in each test and standard phosphate solutions were prepared by dissolving pre-weighed potassium dihydrogen phosphate (KH_2PO_4) or sodium dihydrogen phosphate (NaH_2PO_4) in deionised water. Analytical grade chemicals were used for all the experiments. A Hach HQ30d pH probe with a glass electrode was used for the all pH measurements and the pH probe was calibrated with standard buffer solutions prior to each use. A TOC analyser (Shimadzu TOC-V) was used for the analysis of DOC concentrations.

Experiments were carried out with the synthetic wastewater with various carbon compounds (phthalate, tannic acid, humic acid and soluble starch) that acted as surrogates for wastewater DOC. Another set of experiments was carried out with real municipal wastewater samples with different DOC concentrations.

In the first set of experiments, the aluminium ion dose (Al^{3+}) was varied with an initial dissolved organic carbon concentration of 100 mg/L-C. The initial pH of all the samples was set to 6.5. One set of experiments was done with the presence of phosphorus with the initial phosphorus concentration of 10 mg/L and the other set of experiment was done in the absence of phosphorus. In the next set of experiments, the aluminium ion dose (Al^{3+}) was varied with the presence of an initial dissolved organic carbon concentration of 100 mg/L-C and without the presence of DOC. The initial pH of this set of experiments was also set to 6.5 and the final samples were taken for the residual phosphorus analysis. All tests were done with the laboratory prepared synthetic wastewater with the above-mentioned different types of carbon compounds.

Another set of experiments was carried out with four types of municipal wastewater samples with varying DOC concentration. The DOC concentration of the sample solutions was varied at 10, 20, 30, 60, 80, 90, 100 and 120 mg/L either by diluting or concentrating the wastewater samples. The initial phosphorus concentration was 10 mg/L and a 10 mg/L of Al^{3+} ion dosage was added to each solution. The initial pH of all the samples was set to 6.5 using either acid (H_2SO_4) or base (NaOH).

All the sample solutions were stirred for 1 minute at 200 rpm followed by 30 minutes continuous stirring with 45 rpm. Solutions were allowed to settle for 15 minutes and sub samples were filtered through 0.45 μm Millipore Millex HP Hydrophilic PES membrane filters prior to analysis for residual phosphate and DOC. The final pH of the samples was also recorded at the end of each experiment.

Same methods as in Section 3.3.2 and Section 3.3.3 in Chapter 3 (test for initial pH) were followed to prepare synthetic wastewater samples and municipal wastewater samples. Also the same analytical procedures mentioned in Section 3.3.4 in Chapter 3 were followed for these sets of experiments.

6.4 Results and Discussion

The effect of Al^{3+} dosage on DOC removal in synthetic wastewater with and without the presence of phosphate was studied with different organic carbon compounds including phthalate, tannic acid, humic acid and soluble starch. The Al^{3+} dosage was changed as 0.5 mg/L, 1 mg/L, 2 mg/L, 3 mg/L, 5 mg/L and 10 mg/L. The final pH level was also monitored. The residual P concentration for each sample was measured and the results are shown below in Figure C6.1 to Figure 6.5.

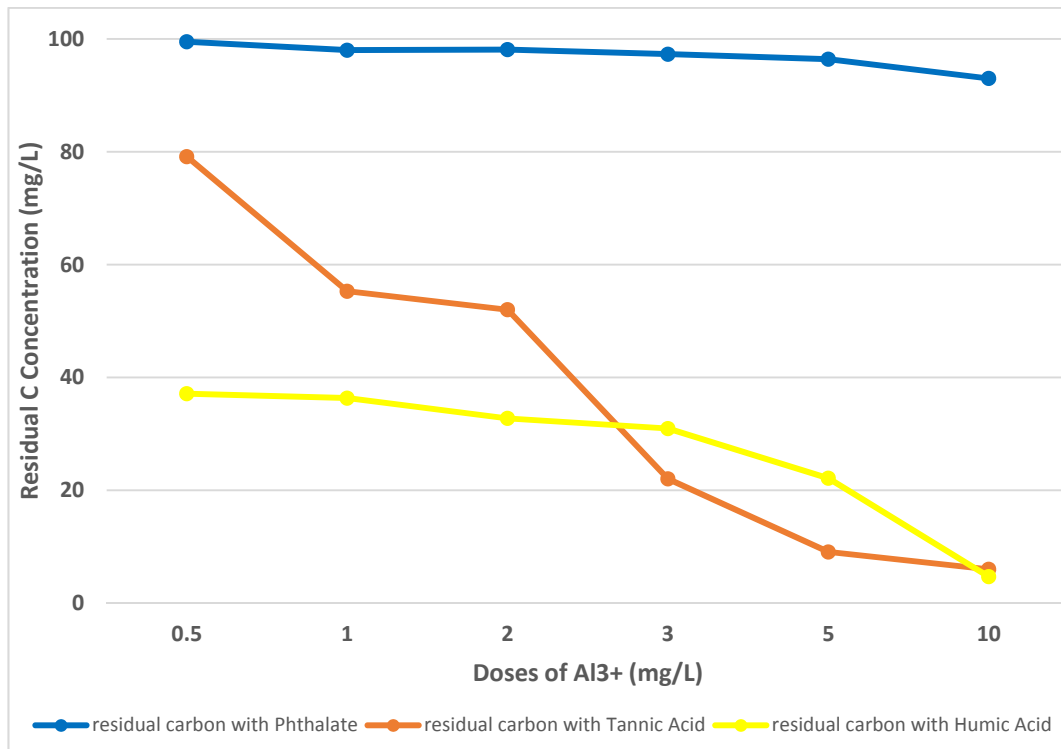


Fig. C6.1: The Effect of Varying Al^{3+} Dosage on DOC Removal without the Presence of Phosphate – with Phthalate, Tannic Acid and Humic Acid (in Synthetic WW)

