# PHOSPHORUS RECOVERY FROM A MEMBRANE ENHANCED BIOLOGICAL PHOSPHORUS REMOVAL (MEBPR) PROCESS

by

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# Abstract

Phosphorus is an essential yet limited element for sustaining life of human beings. Municipal wastewater contains rich phosphorus, which is not sufficiently recovered or recycled. This dissertation developed a system that could recover phosphorus from wastewater as struvite fertilizer ($MgNH_4PO_4 \cdot 6H_2O$). Such a system included three major components — a membrane enhanced biological phosphorus removal (MEBPR) process, a side-stream unit to extract $PO_4^{3-}$ and $NH_4^+$ from wasted solids, and a struvite crystallizer. This dissertation focused on optimizing the first two steps through pilot- and bench-scale studies, respectively.

The MEBPR process was tested at increasing solids retention time (SRT) to increase total phosphorus (TP) concentration in mixed liquor (ML). The operation at SRT = 60 days proved to be technically feasible and achieved comparable phosphorus removal (95−96 %) and organic carbon removal (91−92 %) to that observed during operation at the control SRT (25 days). The 60-day SRT operation also removed 14 % more nitrogen, wasted 17 % less dry solids, more than doubled the TP concentration of aerobic zone ML, but did not increase membrane fouling rates. Cost analyses showed that the energy requirements were 0.94 and 2.1 kWh/m$^3$ of permeate for SRT = 25 and 60 days, both within the reported range for full-scale membrane bioreactors.

To solve foaming problem in the MEBPR process, foam was characterized as an alternative resource for phosphorus recovery. Methods were assessed to extract  phosphorus from ML and foam. With suitable conditions, microwave-based hydrogen peroxide advanced oxidation process (MW-$H_2O_2$ AOP) could extract > 90 % of TP as $PO_4$-P from foam, and anaerobic P-release could extract up to 60 % from ML. Anaerobic digestion could extract 44−46 % of TP under

digestion pHs, 64−65 % with pH ≤ 5.5, and generate sufficient $NH_4^+$ that matched the quantities of $PO_4^{3-}$ extracted.

Finally, a system was proposed that included an MEBRP process operating at SRT = 60 days, and an anaerobic digester to extract both $PO_4^{3-}$ and $NH_4^+$. This system could recover about 60 % of the incoming phosphorus in the influent. To recover more phosphorus, MW-$H_2O_2$ AOP could be used after anaerobic digestion, whenever justified.

# Preface

I planned, designed, and conducted all the batch experiments by myself, and led the operation of the UBC pilot plant with some help from other students. Chemical analyses of $PO_4$-P, $NH_4$-N, $NOx$-N, VFA, TP, and TKN were conducted by our Environmental Lab technician Mr. Timothy Ma. I analyzed all other data.

# Table of Contents

**Chapter 3: Foam In A Membrane Enhanced Biological Phosphorus Removal (MEBPR)**

**Process: From Operational Nuisance To Valuable Resource For Phosphorus Recovery ....82**

**Chapter 4: Evaluation of Methods To Extract Phosphorus From Activated Sludge Mixed**

**Liquor And Foam From An MEBPR Process ........................................................120**

# List of Tables

# List of Figures

# List of Symbols

$g$ —gravity acceleration ($9.8 \text{ m/s}^2$)

$\Delta h$ —vertical height difference between water intake level and discharge pipe exit (m)

$P_0$ —power consumption of pump (W)

$\Delta P$ —differential pressure between pump inlet and outlet (Pa)

$\Delta P\text{m}$ —average TMP (Pa)

$Q_L$ —liquid flow rate ($\text{m}^3/\text{s}$)

$Q\text{p}$ —permeate flow rate ($\text{m}^3/\text{s}$)

$Q\text{s}$ —internally recycled activated sludge ($\text{m}^3/\text{s}$)

$V_L$ —liquid velocity in pump outlet (m/s)

$W\text{p}$ —power consumption for permeate pumping (W)

$W\text{s}$ —power consumption for sludge recycle pumping (W)

$\rho$ —liquid density ($\text{kg/m}^3$)

$\varepsilon_P$ —pump efficiency (-)

$\varepsilon_M$ —motor efficiency (-)

$\eta$ —($\varepsilon_P * \varepsilon_M$), combined efficiency of pump and motor

# List of Abbreviations

AHP — Acid-hydrolyzable phosphorus

AOTR — Actual oxygen transfer rate

AR — Aerobic recycle ratio

AS — Activated sludge

BNR — Biological nutrient removal

CASPs — Conventional activated sludge processes

CEBPR — Conventional enhanced biological phosphorus removal

COD — Chemical oxygen demand

COV — Coefficient of variation

CSH — Cell surface hydrophobicity

CST — Capillary suction time

DO — Dissolved oxygen

EBPR — Enhanced biological phosphorus removal

EPSc — Carbohydrate components of EPS

EPSp — Protein components of EPS

EPSs — Extracellular polymeric substances

F/M — Food to microorgansim ratio

HF — Hollow fibre

HRT — Hydraulic retention time

MBR — Membrane bioreactor reactor

MEBPR — Membrane enhanced biological phosphorus removal

MLSS ― Mixed liquor suspended solids

MW ― Microwave

MW-$H_2O_2$ AOP ― Microwave hydrogen peroxide advanced oxidation process

NR ― Mixed liquor recirculation from aerobic zone to anoxic zone

RAS ― Return activated sludge

SADm ― Specific aeration demand (based on membrane area)

SCFA ― Short-chain fatty acid

SMPs ― Soluble microbial products

SND ― Simultaneous nitrification and denitrification

SRT ― Solids retention time

SOTE ― Standard oxygen transfer efficiency

SOTR ― Standard oxygen transfer rate

TCOD ― Total chemical oxygen demand

TKN ― Total Kjeldahl Nitrogen

TMP ― Trans-membrane pressure

TP ― Total phosphorus

TSS ― Total suspended solids

UBC ― The University of British Columbia

UCT ― The University of Cape Town

VFA ― Volatile fatty acids

VSS ― Volatile suspended solids

WWTPs ― Wastewater treatment plants

# Acknowledgements

It has been a long journey to come to this point, a journey filled with lots of hardworking, sweating, anxiety and joy. So it is the time to acknowledge those who have helped with my PhD study, beginning with my supervisor Professor Eric R. Hall. He is such a wonderful advisor, very knowledgeable and patient in guiding me all the time through this study. His advice was always timely and enlightening when I was confused or lost. His penetrating questions taught me to think more deeply.

I thank my supervisory committee, including Professor Donald S. Mavinic, Professor Victor Lo, and Dr. Rob Simm, for their precious time and advice put into this research.

A special thank-you goes out to our lab technicians Paula Parkinson and Timothy Ma. Their generous help can be seen almost every day through the experimental time. Many thanks are given to Rony Das, Xiaoyu Zheng, Marcia Fromberg, and many other students to help run the pilot plant. I also thank the faculty and staff of Department of Civil Engineering for their support.

NSERC is acknowledged for providing financial support to my study.

Finally, the continual encouragement and support of my family, my parents and my friends has been a source of strength, which is sincerely appreciated.

# Dedication

In memory of Frederic Koch.

# Chapter 1: Introduction

## 1.1    Engineering Problem

Phosphorus is an essential element for sustainable life of human beings (Ashley et al., 2011; Cordell et al., 2011; Cornel and Schaum, 2009). It is a building block of deoxyribonucleic acid (DNA) and cellular membranes, and is a key compound of energy metabolism, and also one of the three key constituents of fertilizers. However, natural reserves of known, high-quality phosphate rock are limited in the world, and over 95 % of them are distributed in a few countries, with Morocco holding 82−85 %, followed by China owning about 12 % (Ashley et al., 2011). On the other hand, phosphorus demands continuously increase, especially due to increased uses in agriculture and electronics (e.g., cell phones, computers), which results in increasing phosphate prices. Municipal wastewater contains phosphorus due to human urine and the use of detergents; however, most of the phosphorus is wasted, ending up in either receiving waters, or landfills, or incinerators. If excess phosphorus enters into receiving waters , eutrophication occurs that lowers aquatic water quality. When phosphorus is recycled back to wastewater treatment plants (WWTPs) from sludge dewatering reject water, it may form a precipitate (e.g., struvite) that clogs the reject water piping and incurs expensive maintenance or pipe replacement (Britton et al., 2007). All these facts point to the need to recover phosphorus from WWTPs.

Phosphorus recovery is conventionally achieved through chemical precipitation, which is expensive and generates more sludge with chemicals. Among all technologies, recovering phosphorus through struvite ($MgNH_4PO_4 \cdot 6H_2O$) crystallization may represent the most desirable approach. The University of British Columbia (UBC) has developed a novel fluidized-bed

crystallizer, that efficiently converts soluble orthophosphate ($PO_4^{3-}$) to struvite pellets—a

fertilizer with high purity that minimizes soil contamination, and with a slow release rate that

prevents overdose and runoff with rain (Bhuiyan et al., 2008). As shown in Equation (1.1), this

technology also recovers equivalent moles of $NH_4^+$:

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \leftrightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow \qquad (1.1)$$
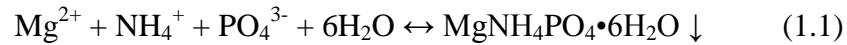
Typically, it is economically feasible to recover phosphorus from an enhanced biological

phosphorus removal (EBPR) process (Cornel and Schaum, 2009), which produces activated

sludge with higher phosphorus concentrations ($\geq$ 5 weight % dry P) than a non-EBPR process

(2−3 %) (Strom, 2006). An even better option is to combine a membrane bioreactor technology

(MBRs) with EBPR, and the combination is called the membrane enhanced biological

phosphorus removal (MEBPR) process. The MBRs bring extra advantages, e.g., high effluent

quality and small footprint, by utilizing membranes for solids-liquid separation. By comparison,

conventional EBPR (CEBPR) uses a secondary clarifier to separate liquid from solids, where

settling can be easily disturbed. MBRs were once very expensive, but with the development of

hollow fibre membrane technologies, their costs keep reducing these days and the costs are now

comparable to those of conventional WWTPs using sand filtration as tertiary treatment (Brepols

et al., 2010).

Research on MEBPR has been conducted at UBC for many years since UBC possesses a

MEBPR pilot plant, a research facility that has two treatment trains with capacity of treating real

domestic wastewater of $2 \times 5,300$ L/day. One, long-observed problem with the UBC MEBPR

train is foaming, which is a nuisance as reported by many other biological WWTPs. When the

UBC pilot plant was operated with both MEBPR and CEBPR trains in parallel, foaming was

consistently observed in the MEBPR (Figure 1.1), but only rarely in the CEBPR. To solve this

problem, foam was suppressed with pressurized water and re-suspended back into the underlying

mixed liquor daily. This simple solution worked temporarily, but with some problems. First,

foam accumulated over time and eventually exceeded the available freeboard. As an example,

after eight months of operation at a solids retention time (SRT) of 25 days, the total suspended

solids (TSS) in the foam accounted for $51 \pm 2$ % of the total suspended solids in the anoxic zone

and $64 \pm 2$ % of that in the anaerobic zone, respectively. The combined TSS in the foam from

these two zones accounted for $23 \pm 1$ % of the TSS in the entire system (Figure 1.2). Foaming

also interfered with the estimation of TSS inventory and with SRT control. The TSS inventory is

routinely measured by sampling mixed liquor suspended solids (MLSS) from each zone without

counting the solids in the foam. As a result, the TSS in the whole system is always

underestimated, along with the wasting rate. This makes precise SRT control problematic.



**Figure 1.1 Foaming in the UBC pilot plant (MEBPR system).**
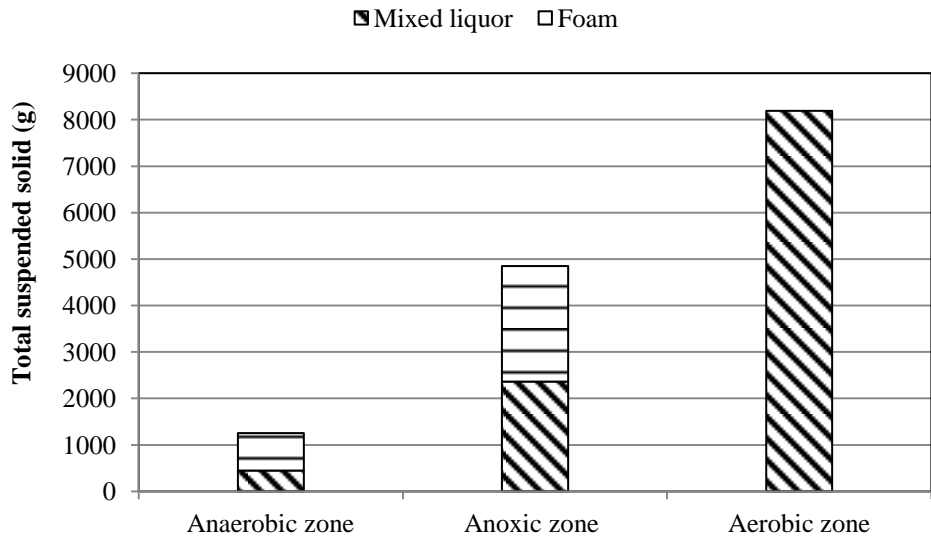
**Figure 1.2 Foam accumulation in different zones of the UBC MEBPR pilot plant after eight-months' operation at SRT = 25 days.**

Finally, foam suppression interfered with the maintenance of dissolved oxygen (DO) in the aerobic zone reactors. In Figure 1.3, the initial DO concentration before foam suppression (t = 0) was 1.6 mg/L. When the suppression/mixing was complete (for a heavy foaming, this normally takes 3−5 minutes), the DO decreased to about 0.4 mg/L (t = 8), and it took more than 10 hours to recover to the original value. This DO change was observed without a DO controller in place, and the rapid decrease in DO concentration in the aerobic zone was attributed to the strong mixing in the anoxic zone, which pushed a large volume of the anoxic zone mixed liquor (and some foam) to the aerobic zone in a short period time. For a system with a DO controller, although the recovery time can be shorter, it indeed requires extra work from the system air compressors to provide oxygen.

**Dissolved oxygen in aerobic zone**
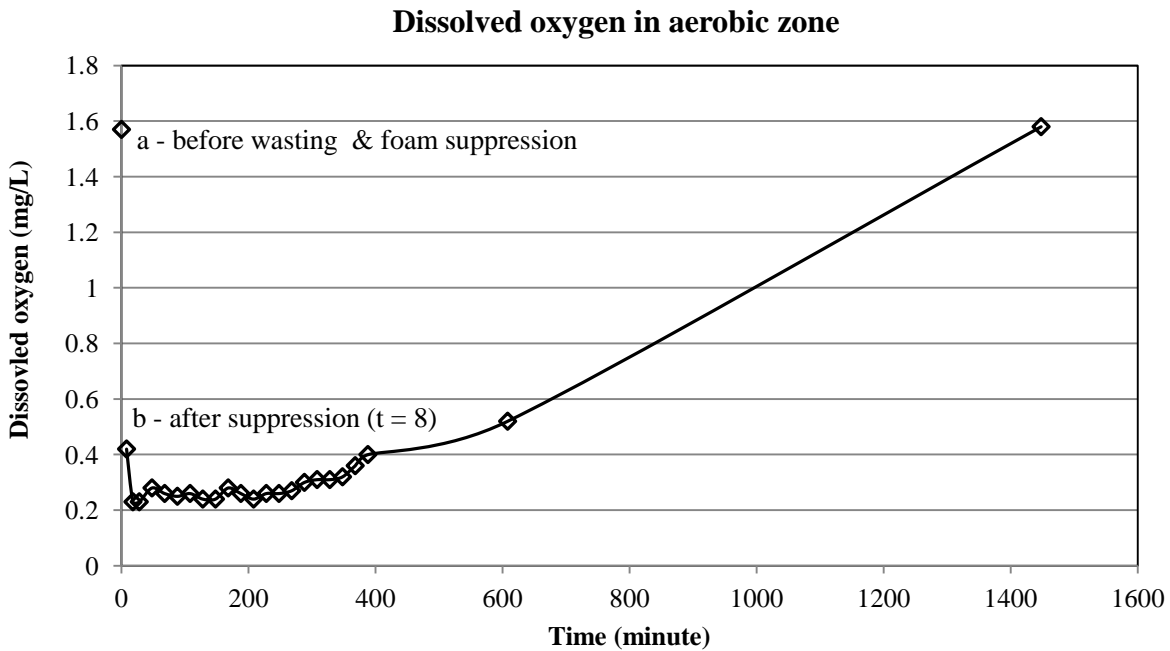


**Figure 1.3 DO concentration in aerobic zone following foam suppression and re-mixing into mixed liquor in the anoxic zone. Experiment was conducted before DO control was installed.**

To find a better solution than the temporary remixing, researchers at UBC performed some preliminary studies on the foam. For example, Hall et al. (2011) reported that the foam contained substantial amounts of nutrients (i.e., P, N, and C). The TSS concentration in anoxic foam was about 10 times the MLSS concentration in aerobic zone activated sludge (4 % vs 0.4 %) at SRT = 15 days, therefore representing a valuable resource for nutrient recovery. Lo et al. (2010) investigated nutrient extraction from the foam using MW-$H_2O_2$ AOP (microwave hydrogen peroxide advanced oxidation process) technology and found that, under conditions of 160 °C and addition of acid, nearly 100 % of the total phosphorus (TP) (650 mg/L) could be extracted as orthophosphate from the foam, suggesting that MW-$H_2O_2$ AOP is a promising technology to extract phosphorus. The obvious advantages of removing foam, instead of ML, for extraction of

5

nutrients are these: (1) foam is more concentrated than ML, therefore pre-thickening might be avoided; and (2) it removes an operational nuisance and related problems from the system. Therefore, the big research problem asked here was "How can we efficiently recover phosphorus as struvite from an MEBPR process by utilizing foam as the major source of recoverable phosphorus?" Key words in the question included biological phosphorus removal, phosphorus recovery as struvite, membrane bioreactor, and foam. The following literature review provides background on these topics.

## 1.2   Literature Review

### 1.2.1          Enhanced Biological Phosphorus Removal (EBPR)

Phosphorus removal came to practice mainly because of the eutrophication phenomenon. When excess nutrients (phosphorus and nitrogen) in WWTP discharges and stormwater runoff enter receiving waters, they promote algae blooms and degrade the water quality. Phosphorus can be removed through chemical precipitation, crystallization, enhanced biological phosphorus removal (EBPR), ion exchange, and filtration (for particulate phosphorus) (Morse et al., 1998). This section only reviews the EBPR.

#### 1.2.1.1   Mechanisms of EBPR

The biological removal of phosphorus can be achieved by phosphorus-accumulating organisms (PAOs) through alternating anaerobic and aerobic environments (Grady et al., 2011). Under anaerobic conditions, PAOs take up acetate and convert it to acetyl coenzyme A (acetyl−CoA) coupled with the energy compound adenosine triphosphate (ATP). ATP comes from cleaving

stored polyphosphate (poly-P) inside of PAOs, with simultaneous release of orthophosphates and light metals (e.g., $K^+$, $Mg^{2+}$). Degradation of glycogen to pyruvate also releases ATP and reducing power. With the reducing power, acetyl−CoA compounds are then converted to poly-hydroxy-alkanoate (PHA). Under aerobic conditions, the PAOs grow normally by utilizing PHAs as energy and carbon sources. They can take up more orthophosphate than previously released, therefore achieving net phosphorus removal. Meanwhile, polyphosphate and glycogen are replenished inside the PAOs, making them ready for the next cycle.

Two models are often referred to to explain the mechanisms related to the EBPR: the Comeau-Wentzel model (Comeau et al., 1986; Wentzel et al., 1986) and the Mino model (Mino et al., 1987). Acetate is a favorable carbon source for EBPR but needs reducing power to be converted to PHA (Mino et al., 1998). The key difference between the two models lies in the pathway used to generate the reducing power necessary for anaerobic PHA synthesis — the degradation of glycogen (the Mino model) or the TCA cycle (the Comeau-Wentzel model). In a review paper, Mino et al. (1998) concluded that the required reducing power is primarily supplied by the degradation of stored glycogen based on experimental observations; however, this is not sufficient for all PHA production. A small fraction of acetate is also metabolized through the TCA cycle under anaerobic conditions, which contributes about 30 % of the required reducing power. The development of EBPR processes is one of the most fascinating histories in environmental engineering (Grady et al., 2011). Oehmen et al. (2007) provided a detailed review on this history.

### 1.2.1.2    Configurations for EBPR

The basic configuration for EBPR requires only an anaerobic zone and an aerobic zone, as the anaerobic/oxic (A/O) process. Several variations exist for removing both phosphorus and nitrogen including the five-stage Bardenpho process, the anaerobic/anoxic/oxic ($A^2O$) process, and the University of Cape Town (UCT) process (Grady et al., 2011). Both the $A^2O$ and the UCT processes utilize anaerobic, anoxic, and aerobic zones in sequence and a secondary clarifier to separate liquid from solids. However, the $A^2O$ process incorporates two recycle streams, i.e., an internal mixed liquor recirculation from the aerobic zone to the anoxic zone (NR), and a return activated sludge (RAS) from the secondary clarifier to the anaerobic zone. The UCT process utilizes three recirculations. In addition to NR, the RAS is also turned to the anoxic zone, and a third recirculation is maintained from the anoxic zone to the anaerobic zone. Compared to the five-stage Bardenpho and $A^2O$ processes, the UCT process is able to reduce nitrate recycled into the anaerobic zone due to denitrification occurring in the anoxic zone.

### 1.2.1.3    Parameters Affecting the EBPR Process

Al-Atar (2007) listed sudden disturbances, volatile fatty acids (VFAs), nitrate load in the anoxic zone, presence of nitrite, metal cations (i.e., Mg and K), temperature, dissolved oxygen (DO), phosphorus load (i.e., P/COD), pH, and SRT as key parameters that influence stability and efficiency of EBPR. Among these, some parameters have explicit impacts on the process based on the above-mentioned mechanisms, but their optimal values need to be identified. Others, however, need a little more explanation.

*DO, VFA, pH, and SRT*. Organic removal, nitrification, and phosphorus uptake all need oxygen. Shehab et al. (1996) indicated that a DO concentration of 2 mg/L in the aerobic zone is sufficient for EBPR, but a DO of 3−4 mg/L is required if nitrification is also considered. Volatile fatty acids (VFAs) are essential for anaerobic phosphorus release. Barnard (1993) reported that 7-9 mg of VFA is required to remove 1 mg of phosphorus. When the influent COD/P ratio is low (< 50), acetate is often supplemented to achieve the desired level of P in the effluent. Manoharan (1988) reported that the addition of 7.5 mg acetate/L of influent contributed to an extra removal of 1.0 mg P/L. pH is a key parameter that affects activities of microorganisms. Mulkerrins et al. (2004) reported that the optimal operating pH ranges were 7.5−9.0, 7.0−8.0, and $6.8 \pm 0.7$ for nitrification, denitrification, and anaerobic acetate metabolism, respectively. The nitrification rate becomes zero at approximately pH 6.0. SRT is one of the most important design parameters. Oldham and Ranbinowitz (2001) indicated that an SRT of 10 days was typical in North America to achieve good P and N removal. Other research groups have also reported that the same SRT gave the best P-removal efficiency (Chang et al., 1996; Choi et al., 1996).

*Nitrate Load, Nitrite, and Metal Cations*. The nitrate load in the anoxic zone should be closely controlled. On one hand, denitrifying PAOs and the associated anoxic P-uptake utilize nitrate. Therefore sufficient nitrate should be available for both denitrifying PAOs and nitrifying bacteria, with the latter out-competing the former (Hu et al., 2002). Extra nitrate should also exist to prevent anaerobic conditions (in anoxic zone) where secondary P-release may occur (Meinhold et al., 1999). However, excess nitrate in the anoxic zone should be avoided to minimize nitrate recycle to the anaerobic zone, otherwise the anaerobic P-release can be negatively impacted. Saito et al. (2004) demonstrated that the presence of nitrite ($NO_2^-$) inhibited

both aerobic and anoxic P-uptake while aerobic P-uptake was more affected. Barat et al. (2005) mentioned that Mg and K are necessary for stability of EBPR because they co-transport with phosphates in and out of bacterial cells, are incorporated into the structure of polyphosphate granules as $(K_aMg_bPO_3)_n$, and maintain electroneutrality inside the bacterial cells.

### 1.2.1.4   EBPR Coupled with MBR (MEBPR)

When membrane modules are used to separate liquid from solids in place of a secondary clarifier, they bring obvious advantages such as higher effluent quality, smaller process footprints, and more flexible operating conditions. When proper membrane pore sizes are selected, the effluent can be essentially free of suspended solids (and microorganisms). Membranes can be compactly installed either inside or outside the bioreactor, therefore resulting in smaller footprints than a secondary clarifier. To achieve good suspended solids settling at a secondary clarifier, conventional WWTPs are normally operated at SRTs of 3 to 15 days (Fenu et al., 2010), with an MLSS concentration limited to between 1500 and 4000 mg/L in the aerobic tank. By comparison, MBRs are free of these limits and have the potential to be operated at a longer SRT with higher MLSS concentrations. However, a longer SRT is often accompanied by a lower α-factor, and therefore, a reduced oxygen transfer efficiency (Section 1.2.3).

MBRs also remove other common problems facing a secondary clarifier, for example, a bulking sludge related to the existence of filamentous microorganisms and a rising sludge caused by nitrogen gas that is produced in the clarifier through denitrification (Jenkins et al., 2004). Both situations deteriorate sludge settling properties and result in higher suspended solids concentrations in the effluent of a conventional process. In addition, the installation of membrane

elements has profound impacts on the design of MBR-coupled BNR systems due to the flexibility in changing mass fractions within different zones (Ramphao et al., 2005). However, for the MBR-coupled BNR systems, DO poisoning of the anoxic or anaerobic zone may easily occur, since more DO can be recycled due to the additional aeration that is used for membrane scouring.

Monti et al. (2006) compared performances of MEBPR and CEBPR systems side-by-side at the UBC pilot plant. Compared to the CEBPR system, the MEBPR counterpart exhibited lower effluent TP concentrations, a 15 % lower sludge yield, and a faster recovery from a loss of bio-P performance. The CEBPR, however, generated effluent with significantly lower nitrates due to the extra denitrification occurring in the sludge blanket of the secondary clarifier. Hall et al. (2010) compared the bacterial populations of an MEBPR and a CEBPR at the UBC pilot plant, and they found that the CEBPR community exhibited greater diversity and demonstrated superior functional stability, while the MEBPR configuration favored the growth of foam-associated microorganisms *Microthrix parvicella* and *Gordonia sp*.

There are a few disadvantages related to MBRs. In addition to the potential DO poisoning of the anoxic (or anaerobic) zone and a reduced α-factor associated with a longer SRT, one major problem is membrane fouling. Membrane fouling has been intensively studied according to a literature review by van Nieuwenhuijzen et al. (2008), and the fouling mechanism is considered to be closely related to the existence of extracellular polymeric substances (EPSs) (Geng et al., 2007a, 2007b, 2006). Another problem is foaming, which occurred more severely in MBRs than conventional WWTPs, as observed at the UBC MEBPR pilot plant (Hall et al., 2011). Many

factors could contribute to the foaming problem in MBR systems, for example, the presence of membranes as a physical barrier, filamentous bacteria, and EPSs (Nakajima and Mishima, 2005; You and Sue, 2009; Di Bella et al., 2011). Finally, MBRs are relatively expensive to operate compared to conventional WWTPs. The energy costs of MBRs can be twice those of conventional activated sludge plants (van Nieuwenhuijzen et al., 2008).

### 1.2.2 Phosphorus Recovery

Phosphorus recovery becomes increasingly important due to a few reasons. First, the natural reserves of high-quality, readily available phosphate rock are rapidly depleting, resulting in increased prices of phosphate rock (Section 1.1). Second, phosphorus in the discharge of WWTPs, together with phosphorus in the runoff of storm water, has been a major source of nutrients causing eutrophication (Ashley et al., 2011; Cordell et al., 2011). Third, since phosphorus cannot evaporate (no gas phase), and its discharge to receiving waters from WWTPs is restricted by many regulations, phosphorus eventually accumulates in the treatment plant piping (Britton et al., 2007). At certain points, phosphorus precipitates as struvite and blocks the piping. Cornel and Schaum (2009) calculated a phosphorus balance over a typical municipal WWTP in Germany. Assuming an influent TP concentration of 9 mg/L and 1 mg TP/L in effluent, the authors demonstrated that only 28 % of the influent TP could be removed in the surplus sludge, without a specific phosphorus removal process. An extra 50 % of the phosphorus could be removed specifically, either by an EBPR process or physical-chemical method or their combination. The remaining 22 % was distributed in primary sludge (11 %) and the effluent (11 %).

