

**FACTORS AFFECTING PHOSPHORUS RELEASE FROM WASTE
ACTIVATED SLUDGE**

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BY

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Abstract

Waste activated sludge (WAS) derived from municipal wastewater treatment plant contains relatively high amounts of P and is a potential source of recoverable P. Phosphorus release into the aqueous phase is an important step for its recovery. The thesis investigated key questions related to engineering systems for P release from WAS using batch experiments.

Aqueous P forms measured were Dissolved Reactive (Ortho) P (DRP) and Total Dissolved P (TDP). An extraction protocol was used to find five solid P fractions: (1) Total P (TP), (2) Inorganic P (IP), (3) Organic P (OP), (4) Non-Apatite Inorganic P (NAIP) and (5) Apatite P (AP). In all cases, the phosphate concentration of extracted solutions was determined spectrophotometrically using a HACH DR/2500 spectrophotometer.

Samples were placed in air-tight, 20 litre plastic containers, transported to the laboratory, and analysed for initial parameters of WAS within one hour of collection. In the same day, any treatments (e.g., pH adjustment with acids and base, incubation different temperatures and maintaining aerobic/anaerobic condition) were applied and the P release tests started.

Five replicate reactors were run for 11 days to test the reliability of results. The coefficient of variation (standard deviation/mean) of the DRP and TDP of the five replicates over the eight sampling days averaged approximately 5%. The solid fractionation was conducted for four replicates of biosolids. The coefficient of variations were all 10% or less, showing high replicability.

P release was found to be increased by use of (1) anaerobic rather than aerobic conditions, (2) temperature of 35 °C rather than ambient temperature, and (3) a pH of 4 to 6 rather than unmodified pH of near 7. pH depression to 6 was sufficient to release NAIP. A lower pH of 4 released effectively all AP. Organic P was found to be more difficult to release from WAS under the range of conditions tested.

P release under favourable conditions (pH4, 35 °C and anaerobic) was studied for WAS from three treatment plants with different designs: activated sludge (AS), carousel biological nutrient removal (CBNR), and sequencing batch nutrient removal (SBNR). The varying levels of P release from sludge solids can be explained by differences in the P fractionation of the WAS, which in turn arise from differences between wastewater treatment processes. Under favourable conditions, total P release from the AS, CBNR, and SBNR sludge solids were 52, 75 and 48 %, respectively, in 21 days, with the CBNR and SBNR releases the most rapid.

It was observed that both inorganic and organic acids effectively released phosphorus from WAS samples. No evidence was found that acetic acid is better than hydrochloric acid for P release. Visual identification of poly-P in staining test results indicated that poly-P was present and not greatly affected by the treatments tested. Testing with glutaraldehyde indicated that P release was not from cell lysis and indicated a biological process was involved in P release.

A series of preliminary tests considered broader issues related to any future development of P release reactors. There was no large adverse effect of using hydrochloric acid on settleability and filterability. COD increase was observed after acid addition, which could improve subsequent gas production. Zn was the only trace metal found to increase significantly during P release treatment. Fe, Ca, Mg also increased, which could have implications for P recovery depending on what process is used.

The findings of this thesis will benefit future work to design reactors to optimise P release from WAS, and provide increased knowledge for the further development of P recovery technology.

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Abbreviations and acronyms

AD = Anaerobic Digestion

ADS = Anaerobic Digested Sludge

AP = Apatite Phosphorus

AS = Standard Activated Sludge Design Treatment Plant

BNR = Biological Nutrients Removal

CBNR = Carousel Design Biological Nutrients Removal Treatment Plant

DOP = Dissolved Organic Phosphorus

DRP = Dissolved Reactive Phosphorus

TDP = Total Dissolved Phosphorus

EBPR = Enhanced Biological Phosphorus Removal

EDCs = Endocrine Disrupting Chemicals

g = Gram

IP = Inorganic Phosphorus

KG = Kilograms

L = Litre

M = Molarity

mg = Milligrams

mL = Millilitre

mmol/L = Millimoles per litre

MT= Metric tones

NAIP = Non Apatite Inorganic Phosphorus

SBNR = Sequencing Batch Reactor Design Biological Nutrients Removal Treatment Plant

TN = Total Nitrogen

TP = Total Phosphorus

VFA = Volatile Fatty Acids

WAS = Waste Activated Sludge

WWTP = Wastewater Treatment Plant

µm = Micrometre

Research outputs

Journal papers

Pokhrel, S. P., Milke, M. W., Bello-Mendoza, R., Buitrón, G., & Thiele, J. (2018). Use of solid phosphorus fractionation data to evaluate phosphorus release from waste activated sludge. *Waste Management*, 76, 90-97. doi:10.1016/j.wasman.2018.03.008

Peer-reviewed conference proceedings

Pokhrel, S. P., Milke, M. W., & Bello-Mendoza, R. (2018) Variation in phosphorus release from different types of waste activated sludge. IWA Specialist Conference on Sludge Management in Circular Economy, Rome, Italy 23-25 May 2018. In proceedings: 172-174. (Conference-Published)

Conference abstracts (oral and poster presentation)

Pokhrel, S. P., Milke, M. W., & Bello-Mendoza, R. (2017) Fractionation of phosphorus during anaerobic release from sludge at a normal and nutrient removal facility. The 14th IWA Leading Edge Conference on Water and Waste Water Technology. 29 May-2 June 2017, Florianopolis, Brazil. (Conference Poster Presentation)

Pokhrel, S. P., Milke, M. W., & Bello-Mendoza, R. (2017) Phosphorus recovery from waste activated sludge. The 2nd international conference on biological waste as resource. 25-28 May 2017-Z Core, the Hong Kong Polytech University, Hog Kong. (Conference keynote presentation)

Pokhrel, S. P., Milke, M. W., & Bello-Mendoza, R. (2016) Differences in phosphorus release from waste activated sludges. *Water New Zealand Annual*

Conference 19-21 October 2016, Rotorua, New Zealand. (Conference Poster Presentation)

Pokhrel, S. P. (2016) Phosphorus release from waste activated sludge under different pH, temperature and anaerobic conditions. 2016 Waterways Postgraduate Student Conference November 15, 2016 Lincoln University, Christchurch, New Zealand. (Conference Oral Presentation)

Pokhrel, S. P. (2018) Phosphorus release from activated sludge and effect of different acids. 2016 Waterways Postgraduate Student Conference November 20, 2018 Lincoln University, Christchurch, New Zealand. (Conference Oral Presentation)

Chapter One: Introduction

Agriculture is the backbone of the New Zealand economy but is an activity that relies heavily on the use of large quantities of nutrients, mainly nitrogen and phosphorus (P). Phosphorus fertiliser is mostly derived from mineral phosphate rock. New Zealand has very substantial P reserves, but they are in ocean sediments on the Chatham Rise (Cullen, 1980). There are active plans to mine this resource if or when the price of phosphorus fertiliser rises. Thus, the New Zealand food system is vulnerable to the volatility of international phosphate rock and fertiliser markets. The New Zealand government has set a target to double the country's agricultural export value by 2025 (MPI, 2013). Achieving this goal will require an increase in P inputs from fertiliser. Given the increasing demand for food and the limited reserves of phosphate rock, it is envisaged that the consumption will increase, and the availability of P will diminish over the following decades (Shu et al., 2006).

Agricultural systems need the application of fertilisers containing P, nitrogen and potassium on farming fields in order to sustain crop yields. However, the modern system is dependent on P derived from phosphate rock, which is a non-renewable resource, and it has been estimated that current global reserves may be depleted in 50 – 100 years (Steen, 1998; Smil, 2000; Gunther, 2005). The global peak in P production is predicted to occur around 2035 (Cordell et al., 2009). Therefore, alternative methods should be developed to recycle P from P-rich residuals (Rittmann et al., 2011).

Supply and demand mean that the question is not “are there enough P reserves?”, but “how high will the cost become before new reserves become economical to extract?” This applies to extraction of P from waste as well. Phosphorus recovery from waste could provide significant assistance towards meeting the government target, reducing the dependency on the

international market for P fertiliser, and reducing environmental pollution such as eutrophication.

There is a need to find ways to recover and reuse P throughout the food production and consumption system. Recovering P from domestic and agro/industrial waste offers great potential. For example, it is estimated that 3 Mt of P are lost annually as human waste. Theoretically, 15% – 20% of world demand for phosphate rock could be substituted by recovering P from domestic waste streams alone (Cordell et al., 2009). However, research is still needed to maximize P release and its recovery from P-rich waste.

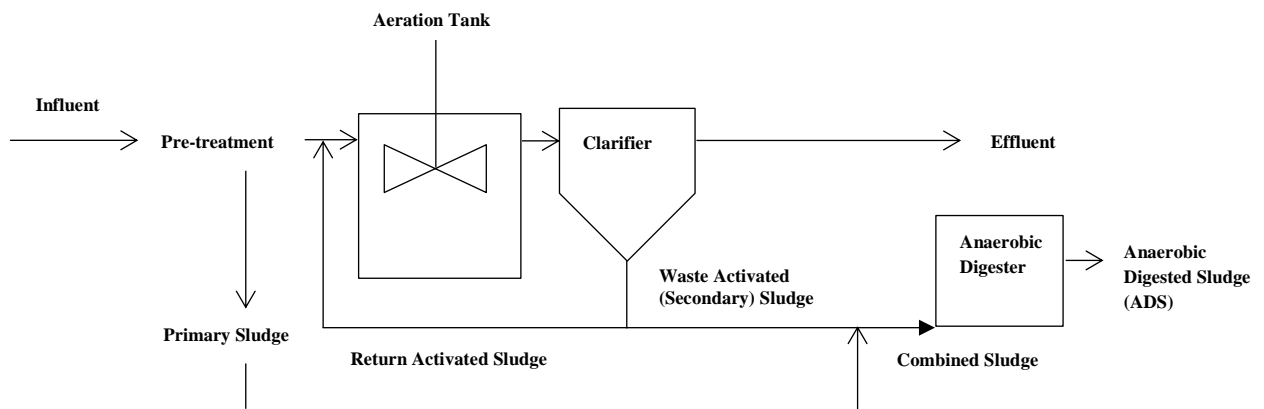


Figure 1.1: Different types of sludges within treatment processes

Wastewater treatment plants (WWTPs) generate large amounts of various types of sludges. Figure 1.1 provides a representation of the various sludges generated by a typical WWTP. The treatment system aims partially to remove P from sewage before it is discarded in the environment. Significant amounts of P are available in the waste activated sludge (WAS) from a WWTP relative to other waste materials (Table 1.1 shows the P concentration of different wastes and intermediates). Anaerobic digested sludge (ADS) is often used as a fertiliser on farmland. However, the main challenge of using this valuable resource as a fertiliser on farmland can be the content of other hazardous substances such as chromium, nickel, and polyaromatic hydrocarbons. If permissible values of the above hazardous substances are exceeded, then it cannot be used on farmland.

Table 1.1: Typical phosphorus concentrations of different waste and intermediates (Source: Cordell et al., 2011)

Organic material	P (% P by weight)
Human urine	0.02 – 0.07
Human faeces	0.52
Human excreta	0.35
Activated sludge	1.4
Anaerobic digested sludge	0.48 – 0.77
Struvite	13 – 14
Cow dung	0.04
Poultry manure	1.27
Farm Yard Manure (FYM)	0.07 – 0.88
Rural organic matter	0.09
Vermicompost	0.65
Crop residues	0.04 – 0.33
Urban composted material	0.44
Oil cake (by-product from oilseed processing)	0.39 – 1.27
Meat meal	1.09
Bone meal	8.73 – 10.91

Awareness of sewage sludge contamination by persistent organic compounds has cast doubt on the sustainability of using ADS as fertiliser in agricultural field (Harrison et al., 2006).

Endocrine disrupting chemicals (EDCs) are among the organic contaminants that can bioaccumulate in the food chain (Sartorius & von Horn, 2010). Therefore, in some countries (Switzerland, Netherlands & Germany), the agricultural use of ADS has been banned.

Extraction of P from WWTP sludges could provide the possibility of efficient P use for fertiliser and other purposes without the problems of land application of sludges.

Process efficiencies, costs and benefits for the recovery of P, have been the focus of many past studies (Morse et al., 1998; Sørensen et al., 2015; Egle et al., 2016). The findings of various research indicates that P can be recovered from ADS or recovered from the ADS ash, but the cost and environmental impact of these methods has been questioned (Cornel and Schaum, 2009).

Sørensen et al., 2015 analyse the recovery of phosphorus from waste activated sludge instead of ADS, and the opportunities regarding its reuse. The assessment showed that phosphorus recovery from WAS can be done with comparable or less environmental effect than applying the sludge directly to agricultural fields or production of fertilizer from primary resources. Recovery of P from WAS is less well studied than recovery from ADS.

There are many approaches including chemical precipitation, sorption, ion exchange, biological phosphorus removal, and crystallisation to recover P from the aqueous phase of treated sludges (Cordell et al., 2011). All these approaches are more efficient when more P can be released from sludge solids to the liquid phase.

If a better process can be designed for P release then the WWTP shown in Figure 1.1 can be modified as in Figure 1.2. This could allow for better P recovery.

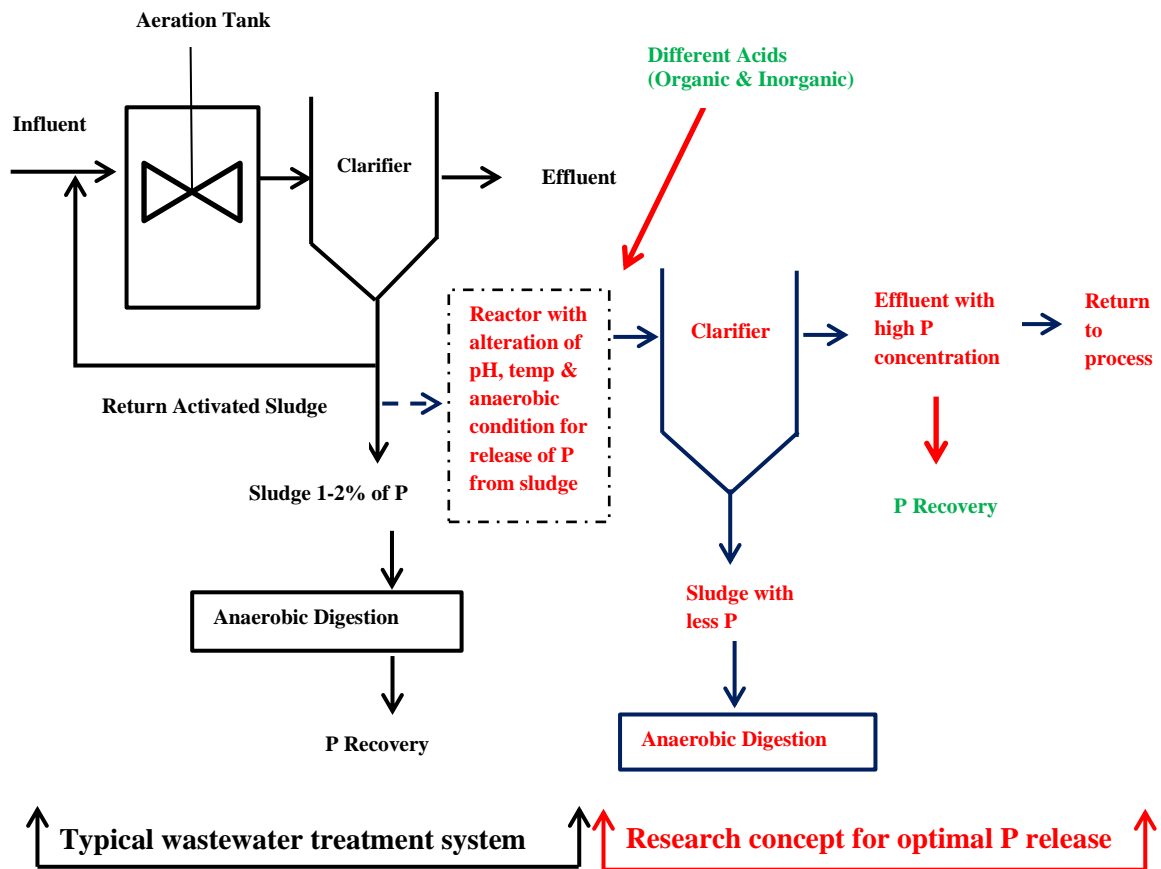


Figure 1.2: Research concept for maximum optimal P release

The focus of this research is on the conditions that can increase the release of P during simple treatments of WAS. The aim of this research project is to identify (1) factors influencing P release and (2) optimal operating strategies to maximise the release of P from WAS.

Although the focus of this study was on municipal WAS, the results would be relevant to wastewater from manufacturing industries such as the detergents, fertiliser, dairy, winery, textile, and beverage industries.

Chapter Two: Literature Review

This chapter provides background relevant to the principal focus of this research on conversion of WAS P from solid to aqueous. The objective is to help engineers design P release reactors in the future. The key questions faced by designers will relate to process control conditions: pH, temperature, redox potential, addition of acids, residence time. The existing literature includes research that has studied one specific aspect of this problem but often with different sludges making it difficult to compare results between studies.

This chapter begins by defining terms related to the types of sludge and the forms of phosphorus in sludge. This allows for some comparison between previous studies. The chapter then considers the major factors affecting P release: pH, temperature, and redox potential. The chapter finishes with a short examination of wastewater treatment processes and their characteristics that help to understand the problem of design of P release reactors. This review helps to figure out the research gaps that need further study in order to maximise P release.

2.1 Types of sludge

Wastewater treatment processes produce different types of sludges due to various stages of the treatment system. Figure 1.1 shows different sludge types within a typical treatment system (Primary Sludge, Return Activated Sludge, Waste Activated Sludge, Combined Sludge and Anaerobic Digested Sludge). The phosphorus availability varies between different sludge types (Xie et al. 2011), and so clear definitions of sludges are needed to interpret past results.

2.2 Forms of phosphorus in sludge

In a typical WAS, much of the P is either bound biologically or exists as solid inorganic P (IP), while dissolved or aqueous P comprises only a small percent of the total P (TP) (Ruban

et al., 1999). Figure 2.1 shows different forms of P available in WAS as considered in this study.

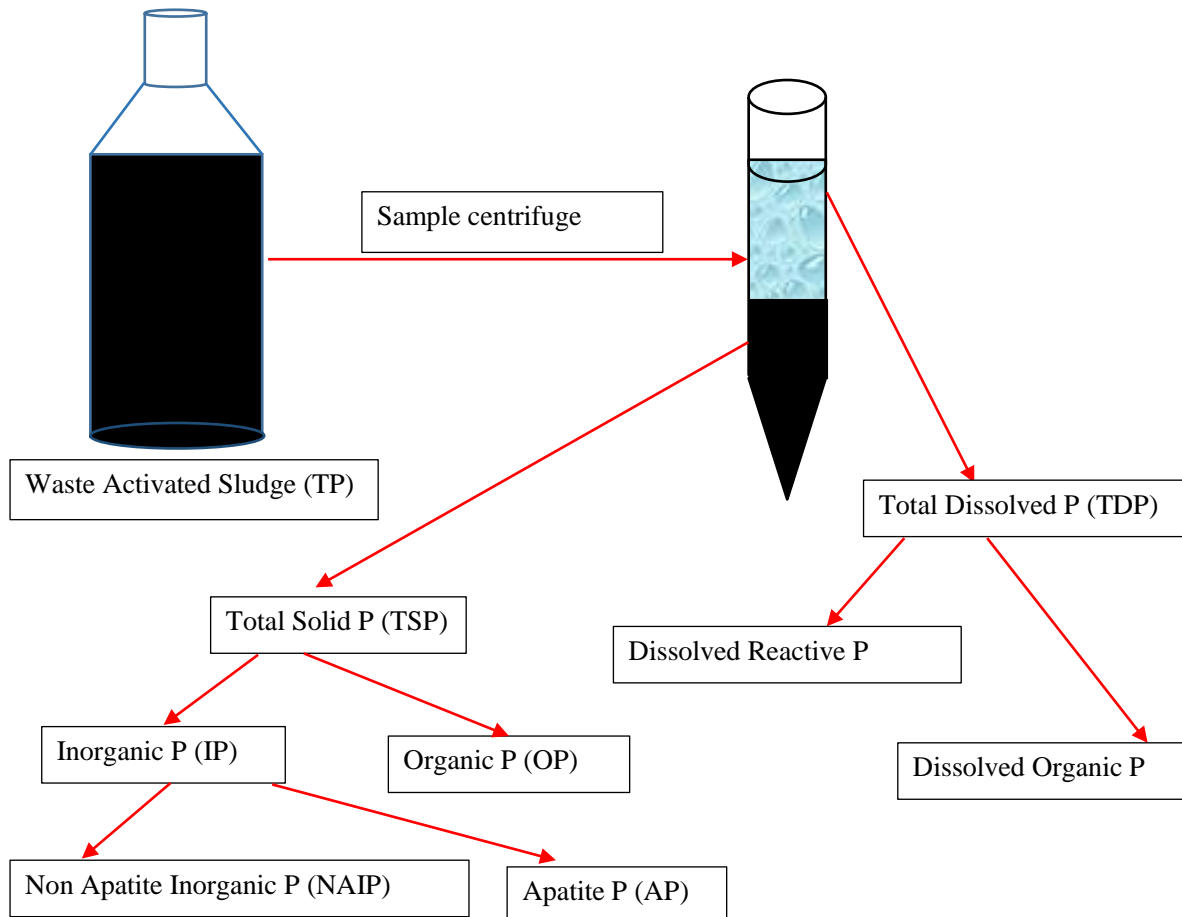


Figure 2.1: Different forms of phosphorus available in WAS

The aqueous P is mostly in the orthophosphate species (i.e. dissolved reactive P (DRP)), though there can be significant amounts of dissolved organic P (DOP) made up of a variety of low molecular weight compounds of biological origin.

Organic P (OP) in WAS solids is a complex fraction reflecting the many uses of P in bacteria-energy cycling (adenosine triphosphate/adenosine diphosphate) and nucleic acids.

One inorganic solid form of P found is in solid mineral compounds generally referred to as apatite P or Ca-bound P (herein termed AP) (Ruban et al., 1999), but which can also include Mg and Fe forms. Another inorganic solid form of P can be either loosely bound by electrostatic forces, or more tightly bound to exchange sites on minerals such as oxides and hydroxides of Al, Fe, and Mn, or sorbed on cells (Ruttenberg, 1992). A final form of solid P is biologically stored inside cells as polyphosphates (poly-P). This P form can be converted readily into soluble orthophosphate forms either within cells or after cell death. This form is more similar to sorbed-P than to P incorporated into complex organic molecules, and it is difficult to analyse for this separate form of solid P, though methods exist (Crocetti et al., 2000; Hung et al., 2002; Hupfer et al., 2008). When considering how the forms of P might vary in their potential for recovery, it can be useful to consider biological polyphosphates as similar in form to sorbed P, rather than to OP (Uhlmann et al., 1990; Kuroda et al., 2002).

The combination of chemically sorbed P and poly-P is referred to herein as non-apatite inorganic phosphorus (NAIP), while recognising that it includes “organic” P in the sense that the P is coming from P compounds formed by microbes.

The different fractions of P can be represented by equations 1, 2, 3 and 4:

$$\text{TP} = \text{TSP} + \text{TDP} \quad \text{Equation 1}$$

$$\text{TDP} = \text{DRP} + \text{DOP} \quad \text{Equation 2}$$

$$\text{TSP} = \text{IP} + \text{OP} \quad \text{Equation 3}$$

$$\text{IP} = \text{NAIP} + \text{AP} \quad \text{Equation 4}$$

In general, NAIP (including polyphosphates) is the most common form of P in WAS and, combined with AP, they account for two-thirds or more of total solid P.

The absolute and relative amounts of the forms of P can also vary with both the waste and water sources. For example, some WWTPs serve communities with calcium-rich waters, and this would lead to more solid P in the calcium phosphate form. In contrast, some WWTPs receive wastes from industrial facilities that discharge high concentrations of soil minerals (e.g. ferric hydroxides) and, in that case, there would be strong potential to sorb phosphates. Finally, some industries may discharge organic-rich food waste which would lead to high total P in the WWTP influent.

A study conducted by Medeiros et al. (2005) examined P fractions in sewage sludge collected from urban wastewater treatment plants. They observed differences in total P content between plants of 23.1 ± 0.2 mg/g and 26.1 ± 0.3 mg/g. In addition, they also found little variation in IP (20.0 ± 0.3 mg/g and 20.2 ± 0.8 mg/g) and more in OP (2.3 ± 0.1 mg/g and 5.8 ± 0.3 mg/g) respectively. The differences in the amount and form of P in sludge make it difficult to compare results between studies.

2.3 Phosphorus release from WAS

Phosphorus release from WAS is a complex process and depends on: (1) physical conditions, e.g. temperature; (2) chemical factors (acid, alkaline, oxidation-reduction potential effects, concentrations of other elements such as Fe); and (3) biological processes (such as uptake, storage, growth, death and biological P release). Consequently, any investigation into P release from WAS should address an understanding of the forms of P and the environmental processes that affect the forms.

2.3.1 Effect of pH

Past research on WAS indicates that pH is one of the dominant factors in P release as it affects sorption-adsorption, precipitation-solubilisation (through its control over the concentration of available iron, aluminium and calcium) and oxidation-reduction reactions (through its effect on iron chemistry) (Chen et al., 2007; Xu et al., 2015; Latif et al., 2015). pH also changes biological reactions because it can stimulate or inhibit specific micro-organisms to uptake or release P.

There are various studies that have examined P release from WAS under extreme pH <4 to pH>9 conditions. These studies are less relevant to this research because any practical reactor for P release would be very expensive to run for extreme pH conditions. The results from these studies are more difficult to compare to results from this study because the extreme pH will tend to cause severe effects on biological communities in WAS not seen at more neutral pH. Still, the results at extreme pH can help understand the general effect of pH. pH-dependent P release from WAS conducted by Xu et al. (2015) shows that the amount of P release significantly depends on pH, with the greatest P at a pH of 2 and the lowest at a pH of 8. A range of pH 2 – pH 11 was applied. The phosphate concentrations in the supernatant was 278.2 mg/L, 160.8 mg/L, 107.0 mg/L and 137.0 mg/L under pH 2, pH 5, pH 8 and pH 11. The WAS sample was obtained from a WWTP with an anaerobic/anoxic/aerobic (A/A/O) process and the WAS had a water content of 97.6%. Stark et al. (2006) conducted a study on P release from different sludge (collected from an incineration plant in central part of Sweden and dried sludge from a WWTP located in Stockholm region, Sweden) using strong acids and bases. They adjusted pH by acid (1 M HCl) and base (1 M NaOH). The phosphate leaching from ash was 85%, 75%, 70% and 55% at pH of 0.3, 1.5, 14 and 13.1 respectively. Similarly,

the phosphate leaching from dried sludge was 80%, 70% and 50% at pH of 0.3, 1.5 and 13.1 respectively. They found that the use of acid (pH < 2) gave a higher P release for all samples.

Research has shown increased P release for pH of 4-6 when compared to pH of 6-9. A past fermentation study on WAS done by Chen et al. (2007) shows that P release and volatile fatty acid production varies over the range of pH 4 – pH 11. Fermentation of WAS resulted in significant increases in soluble P. The levels of P in the mixed liquor appeared to depend on sludge retention time and pH values. The concentrations of P are highest at acidic pH (pH 4 and pH 5). The WAS sample was obtained from the secondary sedimentation tank of a municipal WWTP. Wu et al. (2009) observed 1.92 (48 mg-P soluble L⁻¹) and 1.48 (37 mg-P soluble L⁻¹) times higher soluble P concentration at pH 5 and pH 6 respectively, compared to pH between 7 and 10 (25 mg-P soluble L⁻¹) after 9 days of batch fermentation of primary sludge. Bi et al. (2012) have reported 1.26 times higher P release (213 mg-P soluble L⁻¹) at pH 5 compared to pH 10 (168 mg-P soluble L⁻¹) from WAS sample.

One study conducted by Latif et al. (2015) was on a mixture of WAS and ADS (28 mL and 72 mL) having initial pH 6.5, soluble P 215 mg/L and total P 1060 ± 90 mg/L. The results indicate that during the biochemical methane potential test, the highest soluble P of 799 mg/L was observed at pH 5.25 (75% of the TP), while at neutral pH (pH 7 – pH 7.7) it was around 200 mg/L. The WAS and ADS sample were collected from a sewage treatment plant operated by Queensland Urban Utilities, Brisbane.

Researchers have also studied the mechanisms for the release of P at pH of 4-6. An analysis of nutrient solubilisation and availability following anaerobic digestion by Mehta and Batstone (2013) illustrated that P, Ca and Mg are released from organic matter during anaerobic digestion. The impact of pH on the nutrient release was assessed by adding HCl (8%) to the digestate. The pH of the untreated digestate was 7.6. HCl was added every 120

minutes to the well-stirred beaker; it gave sufficient time to dissolve any inorganic precipitates in the digestate. No significant release of P and Ca was observed at a pH of 5.5. Below pH 5.5, the soluble concentration of P, Ca and Mg increased with a rise in acid concentration. The release of nutrients levelled off at pH 4.5, with no significant release of nutrients with the further addition of HCl. The authors conclude that P is released from solid sludge at a pH of 5.5, but then remains bound (or precipitated) as solid inorganic compounds, which are re-dissolved at low pH of 4. The research at $\text{pH} < 4$ shows that some further release of P can occur at lower pH, but most P release happens by a pH of 4.

There is not a good understanding of how important biological and chemical processes are in the pH effect. For example, previous research has not attempted studies where inoculum is applied to tests to check on biological viability. Instead, previous research has merely adjusted pH and monitored phosphorus release. Further focused research is needed to clarify the extent that P release after pH adjustment is a biological process related to fitness of microbes, or a chemical reaction that occurs with biological cells.

Even without further study of the issue of biological or chemical mechanisms, there is a lack of knowledge about the forms of P released at various levels of pH, about how the time for P release varies with pH, and about how the type of acid affects P release.

2.3.2 Effect of temperature

Temperature, like pH, also affects the physical, chemical and biological processes related to P release. Generally, higher temperature speeds up all reactions, uptake and release. In general, increasing temperature results in a greater release of P (Kuroda et al., 2002). Growth and activity of biological microbes are affected by temperature. As temperature increases, the activity of the living organism is enhanced. This can lead to the removal of dissolved P into biomass.

Research conducted by Yuan et al. (2011) on volatile fatty acid generation from WAS examined the effect of temperature and mixing. Three temperatures were studied: 4 °C, 14 °C and 24.6 °C. The highest P and nitrogen release was achieved in the mixed reactor at 24.6 °C with 14 mg/g and 64 mg/g VSS, respectively. The release of both P and nitrogen from the reactors without mixing was significantly lower than that from the mixed reactors. The WAS used in this study originated from a non-enhance biological phosphorus removal (EBPR) plant and thus had typical low mass P concentrations of 1.2% – 1.5% P in TSS and typical nitrogen content of 8% total nitrogen (TN), by weight.

Some research indicates that higher temperature might not lead to greater P during WAS treatment. Bolzonella et al. (2012) found soluble P concentrations in the digested effluent to be similar at both mesophilic and thermophilic temperatures during a pilot scale operation, suggesting a minimal influence of temperature on P release. The reason is that struvite can form to limit P concentrations. The solubility of struvite increases slightly with temperature until approximately 30 °C, and then decreases slightly with further increases in temperature (Bhuiyan et al., 2007), while hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) solubility increases slightly with temperatures greater than 30 °C (Prakash et al., 2006). The effect of temperature on TDP concentrations in treated WAS could depend on the concentration of magnesium in the aqueous phase, and on the combined effect of pH and temperature.

Research by Ahmad and Idris (2014) shows that P release at high temperatures tends to decrease with the increase in the unadjusted pH of the sample solution. The maximum release of P from sediment to water was observed at pH 2 to pH 4 and at temperature of 175 °C. The high temperature is not typical for WWTP and so we cannot say what the combined effect of pH and temperature is. There is a research gap for the combined effect of pH and temperature on P release from WAS under controlled conditions relevant to wastewater treatment.

2.3.3 Effect of redox potential

Phosphorus-accumulating micro-organisms (PAOs) uptake P under aerobic and anoxic conditions and store as polyphosphates, and subsequently in an anaerobic condition release stored P as a source of energy (Van Starckenburg et al., 1993). This is one important example of how redox potential can affect P release.

Research conducted by Bi et al. (2013) examined P release mechanism during digestion of EBPR sludge under anaerobic, anoxic and aerobic conditions. The result concluded that more P had been released under anaerobic condition while this P release was suppressed under anoxic condition. The sludge used for the digestion experiment was collected from a sludge-thickening tank of an EBPR WWTP. The plant treats about 45,000 m³d⁻¹ of wastewater (almost 100% domestic sewage) using an anaerobic-aerobic process. The phosphorus removal rate is about 80% when the influent concentration varies over the range 3 mg/L – 5 mg/L. The effect of redox potential on P release from non-EBPR WAS is not well understood. There is no research that examines the interrelated effects of pH, temperature, and redox potential on P release under controlled conditions.

2.4 Phosphorus and wastewater treatment processes

2.4.1 Activated sludge process (AS)

The activated sludge (AS) process has primary sedimentation (coupled with a trickling filter as pre-treatment in the case of Christchurch) followed by activated sludge aeration tanks. Clarifiers allow the sludge to settle after aeration. In this process biological growth is managed by controlling the oxygen concentration and recycling flows, such as return activated sludge (RAS) to the reactor. Figure 2.1 shows AS plant processes. Sludge from the activated sludge process has roughly a P concentration of 1.4% (Cordell et al., 2011).

2.4.2 Biological nutrient removal for nitrogen and phosphorus removal process (BNR)

Biological nutrient removal (BNR) is a process used for nitrogen and P removal from wastewater before it is discharged into surface or ground water. A BNR plant contains aerobic, anoxic and anaerobic stages either in a race-track or batch fashion, with sludge being settled in a clarifier. The aerobic zone contain oxygen concentration near or above 2 mg/L and the oxidation–reduction potential (ORP) is kept near or above 100 mV. The anoxic zone has little dissolved oxygen (less than 0.5 mg/L), but chemically bound oxygen (in nitrite and nitrate) may be present in RAS flow (there is also an internal recycle) and ORPs should be between 100 and -200 mV (for rapid denitrification). Anaerobic zones contain neither dissolved oxygen nor chemically bound oxygen and have ORPs below -300 mV. Denitrification is often more important than P removal in the design of BNR systems, and P release is not well studied in BNR systems.

2.4.3 Enhanced biological phosphorus removal process

Numerous literature is available for the EBPR process, but because EBPR sludges are not studied in this research only a brief overview is provided. EBPR is a process to activate the sludge for removal of P by using PAOs. PAOs uptake P under aerobic and anoxic conditions and store it as polyphosphates; and in anaerobic condition PAOs release P as a source of energy for survival (Van Starckenburg et al., 1993). The P concentration in sludge generated from EBPR is 3% – 5%, more than for non-EBPR sludge (Strom, 2006). A study by Bi et al. (2013) examined the P release mechanism during digestion of EBPR sludge under anaerobic, anoxic and aerobic conditions. The result concluded that more P has been released under anaerobic condition. The sludge used for the digestion experiment was collected from a sludge-thickening tank of an EBPR WWTP in Shanghai, China. The plant treats about 45,000 m³d⁻¹ of wastewater (almost 100% domestic sewage) using an anaerobic-aerobic process. The

P removal rate is about 80% when the influent concentration varies over the range 3 mg/L – 5 mg/L.

2.4.4 Phostrip process

The phostrip process is related to the conceptual model for WAS (EBPR or non-EBPR sludge) treatment shown in Figure 1.2. In this process, the main objective is to increase the P of the aerated biomass, and so reduce the P that exits with the effluent. Phosphorus is released from anaerobic treatment of the return sludge, and the P-poor sludge is then used in the aeration basin. The soluble, released P is then locked up into mineral P by the addition of lime. This P is then settled in the primary sedimentation tank, removing it from the recirculation of biological sludge. This system is running on a side-stream so operators can control how much P they remove from the recirculating activated sludge. Figure 2.2 shows a schematic process of phostrip applied to a non-EBPR sludge. This process could be modified to maximise P recovery from WAS.