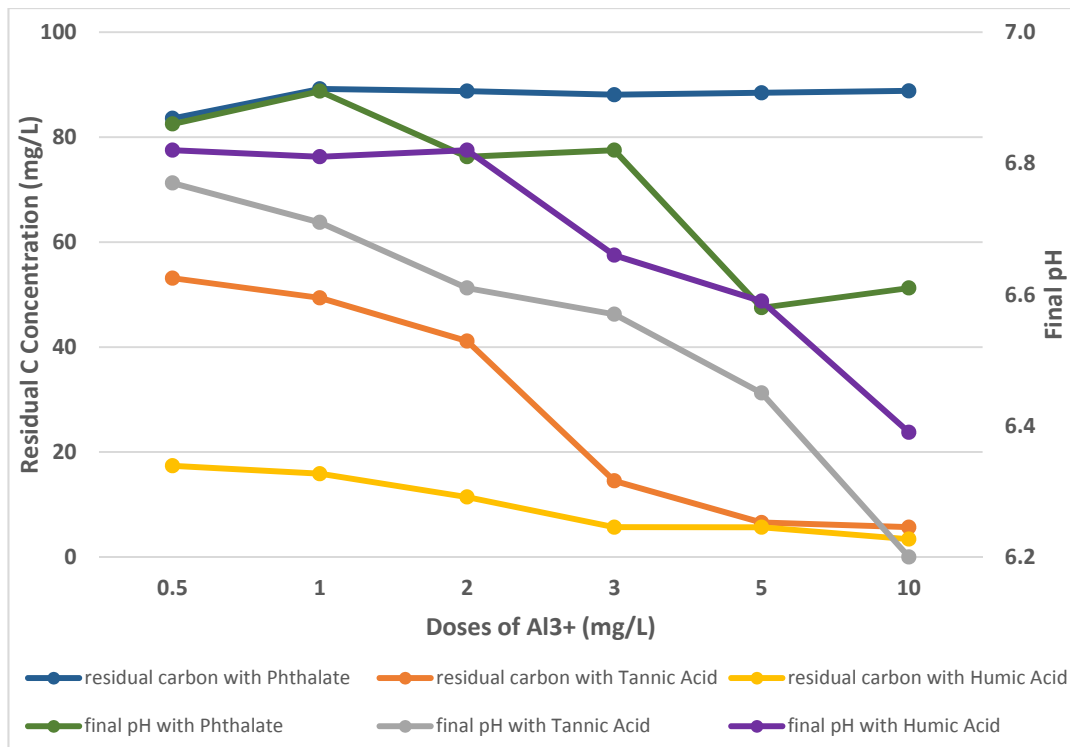


Fig. C6.2: The Effect of Varying Al³⁺ Dosage on DOC Removal with the Presence of Phosphate – with Phthalate, Tannic Acid and Humic Acid (in Synthetic WW)

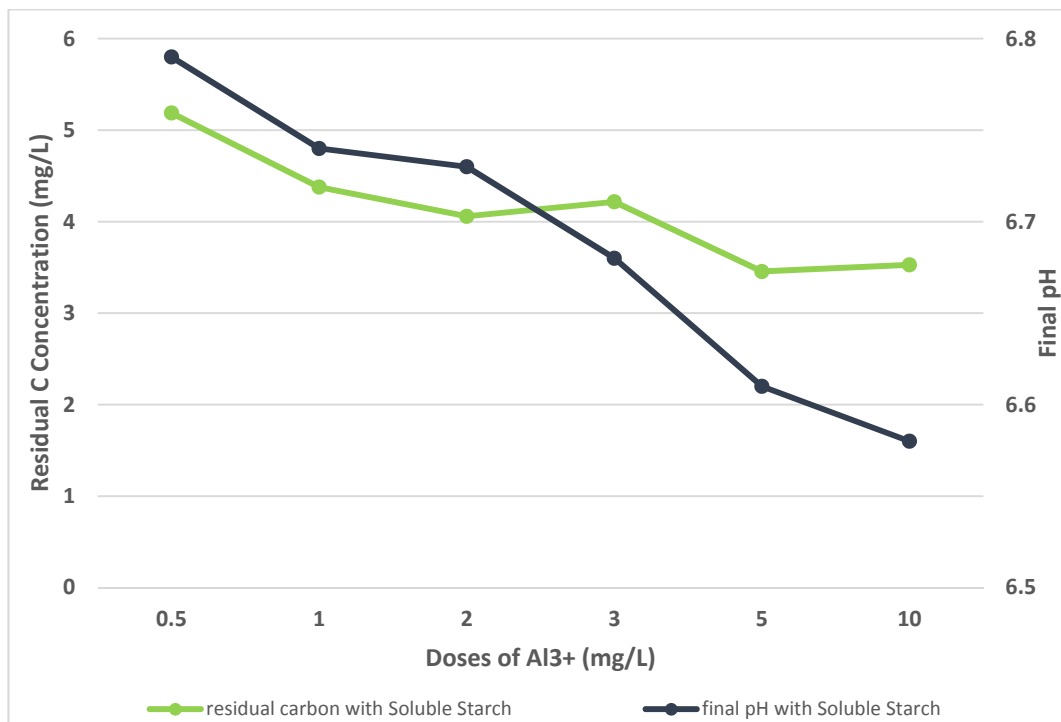


Fig. C6.3: The Effect of Varying Al³⁺ Dosage on DOC Removal with the Presence of Phosphate – with Soluble Starch (in Synthetic WW)

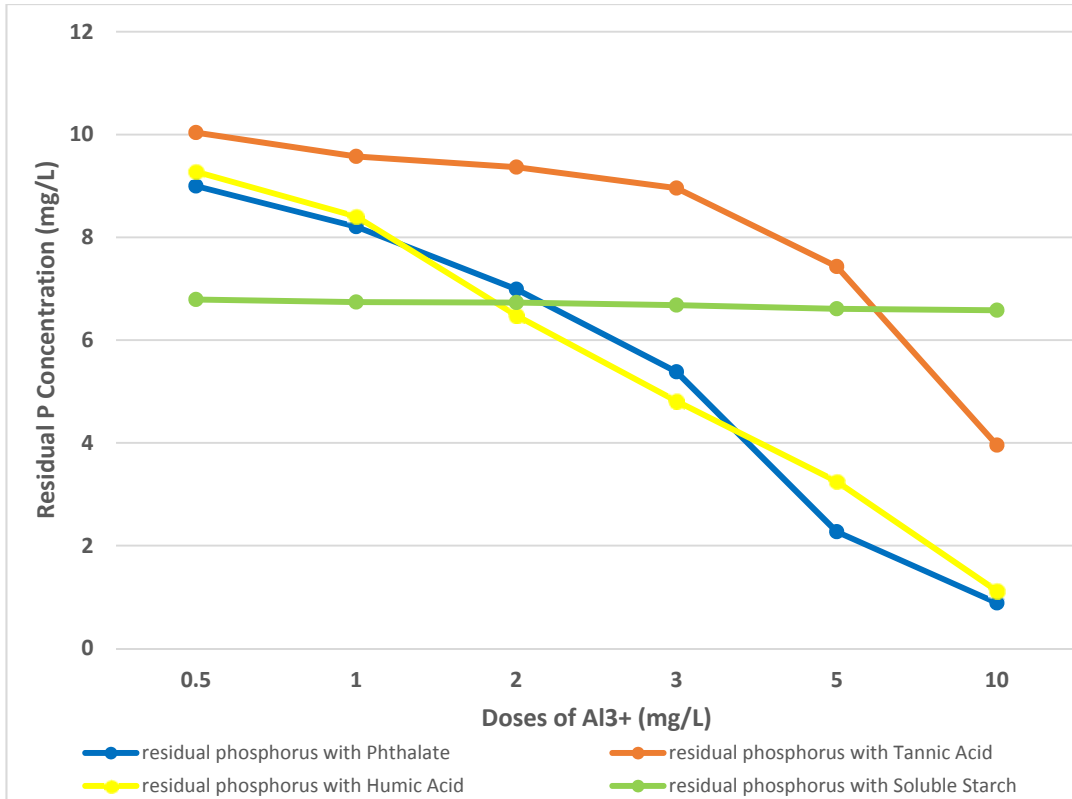


Fig. C6.4: The Effect of Varying Al³⁺ Dosage on Phosphorus Removal with the Presence of Organics – with Phthalate, Tannic Acid, Humic Acid and Soluble Starch (in Synthetic WW)