Cornel and Schaum (2009) also proposed several possible locations for installing processes to recover phosphorus, from either a liquid stream or a solid stream (i.e., sewage sludge and sludge ash). So far, the most successful application is to use a liquid stream, for example, the supernatant liquor of a side-stream anaerobic stripper (as in Phostrip process), or process water produced during sludge treatment. The phosphorus-rich water is then treated by either adding calcium for precipitation or adding magnesium (and ammonium) for crystallization. The precipitated calcium phosphate is a product directly comparable to rock phosphate used in the phosphate industry. The crystallized magnesium ammonium phosphate can be used directly as a fertilizer. Although the theoretical phosphorus recovery is low from the liquid stream ($< 50-60$ %) compared to that from the solid stream (up to 90 %), it might have technical and economic advantages (Berge et al., 2007), because the phosphorus is already in the soluble form, and at a phosphorus concentration of $> 50$ mg/L, phosphorus recovery from a liquid stream could be cost-effective (Cornel and Schaum, 2009). By comparison, to extract phosphorus from the solid phase needs extra mechanical or thermal treatment, or chemical digestion.

### 1.2.2.1    Recovery through Struvite Crystallization

Struvite crystallization is based on the following reaction (Bhuiyan et al., 2008):

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \leftrightarrow MgNH_4PO_4 \bullet 6H_2O \downarrow \qquad (1.1)$$
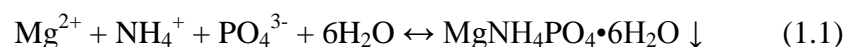
The crystallization/ precipitation of struvite occurs when the activities of magnesium, ammonium and phosphate exceed the thermodynamic solubility product (Ksp) of struvite. While crystallization is referred to as a process which forms larger size solids with defined structure and crystalline facets, precipitation produces small amorphous solids (Britton, 2002). Struvite crystals release nutrients slowly relative to other fertilizers, so that plants can take up more

13

nutrients before the nutrients are leached, which guarantees a reduced fertilizer application frequency (Bhuiyan et al., 2008).

Few reviews can be found in the literature, including those of Le Corre et al. (2009) and Rahman et al. (2014). Historically, struvite appeared as more of a nuisance in WWTPs because it blocked pipes and incurred extra costs for repairing or replacing the pipes. For the two past decades, recovering phosphorus through struvite crystallization has been intensively studied. Japan was the first country to successfully implement full-scale production and to sell the recovered struvite as fertilizer (Le Corre et al., 2009). Liquid from anaerobically digested sludge was used as the feed to fluidized bed reactors (FBRs). However, the particle sizes of their struvite products were relatively small, ranging from 0.5−1.0 mm. No quality data were reported. Fine particles tended to be lost in the effluent due to the high mixing energy imposed. Utilization of a seed material helped to increase the particle size but incurred more energy as the bed of seeds was continuously fluidized. In summary, practical use of struvite as a marketable fertilizer is largely dependent on the size and quality of crystals recovered.

In a pilot-scale study, Bhuiyan et al. (2008) crystallized struvite pellets using liquid of anaerobically digested sludge (i.e., centrate) as feed based on a UBC-patented fluidized bed crystallizer. The recovered strvite pellets possessed larger particle sizes (0.5−3.5 mm) and a high purity of $98.0 \pm 1.0$ % (Bhuiyan et al., 2009). The authors also identified that the optimal characteristics of the feed to the crystallizer were pH 8.0−8.2 and Mg/P molar ratio 1.3:1. Other important operating parameters included supersaturation ratio, recycle ratio, and apparent upflow

velocity. The UBC-patented technology was licensed to the company Ostara Nutrient Recovery Technologies Inc., in 2005.

There are several, full-scale plants that recover phosphorus as struvite, using the UBC-patented crystallizer. All of these plants utilize centrate following an anaerobic digester as the feed to a struvite crystallizer. One problem with these applications is that the $PO_4^{3-}$ concentration in such centrate is very low compared to the $NH_4^+$ concentration, because anaerobic digestion is not designed to extract $PO_4^{3-}$. For example, anaerobic digester centrate at one WWTP in Metro Vancouver (British Columbia) contains an average of about 76 mg /L of $PO_4$-P and around 757 mg/L of $NH_4$-N (Bhuiyan et al., 2008). At another Metro Vancouver WWTP, the averages are about 149 mg /L of $PO_4$-P and 1,057 mg/L of $NH_4$-N (Disha Afrina Zerin, MASc student at UBC, personal communication). The molar ratios in these two cases are about 1:22 and 1:16 (P:N), which are far from the ideal molar ratio of 1:1 (Equation 1.1). More recently, Ostara has been promoting a WASSTRIP process that adds an anaerobic P-release process to increase $PO_4$-P concentration. After centrifugation, the liquid containing a high $PO_4$-P concentration is fed to the struvite crystallizer and the solids are sent to anaerobic digestion.

Britton et al. (2007) conducted a life cycle assessment of integrated struvite recovery from sludge reject water in a wastewater treatment plant, and compared it with the base scenario, i.e., separate treatment of wastewater and fertilizer production. Based on a production capacity of 180 tonne/day struvite per full-scale unit, they reported that struvite recovery could reduce the excess sludge solids mass by 2−5 %, save $100, 000 /year from struvite scaling, and reduce 2,000 tonnes/ year of carbon dioxide-equivalent emissions relative to conventional fertilizer

manufacturing. When these 180 tonnes of struvite are applied to land, they could reduce cadmium, chromium, and arsenic loadings by 7.1, 64, and 0.7 kg, respectively, when compared to other common P- and N-containing fertilizers. This indicated that the struvite recovered by UBC technology was an eco-friendly fertilizer.

### 1.2.2.2 Phosphorus Recovery from MEBPR Process

A conventional EBPR process uses a secondary clarifier to separate suspended solids from liquid. To recover phosphorus by chemical precipitation/ crystallization, a portion of the clarified (and concentrated) sludge either goes to an anaerobic phosphorus stripper (as in the Phostrip process), or to an anaerobic digester (Cornel and Schaum, 2009). However, in an MEBPR process, there is no secondary clarifier. Some possible ways to extract phosphorus from the process are to utilize ML from either the anaerobic (Liao et al., 2003), anoxic (Srinivas, 2006), or aerobic zone (Banu et al., 2009), or from some combinations of these sources.

Based on the UBC MEBPR pilot plant, Srinivas (2006) conducted a preliminary study in which the author diverted a portion of the ML from the anoxic zone (2.5 % of influent) to a side-stream anaerobic phosphorus release unit (PRU), and then recovered the released soluble phosphorus as struvite through crystallization. The anoxic zone ML was selected because it gave the best P:N molar ratio in PRU supernatant for struvite crystallization, although its TP concentration was significantly lower than the TP concentration in the aerobic zone MLSS. Consequently, the $PO_4$-P concentration from the PRU was low (72 mg/L), and the struvite crystallizer only achieved a moderate recovery efficiency (~50 %). As a whole, only 20−25 % phosphorus recovery was achieved based on the influent TP. In addition, poor sludge settling was observed in the

16

sidestream clarifier. As a result, the sludge had to be drained daily from the clarifier to make the supernatant suitable for feeding to the struvite crystallizer.

### 1.2.2.3 Phosphorus Extraction for Struvite Crystallization

Fractions of TP in MLSS consist of ortho-phosphorus ($PO_4$-P), acid-hydrolyzable phosphorus (AHP), and organically-bound phosphorus. Normally three steps may be needed to achieve the conversion of TP in (activated sludge) mixed liquor or foam to $PO_4$-P: (1) breaking up the cell wall to release all the contents inside; (2) converting polyphosphate to $PO_4$-P (the portion of acid-hydrolyzable phosphorus); and (3) oxidizing organic phosphorus into $PO_4$-P. This is how the standard chemical analytical method measures TP after converting all TP into $PO_4$-P. The first step is often called sludge disintegration and can be achieved by physical (e.g., grinding, hydrodynamic cavitation, ultrasonic, microwave), chemical (e.g., ozone, acid or alkaline treatment), or biological (e.g., enzyme lysis in autothermal thermophilic aerobic digestion) processes. Detailed information on sludge disintegration can be found in several reviews (Liu and Tay, 2001; Wei et al., 2003; Perez-Elvira et al., 2006). Sludge production minimization normally needs sludge disintegration as a pretreatment. The second step can be achieved either chemically by strong acid treatment, or biologically under anaerobic conditions (also called anaerobic phosphorus release). The third step needs a strong oxidant such as persulphate to oxidize organic phosphorus to ortho-phosphorus.

The above discussion suggests that a single oxidation treatment is not capable of converting all TP to $PO_4$-P. For example, Saktaywin et al. (2005) reported less than 20 % conversion to $PO_4$-P from particulate phosphate, when up to 187 mg $O_3$/g SS was applied. On the other hand, Lo et al.

(2010) could achieve nearly 100 % conversion of TP for both anoxic and aerobic zone foam obtained from the UBC MEBPR pilot plant. They applied a microwave-hydrogen peroxide advanced oxidation process (MW-$H_2O_2$ AOP) under the conditions of 0.1 weight % $H_2O_2$ dosage, 160 °C, and addition of $H_2SO_4$ (pH = 2.1−2.5). More et al. (2015) completed systematic investigations on treating the foam from the UBC pilot plant with MW-$H_2O_2$ AOP.  They observed that heating temperature was the most significant parameter to maximize orthophosphate release, followed by the combined effects of temperature and hydrogen peroxide dose. Yi (2012) reported that anaerobic digestion of MW-pretreated sludge increased COD solubilization by up to 43 % and biogas production by 25 %, based on a serum bottle test.

Wang et al. (2010) proposed that there are four steps involved in the MW-$H_2O_2$ treatment of sludge: (1) generation of hydroxyl radicals by $H_2O_2$ with microwave radiation; (2) destruction of the sludge floc structure by MW at a temperature of about 80 $^0$C, with particle reduction; (3) the dissolution of extracellular polymeric substances (EPSs), which prevent contact of cell walls with oxidants, followed by break up of bacteria causing nucleic acids, protein etc. to be released into a suspension; (4) oxidation of particulate organics released from lysed cells into soluble forms. The authors also mentioned that there is no clear boundary between these steps, and at a high temperature they may occur simultaneously. One of problems with MW-$H_2O_2$ AOP is that the low pH is not compatible with subsequent struvite crystallization, which requires a pH of about 7.2−7.8. Treatment at relatively low temperature (60 °C) with no acid showed only 40−50 % conversion (Lo et al., 2010).

Orthophosphate can also be released biologically under anaerobic conditions with the addition of a carbon source, for example, acetate. The mechanism involved can be found in the Mino model as introduced in Section 1.2.1.1. This is the first of two steps involved in the biological phosphorus removal (BPR) process, with the second step being aerobic phosphorus uptake. The biggest advantage of anaerobic P-release is that microorganisms are not destroyed so that they can be returned back to the MEBPR process. Of course, this technology only converts the polyphosphate fractions into orthophosphate.

As a conventional technology to stabilize colloidal COD in wasted sludge, anaerobic digestion is rarely used to extract phosphorus, but it does release some $PO_4$-P and a large amount of $NH_4$-N, which is also required for struvite crystallization. Energy recovery from biogas is another attractive feature of anaerobic digestion. Recently, Latif et al. (2015) studied $PO_4$-P release from low-pH anaerobic digestion and found that at pH < 5.7, the soluble phosphorus concentration was 3.6 times greater compared to that released at neutral pH conditions (7−7.7), an 57 % increase based on the initial TP concentration of sludge. They concluded that the increased phosphorus came from dissolution of nearly 100 % of the struvite and about 47 % of the calcium phosphates. As a drawback, they also found that the methane potential decreased by as much as 33 %.

### 1.2.3    MBR Operation at Long SRTs

It is favorable to recover phosphorus from sludge that contains high phosphorus concentration. With an MEBPR process, phosphorus concentration might be increased by operating the MEBPR process at a long SRT. Fenu et al. (2010) defined SRTs from 15 to 40 days as the

"normal" range for MBRs and above 40 days as the "long" SRT range. A long SRT is also useful for reducing excess sludge production. However, long-SRT operation is not commonly applied in full-scale operations because of its associated drawbacks: reduced oxygen transfer efficiency; and possibly an increased membrane fouling rate. It is even rare to find a biological phosphorus removal process using a long SRT, because it is believed that a long SRT causes "secondary P-release" (WDNR, 2009), thereby compromising phosphorus removal efficiency, by elevating phosphorus concentration in the effluent. Since the long-SRT operation was the strategy adopted in this dissertation, this section briefly reviews the impacts of long SRT on these three issues including oxygen transfer, membrane fouling, and phosphorus removal performance.

A longer SRT tends to increase MLSS concentration in a bioreactor, and the MLSS concentration affects oxygen transfer efficiency through the α-factor (Judd, 2011). It appears that the α-factor decreases relatively slowly with increased MLSS concentration up to about 15 g/L (van Nieuwenhuijzen et al., 2008), beyond which the α-factor decreases sharply, along with the oxygen transfer efficiency.

Biological aeration requirements can be evaluated by actual oxygen transfer rate (AOTR), which mainly depends on COD removal, nitrification, and sludge wasting rate. Based on this, no large differences are expected with operation at different SRTs. The major difference comes from the standard oxygen transfer rate (SOTR), which involves with the α-factor defined by the following equation (Judd, 2011):

$$\alpha = \frac{k_L a_{wastewater}}{k_L a_{cleanwater}}$$

where $k_L$ = overall liquid mass transfer coefficient (m/s)

a = specific surface area for mass transfer ($m^2/m^3$)

$k_L a$ = volumetric mass transfer coefficient ($s^{-1}$)

There are many parameters that can affect the α-factor, for example, Cornel et al. (2003) mentioned that α varies with loading rates, surfactant concentrations, air flow rates, mixed liquor suspended solids (MLSS) concentrations, etc. Germain et al. (2007) found that in addition to airflow rate and MLSS concentration, the carbohydrate fraction of the extracellular polymeric substances (EPSc), and the chemical oxygen demand (COD) concentration of the soluble microbial products ($SMP_{COD}$) were also influential. In general, $k_L a$ changes when air bubbles are modified. Specifically, fine bubbles give the most efficient oxygen transfer, while the efficiency reduces when bubble coalescence occurs. The latter often happens with a high MLSS concentration, high viscosity, and small particles in MBRs (Germain and Stephenson, 2005). Based on this information, it is not surprising to see that a wide range of α-factors has been reported in the literature. For example, Cornel et al. (2003) reported an average α = 0.6 ± 0.1 at MLSS = 12 g/L in a full-scale installation, while Germain (2004) and Krampe and Krauth (2003) observed an α-factor of < 0.4 at the same MLSS concentration.

In addition to above-mentioned factors, the method used to determine the α-factor also has an impact. Randall et al. (1992) mentioned that there were limited methods available that can accurately measure oxygen consumption. For example, removing a mixed liquor sample for external measurement in BOD bottles using a dissolved oxygen (DO) probe usually gives

erroneous results. The results can be either underestimated because BOD and ammonia nitrogen are no longer available to the removed mixture, or overestimated if a low DO concentration was maintained in the aeration tank and the mixed liquor was respiring, while high DO of 4−7 mg/L was used in the BOD bottle test. Rather than the external method, *in situ* measurements are more reliable, which include off-gas testing methods or *in situ* oxygen uptake measurements (Randall et al., 1992).

A longer SRT influences membrane fouling propensity through increased MLSS concentration and reduced food-to-microorganism (F/M) ratio (Judd, 2011). The latter alters the characteristics of ML biomass, for example, the concentrations of extracellular polymeric substances (EPSs). Intuitively, it seems obvious that high MLSS increases fouling propensity because there would be more particles clogging the membrane channels. In reality, the relationship between MLSS concentration and fouling propensity is complex. Literature reports indicate positive, negative, and insignificant effects of MLSS concentration on membrane fouling (Judd, 2011). In general, these findings appear more consistent when examined in terms of reduced soluble microbial products (SMPs) and EPSs (colloidal and bound) at SRTs as long as 30 days, beyond which the EPS reduction becomes negligible (Brookes et al., 2003). On the other hand, observations were less consistent related to particle size distribution and air-induced shear stress (Dizge et al., 2013; Huang et al., 2001). These conflicts may result from variations in aerator configurations, membrane materials, pore size, and states of biomass at different SRTs (Dizge et al., 2013). In fact, many researchers have suggested that increasing SRT reduces membrane fouling (Zhang et al., 2006; Ahmed et al., 2007; Dizge et al., 2013; Kimura et al., 2005; Masse et al., 2006; van Nieuwenhuijzen et al., 2008). Cosenza et al. (2013) reported that foaming in a bioreactor reduced

the membrane fouling rate. These observations are encouraging and compatible with our goals for long SRT operations.

On the other hand, there are few reported studies that have demonstrated successful biological phosphorus removal at long SRTs. Ersu et al. (2010) investigated the impacts of different SRTs (i.e., 10, 25, 50, 75 days) on BNR performance in an MBR. Their results showed that TP removal efficiency decreased at higher SRTs, i.e., 80 % and 60 % at SRT = 50 and 75 days, respectively. Their effluent TP concentrations ranged from 2.8 to 5.4 mg/L. In general, longer SRTs could increase phosphorus concentrations in the effluent due to phosphorus accumulation in the bioreactor and/or secondary P release, therefore reducing overall phosphorus removal efficiency.

In summary, a longer SRT may reduce oxygen transfer efficiency by decreasing the α-factor but may not increase the membrane fouling rate. Little research has been done on the influence of long SRTs on the performance of an MEBPR process.

### 1.2.4 Foaming in Bioreactors

Foaming is a common phenomenon in WWTPs and remains one of the last unsolved problems in activated sludge processes ( Stratton et al., 2002). In some earlier days, researchers observed that foaming commonly accompanied the presence of certain types of microorganisms, particularly filamentous microorganisms. Although variations existed in different areas, the *M. parvicella* and members of mycolata, formerly known as "nocardioforms", represented the two most abundant filamentous groups detected in foam in the countries surveyed (Seviour and  Nielsen,

2010). Researchers then tried to relate the foaming events to process operating parameters that promoted the growth of these two filaments. For example, *M. parvicella* is favored by winter temperatures, low dissolved oxygen (DO) concentration, high pH with optimum 8.0 (Slijkhuis and Deinemam 1982), and a longer solids retention time (slow growth). On the other hand, *Nocardia* growth is promoted by low pH with optimum 6.5 (Cha et al., 1992) and *G. amarae* prefers warm temperatures. Asvapathanagul et al. (2012) reported that a change in temperature could trigger changes in operational and physicochemical conditions and eventually promote growth of *G. amarae-like* bacteria. Kocianova et al. (1992) observed correlation between foaming and the food-to-microorganism ratio (F/M). Despite these reports, there has been no systematic study to determine the controllable major factors affecting foaming.

There have been numerous studies on foaming mechanisms. Among others, a foaming mechanism that is similar to the flotation theory of mineral processing has been proposed and generally accepted (Petrovski et al., 2011). In this mechanism, three components must be present in order to form foam—particles with hydrophobic surfaces, surfactants, and gas bubbles. Particles must be hydrophobic so that they can be floated to the water surface by gas bubbles. It is believed that the hydrophobicity of activated sludge mainly comes from filaments like *Mycolatas* and *M. parvicella*. Mycolatas possess hydrophobic cell surfaces due to the presence of hydrophobic mycolic acids in the cell walls, and *M. parvicella* is also hydrophobic and utilizes long-chain fatty acids (LCFAs) as a carbon source while storing excess LCFAs in large globules (Judd, 2011; Rossetti et al., 2005). Hydrophobic compounds in wastewater may also contribute to foaming, and these compounds include hydrocarbons, proteins, and lipids. Khan et al. (1991)

reported that foaming demonstrated a clear relationship to the hydrophobicity of the activated sludge they studied.

Surfactants are surface active compounds which reduce surface tension so that bubbles can be formed from gas. Surfactants also stabilize foam by preventing/reducing liquid drainage from bubble interfaces (Petrovski et al., 2011; Heard et al., 2008). Wastewater contains both synthetic surfactants and biosurfactants. The former are mainly household and industrial detergents, while the latter are surface-active EPSs produced by microorganisms. It has been suggested that microorganisms produce excessive EPSs under nutrient-limited conditions (Jenkins et al., 2004). However, no relationship of surfactant concentration to foaming was observed by Stratton et al. (2002). The influence of gas bubbles from aeration systems has rarely been studied, probably because a sufficient quantity of air must always be supplied, although bubble size may have some impacts on foaming. In a lab-scale anaerobic digester, van Niekerk et al. (1987) found that fine bubble gas ($CH_4$ and $CO_2$) mixing produced more foam than coarse bubble mixing.

More recently, foaming in MBRs has been studied by a few groups. The mechanism involved may be different from that mentioned above, because foaming in MBRs was observed without those "standard" foam-forming filaments. Instead, EPSs play an important role for foaming in MBRs (Nakajima and Mishima, 2005; You and Sue, 2009; Di Bella et al., 2011 and 2013; Cosenza et al., 2013). EPSs are mainly proteins and carbohydrates (soluble and bound), which are hydrophobic and mostly or completely retained in membrane bioreactors by membrane filtration. Studies have shown that protein components of EPS (EPSp) play a more important role than carbohydrate components (EPSc). Di Bella et al. (2013) reported that both bound-EPSp and

filaments are important for foaming, and Nakajima and Mishima (2005) observed that soluble EPSp is important for foaming in MBRs and also a cause of MBR fouling.

Many different methods have been developed or modified to facilitate studies of foaming mechanisms. The foaming potential test is the most common one that measures the combined properties of activated sludge for foaming. Two methods are often used, one involving Alka-Seltzer tablets, and the other, an air diffuser. The Alka-Seltzer method is more standardized and simple, but is temperature dependent. Two Alka-Seltzer tablets are dropped into 250 mL samples of ML in a graduated cylinder, after which the foam height is measured (Ho and Jenkins, 1991). Fryer et al. (2011) improved the method by holding two tablets in a metal cage and reducing the chance of the tablets floating to the surface. The second method involves bubbling air through a sintered disc or a diffuser, with many possible variations in terms of cylinder size, sample size, disc/diffuser pore size, air flow rate, and aeration time (Fryer et al., 2011). There is also an arbitrary rating system developed by Blackall et al. (1991) to evaluate the foaming potential. For MBRs in particular, Nakajima and Mishima (2005) first used a foam power test that originated from the field of food science. Since both EPSs and certain types of filamentous bacteria contribute to foaming in MBRs, Di Bella et al. (2013) developed a modified scum index (MSI) test to determine their separate contributions.

Several methods exist to measure cell surface hydrophobicity (CSH) (Heard et al., 2009). For activated sludge, several research groups (Kreama, 2002; Geng, 2006; Khan et al., 1991; Kocianova, et al., 1992) adopted and modified the method initially developed by Rosenberg et al. (1980). All these methods involve washing of the sludge sample to remove interferences, adding

n-hexadecane to partition hydrophobic matter, and measuring absorbance before and after adding n-hexadecane. Variations exist depending on sample size and dilution, the use of centrifugation, and the types of washing solutions used. Surface tension measurements reported in the literature deal primarily with pure liquid solutions with a few reported on sludge (Verma et al., 2006; Ganidi, 2008; Goddard and Forster, 1986). These methods, however, cannot be used directly in this study, and modifications are necessary.

Although progress has been made to better understand foaming mechanisms, there exist many contradictions. For example, Hug et al. (2005) found that Nocardioform actinomycetes only partially contributed to foaming, and *M. parvicella* exhibited no correlations to foaming. Stratton et al. (2002 and 1998) reported that microorganisms not showing hydrophobicity could also produce a large amount of foam, which is not in agreement with the flotation theory. In addition, they observed no clear relationship between hydrophobicity and foaming, which contradicts the findings of Khan et al. (1991), as noted above. Instead, they suggested that interactions between cell surface and bulk liquid are likely important. A few methodological differences likely contributed to these contradictions. For example, some people worked on *M. parvicella* as the causative bacteria with pure cultures; others focused on different members of mycolata using *in-situ* activated sludge. The lack of consistent or reliable analytical methods might be the biggest contributor. Variation between these methods makes it difficult to directly compare results between different research groups. In summary, foaming in biological WWTPs is a very complicated issue influenced by several physical, chemical, and biological parameters. In spite of the extensive studies that have been carried out over several decades, the foaming mechanism is still not fully understood.

### 1.2.5 Summary of Literature Review

The following conclusions can be drawn from the literature review.

- Phosphorus in wastewater needs not only to be removed but also to be recovered. The driving forces for these practices include reducing eutrophication, reducing the depletion of natural phosphate rock reserves, and saving operational costs caused by pipe scaling

- Recovering phosphorus as struvite crystals represents an eco-friendly strategy, especially when using the UBC-patented technology. The recovered products possess relatively large size, high purity, and a slow phosphorus release rate.

- To crystallize struvite, the phosphorus and nitrogen should be in the soluble forms of $PO_4^{3-}$ and $NH_4^+$, respectively. The ideal molar ratio of $PO_4^{3-}$ and $NH_4^+$ is 1:1. In most cases, $Mg^{2+}$ needs to be supplemented.

- Several full-scale WWTPs utilize UBC-patented technology to recover struvite from the liquid phase of anaerobically digested sludge. However, the $PO_4^{3-}$ concentration is expected to be very low relative to the $NH_4^+$ concentration. An anaerobic phosphorus release, as in the WASSTRIP process of Ostara Nutrient Recovery Technologies Inc., should increase the $PO_4^{3-}$ concentration but little information is available.

- It is desirable to recover phosphorus from an EBPR process because the ML contains higher phosphorus concentrations than that from a non-EBPR process.

- Operation of EBPR at a longer SRT helps to increase phosphorus concentration in the ML, and the long SRT operation is only feasible with an MEBPR process. A longer SRT also promises a lower sludge yield and less waste sludge.

- A long-SRT operation with high MLSS concentration decreases oxygen transfer efficiency, but the observations of long SRT operation on membrane fouling were contradictory.

- Long-SRT operation has generally not been successful with the MEBPR process. Higher effluent phosphorus concentrations and reduced phosphorus removal efficiencies were often observed.

- Foaming was observed to occur more significantly in MEBPR than CEBPR processes. However, foam might be used for phosphorus recovery because of its high suspended solids, phosphorus, and nitrogen concentrations. Utilization of foam also removes an operational nuisance encountered by treatment plant operators.

- Foaming in biological WWTPs is a complex phenomenon that is influenced by physical, chemical, and biological parameters. Consequently, foaming mechanisms are still not fully understood in spite of the tremendous amount of previous research that has been done. Many conflicting observations exist due mainly to three factors: different causative microorganisms studied, a lack of reliable analytical methods, and the different experimental environments (pure culture or in-situ mixed liquor) used.

- The "flotation theory" appeared to be the commonly accepted mechanism, which identifies three key components involved in foaming: surfactants, hydrophobic solids, and gas bubbles.

However, the following knowledge gaps exist.

- Although long SRT operation with an MEBPR process offers many benefits, the technical and economical feasibilities of such an operation are unknown. It is technically

29

a challenge to operate at a long SRT without compromising phosphorus removal efficiency.

- Utilizing foam as a resource to recover phosphorus is a novel idea that could turn a problematic waste into a resource. However, little information is available on MEBPR foam characteristics and the possibility of extracting phosphorus from foam.

- In addition to increasing phosphorus concentration in MLSS, an optimal method of extracting phosphorus from MLSS and foam needs to be determined.

- An integrated system that combines all these attractive features (i.e., MEBPR, high SRT, foam use, optimal phosphorus extraction) is lacking.

## 1.3  Research Objective and Work Scope

Based on the background information, it is understood that global reserves of high quality, economically-recoverable phosphate rock are being depleted. Wastewater contains significant amounts of phosphorus but the phosphorus is usually totally wasted or recovered in a form that is not easily exploitable. Researchers at UBC are currently undertaking a research program to achieve the dual goals of maximizing nutrient recovery and minimizing waste sludge production from an MEBPR system. As a part of this larger research program, the following research focuses on recovering phosphorus as struvite from the MEBPR system. Therefore, the research objective is to propose an integrated system that can efficiently recover phosphorus as struvite from an MEBPR process by utilizing foam as the major source of recoverable phosphorus. Such a system might consist of a mainstream MEBPR process, a side-stream phosphorus extraction unit, and a struvite crystallizer to recover phosphorus (Figure 1.4). The research scope was to focus on the first two parts to produce a suitable feed for the third (struvite crystallizer).