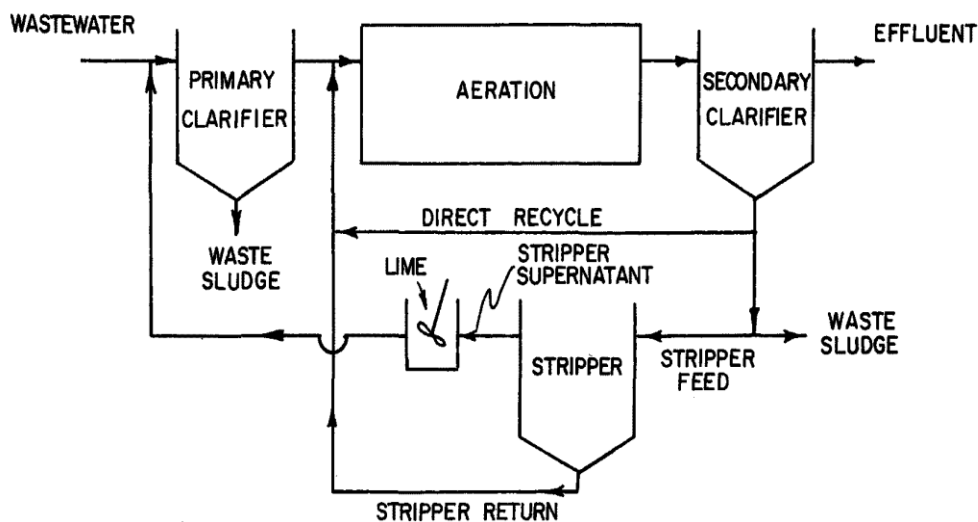


Figure 2.2: Schematic process of Phostrip (Drnevich, 1978)

In phostrip, in order to minimise P returned to the aeration basin, the concentration of soluble P during P release must be as high as possible. Peirano et al. (1983) describe a preliminary design of a P stripping tank with a detention time of 10 to 20 hours with no investigation of the effect of pH or temperature. The main focus and objective of this research is to find the most suitable physical, chemical and biological conditions that maximise the P release from waste activated sludge into water.

2.5 Research objectives

The literature review in this chapter identified poor understanding of the following;

- The combined effect of pH, temperature, and redox potential on optimal conditions for P release
- The amount of variation that can occur in P release between WWTP
- The effect of acid type on P release
- How design of a P release reactor might be designed or how its use might impact on a WWTP.

These knowledge gaps can be considered as the research objectives of this thesis.

The research approaches used to meet these objectives will be:

- Use of batch tests to allow analysis of interrelated influences
- Use of solid P fractionation methods to identify better the source of released P
- Use of simple tests (e.g. settleability and filterability) to begin study of the system effects of a P release reactor.

Chapter Three: Sampling and Analytical Methods

This chapter describes the sampling procedures, the analytical methods used for sample analyses, and the experimental setup for P release studies. Because there are many variables to study in relation to P release, and because controlled conditions are needed, and because WAS must be fresh when tested, the research is designed around a series of tests with WAS tested under various conditions in individual bottles in batch fashion in a laboratory. A test sample size of 1 L is used in this research. Because of a desire to have replicates and controls, and to study multiple test conditions, it was not practical to use a larger test vessel. Because it was important to analyse P within a few hours after sampling, it was not practical to test more than 12 vessels in any one batch test. The sampling methods are described in Section 3.1. Because of the focus on P release, great care is needed in the development of P testing methods. They are described in Section 3.2. Section 3.3 describes the other analytical methods for sludge quality tests. The results for these methods are in various chapters of the thesis.

3.1 Overview of sampling and physio-chemical analyses

Various chemical and physical properties were tested during this research on different WAS samples. Some properties were tested for preliminary data, while others were analysed continuously throughout the batch tests. Phosphorus release batch experiments were performed in 1 L Schott Duran bottles. A similar amount of sludge sample (1 L) was put into each bottle. The bottles were capped tightly, incubated at different temperatures and stirred continuously with magnetic stirrers.

Where there is pH adjustment, the pH of the sludge was adjusted by adding 1 M HCl or 1 M NaOH solution prior to testing. Every 12 hours the pH was measured and readjusted if any fluctuation was noticed. The readjustment process was continued until the desired pH had

been maintained on two subsequent tests in 12 hours intervals. One bottle with 1 L sample was run without pH adjustment at room temperature and considered as a control test.

One twenty mL sample was withdrawn from each bottle tested every 24 hours to study P release kinetics. The sampled aliquots were immediately centrifuged in 50 mL centrifuge tubes at 4000 rpm (roughly, 1250 g) for 10 minutes; temperature fluctuation was monitored which was less than ± 2 °C during this step. The supernatant was used for the analysis of dissolved reactive phosphorus (DRP), total dissolved phosphorus (TDP) and other necessary chemical analysis. After centrifugation, the sludge residue was dried and ground with mortars and pestles to obtain a fine powder. The powdered samples were preserved in sealed plastic pots at room temperature. These preserved samples were used to analyse P fractionations. Figure 3.1 and 3.2 show pictorial views of experimentation, analysis protocol and centrifuge tube used for P fractionation and analyses. Table 3.1 indicates the various properties that were examined during this research.

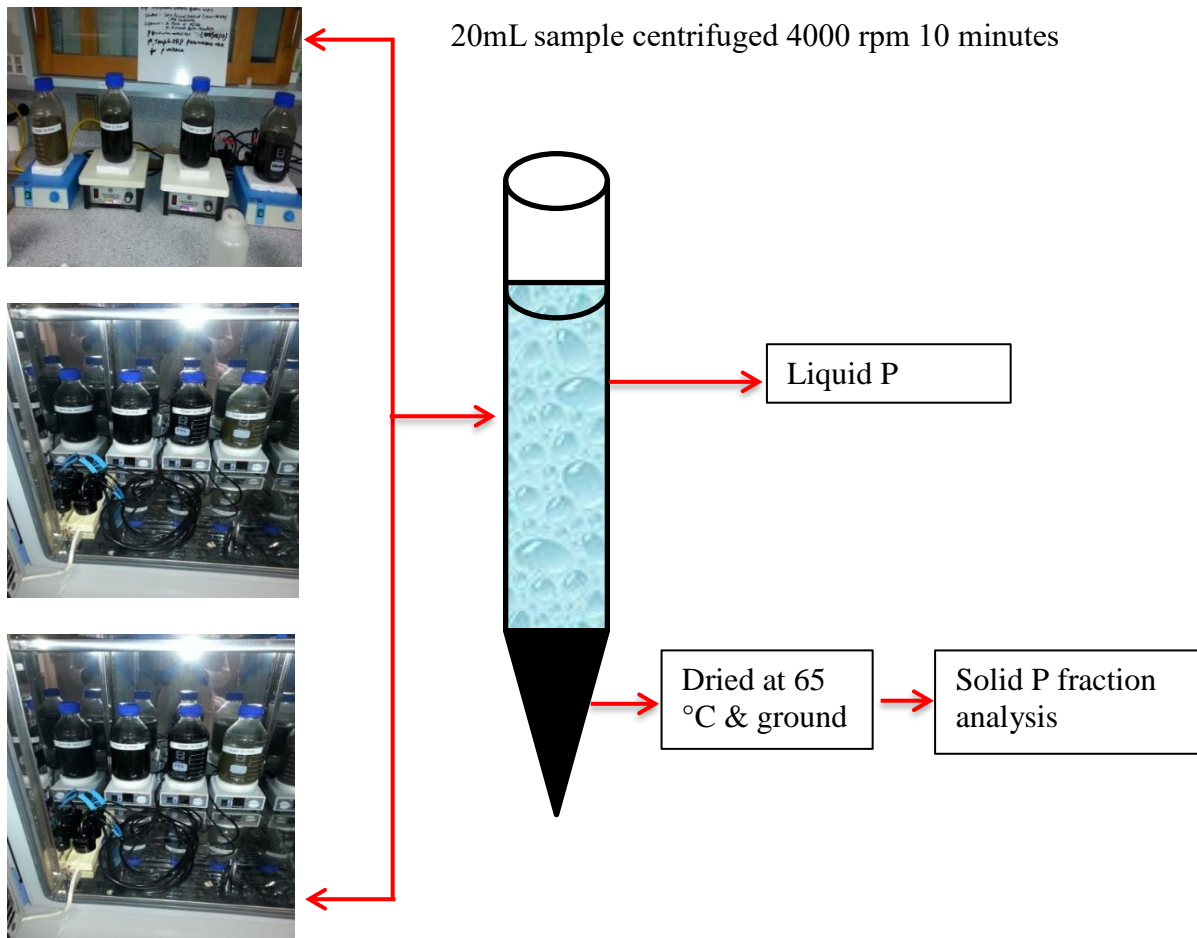


Figure 3.1: Experimental and sample analysis design



Figure 3.2: Plastic centrifuge tube used in this research

Table 3.1: Physical and chemical analyses in this research

Chemical & Physical Properties	Symbol	Unit	Thesis Section
Dissolved Reactive Phosphorus	DRP	mg/L	3.2.1
Total Dissolved Phosphorus	TDP	mg/L	3.2.2
Total Phosphorus in residue	TP	mg/g	3.2.3
Inorganic Phosphorus in residue	IP	mg/g	3.2.4
Organic Phosphorus in residue	OP	mg/g	3.2.4
Non-Apatite Inorganic Phosphorus in residue	NAIP	mg/g	3.2.5
Apatite Phosphorus in residue	AP	mg/g	3.2.5
pH			3.3.1
Dissolved Oxygen	DO	mg/L	3.3.2
Sludge Volume Index	SVI	mL/g	3.3.3
Chemical Oxygen Demand	COD	mg/L	3.3.4
Oxidation Reduction Potential	ORP	mv	3.3.5
Total Suspended Solid	TSS	mg/L	3.3.6
Volatile Suspended Solid	VSS	mg/L	3.3.6
Total Solid	TS	mg/L	3.3.7
Total Volatile Solid	TVS	mg/L	3.3.7
Anions (Cl, SO ₄ & NO ₃)		mg/L	3.3.8
Bio-P bacteria visualization			3.3.9
Filterability		mg/g	3.3.10
Metals and Cations		g/m ³	3.3.11

3.2 Analytical phosphorus methods

WAS samples were centrifuged and filtered. The filtrate was analysed for total phosphorus and for dissolved reactive phosphorus. The difference between the two was taken to be an estimate of the organic phosphorus. The solid was dried, ground, and then analysed in five aliquots to estimate total solid phosphorus, inorganic and organic solid phosphorus, and apatite and non-apatite inorganic solid phosphorus.

3.2.1 Dissolved reactive phosphorus (DRP)

DRP measures the aqueous total orthophosphate concentration, and does not measure the aqueous organic phosphorus. The orthophosphate is commonly called reactive phosphorus because the dissolved (soluble) orthophosphate compounds are readily available for use by plants and algae (Wetzel, R.G. (2001)). Twenty mL samples from each bottle were withdrawn at the beginning and then after every 24 or 48 hours to follow P release kinetics. The sampled aliquots were immediately centrifuged in 50 mL centrifuge tubes at 4000 rpm for 10 minutes. The supernatant was filtered by 0.45 μm and the filtered solution was used for DRP analysis. Chemical analysis of the supernatant for DRP was performed using a HACH DR 3900 instrument with molybdovanadate rapid liquid method (Method 8114). In the molybdovanadate method, orthophosphate reacts with molybdate in an acid medium to give a phosphomolybdate complex. Vanadium in the sample causes a yellow vanadomolybdophosphoric acid to form. The intensity of the yellow colour is proportional to the orthophosphate concentration. The measurement wavelength is 430 nm. Figure 3.3 shows details of this fractionation method.

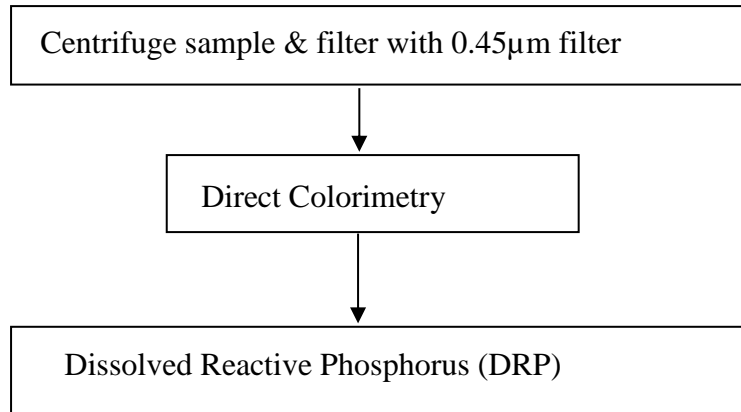


Figure 3.3: Dissolved reactive phosphorus analysis method

3.2.2 Total dissolved phosphorus (TDP)

The method used was HACH method 8190. The supernatant obtained from centrifugation was filtered to 0.45 µm and then an acid persulfate digestion was performed. 25 mL of sample and one potassium persulfate powder pillow were poured into an Erlenmeyer flask and swirled to mix. Two mL of 5.25 N H₂SO₄ was added and the mixture boiled gently for 30 minutes on a hot plate and concentrated to less than 20 mL. The mixture was left to cool down to room temperature. Two mL of 5 N NaOH was added and mixed. The volume of the whole mixture was adjusted by rinsing with deionized water to make a final volume of 25 mL. Chemical analysis of digested solution was analysed for TDP using a HACH DR 3900 instrument with the molybdovanadate rapid liquid method. Figure 3.4 shows details of this fractionation method.

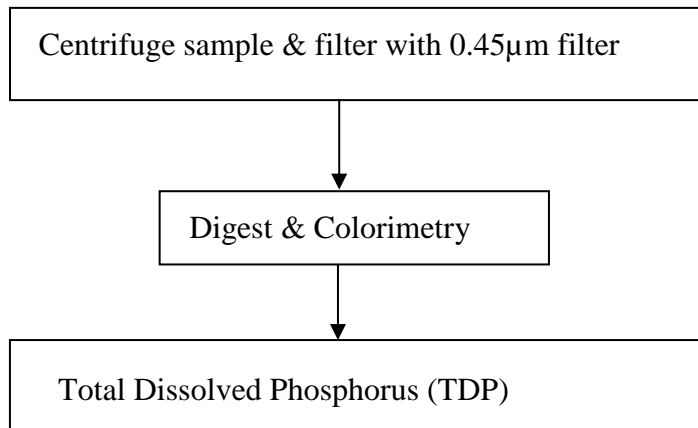


Figure 3.4: Total dissolved phosphorus analysis method

3.2.3 Solid phosphorus analysis

A protocol for sequential extraction of P in sediments (SMT protocol) was used for P fraction analysis in sludge residue. Other methods were not used because they involved expensive equipment (ICP or ICP-MS), or specialised microwave digestion. The selected method was found to be accurate at a reasonable cost. This method was already tested by previous researchers on sludge, soil and lake sediments P (Ruban, et. al 1999; Pardo, et. al. 2003; Medeiros, et. al 2005). The method has three independent extraction procedures applied to separate subsamples of 0.2 gram. The extractions were carried out in 50 mL plastic centrifuge tubes.

3.2.4 Total phosphorus (TP)

About 0.2 gram of dry powder sludge residue was weighed in a crucible and put inside a muffle furnace for 3 hours at 450 °C. The ashed powder was cooled and then dissolved all within 20 mL of 3.5 M HCl. The mixture was shaken 16 hours at room temperature. The supernatant liquid was separated from the solid phase by centrifugation at 2500 rpm for 15 minutes. Total P concentration in the extract was determined using the molybdovanadate spectrophotometric method. Figure 3.5 shows details of this fractionation method.

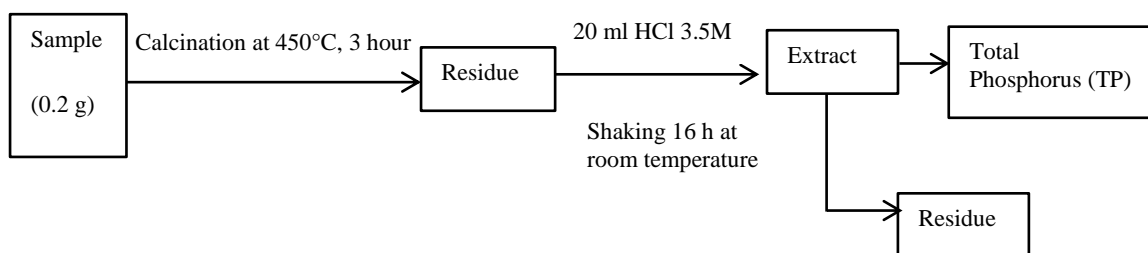


Figure 3.5: Total phosphorus analysis procedure

3.2.5 Inorganic phosphorus (IP) and organic phosphorus (OP)

About 0.2 gram of dry powder sludge residue was weighed in a 50 mL centrifuge tube. 20 mL of 1 M HCl was added and mixed well and then the mixture was shaken for 16 hours at room temperature. The supernatant liquid was separated from the solid phase by centrifugation at 2500 rpm for 15 minutes. Inorganic P concentration in the extract was determined using the molybdovanadate spectrophotometric method. The remaining solid residue was washed by shaking for 5 minutes with 10 mL of deionized water and the washings were discarded after centrifugation and then the residue dried. The dried residue was transferred to a crucible and put inside a muffle furnace for 3 hours at 450 °C. The ashed powder was cooled and then dissolved all within 20 mL of 1 M HCl. The mixture was shaken for 16 hours at room temperature. The supernatant liquid was separated from the solid phase by centrifugation at 2500 rpm for 15 minutes. The organic P concentration in the extract was determined using a molybdovanadate spectrophotometric method. Figure 3.6 shows details of this fractionation method.

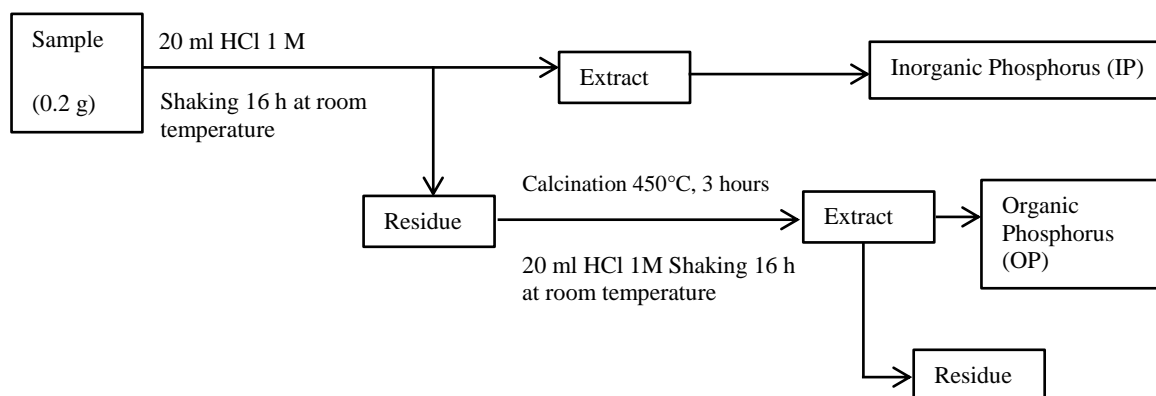


Figure 3.6: Inorganic and organic phosphorus analysis procedure

3.2.6 Non-apatite inorganic phosphorus (NAIP) and apatite phosphorus (AP)

About 0.2 gram of dry powder sludge residue was weighed in a 50 mL centrifuge tube. 20 mL of 1 M NaOH was added and mixed well, and then the mixture was shaken for 16 hours at room temperature. The supernatant liquid was separated from the solid phase by centrifugation at 2500 rpm for 15 minutes. 10 mL extract was pipetted in a 50 mL tube, 4 mL of 3.5 M HCl was added and slowly swirled for mixing and left for 16 hours in the room temperature. Non-apatite inorganic P concentration in the extract was determined using the molybdovanadate spectrophotometric method. The remaining solid residue was washed by shaking for 5 minutes with 10 mL of deionized water and the washings were discarded after centrifugation. 20 mL of 1 M HCl was added in that residue and the mixture was shaken for 16 hours at room temperature. The supernatant liquid was separated from the solid phase by centrifugation at 2500 rpm for 15 minutes. Apatite inorganic P concentration in the extract was determined using the molybdovanadate spectrophotometric method. Figure 3.7 shows details of this fractionation method.

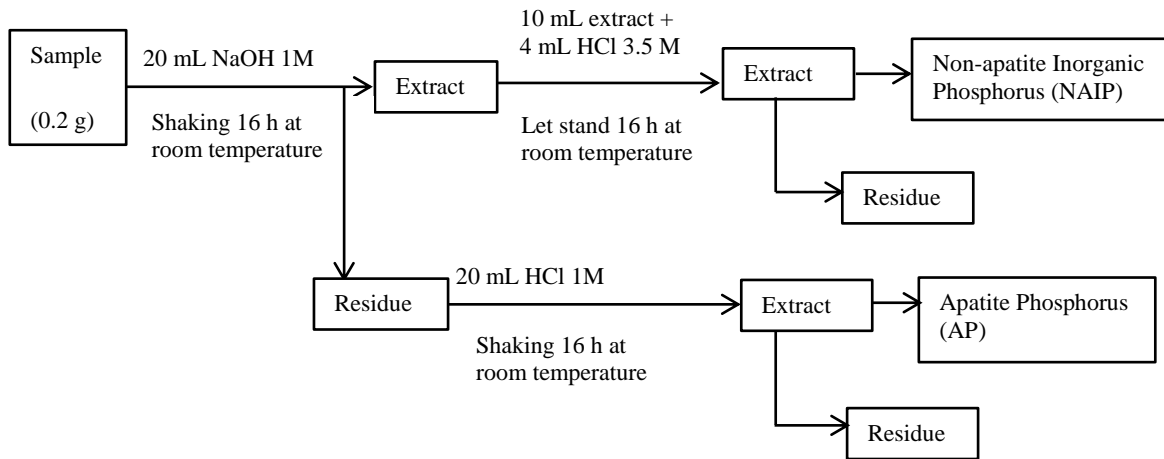


Figure 3.7: Non-apatite and apatite inorganic phosphorus analysis procedure

3.2.7 Reproducibility for phosphorus testing

To test the variability of the P release results, five replicate reactors were run for 11 days. The details of these reactors are described in Section 3.1 and Figure 3.1. The coefficient of variation (standard deviation/mean) of the DRP and TDP of the five replicates over the eight sampling days averaged approximately 5%. The 95% confidence level for 4 degrees of freedom is roughly $5\% * 2.8 = \pm 14\%$. Results are provided in Table 3.2 below.

Table 3.2: Replicate analysis of DRP and TDP release from activated sludge under pH 4, 35 °C and anaerobic condition

S.N.	Temp °C	pH	Days							
			0	1	2	3	4	6	8	11
			Dissolved Reactive Phosphorus (DRP) as mg P/L							
1	35	4	6.9	48	74	78.6	74.7	77.6	79.6	84.2
2	35	4	6.9	48.6	77	76.7	75.4	79.6	81.6	84.8
3	35	4	6.9	54.5	76	78.3	76.3	78	77	82.5
4	35	4	6.9	49.9	75.7	79.3	77.6	80.2	80.2	82.5
5	35	4	6.9	52.5	78.3	79.9	78	80.2	82.2	84.8
Average			6.9	50.7	76.2	78.5	76.4	79.1	80.1	83.8
Std. Dev.			0	2.5	1.4	1.1	1.3	1.1	1.8	1
C.V.%			0	4.8	1.8	1.4	1.7	1.4	2.3	1.2
			Total Dissolved Phosphorus (TDP) as mg P/L							
1	35	4	7.5	49.6	78	81.6	80.2	83.8	83.2	84.8
2	35	4	7.5	50.6	80.9	81.6	79.9	83.5	83.8	84.5
3	35	4	7.5	56.4	78.3	80.9	79.3	80.6	79.9	83.2
4	35	4	7.5	50.9	76.7	81.2	80.9	83.5	83.2	82.5
5	35	4	7.5	54.1	82.9	81.2	79.6	83.8	84.2	84.8
Average			7.5	52.3	79.3	81.3	80	83.1	82.9	84
Std. Dev.			0	2.6	2.2	0.2	0.6	1.2	1.5	0.9
C.V.%			0	4.9	2.8	0.3	0.7	1.5	1.8	1.1

Four replicates of the solids fractionation were conducted on biosolids produced from primary and secondary sludge after anaerobic digestion collected from the Christchurch WWTP using the solid P fractionation protocol. The standard deviations were all 0.4 mg/g or less (roughly +/- 1 mg/g or less as 90% confidence limits), showing high replicability. Table 3.3 demonstrates the detail of the findings.

Table 3.3: Replicate solid sludge fractionation analysis on biosolids (mg P/g)

Sample Num.	TP	IP	OP	NAIP	AP
1	20.3	15.7	3.0	8.6	7.6
2	20.0	15.2	3.1	8.7	7.9
3	20.4	15.9	2.9	8.6	7.4
4	19.6	16.1	2.9	8.6	7.4
Average	20.1	15.7	3.0	8.6	7.6
Std. Dev.	0.4	0.4	0.1	<0.1	0.2
C.V.%	1.8	2.5	3.2	0.6	3.1

The fractionation method also demonstrated internal consistency between the three subsamples where values agreed to within 10%. Table 3.4 demonstrates the details of the findings.

Table 3.4: Comparisons of separate analysis with different phosphorus fraction forms

Sample Num.	TP-IP-OP (mg/L)	(IP+OP)/TP %	AP+NAIP-IP (mg/L)	IP/(NAIP+AP) %
1	1.6	92.1	0.5	96.6
2	1.7	91.5	1.4	91.6
3	1.6	92.2	0.1	99.4
4	0.6	96.9	-0.1	100.6
Average	1.4	93.2	0.5	97.1

The results presented in this thesis are based on different batches of WAS. Over different batches of WAS, the P release pattern under control conditions (room temperature, without pH adjustment and anaerobic) showed similar trends. Separate tests of the effects of pH and temperature were conducted using two batches under slightly different conditions. High reproducibility was found between separate batches of WAS.

3.3 Other analytical methods

3.3.1 pH

A pH electrode (RE357Tx Microprocessor pH Meter) was used to measure the pH. The pH meter was calibrated with reference solutions of pH 4, pH 7 and pH 10 before analysis.

3.3.2 Dissolved oxygen (DO)

The DO concentration was measured using a DO probe and meter (YSI Model 57 Oxygen Meter). The DO meter was calibrated according to the manufacturer guidelines before analysis.

3.3.3 Sludge volume index (SVI)

Sludge volume index (SVI) is the volume in mL occupied by 1 gram of a mixed liquor after 30 minutes settling. SVI typically is used to monitor settling characteristics of activated sludge and other biological suspensions in wastewater treatment processes (Dick & Vesilind, 1969). During this study, SVI was measured to monitor the settling characteristics of the sludge after treatments. One litre of a well-mixed sludge was taken in a one litre graduated cylinder and it was then allowed to settle for 30 minutes. In the meantime, a sample was taken for TSS analysis as well. The 30 minutes settled sludge volume was noted and the SVI was calculated according to the formula;

$$\text{SVI (mL/ g)} = \frac{\text{Settled sludge volume (mL/ L)} \times 1000}{\text{TSS (mg/L)}}$$

3.3.4 Chemical oxygen demand (COD)

COD is a measurement of the oxygen demand of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. The COD was measured by digesting the sample in a digester using potassium dichromate. Silver sulfate (Ag_2SO_4) is used as an oxidation catalyst and mercury sulfate (HgSO_4) is used to reduce interference by chloride ions. The oxidation process was carried out by mixing 2 mL of a sample with 5 mL of high range (0 mg/L to 600 mg/L) digestion solution in glass tubes with a screw cap (10 x 100 mm). This was allowed to digest in a HACH Digital Reactor Block 200 (DRB200) at 150 °C for 2 hours (Method 8000). After the oxidation step, the amount of dichromate consumed was determined with a colorimetric method using a HACH digital DR 3900 spectrophotometer.

3.3.5 Oxidation reduction potential (ORP)

An oxidation reduction potential (ORP) probe was used to monitor anaerobic condition. The probe was manufactured by YSI Company. The range of measurement was reported to be -1999 mV to +1250 mV (millivolts) with an accuracy of $\pm 0.1\% \pm 1$ digit. Ag/AgCl and 3.5 M KCl (Potassium Chloride) gels were reference electrodes and the redox electrode was platinum. The probes were calibrated using quinhydrone buffer solutions (at pH of 4 and pH of 7) according to the manufacturer guidelines before they were used for analysis.

3.3.6 Total suspended solid (TSS) and volatile suspended solid (VSS)

Total suspended solid (TSS) and volatile suspended solid (VSS) were determined using standard glass-fiber filter (Whatman glass fiber filter circles; grade GF/C; 90 mm). First the filter was oven dried at 103 °C to 105 °C for at least 24 hours prior to the test. The weight of the filter paper alone was first taken using an analytical balance (capable of weighing to four decimals). Then, the filter paper was wetted with a small volume of distilled water to seat it on the filtering apparatus. For a more rapid filtering process, a vacuum was applied. After that, a measured volume (normally 10 mL) of well-mixed sample was passed through the filter. The sample volume for TSS was chosen so that it normally yielded a residue of 10 mg to 200 mg. Then, the filter paper was put in the oven (103 °C to 105 °C) for at least one hour to evaporate the entire water content from the filter paper. Before reading the weight of the filter with the suspended solids, it was cooled down in a desiccator to achieve a constant mass. The difference in the mass of the filter before and after the filtration yielded the TSS. To obtain the VSS, the filter paper with the solid mass was ignited in a furnace at 550 °C for 1 hour and cooled in a desiccator for 0.5 hour before weighing. The difference in the mass of the filter plus solid before and after ignition at 550 °C was calculated as the VSS.

3.3.7 Total solids (TS) and Total volatile solids (TVS)

Total solids (TS) and total volatile solids (TVS) were determined according to standard methods (APHA, 1992). According to this method a well-mixed sample is evaporated in a weighed dish by drying to a constant weight in an oven at 103 °C to 105 °C. To obtain the TVS the sample is ignited to a constant weight at 500 ± 50 °C. The increase in weight over that of the empty dish represents the TS, while the weight lost per unit volume of sample on ignition was calculated as the TVS. Clean 90 mm (millimetre) porcelain evaporating dishes were first ignited at 500 ± 50 °C for about 1 hour in a furnace and stored and cooled in a desiccator until needed. A well mixed 50 mL sample then was poured into a pre-weighed dish. The sample was evaporated in an oven at 103 °C to 105 °C. The dish then was cooled in a desiccator to a constant temperature, and weighed in a very sensitive analytical balance (capable of weighing to four decimals) to get the mass of the residue for TS. This residue was ignited to a constant weight at 500 ± 50 °C in a furnace for 1 hour or more according to the mass of residue present in the dish. After ignition, the dish was taken out and allowed to cool partially in air and then it was transferred to a desiccator. As soon as the dish reached a constant room temperature it was weighed. The weight lost per unit volume of sample on ignition was calculated as the TVS.

3.3.8 Anions analysis

Subsamples of treated sludge were also collected for anion analysis (Chloride, Sulphate, and Nitrate) analysis using Ion Chromatography System (Dionex DX-2100). The system has Anion Self-Regeneration Suppressor (AERS 500, 4 mm) with conductivity detector. Eluent Source was EGC III KOH cartridge with CR-TC and flow rate of 1.0 mL/minute. Auto-sampler was Dionex AS-AP. Analytical columns was IonPac AS18 (4 × 250 mm) and guard column was IonPac AS18 (50 x 4mm). The column temperature was 30 °C. All samples were filtered with 0.45 µm NY membrane filter and 25µl (microlitre) sample was injected in the

system. A standard stock solution of 1000 ppm (parts per million) anions was used for preparing calibration curve with deionised water. The concentration range of the calibration curves was from 0.02 ppm to 100 ppm.

3.3.9 Visualization of bio-P bacteria

Neisser staining was performed to test the presence of polyphosphates stored in sludge samples (Tarayre et al., 2016). This is also a method for identification of certain strains of filamentous bacteria.

Necessary solutions

A.	Methylene blue	0.1 gm
	Glacial acetic acid	5 mL
	Ethanol 96%	5 mL
	Distilled water	100 mL
B.	Crystal violet, 10% in 96% ethanol	3.3 mL
	Ethanol 96%	6.7 mL
	Distilled water	100 mL
C.	Chrysoidin Y, 1% aqueous solution	33.3 mL
	Distilled water	100 mL

Staining procedure: A fixed smear of WAS sample was prepared on a glass slide by placing one needle drop of WAS in the centre of a clean slide; this was spread out to cover half of the total slide and the slide left to air dry. A freshly made mixture of 2 parts of solution A and 1 part of solution B was put onto the slide for a contact period of 10 – 15 seconds. Then, the excess dye allowed to run off the slide. Solution C was added and left for a contact period of 45 seconds. The slide was rinsed with deionised water (with the flow against the back of the

slide). The slide was allowed to dry and then viewed in an Olympus BX53, DP21 upright microscope with a 100x bright field objective. Colonies of blue-black colour cells were taken as those of bio-P bacteria. There are some variations in the manner in which these types of colonies stain with Neisser. The shade is sometimes much lighter, or only a part of the cell stains darkly.

3.3.10 Filterability test

The filterability test was conducted by using the specific resistance to filtration (SRF) method. The test was conducted by pouring a reasonable volume of sludge into a funnel with filter paper and applying vacuum (measured with a vacuum gauge) at time zero. During the filtration, filtrate volume was recorded as a function of time. These data were then plotted with inverse flux (time/filtrate volume) versus filtrate volume. The line's slope gives the specific resistance (Christensen & Dick, 1985).

$$SRF = \frac{2\Delta P A^2 b}{\mu w}$$

ΔP = Pressure difference (for filtration process, it refers to liquid pressure)

A = Filtration area

b = the line's slope

μ = Viscosity

w = Weight of dry cake solids per unit volume of filtrate

3.3.11 Heavy metals and cation analysis

Heavy metals and cation analysis in WAS samples were carried out by a commercial laboratory. Nitric acid digestion APHA 3030 E 22nd ed. 2012 (modified) and Nitric acid digestion, ICP-MS, screen level, APHA 3125B E 22nd ed. 2012 (modified) methods were used for total digestion and total metals and cation analysis.

3.4 Data Analysis Methodology

3.4.1 First Order Kinetic Coefficients

P release data over time tends to follow first-order kinetics. Many chemical, biochemical, and biological degradation processes follow first-order kinetics, which is characterized by a single exponential rate constant.

For P release into solution, DRP and TDP data over time were fit to equation (1) below. For P loss from solid WAS, TSP data over time were fit to equation (2).

$$P(t) = P_{\text{initial}} + [(P_{\text{total}} - P_{\text{initial}}) * (1 - e^{-kt})] \dots\dots\dots 1$$

$$TSP(t) = TSP_{\text{total}} * e^{-kt} \dots\dots\dots 2$$

Non-linear regression in the Excel solver was used to fit the first order decay constant (k) and the total P. Minimisation of square residuals was used. More details can be found in Simonin (2016).

3.4.2 Parameter Estimation

Kinetic coefficients (k), P release, P maximum release and average misfit of DRP, TDP and TSP released under different combinations (pH and temperatures) were estimated. Table 3.5 shows an example after use of the Excel solver. Data analysis results are reported with the fit P_{total} , the fit k, and the average error.