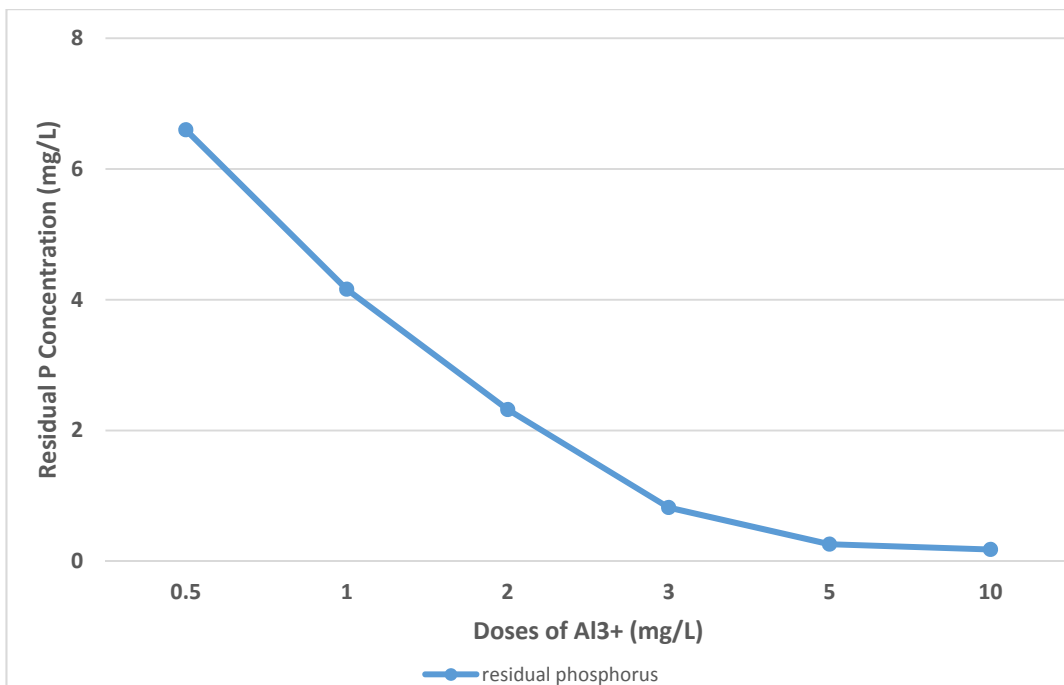


Fig. C6.5: The Effect of Varying Al³⁺ Dosage on Phosphorus Removal without the Presence of Organics (in Synthetic WW)

As shown in Figures C6.1 and C6.2, the dissolved organic carbon removal with the presence of phosphate was higher than that of without the presence of phosphate in all cases with phthalate, tannic acid and humic acid. The least dissolved organic carbon removal was observed with the presence of phthalate in both cases of with and without the presence of phosphorus. Similar trend of gradual decrease of residual carbon concentration was observed with the presence of tannic acid and humic acid; and with a 10 mg/L of Al^{3+} dosage, both carbon sources showed nearly a same residual DOC concentration. The DOC removal with the increase of Al^{3+} dosage was increased with the presence of soluble starch as the organic carbon source. This is illustrated in Fig. C6.3. The final pH of the solutions with tannic acid and humic acid with the presence of phosphorus were dropped (6.20 and 6.39 respectively) from their initial values and a slight increase in the final pH values of solutions can be seen with phthalate and soluble starch (6.61 and 6.58 respectively).

Even though, the increase of Al^{3+} dosage did not show a significant effect on phosphorus removal with the presence of soluble starch, the residual phosphorus concentration was decreased with the presence of other three organic carbon sources with the increase of Al^{3+} dosage. Nearly a same phosphorus removal can be seen with phthalate and humic acid as depicted in Fig. C6.4. A gradual decrease of the residual phosphorus concentration can be seen in Fig. C6.5 with the increase of Al^{3+} dosage without the presence of dissolved organic carbon sources.

Significant removal of phosphorus occurred even with the presence of organic carbon substances. . Nearly 1 mg/L of residual phosphorus could be obtained with a 10 mg/L of Al^{3+} dosage with the occurrence of phthalate or humic acid. This dosage of Al^{3+} is about 63 mg/L of aluminium sulphate. For a stoichiometric removal of phosphorus from the solution, 55.2 mg/L of aluminium sulphate is required. Hence, this amount of aluminium sulphate is bit higher than the amount required for a 1:1 Al:P stoichiometric phosphorus removal. These studies showed that DOC did not have a significant effect on P removal. In fact in some cases alum removed both DOC and P very effectively (e.g. in the case of humic acid).

As stated by Kuo and Amy (1988), aluminium hydroxide is formed with large coagulant dosages and humic matters present in wastewater are adsorbed on to these formed aluminium hydroxide flocs (Kuo and Amy 1988). Hence, the phosphorus

removal efficiency by adsorbing phosphorus on to formed aluminium hydroxide is decreased by the presence of organic matters. Fig. C6.5 reveals that there has been a slight increase in the phosphorus removal without the presence of organic matters (as the Al^{3+} dosage increased) when compared to the results in Fig. C6.4 which shows the phosphorus removal with the presence of organic matters. A possible explanation for this might be the reason stated by Kuo and Amy (1988).

Figures 6.6 illustrates the results obtained with varying dissolved organic carbon concentration with PST inlet, PST outlet, SST inlet and SST outlet municipal wastewater samples.

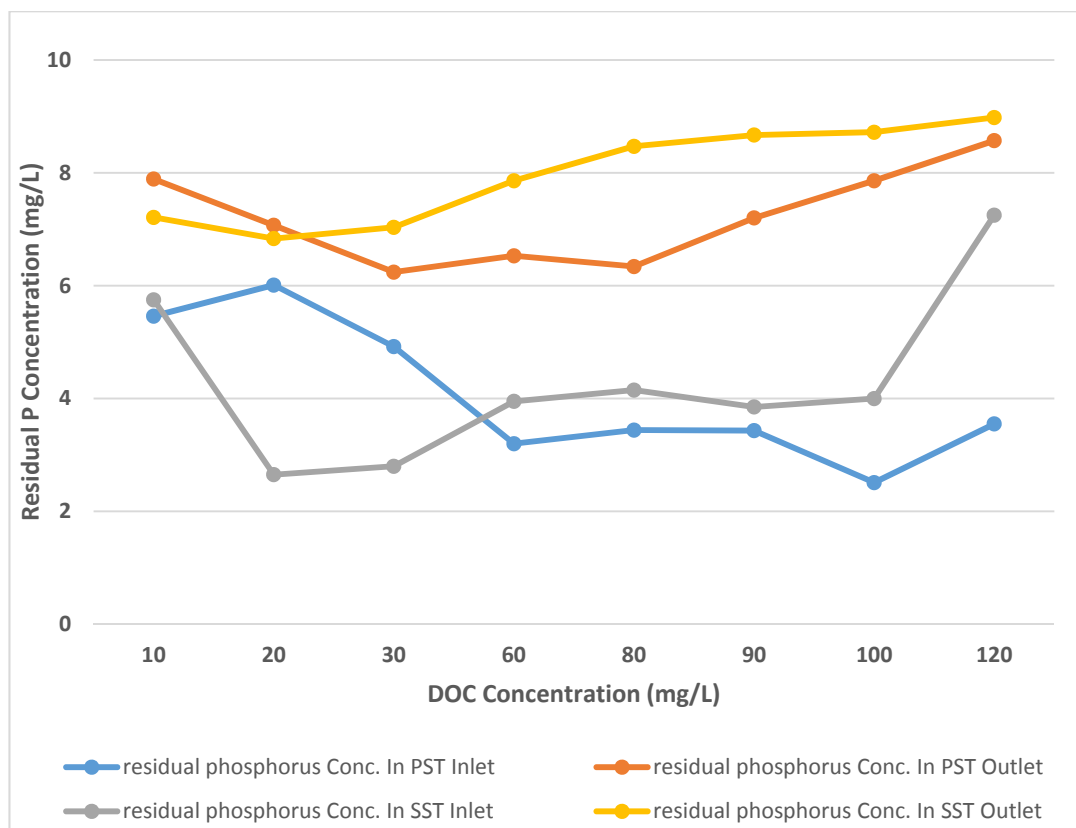


Fig. C6.6: The Effect of Varying DOC Concentration for the Removal of Phosphorus in PST Inlet, PST Outlet, SST Inlet and SST Outlet Wastewater Samples