30
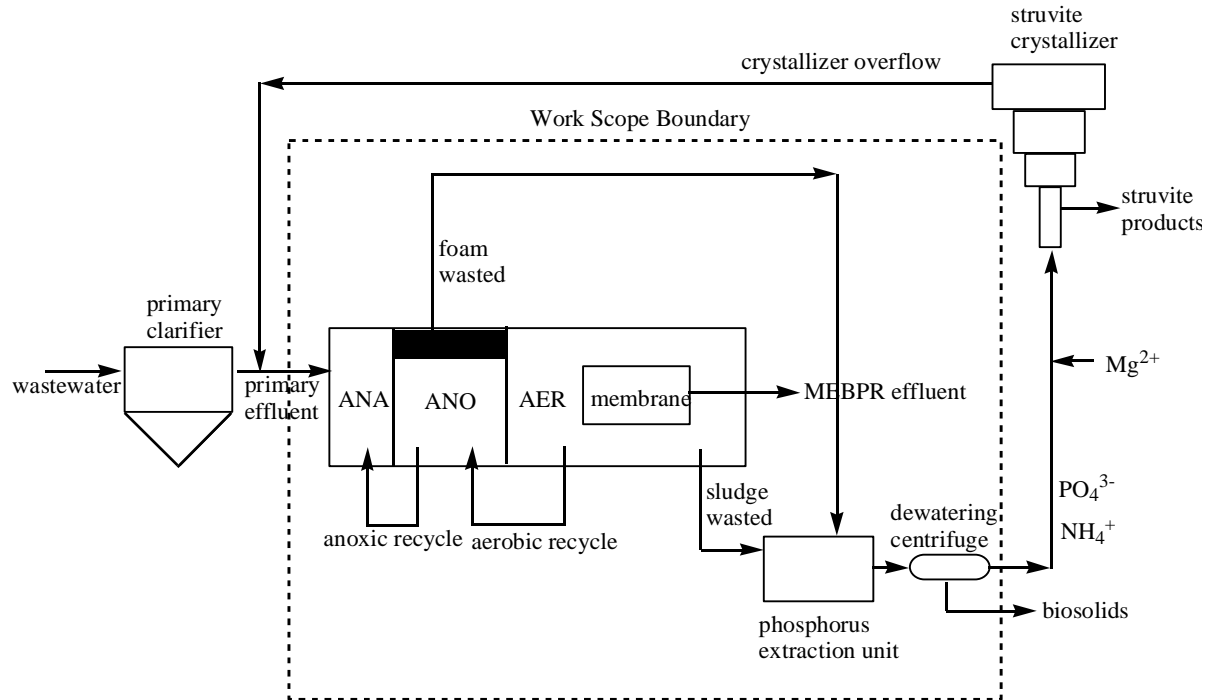
**Figure 1.4 Proposed new system to recover phosphorus and work scope of the thesis.**

Specifically, long SRT operation of the MEBPR process was assessed with the objective of

increasing the phosphorus concentration in mixed liquor, so that phosphorus recovery can be

more cost-effective. Since foaming became a more serious problem with the long SRT operation,

foam was fully characterized as an alternative phosphorus resource. To recover phosphorus as

struvite fertilizer, phosphorus must first be extracted in the form of soluble orthophosphate ($PO_4$-

P) from the waste mixed liquor, wherein phosphorus is mainly stored as polyphosphate and

organically-bound phosphate. Therefore, different technologies were evaluated to find an optimal

solution. In addition, operational costs were compared for operation at typical and long SRTs,

because a change in SRT was believed to have a more significant impact on operational costs

31

than on capital costs. Finally, a new system, illustrated in Figure 1.4 was proposed to overcome the weaknesses of current approaches, by providing a much better P:N molar ratio in the feed to a struvite crystallizer and recovering more phosphorus as well as more nitrogen.

## 1.4    Research Approach

To develop this system, the following approaches were adopted. First, the MEBPR pilot plant was operated at three different SRTs (i.e, 25, 40, 60 days), trying to increase anoxic zone foam generation and TP concentration in aerobic zone mixed liquor. Anoxic foam and aerobic zone mixed liquor were the two sources studied for phosphorus recovery. The operation at SRT = 25 days was considered as a base case (control). The SRT = 40 days was at the top edge of the normal range 15−40 days (Fenu, et al., 2010), therefore representing an initial step toward high SRT operation. A few things were examined in this phase, including the feasibility of wasting foam as an SRT control strategy, the phosphorus removal performance at increased SRT (40 days), and the impacts of a few operating parameters on foam generation through a factorial-design approach. The successful operation at SRT = 40 days provided momentum for operation at a longer SRT of 60 days, during which more foam, higher aerobic zone TP concentration, a lower sludge yield, and equally good phosphorus removal were anticipated.

Second, because of the importance of foam, research was undertaken to characterize the foam that was generated during operation of the UBC MEBPR plant. In addition, the impacts of three controllable operating variables were systematically studied, and the causes of reduced foam generation during periods with significant rain were also investigated. Third, different technologies were assessed to extract $PO_4$-P from mixed liquor and foam. These included MW-

H$_2$O AOP, anaerobic phosphorus release, and anaerobic digestion. In particular, anaerobic digestion was also assessed for NH$_4$-N release and biogas production. The advantages and disadvantages of these technologies were compared. Fourth, an economic analysis was prepared to compare operational costs of a conceptual, full-scale MEBPR plant operated at SRTs of 25, 40, and 60 days. The major operational costs were concluded to result from biological reaction aeration, membrane scouring aeration, and sludge handling. Finally, based on the results obtained above, two integrated systems were proposed to combine attractive features of EBPR, MBRs, long-SRT operation, and phosphorus recovery. At the end of the dissertation, some future work is recommended.

# Chapter 2: Operation Of An MEBPR Process With Increasing Solids Retention Times

## 2.1    Introduction

Phosphorus recovery from WWTPs has received increased interest recently. The driving forces include the depletion of high-quality phosphorus reserves, the increased selling price of phosphate rock, eutrophification caused by excess phosphorus (and nitrogen) discharged into receiving waters, and operational problems caused by phosphorus precipitation in WWTP piping (Ashley et al., 2011; Cordell et al., 2011; Britton et al., 2007). To recover phosphorus, it is economically desirable to utilize an enhanced biological phosphorus removal (EBPR) process (Cornel and Schaum, 2009), because the mixed liquor (ML) contains higher volumetric total phosphorus (TP) concentrations ($\geq$ 5 weight % dry P) than those from non-EBPR processes (2−3 %) (Strom, 2006). In addition, the recovered products should be easily used and environmentally friendly.

The literature review in Chapter 1 indicated that struvite crystallized using the UBC-patented technology is an eco-friendly fertilizer. To crystallize the struvite, phosphorus and nitrogen should be in their soluble forms of $PO_4^{3-}$ and $NH_4^+$, with a ideal molar ratio of 1:1 (Chapter 1, Equation 1.1). However, in reported full-scale facilities, both $PO_4^{3-}$ and $NH_4^+$ are produced from anaerobically digested waste sludge and separated in the liquid portion (i.e, centrate). Data from two WWTPs in Metro Vancouver showed ratios of 1:22 and 1:16 (P:N) in centrate, which are far from the ideal ratio (Chapter 1, Section 1.2.2.1).  A better P:N molar ratio can be achieved using

either or both of two approaches. The first is to increase the total phosphorus (TP) concentration in mixed liquor (ML) (and probably foam). Typically, waste sludge comes from the aerobic zone ML that is wasted to control solids retention time (SRT). The second approach is then to increase the $PO_4^{3-}$ extraction efficiency from the waste sludge. This Chapter deals with the former and Chapter 4 focuses on the latter.

In a membrane bioreactor, volumetric TP concentration in mixed liquor can be increased by increasing the process SRT. A longer SRT may also generate more foam due to the increased viscosity of ML that results. As stated in Chapter 1, foam might be a better source for phosphorus recovery than aerobic zone ML due to its higher TP concentration. Less waste sludge may also be generated due to increased biomass decay at a long SRT. However, three possible obstacles are related to a long SRT operation: potentially reduced phosphorus removal efficiency, reduced oxygen transfer efficiency, and increased membrane fouling rate.

The major research questions asked here were: (1) can we operate an MEBPR process at a long SRT, say 60 days, without compromising removal efficiencies of phosphorus, nitrogen, or carbon? (2) what TP concentrations of aerobic zone ML can be achieved at SRT = 60 days compared with a more commonly used SRT = 25 days, and (3) how much foam and waste sludge are generated at SRT=60 days? Although membrane fouling was not a major focus in this study, trans-membrane pressure (TMP) and membrane cleaning frequency were closely monitored.

## 2.2 Materials and Methods

**UBC (University of British Columbia) Pilot Plant**. The major facility used for this study was

the UBC pilot plant, which has been running for nearly 35 years as a key research facility. A

detailed description of the pilot plant is given in Bahadoorsingh (2010) and Monti et al. (2006).

Briefly, the pilot plant is a UCT-based (University of Cape Town) process with dual trains

(Figure 2.1). In this study, the physical design of these two trains was identical and both were

operated in the MEBPR process mode. The bioreactors consisted of three zones in sequence:

anaerobic, anoxic, and aerobic, each occupying 11 %, 28 %, and 61 % of the total volume of

2,228 L in each train.
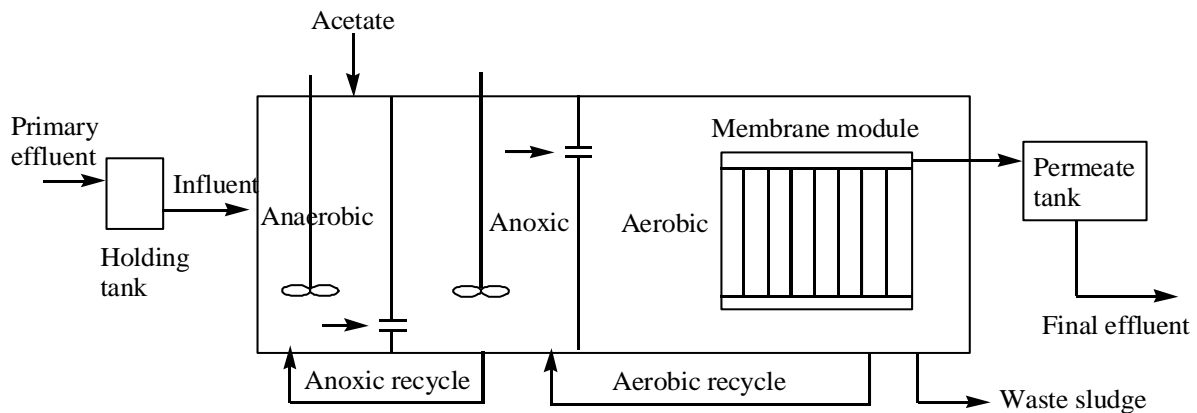


**Figure 2.1 Schematic representation of UBC MEBPR pilot plant. Influent was the effluent of a primary clarifier.**

The wastewater to the pilot plant was pumped from a sewer serving two residential areas on the

UBC campus. Before feeding to the primary clarifier, the wastewater was pumped to three

storage tanks with capacities of about 9,460 L (2,500 USG) per tank. The effluent of a primary

clarifier was used as feed (influent) to each MEBPR train. The standard influent flow rate was

36

set to 3.7 L/min for both trains. In the aerobic zone of each train, two ZeeWeed custom-made hollow fiber membrane modules were installed, with a nominal pore diameter of 0.04 μm. The total membrane area was $2 \times 12$ m$^2$ = 24 m$^2$ per train. The standard permeate flow of each train was set at 4.1 L/min, operating with 9.5 minutes pumping and 0.5 minutes back flush (flow rate ~10 L/min). This gave a membrane flux of about 10 liters per square meter per hour (LMH). Air was supplied by two air compressors (one stand-by) to meet biological and membrane scouring demands. Dissolved oxygen (DO) was controlled in each aerobic zone through a DO probe, controller, and solenoid valves. Air scouring was applied in sequence to each membrane module for 10 seconds on and off, with air flow of 283 to 340 liters per minute (10 to 12 cubic feet per minute) and pressure of 1.9 to 2.2 atmospheres (28 to 32 pound-force per square inch). External sodium acetate was continuously pumped to each anaerobic zone from a stock solution (14 g/L) at a flow rate of about 10 mL/min, which added an extra 29 mg COD/L into the influent to facilitate biological phosphorus removal.

**Experimental Conditions and Schedule**. Operating conditions were controlled at constant values unless otherwise stated in Figure 2.2. One train (A) was operated at an SRT of 25 days as a control for the full experimental program (December 2, 2013 to February 12, 2015, a total of 438 days), while B train was first operated at 40 days SRT (167 days) and then 60 days (271 days, from May 18, 2015 to February 12, 2016). An SRT of 40 days was used as an initial attempt, and 60 days was the targeted SRT that might be adopted in the proposed phosphorus recovery system (Chapter 1, Figure 1.4). For most of time, both anoxic and aerobic recycle ratios were set at 1:1 based on the inflow rate of 3.7 L/min, and the total hydraulic retention time (HRT) was about 10 hours. DO concentration in the aerobic zone was controlled at 1.0 mg/L

unless otherwise stated. This low DO level previously has been proven sufficient for all treatment purposes at the UBC MEBPR plant.
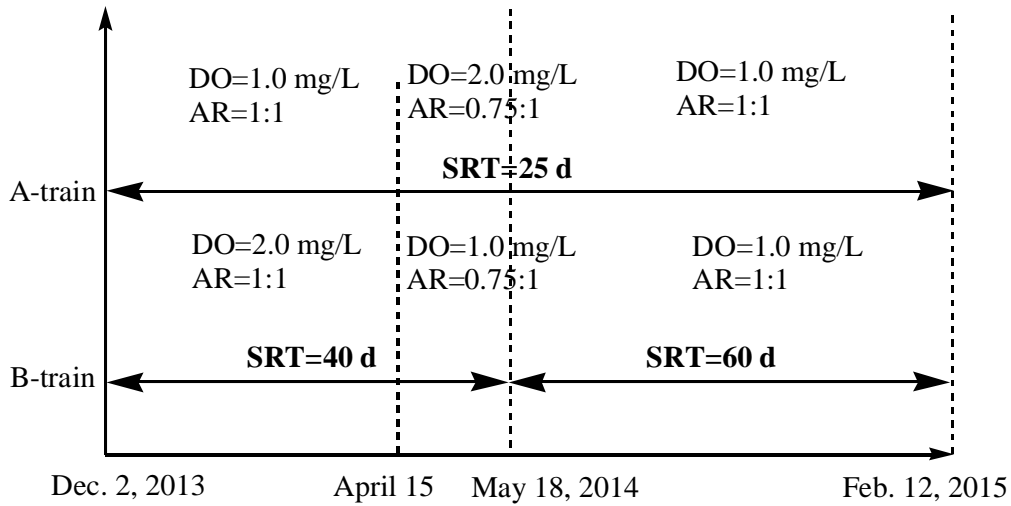


**Figure 2.2 Experimental conditions and timeline.**

Before the experiments were officially started on December 2, 2013, the MLs of two trains were blended and mixed for five days (November 28 to December 2, 2013), so that both trains could start with similar microbial communities (Figure 2.3). After this sludge exchange, MLSS concentrations in A train were 2,410, 4,680, and 9,560 mg/L for the anaerobic, anoxic, aerobic zones, respectively. In B train they were 2,090, 5,700, and 9,160 mg/L. Although the concentrations were not exactly the same for each corresponding zone, the total suspended solids inventories in the two trains were nearly identical (16.50 vs 16.52 kg). Considering that both trains were single-sludge systems and that each started with the same amount of biomass, we considered that the two trains were equivalent after cross-mixing of the ML.
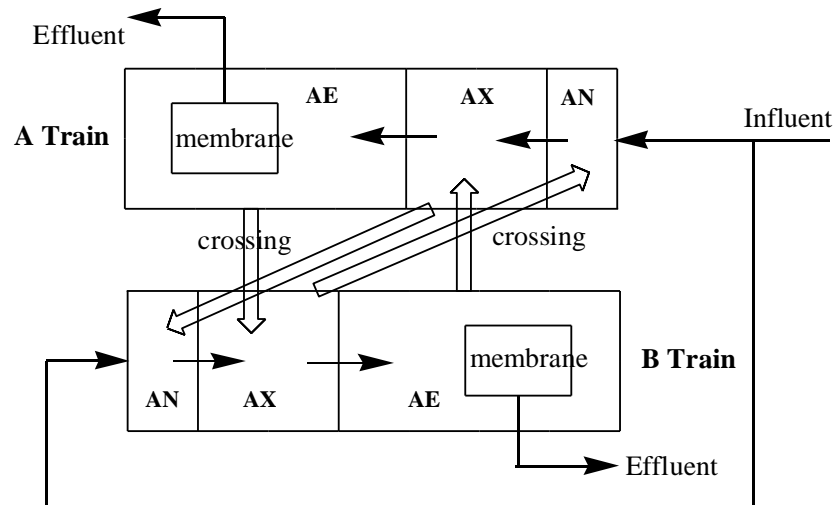
**Figure 2.3 Sludge mixing between A and B trains before factorial experiments.**

**Sampling Procedures and Frequency.** All samples were collected as grab samples. Influent samples were taken from the holding tank using syringes (Figure 2.1). For $PO_4$-P, $NH_4$-N, NOx-N (mixture of $NO_3$-N and $NO_2$-N) analysis, the raw influent samples were filtered with glass microfiber filters (Whatman $\Phi$2.5 cm, A4), and the filtrate was distributed into two 10 mL test tubes. One was for the $NH_4$-N analysis and this was preserved with one drop of 5 % $H_2SO_4$ solution. The other was for $PO_4$-P and NOx-N and was preserved with one drop of phenylmercuric acetate solution (0.1 g phenylmercuric acetate in 20 mL acetone and 80 mL distilled water). Total COD (TCOD) samples of influent were prepared by pipetting 2 mL sample into a 10-mL vial preloaded with 4 mL digestion reagent (200 mL concentrated $H_2SO_4$ plus 134 g $K_2SO_4$, filled up to 1 L with distilled water ). To measure influent TSS concentration, about 150 mL influent sample was taken into a plastic bottle. Since TSS measurement was normally started immediately or in about two hours, no preservative was used. Influent TP and Total Kjeldahl Nitrogen (TKN) samples of about 25 mL were taken by a syringe into a 30 mL plastic bottle, and preserved with five drops of 5 % $H_2SO_4$ solution.

All effluent samples were taken from the permeate tank. The procedures and preservation were similar to those used for influent samples, except that samples did not need filtration. ML samples from each reactor zone were taken either by a syringe connected to a 0.8 meter long plastic tube (Ø4 mm) for anaerobic zone samples, or from the two recycle lines (Figure 2.1). To analyze soluble $PO_4$-P, $NO_x$-N, and $NH_4$-N of the ML, an aliquot of 40 mL sample (from each zone) was first centrifuged at 1,500 relative centrifugal force (RCF) for 5 minutes, filtered through the glass microfiber filters into two 10-mL test tubes, and preserved in the same manner as for the influent samples. Mixed liquor TSS, TP, TKN, and TCOD samples were taken without filtration and handled similarly to the influent TSS, TP, TKN, and TCOD samples, except that the TCOD samples needed to be diluted by 1/50 to 1/100. After preservative was added, all but the COD samples were immediately stored in a fridge (4 $^0$C) for further chemical analysis.

Aerobic zone DO data were recorded from the DO controller with a probe inside the zone and cross-checked by a handheld DO meter (YSI 52 dissolved oxygen meter). pH values were measured by a pH meter ( pHTestr BNC with a OakTon probe) calibrated each time before use. Permeate flow and trans-membrane pressure (TMP) were recorded from flow and pressure meters. All flow rates (influent, anoxic and aerobic recycles) were manually measured using a 4L cylinder and a stop watch. The volume of external acetate addition was recorded directly from the solution tank every day, so that the consumption of the acetate could be calculated. A graduated waste tank was used to measure the sludge wasting rate. For the foam, some modifications were necessary because of the high suspended solids concentration and the

heterogeneous nature of foam. A detailed procedure for foam characterization is given in Chapter 3 (Figure 3.1).

The sampling program included daily sampling (from influent and effluent only) and scanning (2−3 times per week from influent, each reactor zone, and effluent) for different parameters, as shown in Table 2.1.

**Table 2.1 Summary of sampling plan and chemical analysis**

| Frequency | Parameters |
|---|---|
| Daily | **Influent**: $PO_4$-P, $NH_4$-N, NOx-N |
| | **Effluent**: $PO_4$-P, $NH_4$-N, NOx-N |
| | **Others**: foam mass, waste rate, aerobic DO and temperature, external acetate addition, permeate flow, TMP |
| Scan (2−3 times per week) | **Influent**: Total COD, TSS, VSS, pH, TKN, TP |
| | **Effluent**: COD, pH, TKN, TP |
| | **Mixed liquor in each reactor zone**: TSS, VSS, COD, TKN, TP, pH |
| | **Centrate from mixed liquor**: $PO_4$-P, $NH_4$-N, $NO_X$-N |
| | **Others**: influent flow, anoxic recycle flow, aerobic recycle flow |

**Chemical Analysis**. All chemical analyses were conducted at the UBC Environmental Laboratory. Activated sludge concentrations of TS, TSS, VSS, $PO_4$-P, TP, $NH_4$-N, TKN, $NO_X$-N, and COD were measured according to standard methods (APHA et al., 2005). A flow injection analyzer (QuikChem, Lachat Instruments) was used to measure $PO_4$-P, TP, $NH_4$-N, TKN, and $NO_X$-N concentrations.

**SRT Control Strategy**. SRT was controlled by wasting the required mass of suspended solids every day according to Equation (2.1). As a rule, foam in both anoxic and anaerobic zones was weighed and wasted first; if the foam did not contain sufficient suspended solids, aerobic zone ML was also wasted based on Equation (2.2).

$$\text{Suspended solids wasting rate (g/d)} = \frac{\text{total mass of suspended solids in system}}{\text{SRT}}$$

$$= \frac{\text{total mass of suspended solids in ML} + \text{mass of suspended solids in all foam}}{\text{SRT}}$$

$$(2.1)$$

$$\text{Aerobic sludge wasting (L/d)} =$$
$$\frac{\text{suspended solids wasting rate} - \text{mass of suspended solids in wasted foam}}{\text{aerobic sludge TSS concentration}}$$
$$(2.2)$$

where the total mass of suspended solids in ML was calculated as the sum of mixed liquor TSS concentration (mg/L) in each zone multiplied by the ML volume (L) in the same zone. The mass of suspended solids in all foam was calculated by the average foam TSS concentration (g/kg wet foam) multiplied by the mass of all foam (kg), manually removed from the system and weighed each day (Figure 3.1, Chapter 3). The mass of suspended solids in wasted foam was calculated similarly by multiplying the average foam TSS concentration and the mass of wet foam wasted each day (kg).

**Quality Control.** Every effort was made to minimize errors during sampling and chemical analysis events. All the glassware was carefully cleaned before use. Duplicate or triplicate samples were measured for mixed liquor TSS, VSS, and all foam parameters. Internal standards

42

were used to correct matrix effects and to assess analytical accuracy. Coefficients of variation

(COV) were determined to quantify the precision for several methods, as shown in Table 2.2. For

each method, one grab sample was collected from the process, then multiple split samples (10 to

40) were taken from the same grab sample and analyzed separately. The average and standard

deviation were determined and used to calculate the COV.

**Table 2.2 Coefficients of variation (COV) for different methods**

| Sample | Split sample number | Sample size | Average | Standard deviation | COV (%) |
|---|---|---|---|---|---|
| Anoxic zone foam | | | | | |
|    TP (µg/g foam) | 40 | ~ 0.1 g | 976 | 31 | 3.2 |
|    TKN (µg/g foam) | | | 2147 | 116 | 5.4 |
| Anoxic zone ML, SRT=25 d | | | | | |
|    TP (mg/L) | 10 | 1.0 mL | 98 | 3.28 | 3.4 |
|    TKN (mg/L) | | | 242 | 6.58 | 2.7 |
| Anoxic zone ML, SRT=40 d | | | | | |
|    TP (mg/L) | 10 | 0.5 mL | 308 | 7.91 | 2.6 |
|    TKN (mg/L) | | | 595 | 32 | 5.4 |
| Anoxic zone ML | 12 | 5-10 mL | | | |
|    $PO_4$-P (mg/L) | | | 3.51 | 0.15 | 4.0 |
| Anoxic zone ML | 12 | 5-10 mL | | | |
|    $NO_x$-N (mg/L) | | | 0.20 | 0.037 | 19.0 |
| Anoxic zone ML | 12 | 5-10 mL | | | |
|    $NH_4$-N (mg/L) | | | 14.4 | 0.88 | 6.0 |

In particular, foam TP and TKN measurement was based on mass rather than volume because of

the high TSS concentrations and sticky nature of foam. The sample size of ML from B train was

either reduced to 0.5 mL (for anoxic and aerobic zone ML at SRT = 40 days) from the typical 1.0

mL, or the samples were 4 times diluted (for aerobic zone ML at SRT = 60 days) to ensure

complete TP/TKN digestion. The other methods were all well developed and used routinely for

pilot plant monitoring. Table 2.2 demonstrates that all the methods were reliable with COV ≤ 6

%, except for mixed liquor NOx-N, which was normally present at a low concentration in the

anoxic zone. These low COV values confirmed that the small sample sizes 0.1 g (for foam) and

0.5 mL (for ML) could be representative of the suspended solids.


**Data Processing and Statistical Analysis**. A large amount of data was obtained during the

study, especially for the long SRT experiments. These data were carefully screened and then

processed. Statistical analysis using Minitab was performed whenever necessary. To identify

outliers, outer fences were calculated using the following equations (Tukey, 1977). Any data

outside of the outer fences were flagged as potential major outliers and they were discarded if

they were related to a mechanical failure.

$$\textbf{Outer fences: } [Q1 - IQ \text{ rang}*3, Q3 + IQ \text{ rang}*3] \tag{2.3}$$

Where Q1 = lower quartile of data

Q3 = upper quartile of data

IQ rang = interquartile range = Q3 − Q1


To obtain statistics, all operational data were tested for normality using the Anderson-Darling

test (Montgomery, 2005). If the data followed a normal distribution, the average and standard

deviation were used; otherwise, box plots were utilized with percentiles. In the present study, the

data related to effluent TP, $PO_4$-P, TN, $NO_X$-N, $NH_4$-N, and COD concentrations did not follow

a normal distribution (Appendix B). Consequently, these data are presented using box (and

whisker) plots to show percentiles 5 %, 25 % (quartile 1), 50 % (median), 75 % (quartile 3), and

95 % values. Paired t-tests were performed to determine whether differences between two sets of

data were significant at a 95 % confidence level. Paired t-tests were suitable for those naturally paired samples and required the differences between two sets of data to follow a normal distribution (Manly, 2009). In the present research, this requirement was always checked before a paired t-test was conducted. These tests were used mainly to compare the data between SRT = 60 and 25 days due to two reasons: (1) a 60-day SRT was the target of the present research; (2) a paired test was not very suitable for 25 and 40 days, because these two operations differed, not only in SRT, but also in other operating conditions (Figure 2.2).

## 2.3    Results and Discussion

### 2.3.1        Characteristics of Influent Wastewater

Influent wastewater (i.e., primary effluent) was characterized routinely throughout the study. The averaged concentrations of various parameters are given in Table 2.3. The averaged concentration of total VFA (acetate + propionate) was moderate (43 mg COD/L), suggesting that considerable fermentation occurred in the three influent storage tanks (Section 2.2). If it is assumed that primary sedimentation removed 35 % of $BOD_5$, 65 % of TSS, 16 % of TP, 0 % of $NH_4$-N (Qasim, 1999), the raw, untreated wastewater can be categorized as medium strength in COD and TSS concentrations, low strength in TP concentration, and close to high strength in $NH_4$-N concentration, according to the classifications given by Metcalf and Eddy (2003).

**Table 2.3 Characteristics of influent wastewater (primary effluent) at UBC pilot plant**

| Parameters | Average | Standard deviation | Sample size |
|---|---|---|---|
| TCOD (mg/L) | 292 | 58 | 192 |
| $PO_4$-P (mg/L) | 2.42 | 0.50 | 419 |
| TP (mg/L) | 4.50 | 0.74 | 120 |
| $NH_4$-N (mg/L) | 36.4 | 6.8 | 420 |
| $NO_X$-N (mg/L) | 0.05 | 0.11 | 420 |
| TKN (mg/L) | 43.5 | 6.2 | 117 |
| Total VFA (mg/L as COD) | 43.0 * | 11.4 | 205 |
| TSS (mg/L) | 89 | 24 | 126 |
| VSS/TSS | 0.84 | 0.08 | 46 |
| Temperature (°C) | 17.2 | 3.6 | 247 |
| pH | 7.3 | 0.2 | 131 |

* Without external acetate addition.