Table 3.5: Sample calculation for estimation of k and total P_{total}

DRP						
Batch 1					$P_{total} =$	44.0
pH 7, Temp 20	t (days)	P(t)	P fit (mg P/L)	Error	$P_{released} =$	32.9
	0	11.1			$K (1/day) =$	1.34
	1	34.3	35.4	1.2		
	2	44.4	41.7	7.1		
	3	42.4	43.4	1.0		
	4	42.7	43.8	1.3		
	5	42.7	44.0	1.6		
	6	44	44.0	0.0		
	7	45.7	44.0	2.9		
	N=7		Av. Error=	2.1		

Chapter Four: Influence of pH, Temperature, and Redox Potential on Phosphorus Release¹

The aim of this chapter is to explore the effect of pH, temperatures, and aerobic/anaerobic conditions on P release. This is done through the use of either single factor or combined factor batch tests. Because of laboratory and analytical limitations, all test conditions could not be tested with the same batch of WAS. The slight differences between batches complicates analysis of the results. The pH was tested at 4, 6 and 8, because most of literature shows pH (4-6) increased P released when compare to pH (6-9) and was practical to apply in actual reactors. The temperature was tested at 10, 20, 30 and 35 °C, because this range of temperatures can be managed in real scenarios, and more than 35 °C temperature may be more costly for operation. The aerobic/anaerobic state was tested at ORP range (+50 mV to +150 mV) / (-150 mV to -250 mV) because this range of ORP maintains aerobic/anaerobic conditions. The control conditions tested were pH 7, temperature 20 °C.

The purpose of this research is to help identify the most appropriate operating conditions for P reactors. Because of that, research has not examined the underlying mechanisms that might cause the behaviour. The focus is on identifying key behaviours that might be explored in more detail by others. The findings from these batch tests were compared with the literature to reach conclusions.

The chapter gives a summary of all the related tests conducted. An overview of the different experimental designs is provided (4.1), and then a summary of the WAS used (4.2). Results are presented in order for study of the aerobic/anaerobic effect (4.3), the combined effect of

¹ This chapter is an extended version of “Use of solid phosphorus fractionation data to evaluate phosphorus release from waste activated sludge” published in Waste Management, volume 76, pages 90-97.

pH and temperature during two batch tests - batch 3 (4.4), and batch 4 (4.5). There follows an overall discussion of pH and temperature effects (4.6).

4.1 Experimental design

Four batch tests were conducted to examine pH/temperature, aerobic and anaerobic effect on P release. The purpose of these batch tests are summarised in Table 4.1.

Table 4.1: Summary of purpose of different batch tests

Batch	Purpose	Thesis Section
1	Aerobic/Anaerobic	4.3
2	Preliminary study of effect of elevated temperature	Appendix H
3	Combined effect of pH/Temperature (30°C)	4.4
4	Extended analysis of combined effect of pH/temp (35°)	4.5

The process of P release and the effect of pH, temperature, and aerobic/anaerobic condition were tested with four different batches of standard activated sludge (AS). The details of the experimental designs are shown in Table 4.2, 4.3 and 4.4 below. The complete data are provided in Appendix A.

Table 4.2: Operating parameters tested for study of aerobic/anaerobic condition effect on P release (results in section 4.3)

Factors	pH	ORP (mV)	Temp °C	Days test conducted	Replicates	Parameter tested	Batch
Aerobic	6.9	+50 to +150	20	12	3	DRP	1
Anaerobic	6.9	-150 to -250	20	12	3	DRP	1

Table 4.3: Operating parameters tested for preliminary study of temperature effect on P release (results in Appendix H)

pH	Temperature °C	Days test conducted	Replicates	Parameters tested	Batch
6.9	20	12	3	DRP	2
6.9	35	12	3	DRP	2

Table 4.4: Operating parameters tested for study the effect of pH, temperature and anaerobic conditions on P release (results in Sections 4.4 and 4.5)

pH	Temp °C	Days test conducted	Test Vessels	Parameters tested	Batch
4	10	7	1	DRP, TDP, NAIP, AP and OP	3
4	20	7	1	DRP, TDP, NAIP, AP and OP	
4	30	7	1	DRP, TDP, NAIP, AP and OP	
6	10	7	1	DRP, TDP, NAIP, AP and OP	
6	20	7	1	DRP, TDP, NAIP, AP and OP	
6	30	7	1	DRP, TDP, NAIP, AP and OP	
7	20	7	1	DRP, TDP, NAIP, AP and OP	
8	10	7	1	DRP, TDP, NAIP, AP and OP	
8	20	7	1	DRP, TDP, NAIP, AP and OP	
8	30	7	1	DRP, TDP, NAIP, AP and OP	
4	10	22	1	DRP, TDP, TSP NAIP, AP and OP	4
4	20	22	1	DRP, TDP, TSP NAIP, AP and OP	
4	35	22	1	DRP, TDP, TSP NAIP, AP and OP	
6	10	22	1	DRP, TDP, TSP NAIP, AP and OP	
6	20	22	1	DRP, TDP, TSP NAIP, AP and OP	
6	35	22	1	DRP, TDP, TSP NAIP, AP and OP	
6.9	20	22	1	DRP, TDP, TSP NAIP, AP and OP	
8	10	22	1	DRP, TDP, TSP NAIP, AP and OP	
8	20	22	1	DRP, TDP, TSP NAIP, AP and OP	
8	35	22	1	DRP, TDP, TSP NAIP, AP and OP	

No replicates were used for testing with batches 3 and 4. The practical maximum for testing of P release was 10-12 vessels. This maximum was because of the time needed to test for aqueous P. For this scoping research, many combinations of test conditions were needed. The research relied on a separate detailed study of reproducibility to allow for a good estimate of variability to expect between replicates (see Section 3.2.6).

4.2 WAS sampling and characteristics

The WAS used in this chapter's tests was obtained from a WWTP located in Christchurch, New Zealand, that receives municipal wastewater with a small industrial contribution. That plant uses primary sedimentation, a trickling filter as pre-treatment of a fraction of the wastewater, and then aeration tanks operated in a contact stabilisation fashion. Table 4.5 shows information of the treatment plant and basic characteristics of the sludge. The sludge was directly collected from the main WAS pipe (as shown in Figure 2.2). Samples were placed in air-tight 20 litre plastic containers, transported to the laboratory, and analysed for initial parameters of WAS within one hour of collection. In the same day, treatments (e.g., pH adjustment) were applied and the P release tests started.

Table 4.5: Information on the wastewater treatment plant and sludge type studied in this chapter (Source: Water New Zealand, 2018 and this research)

Parameter	Activated Sludge Plant (AS)
Sludge suspended solids (g/m ³)	4350
Total Phosphorus in sludge (g/m ³)	4.5
Total ADS production t dry solids/year	3323
pH	7.5
Total Hardness (as CaCO ₃) g/m ³	45
Volume of water treated (Mm ³ /year) (2015-2016)	62.1
Industrial waste inflow	10%

The WAS was characterised within one hour of sampling for both dissolved and solid forms of P. All four batches had a similar initial pH of 6.9-7.0 and total solids near 4900 mg/L (± 200 mg/L). Figure 4.1 shows the initial P forms in both the water and solid phases. For this figure, the coefficients of variation are 5% for the liquid P fractions and 10% for the solid P fractions. The WAS had roughly 93 mg P/L with 92% in the sludge solids. The P in the WAS solids was 1.7% by dry mass. NAIP was the major form of P in the WAS studied.

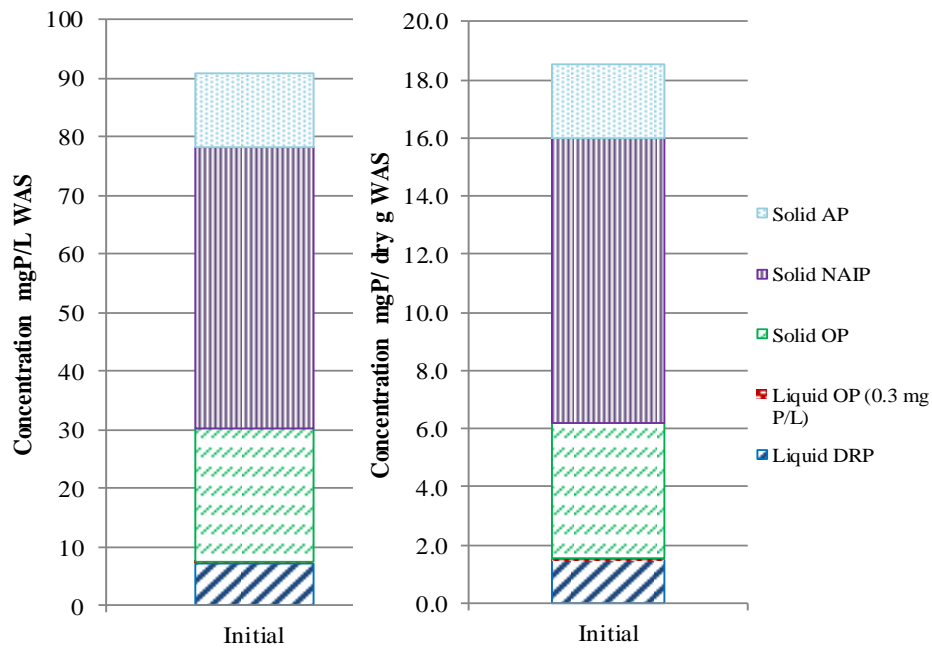


Figure 4.1: Overall phosphorus fractionation for WAS (AP = apatite phosphorus; NAIP = non-apatite inorganic phosphorus; OP = organic phosphorus; DRP = dissolved reactive phosphorus (orthophosphate)). (Estimated coefficient of variations of 5% for aqueous P and 10 % for solid P)

4.3 Effect of aerobic vs anaerobic condition on phosphorus release

A batch test (batch 1) was conducted to determine P release under aerobic and anaerobic conditions at 20 °C and a pH of 6.9 (without pH adjustment). Higher release in anaerobic conditions was expected, and the tests were for confirmation of expected results using the sludge and methods of this research. Three replicates were conducted for both aerobic and anaerobic conditions. The aerobic condition was maintained by purging bubbling air continuously, and the anaerobic condition maintained through tightening the bottle cap. Oxidation reduction potential (ORP) was measured using ORP probe throughout the test to monitor aerobic and anaerobic condition. The ORP range +50 mV to +150 mV was observed under aerobic condition and -150 mV to -250 mV for anaerobic condition.

The batch test was run for 12 days. The standard deviation of DRP between three replicates ranged from 0 to 0.8 mg P/L from 0 to 12 days. The concentration of DRP under aerobic condition increase from 7.2 mg/L initially to 32.8 mg/L at day 12. Phosphorus under anaerobic condition increased from 7.2 mg/L initially to 52.3 mg/L at day 12. Figure 4.2 shows the aerobic and anaerobic P release. The detailed results of this batch test are shown in Table A.1 in Appendix A. The findings of this study indicated that there was a significant difference of P release from activated sludge under aerobic and anaerobic conditions, with more and quicker release in an anaerobic condition.

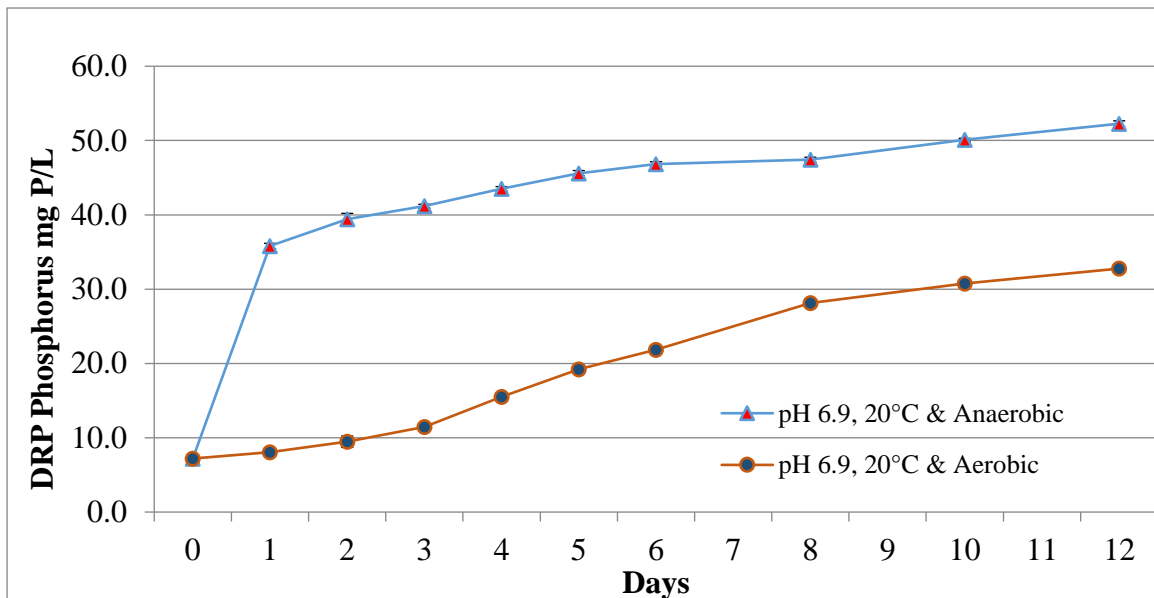


Figure 4.2: Average DRP release under pH 6.9, temperature 20 °C, anaerobic and aerobic conditions. (Estimated standard deviation between three replicates was roughly 1mg P/L (Table A.1))

Without adding food to the batch containers, the cell biomass can be expected to die over time, and this explains the P release in the aerobic vessels, and some of the P release in anaerobic conditions. The extra P release in anaerobic conditions is expected to be from release of poly-P by PAOs. Figure 4.1 shows high P in NAIP and that can include poly-P

ready for release in anaerobic conditions. PAOs uptake P under aerobic and anoxic conditions and store it as polyphosphates, and then in anaerobic conditions release the P from storage as a source of energy to ensure survival when other aerobic bacteria lose activity (Van Starckenburg et al., 1993). Even in a non-EBPR system like this, the WAS will have a number of PAO, and they would be expected to release more P under an anaerobic condition. Thus it was concluded that the anaerobic condition was better for maximum P release. All further experiments used anaerobic conditions for P release tests.

4.4 Effect of pH and temperature on P release (Batch 3)

Batch tests (batch 3) were conducted to examine the combined effect of pH (4, 6 and 8), temperature (10, 20 and 30) and anaerobic condition on P release from WAS. Before the Batch 3 tests, there was a preliminary study of the effect of temperature on P release (Batch 2). The initial pH of batch 2 WAS was pH 6.9, and were conducted for 12 days. The findings of this study indicated that there was 1.24 times more P after treatment at 35 °C than at 20 °C. The detailed results are available in Table H.1 in Appendix H. The preliminary study indicated that further testing of the effect of temperature was needed.

The batch 3 test was a study of the combined pH/temp effect on P release. The initial pH of batch 3 WAS was pH 7, and tests were conducted for 7 days. Phosphorus fractions were examined both in the liquid and solid phase of WAS. The highest DRP and TDP concentration in the soluble phase were noticed under pH 4 and 30 °C. The DRP was 11.1 mg/L at start and it reached 66.5 mg/L at day 7. The TDP was 12.4 mg/L at start and it reached 69.2 mg/L at day 7. Figures 4.3 and 4.4 show details of soluble P (DRP and TDP) release under different pH (4, 6, 7 and 8), temperature (10, 20 and 30 °C) and anaerobic condition. The detailed results of this batch test are shown in Table A.2 in Appendix A.

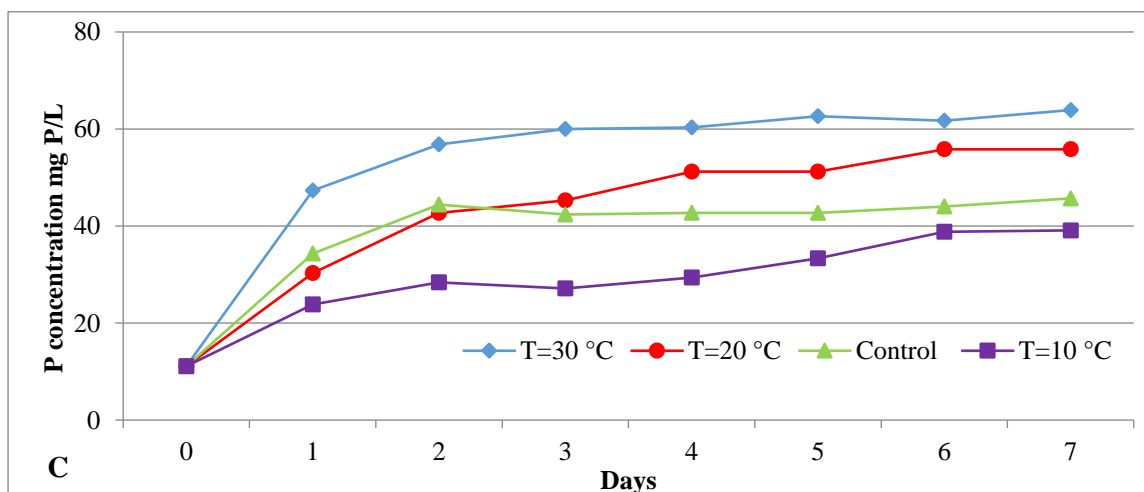
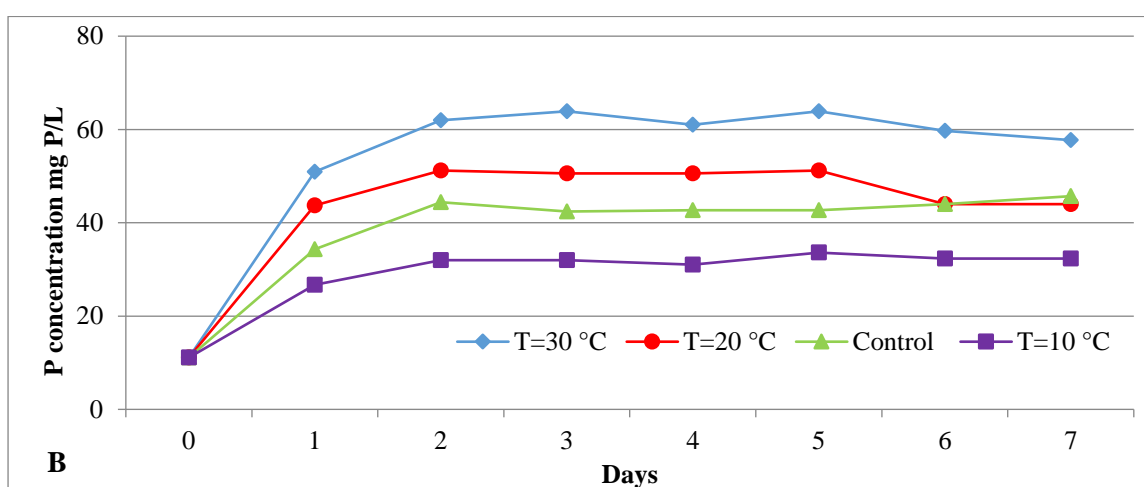
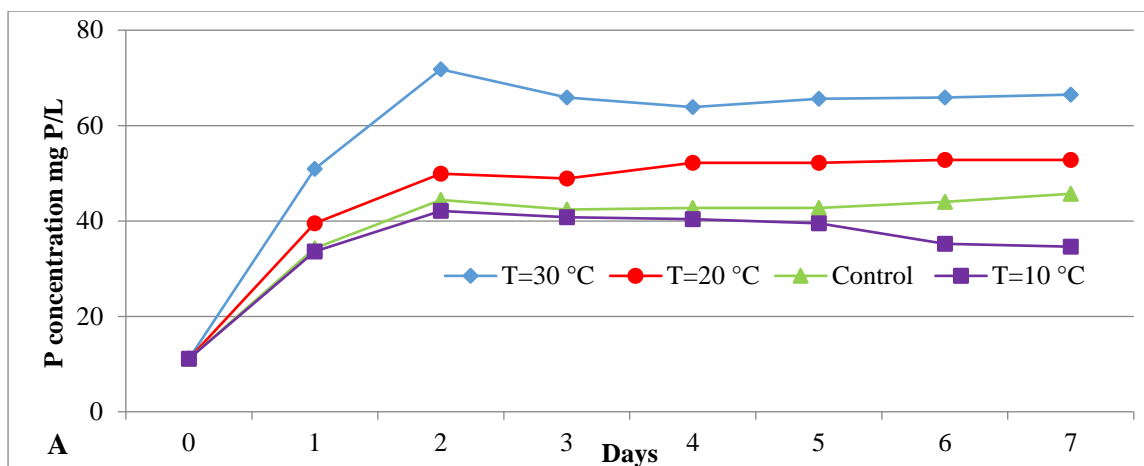


Figure 4.3: DRP release as a function of temperature after pH adjustment. (A) pH of 4, (B) pH of 6 and (C) pH of 8. Control at 20 °C and no pH adjustment with initial pH of 7. (Batch 3)

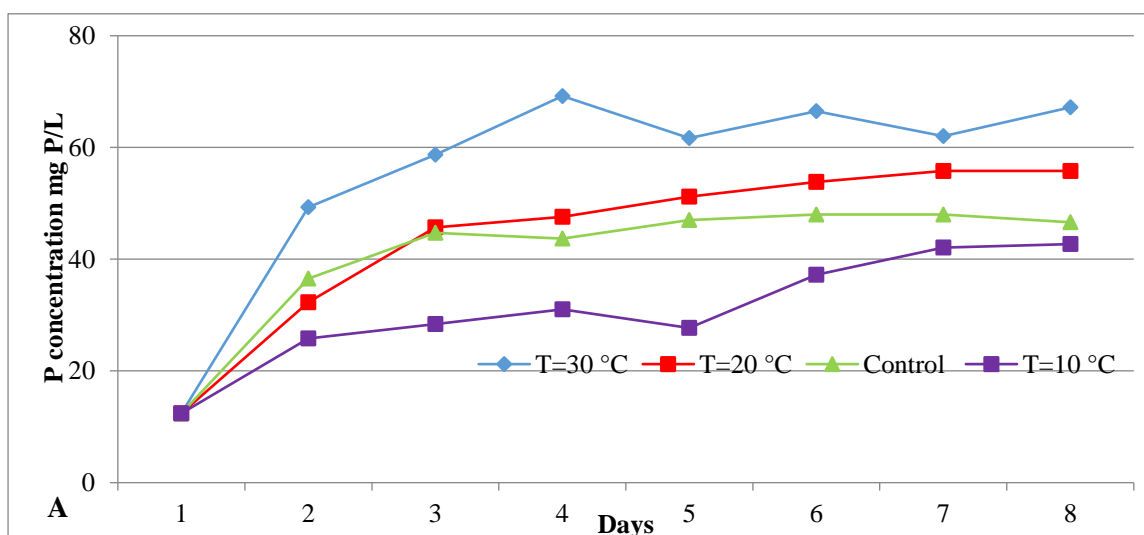
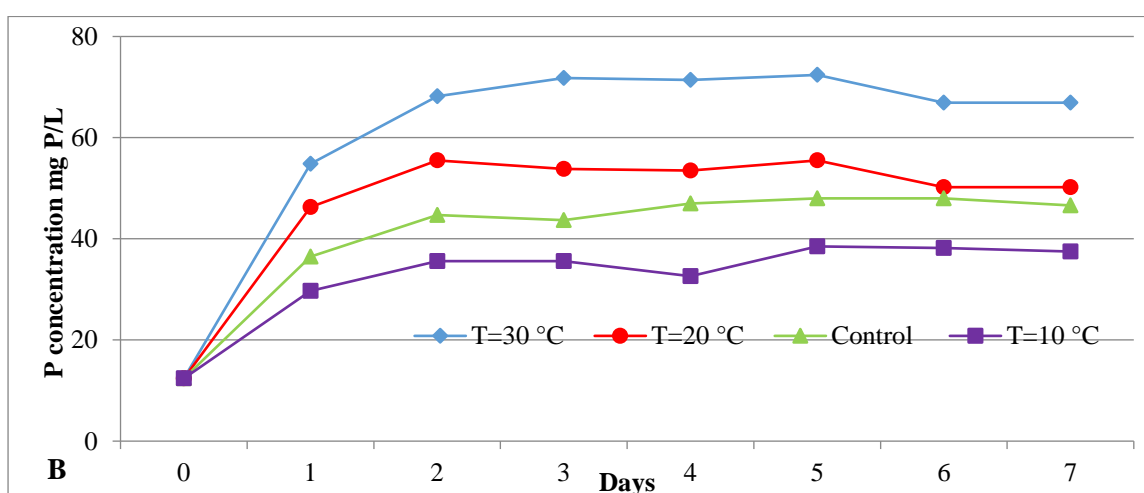
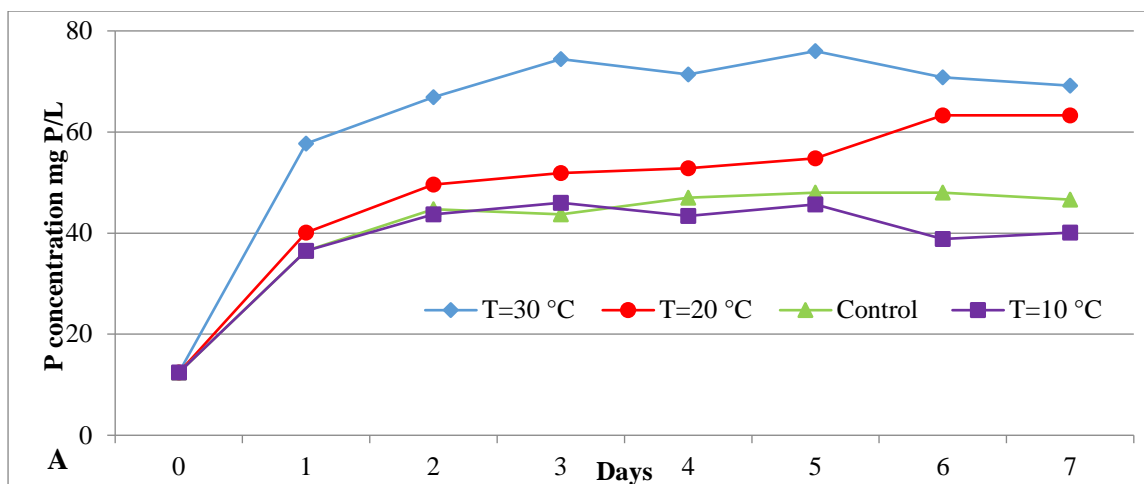


Figure 4.4: TDP release as a function of temperature after pH adjustment. (A) pH of 4, (B) pH of 6 and (C) pH of 8. Control at 20 °C and no pH adjustment with initial pH of 7. (Batch 3)

Phosphorus fractionation on solid sludge was conducted initially and after 7 days treatment. The initial TSP in the WAS sample was 18.1 mg/g. The distribution of P fractions was observed under various pH and temperatures after 7 days treatment. The lowest TSP of 9.5 mg/g dry WAS was observed under pH 4, 30 °C and after 7 days treatment. Figure 4.5 shows the details of P fraction results. The details of all results are presented in Table A.3 in Appendix A.

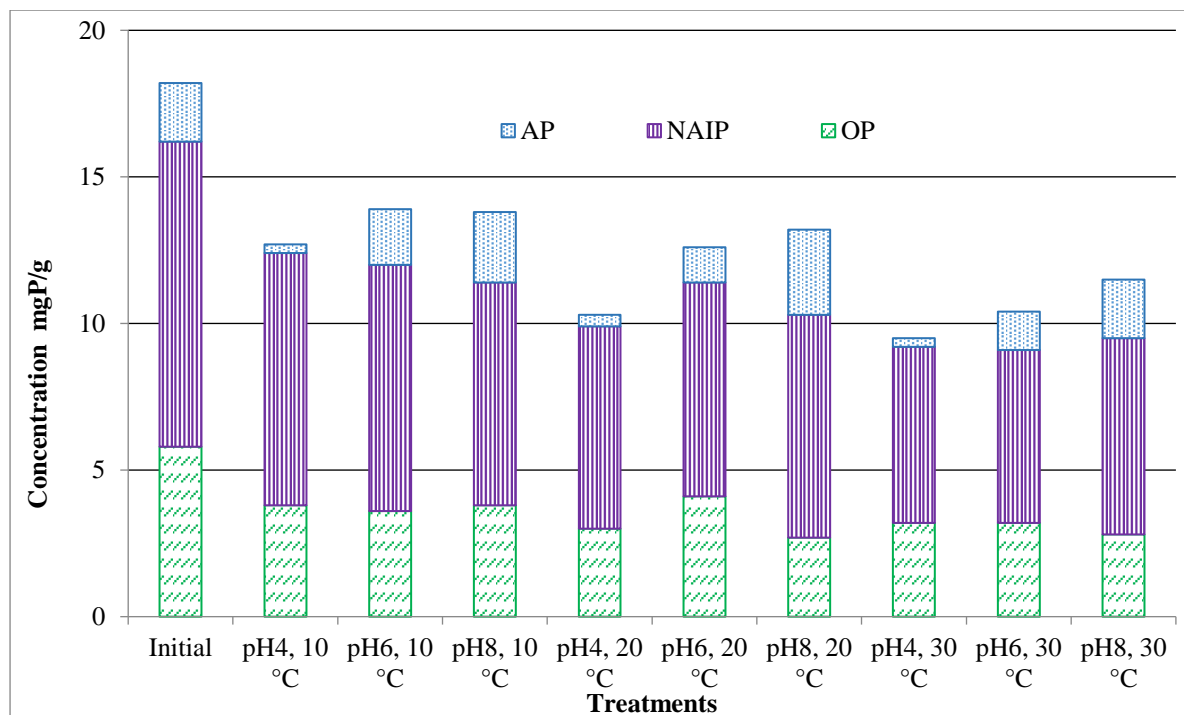


Figure 4.5: Solid phosphorus fractions initially and after 7 days (Batch 3)

The results showed higher P release at higher temperature and some increase in P release at lower pH. In order to have stronger conclusions, further tests were conducted (Batch 4, section 4.5). Discussion of the Batch 3 results is combined with the discussion of the Batch 4 results in section 4.6.

4.5 Extended analysis of effect of pH, temperature on P release (Batch 4)

A set of vessels were tested, here named as batch 4, in an extended analysis of pH/temp effect on P release. This batch examined the combined effect of pH (4, 6 and 8), temperature (10, 20 and 35 °C) on P release and help to justify the findings of previous batch 3 results.

The batch 4 tests had changes from the batch 3 tests:

- 35 °C and not 30 °C (to increase temperature to a maximum for our laboratory)
- Solids P fractionation studied at intermediate times to better understand kinetics
- Testing for total solids to allow for a P balance
- Testing for 22 and not 8 days to study any long-term effects on P release

The effect of temperature at pH 4 and pH 6 on P release in liquid phase from WAS is shown in Figure 4.6A and 4.6B. Full data are presented in Table A.4 in Appendix A. The maximum release of TDP from 7.5 mg/L to 83.2 mg/L was observed at a pH of 4, and temperature of 35 °C after 19 days. This increased the aqueous P from 8% to 54% of the total P in the WAS.

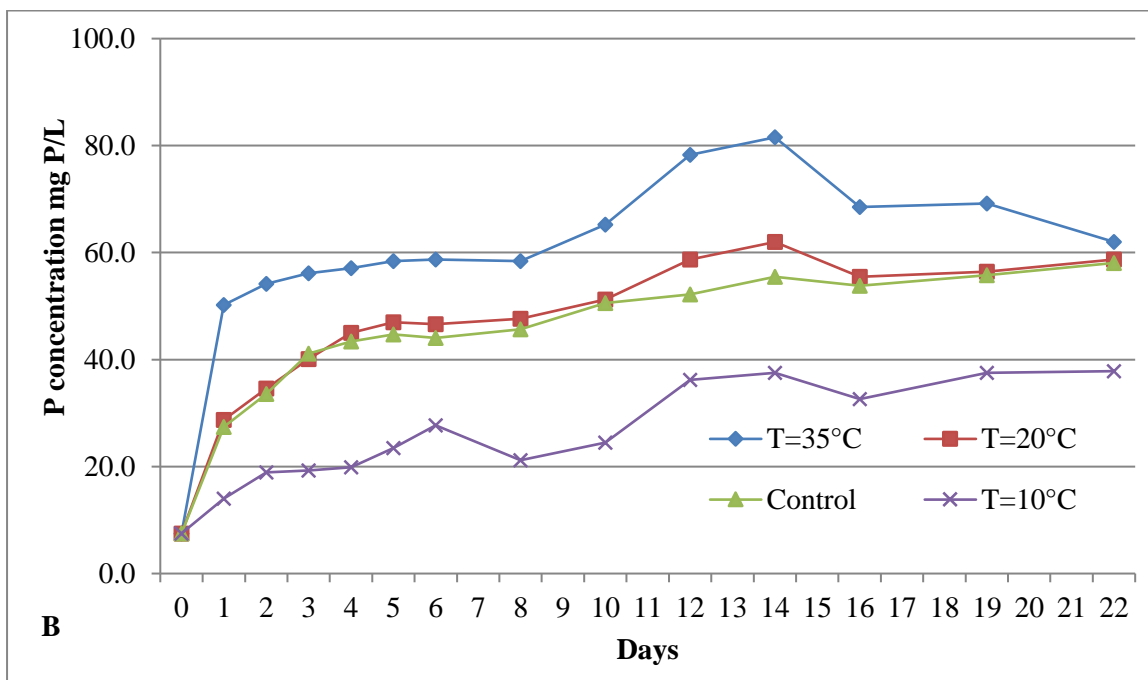
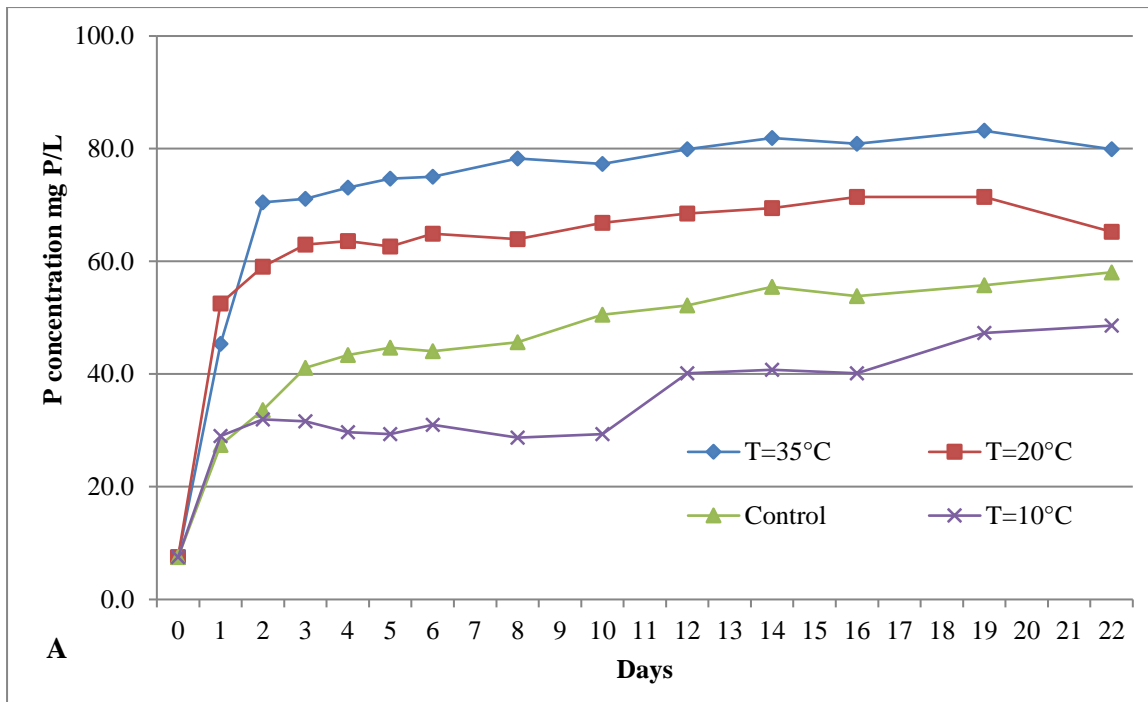


Figure 4.6: TDP release as a function of temperature after pH adjustment. (A) pH of 4, (B) pH of 6. Control at 20 °C and no pH adjustment with initial pH of 6.9. (Batch 4)

The effect of pH on TDP release at 35 °C is shown in Figure 4.7. The results show more total release and more rapid release of P for a pH of 4 than pH of 6, which in turn has more release than pH of 8. Further discussion is included in 4.6. In batch 3 (Figure 4.4), pH 4 had little more TDP than pH 6, but in batch 4 (Figure 4.7), pH 4 had notably more TDP than pH of 6.