In the PST inlet, the residual phosphorus concentration decreased with increasing DOC concentration up to 100 mg/L DOC and afterwards it increased. As shown in Fig. C6.6, in the PST outlet, the residual phosphorus concentration decreased with increasing DOC concentration up to 30 mg /L of DOC concentration and after this, the residual phosphorus concentration increased again. For SST inlet, a drop of residual phosphorus concentration was observed from 10 mg/L of DOC to 20 mg/L of DOC and this is illustrated in Fig. C6.6. At DOC concentrations greater than 20 mg/L, the residual phosphorus concentration increased with increasing DOC concentration and a high residual phosphorus concentration of 7.5 mg/L was obtained with a 120 mg/L of DOC concentration in the SST inlet wastewater sample. In the SST outlet wastewater sample, a much different of the phosphorus removal cannot be seen with the increase of DOC concentration from 10 mg/L to 30 mg/L. After 30 mg/L of DOC concentration, the residual phosphorus concentration gradually increased with the increased concentration of DOC. Moreover, except in the PST inlet wastewater sample, in all other three cases, the phosphorus removal efficiency was hindered by the increasing DOC concentration.

6.5 Conclusion

With the presence of phthalate, tannic acid and humic acid in synthetic wastewater, the dissolved organic carbon removal with the presence of phosphorus was higher than that of without the presence of phosphorus. The aluminium ion dosage had an effect on the DOC removal in the synthetic wastewater as the DOC removal was increased with the increase of aluminium ion dosage except in the experiment with phthalate. It is well known that alum removes organic carbon. This is the basis of conventional water treatment, by far the most common form of water treatment. Humic and tannic acids are known to be well removed by this process, because they are macromolecules with a diffuse negative charge but phthalate is probably not so well removed because it is a much smaller anion. Therefore, alum can form colloids with humic and tannic acids but not with phthalic acid. The fact that DOC has little effect on P removal suggests that phosphate is removed by adsorbing onto colloidal material formed via the reaction of alum and DOC, rather than via the precipitation of $AlPO_4$.

The phosphorus removal with the presence of organic carbon substances was quite high with the presence of phthalate and humic acid when compared with tannic acid and soluble starch.

With the formation of aluminium hydroxide with high coagulant dosages, the organic matters present in wastewater adsorb onto this aluminium hydroxide and the phosphorus removal efficiency by adsorbing phosphorus on to formed aluminium hydroxide was decreased by the presence of organic matters.

In all three locations in the municipal wastewater treatment plant except in the PST inlet, the phosphorus removal efficiency was hindered by the increasing DOC concentration.

CHAPTER 7

Phosphorus Removal by Aluminium Hydroxide ($\text{Al}(\text{OH})_3$)

7.1 Introduction

Aluminium hydroxide which is produced during wastewater treatment after the addition of alum (Georgantas & Grigoropoulou, 2007) has a high adsorptive capacity (van Riemsdijk & Lyklema, 1980b). Alum has been widely used for the removal of phosphate in municipal wastewater (Kawasaki, Ogata, & Tominaga, 2010) and presumably one of the mechanisms of phosphorus removal is the adsorption of phosphate onto the precipitated aluminium hydroxide.

In the set of experiments done in order to find the effect of alum dosing regime in synthetic wastewater with incremental alum addition (in Fig. C5.4 in Chapter 5), more phosphate was removed than the expected amounts according to the stoichiometry with the adjustment of pH. A possible explanation for this removal might be due to the adsorption of phosphate by already formed aluminium hydroxide. As mentioned earlier, this phosphate adsorption by aluminium hydroxide has been studied previously and the following experiments were carried out with the aim of explaining the observations in Fig. C5.4 in Chapter 5.

Over the past few decades, a considerable amount of literature has been published on the phosphorus adsorption by aluminium hydroxide. In the process of alum coagulation, alum quickly dissolves in the water and produces aluminium ions which then form hydrolysed complexes. Nail et al. (1976) reported that with a certain aluminium concentration and pH, a gelatinous precipitate of aluminium hydroxide is formed and the structure of this precipitate changes with the time (Nail, White, & Hem, 1976). Considerable amount of studies have been carried out to find the phosphate adsorption by aluminium hydroxide (for example Rebhun et al. (1993), Pommerank et al. (2005) and Georgantas et al. (2007)) (Georgantas & Grigoropoulou, 2007; Pommerenk & Schafran, 2005; Rebhun & Lurie, 1993). The solubility of aluminium hydroxide is highly pH dependent: the lowest solubility is within the pH range of 6.0 to 6.5 and its solubility increases as the pH increases or decreases beyond those limits (Snoeyink & Jenkins, 1980).

Although different aluminium phosphate complexes are formed during the addition of alum, the phosphate uptake by aluminium hydroxide has a major impact on phosphorus removing process (Boisvert, To, Berrak, & Jolicoeur, 1997; Hsu, 1975). Rebhun et al. (1993) and Georgantas et al. (2007) have reported that aluminium hydroxide is extensively used for the phosphate adsorption as a phosphate removal mechanism in water treatment plants (Georgantas & Grigoropoulou, 2007; Rebhun & Lurie, 1993). It has been demonstrated by a number of authors that aluminium hydroxide is used for the refurbishment of lakes which is affected by the eutrophication (Auvray, van Hullebusch, Deluchat, & Baudu, 2006; Reitzel, Hansen, Andersen, Hansen, & Jensen, 2005; Rydin & Welch, 1998).

According to Kawasaki, aluminium hydroxide gel selectively adsorbs phosphate ions and the maximum adsorption occurs at pH 4 – 6 (Kawasaki et al., 2010). In 2003, Tanada et al. published a paper in which they described the use of aluminium hydroxide to remove orthophosphate in comparison with other ions and showed that phosphate adsorption by aluminium hydroxide was the highest amongst all the ions studied. They also stated that aluminium hydroxide easily adsorbs ions with higher charges (Tanada et al., 2003).

A number of authors have showed that the adsorption of phosphate by different aluminium compounds is associated with their specific surface area and this adsorption depends on ion exchange with the surface hydroxyl groups of the compound (Georgantas & Grigoropoulou, 2007; Kabayama, Kawasaki, Nakamura, & Tanada, 2005). This adsorption of ions is influenced by the pH value of the solution (Kawasaki et al., 2010).

As a result of the small crystals on the surface of the aluminium hydroxide, condensed phosphate is quickly adsorbed to it and this does not occur evenly through the aluminium hydroxide surface (Guan, Chen, & Shang, 2007).

A study done by Mezenner et al. (2009) showed that if the initial concentration of phosphate is high, then the amount of phosphate removed is also high, because of the increase of phosphate ions amount present in the solution. In the beginning, the surface of the aluminium hydroxide is vacant and the adsorption rate is quite high. With the time, the phosphorus removal efficiency decreased as the vacant surface sites are reduced. They also mentioned that the speedy initial adsorption process occurred if the adsorption contains a surface reaction process (Mezenner & Bensmaili, 2009).

According to Jenkins et al. (1971), the precipitation of aluminium phosphate is kinetically and thermodynamically preferred over the precipitation of aluminium hydroxide (Jenkins, Ferguson, & Menar, 1971).