### 2.3.2        MEBPR Performance at Long SRTs

### 2.3.2.1    Phosphorus Removal

Since the essential goal of biological WWTPs is to remove organic pollutants and sometimes

nutrients (P and N), the practice of phosphorus recovery should not compromise the performance

of these WWTPs. For an MEBPR system, the biggest concern was the phosphorus removal

efficiency at increased SRTs. The removal efficiency is usually evaluated based on the ratio of

effluent TP to influent TP concentration. For nearly nine months of operation, the process

provided excellent total phosphorus removal (Figure 2.4). The time series of effluent $PO_4$-P

concentrations is also plotted in Figure 2.5, serving as a cross-check. $PO_4$-P is a soluble

component and was analyzed daily. $PO_4$-P data were considered more reliable than those for TP

due to two reasons—$PO_4$-P is homogenously distributed in solution and its concentration is less

46

affected by membrane leaking. Time series of influent TP and PO$_4$-P concentrations are shown in Figure 2.6.
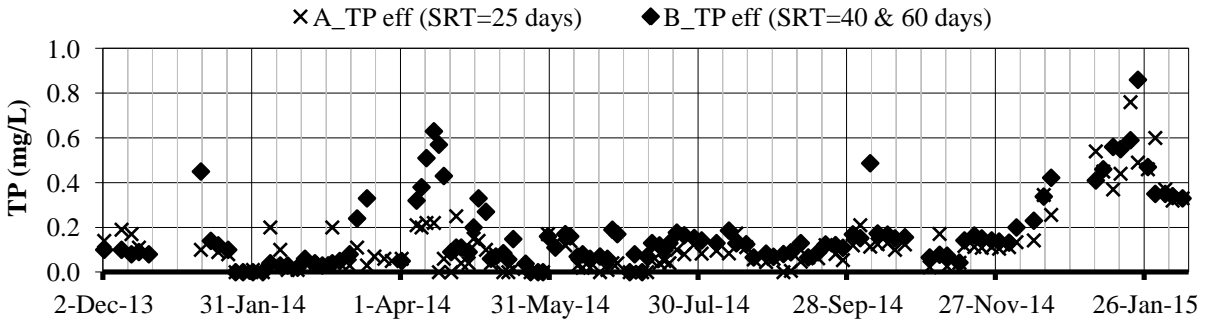


**Figure 2.4 Effluent TP concentrations at three SRTs.**
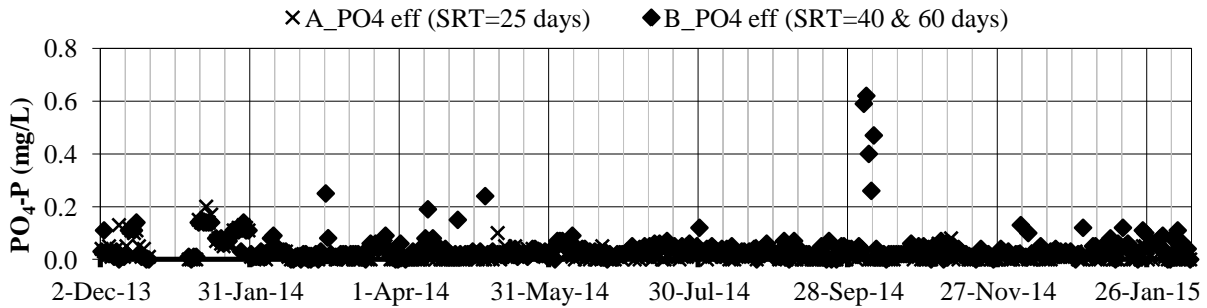


**Figure 2.5  Effluent PO$_4$-P concentrations at three SRTs.**
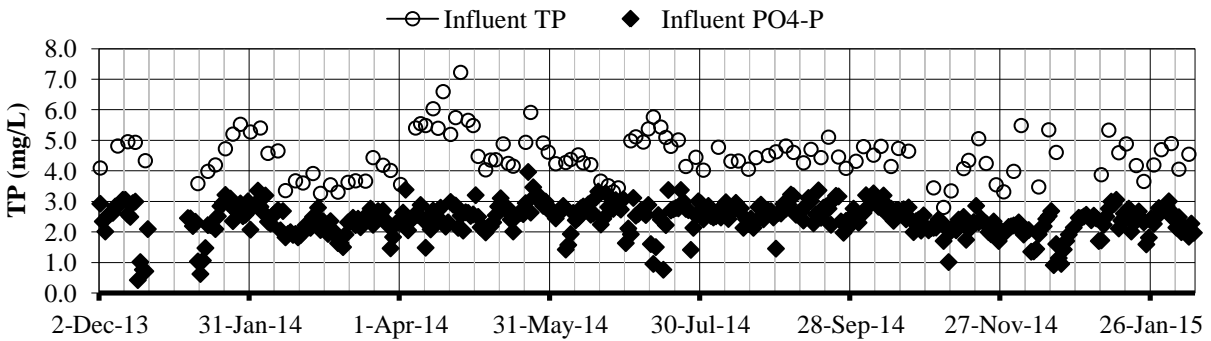


**Figure 2.6 Influent TP and PO$_4$-P concentrations.**

In general, operations at the three selected SRTs were very successful. A summary of effluent TP data is illustrated in Figure 2.7 to show the data distribution. Data from the operation at SRT = 25 days were separated into two parts, 25 (1) and 25 (2), to compare with the data from the parallel operations at 40 and 60 days. The TP median values were 0.06, 0.09, 0.10, 0.13 mg/L for SRT = 25 (1), 40, 25 (2), and 60 days, respectively. Their corresponding 95th percentile concentrations were 0.24, 0.83, 0.47, and 0.51 mg/L. Using the median values of effluent TP and the average influent TP concentration (4.5 mg/L) from Table 2.3, the average phosphorus removal efficiencies were calculated as 98−99 % for SRT = 25, 98 % for 40 days, and 97 % for 60 days. A paired t-test confirmed that the difference in effluent TP concentrations was significant at a 95 % confidence level at SRT = 60 days and 25 days ($p = 0.000$, Appendix B.2). However, since both median values were very low, the removal efficiencies would not be significantly different. Consequently, these two operations achieved comparable phosphorus removal efficiencies (98 % vs 97 %).

A summary of the effluent $PO_4$-P data from the three SRTs is also presented in Figure 2.7. The median values were 0.01, 0.02, 0.01, and 0.03 mg/L for SRTs = 25 (1), 40, 25 (2), and 60 days, respectively, and their corresponding 95th percentiles were 0.13, 0.14, 0.04, and 0.09 mg/L. A paired t-test confirmed that the difference in $PO_4$-P concentrations was significant at a 95 % confidence level between the 60 and 25 days SRT runs ($p = 0.000$, Appendix B.2).
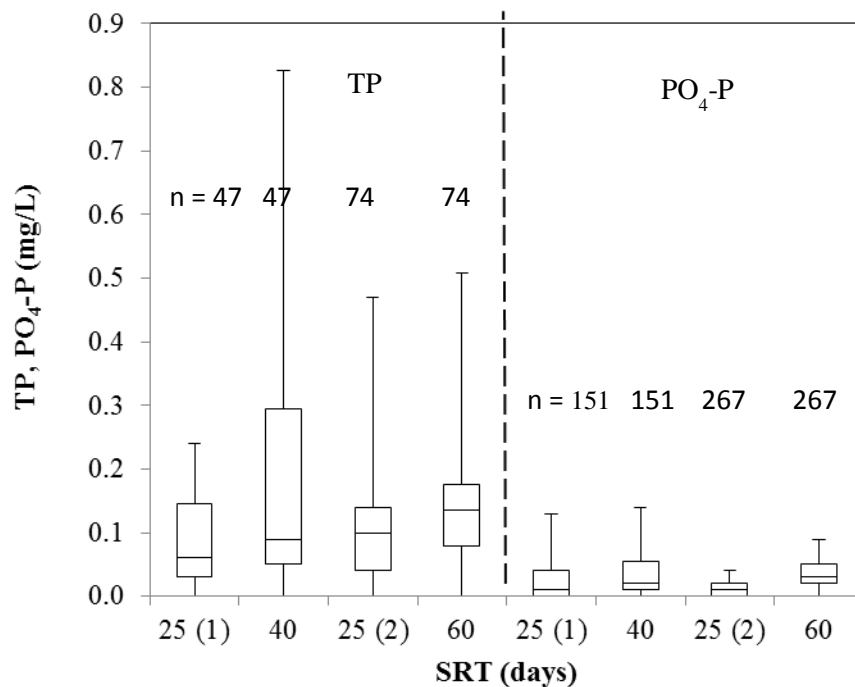
**Figure 2.7 Box plots of effluent TP and PO$_4$-P concentrations at SRTs = 25, 40, and 60 days. 25 (1) and 25 (2) represent the operations parallel to 40 and 60 days, respectively. Percentiles shown: 25th, 75th, and 95th (25th percentile of PO$_4$-P at 25 days and all 5th percentiles were zero). The horizontal line inside the box represents the median. n is sample size.**

Only a few previous studies have reported on the operation of an MEBPR process at a long SRT. Ersu et al. (2010) reported TP removal efficiencies of 80 % and 60 % at SRT = 50 and 75 days, with the effluent TP concentrations of 2.8 and 5.4 mg/L. No VFA concentrations were reported for the influent wastewater, and it seemed they did not supplement any acetate. Monti (2006) compared MEBPR and conventional enhanced biological phosphorus removal (CEBPR) processes at SRT = 12 days using the UBC pilot plant. The major problem in his study was that the phosphorus removal in the MEBPR process was not very stable. Two performance failures were observed even when external acetate at 30 mg COD/ L was supplemented. The author

attributed the first major failure to a quick decrease of temperature and a relatively small anaerobic mass fraction. The second failure was relatively minor, lasting 2−3 weeks without a clear cause being identified.

The low effluent $PO_4$-P concentrations observed in the present study were surprising at a long SRT of 60 days, considering that phosphorus might have accumulated in the system due to reduced sludge wasting at SRT = 60 days relative to that at 25 days (Section 2.3.3.2). One explanation was that at SRT= 60 days, although a reduced mass of suspended solids (as TSS) was wasted each day, the TP/ TSS ratios of waste ML were higher than those at 25 days (Figure 2.8). Consequently, the wasted TP mass at both SRTs could be equivalent over a long enough period; therefore, no significant phosphorus accumulation occurred even at SRT = 60 days. As shown in the following Section (2.3.2.2), the total wasted phosphorus ($TP_{FOAM}$ + $TP_{AS}$) was 5,707 g at SRT = 25 days and 5,804 g at 60 days for a total of 271-day operation (Table 2.4). Figure 2.8 also shows that the TP/ TSS ratios kept changing with time in an "Up−Down" pattern. The "Up" period indicated that phosphorus accumulated in the system (i.e., phosphorus in > out), while a "Down" period suggested that phosphorus was depleting.
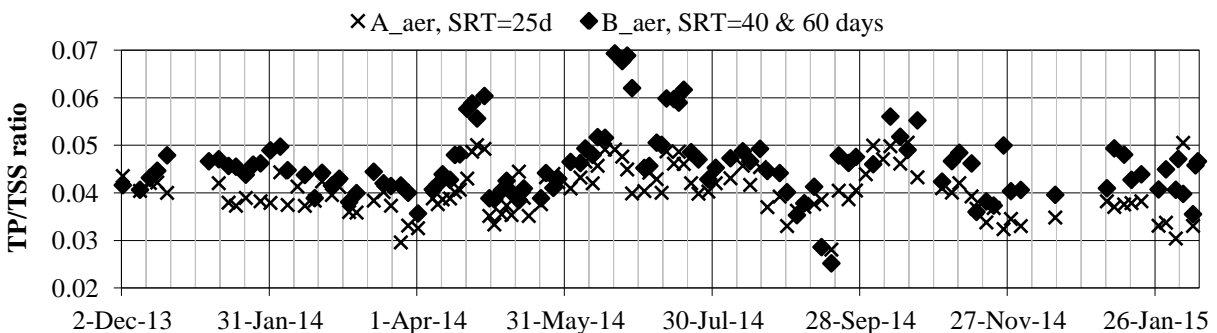


**Figure 2.8 TP/TSS ratios of aerobic zone ML at three SRTs.**

In addition to the TP/TSS self-regulation by the system, control of the NOx-N entering the anaerobic zone from the anoxic zone recycle was critical to maintain stable performance. At SRT = 60 days, one upset occurred around October 4 to 8, 2014, which was believed to be due to an accidently increased aerobic recycle ratio. This accident occurred when the TMP was extremely high but membrane modules could not be replaced in time. To reduce the TMP, the permeate and influent flows were lowered to about 2.1 L/min, but the aerobic recycle flow remained at 3.7 L/min. This resulted in a recycle ratio of about 2:1 during these five days, rather than the original setting of 1:1. This higher recycle ratio resulted in some higher $NO_X$-N concentrations in the anoxic zone, which was evidenced by a value of 4.87 mg/L observed during the upset period on October 7, 2014 (Figure 2.9). Because $NO_X$-N concentrations in the bioreactor were measured twice a week (Table 2.1), only one point was captured.

In an EBPR system, recycling nitrate from the anoxic zone to the anaerobic zone has a deleterious effect on phosphorus removal (Grady et al., 2011). When nitrate is present in the anaerobic zone, ordinary heterotrophic organisms (OHOs) can grow using the nitrate as electron acceptor (i.e., denitrification), therefore competing for the available VFAs with PAOs. Wentzel and Ekama (1997) indicated that every 1 mg $NO_3$-N and 1 mg O recycled to the anaerobic reactor uses 8.6 and 3.0 mg COD, respectively. In addition, the presence of nitrate also interferes with fermentation in the anaerobic zone (Grady et al., 2011)
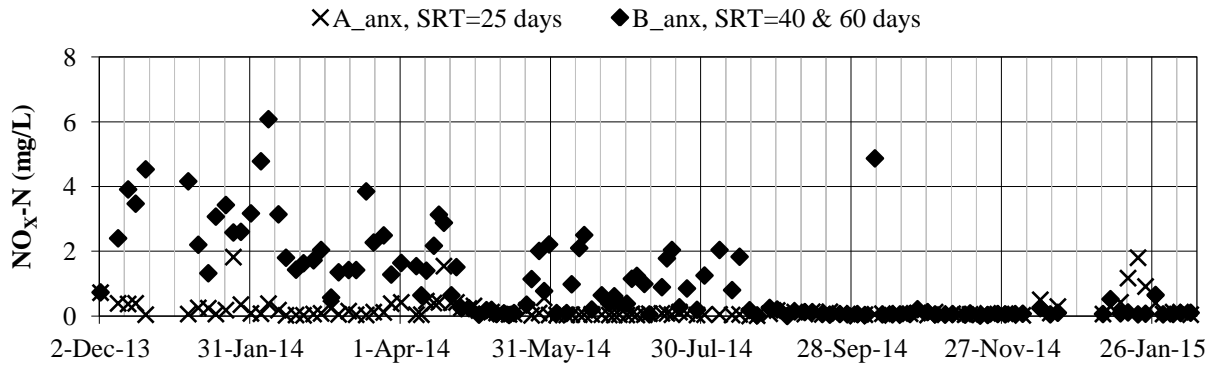
**Figure 2.9 Anoxic zone NO$_X$-N concentrations at three SRTs.**
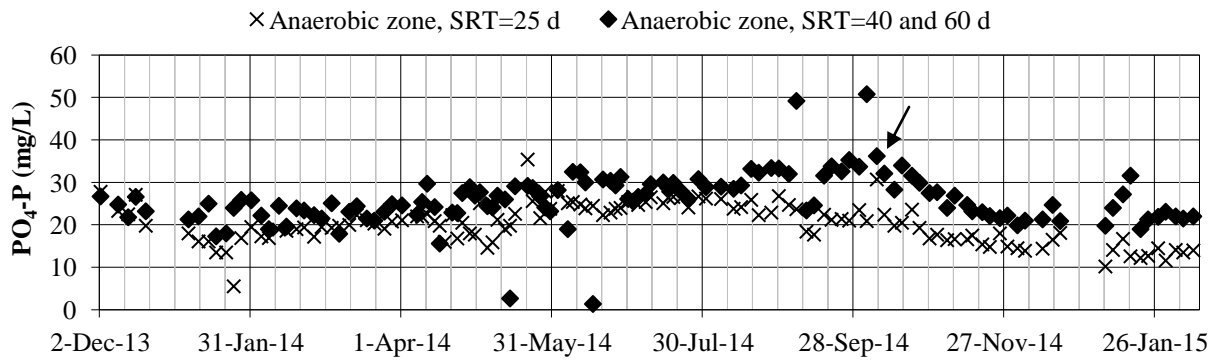


**Figure 2.10 Anaerobic zone PO$_4$-P concentrations at three SRTs.**
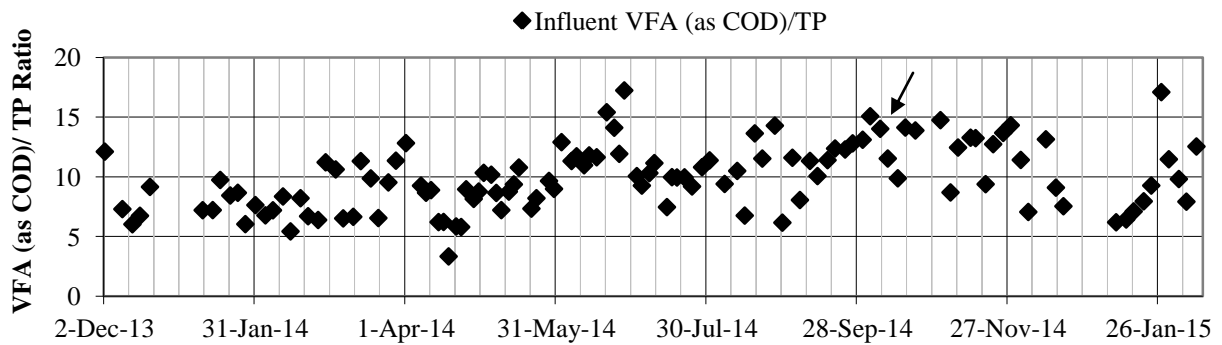


**Figure 2.11 Measured VFA/TP ratio (as COD mg/ P mg) in influent water (without acetate addition).**

However, the high $NO_X$-N concentration on October 7, 2014 did not seem to negatively affect the phosphorus release in the anaerobic zone. In fact, the observed $PO_4$-P concentration (36.20 mg/L) was one of the highest values, as shown in Figure 2.10 (indicated by the arrow). The measured influent VFA/TP ratio on this day (14.0) was also higher than most of other values (Figure 2.11). The ratio did not include the external acetate addition (29 mg COD/L, Section 2.2). It seemed that sufficient VFAs were available for PAOs to take up and release phosphorus, but the released phosphorus was either not sufficiently taken up in the aerobic zone, or secondary phosphorus release took place during October 4 to 8, 2014, There was another upset that started on December 5, 2014. The cause was not clear, but since the upset occurred at SRT of both 25 and 60 days, it can be concluded that this was not caused by the longer SRT.

TP removal at SRT = 40 days was slightly less stable. An upset was observed at SRT = 40 days from March 14 to May 5, 2014 (Figure 2.4). The beginning of the upset might be attributed to leaking membranes which were used from March 7 to April 1. A higher DO setpoint (2.0 mg/L) in the aerobic zone (see Figure 2.2) could also have contributed to the upset. Some high $NO_X$-N concentrations were detected in the anoxic zone during this period (Figure 2.9), and the presence of these high $NO_X$-N concentrations indicated that denitrification was not complete. This incomplete denitrification may have been caused by excessive DO recycled from the aerobic zone due to the higher DO setpoint of 2.0 mg/L. In general, these higher $NO_X$-N concentrations indeed caused some upset as shown in Figure 2.5; however, the negative effect seemed to less than that observed with SRT = 60 days when a similarly high $NO_X$-N concentration was present in the anoxic zone. In other words, the operation at SRT = 60 days appeared to be more sensitive to a high anoxic zone $NO_X$-N concentration than operation at SRT = 40 days. For example, on

February 4, 2014, the anoxic zone $NO_X$-N concentration was observed as 4.78 mg/L at SRT = 40

days (Figure 2.9), very close to the concentration of 4.87 mg/L noted on October 7, 2014. The

corresponding anaerobic zone $PO_4$-P concentration (22.20 mg/L, Figure 2.10) and influent

VFA/TP (6.76, Figure 2.11) on February 4, 2014 were both lower than the values on October 7,

2014, but the phosphorus removal seemed to be unaffected.

After the membrane was replaced on April 1, and the DO was lowered to 1 mg/L on April 15

(Figure 2.2), the TP concentration returned to below 0.2 mg/L after May 5. Comparing the

anoxic zone $NO_X$-N concentrations (Figure 2.9) and the effluent phosphorus concentrations

(Figures 2.4 and 2.5) suggests that the process can withstand anoxic zone $NO_X$-N concentrations

of up to 2.0 mg/L.

### 2.3.2.2    Phosphorus Mass Balance

Although the effluent $PO_4$-P and TP concentrations were significantly higher at SRT = 60 days

than at 25 days, the performance in terms of phosphorus removal was still exceptionally good

(median $PO_4$-P 0.03 mg/L, TP 0.13 mg/L at SRT = 60 days), and the systems were also stable.

Therefore, phosphorus mass balances were calculated to determine how incoming phosphorus

was removed out of the system through different streams (i.e., effluent, wasted foam and sludge).

In addition, since all phosphorus is preserved and measurable in the system, such balances

therefore can be used to roughly evaluate the quality of data.

Phosphorus mass balances were calculated by considering TP over the entire system (Figure

2.12) and based on the following equation.

$$\Delta TP = TP_{INF} - TP_{FOAM} - TP_{AS} - TP_{EFF} \qquad (2.4)$$

where   $\Delta TP$ = TP increase in system (g) within a time period $\Delta t$

= total phosphorus (g) in entire system (including foam) at t2 − total phosphorus (g)

in entire system at t1

$TP_{INF}$ = cumulative mass TP loading in influent (g) within $\Delta t$

$TP_{FOAM}$ = cumulative mass of TP wasted in foam (g) within $\Delta t$

$TP_{AS}$ = cumulative mass of TP wasted in aerobic zone mixed liquor (g) within $\Delta t$

$TP_{EFF}$ = cumulative mass of TP leaving in effluent (g) within $\Delta t$
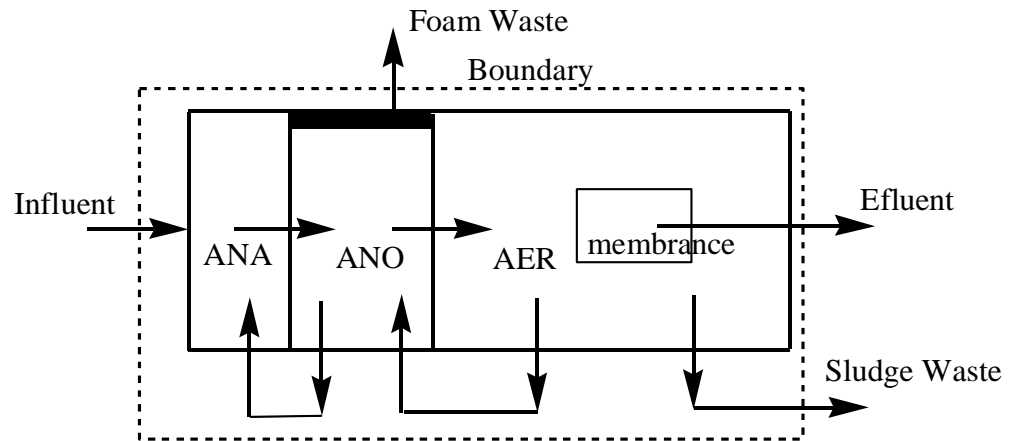


**Figure 2.12 TP (and TN) balance over entire system.**

Moving $\Delta TP$ to the right-hand side, we then have

$$0 = TP_{INF} - TP_{FOAM} - TP_{AS} - TP_{EFF} - \Delta TP \qquad (2.5)$$

Each term on the right-hand side can be calculated. $TP_{INF}$, $TP_{AS}$, and $TP_{EFF}$ were obtained by

multiplying flow rates by the respective measured TP concentrations. $\Delta TP$ was calculated from

the difference in the TP inventory in the system (all three zones) at two different times. $TP_{FOAM}$

was calculated in a different way as explained in the following paragraph. To calculate the

balances, the daily mass (g/day) of each term in Equation (2.5) was estimated and then accumulated over time. Since process samples were not measured daily (see Table 2.1), a linear interpolation method was used to estimate any missing daily data.

The daily mass of TP in the wasted foam was estimated using the following equation.

$$TP_{FOAM, d} = W_{FOAM} \times TSS_{FOAM} \times (TP/TSS)_{FOAM} \qquad (2.6)$$

where $TP_{FOAM, d}$ = daily mass of TP in the wasted foam, g/ day

$W_{FOAM}$ = foam wasting rate, kg wet foam/ day

$TSS_{FOAM}$ = TSS concentration in wet foam, g/ kg wet foam

$(TP/TSS)_{FOAM}$ = TP to TSS ratio in foam, unitless

$TSS_{FOAM}$ concentrations at the three experimental SRTs were measured. The Anderson-Darling tests showed that only the data from the SRT = 25 and 40 day runs were normally distributed (Appendix B.1). The mean and 95 % confidence interval (CI) were 33.2 and (31.8, 34.6) g/ kg wet foam at SRT = 25 days, and 35.2 and (32.6, 37.9) g/kg wet foam at SRT = 40 days. Because the data from SRT = 60 days did not exhibit a normal distribution, the median value and 95 % CI were estimated using 1-sample sign test. This test does not require normally distributed data and does not make assumptions about population symmetry. The median and 95 % CI were 38.4 and (37.5, 39.3) g/ kg wet foam at SRT = 60 days. These data were summarized in box plots and are shown in Figure 2.13.
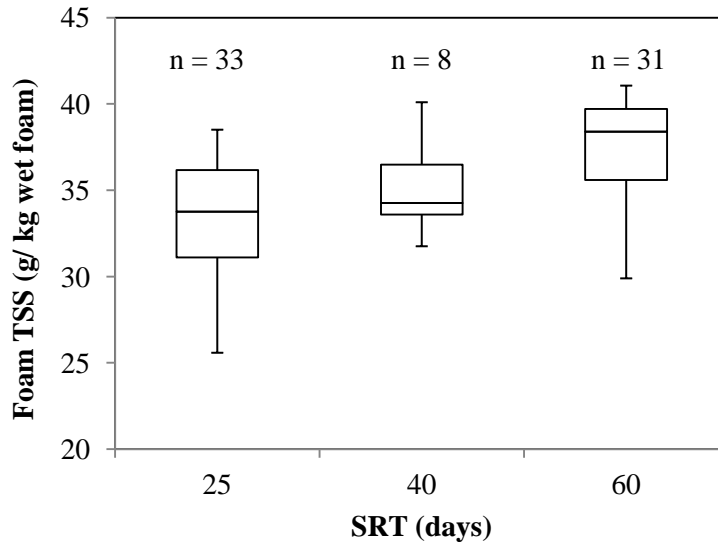
**Figure 2.13 TSS concentrations of mixed foam from both anoxic and anaerobic zones of the UBC MEBPR process at three experimental SRTs. Percentiles shown: 5th, 25th, 75th, and 95th. The horizontal line inside the box represents the median. n is sample size.**

In addition, there were limited numbers of measured $(TP/TSS)_{FOAM}$ values compared to those available for the mixed liquor (ML). To estimate daily $(TP/TSS)_{FOAM}$, the measured $(TP/TSS)_{FOAM}$ values were first compared to measured TP/TSS ratios of the ML in the different reactor zones. Surprisingly, the $(TP/TSS)_{FOAM}$ was found to be significantly lower than the TP/TSS of anoxic and aerobic zone ML, but comparable to the TP/TSS of anaerobic zone ML, $(TP/TSS)_{ANA}$ (see Chapter 3 for details). Consequently, $(TP/TSS)_{ANA}$ was adopted whenever available, and a linear interpolation was used to estimate the rest of the missing $(TP/TSS)_{FOAM}$ data for mass balance calculations.

In theory, the TP balance (i.e., the right-hand side of Equation 2.5) should be zero. To check this, phosphorus balance data were plotted in Figures A1 and A2 in Appendix A and summarized in

Table 2.4. Mean values of foam TSS were used for SRT = 25 and 40 days, and the median value

was used for SRT = 60 days. This table shows that aerobic waste sludge was the major pathway

to remove phosphorus at SRT = 25 days, accounting for 65 % of the influent phosphorus.

However, 78 % of the incoming phosphorus was removed through waste foam at SRT = 60 days.

Operation at SRT = 40 days fell in between, removing 52 % in foam and 34 % in waste aerobic

zone ML. Effluent discharges were 4 %, 5 %, and 4 % from SRT = 25, 40, and 60 days,

respectively. This was equivalent to 96 % phosphorus removal at 25 and 60 days, and 95 % at 40

days. These removal efficiencies were slightly lower than those calculated based on effluent

median and influent concentrations in Section 2.3.2.1 (97−98 %).