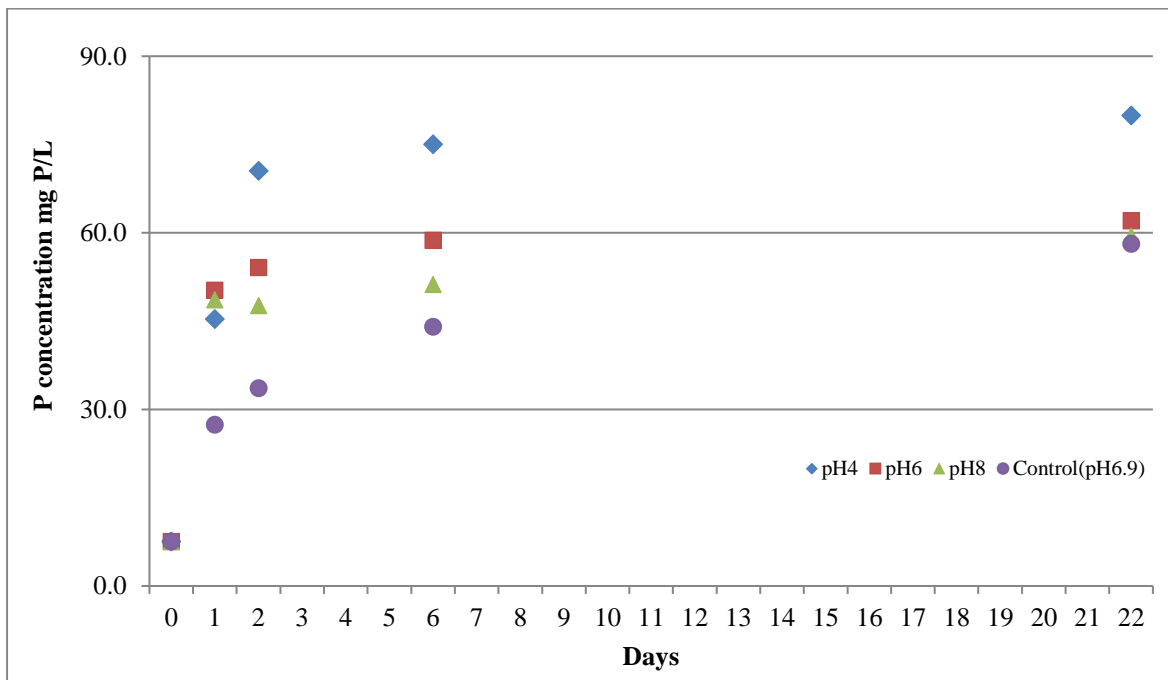


Figure 4.7: TDP release as function of pH at 35 °C and control at 20 °C and without pH adjustment initial pH of 6.9. (Batch 4)

The organic P in the aqueous phase was monitored through subtraction of DRP from TDP. Tests at all temperatures showed small dissolved organic P of 2% – 10% (typically, 4%) of the total aqueous P. There are no clear discernible trends in DOP and so only DRP and TDP results are discussed in this research.

Figure 4.8 shows the results comparing the initial distribution of P in the WAS with that after pH adjustment to 4 and 22 days of anaerobic incubation for batch 4. The effect shown in

Figure 4.8 is that P is released from NAIP relatively effectively, as is AP, while the OP results are less conclusive. These results are consistent with the increase in DRP and TDP above; further discussion of the agreement between solids and liquid P results is provided in section 4.6.

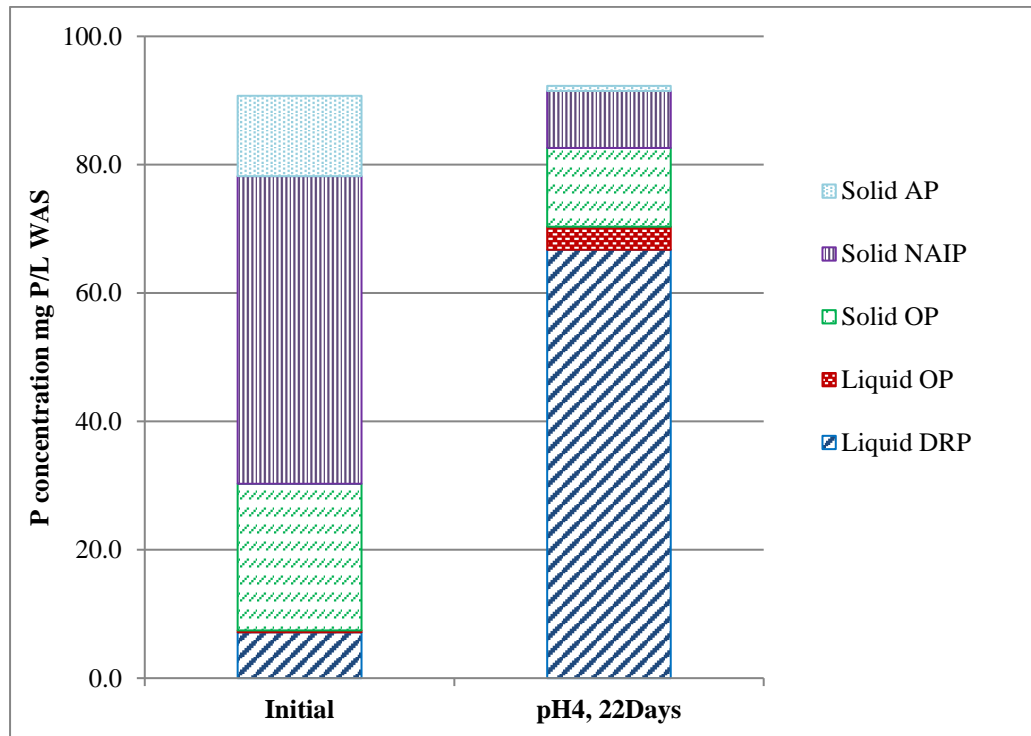


Figure 4.8: Overall phosphorus fractionation for WAS initial and after 22 days at pH 4 and 35 °C (Batch 4) (Estimated coefficient of variation of 5% for aqueous P and 10% for solid)

The TSP in the WAS samples were 1.8% and 1.7% by dry mass (18.1 mg P/g dry WAS for batch 3 and 16.8 mg P/g dry WAS for batch 4). These are higher than the 1.4% by dry mass reported as typical for activated sludge by Cordell et al. (2011). NAIP was the major form of P in both batches WAS studied. Combined with the AP, the total IP was 69% of the total solid P for batch 3 and 73% of the total solid P for batch 4. IP fraction of both batches were

slightly lower than past findings. Previous research has found a combined NAIP and AP of between 75% – 85% of the total solid P in sewage sludge (Medeiros et al., 2005).

Figure 4.9 shows the loss in TSP at a pH of 4 and at three temperatures (10, 20 and 35 °C). Full results are provided in Table A.6 in Appendix A. Roughly 40% of the TSP was solubilized in 2 days and 50% within 7 days under the best conditions tested (35 °C and pH 4). The higher temperature had a greater effect on increasing the rate of P solubilisation than on the total solubilisation after 22 days. At 35 °C, most of the TSP release from the solids happened in the first two days for tests at pH of 4, 6 or 8. TSP at the start was 16.8 mg/g, and with pH of 4 this reduced to 9.9 mg/g after 2 days, further decreasing to 8.2 mg/g after 22 days. A lower pH shows a greater total release of P.

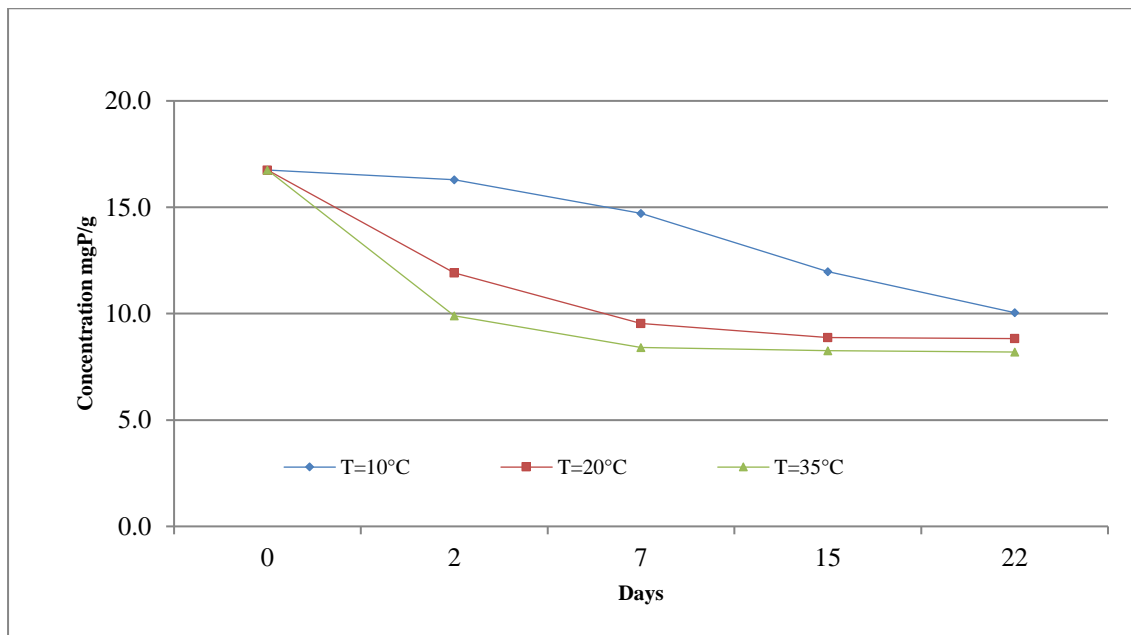


Figure 4.9: TSP in WAS under different temperature and at pH of 4 (Batch 4)

The liquid and solid results can be combined to give an overall picture of the changes in P fractionation during these treatments. TSP loss from solid side (Figure 4.9) reflected the TDP increased in liquid phase (Figure 4.7).

Figure 4.10A also shows that at pH 4 the higher temperatures release more from both the NAIP and AP fractions, with little change in the OP. Most of the P released at any temperature was from the NAIP fraction because of its predominance in the raw WAS. The effect of pH on total P and P fractions in residual WAS is shown in Figure 4.10B. Full results are provided in Table A.5 in Appendix A.

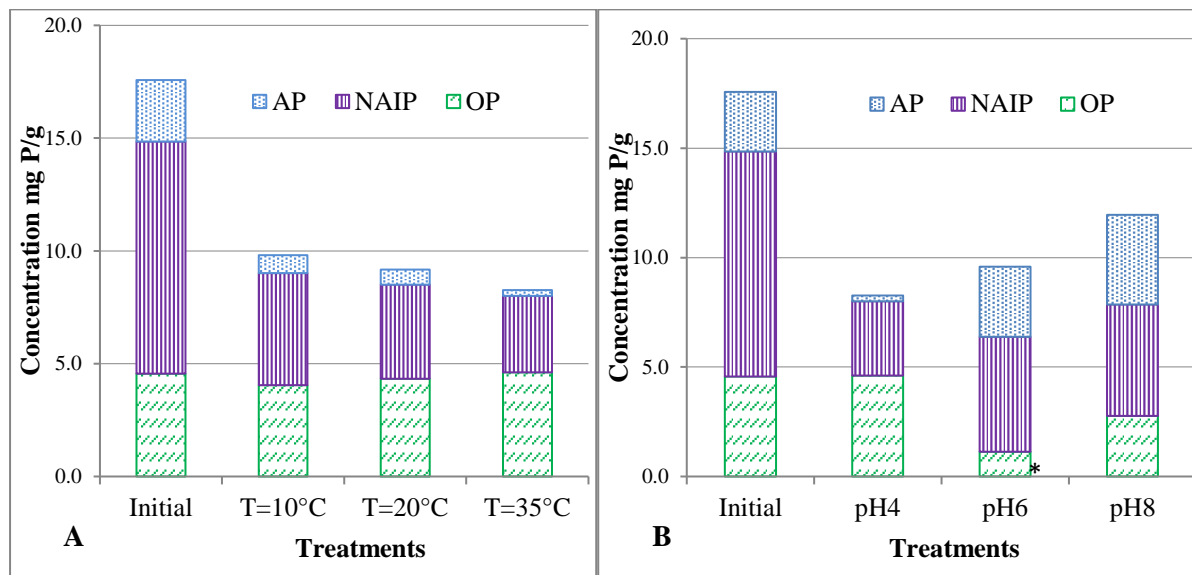


Figure 4.10: Solid phosphorus fractionation results. (A) Temperature effects at pH 4 after 22 days. (B) pH effects at 35 °C after 22 days. (* Value of 1.1 mg OP/g is likely an analytical error).

The OP measurement at pH of 6 and 35 °C shown in Figure 4.10B merits separate consideration. Throughout these and other batch testing, the OP measured from 2.8 mg P/g – 4.6 mg P/g, except for this value of 1.1. In batch 3 the OP fraction at a pH of 6 and temperature 30 °C and after 7 days was 3.2 mg P/g. There is no reason to expect the OP to be lower at a pH of 6 than at pH of 4 or pH of 8 considering that Xu et al. (2015) show no variation in OP over this pH range. It was concluded that the OP value of 1.1 is most likely an analytical error.

The effect of pH is the greatest on the AP fraction. Figure 4.10B shows release of practically all AP from solids at a pH of 4, with little change at a pH of 6, and an increase in AP at a pH of 8. Lowering the pH to 4 from pH 6 seems to also have an effect on the NAIP release.

4.6 Overall discussion of effect of pH and temperature (Batch 3 and 4)

Although these two batches examined the WAS from one WWTP, the changes in the amounts of the various solid P fractions provides an opportunity to consider broader implications. The total inorganic P in the WAS of this study was 68% and 73% of TSP for batch 3 and 4, slightly lower than results by Medeiros et al. (2005), and showing similar characteristics of typical WAS.

Relatively independent of pH, higher temperature led to generally higher TDP concentrations. These observations agree with previous studies; Brdjanovic et al. (1998); Wu et al. (2009); Yuan et al. (2011). The relationship between pH and temperature over time appears to be complex over the ranges studied. For example, Figure 4.8B shows the total aqueous phosphorus at 35 °C and a pH of 6 increasing over 14 days, and then decreasing at day 22 to the value originally reached on day 10. A similar pattern of P release was shown at 30 °C by Wu et al. (2014). Because of the dependence of the chemical and biological

processes controlling P release on both pH and temperature, further study is needed to understand the intricacies of their joint effects.

A pH less than 6 during anaerobic incubation of WAS can be expected to promote P solubilisation because of the higher solubility of P solids such as apatite under acidic conditions, with maximum solubilisation of P solids expected near or below pH 4 (Mehta & Batstone, 2013). Greater P release can also be expected at lower pH because of decreased microbial activity at lower pH, leading to less P uptake, plus the increased death of microbial biomass and consequent P release.

The key to understanding these batch results are the changes in AP and NAIP solid concentrations. As shown in Figure 4.12, at 35 °C, 50% of the NAIP was released at a pH of 6 after 22 days, while no AP was released. At a pH of 4 after 22 days, 70% of the NAIP and 90% of the AP were released (data in Table A.6 in Appendix A). These findings indicate that WAS higher in NAIP (including microbial polyphosphates) will be more suitable for P recovery because of less need to reduce pH, and that a pH of 4 could be suitable for P recovery when WAS have high quantities of AP.

These results are consistent with recent findings of Latif et al. (2017). Their tests with a WAS thickened by dissolved air flotation showed high release of solid P at a pH of 5 in a continuous reactor at 37 °C. They also show a greater release of P from the inorganic rather than organic solid P. Their research did not fractionate inorganic solid P into apatite and non-apatite inorganic P.

A further batch test was conducted on WAS sample collected from same AS plant to test the behaviour of lower pH (pH<6). The initial characteristics of WAS was pH 7 and TSS 2850 mg/L. The sample was adjusted to pH 4, pH 5 and control at pH 7 and anaerobically incubated at 20 °C. P release was monitored throughout 21 days. The higher soluble P 57.1

mg/L was noticed under pH 4. This test results are in agreement with the previous batch results of this research. This reconfirmation test gives greater confidence in the results described in this chapter. The details of this test are shown in Table E.1 in Appendix E.

Non-linear regression in the Excel solver was used to fit the first order decay (k) and P release. Minimisation of square residuals was used. Kinetic coefficients (k) of DRP and TDP released under different combinations (pH and temperatures) were calculated using first order of relationship for batch 3 and 4. Detailed results are provided in Appendix G. There was no trends seen on different k values between different pH and temperature combinations.

The combination of lower pH 4 and higher temperature 30 °C in batch 3 reached maximum DRP 66.7 mgP/L level in aqueous phase having 55.6 mgP/L P released. Same combination also reached maximum TDP 72.3 mgP/L level in aqueous phase having 59.9 mgP/L P released. Similarly, combination of lower pH 4 and higher temperature 35 °C in batch 4 reached maximum DRP 77.9 mgP/L level in aqueous phase having 70.7 mgP/L P released. Same combination also reached maximum TDP 79.1 mgP/L level in aqueous phase having 71.6 mgP/L P released.

A first order equation was also fitted to the data on TSP. The results for k on TSP losses from day 0 to 22 days under different pH/temp treatment also didn't show any trends. The regression did show a lower final TSP (8.2 mg/g dry sludge) after 22 days treatment under pH 4 and temperature 35°C.

The implications of these batches and related research are significant for those considering P recovery. The aqueous P and solid P results in this study indicate that a higher temperature (up to 35 °C) can release more P from WAS. Because 80 mg TP/L at 35 °C for pH of 4 and pH of 6 represents 88% of the total P, higher temperatures are likely to have decreasing effectiveness at increasing soluble TP. The high release of P from NAIP/AP at a pH of 4 and

a temperature of 35 °C after 2 days, indicates that design engineers will not have a strong motivation to implement P recovery from WAS under more expensive design conditions with even lower pH and or even higher temperature. Latif et al. (2015) also point out that greater acidification to allow for more P release can be expected to decrease the degradability in any subsequent anaerobic digestion of the activated sludge.

It was hard to draw conclusion regarding suitable pH (4 or 6) for maximum releases of P. In batch 3; TDP released at pH 4 was as similar as compared at pH 6. In batch 4; better TDP release was monitored at pH 4. Solid WAS analysis shows better AP release at pH 4, but in application many factors can influence choice of using pH 4 or 6.

The results of these batch studies highlight that recovery of solid OP from WAS will be more challenging. The results presented here indicate that temperature up to 35 °C released little solid OP, and pH as low as 4 shows some OP release, but at a lower percentage than for either AP or NAIP. Xu et al. (2015) examined OP release over the pH range of 2 to 11 and found some increase in OP release at the highest pH. This study supports earlier work that WAS that is rich in OP (excluding microbial polyphosphates) could be particularly challenging in terms of the practicality of P recovery. These results also suggest a need for further research into the behavior of OP from WAS.

4.7 Conclusions

Although WAS can be a relatively rich source of P, the design of P recovery systems has been hampered by a lack of understanding of how process variables control the amount of P release. This chapter examined the use of elevated temperature and lowered pH conditions for release through anaerobic fermentation. The results indicate that 35 °C greatly accelerates P release relative to ambient temperatures, and that a decrease of the pH to 4 or 6 would increase the total P release.

More significantly, the results point to the value of conducting P fractionation analyses of solid WAS. Solid P fractionation in this study points to the following conclusions:

- Little pH depression is needed to release NAIP; therefore WAS high in NAIP will be more promising for P recovery;
- Lowering the pH from 6 to 4 is needed to release AP; thus, a more expensive treatment would be needed for WAS higher in AP;
- OP is more difficult to release from WAS; WAS rich in OP would be more challenging to economically recover.

Chapter Five: Influence of Different Types of WAS on Phosphorus Release

The previous chapter four examined the effect of pH, temperatures and ORP on P release from an activated sludge (AS) plant's samples. The previous chapter indicated that a pH of 4-5 and a temperature of 30-35 °C were good conditions to consider for a P release reactor. Previous work has not examined P release from WAS across multiple treatment plants raising issues of comparability of results, and/or has not conducted solids fractionation analyses thereby limiting an ability at inter-plant interpretability. It could be that each P release reactor would need to be designed differently and that certain WWTPs are better candidates for P recovery with P release reactors. This chapter provides details of P release from WAS sample collected from three different WWTPs and also solid P fractionation on these samples to help evaluate at a scoping level the implications of WAS source on P release reactors.

5.1 Introduction

The many different types of activated sludge systems around the world means there is potentially wide variation in P content, form and P release from different sludges. For example, Medeiros et al. (2005), examining P fractions in sewage sludge collected from urban WWTPs observed differences in TP content between plants of 23.1 ± 0.2 mg/g and 26.1 ± 0.3 mg/g. In addition, they found variations in IP (20.0 ± 0.3 mg/g and 20.2 ± 0.8 mg/g) and OP (2.3 ± 0.1 mg/g and 5.8 ± 0.3 mg/g). Similarly, research carried out by Xie et al. (2011) observed variations in P content and type from four different activated sludge systems (see Table 5.1).

The total and relative amounts of the forms of P, even within the same treatment plant, can vary as a function of both the waste and water source. For example, if a WWTP served a community with calcium-rich waters, this would lead to more solid P in the calcium phosphate form, with implications for P recovery. If a WWTP received waste from industrial

facilities that discharged high concentrations of soil minerals (e.g. ferric hydroxides), there would be strong potential to sorb phosphates in NAIP. Finally, some industries may discharge organic-rich food waste, which could lead to high total or organic phosphorus in the WWTP influent. As a case in point, Chapter 4 reported TP, IP and OP fractions in activated sludge obtained from the same municipal wastewater treatment but at different times. The plant received trade waste of approximately 10%. Different fractions of TP (18.1 mg/g vs. 16.8 mg/g), IP (12.4 mg/g vs. 12.2 mg/g) and OP (5.8 mg/g vs. 4.6 mg/g) are reported (see Table A.4 and A.6 in Appendix A). At least part of the difference in sludge make-up (in terms of P fractionation) could have arisen because the contribution of the trade waste varied as a function of time.

Table 5.1: Analytical results obtained in activated sludge (expressed in mg/g of solid sludge or biomass) (Source: Xie et al., 2011)

Wastewater Flow	Process	Source of wastewater	Sample collection	TP	IP	OP	NAIP	AP
2×10^6 m ³ /d	A/O	Domestic	Anoxic	16.3 ± 0.5	13.1 ± 0.4	2.8 ± 0.1	10.6 ± 0.3	1.7 ± 0.0
			Aerobic	16.9 ± 0.3	12.8 ± 0.9	3.6 ± 0.2	11.3 ± 0.2	1.6 ± 0.1
6×10^6 m ³ /d	A ² /O- Flocculating	Domestic	Anaerobic	17.3 ± 1.1	15.0 ± 0.5	2.4 ± 0.1	13.2 ± 0.2	1.6 ± 0.1
			Anoxic	17.0 ± 0.5	14.4 ± 0.8	2.5 ± 0.3	12.4 ± 0.4	2.0 ± 0.2
			Aerobic	16.2 ± 0.8	13.3 ± 0.6	3.3 ± 0.2	12.5 ± 0.3	1.2 ± 0.1
2×10^4 m ³ /d	A/O	Industrial (dyeing)	Anoxic	2.7 ± 0.3	1.5 ± 0.2	1.4 ± 0.2	1.2 ± 0.1	0.2 ± 0.1
			Aerobic	3.9 ± 0.3	2.2 ± 0.3	1.7 ± 0.2	1.9 ± 0.1	0.4 ± 0.2
1×10^4 m ³ /d	A/O- A/O	Industrial (tannery)	Anoxic 1	4.5 ± 0.3	3.2 ± 0.2	1.4 ± 0.1	2.5 ± 0.2	0.9 ± 0.1
			Aerobic 1	5.1 ± 0.2	3.5 ± 0.3	1.6 ± 0.1	2.4 ± 0.2	1.1 ± 0.2
			Anoxic 2	6.3 ± 0.4	4.5 ± 0.2	1.6 ± 0.2	3.4 ± 0.3	1.2 ± 0.2
			Aerobic 2	5.3 ± 0.3	3.4 ± 0.2	1.6 ± 0.2	2.6 ± 0.2	0.9 ± 0.2

Although the ability of different biological nutrient removal systems to uptake P has been well studied (Kern-Jespersen & Henze, 1993; Lee et al., 1997; Lee et al., 2001; Oehmen et al., 2007), the release of P (particularly between different treatment plants) is less well understood. In addition, an understanding of the partitioning of solid P under controlled conditions is largely absent in the literature. As such, the aim of this chapter is to understand the differences in P fractionation between treatment plants having different wastewater sludges; with this difference investigated under controlled laboratory conditions known to

enhance P release. Understanding how these P fractions change during P release may influence the potential for P recovery.

The goal of this part of the research is not to analyse all types of WAS that could be produced by different WWTPs. For example, this chapter does not examine WAS produced by EBPR plants. The scope is limited to studying the potential for variation between plants. The plants chosen are relatively similar because they were within a day's drive of the research base.

They are within a day's drive of the research base because it was important to analyse P quickly when sampling and bring the pH-adjusted samples to the lab for controlled testing.

The focus of this research is to identify behaviour in P release and issues related to potential P recovery from WAS to support future research into mechanisms to explain the behaviour.

5.2 Sources of WAS

The WAS used in this study was obtained from three different WWTP and the relevant characteristics are shown in Table 5.2. The activated sludge (AS) plant had primary sedimentation (coupled with a trickling filter as pre-treatment) followed by activated sludge aeration tanks equipped with fine bubble diffusers. Clarifiers allowed the sludge to settle after aeration. The carousel biological nutrient removal (CBNR) plant contained aerobic, anoxic and anaerobic stages in a race-track fashion, with sludge being settled in a clarifier. Finally, sludge was taken from a sequencing batch reactor (SBR) biological nutrient removal (SBNR) plant that used dual trains to allow a four-stage Bardenpho configuration of anoxic, aerobic, anoxic and aerobic oxygen tensions at different times in the SBR. Both the CBNR and SBNR plants were designed and operated for N rather than P removal.

Table 5.2: Information on three wastewater treatment plants (Source: Water New Zealand, 2018 and measured in this research)

Parameter	Activated Sludge Plant (AS)	Carousel Biological Nutrient Removal Plant (CBNR)	Sequencing Batch Nutrient Removal Plant (SBNR)
Sludge suspended solids (g/m ³)	4350	3960	4920
Total Phosphorus in sludge g/m ³	4.5	7.2	3.7
Total sludge production t dry solids/year	3323	245	260
pH	7.5	7.4	7.6
Total Hardness (as CaCO ₃) g/m ³	45	54	40
Volume of water treated (Mm ³ /year) (2015-2016)	62.1	2.1	1.1
Industrial waste inflow	10%	<1%	<1%

The sludge was directly collected from main WAS pipe for the AS, CBNR and SBNR plants. The CBNR plant wasted activated sludge from the carousel reactor and not from the underflow of the clarifier. Samples were placed in air-tight plastic containers, transported to the laboratory, and analysed for initial parameters of WAS within one hour of collection. Acidic conditions during incubation of WAS were expected to promote P solubilisation based on previous literature (Mehta & Batstone, 2013) and the results in Chapter 4. pH adjustment with HCl was applied on the same day of sample collection. For elevation of temperature samples were incubated in incubator at 35 °C and for 20 °C at room temperature.

5.3 Characterization of phosphorus in WAS

The WAS samples were characterized immediately after sampling for both dissolved and solid forms of P. The initial pH of the samples was 7, while the total solids were 4900, 4610 and 5181 mg/L for the AS, CBNR and SBNR samples respectively. The initial P in solid form for the AS, CBNR, and SBNR sludges were 17.2, 19.7 and 18.1 mg P/g dry sludge respectively. Note that neither the CBNR nor the SBR plant were optimised for P removal. Figure 5.1 shows details of the initial P forms as mg/L WAS and mg/g dry sludge. The results are slightly higher than the 1.4 % (14 mg P/g) by dry mass reported as typical for activated sludge by Cordell et al. (2011). NAIP was the most common form of P in the sludges measured in the present research, which agrees with earlier findings (Xie et al., 2011). Combined with AP, the total initial IP was 72.6, 88.0, and 69.5 % of the total solid P for the AS, CBNR, and SBNR sludges respectively. Other research has found a combined NAIP and AP of between 75% and 85% (Medeiros et al., 2005) and 66% to 77% (Chapter 4) of the total solid P in sewage sludge.

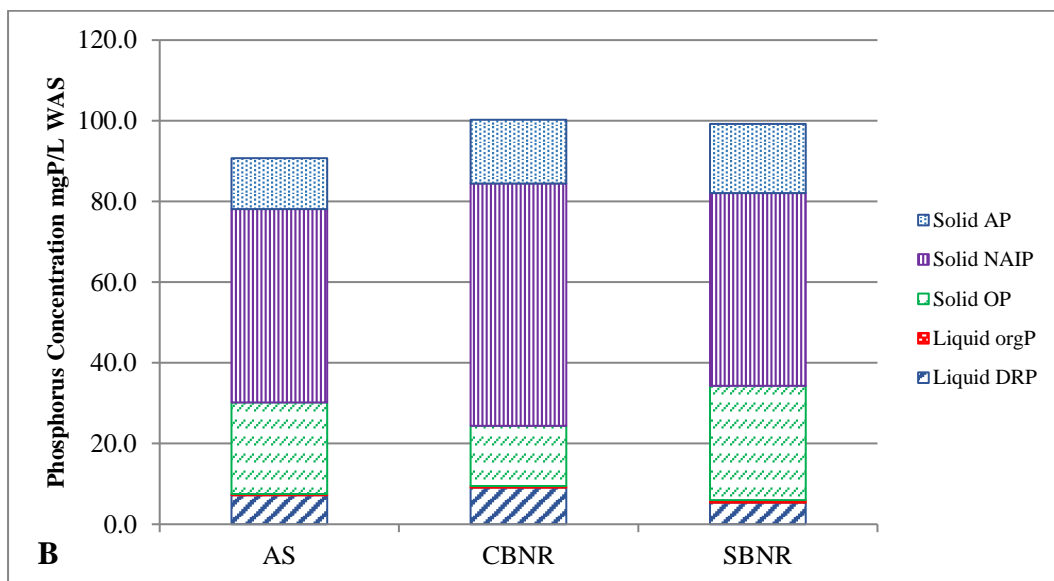
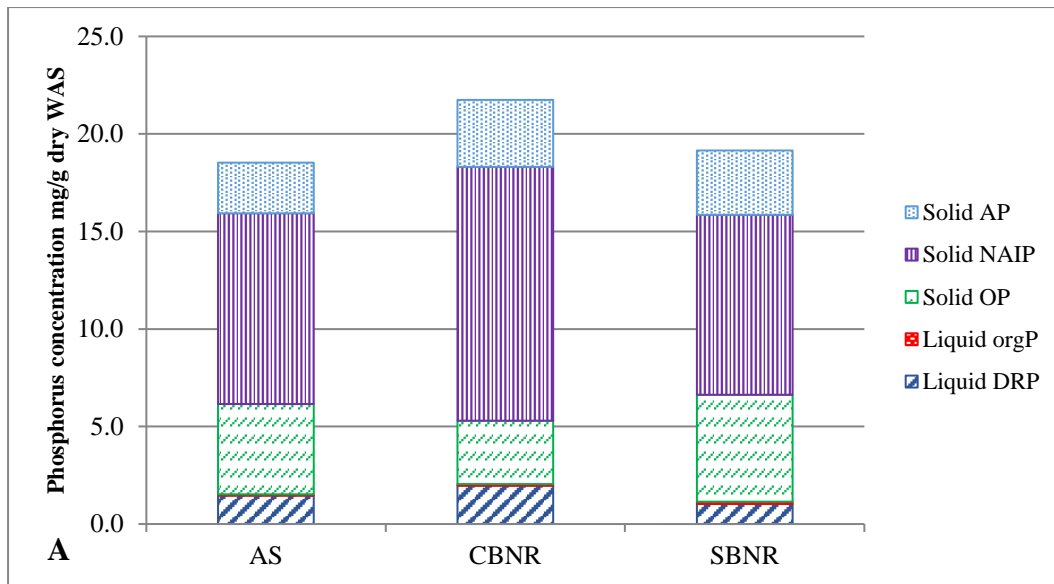


Figure 5.1: Overall phosphorus fractionation for WAS (AP = apatite phosphorus; NAIP = non-apatite inorganic phosphorus; OP = organic phosphorus; DRP = dissolved reactive phosphorus (orthophosphate)); (A) estimated as g/g dry sludge and (B) estimated as mg P/L WAS

5.4 Aqueous phosphorus results

Phosphorus release and fractionation were studied in tests lasting 21 days. The temperature and pH of the samples were 35 °C and pH 4 for treatment, and 20 °C and pH 7 for the control. Table 5.3 shows the initial soluble P, soluble P after 1 day and final soluble P (i.e. after 21 days) for all sludge types. All WAS types showed similar levels of initial soluble liquid P, with Table 5.3 indicating substantial levels of soluble P released with time for the different sludges. The most release occurred in the 1st day while the maximum release of P from 9.1 mg/L to 147.1 mg/L (after 21 days) was observed at a pH of 4 and a temperature of 35 °C for the CBNR WAS. Less release of P (5.4 mg/L to 77.5 mg/L and 7.2 mg/L to 82.5 mg/L) was observed with the SBNR and AS sludges respectively. The CBNR and SBR sludges released 78% and 70%, respectively, of its 21 days total release in one day, while the AS sludge released only 53% of its 21 day release after one day.

A replicated batch test was conducted on CBNR WAS under pH 4, temperature 35 °C and anaerobic condition for verify CBNR finding. Three replicates samples were run under above parameters. The test was conducted for 21 days. The average DRP concentration at day 21 was 149.4 mg/L and standard deviation was 0.8 mg/L. The replicate study results show similar DRP release from CBNR WAS. Full data are presented in Table B.3 in Appendix B.

Table 5.3: Change in soluble phosphorus in WAS after 21 days of incubation under anaerobic condition

Sludge source	Initial DRP ((mg P/L WAS)/(mg/g dry WAS))	pH 7, 20 °C (control)		pH 4, 35 °C (treatment)	
		DRP after 1 day ((mg P/LWAS)/(mg/g dry WAS))	DRP after 21 days ((mg P/L WAS)/mg/g dry WAS))	DRP after 1 day ((mg P/L WAS)/(mg/g dry WAS))	DRP after 21 days ((mg P/L WAS)/(mg/g dry WAS))
AS	7.2/1.5	35.9/7.3	55.8/11.4	43.4/8.9	82.5/16.8
CBNR	9.1/2.0	88.1/19.1	123.3/26.7	114.3/24.8	147.1/31.9
SBNR	5.4/1.0	39.1/7.5	67.7/13.1	53/10.2	77.5/15.0

The effect of pH 4 and temperature 35 °C on P release in the liquid phase for the three sludges is also shown by the track profiles presented in Figure 5.2.

As can be seen, the majority of the P was released in the first few days. Although a pH of 4 and a temperature of 35 °C led to the greatest aqueous P release for all sludges, there was a different amount of P release for each sludge implying that the type of sludge (which directly relates to the type of plant) may prove an important factor in P release. Note that the AS results here are for a different batch from the same plant considered in Chapter 4.