7.2 Objective of the Study

This study was carried out to find the effect of pre-formed aluminium hydroxide ($\text{Al}(\text{OH})_3$) on the phosphorus removal process in real and synthetic municipal wastewater with aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$).

7.3 Materials and Methods

7.3.1 Apparatus and Experimental Procedure

A series of jar test experiments were carried out at laboratory temperature using a six paddle jar test apparatus (VELPSCIENTIFICA (JLT6 flocculator)). Synthetic wastewater samples (500 ml) were used in each test and standard phosphate solutions were prepared by dissolving pre-weighed potassium dihydrogen phosphate (KH_2PO_4) or sodium dihydrogen phosphate (NaH_2PO_4) in deionised water. Analytical grade chemicals were used for all the experiments. A Hach HQ30d pH probe with a glass electrode was used for the all pH measurements and the pH probe was calibrated with standard buffer solutions prior to each use. An Eppendose Centrifuge 5810 R was used for the centrifuging of prepared aluminium hydroxide.

Three sets of experiments were carried out with the synthetic wastewater with three different mixing speeds. The aluminium hydroxide concentration was kept constant at 30 mg/L and the initial phosphorus concentration of the sample solutions was varied at 5, 20, 40, 60, 80 and 100 mg/L respectively. The initial pH of all the samples was set to 6.5 using either acid (H_2SO_4) or base (NaOH). All the samples were continuously stirred at 60, 80 and 200 rpms for 48 hrs and the sub samples for the analysis of residual phosphorus concentration were taken at 1 hr, 3 hrs, 5 hrs, 24 hrs and 48 hrs after filtering through a 0.20 μm membrane filter. The final pH of the samples was also recorded at the end of each experiment.

The method to prepare synthetic wastewater and the analytical procedure were described in Section 3.3.2 and Section 3.3.4 in Chapter 3.

7.3.2 Preparation of Aluminium Hydroxide ($\text{Al}(\text{OH})_3$)

Amorphous aluminium hydroxide was prepared according to the procedure described by Georgantas et al. (2005). In brief, aluminium sulphate hexadecahydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) (46.3 g) was dissolved in deionized water (350 mL) and 1 N of sodium hydroxide (NaOH) was prepared by dissolving NaOH pellets (40 g) in deionized water (1 Litre). Prepared NaOH was added to an aluminium sulphate solution by a peristaltic pump at a rate of 3 ml per minute. The solution was stirred during the addition of base and the pH of the solution was monitored using a pH probe. At about pH 5, an increase of the viscosity of the solution was observed, together with a sharp increase in the pH increase with the addition of the base. The addition of the base was stopped when the pH of the solution reached at 7 and the solution was stirred for an hour while keeping the pH at 7. Then the gel was centrifuged using Eppendose Centrifuge 5810 R, the supernatant was decanted and washed several times with deionised water to remove excess sulphate ions (Georgantas & Grigoropoulou, 2005).

7.4 Results and Discussion

The figure below illustrates the titration curve of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ with 1N NaOH.

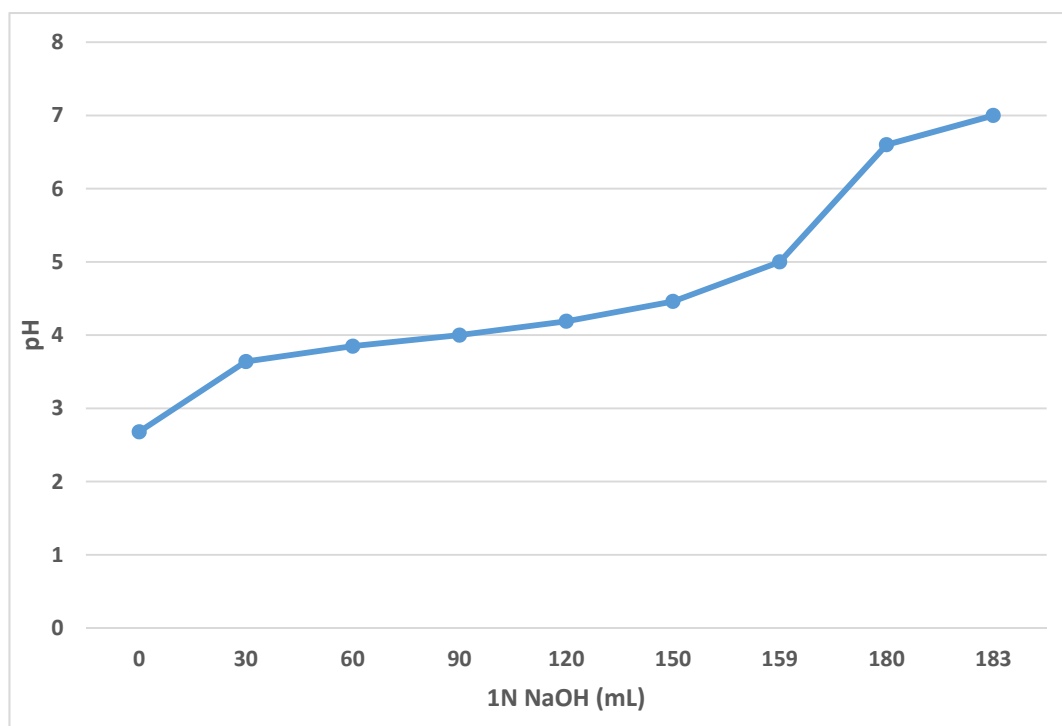


Fig. C7.1: Potentiometric Titration of Alum using 1N NaOH

During the first phase of the titration the pH increase was slow in comparison to the NaOH added until a pH of 5. This phase of slow increase in pH indicates that the hydroxide ions reacted with aluminium ions (Al^{3+}), forming aluminium hydroxide. After about pH 5, a sudden increase of the pH of the solution was observed. This was because no further aluminium was available to react with hydroxide. This observation therefore provided confidence that all of the available alum had reacted to form $\text{Al}(\text{OH})_3$.

This pre-formed $\text{Al}(\text{OH})_3$ was then used to test the adsorption of phosphate, including the effect of varying mixing speeds, and the effect of aging on adsorption. The results obtained from the three different mixing speeds for the phosphate uptake by aluminium hydroxide are presented in Figures C7.2 (a), (b) and (c).