**Table 2.4 Phosphorus mass balance components at different SRTs**

| Parameters | A train, SRT = 25 d (in parallel with SRT = 60 d, 271 days) | B train, SRT = 40 d (167 days) | B train, SRT=60 d (271 days) |
|---|---|---|---|
| $TP_{INF}$, g | 6,026 | 3,882 | 6,205 |
| $TP_{FOAM}$, g | 1,794 (30 %) [c] | 2,010 (52 %) | 4,868 (78 %) |
| $TP_{AS}$, g | 3,913 (65 %) | 1,317 (34 %) | 936 (15 %) |
| $TP_{EFF}$, g | 215 (4 %) | 193 (5 %) | 276 (4 %) |
| $\Delta TP$ in system, g | 32 | 134 | 360 |
| Balance [a], g | 72 | 228 | -235 |
| Error, % [b] | 1.2 | 5.9 | -3.8 |

Notes: (a) balance is equal to the right-hand side of Equation 2.5; (b) error was calculated by balance / $TP_{INF}$; and (c) percentages were based on $TP_{INF}$.

Table 2.4 also shows that the relative errors in the mass balance calculations were 1.2 %, 5.9 %,

and -3.8 % for the three different SRTs. To evaluate the variations of these errors, mass balance

was also calculated using the low- and high-end foam TSS values defined by the 95 % CIs, considering that the sample sizes for foam TSS data were relatively small. These calculations only resulted in different $TP_{FOAM}$ in Table 2.4 and exhibited an error range of 2.3 % to 0.05 % at SRT = 25 days and -2.1 % to -5.4 % at 60 days (Appendix A, Table A1). The resulting errors, however, did not changed significantly from those obtained using mean or median foam TSS values. These small errors suggested that the quality of the data was very good. The major error sources may come from chemical analyses and estimations of missing data, particularly those parameters related to the foam due to its heterogeneous nature, limited sampling frequency, and sample dilution. Consequently, it is not surprising to see the smaller error related to the lower SRT because fewer foam measurements were involved.

In summary, phosphorus mass balance calculations demonstrated that waste foam carried up to 78 % of incoming TP, therefore representing a major resource for phosphorus recovery at SRT = 60 days. On the contrary, at SRT = 25 days, aerobic zone mixed liquor was the major resource. Phosphorus mass balance calculations also indicated that the methods used to estimate missing data, particularly those for TSS and TP/TSS data for the foam, were satisfactory with a combined error $< \pm 5.5$ % (considering the 95 % CI).

### 2.3.2.3    Nitrogen Removal

Nitrogen removal can be evaluated through both $NH_4$-N and TN measurements. $NH_4$-N is an important parameter of effluent quality because it may lead to depletion of $O_2$ in receiving waters, just like organic carbon. Effluent TN concentration reflected total nitrogen removal efficiency and was calculated by summing the concentrations of effluent TKN and NOx-N.

The time series of effluent $NH_4$-N, $NO_X$-N, TKN, and TN concentrations are presented in Figures 2.14−2.17. In general, the operations with SRT = 40 and 60 days exhibited a more stable performance in removing $NH_4$-N than that at 25 days. This was expected since longer SRTs usually result in a greater extent of nitrification, through complete nitrification of the ammonia in influent wastewater plus the ammonia released from cell decay at long SRTs. There was some $NH_4$-N breakthrough with SRT = 25 days between November 13 and 16, 2014, which was caused by a partial blockage of an air diffuser (resulting in a DO of ~0.5 mg/L). These few high $NH_4$-N concentrations were consistent with the high TKN value measured on November 14 (Figure 2.16). It was not clear why $NH_4$-N values were high on November 2 and 3 at SRT = 60 days. There might have been some measurement errors, but no corresponding TKN value was available to confirm this. In general, operation at the two longer SRTs showed more stable nitrification than the control, particularly when the DO setpoint was low.
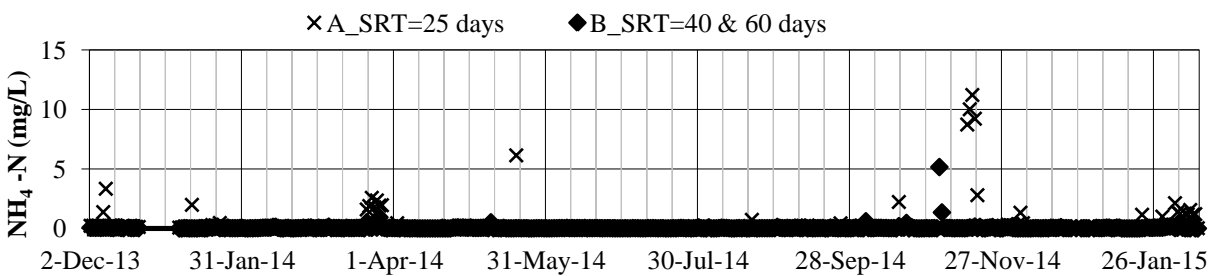


**Figure 2.14 Effluent $NH_4$-N concentrations at three SRTs.**
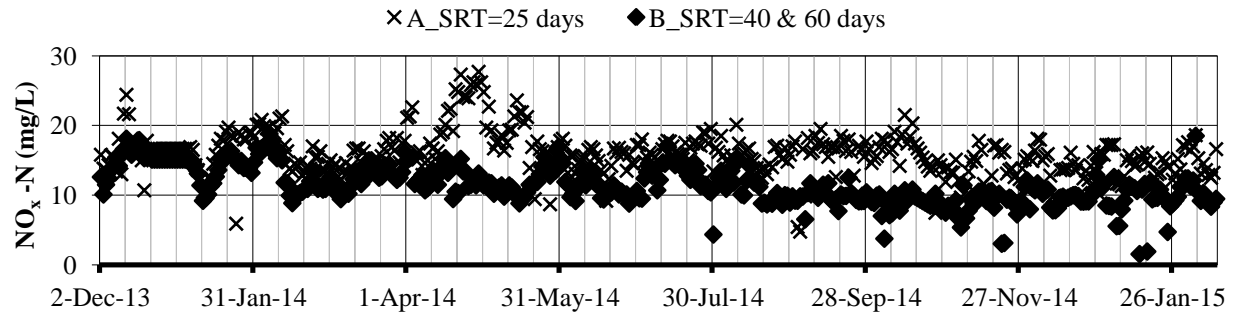
**Figure 2.15 Effluent NO$_X$-N concentrations at three SRTs.**
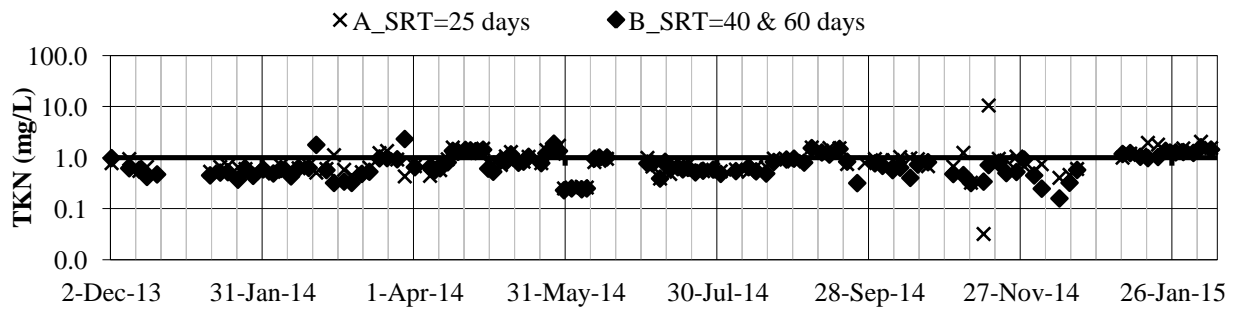


**Figure 2.16 Effluent TKN concentrations at three SRTs.**
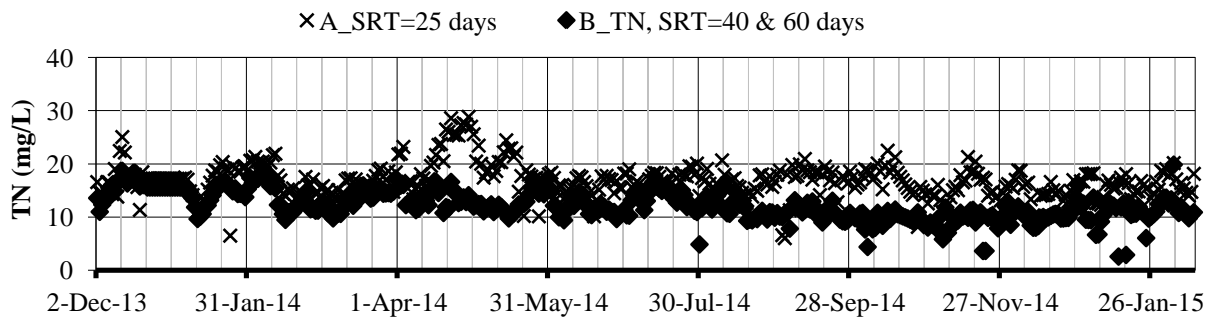


**Figure 2.17 Effluent TN concentrations at three SRTs.**

61

Figure 2.18 Box plots of (a) effluent TN and NOx-N (b) NH$_4$-N concentrations at SRTs = 25, 40, and 60 days. Percentiles shown: 5th, 25th, 75th, and 95th (5th percentiles were zero for NH$_4$-N). The horizontal line inside the box represents the median. n is sample size.

A summary of the effluent TN, NO$_X$-N, and NH$_4$-N data is presented in Figure 2.18. To simplify the discussion, from this point on, data from the operation at 25 days were no longer separated

into two parts in the box plots. Operations with longer SRTs consistently achieved lower effluent TN concentrations, with median values of 17.1, 13.5, and 10.7 mg/L for SRT = 25, 40, and 60 days, respectively. With an average of 43.5 mg/L TN in the influent, the average TN removal efficiencies were 61 %, 69 %, and 75 % for SRT = 25, 40, and 60 days, respectively. The corresponding effluent median $NO_X$-N concentrations were 15.8, 12.7, 10.1 mg/L. The median $NH_4$-N concentrations were 0.07, 0.03, 0.02 mg/L for SRT = 25, 40, and 60 days, respectively. The 95 % percentiles were 0.12 mg/L $NH_4$-N for both SRT = 40 and 60 days. Paired tests confirmed that effluent TN, $NO_X$-N, and $NH_4$-N values were all significantly lower at the 60 day SRT than at the 25 day SRT, with a 95 % confidence level (p = 0.000, 0.000, 0.003, respectively, Appendix B.2).

The lower effluent NOx-N concentrations at longer SRTs were unexpected since longer SRTs should have led to greater extent of nitrification, therefore higher NOx-N concentrations. Figure 2.18 (b) indicates that operations at three SRTs all achieved nearly complete nitrification. Therefore, the lower effluent $NO_X$-N concentrations at two longer SRTs should be indicative of greater denitrification. One possible explanation may be that simultaneous nitrification and denitrification (SND) was occurring in the aerobic reactor (Zhao et al., 1999; Zhao, 1998). Grady et al. (2011) pointed out that when the SRT is long enough, a lower DO concentration helps to encourage denitrification in the aerobic zone. Any extra nitrogen removal is attractive for a biological process removing both phosphorus and nitrogen. Normally these two goals are somewhat conflicting. A complete denitrification requires extensive recycling of nitrates to the anoxic zone from the aerobic zone, which means the recycle ratio could be anywhere from more than 1:1 to 5:1 (based on influent flow). However, elevated nitrates in the anoxic zone pose a

63

threat to optimal phosphorus removal if these are further recycled to the anaerobic zone, as discussed in Section 2.3.2.1. Considering this challenge, the suspected SND at SRT = 60 days represents an attractive feature of long-SRT operation.

### 2.3.2.4   Nitrogen Mass Balance

To estimate the unaccounted-for nitrogen removal, nitrogen balances were performed on the whole system and around the anoxic zone. The former estimated the total nitrogen removal from the whole system, and the latter estimated $N_2$ removal from the anoxic zone. The difference therefore, represents the unaccounted-for nitrogen removal, which might be attributed to the occurrence of SND. The nitrogen balances were performed based on Equations (2.7) and (2.8), and Figures 2.12 and 2.19.

$$\text{Total nitrogen removed as } N_2 \text{ from system} = TN_{INF} - TN_{FOAM} - TN_{AS} - TN_{EFF} - \Delta TN \quad (2.7)$$

$$N_2 \text{ removed from anoxic zone} = NO_X\text{-N in} - NO_X\text{-N out} = 2fC_1 + fC_3 - 3fC_2 \quad (2.8)$$

where f is influent flow rate, and $C_1$, $C_2$, and $C_3$ are $NO_X$-N concentrations in the anaerobic, anoxic, and aerobic zones, respectively. Terms in Equation (2.7) were defined similarly to those of Equation (2.4). Missing $TN_{FOAM}$ data were estimated using linear interpolation of experimentally measured data.
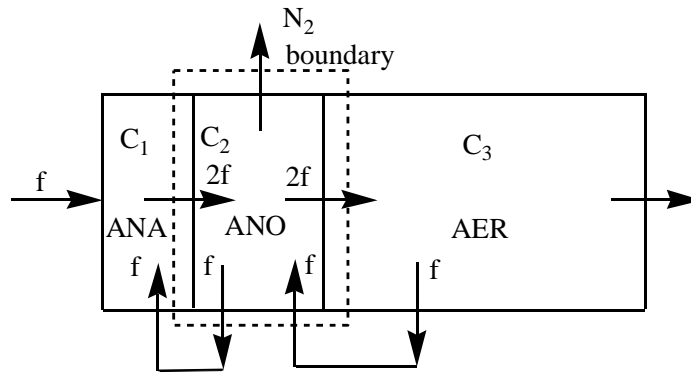
**Figure 2.19 NO$_X$-N balance over anoxic zone.**

The nitrogen balance data are plotted in Figures A3−A5 in Appendix A and summarized in Table 2.5. Mean values of foam TSS were used for SRT = 25 and 40 days, and the median value was used for SRT = 60 days. It is interesting to see from the table that the SRT = 60 days operation exhibited greater TN total removal but less denitrification (in the anoxic zone) than that at SRT = 25 days. The unaccounted-for portion of the nitrogen removal was estimated to be about 22 % of total removal for SRT = 25 days and 64 % for 60 days. These also account for about 9 % and 37 % of the TN in influent. By comparison, Zhao et al. (1999) reported that NOx removal due to SND could reach 50 % of the TN in the influent with a two-stage, intermittent aeration process. Since the TN balance (Equation 2.7) was performed using a very similar approach to that for the TP balance, and TP and TKN were measured from same samples with similar precisions (Table 2.2), comparable errors ($< \pm 5.5$ %) were expected for TN balance calculations. If considering the errors, it can be concluded that the unaccounted-for nitrogen removal was about $22 \pm 5.5$ % at SRT = 25 days and about $64 \pm 5.5$ % at 60 days. The operation at SRT = 40 days gave an even higher value of 70 %. Therefore, the unaccounted-for nitrogen removal was significant, especially at longer SRTs.

**Table 2.5 Nitrogen mass balance at different SRTs**

| Cumulative mass flows | A train, SRT = 25 days (in parallel with SRT = 60 days, 271 days) | A train, SRT = 40 days (167 days) | B train, SRT = 60 days (271 days) |
|---|---|---|---|
| $TN_{INF}$, g | 58,152 | 38,093 | 59,872 |
| $TN_{FOAM}$, g | 3,627 | 3,859 | 9,112 |
| $TN_{AS}$, g | 7,359 | 2,397 | 1,440 |
| $TN_{EFF}$, g | 22,088 | 12,155 | 15,700 |
| $\Delta TN$ in system, g | 42 | 409 | 493 |
| Total N removed as $N_2$ [a], g | 25,036 | 19,273 | 33,127 |
| $N_2$ removed from anoxic zone, g | 19,445 | 5,707 | 12,097 |
| Unaccounted-for N removal [b] | 22 % | 70 % | 63 % |

Note: (a) calculated based on Equation 2.7; (b) = (total removal − removal from anoxic zone)/ total removal.

Similarly to the phosphorus mass balance, nitrogen mass balances were also calculated using the low- and high-end values of the 95 % CI for foam TSS. The results are shown in Appendix A (Table A2). At SRT = 25 and 60 days, the unaccounted-for N removal did not change from the values in Table 2.5, suggesting that using the mean or median foam TSS would be sufficient to estimate the unaccounted-for N removal.

In a typical UCT-EBPR design, the aerobic recycle ratio can be increased to increase the amount of denitrification in the anoxic reactor. For the UCT process, this ratio can be as high as 3 or 5 (Ramphao et al., 2005). In the present study, both aerobic recycle and anoxic recycle ratios were controlled at 1:1 for most of the experimental period. Experience showed that this ratio gave the most stable phosphorus removal in the UBC pilot plant. Control of the aerobic recycle ratio is

critical for simultaneous removal of phosphorus and nitrogen (Wentzel and Ekama, 1997; Grady et al., 2011). As mentioned previously, a ratio of 2:1 was thought to have caused an upset in the present study. Considering this, SND provides an alternative way to remove extra nitrogen while keeping phosphorus removal under control. Obviously, more research will be needed on how to properly manage a suitable environment for SND. In addition to setting a low DO concentration (as in the present study), an air on-off mode in the aerobic zone might also be an option.

In summary, nitrogen mass balance calculations demonstrated that the unaccounted-for nitrogen removal was significantly higher at two longer SRTs (70 % and 64 %) than that at the SRT = 25 days (22 %). Since the calculations followed similar approaches to those used in the phosphorus mass balance calculations, the results here were expected to bear a similar error $< \pm 5.5$ %. This extra nitrogen removal is an attractive feature for the EBPR process, in which maximum nitrogen removal is often limited by the optimal phosphorus removal. The unaccounted-for nitrogen removal estimated was here assigned to SND that was caused by a combination of a low DO setpoint (1.0 mg/L) in the aerobic zone and the high TSS concentrations that accompanied the long SRTs utilized.

### 2.3.2.5    COD Removal

COD removal is normally not a concern for a long SRT operation. Figure 2.20 presents the effluent COD concentrations for operations at the three experimental SRTs. In general, these values were below 50 mg/L. Box plots of COD data indicated that the median COD values were 24, 33, 26 mg/L for SRT = 25, 40, and 60 days, respectively (Figure 2.21). These effluent COD values could be considered as representing an inert COD residual that originated from both

influent inert COD and inert soluble microbial products (SMPs). Given the influent total COD of 292 mg/L (after the primary clarifier), the COD removal efficiencies ranged from 89 % to 92 %. Based on paired t-test, we could not conclude that the difference in COD concentrations was significant at a 95 % confidence level between SRT = 60 and 25 days (p = 0.670, Appendix B.2).
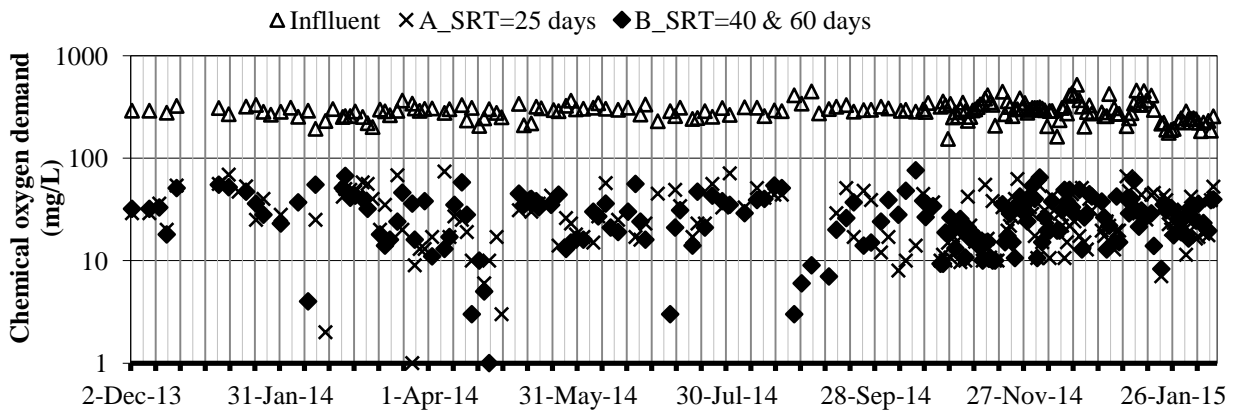


**Figure 2.20 COD concentrations in influent and effluent.**



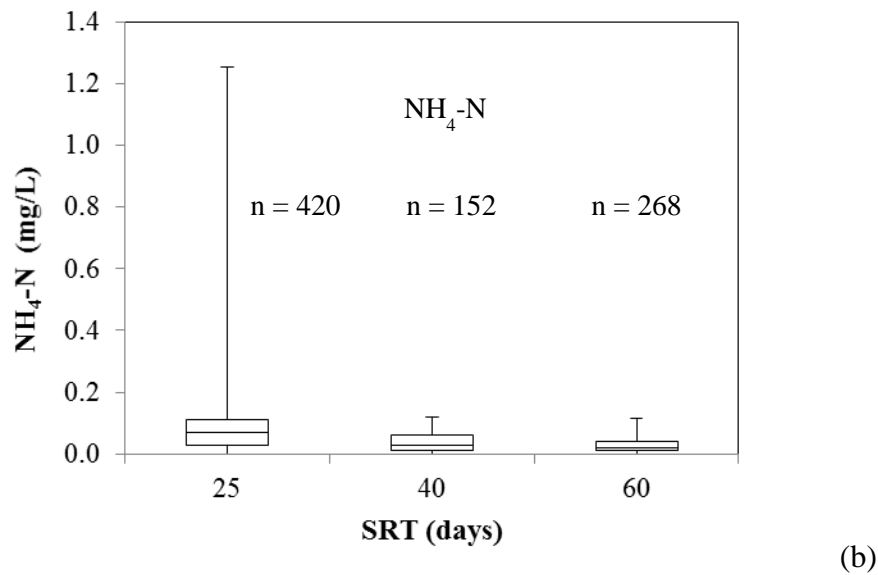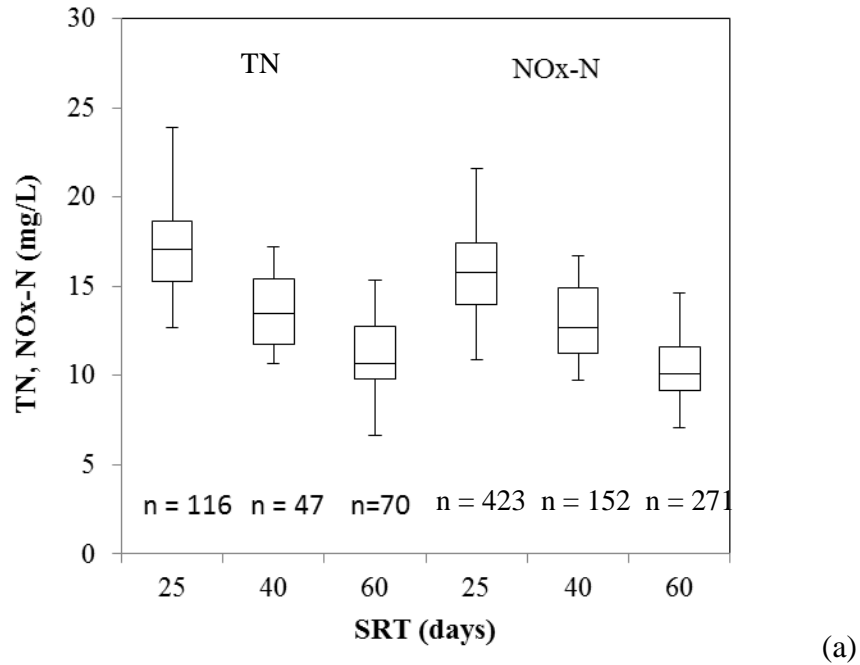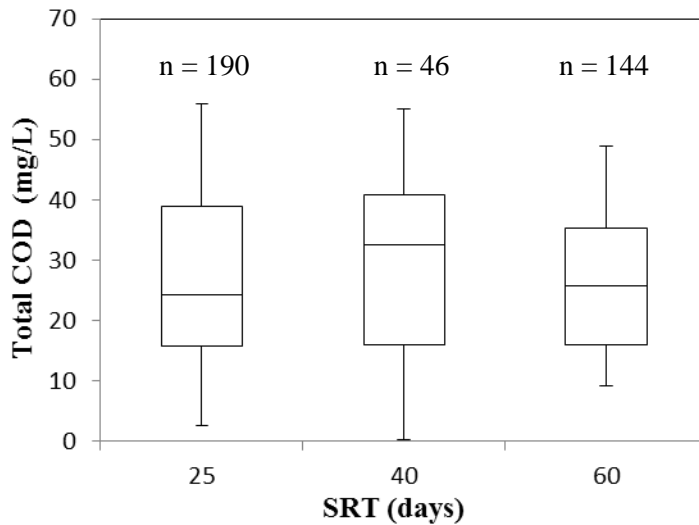**Figure 2.21 Box plots of effluent COD concentrations at SRTs = 25, 40, and 60 days. Percentiles shown: 5th, 25th, 75th, and 95th (5th percentile at 40 days was zero. The horizontal line inside the box represents the median. n is sample size.**

In summary, operation at SRT = 60 days resulted in similar TP and TCOD removal efficiencies to those observed at SRT = 25 days, as well as 14 % better TN removal (based on influent TN). This indicates that operation of an MEBPR at SRT = 60 days offers some advantages and is technically feasible. The key considerations for stable performance include the influent VFA/ P ratio, control of NOx-N concentration in the anoxic zone, and a DO setpoint of 1.0 mg/L in the aerobic zone.

### 2.3.3      Benefits from Long SRTs

Once it was verified that the MEBPR plant continued to perform well at SRT = 60 days, it was possible to assess the benefits that this long SRT brings to the process, by examining TP concentration of the aerobic zone ML, sludge yield,  and foam generation.

### 2.3.3.1    Increased TP Concentration of ML

As stated previously, the major purpose of using a long SRT was to increase the TP concentration in the aerobic zone ML, so that phosphorus recovery would be more cost-effective. TP concentration can be represented by volumetric concentration (mg/L) and specific concentration TP/TSS (mg/mg). The former is associated with the volume (mainly of water) that needs to be dealt with in order to recover a certain amount of phosphorus. The latter is associated with the mass of suspended solids. A good phosphorus resource should have high concentrations expressed in both of these ways. Figure 2.22 shows that operation with a longer SRT increased the TP concentration of the aerobic zone ML, and at pseudo-steady state (after operating for at

69

least 3 SRTs), the averaged TP concentrations and standard deviations were 302 ± 48, 475 ± 80, and 676 ± 56 mg/L for 25, 40, and 60 day SRTs, respectively.
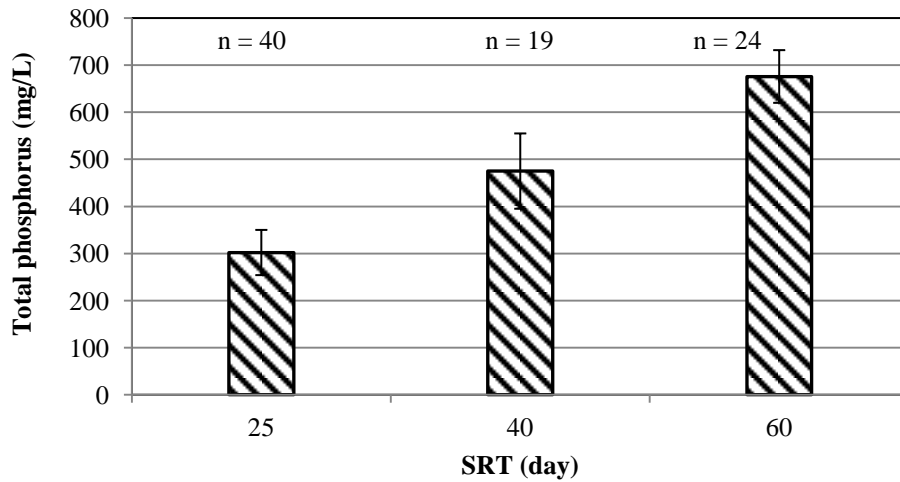


**Figure 2.22 Total phosphorus concentrations in aerobic zone mixed liquor at different SRTs (error bar represents one standard deviation). n is sample size.**
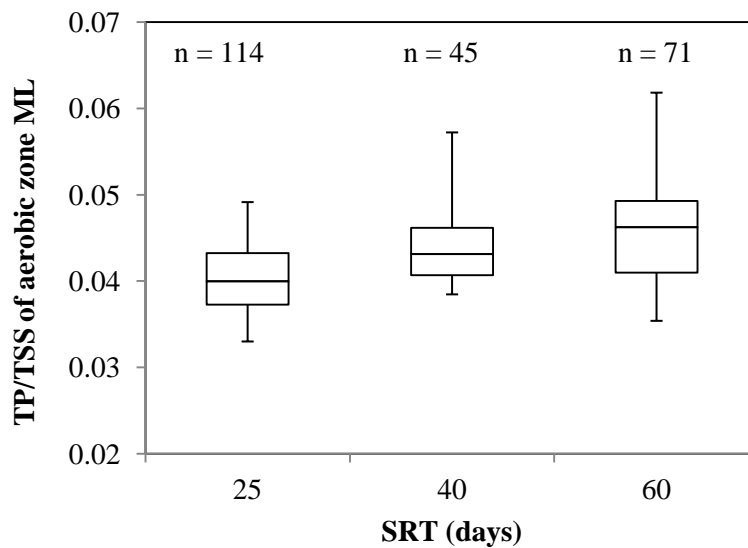


**Figure 2.23 TP/TSS ratios of aerobic zone ML at SRTs = 25, 40, and 60 days. Percentiles shown: 5th, 25th, 75th, and 95th. The horizontal line inside the box represents the median. n is sample size.**

Figure 2.23 summarizes the specific TP concentrations of aerobic zone ML at three SRTs, with the median values of 0.040, 0.043, and 0.046 mg/mg for SRTs = 25, 40, and 60 days, respectively. A paired t-test confirmed that the difference in TP/TSS between 25 and 60 days was significant at a 95% confidence level (p = 0.000, Appendix B.2).