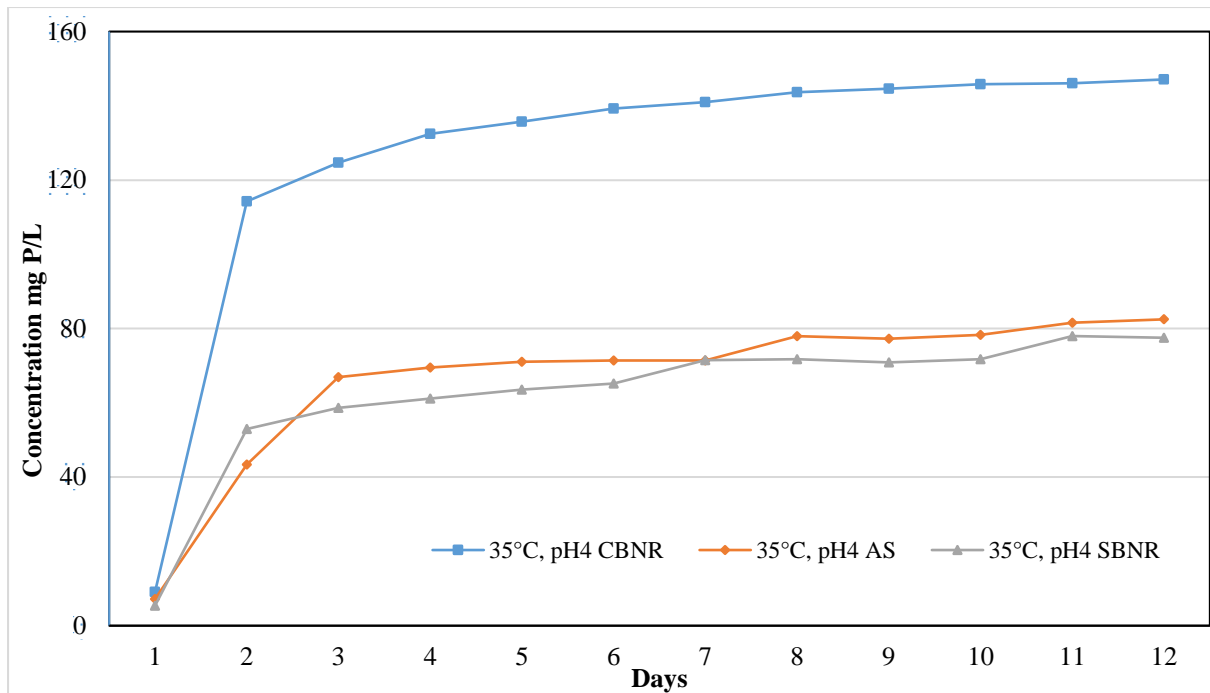


Figure 5.2: Phosphorus release change in WAS from start to 21 days of incubation under anaerobic condition

Table 5.4 shows a summary of non-linear regression results from the Excel Solver routine. The method was used to fit the first order decay (k) and P release. Minimisation of square residuals was used. The estimated (k) values of DRP and TDP among three sludges under 21 days treatment show higher values (1.2-1.4) for CBNR WAS. The estimated TDP release showed a corresponding maximum TDP release of 142.3 mgP/L for CBNR sludge.

Table 5.4: Estimation of kinetic coefficients for DRP & TDP for different sludges

DRP (mg P/L WAS)							
WWTPs	Treatments			k (1/day)	P max (mg/L)	P release (mg/L)	Av. Misfit (mg/L)
	Temp °C	pH	Days				
AS	20	7	21	0.6	49.9	42.7	1.4
AS	20	4	21	0.8	66.5	59.3	0.8
AS	35	4	21	0.8	77.4	70.2	1.0
CBNR	20	7	21	1.2	120.7	111.6	1.0
CBNR	20	4	21	1.1	129.4	120.3	1.1
CBNR	35	4	21	1.4	141.7	132.6	1.5
SBNR	20	7	21	0.6	54.8	49.4	2.2
SBNR	10	4	21	0.5	62.5	57.1	1.9
SBNR	35	4	21	1.0	71.0	65.6	1.4
TDP (mg P/L WAS)							
WWTPs	Treatments			k (1/day)	P max (mg/L)	P release (mg/L)	Av. Misfit (mg/L)
	Temp °C	pH	Days				
AS	20	7	21	0.6	50.5	43.0	1.4
AS	20	4	21	0.9	67.0	59.5	0.7
AS	35	4	21	0.8	78.7	71.2	0.9
CBNR	20	7	21	1.2	121.7	112.2	0.8
CBNR	20	4	21	1.2	130.7	121.2	1.2
CBNR	35	4	21	1.4	142.3	132.8	1.5
SBNR	20	7	21	0.6	55.0	49.0	2.2
SBNR	10	4	21	0.5	63.1	57.1	1.8
SBNR	35	4	21	1.0	71.5	65.5	1.4

For comparative purposes, the results from this research can be contrasted with other studies that have documented P release from sludges held for similar incubation times under low pH conditions. For example, Chen et al. (2007) observed final (i.e. after 20 days) TDP concentration of 81 mg P/L from a WAS held at a pH of 4 at room temperature. The WAS was collected from the underflow to a secondary sedimentation tank treating municipal waste, with the underflow having a TSS value of approximately 14,000 mg/L. Wu et al. (2009) using primary sludge observed soluble phosphorus concentrations of 48 mg/L and 37 mg/L at a pH 5 and pH 6 after 9 days of batch fermentation. The sample was obtained from the underflow from primary sedimentation tanks of a municipal WWTP, with the underflow

having a TSS value of around 19,000 mg/L. Finally, Xu et al. (2015) observed P concentrations of 44 mg/L, 52.5 mg/L and 90.7 mg/L in a sludge under pH of 6.8, pH 5 and pH 2 respectively. The sludge used in their study was obtained from a WWTP with an anaerobic/anoxic/aerobic sequence having a TS value of 26,800 mg/L.

5.5 Phosphorus in solids results

Medeiros et al. (2005) observed 2.3% P and 2.6% P from sewage sludge samples taken from an urban wastewater treatment plant, and some plants designed and operated for maximum P removal can have 5% P to 7% P in the WAS (Yuan et al., 2012). In the present research, the initial WAS total P (1.9% P to 2.2% P) was relatively similar between the three treatment plants (Figure 5.1), with the two BNR plants operated to achieve high N removal. For comparison, Xie et al. (2011) observed 1.63% P and 1.7% P in domestic activated sludge solids in an anoxic phase associated with an EBPR process. The raw sewage of those plants was comprised almost entirely of domestic wastewaters.

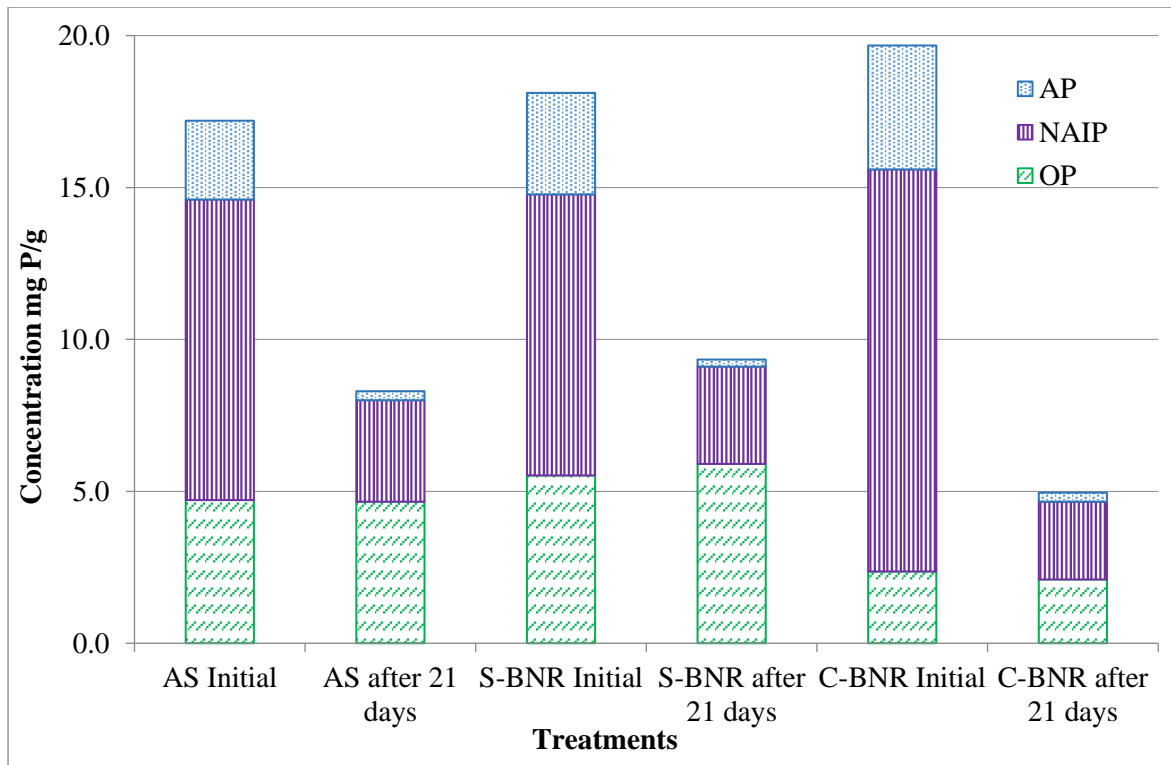


Figure 5.3: Phosphorus fractions in WAS solids before and after 21 days incubation under pH 4 and 35 °C

The CBNR WAS had the highest TSP content (19.7 mg/g) with most of it in the form of NAIP 13.2 mg/g, followed by AP 4.1 mg/g and the smallest fraction of OP 2.4 mg/g.

Although, the AS and SBNR sludges contained a similar amount of initial IP (12.5 mg/g and 12.6 mg/g), the SBNR sludge had more organic P at 5.5 mg/g. The CBNR sludge contained the highest initial NAIP and AP fractions at 68% and 21% of the TP respectively. The CBNR plant has only slightly higher hardness than the AS plant and yet has a greater amount (and fraction) of AP in its dry sludge. Full data are presented in Table B.2 in Appendix B.

5.6 Discussion

The total and relative amounts of the forms of P available initial and after 21 days treatments were calculate and presented in Table 5.5. The Table 5.5 shows the total change in NAIP, AP and OP within the sludge over the 21 days of experiment. After incubation, the sludge with the lowest TSP content was CBNR (5.0 mg/g) followed by AS (8.3 mg/g) and SBNR (9.3 mg/g). The results indicate that compared to the initial amount of TSP in the sludge, the amount retained in the sludge in terms of TSP was 48%, 25% and 52% for the AS, CBNR and SBNR sludges after incubation at 35 °C and pH of 4. Similarly, NAIP fractions retained were 33%, 19% and 35% respectively. The OP fractions remained approximately constant over time, thus the reductions in NAIP and AP fractions corresponded to P release to the bulk liquid. Figure 5.3 also shows how the effect of pH was the greatest on the AP fraction with the release of practically all AP from the solids at a pH of 4.

Table 5.5: Phosphorus release from WAS solid fractions under pH 4 and 35 °C (Expressed as mg/g of dry solid sludge)

Sludge	Initial TP (mg/g dry sludge)	P Fractions	Initial mg/g dry solid sludge	After 21 days	% P Initially Available	% P Released	% P Retained
AS	18.5	TSP	17.2	8.3		52	48
		IP	12.5	3.6	73	71	29
		OP	4.7	4.7	27	0	100
		NAIP	9.9	3.3	58	67	33
		AP	2.6	0.3	15	88	12
CBNR	21.8	TSP	19.7	5.0		75	25
		IP	17.3	2.9	88	83	17
		OP	2.4	2.1	12	13	88
		NAIP	13.2	2.6	67	80	20
		AP	4.1	0.3	21	93	7
SBNR	19.2	TSP	18.1	9.3		49	51
		IP	12.6	3.4	70	73	27
		OP	5.5	5.9	31	-7	107
		NAIP	9.2	3.2	51	65	35
		AP	3.3	0.2	18	94	6

The results from the solids fractionation (Figure 5.3) correlate with the results found in the aqueous tests (Figure 5.2), in that lower P concentrations in the sludge tracked the higher aqueous P concentrations, as P was released to the bulk liquid during the incubation period. Overall, the total P release from the AS, CBNR and SBNR sludge solids were 52%, 75% and 48% respectively. All sludges released more P at a pH of 4 (T = 35 °C) than the control conditions (pH = 7 and 20 °C); for example, the AS sample at a pH 4 and a temperature of 35 °C released 44% more P than the control reactor conditions. The greater P release at the low pH is in agreement with reports of higher P availability in the aqueous phase at pH below 6 (Chen et al., 2007; Latif et al., 2015).

Examining the data in Table 5.3 for aqueous P results, shows CBNR sludge had the highest and the quickest release of P. This finding was observed after estimation of kinetic coefficient

of P release from all three WAS samples. The highest CBNR kinetic coefficient ($k=1.2$ to $k=1.4$) calculated in Table 5.4 justified the highest and quickest release of DRP and TDP from CBNR sludge. The faster release of P from CBNR sludge than from AS sludge is expected because the CBNR sludge should have more bio-P bacteria (though not as much as EBPR sludge). Further investigation would be needed to understand why the CBNR sludge showed faster P release than the SBNR sludge, which should also have been expected to have more bio-P bacteria than AS sludge.

Because of the quicker release of P at pH 4 from the CBNR sludge relative to the other two sludges, an additional set of tests was conducted on the CBNR sludge only with testing at pH 5, pH 6 and at 20 °C. The data for this additional CBNR test are provided in Appendix F. The initial characteristics of the WAS sample was pH 7 and TSS 4905 mg/L. The results show the highest soluble P 134.6 mg/L was noticed under pH 4 and after 11 days treatment. These results support the finding on the AS batch testing in Chapter 4 that greater P release is found under treatment at pH of 4.

There is the potential that the measured NAIP does not include poly-P or that a pH of 4 will kill so many cells that the remaining NAIP is only chemically sorbed P. Quantitative analysis of this issue is beyond the scope of this research, but preliminary testing was done to look for bio-P bacteria at the most harsh conditions tested (pH of 4, temperature of 35 C, anaerobic conditions, 7 days). The methods and results are in Appendix I. Neisser staining showed bio-P bacteria present in the initial WAS, control WAS after 7 days, and pH of 4, 35 C WAS after 7 days.

Development of P release reactors could be limited because WAS treatment at pH 4, 35 °C, and anaerobic conditions could release heavy metals that cause problems. Also, Ca, Mg, and Fe could be released and interfere with later P recovery. Metal and cation concentrations (Ca,

Mg, Mn, Fe, Cd, Cu, Zn, and Ni) released under HCl treatment at different pH (4, 5, 6, 6.9 control & 8) was monitored. The details of these preliminary test results are provided in Appendix J. The key findings of this test are that: (1) of the toxic metals, Zn is the only one that increases significantly during P release at pH of 4, and so there might not be significant issues with a P recovery reactor, and (2) Fe, Ca, Mg also increase which could have implications for P recovery depending on what process is used for P recovery.

Between sludges, it is evident that the P release from the CBNR sludge was the highest for both control and treatment conditions. In order to determine whether this result was an artefact of the system, (i.e. more P was released simply because more P was available); the amount of P release was normalised by the fraction of P in the sludge available to be released. Since as mentioned earlier, the OP fraction in the sludge essentially remained constant (and it is well known that the OP is the hardest fraction to release under acidic conditions (Xu et al. (2005)), the fraction available for release was essentially the NAIP and AP (i.e. the IP). Since the CBNR had the highest initial P (TP 21.8 mg/g dry sludge and NAIP 13.2 mg/g dry solid sludge); the highest % P release (TSP 75% and NAIP 80%) and the highest k fitted value ($k=1.2$ to $k=1.4$), it is evident that it had the most potential to release P once normalisation was taken into account.

5.7 Conclusions

The results show that high non-apatite inorganic phosphorus in WAS is critical to achieving high P release, both on the basis of fractional release and total P released. The results here indicate that P fractionation studies with multiple sludges can indicate which sludges are better for P release. The CBNR sludge showed highest initial P available, the highest P release under optimal condition and highest k fitted value, it is evident that it had the most potential to release P.

These results in turn open the door for future work on development of P release reactors. The results indicate the potential value in evaluation of the forms of P in the solid WAS as well as the total P. Future P recovery using P release reactors might then focus on the more promising wastewater treatment plants.

Chapter Six: Effects of Acid Type on Phosphorus Release and Treatment

Side-Effects

The previous chapter four and five examined the combined effect of pH, temperature and ORPs on P release from AS, CBNR and SBNR samples. The previous results indicated that a pH <6 and a temperature of 30-35°C were good conditions for optimal P release from WAS samples. Comparison of P release between AS, CBNR and SBNR indicated that CBNR sludge had the quickest and the highest P released. Previous chapters work adjusted pH by using only a single acid (HCl). The quantitative effect of other acids on P release at a pH of 4 should be studied for design of P release reactors. The CBNR WAS was studied because it was the most promising for P release. This chapter provides details of P release from CBNR WAS at pH <6 under different acids. Solid P fractionation and soluble liquid phase P analysis was monitored.

This chapter did not examine WAS produced by EBPR plants. The scope is limited to studying the P release potential of certain acids. The acids were selected for different reasons. Acetic acid was selected because it is known to have an effect on P retention in BNR plants. Oxalic and citric acids had been studied in previous research related to P dissolution. Peracetic acid was used as a control because of its oxidising effect on microbes while having a similar structure to other organic acids. Sulphuric and nitric acids were not used because of the reduction reactions that would occur in anaerobic conditions could make interpretation of results difficult. The dissociation constant (pKa) is a quantitative measure of the strength of an acid in solution. The pKa values are shown in Table 6.1 below. Because the tests were conducted at a pH of 4 which is less than the pKa of acetic acid, more acetic acid would need to be added to obtain the target pH. Peracetic acid addition results in a low pH by oxidising cell mass, creating organic acids. Glutaraldehyde was also added in some test vessels as a control to evaluate biological versus not biological origins of P release.

Four batch tests were conducted to examine the effect that different acids have on P release. In addition, preliminary tests were done on the characteristics of sludges after treatment with a variety of acids. Specifically, these tests were on settleability, filterability, and COD. The purpose of each test is summarised in Tables 6.2 below. The specific test conditions for each test vessel are in section 6.2.

Table 6.1: Dissociation constants (pKa) of acids (Kortüm & Andrussow, 1961; Snoeyink and Jenkins, 1980)

Acids	Formula	pKa
Oxalic	$C_2H_2O_4$	1.23
Citric	$C_6H_8O_7$	3.14
Acetic	$C_2H_4O_2$	4.76
Peracetic	CH_3CO_3H	8.2
Hydrochloric	HCl	-3

Table 6.2: Summary of purpose of different batches

Batch	Purpose	pH tested	Temp (°C)	Analysis
1	Effect of hydrochloric/Acetic acid on P release	4 & 6.5 (as control)	20 & 35	DRP, Solid P fractions (NAIP, AP & OP)
2	Effect of hydrochloric/Acetic acid on P release	4, 5 and 6.3 (as control)	20	DRP, Solid P fractions (NAIP, AP & OP)
3	Effect of different acids and glutaraldehyde on P release	4 & 6.7 (as control)	20	DRP, Solid P fractions (NAIP, AP & OP)
4	Effect of different acids on P release	4 & 6.7 (as control)	20	DRP

The aims of this research are (1) to identify the effects of different acids on P release, and (2) to examine how acid treatment for P removal might affect later sludge processing. The results from testing of acetic and hydrochloric acid are presented, then the results from testing of other organic acids are presented, and then the preliminary results of sludge characteristic testing with various acids are presented. Finally, an overall discussion is presented.

6.1 Introduction

Organic acids release protons as with HCl. Addition of organic acids will increase the chemical oxygen demand (COD) and biological oxygen demand (BOD) and likely change the behaviour of specific bacteria species in complicated ways. For these reasons, the choice of acid used to release P from WAS could be important. No literature was found on this specific question. There is literature on the effect of different acids on release of P from phosphate rocks and from ADS. Sample references are summarised here.

One study by Kpombrekou-a and Tabatabai (1994) shows the effect of acids on P release from phosphate rocks. This study used two different types of phosphate rocks (low and medium reactive) and different acid strengths of 1 mmol/L and 10 mmol/L. One gram of

sample was equilibrated with 25 mL of each acid (1 mmol/L and 10 mmol/L) at 25 °C for 25 hours. Under both acid strengths (1 mmol/L and 10 mmol/L), citric and oxalic acids released more P from two rock samples than other organic and inorganic acids (HCl, H₂SO₄ and HNO₃). This study also shows that there is no relation between the dissociation constant and P release.

Research by Pakdil and Filibeli (2007) observed that both inorganic and organic acids were effective at phosphorus release from ADS. The sludge sample was taken from a belt press after digestion at two different wastewater treatment plants. The samples were dried at 103 ± 2 °C and leached with different acids (sulphuric, hydrochloric, nitric, citric and oxalic) under different concentrations up to 4 M. The P release varied between 11.4 and 15.95 mg P/g DS under leaching with inorganic acids for sludge 1 and 2 and with organic acids between 11-12 mg P/g DS at 0.5 M acid concentration with sludge 1. This study also shows that P release decreased at 0.5 M citric acid for sludge 2. Among inorganic acids, nitric acid accomplished higher P release and among organic acids, 0.5 M oxalic acid was more effective in releasing P from dry sludge. The P leaching rapidly decreased with the higher organic acid concentration while it increased with the higher concentration of inorganic acid. This also suggested that P release can be dependent on the origin of the sludge and its composition.

Vaneekhaute et al. (2017) studied four different mechanical pre-treatments (microwave heating, conventional heating, ultrasonic treatment, and orbital shaking) in combination with chemical dosing of three acids (citric, formic and hydrochloric acids) down to pH 4, pH 5 and pH 6 to enhance P release from ADS. The sample was digested and collected from a mesophilic (35 °C) anaerobic digestion plant with an input feed mainly consisting of dairy manure. 5 gm of digestate sample was adjusted to pH 4, pH 5 and pH 6 by adding 2 M acids and then four different mechanical treatments applied and the sample centrifuged to separate solid and liquid. Soluble ortho-P were analysed on liquid aliquot. Citric acid generally

released more soluble ortho-P into the liquid fraction as compared to the other acids at pH 6 for all mechanical treatments and at pH 5 for microwave, orbit shaking and conventional heating. At pH 4, no significant differences were found between the various acids per mechanical treatment, except orbital shaking where citric acid resulted in the highest ortho-P release.

Differences in P release between addition of organic and inorganic acids could be because of active biological processes or because of cell lysis or chemical desorption from surfaces. More standard methods for stopping cell activity (such as sterilisation) would not help because they would lead to cell lysis. Ju et al. (2005) controlled for biological activity in sludge by treatment with glutaraldehyde (3% w/v). Glutaraldehyde is known to crosslink all amino groups in cellular components, especially the proteins (including enzymes), causing cell death while preserving the physical structure of the organism. To differentiate between the P released from the polyphosphate (poly-P) and that from the non-poly-P, Ju et al. (2005) conducted experiments with two sludge samples. One sample was WAS from a smaller plant that used an anaerobic/oxic (A/O) ditch process that consisted of a three-stage anaerobic selector (including a RAS denitrification stage and two subsequent anaerobic stages) and the other sample was from activated sludge plant. Samples were taken before and after the glutaraldehyde treatment for later analysis, to check if and/or how the treatment affected the phosphorus concentration in the water. Ju et al. found little difference in P release after glutaraldehyde addition. It will be worthwhile to apply glutaraldehyde in this research to better understand the biological and chemical effect on P release. If glutaraldehyde is added and P release is not affected, one would expect that P release is dominated by chemical processes, because stopping cell activity has had no impact on P release. If glutaraldehyde is added and P release is increased, one would expect that P release is a biological process where live cells are stopping release of P. If glutaraldehyde is added and P release is

decreased, one would expect that P release is a biological process where live cells are actively releasing P.

There is a lack of knowledge about how acids other than HCl affect P release, and about how the P fractions change due to acid effects. Information about sludge characteristics such as settleability, filterability and methane potential after treatment with acids could be helpful for design of new P release facilities.

6.2 Experimental design

The process of P release and the effect of different acids was tested with four different batches of CBNR sludge. The detail of acids and other parameters are illustrated in Table 6.3 below. The complete data for this chapter is provided in Appendix C.

Table 6.3: Operating parameters tested for study of effect of different acids on P release

Test chemicals	pH	Temp °C	Test Vessels	Days	Parameters Tested	Batch
Hydrochloric	4	35	1	17	DRP, TSP, IP, OP, NAIP & AP	1
Hydrochloric	4	20	1	17	DRP, TSP, IP, OP, NAIP & AP	
Acetic	4	35	1	17	DRP, TSP, IP, OP, NAIP & AP	
Acetic	4	20	1	17	DRP, TSP, IP, OP, NAIP & AP	
Control	6.9	20	1	17	DRP, TSP, IP, OP, NAIP & AP	
Hydrochloric	4	20	1	12	DRP, TSP, IP, OP, NAIP & AP	2
Hydrochloric	5	20	1	12	DRP, TSP, IP, OP, NAIP & AP	
Acetic	5	20	1	12	DRP, TSP, IP, OP, NAIP & AP	
Control	6.3	20	1	12	DRP, TSP, IP, OP, NAIP & AP	
Hydrochloric	4	20	1	7	DRP, TSP, IP, OP, NAIP & AP	3
Acetic	4	20	1	7	DRP	
Citric	4	20	1	7	DRP	
Oxalic	4	20	1	7	DRP, TSP, IP, OP, NAIP & AP	
Glutaraldehyde	6	20	1	7	DRP, TSP, IP, OP, NAIP & AP	
Control	6.7	20	1	7	DRP, TSP, IP, OP, NAIP & AP	
Hydrochloric	4	20	1	7	DRP	5
Citric	4	20	1	7	DRP	
Oxalic	4	20	1	7	DRP	
Peracetic	4	20	1	7	DRP	
Control	6.7	20	1	7	DRP	

The pH of sludge was adjusted from start until stable at pH 4. Table 6.4 shows the amount of acid added and the time needed to reach pH 4. All the acids were diluted to 1 M and then 1 M diluted acids were used for pH adjustment of samples. Every 12 hours the pH of the solution was tested. pH was readjusted by addition of corresponding 1 M acids. The time until the pH stabilised at 4 varied between acids. A pH 6 was noticed after treated with 3% glutaraldehyde sludge and the pH did not change throughout the experiment. Gas bubbles were noticed after addition of peracetic acid in the sludge sample. The HCl sample needed the least volume of acid and the shortest time for pH stabilisation.

Table 6.4: Volume of different acids added to reach pH

Chemicals	Strength	Total chemical used (mL/L)	No of days need to reach pH 4
Hydrochloric	1 M	5.5	3
Acetic	1 M	20	7
Citric	1 M	7.5	6
Oxalic	1 M	11.8	6
Peracetic	1 M	7.5	5
Glutaraldehyde	25%	120	1*(pH6)

There is uncertainty regarding the side-effects that treatment of WAS for P release could have on other parts of sludge management i.e. settleability, filterability and methane production potential. Preliminary tests were designed for identification of the potential importance of these side effects under different acid treatments. Table 6.5, 6.6 and 6.7 shows details of the parameters tested.

Sludge Volume Index (SVI) is used to monitor the settling characteristics of activated sludge and other biological suspensions in a sewage system (Dick & Vesilind, 1969). Another option for the concentration of solids of treated WAS may be a filtration process. The filtration rate of sludge is normally described by the specific resistance to filtration (SRF), which is

calculated from a plot of the inverse flux (t/V) versus filtrate volume (V). The higher the specific resistance, the more difficult it is to dewater sludge and vice versa (Karr & Keinath, 1978). Methane produced by a WWTP can be used for commercial sale or utilised on-site to balance the costs of system installation and operation. Sludge is not only biologically degradable and a source of P, but also a good material for methane fermentation. Anaerobic digestion technology has been widely used as a main process for the stabilization of sludge and the production of biogas (Sreekrishnan et al., 2004). Testing for methane production potential usually involves testing of replicates of sample with and without inoculum, and over multiple weeks. For these preliminary tests, only the COD was measured as a surrogate for methane production potential.

Table 6.5: WAS SVI estimation treated with acids

Test chemicals	pH	Temp °C	Test Vessels	Days	Batch
Control	6.3	20	1	12	A
Hydrochloric	4 & 5	20	1	12	A
Acetic	5	20	1	12	A
Control	6.9	20	1	7	B
Hydrochloric	4	20	1	7	B
Citric	4	20	1	7	B
Oxalic	4	20	1	7	B
Peracetic	4	20	1	7	B

Table 6.6: WAS SRF estimation treated with acids

Test chemicals	pH	Temp °C	Test Vessels	Days	Batch
Control	6.9	20	1	7	B
Hydrochloric	4	20	1	7	B
Citric	4	20	1	7	B
Oxalic	4	20	1	7	B
Peracetic	4	20	1	7	B

Table 6.7: WAS COD estimation treated with acids

Test chemicals	pH	Temp °C	Test Vessels	Days	Batch
Control	6.9	20	1	7	B
Hydrochloric	4	20	1	7	B
Citric	4	20	1	7	B
Oxalic	4	20	1	7	B
Peracetic	4	20	1	7	B

6.3 Source, sampling, and characteristics of WAS

The WAS used in this study was obtained from a carousel biological nutrient removal WWTP (CBNR). The plant contained aerobic, anoxic and anaerobic stages in a race-track fashion, with sludge being settled in a clarifier. The sample was directly collected from the WAS main pipe. Samples were placed in air-tight plastic containers, transported to the laboratory and analysed for initial parameters of WAS within one hour of collection. The different acid treatments (e.g. pH adjustment) were applied on the day of sample collection. The initial characteristics of the different batch samples are shown in Table 6.8.

During these tests, the CBNR plant was undergoing expansion and changes to its incoming wastewater composition. This resulted in variable conditions (pH, DRP and TSS) in the CBNR WAS. The high variability in both pH and TSS between WAS batches makes it difficult to compare results.

Table 6.8: Initial characteristics of WAS samples

Parameters	Batch 1	Batch 2	Batch 3	Batch 4
pH	6.9	6.3	6.7	6.7
DRP in sludge (mg P/L)	4.42	44.9	15.8	24
Sludge TSS (mg/L)	4957	10940	5605	7530

6.4 Effect of acids and glutaraldehyde on phosphorus release

Two batch tests were conducted to examine the difference in P release using hydrochloric (HCl) and acetic acid (AA) at pH 4 and pH 5, temperature 20 °C and 35 °C. Batch 1 examined P release using HCl and AA at pH 4, temperature 20 °C and 35 °C for 17 days and the control at pH 6.9. The highest DRP 150 mg P/L (30 mg DRP/g of dry WAS) was monitored at pH 4 adjusted with HCl at 35 °C on day 11 with 83% of the maximum release happening after 1 day. DRP was greater for HCl than for AA at both 20 °C and 35 °C. There was little difference between the control and the addition of acetic acid to a pH of 4. Figure 6.1 shows the detailed result of this study. The full data are provided in Table C.1 in Appendix C.

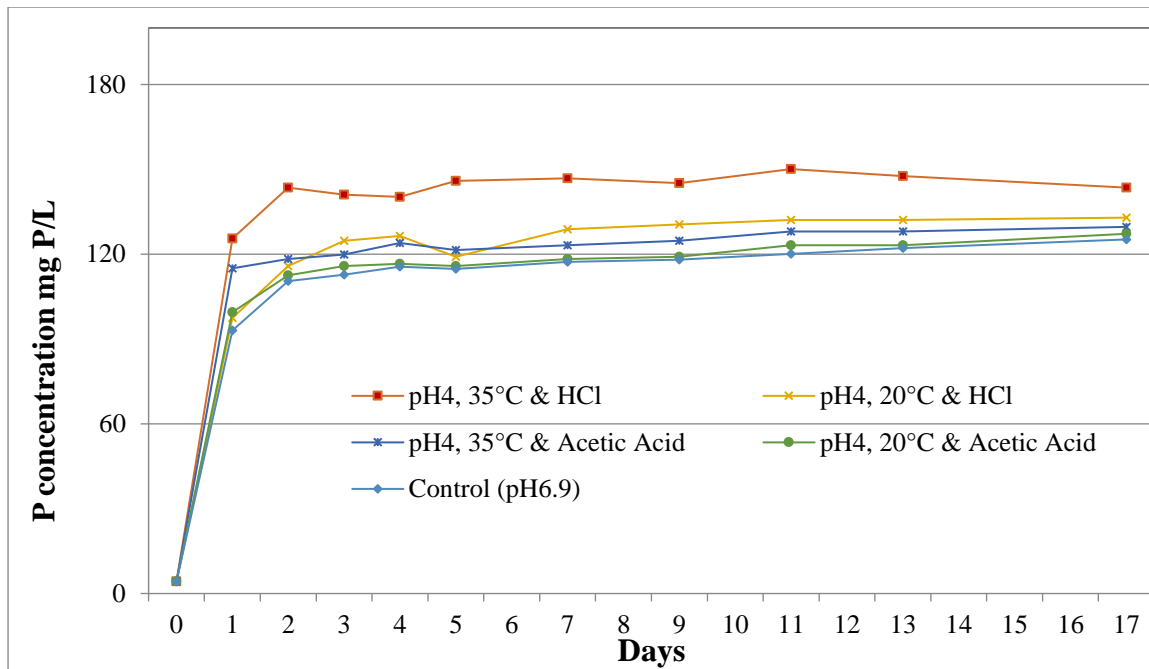


Figure 6.1: DRP release under hydrochloric and acetic acid (Batch 1)

The results from the solid fractionation mirror and corroborate the results found in the aqueous tests. Figure 6.2 highlights the P fraction initially and after 17 days with temperatures of 20 °C and 35 °C, pH of 4 adjusted with HCl and AA, and control at pH 6.9. The lowest P retained (28% of P) was on the sample treated with pH 4 adjusted with HCl, 35 °C and anaerobically. The CBNR sample released the highest AP (91%) and NAIP (80%) fraction but lower OP (7%) fraction. A similar result was found with a different batch of CBNR WAS and reported in Chapter 5 (AP 93%, NAIP 80% and OP 13% released). The detailed data of this Chapter are provided in Table C.2 in Appendix C.

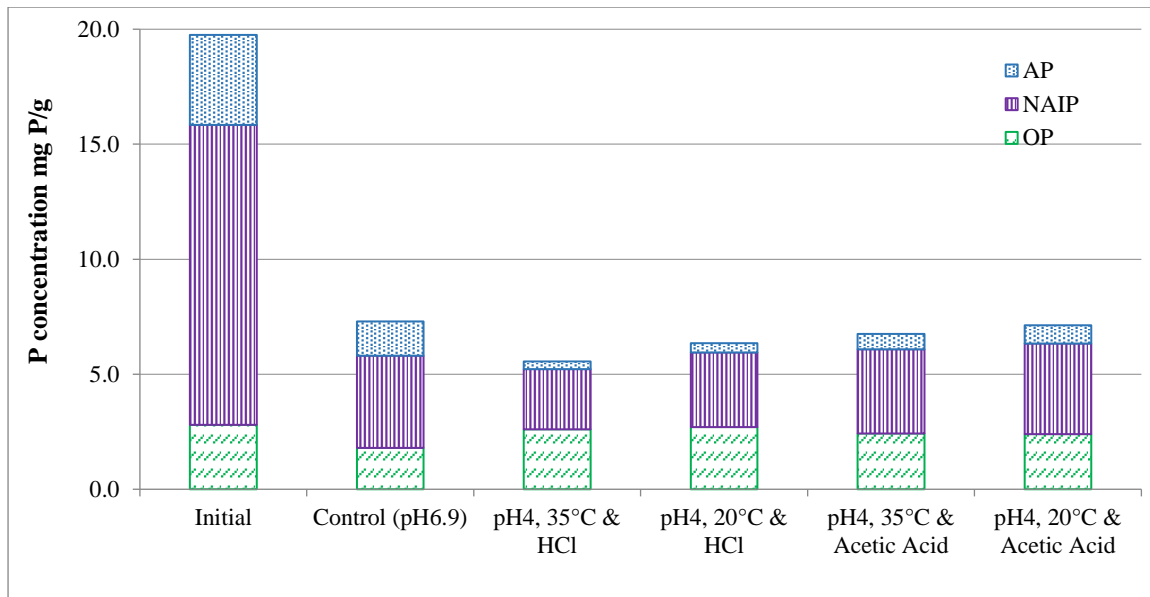


Figure 6.2: Phosphorus fraction under hydrochloric and acetic acid initially and after 17 days (Batch 1)

In batch 2 phosphorus release was examined under pH 4 and pH 5 adjusted with HCl, and under pH 5 adjusted with AA, temperature 20 °C for 12 days and the control at pH 6.3. The highest DRP 408.mg P/L (37 mg DRP/g dry WAS) was monitored at pH 4 adjusted with HCl at 20 °C after 12 days. There was little difference in the final DRP after 12 days for the control, and another two sets at a pH of 5 (HCl and acetic acid adjusted). The slower P release was noted under pH 5 adjustment with AA acid in the first five days. Figure 6.3 shows the detailed results of this study. The full data are provided in Table C.3 in Appendix C. These results indicated that AA was not superior to HCl at a pH of 5. Combined with the results from batch 1, there seemed to be no clear benefit on P release from acetic acid addition.