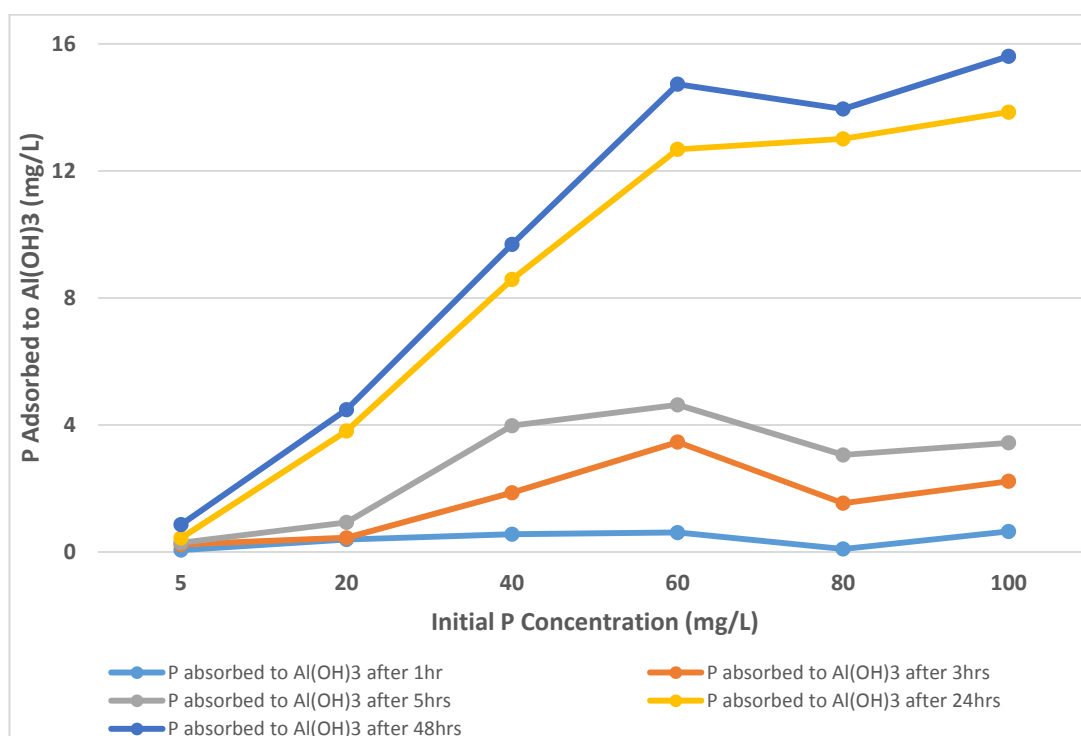


Fig. C7.2 (a): Phosphate Adsorption by $\text{Al}(\text{OH})_3$ with Mixing Speed of 60 RPM

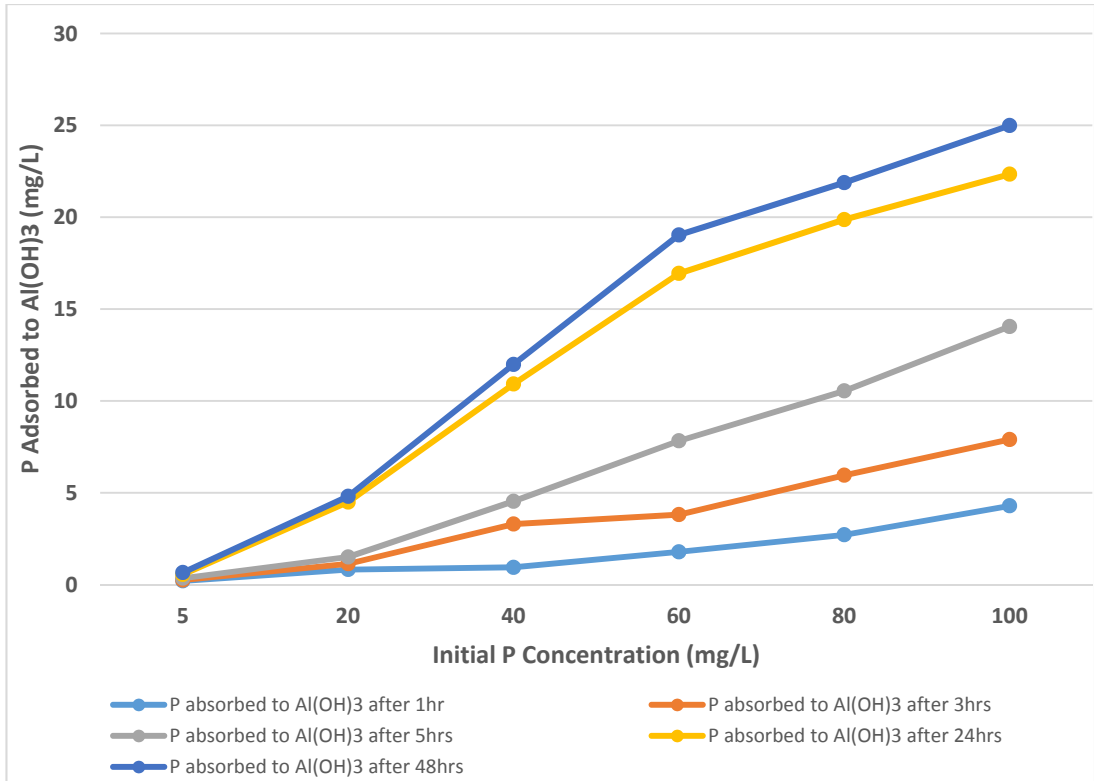


Fig. C7.2 (b): Phosphate Adsorption by Al(OH)₃ with Mixing Speed of 80 RPM

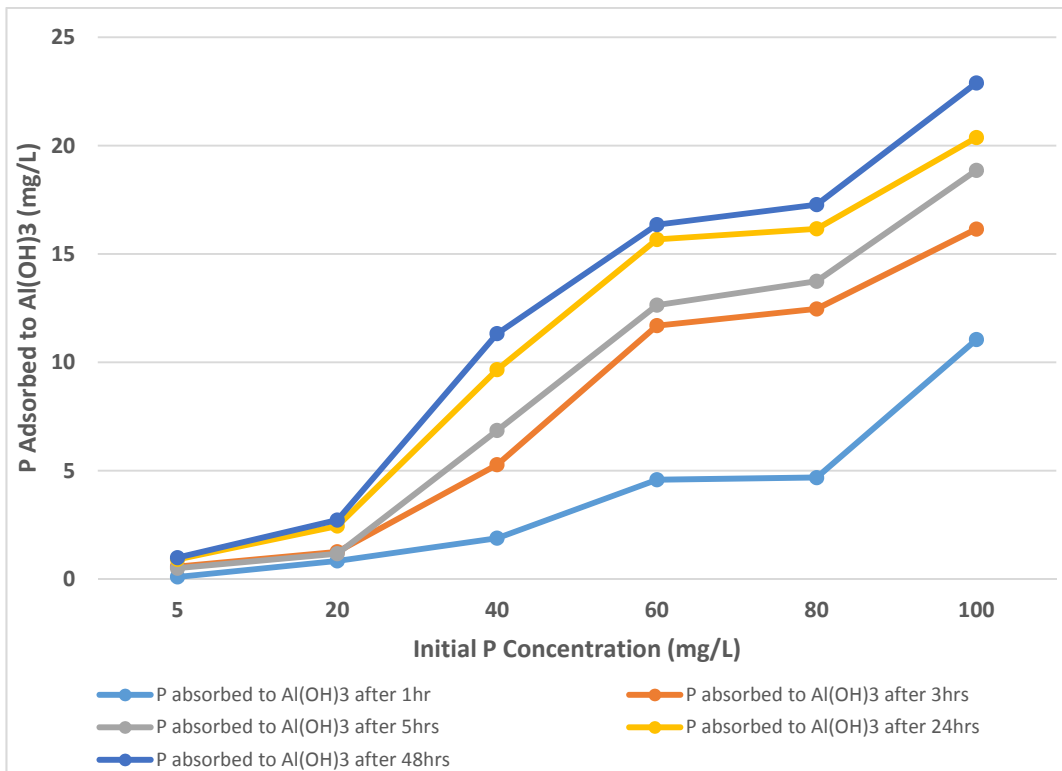


Fig. C7.2 (c): Phosphate Adsorption by Al(OH)₃ with Mixing Speed of 200 RPM

Figures C7.2 (a)-(c) show that the amount of phosphate adsorbed on to aluminium hydroxide increased with time and that increasing stirring rate generally resulted in increased phosphate uptake: the initial phosphate uptake with a speed of 60 rpm was quite low compared with the other two cases (Fig. C7.2 (a)). The highest initial uptake of phosphate by aluminium hydroxide occurred at 200 rpm. The amount of phosphate adsorbed after a day was quite high at 80 rpm. When compared with Fig. C7.2 (a) and (b), there was a slight increase of the phosphorus removal with the increase of the mixing speed. The reason for this could be the formation of new surfaces for the adsorption of more phosphate by breaking down the aluminium hydroxide particles due to the intense mixing speed. However, in a somewhat contradictory result, the phosphate uptake by aluminium hydroxide with a high mixing speed of 200 rpm at 48 hours was less than at 80 rpm as shown in Fig. C7.2 (b) and (c). This may be due to the aging of aluminium hydroxide as the first two experiments were done with fresh $\text{Al}(\text{OH})_3$ and the latter was done with five days aged $\text{Al}(\text{OH})_3$.