The increased TP concentrations resulted from increasing MLSS concentrations. With a fixed reactor volume, longer SRTs result in higher MLSS concentrations, and it is the high MLSS concentration that influences the oxygen transfer efficiency and membrane fouling rate in an MEBPR process. At pseudo-steady state, the observed average aerobic zone MLSS concentrations were 8,075 ± 477 to 8,141 ± 664 mg/L for SRT = 25 days, and 10,368 ± 476 and 15,926 ± 613 mg/L for SRT = 40 and 60 days, respectively. It should be mentioned that the variations in the measured MLSS concentrations were significant due to the variable occurrence of foaming, where some particles were transported between foam and mixed liquor.

### 2.3.3.2 Reduced Sludge Waste

The sludge wasting rate not only depends on SRT but also on parameters such as the influent COD loading, which changes all the time. Therefore, to compare sludge wasting rates at different SRTs, it is desirable to use observed yield ($Y_{H\,obs}$), which is the ratio of MLVSS produced to COD removed and given by the following equation:

$$Y_{Hobs} = \text{VSS produced, g/ COD removed, g} \qquad (2.9)$$

Briefly, the VSS produced was calculated as the VSS actually wasted during the experiment from either foam and/ or aerobic ML. During the operation, the VSS/TSS ratio was observed to be relatively stable for both foam and aerobic ML; therefore, averaged VSS/TSS values were used when VSS/TSS values were not available (Table 2.6). The concentration of TSS in the foam ($TSS_{FOAM}$) was measured less frequently, and missing data were assumed to be average values, i.e., 34 g/kg for SRT = 25 days and 38 g/kg for SRT = 40 and 60 days. The COD removed was calculated to be cumulative total COD (TCOD) in influent plus external acetate, less the cumulative total COD in effluent. Figure 2.24 shows the $Y_{H\,obs}$ values at the three different SRTs. The plots of accumulated VSS wasted vs COD removed for the entire operation time are given in Figures A6 and A7 in Appendix A.

**Table 2.6 VSS/TSS ratios of anoxic foam and aerobic ML**

| SRT (days) | Materials | VSS/TSS | Sample size | Time period (days) |
|---|---|---|---|---|
| 25 | Anoxic foam | $0.84 \pm 0.05$ | 19 | 438 |
| | Aerobic ML | $0.82 \pm 0.02$ | 46 | |
| | Anoxic ML | $0.83 \pm 0.03$ | 45 | |
| 40 | Anoxic foam | $0.81 \pm 0.07$ | 8 | 167 |
| | Aerobic ML | $0.79 \pm 0.03$ | 17 | |
| | Anoxic ML | $0.79 \pm 0.03$ | 17 | |
| 60 | Anoxic foam | $0.85 \pm 0.04$ | 9 | 271 |
| | Aerobic ML | $0.79 \pm 0.01$ | 29 | |
| | Anoxic ML | $0.79 \pm 0.02$ | 29 | |
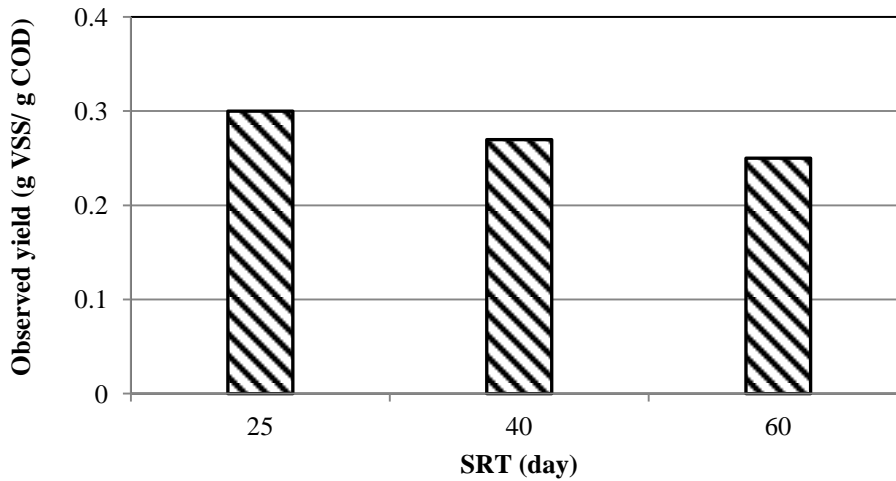
**Figure 2.24 Observed VSS yield at different SRTs.**

**Table 2.7 Observed yield at different SRTs**

| $Y_{H\ obs}$ | SRT = 25 days | SRT = 40 days | SRT = 60 days |
|---|---|---|---|
| g VSS/ g COD | 0.30 | 0.27 | 0.25 |
| g VSS/ g BOD$_5$ | 0.51 | 0.46 | 0.43 |
| g TSS/ g BOD$_5$ | 0.62 | 0.55 | 0.51 |

WEF and ASCE (1992) reported that the observed yield range is from 0.33 to 0.88 mg TSS/ mg BOD$_5$ for domestic wastewater with a primary clarifier for SRTs up to 30 days and temperatures between 10 and 30 $^0$C. To compare our data with the reported range, the units needed to be consistent. The observed yield in units of g VSS/ g BOD$_5$ was calculated by assuming biodegradable COD = 1.7 BOD$_5$ (Grady et al., 2011). In addition, an average VSS/TSS = 0.82 was measured for aerobic ML, which was the major wasting source at SRT = 25 days, and VSS/TSS = 0.85 was measured for anoxic foam, which was the major wasting source at SRT =

60 days. These two VSS/TSS ratios are used to convert $Y_{H\,obs}$ from g VSS/ g $BOD_5$ to g TSS/ g

$BOD_5$ in Table 2.7.

The observed $Y_{H\,obs}$ value (0.62 g TSS/ g $BOD_5$) at SRT = 25 days in the present study was in the

range given by WEF and ASCE (1992). The results in Table 2.7 are comparable to the data

reported by Monti et al. (2006), $Y_{H\,obs}$ = 0.23−0.28 g VSS/ g COD, also from the UBC MEBPR

pilot plant at an SRT = 12 days. Based on a submerged MBR, Masse et al. (2006) reported that

when SRT was increased from 10 to 37 days, the $Y_{H\,obs}$ decreased from 0.31 to 0.22 g VSS/ g

COD. These values were also comparable to the results in Table 2.7.

It should be noted that in the present study, the daily wastage was calculated including foam in

the suspended solids inventory (Section 2.2).  Evidence suggested that foam was an active

component in the MEBRP process (Section 4.3.2); therefore it was reasonable to include the

foam in SRT control calculations for the process (SRT). Jenkins et al. (2004) stated that "Surface

wasted material should be combined with WAS for treatment and the solids contained in it

should be accounted for in sludge wasting calculations."

When the foam was included in the solids inventory and used to control the process (SRT), the

observed yield was expected to be higher than that anticipated without considering the foam,

particularly at SRT=60 days. Two factors will contribute to higher observed yield: (1) foam was

included in solids inventory; therefore, the calculated, daily waste TSS was higher based on

Equation (2.1); and (2) VSS /TSS in foam (0.85 ± 0.04) was significantly higher than VSS/TSS

(0.79 ± 0.01) in aerobic zone ML (Table 2.6). At SRT = 60 days, SRT control was achieved

mainly through wasting of foam, rather than by wasting aerobic zone ML. Therefore, when the same amount of TSS was wasted, more VSS was removed from foam than from aerobic zone ML. This should result in a higher observed sludge yield, based on Equation (2.9).

The reduced sludge waste was an extra benefit for the two longer SRTs. Labelle et al. (2015) combined the Cannibal process with a long SRT of 400 days to minimize sludge production in a full-scale facility. The Cannibal process utilizes a microscreen and hydrocyclone to remove the trash and grit from return activated sludge (RAS), and an interchange tank to condition the RAS with a low, controlled oxidation reduction potential (ORP). The observed yield was estimated by Labelle et al. (2015) to be 0.14 g TSS/ g COD removed. While the Cannibal process can effectively reduce sludge production, it has the problem to sufficiently remove phosphorus due to phosphorus release in the interchange tank (Johnson et al., 2007). Consequently, chemical precipitation is needed to achieve a high phosphorus removal efficiency.

**Cumulative Solids Wasted**. During pseudo-steady state operation between November 14, 2014 and February 12, 2015, the total masses of suspended solids wasted were 52.3 and 45.5 kg (dry solids) from the SRT = 25 days and 60 days systems, respectively, which represents a 13 % reduction with increased SRT; however, the total waste volume decreased from 4,539 to 1,446 L, a reduction of 68 %. The significant reduction was due to the different TSS concentrations of the wasted material. Wasting at SRT = 60 days was mostly carried out with foam (~ 40 g TSS/L), while at SRT = 25 days aerobic zone mixed liquor (~ 8 g TSS/L) was the major waste source. This means that the operation at SRT = 60 days requires much smaller storage tanks/ reactors for further treatment and disposal of the waste sludge. The accumulated wasted dry solids and total

waste volume (activated sludge + foam) from both trains are given in Figures A8 and A9 in Appendix A.

### 2.3.3.3    More Foam Generated

Foam generation at the three different SRTs was also closely monitored. In general, longer SRTs produced more foam. The median foam generation rate was 4.9 and 11.3 kg wet foam/ day at SRT = 25 and 60 days, respectively (see Chapter 3 for details), or about 0.9 and 2.1 kg wet foam/ $m^3$ wastewater treated, based on a constant influent flow rate of 5,328 L/day (3.7 L/min). A paired t-test confirmed that the difference between the two foam generation rates was significant at a 95 % confidence level (p = 0.000, Appendix B.2). However, foam generation varied greatly. It was found that foam generation was influenced by precipitation events, which was studied separately and reported in the next chapter.

### 2.3.4        Membrane Cleaning Frequency

One of the biggest concerns associated with long-SRT operations in MBRs is membrane fouling because of the associated high MLSS concentrations. Although membrane fouling was not a subject of research in the present study, the TMP was closely monitored every day. A chemically cleaned membrane module normally started operation with TMP of 0.1−0.13 atmospheres (3−4 inches of mercury) and was replaced when the TMP reached 0.53−0.57 (16−17 inches of mercury). During the study, two complete service cycles were observed within the control train, one lasting for five months and the other for seven months (Figure 2.25, point "2" to "3", and "3" to "4"). Another complete cycle (about six months) was also recorded within the longer-SRT train but this included operation at SRT of 40 and 60 days (points "b" to "c"). Mechanical

problems were encountered including membrane leaking and pinched tubing, with the former

requiring a temporary membrane replacement (points "1" to "2" and "a" to "b") and the latter

increasing TMP unexpectedly (May 27 to June 20, 2014 in Figure 2.25).  There was also an

unresolved issue resulting in a TMP jump over a short period between May 4 and 22, 2014.

Since this problem occurred in both trains, the cause was thought to be related to the influent

quality. During this time, a lot of construction work was occurring at UBC. It was thought that

some materials from construction sites (e.g., gypsum) were washed into the sewer and caused

blocking of the membranes.
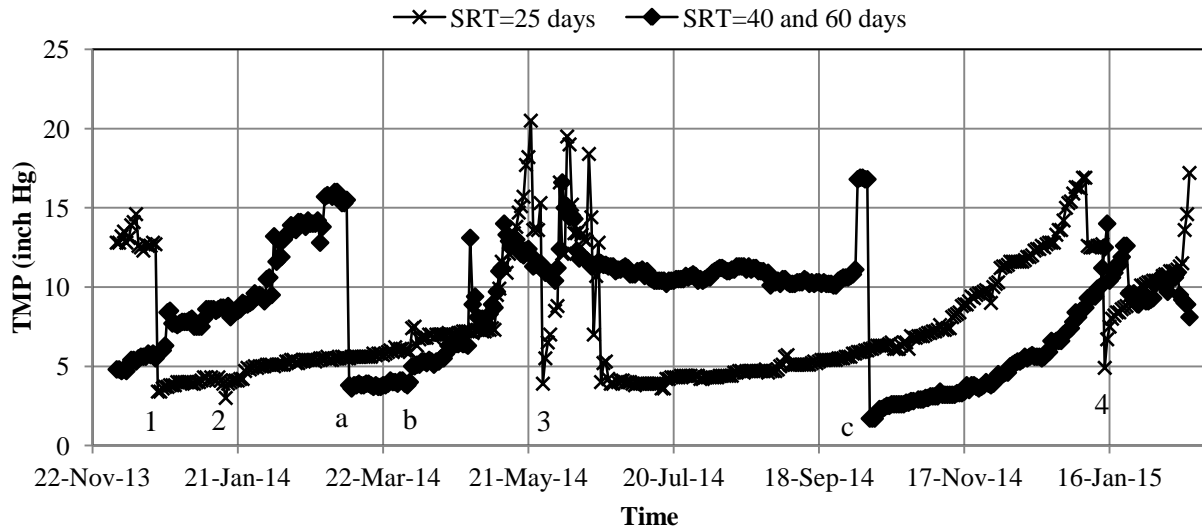


**Figure 2.25 TMPs in both trains from Dec. 2, 2013 to Feb. 18, 2015.**

Although there was not a complete cycle observed for SRT = 60 days, a very interesting

phenomenon was observed from June 10 to October 4, 2014. For nearly 4 months the TMP

basically remained at 0.33 to 0.4 atmospheres (10 to 12 inch mercury, Figure 2.25), but suddenly

jumped one day following the malfunction of a solenoid air valve. After changing the solenoid

valve, the membranes did not recover over the next four days and had to eventually be replaced.

Membrane fouling is typically considered to be a three-stage process wherein various

mechanisms prevails—conditioning fouling, slow/steady fouling, and TMP jump (Judd, 2011).

The observed TMP jump might have coincided with the third fouling stage, or perhaps the

malfunction of the solenoid valve triggered the TMP jump. In any case, the membrane cleaning

frequency at longer SRTs seemed comparable to that of the control (SRT = 25 days). Following

the present study, another PhD student operated the two pilot plant trains at SRT = 40 and 80

days. A complete membrane cycle of six and half months was observed for SRT = 40 days (July

1, 2015 to January 14, 2016), and about seven and half months for SRT = 80 days (April 28,

2015 to December 7, 2015). Furthermore, a cycle of nearly nine months was observed in the

operation crossing SRT of 60 days and 40 days (October 8, 2014 to June 30, 2015). Based on

these experiments, longer SRT operation does not seem to increase bio-fouling of membranes.

As mentioned in the literature review (Chapter 1, Section 1.2.3), the impacts of MLSS

concentration on membrane fouling have been reported to be positive, negative, and

insignificant. There may be several reasons why a high MLSS concentrations (at a long SRT) did

not increase observed membrane fouling rates. First, studies showed that membrane fouling was

mainly caused by the adsorption of dissolved organic matter, such as EPSs and humic or humic-

like substances, onto membrane surface and pores (Geng, 2006). Second, EPSs concentrations

have been reported to decrease with increasing SRT up to 30 days, beyond which the EPSs

remained relatively constant (Brookes et al., 2003). Third, at high MLSS concentrations, a cake

layer forms rapidly on the filtration membrane surface, acting as a protective barrier for

membrane pores, therefore reducing the fouling rate and permeate flux (Cao et al., 2004). Fourth,

under constant flux operation, where the flux is normally controlled below the apparent "critical

flux", the large floc particles did not interact significantly with the membrane surface. Consequently, a high MLSS concentration should not affect membrane fouling (Zhang et al., 2006). Cosenza et al. (2013) reported that foaming also helped to reduce the observed membrane fouling rate because EPSs, which are considered as the major fouling contributors, remained trapped in the floating scum. A higher MLSS concentration tends to generate more foam.

## 2.4 Conclusions and Engineering Significance

A pilot-scale MEBPR plant was operated for 438 days at SRTs of 25, 40, and 60 days to increase the TP concentrations of the mixed liquor. These following conclusions were made.

- It was technically feasible to operate an MEBPR process at a long SRT = 60 days, with TP, TN, and TCOD removal efficiencies of 97 %, 75 %, and 91 %, respectively, based on the effluent median values. Mass balance calculations showed similar, but slightly, lower TP (96 %) and TN (74 %) efficiencies.

- Compared to SRT = 60 days, the operation at SRT = 25 days showed marginally higher TP (98 %) and TCOD (92 %) removal but a significantly lower TN removal efficiency (61 %).

- The phosphorus removal efficiency at SRT = 60 days was fully satisfactory. The median concentrations of effluent $PO_4$-P and TP were 0.03 and 0.13 mg/L, and 95 % of the data were below 0.09 and 0.51 mg/L. By comparison, the median $PO_4$-P and TP concentrations were 0.01 and 0.08 mg/L at SRT = 25 days, and their corresponding 95 % percentiles were 0.08 and 0.46 mg/L.

- Paired t-tests confirmed that operation at SRT = 60 days exhibited significantly higher effluent TP and $PO_4$-P, but lower TN, NOx-N, and $NH_4$-N concentrations than operation

at SRT = 25 days at a 95 % confidence level. No significant difference was found for TCOD.

- Although the differences for effluent TP or $PO_4$-P were statistically significant, all the concentrations were fairly low. Consequently, both 60 and 25 days achieved comparable phosphorus removal (97 % vs 98 %). On the contrary, the significantly lower effluent TN concentration (10.7 vs 17.1 mg/L at 25 days) provides an extra advantage to operation at SRT = 60 days.

- The average TP concentration of aerobic zone ML was $676 \pm 56$ mg/L at SRT = 60 days compared with $302 \pm 48$ at SRT = 25 days, a 220 % enhancement.

- The median foam generation rate was 4.9 kg foam/ day (or 0.9 kg/ $m^3$ wastewater treated) at SRT = 25 days, with an interquartile range of (3.6, 7.0). By comparison, the median at SRT = 60 days was 11.3 kg/d (or 2.1 kg $m^3$ wastewater treated), and its interquartile range was (7.1, 16.0).

- Operations at SRT = 40 and 60 days reduced the waste solids by 10 % and 17 %, respectively, and waste sludge volumes by 45 % and 68 %, compared to operation at SRT = 25 days. The dramatic volume reduction was due to the fact that foam could be used increasingly as the major waste sludge source at SRT=25 days.

- Observed membrane cleaning frequencies were comparable at three different SRTs, suggesting that operation at a long SRT = 60 days did not increase the membrane fouling rate.

It is a challenge to operate a biological phosphorus removal (BPR) process at long SRTs without compromising phosphorus removal efficiency. It is even more difficult to maintain good

phosphorus removal performance while maximizing nitrogen removal. These two goals are somewhat conflicting. To stabilize phosphorus removal in a UCT process, the NOx-N concentration in the anoxic zone should be kept low (< 2 mg/L in the present research). This limits the applicable ML recycle ratio from aerobic zone to the anoxic zone. Consequently, NOx-N was not sufficiently returned to the anoxic zone, resulting in sub- optimized nitrogen removal through denitrification.  The present research proved that 14 % more nitrogen (based on influent TN) could be removed while maintaining satisfactory phosphorus removal, when the SRT was increased from 25 to 60 days and a low DO concentration (e.g., 1.0 mg/L) was maintained in the aerobic zone. A low DO concentration reduces aeration demand and the risk of upsetting phosphorus removal.

From a technical point of view, an MEBPR operating at SRT = 60 days is the most desirable option among the three SRTs examined. It could achieve the goal of increasing mixed liquor TP concentrations without compromising TP and TCOD removal performances, and could also increase TN removal efficiency and reduce sludge production. Consequently, the SRT = 60 was selected for the proposed system in Chapter 6. A cost analysis of this long-SRT operation is presented in Chapter 5.

# Chapter 3: Foam In A Membrane Enhanced Biological Phosphorus Removal (MEBPR) Process: From Operational Nuisance To Valuable Resource For Phosphorus Recovery

## 3.1    Introduction

Foaming has been a long-term operational nuisance in biological WWTPs, since it can interfere with operations, pose health threats for personnel, and incur significant cost to cure the problem (Jenkins et al., 2004; Seviour and Nielsen, 2010). While certain types of filamentous bacteria, for example the *M. parvicella* and members of mycolata, are considered to be the major causes of foaming in conventional WWTPs, the extracellular polymeric substances (EPSs) retained by membranes also play a significant role in the foaming in membrane bioreactors (MBRs) (Nakajima and Mishima, 2005; You and Sue, 2009; Di Bella et al., 2011). Consequently, foaming in MBRs tends to be more severe than in conventional WWTPs (Hall et al., 2011). Traditional solutions to the foaming problem may include mechanically removing foam, adding chemical coagulants to suppress foaming, or reducing activated sludge age (Madoni et al., 2000). Some solutions have achieved only moderate success, others have achieved great success but under specific conditions, and the rest caused additional sludge treatment and disposal problems (Madoni et al., 2000). Therefore, a better solution to control foaming is desirable.

Foaming is a complicated phenomenon and the mechanisms are still not fully understood (Stratton et al., 2002). One commonly accepted mechanism is similar to the "flotation theory" proposed for the mineral flotation process (Petrovski et al., 2011). Flotation theory emphasizes three key components for foaming: surfactants that reduce surface tension, hydrophobic

82

suspended solids (e.g., certain filamentous microorganisms), and gas bubbles that float the hydrophobic particles to the liquid surface. Unfortunately, no standard methods have been agreed on to measure the hydrophobicity and surface tension of mixed liquor. Instead, many approaches have been reported by different research groups (Kreama, 2002; Geng, 2006; Khan et al. 1991, Kocianova, et al., 1992; Verma et al., 2006; Ganidi, 2008; Goddard and Forster, 1986). To measure the combined properties of a mixed liquor (ML) for foaming, foaming potential tests have been developed using either Alka-Seltzer tablets or an air diffuser (Fryer et al., 2011). The former method is more standardized and the latter has many variations.

Chapter 1 demonstrated that foam can be a more appealing source for phosphorus recovery than ML, because foam contains higher total phosphorus (TP) concentrations. Treating foam as a resource, rather than an operational nuisance, is a novel approach, and incorporating the foam into the operation of an MEBPR process requires that we know its characteristics for the purposes of solids retention time (SRT) control and phosphorus recovery. It is also important to understand how the treatment process operating parameters influence foam generation and if the foam can be consistently generated. Some previous research publications reported the characteristics of foam, but the data were limited and based on operation at relatively short SRTs (Lo et al., 2010; Hall et al., 2011). Some research explored the impacts of operating parameters (e.g., pH, DO, temperature, etc.) on foaming, but none of these studies was executed systematically, for example, using a set of carefully designed factorial experiments. In Chapter 2, we observed that foam generation appeared to be strongly influenced by rain precipitation, therefore the "flotation theory" was adopted in this Chapter to investigate rain precipitation impacts.

The present study employed a novel approach, which focused on considering the foam in an MEBPR process as a resource. Therefore, the objectives of this chapter included: (1) fully characterizing foam for the purposes of SRT control, P recovery, and N balance; (2) determining possible main factors influencing foam formation through factorial design experiments; (3) exploring why rain precipitation reduces foam formation (4) modifying the available methods for estimating hydrophobicity and surface tension tests to suit objective (3).

## 3.2    Materials and Methods

**Source of Foam.** All the foam used in the present study was produced by the UBC MEBPR pilot plant operated at three SRTs, i.e, 25, 40, and 60 days (Chapter 2, Section 2.2). Typically, the majority of the foam was generated at the anoxic zone of the MEBPR process, with < 10 % generated at the anaerobic zone. Except for direct comparison between the anoxic zone foam and its underlying mixed liquor (Section 3.3.1.3), mixed foam from both anoxic and anaerobic zones was collected for characterization.

**Foam Characterization.** Figure 3.1 shows the general procedures used to characterize the foam. In each sampling case, all the foam was removed into a 20 L bucket from the anaerobic and anoxic zones, weighed on a scale, and mixed for 2−3 minutes with a battery-powered blender to drive off gases. From the bucket, samples were taken for measurements with proper dilution (in most cases). In general, the characterization of foam was difficult due to its heterogeneous nature and the high concentrations of all the constituents. Usually, pre-mixing and dilution were required before analysis. In addition, the foam was sticky and could only be measured by mass,

rather than by volume. Foam density (g/mL) was measured to convert concentration units from "mg/ kg foam" to "mg/L".



take foam from anaerobic and anoxic zones

weigh on scale

mix for 3-5 min.

store in fridge for TP&TKN analysis

centrifuge 1000 RCF for 30 minutes

supernatant

weigh ~ 4 g

weigh ~ 1 g

add 96 mL distilled water

add 99 mL distilled water

pipet 1 mL foam, weigh for density (duplicate)

mix 3-5 min.

mix 3-5 min.

syringe + glass fiber filtration (1.2 µm)

test tube

store in bottle for TSS and VSS analysis (duplicate)

add 1 drop 5% $H_2SO_4$, store in fridge for $NH_3$-N analysis

add 1 drop phenol mercuric acetate, store in fridge for $NO_X$-N and $PO_4$-P analysis

pipet 2 mL into each COD vial (high-range) for TCOD analysis

**Figure 3.1 Procedures for foam characterization.**

85

**Fractional Factorial Experiment**. Fractional factorial experiments have several advantages. They are more efficient than one-factor-at-a-time experiments to determine factors having significant effects. Furthermore, factorial experiments are necessary to avoid misleading conclusions when interactions of factors may be present. According to Montgomery (2005), interactions occur if the difference in response between the levels of one factor is not the same at all levels of the other factors. Finally, factorial experiments allow the effects of a factor to be estimated at several levels of the other factors, yielding conclusions that are valid over a range of experimental conditions (Montgomery, 2005).

(a) *Selection of independent variable levels*. Two levels of each independent variable were selected based on operational experiences of the UBC pilot plant and a literature review (Table 3.1). Specifically, SRTs were selected based on the low and high levels of an MBR system (15 to 40 days) (Fenu et al., 2010). A low level of 25 days was used in the current study, rather than 15 days, because we have long observed more stable performance from the former. DO levels of 1.0 and 2.0 mg/L are typical at the UBC pilot plant. An aerobic recycle ratio of 1 (i.e., 1:1 based on influent flow rate) is also the most commonly used value. Beyond this level, high $NO_X$-N concentrations in the anoxic zone (1.0 to 4.0 mg/L) were often observed. This $NO_X$ breach, when recycled to the anaerobic reactor, compromised $PO_4$-P release in the anaerobic reactor and subsequent uptake in the aerobic reactor. For this reason, a recycle ratio of 1.0 was selected as the high level and the low ratio of 0.75 was determined from the low-limit capacity of the recycle pump.

(b) *Fractional factorial design* ($2^{3-1}$). Because of the time-consuming nature of these pilot scale experiments, only one-half of the full factorial experiments was feasible, and the experimental conditions were determined using statistical software Minitab (Table 3.2).

**Table 3.1 Selected two levels of three independent variables**

| Parameters | SRT (day) | DO (mg/L) | Aerobic recycle ratio |
|---|---|---|---|
| Low level | 25 | 1 | 0.75 |
| High level | 40 | 2 | 1 |

**Table 3.2 $2^{3-1}$ fractional factorial design table**

| Experiment | Operation time (days) | Sampling days (replicates) | SRT (days) | DO (mg/L) | Aerobic recycle ratio | Train |
|---|---|---|---|---|---|---|
| 1 | 135 | 4 [a] | 25 | 1 | 1 | A |
| 2 | 32 | 4 [b] | 25 | 2 | 0.75 | |
| 3 | 135 | 4 [a] | 40 | 2 | 1 | B |
| 4 | 32 | 4 [b] | 40 | 1 | 0.75 | |

Notes: (a) from April 12 to 15, 2014; and (b) on May 2, 3, 15, and 16. During the experiments, anoxic zone temperature ranged from 15.7−20.0 $^0$C, pH 6.96−7.50.