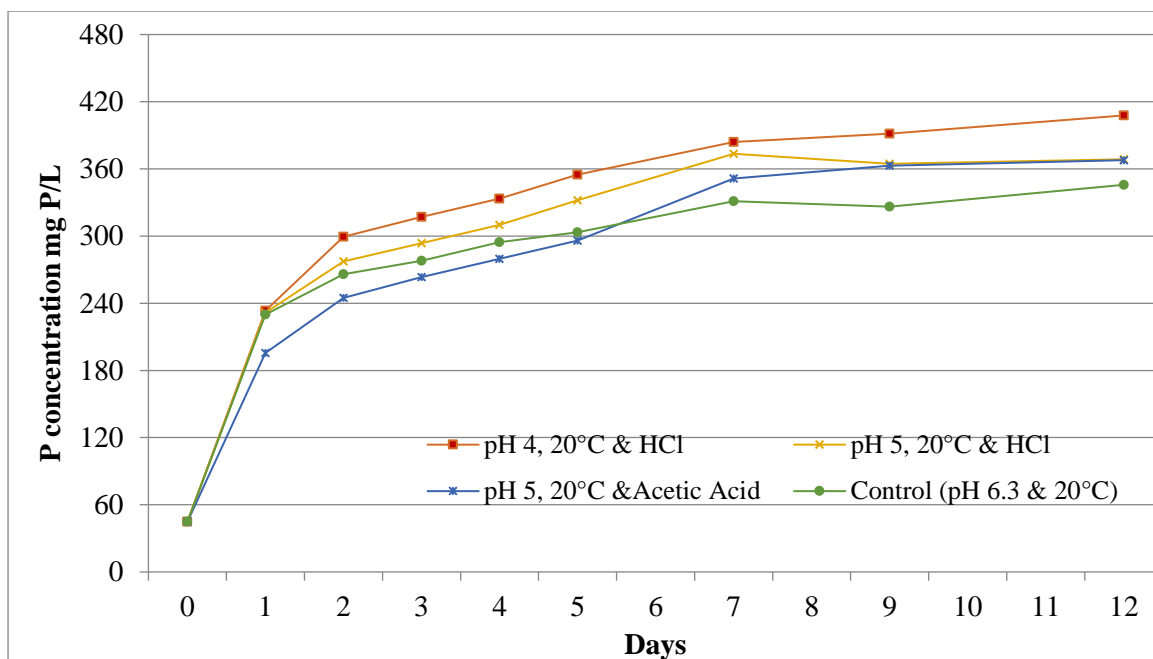


Figure 6.3: DRP release under pH 4, pH 5 and pH 6.3 at 20 °C, anaerobic adjusted with HCl and AA (Batch 2)

The results from the solid fractionation support the P release results found in the aqueous tests. Figure 6.4 highlights the P fraction initially and after 12 days with a temperature of 20 °C, pH of 4 and pH of 5 adjusted with HCl and pH of 5 adjusted AA, and control at pH 6.3. The highest P release was 71% for the sample treated with pH 4 adjusted with HCl and 20 °C. The similar treatment also releases the highest AP (97%) and NAIP (83%) fractions. The solid results support the finding that there is little difference between acetic acid and HCl at a pH of 5. The results show that a pH of 4 with HCl gives less AP and also less NAIP than for treatment with HCl and a pH of 5. The detailed data is provided in Table C.4 in Appendix C.

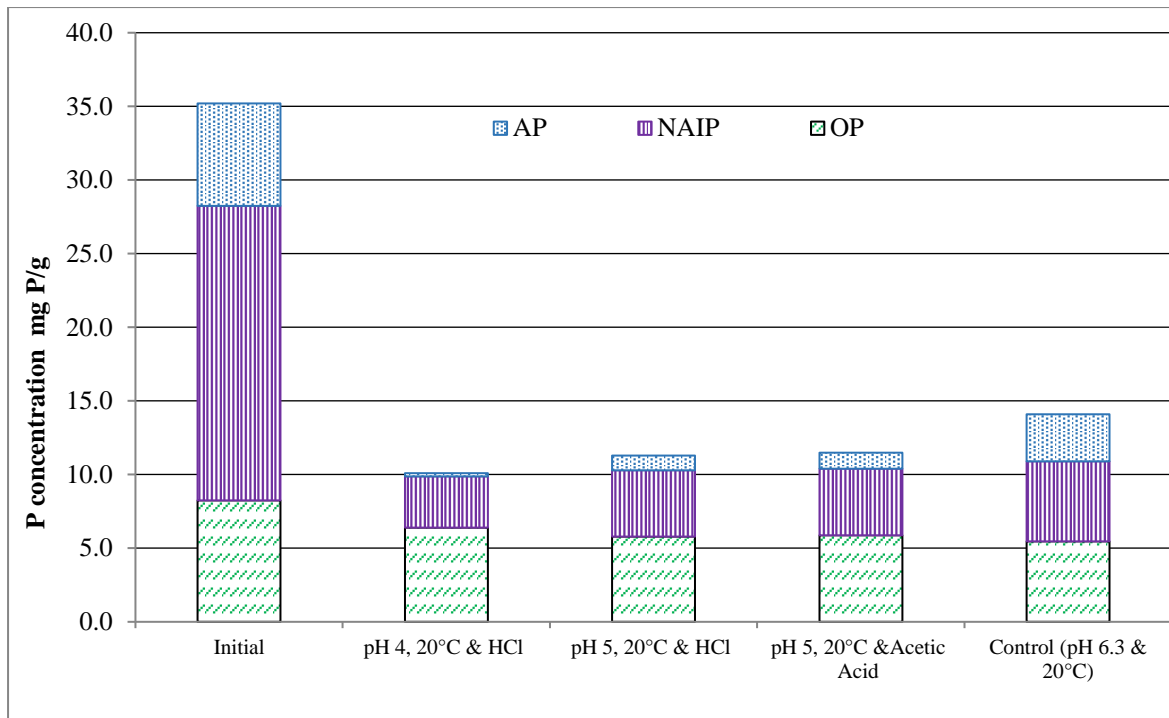


Figure 6.4: Phosphorus fraction release initially and after 12 days under pH 4, pH 5 adjusted with HCl, AA and control at pH 6.3 at 20 °C (Batch 2)

Further two batch tests (batch 3 and batch 4) were performed to evaluate the P release variation using different acids. Organic and inorganic acids (1 M strength) are used to adjust pH to 4, at 20 °C and anaerobic condition for both batches. Both batch samples were collected from the same biological nutrient removal plant having aerobic/anoxic and anaerobic cycles (CBNR).

The third batch sample was adjusted to pH 4 using hydrochloric, acetic acid, citric acid, and oxalic acid, temperature at 20 °C, one control at pH 6.7 and one more sample treated with glutaraldehyde to inhibit microbial P release. The sample was run for seven days and both solid and liquid P fractionation were done. Figure 6.5 shows details of DRP release from start to day 7.

The maximum DRP of 178 mg/L (32 mg DRP/g dry WAS) was observed on WAS after pH adjustment with oxalic acid. Among different samples, WAS adjusted with HCl followed a similar trend to oxalic acid and DRP release reached 166 mg/L (30 mg DRP/g dry WAS) after 7 days treatment. Although there were quantitative variations in the DRP released, all samples showed a similar releasing pattern after day 1. The full data is provided in Table C.5 in Appendix C.

The glutaraldehyde killed the cells while preserving their physical structure. This allows for informed speculation on the relative role of chemical and biological processes in P release. There is a significant DRP release difference between the control and glutaraldehyde treatments. The glutaraldehyde sample released roughly 45% of the P of the acid-treated samples, and roughly 55% relative to a control. The difference is greatest during the first day of treatment, with little change in the difference over the next six days. These results are discussed in section 6.6.

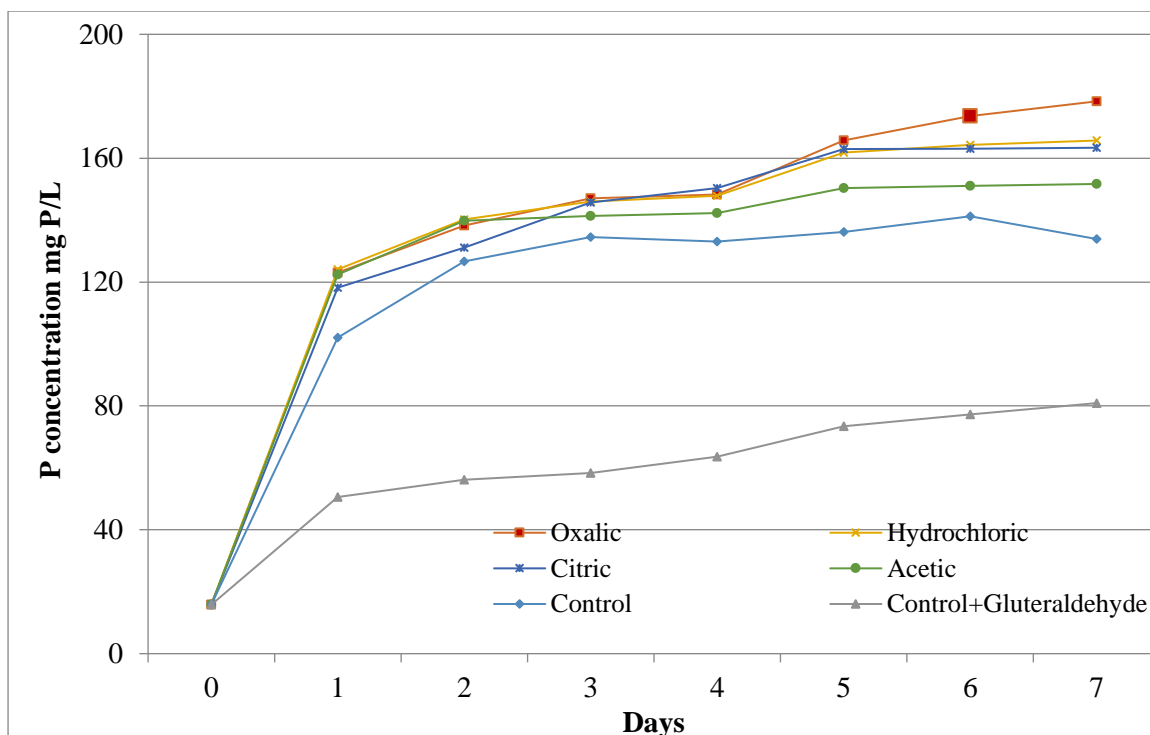


Figure 6.5: DRP release at pH 4 using different acids and 20 °C and control at pH 6.7 (Batch 3)

The results from the solids fractionation reinforce or support the results found in the aqueous tests. Figure 6.6 highlights the P fraction initially and after 7 days with a temperature of 20 °C, pH of 4 adjusted with oxalic and HCl acids, control at pH 6.7 and glutaraldehyde at pH 6. The highest P release was 67% from the sample adjusted with the oxalic acid, followed by 65% released from the sample adjusted with HCl. Both oxalic and HCl treated samples release similar percentages of NAIP (77% and 74%) and AP (88% and 85%) fraction. The detailed data are provided in Table C.6 in Appendix C.

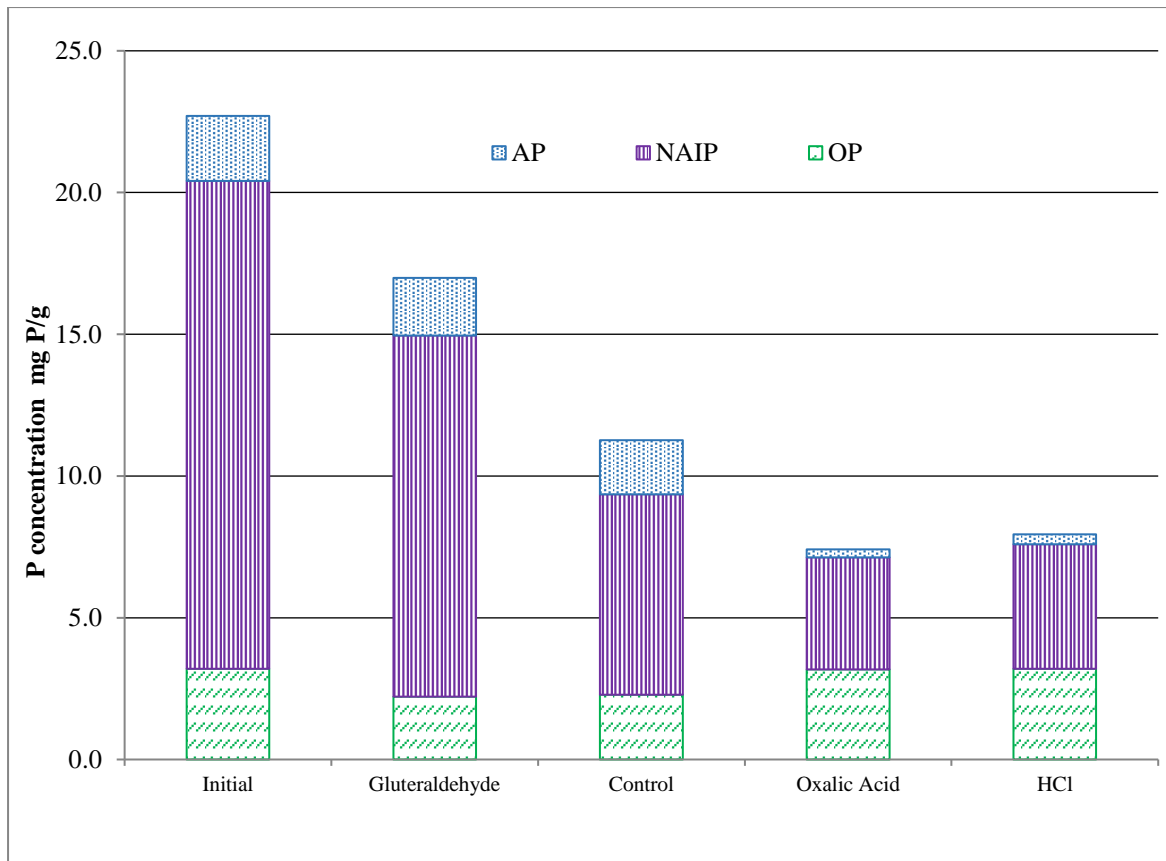


Figure 6.6: Phosphorus fraction initial and after 7 days under pH 4 adjusted with oxalic and HCl, glutaraldehyde at pH 6, control at pH 6.7 at 20 °C and anaerobic (Batch 3)

The fourth batch samples were also adjusted to pH 4 using different acids: hydrochloric, citric, oxalic and peracetic acid, temperature 20 °C and one control at pH 6.7. This batch was also observed over seven days. Figure 6.7 shows details of DRP release from the start to day 7. The maximum DRP 266 mg/L (35 mg DRP/g dry initial WAS) was measured for the sample adjusted with oxalic acid at pH of 4. pH adjustment with HCl followed a similar trend to oxalic acid and reached 261 mg/L (35 mg DRP/g initial WAS) after 7 days treatment. The full data are provided in Table C.7 in Appendix C.

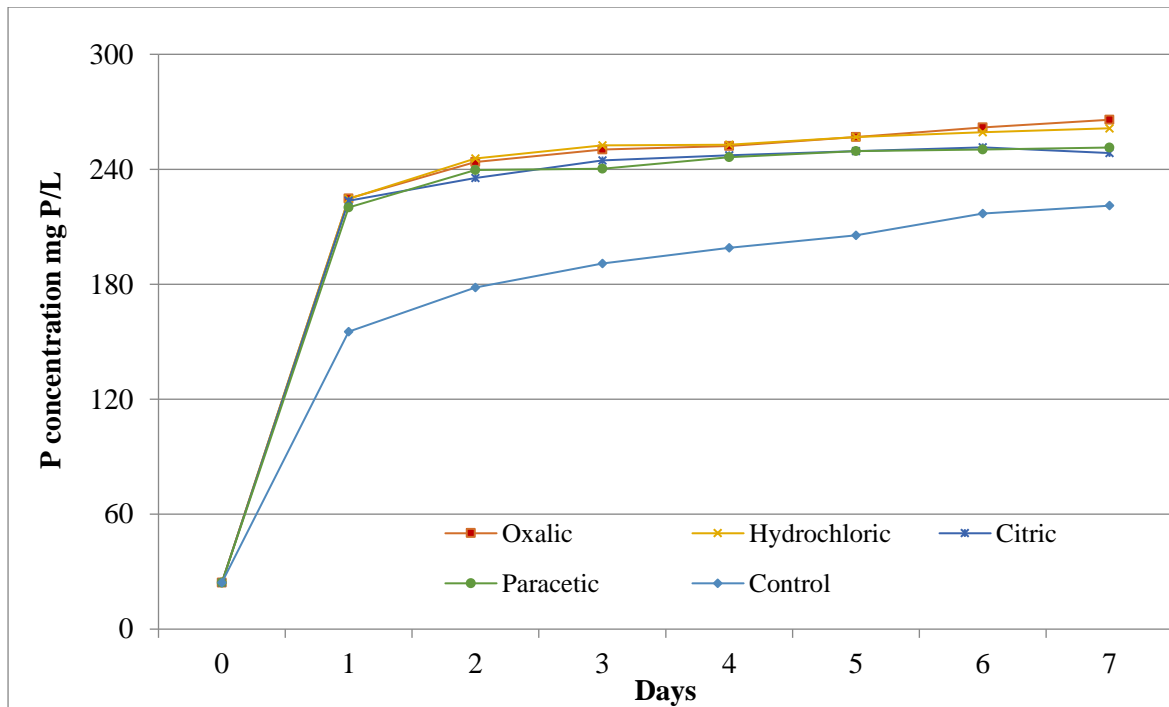


Figure 6.7: DRP release at pH 4 using different acids and control at pH 6.7 (Batch 4)

6.5 Other Sludge Parameters

6.5.1 Settleability

It is important that, after optimal P release under different treatments, the sludge needs to be well settled. It can be uneconomical to recover P if a large reactor is needed for settling after treatment. P release is efficient only when the settling characteristics of P-treated WAS do not greatly change from non-treated WAS. In general, the range of 50 to 150 ml/g indicates a good settling sludge.

SVI was measured to monitor the settling characteristics of the sludge at the beginning, day 1 and day 12 at pH 4, pH 5 and control at pH 6.3 adjusted with HCl and AA in batch A, and pH 4 and control 6.7 adjusted with different acids and after 7 days in batch B. There was similar settling characteristics of all samples in the range SVI 63 ml/g to 73 ml/g for batch A. In batch B, there was more variable SVI under different acid treatments and range from 82 ml/g

to 122 ml/g. The details of SVI results are provided in Table 6.9 and 6.10. An SVI of 80 ml/g or less usually indicates a sludge that is dense and has rapid settling characteristics. The findings of the SVI result shows that there were no significant effects of using different acids on the settling characteristics of WAS but when comparing with acids, HCl has lower SVI value and slightly better settling than others.

Table 6.9: SVI at pH 4, pH 5 and control at pH 6.3 using HCl and acetic acid (batch A)

Treatments	Sludge Volume Index as (ml/g)		
	Day 0	Day 1	Day 12
Control (pH = 6.3)	73	71	66
pH4 HCl Acid	73	63	66
pH5 Acetic Acid	73	71	73
pH5 HCl acid	73	69	70

Table 6.10: SVI of CBNR sludge at pH 4 and control at pH 6.7 using different acids, 20 °C initial and after 7 days treatment (batch B).

Treatments	Sludge Volume Index (ml/g)
Control (pH = 6.7)	82
HCl	95
Citric	116
Oxalic	122
Peracetic	122

6.5.2 Filterability

The SRF of CBNR sludge was calculated at pH 4 and control at pH 6.9 using different acids, 20 °C and after 7 days treatment (batch B). There was variation of SRF for the CBNR WAS sample treated with different acids. The lowest SRF value 3.9×10^{10} (m/kg) was observed under control and the highest value 2.4×10^{12} (m/kg) was measured under peracetic acid treated sample.

In general, sludge with SRF value as low as $10^{10} - 10^{11}$ m/kg is classified as easy to dewater; whereas, sludge with SRF value as high as $10^{14} - 10^{15}$ m/kg is considered as difficult to extract water. Specific resistance varies with applied pressure, filter area and pore size and liquid viscosity, making it more complicated to measure and compare. The higher the specific resistance, the more difficult it is to dewater sludge and vice versa (Karr & Keinath, 1978).

The WAS sample treated with HCl shows slightly higher SRF 1.3×10^{11} (m/kg). The full data are provided in Table 6.11. The findings of SRF testing indicate that HCl treated sludge was more difficult to dewater than the control. The citric, oxalic and peracetic acids treated sludges are more difficult to dewater than the HCl treated sludge.

Table 6.11: SRF of CBNR sludge at pH 4 and control at 6.9 using different acids, 20 °C after 7 days treatment (batch B)

Treatments	Specific Resistance to Filtration (m/kg)
Control	3.9×10^{10}
HCl	1.3×10^{11}
Citric	2.1×10^{12}
Oxalic	1.7×10^{12}
Peracetic	2.4×10^{12}

6.5.3 Impact on Chemical Oxygen Demand

A number of sludge pre-treatments have been studied to maximise methane production during anaerobic digestion (Carrère et al., 2010; Neumann et al., 2016). They generally work by breaking apart bacteria to make anaerobic digestion quicker. The higher temperature and lower pH that favour P release could also help to increase the digestability of sludge. A phosphorus release and recovery reactor could work well on WAS and also be useful to combine with primary sludge before anaerobic digestion.

Soluble Chemical oxygen demand (COD) is used to quantify the amount of organic matter in waste streams and predict the potential for biogas production. The oxygen equivalent of dissolved organic compounds that can be oxidised is measured using a strong chemical oxidising agent in an acidic medium. During anaerobic digestion, the biodegradable COD present in organic material is preserved in the end products, namely methane, carbon dioxide, and the newly formed bacterial mass.

The soluble COD of CBNR sludge sample was analysed at pH 4 after treatment with different acids at 20 °C (batch B). Analyses were done at the start, day 1, 3 and after 7 days of treatments. The highest soluble COD (1120 mg/L) was observed under citric acid, and lowest COD 650 mg/L under hydrochloric acid and control was COD 344 mg/L. To adjust pH at 4 the WAS sample consumed 5 ml of 1 M HCl hydrochloric, 8 ml of 1M citric, 7.5 ml of 1 M peracetic and 11.8 ml of 1 M oxalic acid per litre of WAS. The addition of these acids also added COD to the sample. Full data is provided in Table 6.12. The increasing COD after acid treatment indicated that the sludge has potential for methane production. It should be noted that no correction has been made in Table 6.11 for the COD added through the addition of organic acids, though it is not expected to be change these preliminary conclusions.

Table 6.12: COD of CBNR sludge at pH 4 and control at 6.9 using different acids, 20 °C initial and after 1, 3 and 7 days treatment (batch B)

Treatments	COD Analysis mg/L			
	Day 0	Day 1	Day 3	Day 7
Control	41	237	278	344
HCl	41	636	641	650
Oxalic Acid	41	642	702	716
Peracetic Acid	41	900	952	961
Citric Acid	41	1038	1115	1120

6.6 Discussion

The sample sludge characteristics varied greatly between batches. So it was difficult to compare results of various batches. Observation after four batches test are summarised below.

- Very little difference of P release is seen between various acids after 7 to 17 days of treatment
- For batch 1, HCl had greater P release than AA, but the actual difference after 17 days was 14 mg/L, which was less than the 90% confidence level difference of 19 mg/L ($136.5 * 14\% = \pm 19.11$), so there is no proven difference between HCl and Acetic acid for P release.
- For batch 3, Oxalic had greater P release than HCl, but the actual difference after 7 days was 12.7 mg/L, which was less than the 90% confident level difference of 24.1 ($172.05 * 14\% = \pm 24.1$), so there is no proven difference between HCl and Oxalic acid for P release.
- Rapid release is seen for all acids like that shown in chapter 5 for CBNR WAS.

Table 6.13 shows initial DRP and the highest DRP release after acids treatment observed in different batches. Calculation of 90% confident interval (on the basis of reproducibility section 3.2.7) shows similar initial DRP (3.2 ± 0.5 mg/g dry WAS) and the highest DRP (33.7 ± 4.7 mg/g dry WAS) released for all batches.

Table 6.13: Initial and Peak DRP concentration (as mg/L WAS and mg/g dray WAS)

Batch 1	Acids	pH4	Temp °C	Peak DRP mg/L WAS	Peak DRP mg/g dry WAS	Initial DRP mg/L WAS	Initial DRP mg/g dry WAS
1	HCl	4	35	150.1	30.28	4.2	0.8
2	HCl	4	20	407.8	37.28	44.9	4.1
3	HCl	4	20	165.7	29.56	15.8	2.8
3	Oxalic	4	20	178.4	31.83	15.8	2.8
4	HCl	4	20	261.4	34.71	24.3	3.2
4	Oxalic	4	20	265.9	35.31	24.3	3.2

Non-linear regression in the Excel Solver was used to fit the first order decay (k) and P release. Minimisation of square residuals was used. Kinetic coefficients (k) of DRP released under different acids in various batches (1, 2, 3 & 4) were calculated using a first order relationship. There were no trends seen on k values between different acids. In batch 1, results from experiment (150 mg/L) and calculated (145 mg/L) using kinetics shows higher total P release under hydrochloric acid at pH 4 and 35 °C. Batch 2 results show similar P release under acetic (356 mg/L) and hydrochloric acid (356 mg/L) acid at pH 5 and 20 °C. Both batch 1 and 2 were comparison of acetic and hydrochloric acid performance at pH 4 and 5 on P release. Excel calculation of non-linear regression and laboratory values both indicated that at lower pH 4, hydrochloric acid is better option for P release than acetic acid. Table 6.14 shows the details of all values.

The linear regression results highlight the effect of glutaraldehyde on P release. Table 6.14 shows a total P release of 65.1 mg/L for the glutaraldehyde treatment and 132-149 mg P/L for the various acid treatments, with 121 mg P/L for the control using that WAS batch. Because glutaraldehyde is assumed to stop biological activity without damaging the cells, the results indicate that roughly half of the P release measured is due to processes of active biological cells, while roughly half is due to chemical processes of dissolution or desorption.

Before this research, the ability of poly-P bacteria from EBPR plants to release P under stressed conditions was well known. These results indicate that even for BNR plants not designed for P removal that a large amount of P release can occur through biological processes. This is notable because the total P in the BNR sludge was roughly 23 mg P/g dry sludge (2.3%), which is less than 5% to 15% reported for EBPR sludge (Mino et al. 1998). Staining tests indicated the presence of bio-P bacteria in the CBNR sludge (true that staining was on CBNR sludge?) both before and after treatment to pH of 4. Taken together, the results point to a large biological influence on P release in any future P release reactor. There is some release of P with glutaraldehyde treatment, and Figure 6.6 shows that this is NAIP release, indicating that there is significant P release through chemical processes when there is none expected from biological processes. The rapid release of P seen without glutaraldehyde indicates that bacteria from BNR plants could release large amounts of P within one day with only moderate decreases in pH, increases in temperature, and maintenance of anaerobic conditions. Cell death and cell lysis do not appear necessary to maximise P release. Although glutaraldehyde was not tested with activated sludge from the plant examined in chapters 4 and 5, the high P release from AS found indicates that it is likely that biological processes are major factors in the release of P from AS sludge where there is no known selection for P retention. One hypothesis could be that WAS cells in these conditions are stressed and release

stored P to generate internal energy to keep them viable, and this occurs for a WAS from a wider variety of WWTP than might have been expected.

Table 6.14: Fitted coefficients using a first order relationship for DRP (Batch 1, 2, 3 & 4)

Batch	Acids	Treatments			K (1/day)	P max (mg/L)	P release (mg/L)	Av. Misfit (mg/L)
		Temp °C	pH	Days				
1	HCl	35	4	17	2.0	145.3	141.1	0.8
	HCl	20	4	17	1.3	128.6	124.4	1.1
	Acetic	35	4	17	2.7	125.6	121.4	0.9
	Acetic	20	4	17	1.7	119.8	115.6	1.0
	Control	20	6.9	17	1.4	118.5	114.3	0.9
2	HCl	20	4	12	0.7	383.8	338.9	6.4
	HCl	20	5	12	0.7	356.0	311.1	6.9
	Acetic	20	5	12	0.5	356.1	311.2	7.5
	Control	20	6.3	12	0.9	320.2	275.3	6.2
3	HCl	20	4	7	1.3	157.8	142	2.4
	Acetic	20	4	7	1.6	147.5	131.7	1.4
	Citric	20	4	7	16.2	147.8	132	6.2
	Oxalic	20	4	7	1	165.1	149.3	4.0
	Glutaraldehyde	20	6	7	1	80.9	65.1	4.4
	Control	20	6.7	7	1.3	136.6	120.8	0.9
4	HCl	20	4	7	1.9	255.9	231.6	1.4
	Citric	20	4	7	2.2	247	222.7	1.5
	Oxalic	20	4	7	1.9	256.6	232.3	2.2
	Peracetic	20	4	7	2.1	247.1	222.8	1.4
	Control	20	6.7	7	1.1	209.1	184.8	3.4

6.7 Conclusions

It was observed that both HCl and organic acids effectively released phosphorus from WAS samples. There is no clear evidence that the organic acids tested will be better than hydrochloric acid at P release under pH 4 condition. Acid use and P release in this study points to the following conclusions:

- Glutaraldehyde treatment concludes that the P release from WAS is not only a chemical but also a biological process
- No evidence that acetic acid is better than HCl for P

The preliminary test studies of other parameters examined broader issues that might be related to any future development of P release reactors for WAS. The preliminary conclusion is that HCl acid is at least as good, if not better, than other organic acids in terms of settleability and filterability, and that no major problems from acid treatment appear likely.

Chapter Seven: Conclusion and Recommendations

Phosphorus recovery from liquid phase should be improve by releasing P available in solid WAS. However, the release of P from solid in to liquid phase is affected by different factors (pH, temperature, aerobic/anaerobic). The effects of these factors (single or combination of multiple factors) on P release were tested and optimal condition was identified. The optimal condition was tested on different WAS and outcomes of P release was observed. Other important aspects of sludge such as effect of different acids, settleability, filterability and COD were monitored for future baseline data to help in design of P release reactors. A number of conclusions can be drawn from this research and these are summarised in this chapter.

7.1 P Release experimental conclusions

Research Aim: Understand the combined effect of pH, temperature, and redox potential on optimal conditions for P release

Different fractions of P exist in aqueous (DRP, TDP, and DOP) and solid (IP, OP, NAIP, and AP) phase in sludge and these fractions are released differently under various treatments. The use of elevated temperature and lowered pH conditions for release through anaerobic fermentation indicates that 35 °C greatly accelerates P release relative to ambient temperatures and that a decrease of the pH to 4 or 6 would also increase the total P release. Little pH depression is needed to release non-apatite inorganic P (including microbial polyphosphate). A lower pH of 4 rather than pH 6 is needed to release more apatite inorganic P. Thus, WAS high in NAIP is better for P recovery and a more acid treatment would be needed for WAS higher in apatite P. Organic P is more difficult to release from WAS. That is to say, WAS rich in organic P would be the most challenging in terms of economical P recovery.

Research Aim: Understand the amount of variation that can occur in P release between WWTPs WAS

The study of P release from AS, CBNR and SBNR WAS concluded that the varying levels of P release from sludge solids can be explained by differences in the P composition of the WAS which in turn arise from differences between wastewater treatment processes.

Anaerobic incubation of WAS at a pH of 4 and 35 °C gave total P release from the AS, CBNR, and SBNR sludge solids of 52, 75 and 48 %, respectively, in 21 days, with the CBNR and SBNR releases the most rapid.

Research Aim: Understand the effect of acid type on P release

It was observed that both inorganic and organic acids effectively released phosphorus from WAS samples. No evidence was found that acetic acid is better than HCl for P release. The visual identification of poly-P in staining test results and glutaraldehyde treatment concludes that the presence of poly-P under lower pH 4 and much of the P release is not only chemical but also a biological process

Research Aim: Towards design of P release reactors

Preliminary test studies observed broader issues that related to any future development of P release reactors. There was no adverse effect of using HCl on settleability and filterability. Conceptual design shown in Figure 1.2 (Chapter 1) and reprinted (Figure 9.1) below is closer to implementation after this research. The baseline information gathered a P release reactor is presented in Table 9.1.

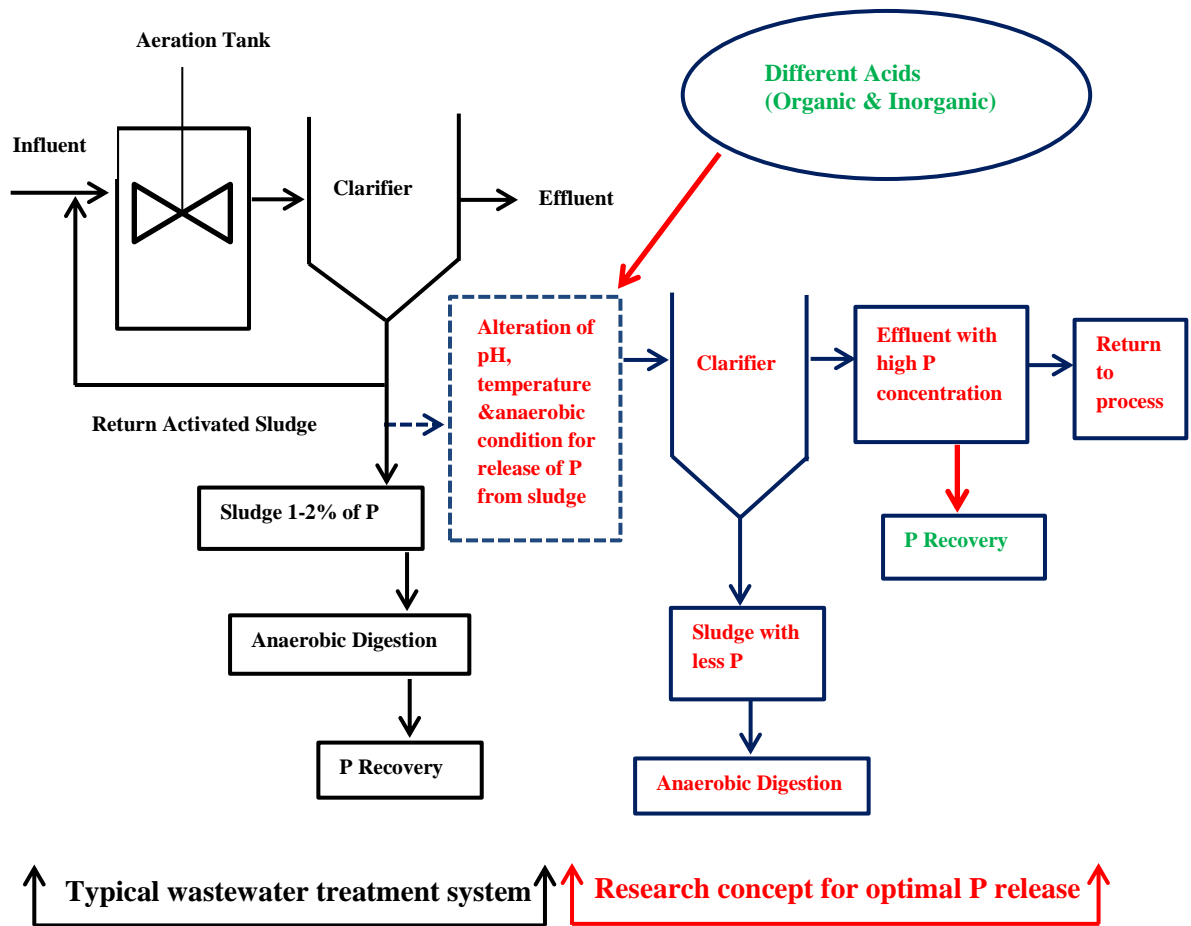


Figure 7.1: Research concept for maximum optimal P release

Table 7.1: Design consideration of P release reactors

Design consideration of P release reactors	Knowledge after this research
pH	pH 5 is important, though pH 4 better with high AP sludge
Choice of acid	Similar P release under acids but hydrochloric likely an option due to low cost and easily available
Temperature	Improved performance shown to 35 °C
ORP level	Below -150 mV
Residence time	1 to 3 days, detailed study hasn't been conducted
Type of treatment plants to select	AS and BNR positive, CBNR better. BNR performed better. EPBR plant sludge hasn't been tested. The WAS from EBPR plant could be even better than BNR.
Metal and cation release	Toxic metals: only Zn increases significantly, might not be significant toxicity issues in downstream water. Fe, Ca, Mg also increase which could have implications for P recovery depending on what process is used for P recovery.
Effect on anaerobic digestion of sludge	The increase in soluble COD after acid addition could be a benefit for methane production. Mixing of post-treated WAS at pH of 4 with primary sludge might remove need to add buffer before anaerobic digestion.
Settleability after treatment	Preliminary test shows little change, need further investigation
Filterability after treatment	Preliminary test shows little change, need further investigation
Effects of P release reactor design on P recovery	Not studied.