There are several reports on the impact of aging on the capacity of $\text{Al}(\text{OH})_3$ to adsorb phosphate (Georgantas & Grigoropoulou, 2007; Sims & Ellis, 1983) There is general agreement amongst these studies that as aluminium hydroxide experiences change with ageing, its phosphorus removal capability decreases.

In two studies conducted by Kabayama et al. in 2003 and 2005, it was shown that phosphate adsorption onto aluminium compounds was affected by ion exchange with the hydroxyl groups on the surface of the compound, i.e. aluminium hydroxide in this study (Kabayama et al., 2005; Kabayama et al., 2003).

Phosphorus adsorption by aluminium hydroxide is based on the non-structural OH^- ion exchange with phosphate ions and hence the decrease of OH^- ions due to the ageing of aluminium hydroxide lead to a significant drop of phosphate adsorption (Georgantas & Grigoropoulou, 2007).

7.4.1 Isotherms Modelling of Phosphate Adsorption Mechanism

Modified Freundlich and Langmuir isotherms were used to model the phosphate adsorption mechanism on aluminium hydroxide. The Modified Freundlich isotherm reflects heterogeneous adsorption on surface sites and the Langmuir isotherm reflects a homogeneous monolayer adsorption on surface sites. Figures C7.3 and C7.4

illustrate the plotted Modified Freundlich and Langmuir isotherms for the above experiments for the adsorption of aluminium hydroxide.

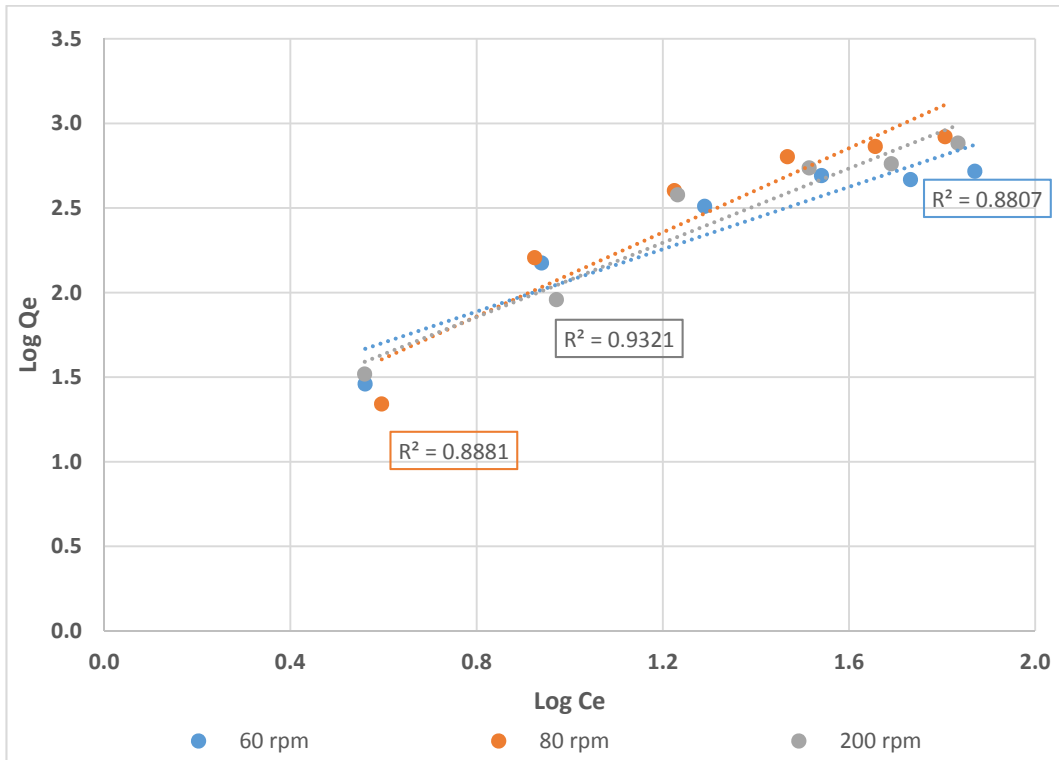


Fig. C7.3: Modified Freundlich Isotherm for 60, 80 and 200 RPMs

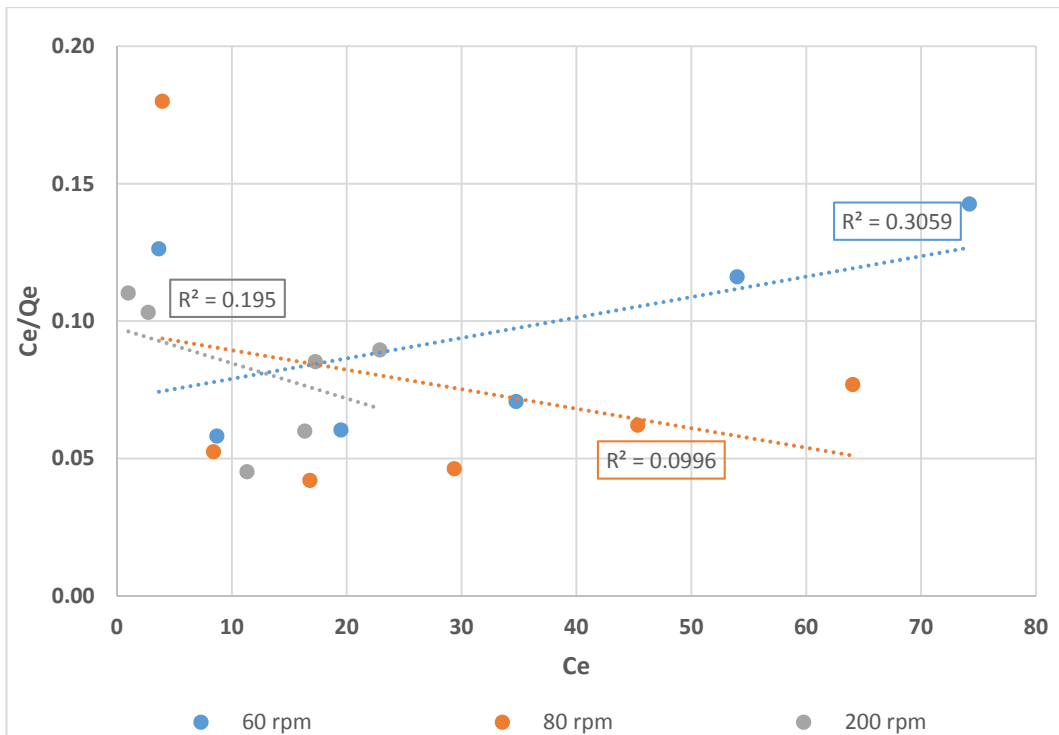


Fig. C7.4: Langmuir Isotherm for 60, 80 and 200 RPMs

Where Q_e is the amount of phosphate adsorbed per unit weight of sorbent at equilibrium (kgkg^{-1}) and C_e is the equilibrium concentration in solution (kgm^{-3}) (Georgantas & Grigoropoulou, 2007).