**Variable Control Strategy**. Factorial experiments require that in all experiments, the studied independent variable be carefully controlled at the specified levels while the other conditions remained the same. This is a challenge for a pilot-scale, biological treatment plant, which relies completely on the microorganisms to do all the work. In addition, precise control at pilot scale (if not impossible) is much more difficult than at lab scale. In the present study, DO was controlled using a DO controller and solenoid valve in an on/off mode. A data logger (Hoboware) was

employed to record DOs from both trains every 30 seconds. The logger generated a huge amount

of DO data. As an example, Figure 3.2 shows the DO data controlled at 1 and 2 mg/L during the

first hour for Exp. 1 and Exp. 3 (Table 3.2). SRT was controlled based on the wasting of a

designated mass of suspended solids every day. The details are given in Chapter 2 (Section 2).

Aerobic recycle ratios, based on influent flow rate, were measured using a 4-L cylinder and a

stop watch normally two to three times per week.
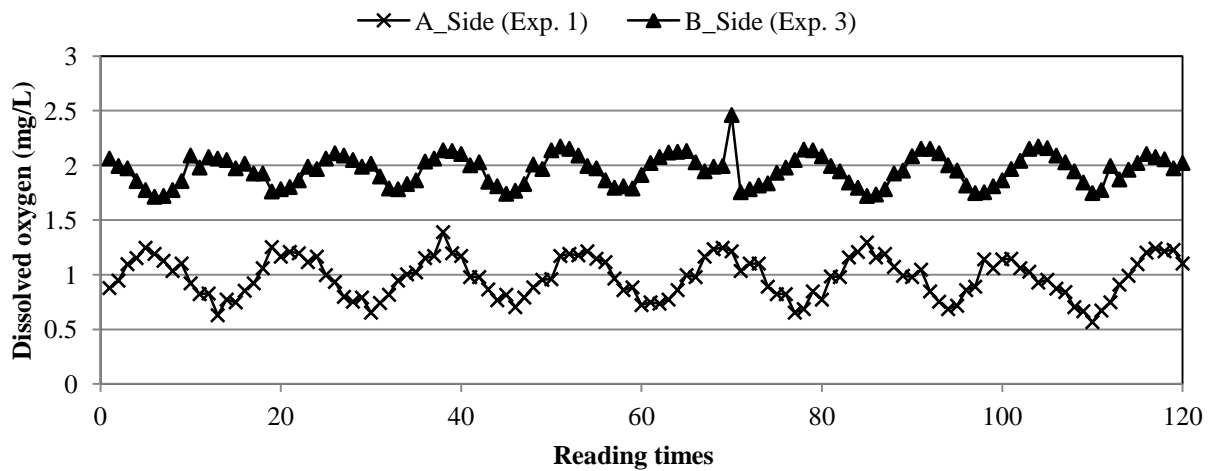


**Figure 3.2 A sample DO plot for the first hour (120 reading times) .**

**Measurement of Surface Tension.** A Surface Tensiometer 20 (Fisher Scientific) with platinum

ring was used for the measurement of surface tension. Before measurement, the tensiometer was

calibrated with a 600 g mass, as described in the equipment manual. Pure Milli-Q water was

measured at room temperature ($22\ ^0C$) to check the accuracy and any system bias was corrected.

To develop a suitable method for sludge, several procedures were tried. It was found that

centrifugation at 8,000 ($\times$ g) for 10 min was required, after which centrate filtration using a 0.45

μm filter was necessary. Filtration with glass fiber (~1.2 μm) filters significantly increased

measurement results (see Table 3.3). Since surface tension is a characteristic of liquid, and the

liquid passing through the 0.45 μm filter paper contains fewer fine particles than through the 1.2

μm one, the results obtained after 0.45 μm filtration should be closer to the true value. On the

other hand, filtration using smaller-than-0.45 μm filter paper was too slow to be practical.

Table 3.3 Surface tension comparison with different filtration pore sizes

| | Filtration After 0.45 μm | Filtration after glass fiber G4 (~1.2 μm) |
|---|---|---|
| Surface tension (millinewton/ meter) | 65.0 | 71.3 |
| | 65.2 | 71.0 |
| | 65.0 | 70.6 |
| | 64.4 | 71.2 |
| | 65.0 | 71.4 |
| | 64.0 | 71.1 |
| | 64.6 | 71.1 |
| | 65.3 | 71.0 |
| | 65.0 | 71.3 |
| | 64.6 | 70.3 |
| Average | 64.8 | 71.0 |
| Stdev | 0.40 | 0.34 |
| COV (%) | 0.62 | 0.48 |

Notes: sludge centrifugation at 8000 × g, 10 min.; room temperature 22 $^0$C.

Aliquots of 90 mL mixed liquor were placed into two centrifugation vials (~ 45 mL each), and

these were centrifuged at 8,000 (× g) for 10 minutes. The resulting supernatants were then

filtered through 0.45 μm filter papers (Ø25 mm) with a syringe. If a 100 mL beaker (diameter 50

mm) was used, at least 40−45 mL filtrate (from two vials) was needed to ensure the platinum

ring of the tensiometer could reach the liquid. This normally required 3−4 filter papers. The

manual mentioned that the minimum diameter of the container should be at least 45 mm. With

this 100-mL beaker, the ring had the tendency to be pulled to the wall of the beaker which

resulted in an faulty measurement. Alternatively, a 150-mL beaker (diameter 60 mm) could have been used, but this required about 80 mL filtrate, which in turn needed 6−7 filter papers. With this option, the chance of error could be reduced, but more time and filter papers were required. At the end of each set of five measurements, the platinum ring was cleaned by heating to red hot in a bunsen flame. The sample vessel used was washed in tap water, followed by chloroform, then tap water again, and finally washed with distilled water before introducing the next sample (Goddard and Forster, 1986).

**Hydrophobicity Measurement.** Based on the literature and after several attempts, a method was developed from that of Rosenberg et al. (1980). A PUM buffer solution was made by dissolving 22.2 g of $K_2HPO_4$, 7.26 g of $KH_2PO_4$, 1.8 g of urea, 0.2 g of $MgSO_4 .7H_2O$ in 1 L distilled water. The PUM solution was used to wash mixed liquor samples twice and also to dilute the samples before hydrophobicity measurement. Due to its high ionic strength, the PUM solution helped to minimize electrostatic effects and to accentuate the hydrophobic interactions (Rosenberg, 2006). It was also important to use clean, acid-washed glassware and fresh (non-oxidized) hexadecane.

In the present study, 10 mL PUM solution was added to 5 mL of mixed liquor in a 50 mL conical vial. After brief mixing by hand, the vial was centrifuged at $3,000 \times g$ for 5 minutes. After centrifugation, 10 mL of supernatant was discarded carefully using a pipette, and 10 mL of the PUM buffer solution was added. An attempt to discard all the supernatant likely resulted in some suspended solids loss, leading to wider variations of initial absorbance of samples with reduced reproducibility. The suspension was then re-suspended by vortex for 5−10 seconds and centrifuged at $3,000 \times g$ for another 5 minutes. Again, 10 mL of supernatant was discarded

leaving only 5 mL of pellet in the vial. Then 25 mL PUM solution was added to the vial and the

pellet was re-suspended by vortex for 5−10 seconds again. An aliquot of 5 mL of the mixture

was withdrawn by pipette and put into a10-mL test tube, and the initial absorbance ($ABS_{initial}$)

was measured at 400 nm using a HACH Spectrophotometer DR 2800. The TSS for initial

measurement was about 1/6 of the original concentration, and the initial absorbance normally

ranged from 1.3−1.5 at 400 nm. The rest of the mixture was transferred into a separatory funnel

with 1 mL of n-hexadecane, shaken for 2 minutes, and set aside for 15 minutes to allow for

settling. Different quantities of n-hexadecane were assessed and 1.0 mL was found to be

sufficient for our samples (Figure 3.3). After settling, an aliquot of 5 mL of the bottom, aqueous

layer was then transferred to a 10-mL test tube, and the final absorbance ($ABS_{final}$) was

measured. The relative hydrophobicity was expressed using Equation (3.1):

$$\text{relative hydrophobicity} = 1- (ABS_{final}/ABS_{initial}) \tag{3.1}$$
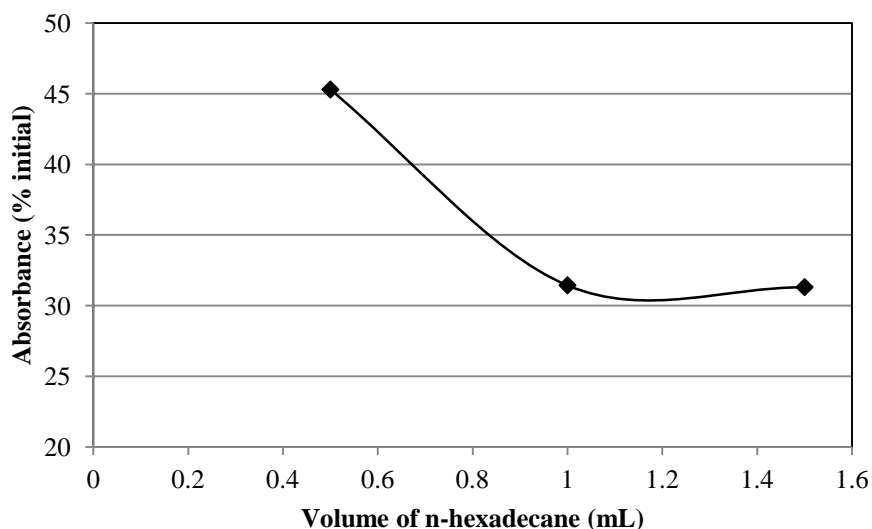


**Figure 3.3 Absorbance as a function of volume of n-hexadecane.**

**Measurement of Foaming Potential.** In the present study, both the aeration and the Alka-Seltzer methods were used. In the aeration method, compressed $N_2$ gas replaced the air because our samples were anoxic zone mixed liquor, and using $N_2$ gas resembled the situation in reality. Several attempts were made on different samples with different sample sizes (150 to 500 mL) and $N_2$ flow rates (0.1 to 1 L/min). A stone ball diffuser, with averaged pore size of 60 µm, was also tried with a 1-L Ø60mm cylinder. Hug's rating scales were used (Hug, 2006). However, with a strongly foaming sample, only sample sizes larger than 450−500 mL and 0.1−0.2 L/min gas flow rate generated a foaming rating of 6 and stability of 3. At a smaller sample size and higher flow rate, there was no stable foam layer produced on the surface (foam was broken by the bubbles), but only films were observed covering the whole cross-section of the cylinder continuously rising from the liquid. Since the results from the $N_2$ bubbling method were very subjective, the Alka-Seltzer test was used as the preferred method in this study. Figure 3.4 shows the apparatus for the Alka-Seltzer test. Foaming potential was evaluated by the relative volume of foam produced (Hug, 2006), as shown in Equation (3.2):

$$\text{Vrel} = V_{foam} / \text{ original sample size (250 mL)} \qquad (3.2)$$

where Vrel = relative foaming potential, unitless

$V_{foam}$ = foam volume measured at the end of the Alka-Seltzer test, mL

**Figure 3.4 Apparatus used for foaming potential with Alka-Seltzer tablet (stainless steel cages were used to hold the tablets)**

**Statistical Methods.** Normal probability plots of effects, main effects plots, and interaction plots were obtained using statistical software Minitab to determine significant factors and possible interactions. Paired t-tests were conducted to determine if two naturally paired samples were significantly different at a 95 % confidence level. The paired t-test requires that the differences between two sets of data follow a normal distribution (Manly, 2009), which can be checked by the Anderson-Darling test. These samples included TP/TSS and TKN/TSS ratios between anoxic zone foam and either the underlying anoxic zone ML or the anaerobic zone ML, as well as foam generation rates between SRT = 60 and 25 days. Two-sample t-tests were used in the exploratory foaming study to determine whether the differences in surface tension, hydrophobicity, and

foaming potential were significant between samples collected on a dry day and a wet day. Two-sample t-tests require that both sets of data follow a normal distribution.

## 3.3    Results and Discussion

### 3.3.1        Characteristics of Foam

Since foam was considered to be a potential source of phosphorus for recovery, it was characterized through all the experimental runs at three different settings of SRT.

#### 3.3.1.1    TP Concentrations

Foam was considered to be a good resource in terms of phosphorus recovery because it has higher phosphorus concentrations than mixed liquor. Therefore, TP is one of the most important characteristics of foam. Figure 3.5 shows that the average TP concentrations and standard deviations were $1{,}060 \pm 176$, $1{,}324 \pm 85$, and $1{,}375 \pm 183$ mg/L at SRT = 25, 40, and 60 days, respectively. It is clear that TP concentrations increased as SRT increased from 25 to 40 days, but stayed relatively constant from 40 to 60 days. In all cases, foam exhibited significantly higher volumetric TP concentrations than aerobic ML, as shown in Figure 3.5. Specific TP concentrations in foam, as represented by TP/TSS ratios (mg/mg), were evaluated by from mean values and 95 % confidence intervals, since the foam TP/TSS ratios followed a normal distribution. Table 3.4 shows that the average specific TP concentrations of foam were significantly higher at SRTs = 40 and 60 days than at 25 days.

It is clear that operation at SRT = 60 days significantly increased the prevailing TP concentrations above those at SRT = 25 days (volumetric and specific concentrations in aerobic

zone ML and foam). When comparing foam with aerobic zone ML generated at SRT = 60 days, the foam (mainly from anoxic zone) showed much higher volumetric TP concentration (1,375 vs 676 mg/L), but a slightly lower specific concentration TP/TSS (0.044 vs 0.046). This indicates that foam may be the best source for P recovery. The average density of the foam was 0.926 mg/L, and the 95 % confidence interval (CI) was (0.911, 0.940).
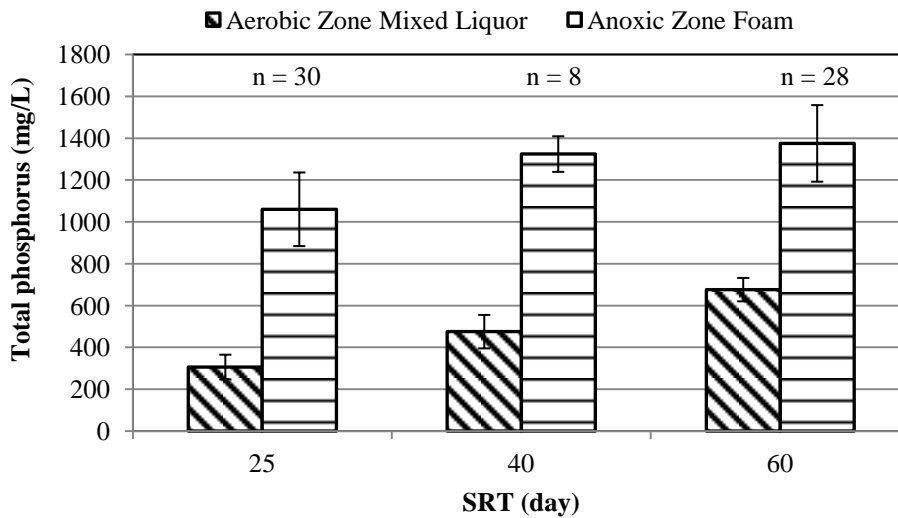


**Figure 3.5 TP concentrations in aerobic zone mixed liquor and anoxic zone foam at different SRTs (error bars represent one standard deviation). n is sample size.**

**Table 3.4 Specific TP concentration of foam (TP/TSS, mg/mg) at three SRTs**

| SRT (day) | Mean | 95% CI | Sample size |
|---|---|---|---|
| 25 | 0.033 | (0.031, 0.034) | 28 |
| 40 | 0.038 | (0.035, 0.041) | 8 |
| 60 | 0.044 | (0.041, 0.047) | 27 |

Notes: CI — confidence interval.

### 3.3.1.2    TSS, VSS, TKN, and TCOD Concentrations

If foam is to be removed for phosphorus recovery, it would create a second waste stream, in addition to conventional wasting of aerobic zone MLSS. Therefore, it is important to measure the TSS of foam for use in SRT control. Other parameters also need to be analyzed, for example, VSS for calculating the observed sludge yield, and TP and TKN for mass balance calculations (see Chapter 2). It was advantageous to find correlations between these parameters in foam and those of anoxic zone ML, because the majority of the foam was formed in the anoxic zone and anoxic ML was routinely analyzed on a scanning day (i.e., two to three times per week). To find potential correlations, TSS, VSS, TP, TKN, and TCOD concentrations of foam were analyzed from time to time during operation with SRTs from 25 to 60 days. Due to the different TSS concentrations in foam and anoxic zone ML, the parameters VSS, TP, TKN, and TCOD needed to be normalized to their respective TSS before they could be reasonably compared. In addition, efforts were made to find a possible correlation between the TSS concentration of foam and its wet mass. Foam was removed from the surfaces of both anoxic and anaerobic zones and weighed in a wet form every day. Therefore, by using the wet mass and the correlation, it was quicker and easier to estimate the TSS concentration of foam than to measure it directly according to the standard method.

Figure 3.6 shows that when foam mass was ≥ 7 kg/d, the TSS had an average value of 38 g/ kg foam (standard deviation ± 3 g/ kg). Under 7 kg/d, TSS varied greatly with an average of 33 g/ kg foam (standard deviation ± 4 g/ kg). When there was more foam in the reactor, the foam layer became thicker. Consequently, the upper part was exposed to the air and became relatively dry, resulting in a higher average TSS concentration.
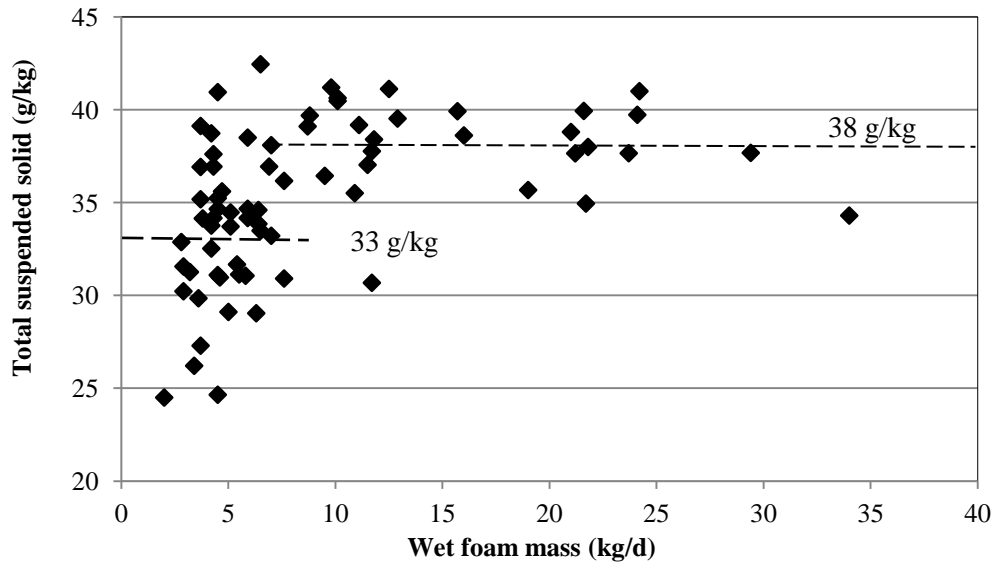
**Figure 3.6 Correlation between foam TSS and its wet mass (foam weighed in an original wet state).**

Figure 3.7 shows the normalized VSS correlations between foam and anoxic zone MLSS at different SRTs. It is clear that foam exhibited higher VSS/TSS ratios than anoxic zone MLSS especially for the two higher SRTs 40 and 60 days. The higher values suggest that more volatile organic matter was present in foam. Wentzel and Ekama (1997) reported that the VSS/TSS ratio of PAOs is much lower than that of ordinary heterotrophs (0.46 vs 0.75 to 0.85) because of the higher inorganic content of PAOs; therefore the higher the PAO fraction of the mixed liquor is, the lower is the VSS/TSS ratio of the mixed liquor. The average VSS/TSS ratios of anoxic zone foam and anoxic ML were 0.84 vs 0.83, 0.81 vs 0.79, and 0.85 vs 0.79 for SRT = 25, 40, and 60 days, respectively (Chapter 2, Table 2.6). The significantly lower VSS/TSS and higher TP/TSS (see next paragraph) ratios in anoxic zone ML at SRT = 60 days, than in anoxic zone foam, suggest that PAOs tend to stay in the anoxic zone ML.
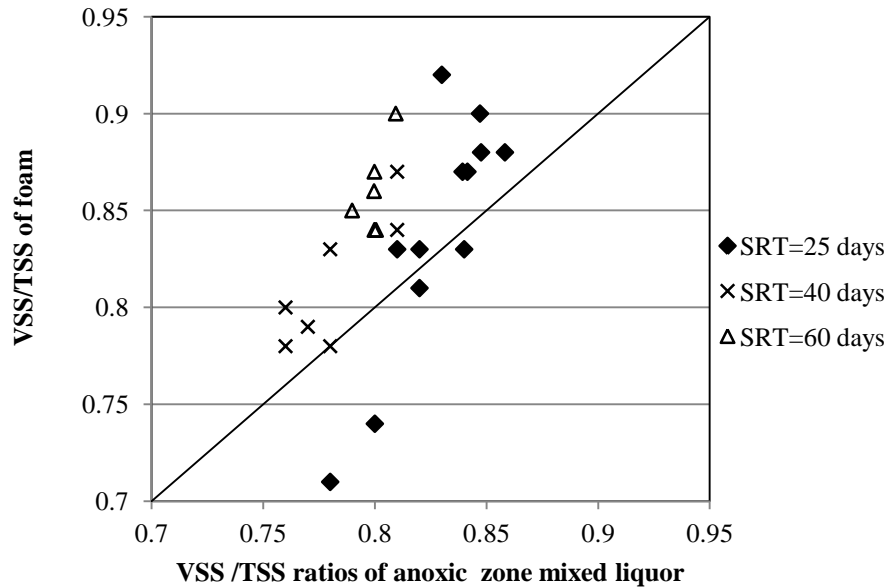
**Figure 3.7 Correlation of VSS/TSS between foam and anoxic zone ML.**

Correlations of TP/TSS between foam and anoxic zone ML are given in Figure 3.8. Visual

observation suggests that the TP/TSS ratios of both foam and anoxic zone ML increased

significantly, as SRT was increased from 25 to 60 days. Between 25 and 40 days, only the

difference in foam TP/TSS ratio was significant, as confirmed in Section 3.3.1.1. The ratios of

anoxic zone foam were generally lower than the ratios of anoxic zone MLSS at 25 and 60 days.

Statistical paired t-tests at 95 % confidence level demonstrated that differences of mean TP/TSS

between anoxic zone foam and anoxic ML were significant for SRT = 25 and 60 days (p = 0.000

and 0.002, respectively, Appendix B.2), but a significant difference could not be concluded for

SRT = 40 days (p = 0.131). A paired t-test requires the assumption that the paired differences are

normally distributed (Manly, 2009), and this was confirmed by the Anderson-Darling normal test

(see Appendix B for an example). These conclusions do not completely agree with that reported

by Hall et al. (2011), which did not indicate a significant difference in TP/TSS between anoxic

zone foam and the underlying ML at lower SRTs (15−20 days). The discrepancy might be due to the wider range of operating conditions used here (i.e., SRTs = 25−60 days).
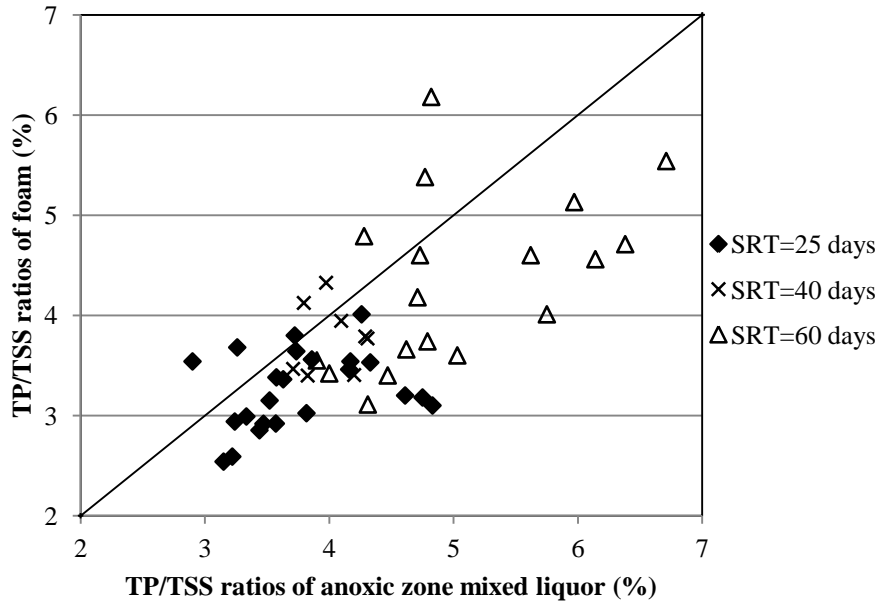


**Figure 3.8 Correlation of TP/TSS between foam and anoxic zone ML.**

The differences in TP/TSS ratio suggest that foaming in the anoxic zone is a selective process with some random nature. In other words, not all anoxic ML is equally floated to the surface to form foam, and the opportunity at least depends on the size and surface properties of particles, and the chance of them colliding with gas bubbles (where denitrification occurred). This "selective process" conclusion is also evidenced by the difference in VSS/TSS ratios discussed above, and becomes even clearer at SRT = 60 days. Further examination of the data could not conclude that significant difference existed between the means of TP/TSS ratios of anoxic zone foam and anaerobic zone ML at SRT = 60 days (p = 0.073, Appendix B.2). Consequently, the TP/TSS ratios of anaerobic zone ML were used to estimate those missing TP data of foam for

phosphorus balance calculations in Chapter 2. A comparison of the TP/TSS ratios of anaerobic, anoxic, and aerobic MLSS is given in Appendix A (Figures A10 and A11).

Figures 3.9 and 3.10 show correlations of TKN/TSS and TCOD/TSS ratios between foam and anoxic zone ML. It appears that TKN/TSS ratios of foam are comparable to the ratios of anoxic zone ML at SRT = 25 and 40 days (p = 0.808 and 0.196, respectively, Appendix B.2), but higher at SRT = 60 days. A paired t- test indicated that the difference was statistically significant for SRT = 60 days (p = 0.012, Appendix B.2). Further t-tests indicated that the TKN/TSS ratios of foam were also significantly higher than those of anaerobic zone ML. The TCOD/TSS ratios decreased with increasing SRT from 25 to 60 days, and did not show significant differences between foam and anoxic zone ML.
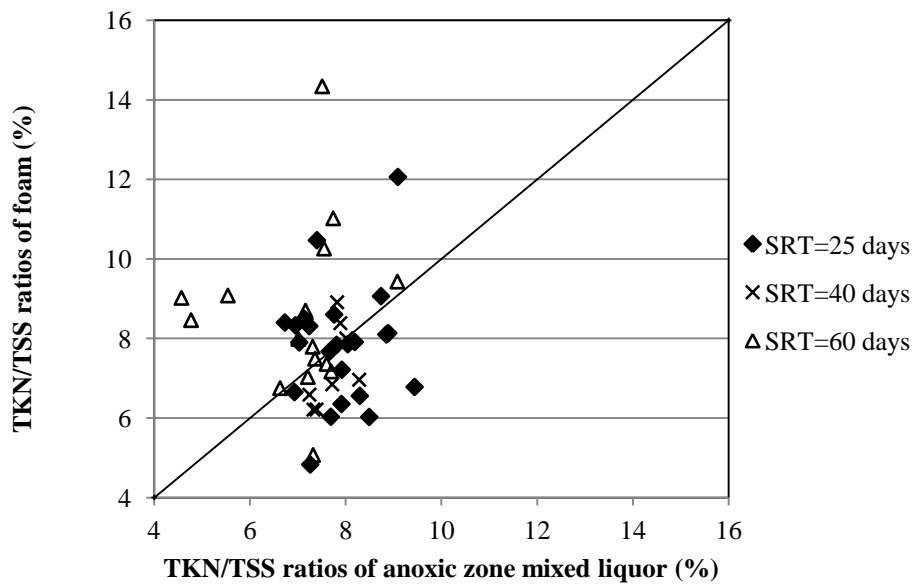


**Figure 3.9 Correlation of TKN/TSS between foam and anoxic zone ML.**
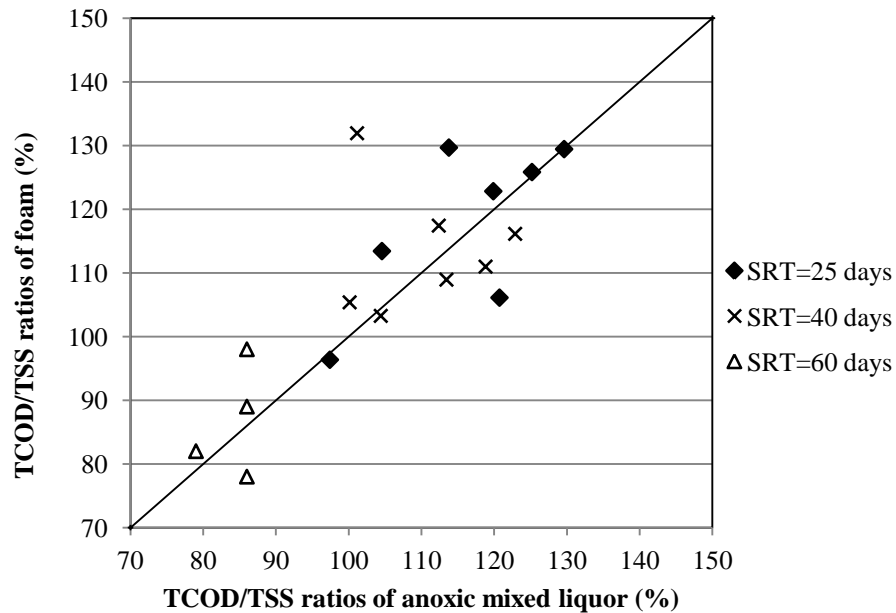
**Figure 3.10 Correlation of TCOD/TSS between foam and anoxic zone ML.**

In summary, when SRT was increased from 25 to 60 days, TP/TSS ratios increased and

TCOD/TSS ratios decreased for both foam and anoxic zone ML. At SRT = 60 days, VSS/TSS

and TKN/TSS of foam were significantly higher than the respective ratios of anoxic zone MLSS,

while TP/TSS was significantly lower and TCOD/TSS stayed the same. For estimation purposes,

the VSS/TSS ratio of foam could be estimated using the averaged values from Table 2.6. TP/TSS

values of foam at SRT = 60 days were estimated from anaerobic ML rather than from the values

of underlying anoxic zone MLSS. Foam TSS concentration was estimated to be 38 g/ kg wet

foam when the wet foam mass was ≥ 7 kg/ day, and 33 g/ kg wet foam when the wet foam mass

was < 7 kg/ day. These estimation methods were shown to be valid by the phosphorus mass

balance calculations, showing a small combined error < 5.5 %). With these established

correlations, process control (e.g., SRT) and assessment (e.g., sludge yield, P and N balances)

can be achieved with minimized analytical monitoring of the foam. However, the correlations

were specific to the conditions of the experiments. The characteristics of the foam may change with other operating conditions.