7.2 Analytical conclusions

The findings of this research show the value of fractionation testing to significantly improve society's ability to recover phosphorus from waste activated sludge. Phosphorus fractionation testing will be useful before considering P recovery from a wastewater treatment plant.

After successfully conducting different batch tests on P fraction release, here are some conclusions associated with analytical techniques for conducting similar experiments in future:

- ✓ Washing of samples with deionized water in-between the fractionation process of IP and OP; and NAIP and AP is necessary to get precise results;
- ✓ First couple of drops of samples should be discarded while doing sample filtration with 0.45 μm syringe filter to avoid filter paper associated impurities contaminating a sample;
- ✓ The P fractions in WAS change quickly and are influence by environmental factors that change with time, so analysis of these fractions should be carried out immediately after sampling (within an hour of sampling).

7.3 Limitations of research

There are some limitations in this study that could be addressed in further research. The first, insufficient replicates were used to provide strong statistical analysis on P release. The second is that EBPR WAS has not been tested. A test of EBPR WAS gives a better idea for comparison between WWTPs WAS P releases. The third was that a P mass balance was not conducted due to lack of TSS, VSS, TS or VS information of WAS initially and after different treatments.

7.4 Recommendations for further work

This thesis focuses on the optimal condition for phosphorus release by testing different factors (pH, temperature, aerobic/anaerobic) on waste activated sludges, followed by preliminary investigation of the effect of lower pH 4 condition on settleability, filterability, and COD. More P release research should be on WAS and not mixed sludge and not digested sludge. This research shows that simple treatment such as lowering pH and elevation of temperature can yield a high percentage of P release from WAS, but this might not be the case for other sludges. Special attention should be given to the ability to recover P from EBPR WAS because of the higher P content and more bio-P organisms than the CBNR WAS tested in this research.

The research has not been able to explain the results in terms of mechanisms. Further research into mechanisms would add scientific significance to this P release research work.

This research indicates the importance of NAIP release for total P release. Further exploration of NAIP composition would be valuable before and after application of pH, temperature, aerobic/anaerobic condition. This research could clarify the role of chemical and biological processes in P release. Another topic to study in a more detailed manner would be organic P release from WAS and the role of PAOs. The staining, glutaraldehyde addition and sonication tests did not provide the detailed mechanics of OP behaviour. Detailed microbial test analysis is recommended to explain the phenomenon.

This research has not estimated the cost and benefit of P release and recovery. An estimation of P release cost and recovery benefit will be needed for economical evaluation of this P released from WAS. This would require selection of a method for P recovery, and testing of that method. To test the implication of this research in a real situation, a pilot- scale reactor is recommended under pH 4, temperature 35 °C and anaerobic condition for a CBNR WAS to investigate if these results can be repeated at a larger scale.

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Appendix A: Full Data of Relative Influence of Factors Affecting Phosphorus Release

Table A.1: Aerobic and anaerobic phosphorus release from standards WAS under 20 °C and pH 6.9 without initial pH adjustment

Parameters			Days									
			Dissolved Reactive Phosphorus (mg/L)									
Temp °C	pH		0	1	2	3	4	5	6	8	10	12
20	6.9	Aerobic	7.2	7.9	9.5	11.2	15.7	19.7	21.6	27.9	31.6	33.7
20	6.9	Aerobic	7.2	8.1	9.2	11.7	15.9	19.1	22.1	28.4	30.6	32.8
20	6.9	Aerobic	7.2	8.2	9.7	11.5	14.9	18.8	21.8	28.1	30.1	31.8
Average			7.2	8.1	9.5	11.5	15.5	19.2	21.8	28.1	30.8	32.8
Standard Deviation			0.0	0.2	0.3	0.3	0.5	0.5	0.3	0.3	0.8	1.0
			Dissolved Reactive Phosphorus (mg/L)									
20	6.9	Anaerobic	7.2	35.9	38.6	41.2	43.5	45.2	46.5	47.8	50.1	52.1
20	6.9	Anaerobic	7.2	36.1	39.6	40.9	43.2	45.7	46.9	47.2	50.3	52.7
20	6.9	Anaerobic	7.2	35.4	40.1	41.4	43.8	45.9	47.1	47.3	49.9	52.0
Average			7.2	35.8	39.4	41.2	43.5	45.6	46.8	47.4	50.1	52.3
Standard Deviation			0.0	0.4	0.8	0.3	0.3	0.4	0.3	0.3	0.2	0.4

Table A.2: DRP and TDP release from standard activated sludge under different pH, temperature and anaerobic condition

Temp °C	pH	Days							
		0	1	2	3	4	5	6	7
Dissolved Reactive Phosphorus (DRP) as mg/L									
20	7	11.1	34.3	44.4	42.4	42.7	42.7	44	45.7
10	4	11.1	33.6	42.1	40.8	40.4	39.5	35.2	34.6
10	6	11.1	26.7	32	32	31	33.6	32.3	32.3
10	8	11.1	23.8	28.4	27.1	29.4	33.3	38.8	39.1
20	4	11.1	39.5	49.9	48.9	52.2	52.2	52.8	52.8
20	6	11.1	43.7	51.2	50.6	50.6	51.2	44	44
20	8	11.1	30.3	42.7	45.3	51.2	51.2	55.8	55.8
30	4	11.1	50.9	71.8	65.9	63.9	65.6	65.9	66.5
30	6	11.1	50.9	62	63.9	61	63.9	59.7	57.7
30	8	11.1	47.3	56.8	60	60.3	62.6	61.7	63.9
Total Dissolved Phosphorus (TDP) as mg/L									
20	7	12.4	36.5	44.7	43.7	47	48	48	46.6
10	4	12.4	36.5	43.7	46	43.4	45.7	38.8	40.1
10	6	12.4	29.7	35.6	35.6	32.6	38.5	38.2	37.5
10	8	12.4	25.8	28.4	31	27.7	37.2	42.1	42.7
20	4	12.4	40.1	49.6	51.9	52.8	54.8	63.3	63.3
20	6	12.4	46.3	55.5	53.8	53.5	55.5	50.2	50.2

20	8	12.4	32.3	45.7	47.6	51.2	53.8	55.8	55.8
30	4	12.4	57.7	66.9	74.4	71.4	76	70.8	69.2
30	6	12.4	54.8	68.2	71.8	71.4	72.4	66.9	66.9
30	8	12.4	49.3	58.7	69.2	61.7	66.5	62	67.2
Dissolved Organic Phosphorus (DOP) as mg/L									
20	7	1.3	2.2	0.3	1.3	4.3	5.3	4	0.9
10	4	1.3	2.9	1.6	5.2	3	6.2	3.6	5.5
10	6	1.3	3	3.6	3.6	1.6	4.9	5.9	5.2
10	8	1.3	2	0	3.9	-1.7	3.9	3.3	3.6
20	4	1.3	0.6	-0.3	3	0.6	2.6	10.5	10.5
20	6	1.3	2.6	4.3	3.2	2.9	4.3	6.2	6.2
20	8	1.3	2	3	2.3	0	2.6	0	0
30	4	1.3	6.8	-4.9	8.5	7.5	10.4	4.9	2.7
30	6	1.3	3.9	6.2	7.9	10.4	8.5	7.2	9.2
30	8	1.3	2	1.9	9.2	1.4	3.9	0.3	3.3

Table A.3: Solid sludge phosphorus fractionation (mg/g) initial and after 7 days under different pH, temperature and anaerobic condition (AS WAS)

Treatments			TP	IP	OP	NAIP	AP
Temp °C	pH	Day					
20	7	0	18.1	12.3	5.8	10.4	2.0
20	7	7	13.0	8.8	4.2	7.6	1.2
10	4	7	12.7	8.9	3.8	8.6	0.3
10	6	7	13.9	10.3	3.6	8.4	1.9
10	8	7	13.8	10.0	3.8	7.6	2.4
20	4	7	10.4	7.4	3.0	6.9	0.4
20	6	7	12.6	8.5	4.1	7.3	1.2
20	8	7	13.3	10.6	2.7	7.6	2.9
30	4	7	9.5	6.3	3.2	6.0	0.3
30	6	7	10.3	7.1	3.2	5.9	1.3
30	8	7	11.5	8.7	2.8	6.7	2.0

Table A.4: DRP and TDP release from standard activated sludge under different pH, temperature and anaerobic condition (AS WAS)

Temp °C	pH	Days													
		0	1	2	3	4	5	6	8	10	12	14	16	19	22
		Dissolved Reactive Phosphorus (DRP) as mg P/L													
20	6.9	7.2	35.9	34.9	41.4	43.1	46	45.3	47.3	50.6	52.2	54.8	52.5	57.1	57.1
10	4	7.2	28.7	30.3	29	27.4	27.1	26.1	28.4	29.4	39.5	39.8	40.1	47.6	48.9
10	6	7.2	13.7	18.9	18.9	19.6	24.1	28.4	22.5	25.1	36.2	37.2	31	36.9	38.2
10	8	7.2	15	18.3	20.2	21.5	22.2	27.4	29.7	33.3	40.4	40.8	41.1	44	45.3
20	4	7.2	51.5	56.8	60.7	62.6	63.3	63	63.9	67.5	68.5	69.5	71.4	71.4	66.9
20	6	7.2	30.3	36.2	41.8	45.7	48	47.6	50.2	51.2	58.7	61	54.8	56.8	61.7
20	8	7.2	25.8	36.2	39.8	42.7	44.7	43.7	50.9	53.5	59.4	59.7	56.1	59.4	59.7
35	4	7.2	43.4	66.9	69.5	71.1	71.4	71.4	78	77.3	78.3	81.6	79.9	82.5	78.3
35	6	7.2	52.5	54.1	56.1	58.1	59.4	58.4	58.7	64.6	78.9	83.2	67.2	67.2	61.3
35	8	7.2	51.9	51.5	50.2	54.8	55.1	53.8	55.5	63.6	65.2	67.2	65.2	64.3	58.1
		Total Dissolved Phosphorus (TDP) as mg P/L													
20	6.9	7.5	27.4	33.6	41.1	43.4	44.7	44	45.7	50.6	52.2	55.5	53.8	55.8	58.1
10	4	7.5	29	32	31.6	29.7	29.4	31	28.7	29.4	40.1	40.8	40.1	47.3	48.6
10	6	7.5	14	18.9	19.2	19.9	23.5	27.7	21.2	24.5	36.2	37.5	32.6	37.5	37.8
10	8	7.5	14.7	17.6	20.6	21.5	22.2	24.8	28.4	33.3	39.1	42.4	40.8	45	45.7
20	4	7.5	52.5	59	63	63.6	62.6	64.9	63.9	66.9	68.5	69.5	71.4	71.4	65.2
20	6	7.5	28.7	34.6	40.1	45	47	46.6	47.6	51.2	58.7	62	55.5	56.4	58.7
20	8	7.5	26.7	34.6	37.8	41.8	43.1	43.7	47	53.5	59.4	58.7	55.5	60.3	58.7
35	4	7.5	45.3	70.5	71.1	73.1	74.7	75	78.3	77.3	79.9	81.9	80.9	83.2	79.9
35	6	7.5	50.2	54.1	56.1	57.1	58.4	58.7	58.4	65.2	78.3	81.6	68.5	69.2	62

35	8	7.5	48.6	47.6	47.3	47.3	49.3	51.2	53.8	62	65.2	68.5	65.2	64.6	59.4
Dissolved Organic Phosphorus (DOP) as mg/L															
20	6.9	0.3	-8.5	-1.3	-0.3	0.3	-1.3	-1.3	-1.6	0	0	0.7	1.3	-1.3	1
10	4	0.3	0.3	1.7	2.6	2.3	2.3	4.9	0.3	0	0.6	1	0	-0.3	-0.3
10	6	0.3	0.3	0	0.3	0.3	-0.6	-0.7	-1.3	-0.6	0	0.3	1.6	0.6	-0.4
10	8	0.3	-0.3	-0.7	0.4	0	0	-2.6	-1.3	0	-1.3	1.6	-0.3	1	0.4
20	4	0.3	1	2.2	2.3	1	-0.7	1.9	0	-0.6	0	0	0	0	-1.7
20	6	0.3	-1.6	-1.6	-1.7	-0.7	-1	-1	-2.6	0	0	1	0.7	-0.4	-3
20	8	0.3	0.9	-1.6	-2	-0.9	-1.6	0	-3.9	0	0	-1	-0.6	0.9	-1
35	4	0.3	1.9	3.6	1.6	2	3.3	3.6	0.3	0	1.6	0.3	1	0.7	1.6
35	6	0.3	-2.3	0	0	-1	-1	0.3	-0.3	0.6	-0.6	-1.6	1.3	2	0.7
35	8	0.3	-3.3	-3.9	-2.9	-7.5	-5.8	-2.6	-1.7	-1.6	0	1.3	0	0.3	1.3

Table A.5: Solid sludge phosphorus fractionation (mg/g) initial and after 22 days under different pH, temperature and anaerobic condition (AS WAS)

Treatments			TP	IP	OP	NAIP	AP
Temp °C	pH	Day					
20	6.9	0	16.8	12.2	4.6	9.7	2.5
20	6.9	22	13.2	9.8	3.4	6.1	3.7
10	4	22	10.0	5.9	4.1	5.1	0.8
10	6	22	12.8	10.0	2.8	6.6	3.4
10	8	22	13.9	10.8	3.1	7.3	3.4
20	4	22	8.9	4.6	4.3	3.9	0.7
20	6	22	11.8	8.5	3.3	5.6	3.0
20	8	22	12.6	9.8	2.8	5.8	4.1
35	4	22	8.3	3.6	4.7	3.3	0.3
35	6	22	11.0	9.9	1.1	6.1	3.8
35	8	22	12.8	10.0	2.8	5.6	4.5

Table A.6: Total phosphorus (mg/g) initial and after 22 days under different pH, temperature and anaerobic condition (AS WAS)

Parameters		Days				
pH	Temp °C	0	2	7	14	22
6.9	20	16.8	14.8	13.2	13.0	12.5
4	10	16.8	16.3	14.7	12.0	10.0
6	10	16.8	15.7	13.9	13.0	12.8
8	10	16.8	16.2	14.9	13.8	13.9
4	20	16.8	11.9	9.5	8.9	8.8
6	20	16.8	13.9	12.1	11.8	11.4
8	20	16.8	15.4	14.6	13.9	13.1
4	35	16.8	9.9	8.4	8.3	8.2
6	35	16.8	12.1	11.9	11.6	11.4
8	35	16.8	14.9	13.1	12.6	12.0

Appendix B: Full Data of Influences of Differences in WAS on Phosphorus Release

Table B.1: Anaerobic DRP, TDP and DOP release from AS, CBNR and SBNR WAS under pH 4, pH 7, and temperature 20 °C and 35 °C

Temp °C	pH	Days											
		0	1	2	3	4	5	7	9	11	13	17	21
Dissolved Reactive Phosphorus mg P/L (AS)													
35	4	7.2	43.4	66.9	69.5	71.1	71.4	71.4	78	77.3	78.3	81.6	82.5
20	4	7.2	41.5	56.8	60.7	62.6	62.6	63.0	63.9	66.9	68.5	69.5	71.4
20	7	7.2	35.9	33.6	41.1	43.1	44.7	44.0	45.7	50.6	52.2	54.8	55.8
Total Dissolved Phosphorus mg P/L (AS)													
35	4	7.5	45.3	70.5	71.1	73.1	74.7	75	78.3	77.3	79.9	81.9	83.2
20	4	7.5	42.5	59.0	63.0	63.6	63.3	64.9	63.9	67.5	68.5	69.5	71.4
20	7	7.5	37.4	34.9	41.4	43.4	46.0	45.3	47.3	50.6	52.2	55.5	57.1
Dissolved Organic Phosphorus mg P/L (AS)													
35	4	0.3	1.9	3.6	1.6	2.0	3.3	3.6	0.3	0.0	1.6	0.3	0.7
20	4	0.3	1.0	2.2	2.3	1.0	0.7	1.9	0.0	0.6	0.0	0.0	0.0

20	7	0.3	1.5	1.3	0.3	0.3	1.3	1.3	1.6	0.0	0.0	0.7	1.3
Dissolved Reactive Phosphorus mg P/L (CBNR)													
35	4	9.1	114.3	124.7	132.5	135.7	139.3	141.0	143.7	144.6	145.8	146.1	147.1
20	4	9.1	93.0	115.8	124.8	126.4	119.1	128.8	130.5	132.1	132.1	132.9	132.5
20	7	9.1	88.1	109.3	114.2	116.1	115.8	117.8	126.9	120.0	123.3	123.1	123.3
Total Dissolved Phosphorus mg P/L (CBNR)													
35	4	9.5	114.3	125.1	132.7	137.2	141.3	141.0	144.0	144.6	146.0	147.0	147.5
20	4	9.5	95.0	116.5	126.0	128.3	120.2	130.0	131.0	133.0	134.0	135.0	134.2
20	7	9.5	89.3	110.2	115.0	118.3	118.0	120.1	126.9	121.0	123.3	124.0	123.5
Dissolved Organic Phosphorus mg P/L (CBNR)													
35	4	0.4	0.3	0.4	0.2	1.5	2.0	0.0	0.3	0.0	0.2	0.9	0.4
20	4	0.4	2.0	0.7	1.2	1.9	1.1	1.2	0.5	0.9	1.9	2.1	1.7
20	7	0.4	1.2	0.9	0.8	2.2	2.2	2.3	0.0	1.0	0.0	0.9	0.2
Dissolved Reactive Phosphorus mg P/L (SBNR)													
35	4	5.4	53.0	58.7	61.2	63.6	65.2	71.5	71.8	70.9	71.8	78.0	77.5
20	4	5.4	41.5	44.9	46.5	47.3	53.0	59.0	59.5	59.5	62.8	70.0	70.7

20	7	5.4	39.1	40.0	41.6	43.2	45.7	50.5	50.5	50.6	51.4	66.1	67.7
Total Dissolved Phosphorus mg P/L (SBNR)													
35	4	6.0	54.0	59.0	62.5	64.0	66.0	71.8	72.0	72.1	72.5	78.3	77.5
20	4	6.0	41.6	45.1	47.0	47.3	54.0	59.5	60.0	60.0	63.0	70.9	70.7
20	7	6.0	40.0	40.0	42.0	44.0	46.0	50.6	50.6	51.0	51.5	66.5	68.0
Dissolved Organic Phosphorus mg P/L (SBNR)													
35	4	0.6	1.0	0.3	1.3	0.4	0.8	0.3	0.2	1.2	0.7	0.3	0.0
20	4	0.6	0.1	0.2	0.5	0.0	1.0	0.5	0.5	0.5	0.2	0.9	0.0
20	7	0.6	0.9	0.0	0.4	0.8	0.3	0.1	0.1	0.4	0.1	0.4	0.3

Table B.2: Phosphorus fractions mg/g of AS, CBNR and SBNR initial and after 21 days treatment.

Temp °C	pH	Days	Sludge	TP	IP	OP	NAIP	AP
20	6.9	0	AS	17.2	12.5	4.7	9.9	2.6
35	4	21	AS	8.3	3.6	4.7	3.3	0.3
20	4	21	AS	8.9	4.6	4.3	3.9	0.7
20	6.9	21	AS	13.2	9.8	3.4	6.1	3.7
20	6.9	0	CBNR	19.7	17.3	2.4	13.2	4.1
35	4	21	CBNR	5.0	2.9	2.1	2.6	0.3
20	4	21	CBNR	6.9	4.7	2.3	3.9	0.7
20	6.9	21	CBNR	8.0	6.0	2.2	4.1	1.7
20	6.9	0	SBNR	18.1	12.6	5.5	9.2	3.3
35	4	21	SBNR	9.3	3.4	5.9	3.2	0.2
20	4	21	SBNR	10.3	4.6	5.7	3.7	0.9
20	6.9	21	SBNR	11.3	5.2	6.1	4	1.2

Table B.3: Replicate DRP release test on CBNR WAS under pH 4, 35 °C, anaerobic condition and control at pH 6.9 and 20 °C

Parameters		Dissolved Reactive Phosphorus (mg/L)											
Temp °C	pH	Days											
		0	1	2	3	4	5	7	9	11	13	17	21
35	4	10.5	107.6	121.8	129.1	133.1	138.5	140.2	141.8	142.1	143.5	146.5	149.9
35	4	10.5	103.9	124.9	128.1	132.7	139.3	139.9	140.5	144.5	144.8	147.5	148.5
35	4	10.5	105.5	121.1	132.7	134.7	137.7	141.9	142.8	142.8	143.8	145.5	149.9
Average		10.5	105.7	122.6	130.0	133.5	138.5	140.7	141.7	143.1	144.0	146.5	149.4
Std. Dev.		0.0	1.9	2.0	2.4	1.1	0.8	1.1	1.2	1.2	0.7	1.0	0.8
C.V.%		0.0	1.8	1.6	1.9	0.8	0.6	0.8	0.8	0.9	0.5	0.7	0.5
20	6.9	10.5	85.1	99.3	103.5	107.3.5	108.6	109.3	113.2	114.8	113.8	114.9	117.2

Appendix C: Full Data of Effect of Acid Type on Phosphorus Release

Table C.1: DRP release under pH 4, 20°C, 35 °C and using hydrochloric and acetic acid and anaerobic condition (CBNR WAS)

Temp °C	pH	Acid Used	Days										
			0	1	2	3	4	5	7	9	11	13	17
35	4	Hydrochloric Acid	4.2	125.6	143.5	141.1	140.3	146.0	146.8	145.2	150.1	147.6	143.5
35	4	Acetic Acid	4.2	115.0	118.2	119.9	124.0	121.5	123.1	124.8	128.0	128.0	129.7
20	4	Hydrochloric Acid	4.2	97.5	115.8	124.8	126.4	119.1	128.8	130.5	132.1	132.1	132.9
20	4	Acetic Acid	4.2	99.5	112.5	115.8	116.6	115.8	118.2	119.1	123.1	123.1	127.2
20	6.9	Control	4.2	93.0	110.5	112.8	115.6	114.8	117.2	118.1	120.1	122.1	125.2

Table C.2: Solid sludge phosphorus fractionation (mg/g) initial and after 17 days under pH 4, pH 6.9, temperature 20 °C, 35 °C, hydrochloric acid, acetic acid and anaerobic condition (CBNR WAS)

Temp °C	pH	Days	Acid Used	TP	IP	OP	NAIP	AP
20	6.9	0		19.8	16.4	3.5	12.6	3.8
35	4	17	Hydrochloric Acid	4.9	2.9	2.0	2.7	0.2
35	4	17	Hydrochloric Acid	5.0	2.9	2.1	2.7	0.2
35	4	17	Acetic Acid	7.6	5.5	2.1	3.5	1.9
35	4	17	Acetic Acid	7.7	5.7	2.0	3.6	2.1
20	4	17	Hydrochloric Acid	5.2	3.4	1.8	3.1	0.3
20	4	17	Acetic Acid	5.7	4.0	1.7	2.8	1.2

Table C.3: DRP and COD release at pH 4, pH 5, pH 6.3 and 20 °C using hydrochloric and acetic acid under anaerobic condition (CBNR WAS)

Acid Used	Temp °C	pH	Days								
			0	1	2	3	4	5	7	9	12
Acid not Used	20	6.3	44.9	230.0	265.9	278.1	294.4	303.4	331.1	326.2	345.8
Acetic Acid	20	5	44.9	195.7	244.7	263.4	279.7	296.0	351.5	362.9	367.8
Hydrochloric Acid	20	5	44.9	231.6	277.3	293.6	309.9	331.9	373.5	364.5	368.6
Hydrochloric Acid	20	4	44.9	233.2	299.3	317.2	333.5	354.7	384.1	391.4	407.8
			Chemical Oxygen Demand (COD) mg/L								
Acid not Used	20	6.3	46	176	352	490	569	698	1014	1076	1267
Acetic Acid	20	5	46	566	1040	1250	1310	1314	1297	1325	1256
Hydrochloric Acid	20	5	46	717	824	1020	1160	1299	1299	1308	1258
Hydrochloric Acid	20	4	46	695	1137	1297	1344	1303	1310	1315	1256

Table C.4: Solid phosphorus fractionation (mg/g) initial and after 12 days under pH 4, pH 5, pH 6, 20 °C, hydrochloric acid, acetic acid and anaerobic condition (CBNR WAS)

Temp °C	pH	Day	Acid Used	TP	IP	OP	NAIP	AP
20	6.3	0	Initial	35.0	26.8	8.2	19.9	6.9
20	6.3	12	Control	13.9	8.4	5.5	5.3	3.1
20	5	12	Acetic Acid	11.3	5.4	5.9	4.4	1.0
20	5	12	Hydrochloric Acid	11.0	5.2	5.8	4.3	1.0
20	4	12	Hydrochloric Acid	10.6	4.2	6.4	3.9	0.3

Table C.5: DRP release under pH 4, 20 °C, different acids and anaerobic treatment and control at pH 6.7 (CBNR WAS)

Treated Chemical	Temp °C	pH	Days							
			0	1	2	3	4	5	6	7
Control + Gluteraldehyde	20	6	15.8	50.6	56.2	58.4	63.6	73.5	77.3	80.9
Control	20	6.7	15.8	102.1	126.6	134.5	133.1	136.2	141.2	133.9
Acetic Acid	20	4	15.8	122.4	139.8	141.4	142.3	150.3	151.1	151.7
Citric Acid	20	4	15.8	118.2	131.1	145.7	150.3	162.9	163.1	163.4
Hydrochloric Acid	20	4	15.8	124.1	140.2	146.0	147.9	161.8	164.3	165.7
Oxalic Acid	20	4	15.8	123.1	138.3	147.0	148.2	165.7	173.6	178.4

Table C.6: Solid sludge phosphorus fractionation (mg/g) initial and after 7 days under different acids and pH 4, pH 6.7 and anaerobic condition

(CBNR WAS)

Temp °C	pH	Day	Treated Chemical	TP	IP	OP	NAIP	AP
20	6.7	0	Initial	22.7	19.5	3.2	17.2	2.3
20	6	7	Control + Gluteraldehyde	16.9	14.7	2.2	12.7	2.0
20	4	7	Control	11.5	9.2	2.3	7.1	1.9
20	4	7	Hydrochloric Acid	7.8	4.8	3.0	4.5	0.3
20	4	7	Oxalic Acid	7.6	4.4	3.2	4.2	0.3

Table C.7: DRP release under pH 4, 20 °C, different acids and anaerobic treatment and control at pH 6.7 (CBNR WAS)

Treated Chemical	Temp °C	pH	Days							
			0	1	2	3	4	5	6	7
Control	20	6.7	24.3	155.3	178.3	190.8	199.0	205.5	216.9	221.0
Oxalic	20	4	24.3	224.8	243.8	250.3	252.2	256.9	261.8	265.9
Hydrochloric	20	4	24.3	224.6	245.6	252.4	252.8	256.9	259.3	261.4
Citric	20	4	24.3	223.6	235.5	244.6	247.4	249.5	251.4	248.5
Peracetic	20	4	24.3	220.2	239.6	240.3	246.3	249.5	250.4	251.4

Table C.8: Anions analysis on WAS at pH 4 and 20 °C using different acids and anaerobic condition (CBNR WAS)

Sample ID	Days							
NO ₃ ⁻ mg/L	0	1	2	3	4	5	6	7
Control	0.1	0.6	0.5	1.4	0.8	0.6	0.6	0.6
Control + Glutaraldehyde	0.1	1.1	1.2	0.3	0.6	0.6	1.0	0.7
Hydrochloric	0.1	0.6	0.6	0.3	0.4	0.5	0.8	0.5
Acetic	0.1	0.4	0.4	0.3	0.4	0.4	0.5	0.4
Citric	0.1	0.3	0.3	0.3	0.3	0.2	0.3	0.3
Oxalic	0.1	3.0	3.5	2.0	2.2	4.5	1.4	2.3
SO ₄ ⁻ mg/L								
Control	25.7	10.3	14.8	7.0	8.1	16.1	18.8	28.3
Control + Glutaraldehyde	25.7	23.7	26.3	20.9	23.9	24.5	22.9	22.4
Hydrochloric	25.7	26.3	28.4	26.9	28.3	23.6	23.3	21.7
Acetic	25.7	27.3	27.9	28.6	29.2	26.6	22.7	23.3
Citric	25.7	30.6	31.4	31.6	33.2	28.0	22.2	22.0
Oxalic	25.7	29.6	32.0	29.1	29.1	29.0	28.0	19.0
Cl ⁻ mg/L								
Control	32.0	21.7	21.5	18.7	21.9	21.7	19.7	19.3
Control + Glutaraldehyde	32.0	40.5	39.8	32.1	41.3	41.1	34.2	16.3
Hydrochloric	32.0	132.5	166.4	214.9	214.5	211.0	252.6	245.1
Acetic	32.0	18.6	17.8	18.4	18.4	18.9	15.2	15.7
Citric	32.0	25.6	21.1	22.6	23.2	20.5	15.3	15.4
Oxalic	32.0	25.3	22.0	22.3	22.0	20.9	18.9	19.0

Appendix D: Full Data of Towards Design of Phosphorus Release Reactors

Table D.1: DRP release initial and after 15 day under pH 4, 20 °C and anaerobic condition and then ultrasonic treatment (AS WAS)

Temp °C	pH	Day	Treatment	DRP mg P/L
20	7	0	Without Ultrasonic Treatment	8.5
20	4	15	Without Ultrasonic Treatment	71.8
20	4	15	Ultrasonic Treatment	74.2

Table D.2: Solid sludge phosphorus fractionation (mg/g) initial and after 15 days under pH 4, pH 6.9, temperature 20 °C and anaerobic with and without ultrasonic treatment (AS WAS)

Treatments				TP	IP	OP	NAIP	AP
Temp °C	pH	Days	Condition					
20	6.9	0		17.1	12.4	4.7	10.2	2.2
20	4	15		8.4	4.2	4.3	3.4	0.8
20	4	15	Ultrasonic Treatment	7.7	3.8	3.9	3.2	0.6

Table D.3: COD analysis under pH 4 using different acids (CBNR WAS)

Treatments	COD Analysis mg/L			
	Day 0	Day1	Day 3	Day 6
20°C, pH ,Citric Acid	41	1038	1115	1120
20°, pH4, HCl Acid	41	636	641	650
20°C, pH4, Oxalic Acid	41	642	702	716
20°C, pH4, Peracetic Acid	41	900	952	961
20°C, pH 6.9, Control	41	237	278	344

Appendix E: Comparisons of pH 4, pH 5 and control at pH 7 (AS WAS)

A batch test was conducted to support the findings of previous results of higher P release under lower pH < 6. The sample was collected from AS treatment plant. The initial characteristics of WAS was pH 7 and TSS 2850 mg/L. The sample was adjusted to pH 4, pH 5 and control at pH 7 and anaerobically incubated at 20 °C. P release was monitored throughout 21 days. The higher soluble P 57.1 mg/L was noticed under pH 4. Figure E.1 and Table E.1 shows detail of P release kinetics. This is a repeat test and the result is agreement with other results of this research. It gives greater confidence in the results.

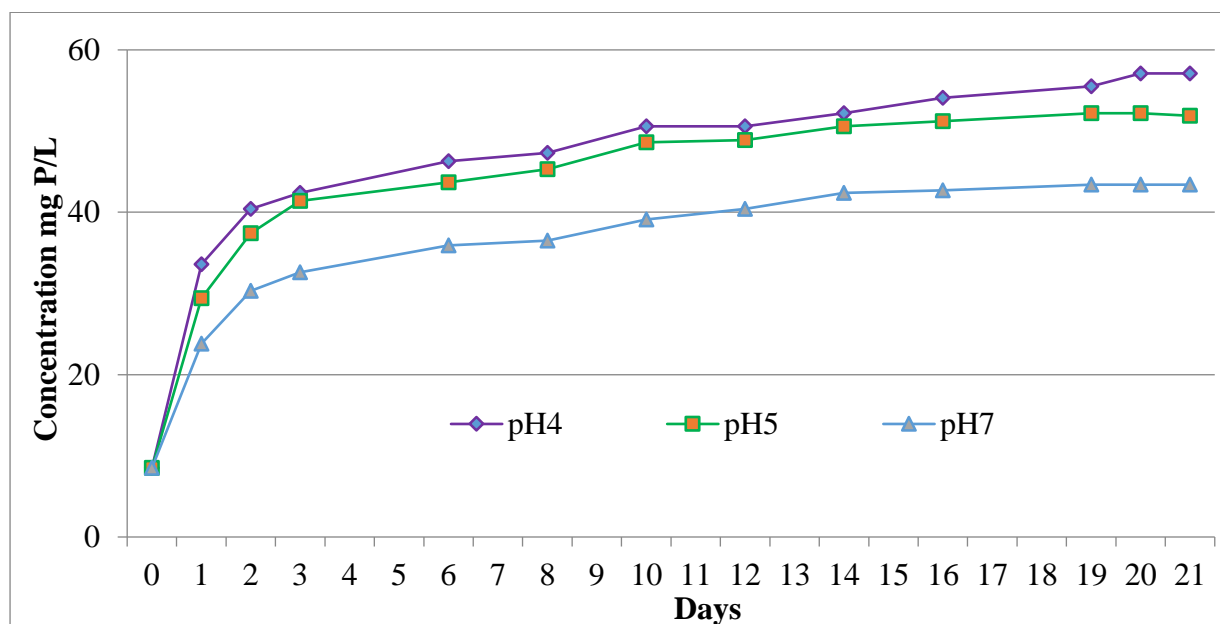


Figure E.1: DRP release at pH 4, pH 5 and pH 7 at 20 °C under anaerobic condition (AS Sludge)

Table E.1: DRP analysis under pH 4, pH 5, pH 7, temperature 20 °C and anaerobic condition (AS WAS)

Temp °C	pH	Days												
		0	1	2	3	6	8	10	12	14	16	19	20	21
		Dissolved Reactive Phosphorus (DRP) as mg P/L												
20	4	8.5	33.6	40.4	42.4	46.3	47.3	50.6	50.6	52.2	54.1	55.5	57.1	57.1
20	5	8.5	29.4	37.4	41.4	43.7	45.3	48.6	48.9	50.6	51.2	52.2	52.2	51.9
20	7	8.5	23.8	30.3	32.6	35.9	36.5	39.1	40.4	42.4	42.7	43.4	43.4	43.4
		Total Dissolved Phosphorus (TDP) as mg P/L												
20	4	8.8	34.3	40.8	43.1	47.0	47.3	50.9	51.2	52.2	54.1	55.5	57.1	57.7
20	5	8.8	29.7	38.2.4	42.1	46.0	46.3	48.3	49.3	50.6	51.2	52.5	52.2	52.2
20	7	8.8	24.1	30.3	32.6	35.9	36.5	39.1	40.8	42.4	42.7	43.4	43.4	44.0

Appendix F: Comparisons of pH 4, pH 5, pH 6 and control at pH 7 (CBNR WAS)

A batch test was conducted to support the findings of previous results of higher P release under lower pH 4. The sample was collected from CBNR treatment plant. The initial characteristics of sample was pH 7.0 and TSS 4905 mg/L. The sample was adjusted to pH 4, pH 5, pH 6 and control at pH 7 and anaerobically incubated at 20 °C. The P release kinetics was monitored throughout 10 days. The higher soluble P 134.6 mg/L was noticed under pH 4 and after 11 days treatments. Figure F.1 and Table F.1 shows detail of P release. In the CBNR WAS sample, did not have another test at pH of 5 or pH of 6, and this gives a more complete picture of the effect of pH on P release.