The modified Freundlich isotherm provided the best fit for the all experimental results with a heterogeneous adsorption, in agreement with previous studies (Georgantas, Matsis, & Grigoropoulou, 2006). As stated by Georgantas et al., the adsorption of phosphate onto aluminium hydroxide is best described by the Freundlich isotherm compared to Langmuir isotherm (Georgantas & Grigoropoulou, 2007). Kuroda and Tanada et al. also reported that phosphate adsorption onto many adsorbents fitted with the Freundlich equation (Kuroda, 1987; Tanada et al., 2003)

The adsorption of phosphate ions onto the surface of aluminium hydroxide occurs via the displacement of OH^- ions from the surface of $\text{Al}(\text{OH})_3$ (Guan, Liu, Chen, & Shang, 2005). When the phosphate attraction with aluminium hydroxide is quite strong, it removes the surface OH^- ions and phosphate will be adsorbed onto the surface. With high phosphate concentrations, there is a tendency to break the large particles into smaller particles by aluminium hydroxide-phosphate attraction and creates new surfaces for the adsorption (Hsu & Rennie, 1962). According to Van Riemsdijk et al. the sorption of phosphate on $\text{Al}(\text{OH})_3$ is related to the concentration of phosphate. The amount of sorption is negligible at low phosphate concentrations and short reaction times (Van Riemsdijk & Lyklema, 1980a). This is in agreement with Goldshmid et al. (1988) and Boisvert et al. (1997) who reported that if the phosphate concentration is low, i.e. 1 – 5 mg/L, then the main phosphate removal is followed by the adsorption of phosphate ions onto the surface of formed aluminium hydroxide (Boisvert et al., 1997; Goldshmid & Rubin, 1988).

7.5 Conclusion

The results of the study confirmed that phosphate adsorption continued over at least 48 hours, particularly in the case of freshly formed $\text{Al}(\text{OH})_3$, the amount of phosphate adsorbed on to aluminium hydroxide was increased. The highest initial uptake of phosphate by aluminium hydroxide was occurred with the speed of 200 rpm and the lowest was with the speed of 60 rpm. When considering the 48 hrs period, the mixing speed does not have much effect on the phosphorus removal process. There was a

slight increase of the phosphorus removal with the increase of the mixing speed from 60 rpm to 80 rpm. But, again the maximum phosphorus removal with the mixing speed of 200 rpm was less than that of 80 rpm. This may be due to the aging of aluminium hydroxide as the first two experiments were done with fresh $\text{Al}(\text{OH})_3$ and the latter was done with aged $\text{Al}(\text{OH})_3$. As aluminium hydroxide experiences change with ageing, its phosphorus removal capability is known to decrease.

When considering the result in Fig. C5.4 in Chapter 5, the experiment ran for a total period of 40 minutes and the speed changed from 200 rpm to 20 rpm after 20 minutes of the commencement of the experiment. More phosphorus removal than the stoichiometric level occurred between 8 and 18 minutes in the experiment. That was within the rapid mixing zone (with the speed of 200 rpm). As the highest initial uptake of phosphorus occurred with the 200 rpm speed in the experiments with aluminium hydroxide, the more phosphorus removal in the result in Fig. C5.4 in Chapter 5 can be considered as the phosphate adsorption by already formed aluminium hydroxide in the solution other than the phosphate precipitation with aluminium sulphate. In addition to that, this intense mixing may break particles creating more surfaces for adsorption of phosphorus.

Also, the modified Freundlich isotherm best fits for the all experimental results with a heterogeneous adsorption, which is in agreement with other published studies and with the known mechanism of removal of phosphate by $\text{Al}(\text{OH})_3$ that is, the exchange of phosphate with hydroxyl groups to form Al-hydroxy-phosphate-based minerals.

CHAPTER 8

Conclusions and Recommendations

8.1 Conclusions

In this study, the effect of different parameters for the phosphorus removal in municipal wastewater was investigated. Evaluation of optimum conditions of these parameters are of great importance for the efficient and economical operation of wastewater treatment plants. A large number of researches have been done in the past on phosphorus removal and this thesis added another literature by studying the effects of these parameters including pH, alum dosage, alum dosing regime, dissolved organic carbon (DOC) and the phosphorus removal by aluminium hydroxide.

Most of the findings of this investigation complement those of earlier studies and contribute additional evidence.

For example, studies in Chapter 3 (Effect of Initial pH) confirmed literature findings that the maximum phosphorus removal occurred at pH 6.5. Secondly, the study shows that there is an optimum dosage of coagulant for the phosphorus removal and further addition of coagulants is counterproductive as it may shift the pH of wastewater from its optimum coagulation zone.

Very little was found in the literature on the effect of varying the alum dosing regime and one of the more significant findings to emerge from this study is that it has been found that the phosphorus removal with incremental alum addition without pH control was much higher than the normal single dosing of alum. Controlling the pH of the synthetic wastewater with incremental alum dosing removed more phosphorus compared to real wastewater.

In addition, it was found that different forms of organic carbon had different effects on phosphate removal by alum (Chapter 6). For example, tannic acid and starch hindered phosphate removal while phthalate and humic acid had no effect or even appeared to aid phosphate removal. This demonstrated that knowledge of the organic carbon types (functional groups) in wastewater and how this affects alum reactivity with phosphate in wastewater is critical to optimisation of alum treatment. In a practical sense, these findings on the importance of organic carbon suggest that alum may be more effective

at some points in the treatment plant, depending on the concentration and nature of organic matter presents at each location.

These findings of this study have a number of important implications for practice in wastewater treatment plants and this information can be used by them for optimising their operating conditions while minimising the operational costs such as minimising the costs for the chemical coagulants with the use of optimum coagulant doses rather than adding them unnecessarily.

8.2 Recommendations for Future Research

It is recommended that future research be undertaken in the following areas:

- The scope of this study was limited to enhance the phosphorus removal efficiency in municipal wastewater using aluminium sulphate. There are many other chemical coagulants used in wastewater treatment plants for the phosphorus removal. Hence, it is recommended that further research should be undertaken to explore how the other chemical coagulants affect phosphorus removal efficiency.
- In this study, only few factors affecting for the phosphorus removal efficiency in municipal wastewater has been considered and there are few other factors which affects for this process. Therefore, more research on the other factors including the temperature, effect of suspended solids, etc. influencing the phosphorus removal efficiency is highly recommended.
- Further investigation and experimentation on the effect of alum dosing regime (single dose or incremental dose) is strongly recommended as there is very little evidence on that on current literature. This would be worthwhile to validate the results of the current study.
- Further experimental investigations are needed to estimate the Cost and benefits analysis of the use of aluminium sulphate for the phosphorus removal in municipal wastewater with the above found conditions.
- Further information is required on the impact of organic matter on phosphate removal using alum, particularly on the effects of different types of organic carbon (different functional groups)

- More information is needed on the chemical mechanisms of phosphate removal under different conditions. Better understanding of the fundamental chemistry in this area could help to tailor treatment regimes to enable phosphate removal to lower final concentrations

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