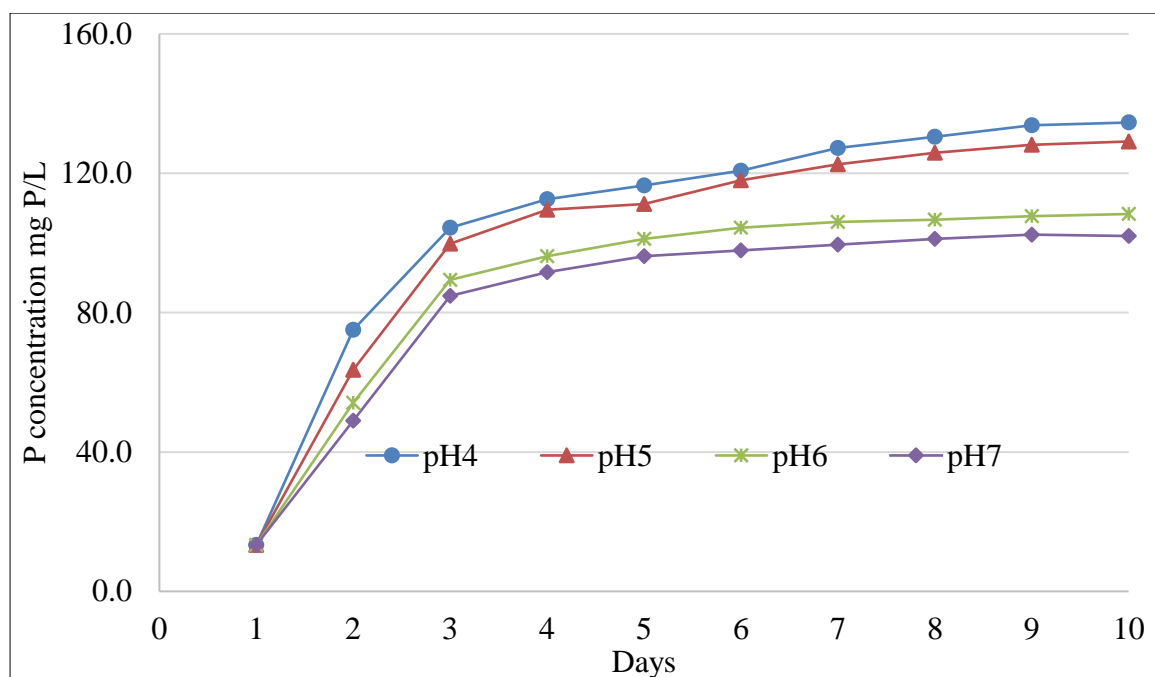


Figure F.1: DRP release under different pH under anaerobic condition (CBNR Sludge)

This tests indicated that below pH 6, phosphorus was release significantly and under pH 4 highest P released was observed. The results are in agreement with the previous batches result.

Table F.1: DRP analysis under pH 4, pH 5, pH 6, pH 7, temperature 20 °C and anaerobic condition (CBNR WAS)

Temp °C	pH	Days									
		0	1	2	3	4	5	6	7	9	11
20	4	13.3	75.0	104.4	112.5	116.5	120.7	127.2	130.5	133.7	134.6
20	5	13.3	63.6	99.8	109.5	111.2	118.0	122.5	125.9	128.1	129.1
20	6	13.3	54.1	89.4	96.2	101.1	104.4	106.0	106.7	107.6	108.3
20	7	13.3	48.9	84.8	91.6	96.2	97.9	99.5	101.1	102.4	102.0

Appendix G: Kinetic coefficient calculation using a first order relationship

Non-linear regression in the Excel solver was used to fit the first order decay (k) and P release. Minimisation of square residuals was used. Kinetic coefficients (k) of DRP and TDP released under different combinations (pHs and temperatures) were estimated using first order of relationship for batch 3 and 4.

There were no trends seen on different K values between different pH and temperature combinations. The combination of lower pH4 and higher temperature 30 °C in batch 3 reached maximum DRP 66.7 mgP/L level in aqueous phase having 55.6 mgP/L P released. Same combination also reached maximum TDP 72.3 mgP/L level in aqueous phase having 59.9 mgP/L P released. Similarly, combination of lower pH4 and higher temperature 35 °C in batch 4 reached maximum DRP 74.3 mgP/L level in aqueous phase having 67.1 mgP/L P released. Same combination also reached maximum TDP 76.4 mgP/L level in aqueous phase having 69.0 mgP/L P released. Calculation of k on TSP losses from day 0 to 22 days under different pH/temp treatment (Table G.5) also didn't show any trends except the lower TSP (8.2 mg/g dry sludge) after 22 days treatment under pH 4 and temperature 35°C.

Table G.1: Kinetic coefficient calculation using a first order relationship for DRP (Batch 3)

Treatments			k (1/day)	P max (mg/L)	P release (mg/L)	Av. Misfit (mg/L)
Temp °C	pH	Days				
20	7	7	1.3	44.0	32.9	0.6
10	4	7	2.0	38.7	27.6	1.1
10	6	7	1.4	32.4	21.3	0.3
10	8	7	0.4	39.7	28.6	1.1
20	4	7	1.2	52.3	41.2	0.4
20	6	7	2.2	48.6	37.5	1.2
20	8	7	0.6	55.7	44.6	0.7
30	4	7	1.5	66.7	55.6	1.3
30	6	7	1.7	61.6	50.5	0.9
30	8	7	1.2	62.1	51.0	0.4

Table G.2: Kinetic coefficient calculation using a first order relationship for TDP (Batch 3)

Treatments			K (1/day)	P max (mg/L)	P release (mg/L)	Av. Misfit (mg/L)
Temp °C	pH	Days				
20	7	7	1.2	47.1	34.7	0.4
10	4	7	1.7	43.0	30.6	1.0
10	6	7	1.2	36.8	24.4	0.7
10	8	7	0.3	46.5	34.1	1.4
20	4	7	0.7	59.7	47.3	1.3
20	6	7	1.9	53.1	40.7	0.8
20	8	7	0.7	55.7	43.3	0.7
30	4	7	1.4	72.3	59.9	0.9
30	6	7	1.4	70.2	57.8	0.9
30	8	7	1.2	65.4	53.0	1.1

Table G.3: Kinetic coefficient calculation using a first order relationship for DRP (Batch 4)

Treatments			K (1/day)	P max (mg/L)	P release (mg/L)	Av. Misfit (mg/L)
Temp °C	pH	Days				
20	6.9	8	1.2	52.2	45.0	1.2
10	4	8	0.2	42.2	35.0	1.9
10	6	8	0.1	37.8	30.6	0.9
10	8	8	0.1	49.2	42.0	0.5
20	4	8	1.13	66.5	59.3	0.9
20	6	8	0.4	56.4	49.2	1.0
20	8	8	0.3	57.7	50.5	0.9
35	4	8	0.7	77.9	70.7	0.9
35	6	8	1.1	65.2	58.0	2.2
35	8	8	1.6	59.2	52.0	1.5

Table G.4: Kinetic coefficient calculation using a first order relationship for TDP (Batch 4)

Treatments			K (1/day)	P max (mg/L)	P release (mg/L)	Av. Misfit (mg/L)
Temp °C	pH	Days				
20	6.9	8	0.4	53.3	45.8	3.2
10	4	8	0.8	36.8	29.3	6.5
10	6	8	0.1	38.9	31.4	3.4
10	8	8	0.1	52.2	44.7	1.9
20	4	8	1.3	66.5	59.0	2.9
20	6	8	0.4	56.3	48.8	3.7
20	8	8	0.3	57.5	50.0	3.6
35	4	8	0.8	79.1	71.6	2.8
35	6	8	0.9	65.8	58.3	7.5
35	8	8	1.0	58.4	50.9	7.2

Table G.5: Kinetic coefficient calculation using a first order relationship for TSP (Batch 4)

Treatments			K (1/Days)	P initial (mg/g of dry sludge)	P final (mg/g of dry sludge)	Av. Misfit (mg/g of dry sludge)
Temp °C	pH	Days				
20	6.9	22	0.4	16.8	12.8	0.1
10	4	22	0.0	16.8	10.2	0.3
10	6	22	0.0	16.8	13.9	1.3
10	8	22	0.1	16.8	13.7	0.0
20	4	22	0.5	16.8	8.9	0.0
20	6	22	0.3	16.8	11.5	0.0
20	8	22	0.2	16.8	12.2	0.1
35	4	22	0.4	16.8	8.2	0.0
35	6	22	8.5	16.8	11.7	0.1
35	8	22	1.2	16.8	12	0.0

Appendix H: Preliminary testing of temperature effects on P release (Batch 2)

Preliminary (batch 2) was conducted to test the effect of temperature under anaerobic condition on P release at 20 °C and 35 °C temperature and a pH of 6.9 (without pH adjustment). Three replicated tests were conducted for both 20 °C and 35 °C temperature. Temperature was maintained through incubation (using Thermo Fisher Scientific high performance incubator having mechanical convection utilises a fan to force heated air throughout the incubator resulting in uniform temperature distribution throughout the unit). The batch test was run for 12 days. The standard deviation of DRP between three replicates ranged from 0 to 0.9 mg P/L within initial to 12 days. Initial soluble P concentration was 7.2 mg/L and it reached 52.3 mg/L after 12 days at 20 °C temperature treatment. Similarly, 7.2 mg/L initial soluble P concentration reached 59.4 mg/L after 12 days at 35 °C treatment. Figure 4.3 shows the effect of temperature on P release under anaerobic condition. The detailed results of this batch test is shown in Table A.2 in Appendix A.

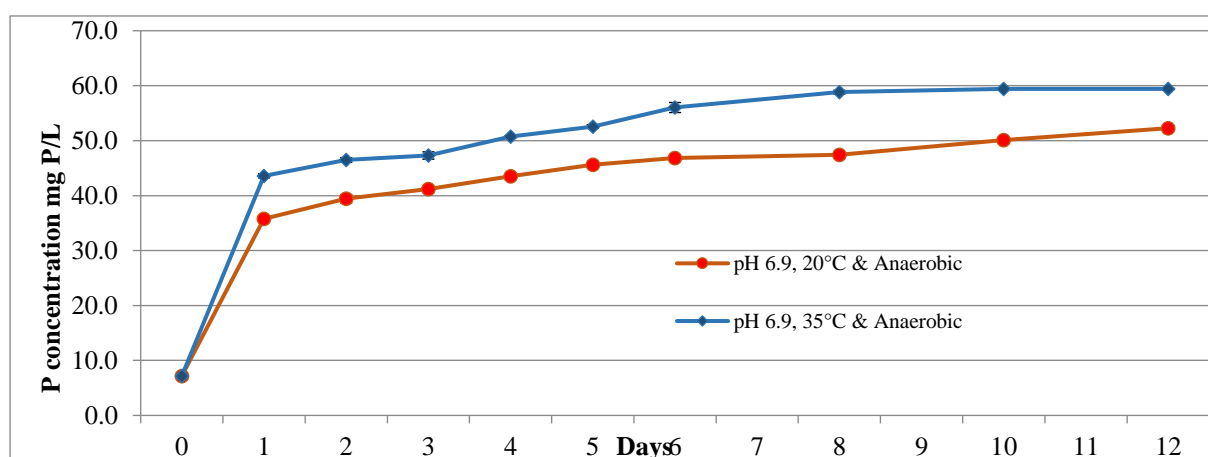


Figure H.1: DRP release at 20 °C and 35 °C temperature under anaerobic condition

(Estimated standard deviation between three replicates was roughly 0.9 mg P/L (Table A.2))

The findings of this study indicated that there was an important difference (25% more DRP under 35 °C than under 20 °C) of P release from the activated sludge at 20 °C and 35 °C temperature which was 1.24 times more at 35 °C than at 20 °C. The higher temperature and anaerobic condition release high P from sludge into the water. This higher P release was either due to temperature effects on growth or other biological microbes activity; speeds of P uptake and release activities or presence/ absence of metals on sludge. Thus it was concluded that the higher temperature (30-35°C) was better for maximum P release and afterward temperature range 30-35°C was tested for P release.

Table H.1: Anaerobic phosphorus release from standard activated sludge under 20 °C and 35 °C and pH 6.9 without adjustment of initial pH

Parameters		Dissolved Reactive Phosphorus (mg/L)										
		Days										
Temp °C	pH		0	1	2	3	4	5	6	8	10	12
20	6.9	Anaerobic	7.2	35.9	38.6	41.2	43.5	45.2	46.5	47.8	50.1	52.1
20	6.9	Anaerobic	7.2	36.1	39.6	40.9	43.2	45.7	46.9	47.2	50.3	52.7
20	6.9	Anaerobic	7.2	35.4	40.1	41.4	43.8	45.9	47.1	47.3	49.9	52.0
Average			7.2	35.8	39.4	41.2	43.5	45.6	46.8	47.4	50.1	52.3
Standard Deviation			0.0	0.4	0.8	0.3	0.3	0.4	0.3	0.3	0.2	0.4
35	6.9	Anaerobic	7.2	44.0	47.0	46.6	50.7	52.7	55.5	59.2	59.4	59.4
35	6.9	Anaerobic	7.2	43.4	46.2	48.0	50.9	52.2	55.5	58.6	59.5	59.5
35	6.9	Anaerobic	7.2	43.4	46.3	47.3	50.6	52.8	57.1	58.7	59.4	59.4
Average			7.2	43.6	46.5	47.3	50.7	52.6	56.0	58.8	59.4	59.4
Standard Deviation			0.0	0.4	0.4	0.7	0.2	0.3	0.9	0.3	0.1	0.1

Appendix I: Staining to test for poly-P bacteria

All the batch test results for this research show a strong release of P from the NAIP fraction. It is not clear if this P release is from polyphosphates stored in cells or just sorbed P on cell surfaces and inorganic matter. A pH of 4 perhaps kills bio-P bacteria and leads to fewer of them and little biological release of P. Quantitative analysis of polyphosphates would be needed to verify the bio-P bacteria behaviour at lower pH such as at pH 4, but the analysis is beyond the scope of this research. It could be useful to do more research on identifying the activity of bio-P bacteria when developing P release reactors. A preliminary study was conducted looking at bio-P bacteria under pH 6.9, pH 4, temperature 35 °C and anaerobic condition after 7 days.

The Neisser staining method (see section 3.3.9 for details) was used to prepare slides, which were then viewed under a microscope. In this test, colonies of blue-black coloured cells are comprised bio-P bacteria. There are some variations in the manner in which these types of colonies stain with Neisser. The shade is sometimes much lighter, or only a part of the cell stains darkly. Figure I.1A and I.1.B shows the view of the slide of control WAS under pH 6.9 at day 1 and day 7 and Figure I.1C shows the view of the slide of WAS treated under pH 4, temperature 35 °C anaerobically and at day 7. The WAS sample was from the CBNR plant. This experiment verifies the presence of polyphosphates under lower pH 4.

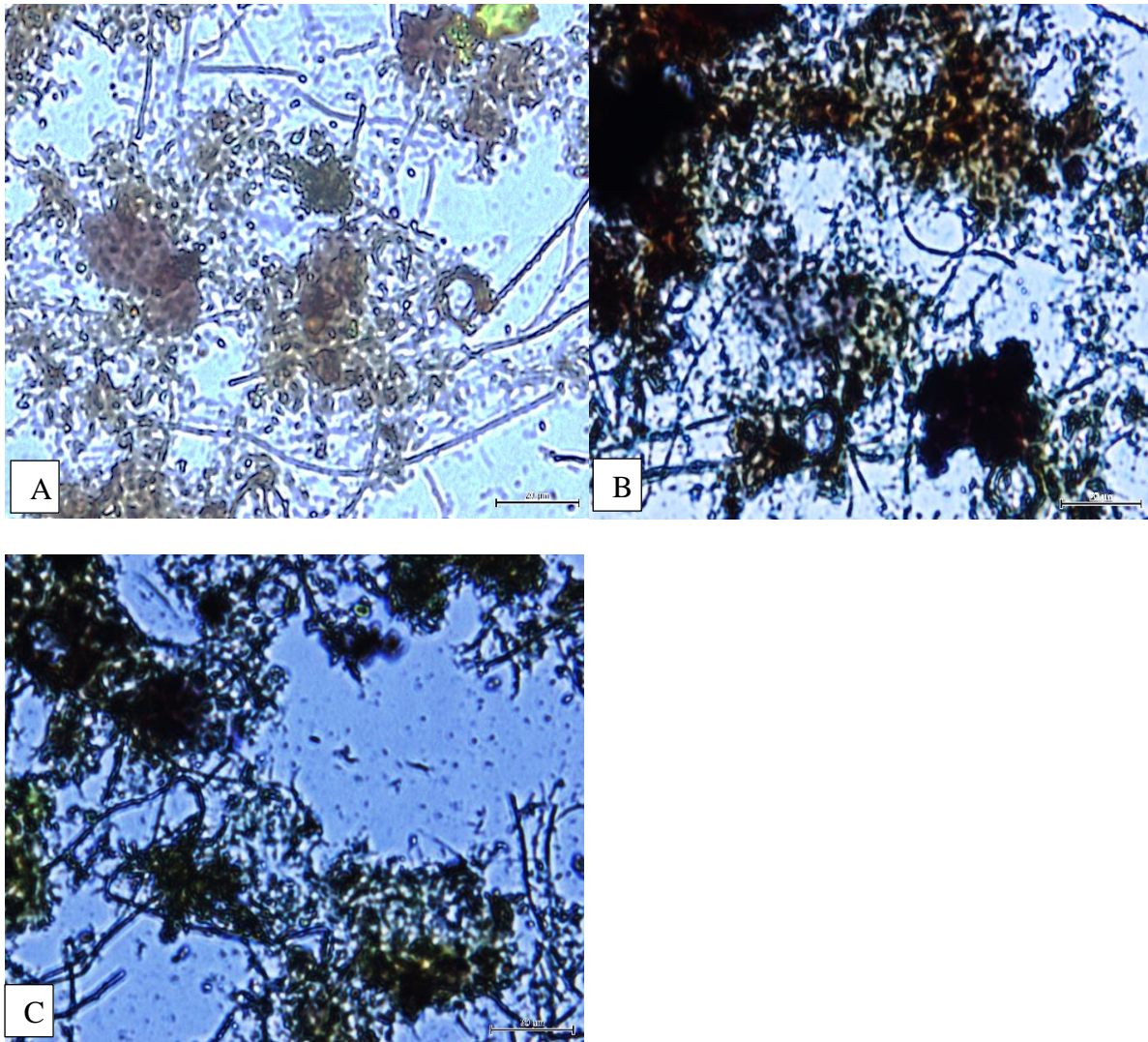


Figure I.1: Neisser positive for polyphosphates; (A) initial WAS, (B) control at pH 6.9, temperature 20 °C and (C) pH 4, 35 °C and anaerobic conditions.

Appendix J: Metal and cation release from WAS under different pH

Metal and cation concentrations (Ca, Mg, Mn, Fe, Cd, Cu, Zn, and Ni) released using HCl acid from CBNR WAS under different pH (4, 5, 6, 6.9 & 8), 20 °C temperature and anaerobic condition was monitored. Figure J.1, Table J.1 and Table J.2 shows findings of some results. The results indicate that lowering pH from 8 to pH 4 significantly increased some metals (Fe and Mn) and cations (Ca and Mg) in the liquid phase, but other metals Cd, Cu, Zn, and Ni are negligibly released.

The metals Ca, Mg, Fe, and Mn are widely recognized for their role in phosphate precipitation. Chemical treatment methods are promising for P recovery, as Ca and Mg precipitates P formed by crystallisation and precipitation methods have the potential to be re-used as P fertilizer if separated from wastewater and dried (Bauer et al., 2007).

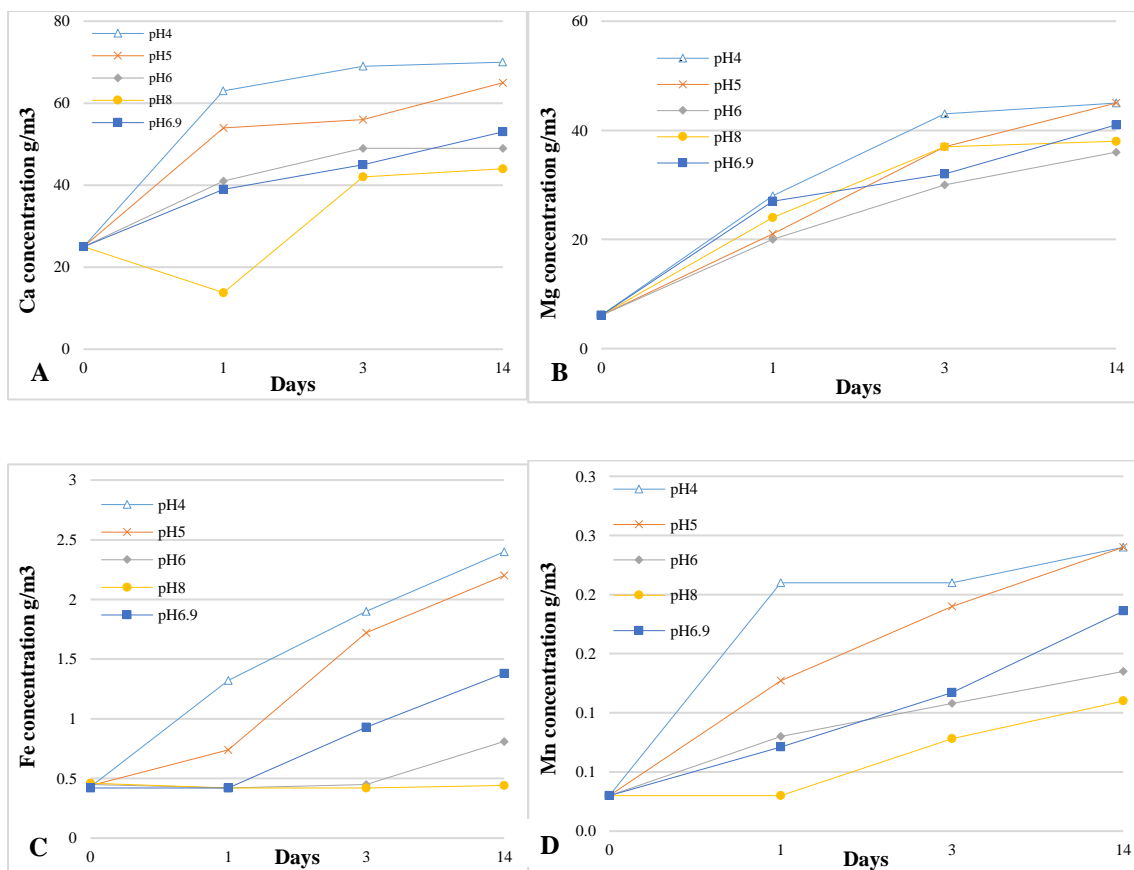


Figure J.1: Metals release from CBNR WAS under different pH, 20 °C and anaerobically (A Calcium, B Magnesium, C Iron and D Manganese)

Table J.1: Metal release from WAS under different pH

Metals	Concentration (g/m ³) from 0 to 14 day under pH 4 to 8
Cd	<0.0011
Cu	0.012 to 0.023
Zn	0.054 to 0.23
Ni	0.015 to 0.053

Table J.2: Metal release from CBNR WAS under different pH

Treatments		Metal release g/m ³	Days			
pH	Temp °C		0	1	3	14
6.9	20	Cd	<0.0011	<0.0011	<0.0011	<0.0011
6.9	20	Cd	<0.0011	<0.0011	<0.0011	<0.0011
4	20	Cd	<0.0011	<0.0011	<0.0011	<0.0011
5	20	Cd	<0.0011	<0.0011	<0.0011	<0.0011
6	20	Cd	<0.0011	<0.0011	<0.0011	<0.0011
8	20	Cd	<0.0011	<0.0011	<0.0011	<0.0011
6.9	20	Ca	25	39	45	53
4	20	Ca	25	63	69	70
5	20	Ca	25	54	56	65
6	20	Ca	25	41	49	49
8	20	Ca	25	13.8	42	44
6.9	20	Cr	<0.011	<0.011	<0.011	<0.011
4	20	Cr	<0.011	<0.011	<0.011	<0.011
5	20	Cr	<0.011	<0.011	<0.011	<0.011
6	20	Cr	<0.011	<0.011	<0.011	<0.011
8	20	Cr	<0.011	<0.011	<0.011	<0.011
6.9	20	Cu	<0.011	0.017	0.011	0.017
4	20	Cu	<0.011	<0.011	0.013	0.022
5	20	Cu	<0.011	<0.011	<0.011	<0.011
6	20	Cu	<0.011	0.012	0.023	0.06
8	20	Cu	<0.011	0.022	0.014	0.017
6.9	20	Fe	<0.42	<0.42	0.93	1.38
4	20	Fe	<0.43	1.32	1.9	2.4
5	20	Fe	<0.44	0.74	1.72	2.2
6	20	Fe	<0.45	<0.42	0.45	0.81
8	20	Fe	<0.46	<0.42	<0.42	0.44
6.9	20	Mg	6.1	20	30	36
4	20	Mg	6.1	28	43	45
5	20	Mg	6.1	27	37	45
6	20	Mg	6.1	21	32	41
8	20	Mg	6.1	24	37	38
6.9	20	Mn	0.03	0.071	0.117	0.186
4	20	Mn	0.03	0.21	0.21	0.24
5	20	Mn	0.03	0.127	0.19	0.24
6	20	Mn	0.03	0.08	0.108	0.135
8	20	Mn	0.03	<0.011	0.078	0.11
6.9	20	Ni	<0.011	<0.011	0.023	0.053
4	20	Ni	<0.012	0.016	0.015	0.031

5	20	Ni	<0.013	<0.011	0.019	0.04
6	20	Ni	<0.014	<0.011	<0.011	0.012
8	20	Ni	<0.015	<0.011	<0.011	<0.011
6.9	20	Zn	0.054	<0.021	<0.021	<0.021
4	20	Zn	0.054	0.23	<0.021	<0.021
5	20	Zn	0.054	0.031	<0.021	<0.021
6	20	Zn	0.054	<0.021	<0.021	0.033
8	20	Zn	0.054	<0.021	<0.021	<0.021

The key findings of this test are that: (1) of the toxic metals, Zn is the only one that increases significantly during P release at pH of 4, and so there might not be significant toxicity issues with a P recovery reactor, and (2) Fe, Ca, Mg also increase which could have implications for P recovery depending on what process is used for P recovery.

Appendix K: Test of Ultrasonic Disruption of Cells for P Release

K.1 Introduction

The previous chapters' results indicate that most of the P released was from the inorganic (NAIP/AP) fraction under lower pH (<6) using hydrochloric acid. So the performance of any P release reactor will depend greatly on P release from these NAIP/AP fractions. There are still questions such as: do chemical changes lead directly to these P release fractions? Or, do chemical changes cause the cells to behave differently? Slight pH reductions to WAS are known to lead to biological release of P, but for very low pH we expect cell death and lysis and a more chemical process of P release from NAIP/AP. Due to lack of quantitative study of the bacterial presence in the WAS initial sample and after different pH, temperatures, aerobic and anaerobic treatments, it is difficult to separate biological and chemical processes.

Ultrasonic disintegration is a well-known method for the break-up of microbial cells to release intracellular materials (Mao et al., 2004). Various research have been conducted on waste activated sludge and ultrasonic treatment effects for disintegration, bacterial population and dewatering (Tiehm et al. (2001); Dewil et al. (2006); Kesari et al. (2011)). Fewer have examined P release by using ultrasonic treatment on WAS. Yan et al. (2010) used ultrasonic treatment on waste activated sludge and then fermented at pH 10. P concentrations of 35.7 mg P/L and 31.8 mg P/L were observed with and without 1.0 kW/L ultrasonic energy density, with pH 10.0 and after 7 days at 20 °C. The sample was collected from the secondary sedimentation tank of a municipal WWTP with initial pH 6.5 and TSS 10119 mg/L.

Ultrasonic treatment can kill many (but not all) cells, and create cell lysis without great changes in the chemistry or temperature. If P release at pH 4 is limited by live microbes retaining NAIP/AP, then it would be expected that ultrasonic treatment would increase P release.

There is a lack of knowledge about the ultrasonic effect on P release. This chapter describes a preliminary study, and the results will be a preliminary indication of ultrasonic disruption as an option for P release and provide information about whether P release at pH 4 is limited by a biological or chemical process.

K.2 Method and materials

One batch test was conducted to test the ultrasonic treatment for bio-P release. The sample was collected from a standard activated sludge WWTP (AS). An initial DRP of 8.5 mg P/L was noted within the sample. The sample was then treated under pH 4, 20 °C and anaerobically for 15 days. One litre of sample was then treated with ultrasonic energy density vibrator (1.0 kW/L) for one hour to break down the cells.

When the WAS was treated under ultrasonic waves, the temperature increased slightly. High temperatures, however, result in thermal degradation or destruction of various components and microorganisms within the WAS. Because this test intended to study the sole effect of ultrasonic treatment on P release, experiments had to be dissociated from thermal effects. Considerable temperature increases should therefore be avoided.

K.3 Results and discussion

The initial DRP 8.5 mg P/L was observed within the AS WAS sample. Under anaerobic condition, 20 °C and at pH 4 for 15 days; DRP increased to 71.8 mg P/L. A similar result was found with different batch of AS WAS and reported in Chapter 4 (DRP 69.5 mg/L under anaerobic, 20 °C, at pH 4 and after 14 days). Further application of ultrasonic treatment, DRP concentration enhanced this to 74.2 mg P/L.

The result indicated that there was no significant additional P released after ultrasonic treatment. Only a little more DRP was released (2.4 mg/L) which was 3% more than without

ultrasonic treatment. The increased 3% DRP is expected to be due to the breakdown of microbial cells. The results are shown in Figure 7.1.

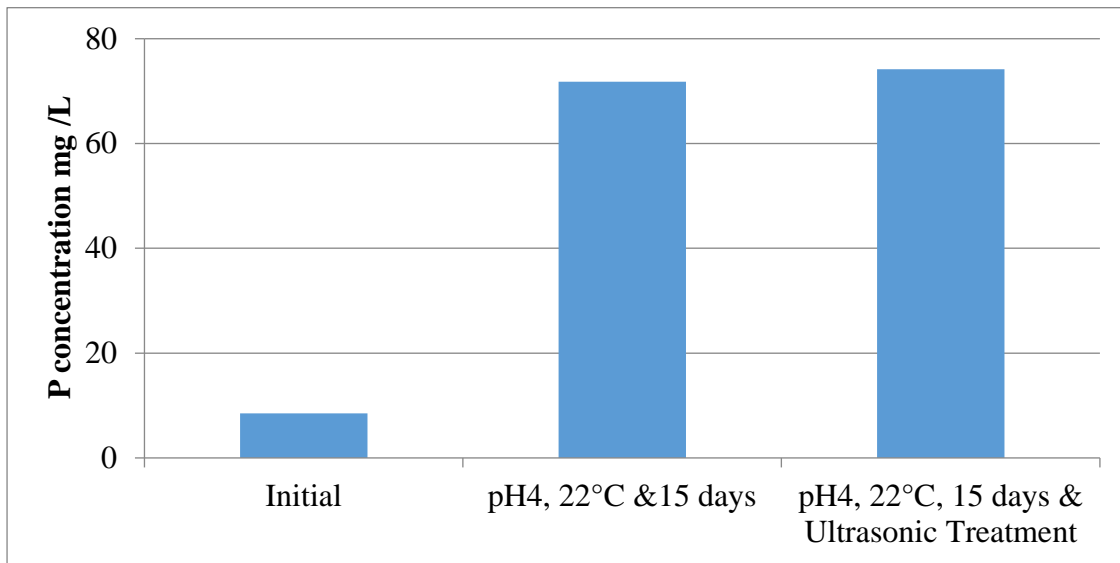


Figure K.1: DRP release with and without ultrasonic treatment

The solid P fractionation analysis was also conducted on this batch test. The details of solid results are shown in Figure 7.2. There was no variation of NAIP and AP release with and without ultrasonic treatment. There was a 10% release of OP fraction before ultrasonic treatment and after treatment released up to 22%. It appears that the extra P release with ultrasonic treatment is from OP and not NAIP, but the change is small relative to the uncertainty in the tests and no strong conclusions can be reached. The full results of both liquid and solid phase P release are provided in Table D.1 and D.2 in Appendix D.

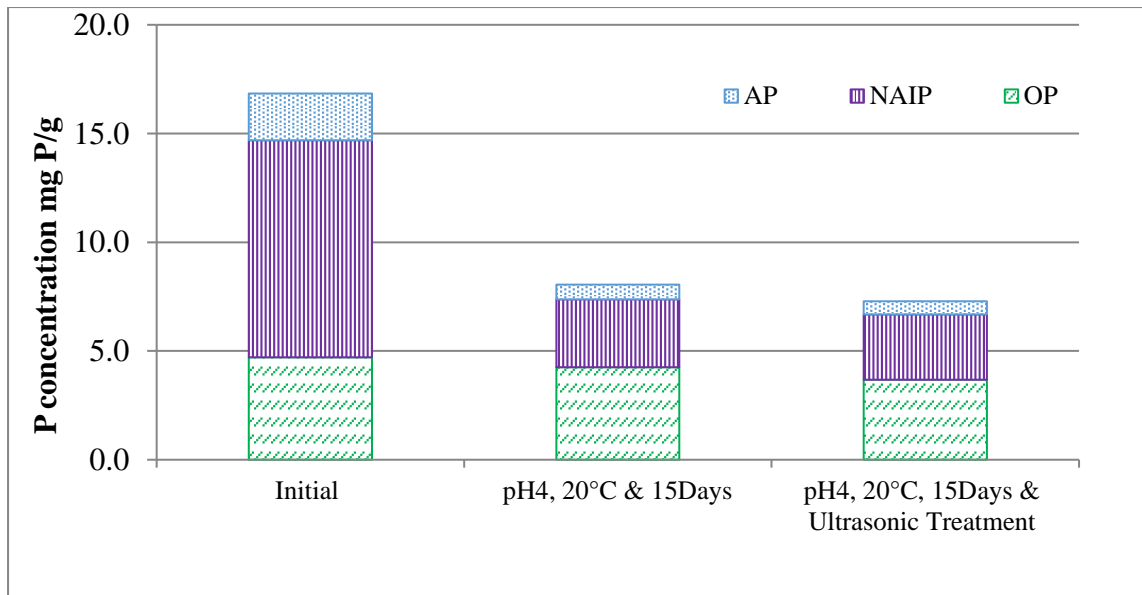


Figure K.2: Phosphorus fraction under ultrasonic and without ultrasonic treatment

The result from this ultrasonic testing also indicates that chemical desorption and cell lysis are not major contributors to P release at pH 4. These preliminary results indicate that more aggressive treatment that kills biomass might not improve P release.

K.4 Conclusions

Ultrasonic disruption may be an option for releasing slightly more of the OP fraction (which was not significantly released under pH 4). The result shows that the ultrasonic treatment does not seem to increase the NAIP release.