### 3.3.1.3 Concentrations of Soluble Constituents

To better understand the characteristics of foam, soluble constituents of the anoxic zone foam were also analyzed and compared side-by-side to those of the underlying anoxic zone mixed liquor. This work was conducted during the factorial experiments (Table 3.2), and the results are plotted in Figures 3.11−3.13 for $NH_4$-N, $NO_X$-N, and $PO_4$-P. Detailed data are given in Appendix A, Table A3. In general, foam samples exhibited higher $NO_X$-N concentrations and lower $NH_4$-N concentrations than mixed liquor samples. The lower $NH_4$-N concentrations in foam might be attributed to filaments like *M. parvicella*. The presence of *M. parvicella* in the UBC pilot plant was confirmed by a few studies (Hall et al., 2010; Lawson et al., 2015). After the foam was separated from mixed liquor, the *M. parvicella* in foam could have used $NH_4$-N as a preferential nitrogen source for growth (Rossetti et al., 2005; Tsai et al., 2003). Without replenishing from the anaerobic reactor, $NH_4$-N could have been largely depleted in foam, resulting in lower concentrations relative to those of the underlying anoxic ML.

While nitrates in the anoxic ML were constantly denitrified to $N_2$ gas, denitrification in foam might be limited after the foam was floated to the liquid surface and exposed to air. This difference could have resulted in higher $NO_X$-N concentrations in foam than in mixed liquor. Although *M. parvicella* in foam also has the denitrifying ability to reduce nitrate to nitrite (Rossetti et al., 2005; Casey et al., 1992), this would not change the $NO_X$-N concentration because both nitrate and nitrite were measured together as $NO_X$-N. Figures 3.11 and 3.12 show

that the differences in $NH_4$-N and $NO_X$-N concentrations between anoxic zone foam and mixed

liquor were particularly obvious in experiments 1 and 3. Examining the experimental conditions

showed that these two experiments had one thing in common, i.e., they both used the high level

aerobic recycle ratio 1 (Table 3.2). It appeared that the high aerobic recycle ratio was related to

the significant differences in $NH_4$-N and $NO_X$-N concentrations between anoxic zone foam and

mixed liquor.

The $PO_4$-P concentrations (Figure 3.13) in foam show considerable variation, and the

polyphosphates in foam may have released $PO_4$-P anaerobically during the mixing and

centrifugation processes, because centrifuging foam required a much longer time than

centrifuging mixed liquor (30 vs. 5 minutes). Or the $PO_4$-P release may have occurred even

before the foam was taken out from the anoxic zone, depending on their residence time and

VFAs available.
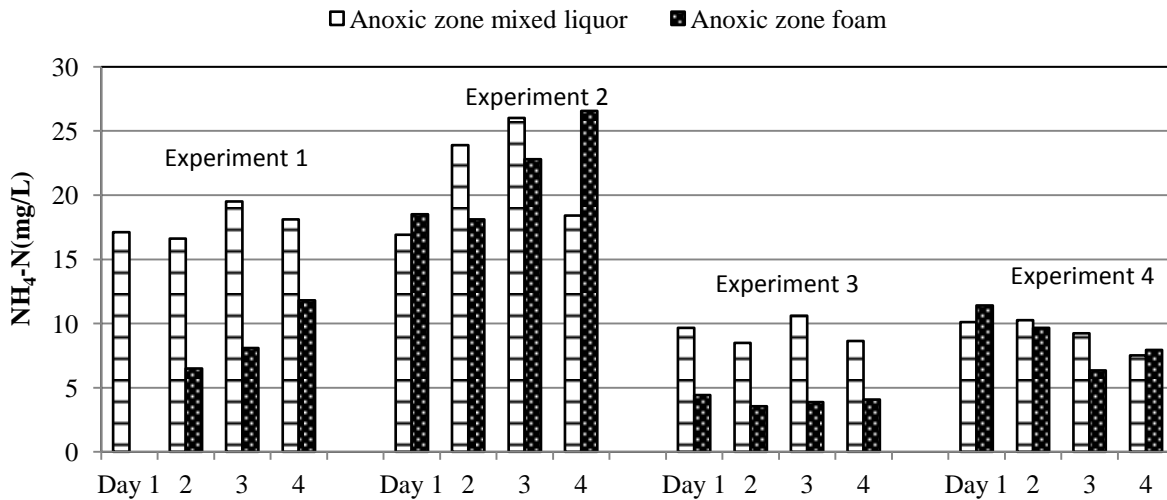


**Figure 3.11 Comparison of $NH_4$-N concentrations in anoxic zone foam and ML. All four experiments were the factorial experiments with conditions given in Table 3.2.**

103
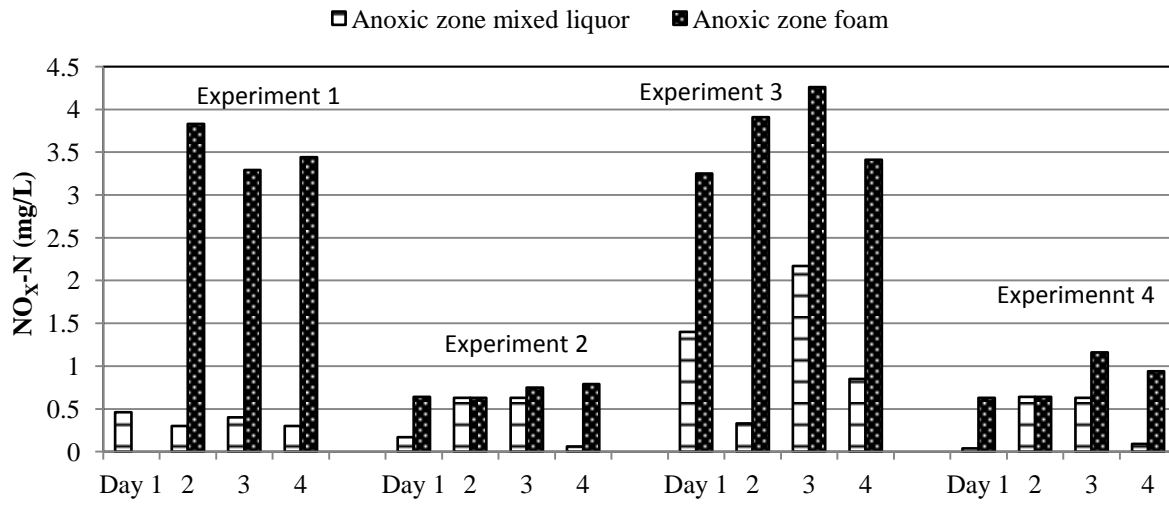
**Figure 3.12 Comparison of NO$_x$-N concentrations in anoxic foam and ML. All four experiments were the factorial experiments with conditions given in Table 3.2.**
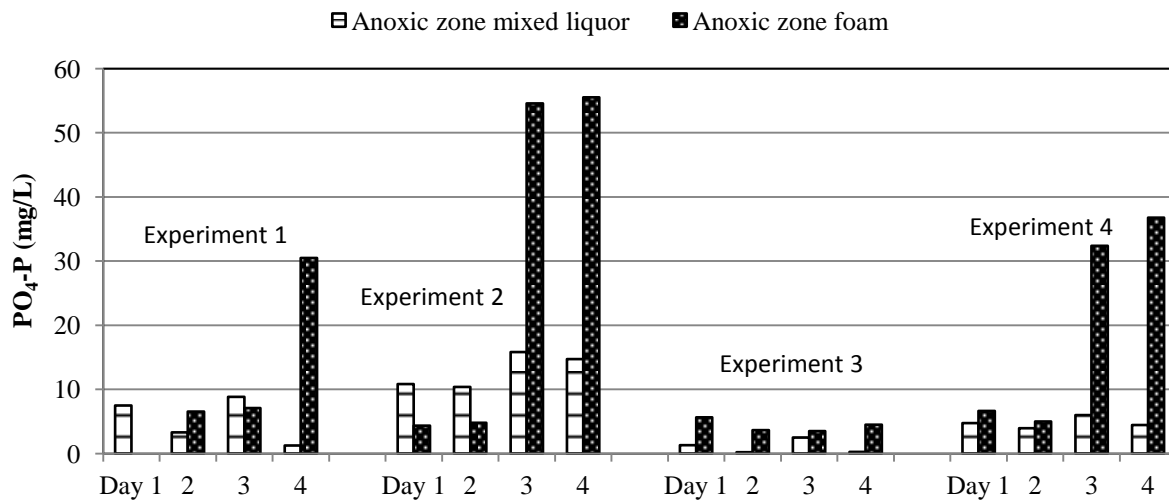


**Figure 3.13 Comparison of PO$_4$-P concentrations in anoxic foam and ML. All four experiments were the factorial experiments with conditions given in Table 3.2.**

### 3.3.2 Impacts of SRT, DO, and ARR on Foam Generation

To determine whether three controllable, operational parameters—SRT, DO, and aerobic recycle ratio (ARR)—could significantly influence foam generation, four factorial experiments were conducted. Each experiment was subjected to a 4−day sampling, and statistical analysis was conducted using foam generation (kg/day) as a response. Foam generation was measured by manually removing all the foam from both the anoxic and anaerobic zones, placing it in a tared bucket and then weighing the bucket on a scale (Section 3.2). For each experiment, one median value of the wet foam mass produced was calculated. This resulted in foam generation rates of 3.2, 3.4, 4.7 and 7.9 kg/day for Experiments 1, 2, 3, and 4, respectively (Table 3.5). Fortunately, the temperature did not change significantly during the sampling periods, ranging from 15.7 to 20.0 $^0$C. Therefore, the temperature effects were minimal.

**Table 3.5 Foam generation from factorial experiments.**

| Experiment | SRT (days) | DO (mg/L) | Aerobic recycle ratio (ARR) | Foam generated (kg/ day), median (4 measurements) |
|---|---|---|---|---|
| 1 | 25 | 1 | 1 | 3.2 (3.4, 2.9, 2.9, 3.7) |
| 2 | 25 | 2 | 0.75 | 3.4 (4.5, 3.2, 2.8, 3.6) |
| 3 | 40 | 2 | 1 | 4.7 (4.6, 4.7, 4.5, 5.1) |
| 4 | 40 | 1 | 0.75 | 7.9 (10.1, 8.7, 6.4, 7.0) |

A Pareto chart of the effects is presented in Figure 3.14. This chart assists in the determination of the magnitude and the importance of an effect, for both main effects and their interactions, which can also be accomplished by analysis of variance (ANOVA). Compared to ANOVA, the Pareto

chart of the effects demonstrates the results in a clearer and more understandable way, by distinguishing the vital few from the trivial many. In addition, in the current study all four experiments were conducted without experimental replication. Therefore, ANOVA could not calculate a p-value for hypothesis test due to lack of the error term (degree of freedom was zero). Instead, Lenth's method was used to estimate a pseudo-standard error (PSE) (Lenth, 1989). From the PSE, a reference line was determined at the effect of 29.54. Figure 3.14 shows that no any effect reached the reference line, indicating that it was not possible to conclude that any of these three factors had a statistically significant effect on foam generation within their ranges studied.
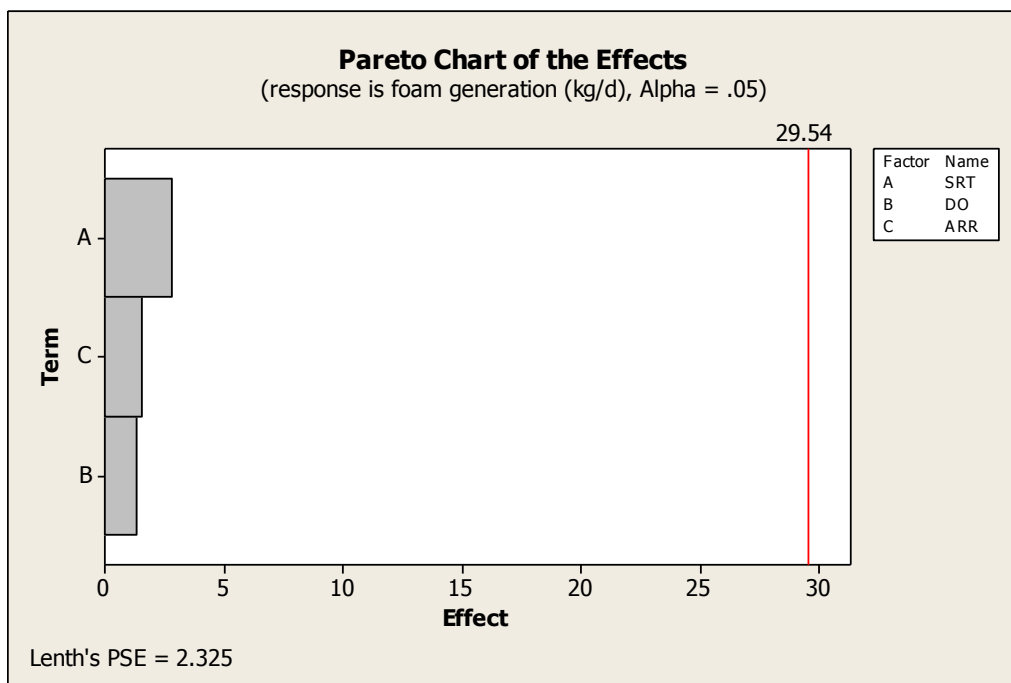


**Figure 3.14 Pareto chart of the effects to determine significant factors (generated by Minitab computer program). All effects were presented with their absolute values.**

Despite their non-significant effects, Figure 3.15 demonstrates that SRT has a positive relationship to foam generation, meaning that a longer SRT resulted in a higher mean generation

rate of foam. For example, Figure 3.15 shows that at the higher level SRT (represented by "1"), the mean generation rate of foam was about 6.3 kg/d. At the low level SRT (represented by "-1"), the mean generation rate was decreased to about 3.2 kg/d. Both DO and ARR are negatively related to foam generation. Interactions were determined between any two of these three factors, but because all the effects of these factors were not significant, their interactions were also deemed insignificant.
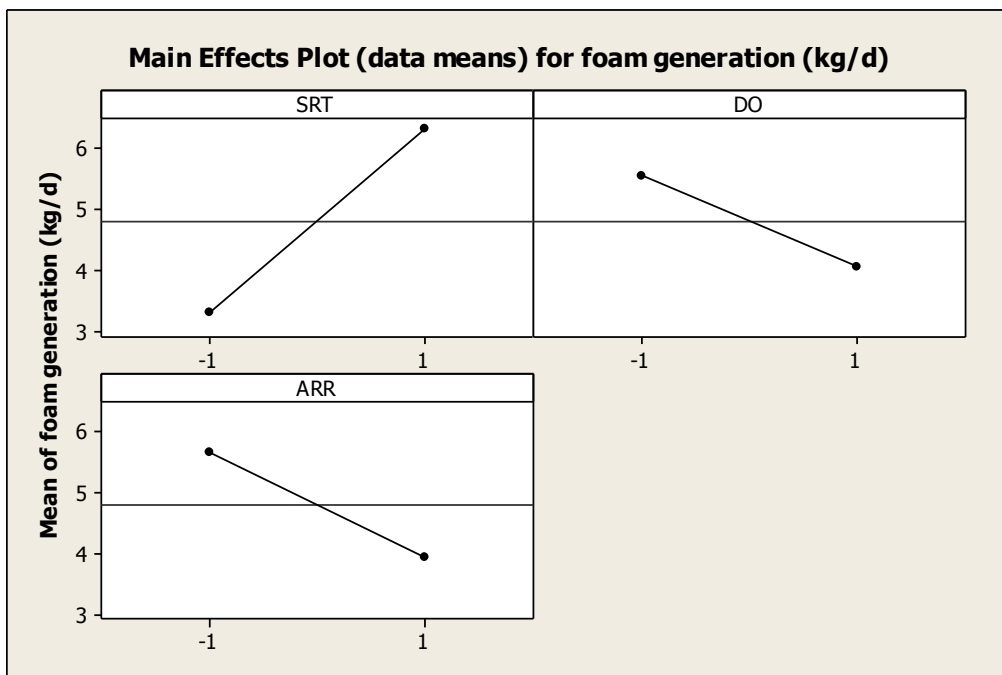


**Figure 3.15 Main effect plot. "-1" and "1" on the abscissa represent low and high levels of each factor, respectively. The vertical axis represents mean values of foam generation rate.**

The results obtained from the factorial experiments were not surprising. Hug et al. (2005) concluded, after a two-year monitoring program, that neither filamentous organisms nor any plant operating condition could fully explain the dynamics of the scumming/foaming that was

observed. The positive effect of SRT might be attributed to the higher MLSS concentrations at the high level SRT. The negative effect of DO was probably related to growth of *M. parvicella*. Rossetti et al. (2005) reported that low DO concentration favors growth of *M. parvicella,* a major type of filamentous microorganism that is involved in foaming events. Its presence in the UBC pilot plant was also confirmed by a few previous studies (Hall et al., 2010; Lawson et al., 2015). Since DO concentrations were controlled in the aerobic zone, the impact of DO on the anoxic zone foaming was not only dependent on the DO concentration in the aerobic zone but also the ARR. With a fixed DO concentration in the aerobic zone, the higher ARR carried more DO to the anoxic zone. This may explain the negative impact of ARR on foaming in Figure 3.14.

In summary, based on the fractional factorial experiments, we could not conclude that any of the three examined variables was a significant factor on anoxic zone foaming within their examined ranges. However, SRT exhibited a positive relationship to foam generation, and both aerobic zone DO and aerobic recycle ratio were negatively related to foam generation. In other words, a higher SRT, a low level aerobic zone DO setpoint, and a low level aerobic recycle ratio favored foam generation. The last two conditions also helped to achieve stable phosphorus removal, as discussed in Section 2.3.2.1 (Chapter 2).

### 3.3.3    Foaming Study

### 3.3.3.1    Correlation between UBC Sewage Flow and Precipitation

Since foam is a potential resource for phosphorus recovery, it is important to know if the MEBPR process can generate a sufficient amount of foam for phosphorus recovery. Figure 3.16 shows that the foam generation rate during the entire experimental period ranged from 1 to 15

kg/d for SRT = 25 days and 2 to 42 kg/d for SRT = 40 and 60 days. These data were observed

with a constant influent flow rate of 5,328 L/day (3.7 L/min.). Anderson-Darling normality tests

indicated that these data did not follow normal distributions; therefore, box plots were used to

represent the data distributions. Figure 3.17 shows that the median value at SRT = 60 days was

11.3 kg/d (2.1 kg/m$^3$ wastewater treated) based on a sample size of 176. The median values at

SRT = 25 and 40 days were 4.9 and 7.8 kg foam/ day (0.9 and 1.5 kg/m$^3$ wastewater treated),

respectively. A paired t-test confirmed that the difference was significant for SRT = 60 and 25

days (p = 0.000, Appendix B.2).
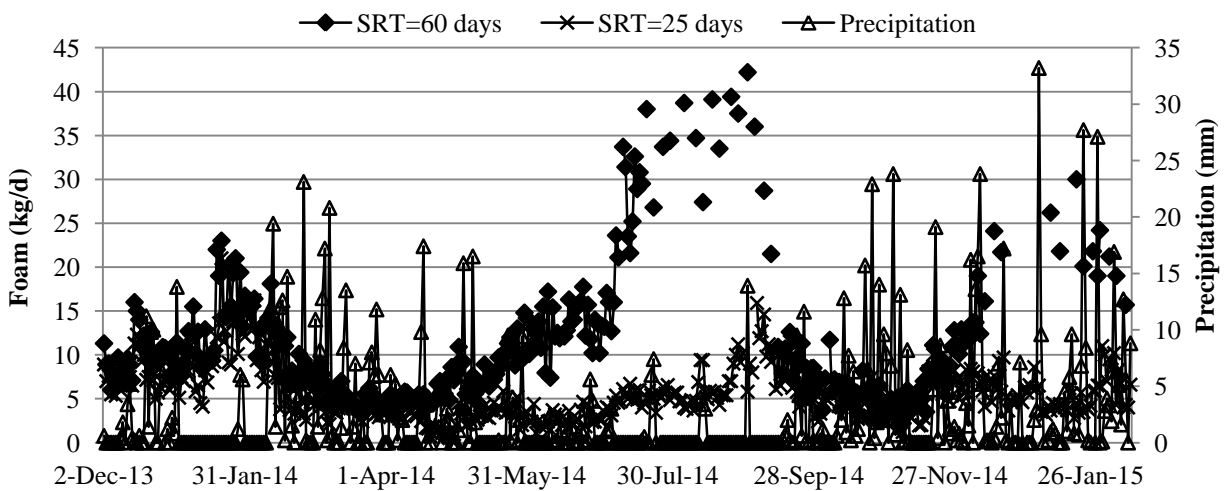


**Figure 3.16 Time series of foam generation and rain precipitation.**
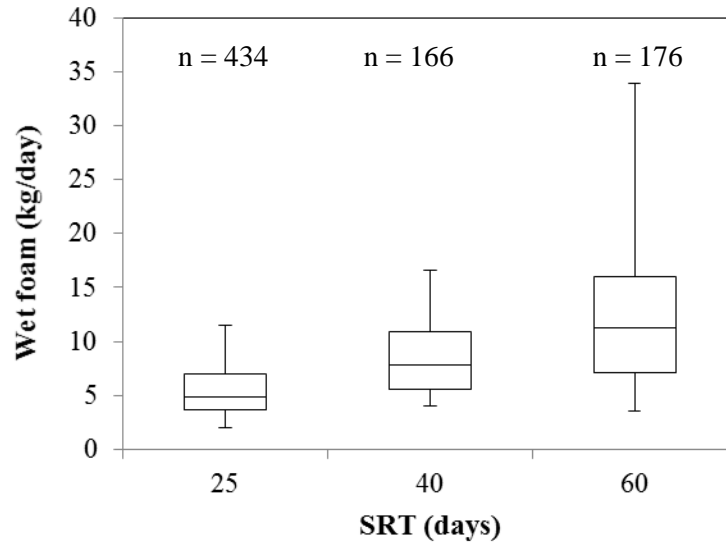
**Figure 3.17 Box plots of wet foam mass observed at SRTs = 25, 40, and 60 days. Percentiles shown: 5th, 25th, 75th, and 95th. The horizontal line inside the box represents the median. n is sample size. Results were obtained with a constant influent flow rate.**

Although, in the present study, the amount of foam wasting required was determined by SRT control (Chapter 2, Section 2.2), it is possible to estimate how much foam needs to be wasted in order to balance the TP loading associated with influent wastewater. Based on the average TP concentration of 4.5 mg/L in influent, and the influent flow of 5,328 L/d (3.7 L/min.), the daily TP loading into the MEBPR plant was about 24 g/day. Assuming the TSS of foam to be 38 g/ kg foam (Figure 3.6) and an average TP/TSS to be 4 % (Figure 3.8), 16 kg foam/day needs to be wasted at SRT = 60 days in order to balance the TP loading. This indicates that for about 25 % of the time (third quartile 16.0 kg foam/day), the MEBPR plant could generate sufficient foam when operating at an SRT = 60 days. For most periods, wasting of aerobic zone mixed liquor would still be needed as a second source for phosphorus recovery. In spite of this, phosphorus mass balance calculations confirmed that foam wasting could still be a major pathway to remove

110

phosphorus at SRT = 60 days, accounting for 74 % of the incoming phosphorus (Chapter 2, Section 2.3.2.2).

The observed foam generation rate was significantly higher at SRT = 60 than at 25 days; however, the foam generation rate appeared to be strongly influenced by rain precipitation at all three SRTs (Figure 3.16). To determine if the rain water infiltrated into the sewer from which influent was taken, correlation between rain precipitation (mm/day) and the UBC south campus sewage flow rate (wastewater source of the pilot plant) was plotted in Figure 3.18. A Pearson correlation coefficient of r = 0.529 was calculated between these two variables (sample size n = 275), suggesting that rain water infiltration into the sewer had, indeed, occurred.
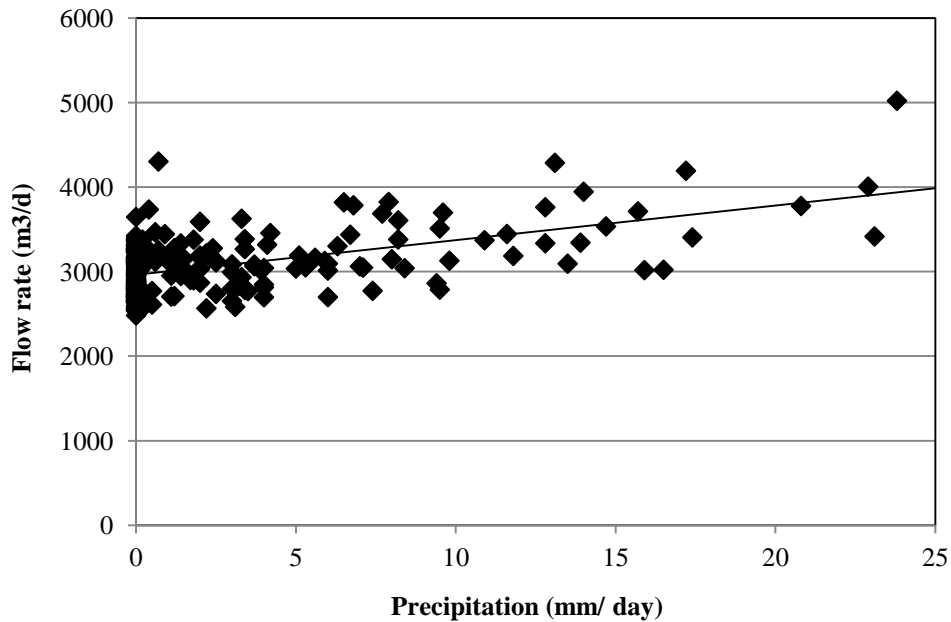


**Figure 3.18 Correlation between UBC south campus sewage flow rate and rain precipitation.**

Once rain water infiltration had been confirmed, its impacts on foaming were evaluated from two perspectives: environmental condition changes caused by the infiltration, and possible changes in the key components of the "flotation" foaming mechanism. When rain water enters into a sewer, it may lower the sewage temperature, and it may reduce the wastewater concentration due to dilution, or it may bring external chemicals (e.g., clay, de-icing salts). Wet days are also usually accompanied by high humidity. However, no significant correlations were found between foam generation rate and influent TCOD, temperature, pH (influent and anoxic zone), and humidity (Appendix A12−16). It should be pointed out that the UBC pilot plant has three raw wastewater storage tanks, each with a capacity of 9,460 L (2,500 USG) . These tanks provide some equalization which could dampen changes in these parameter values.

Although rain water infiltration was confirmed, no parameter examined seemed to correlate with foam generation rate. Therefore, work was focused on the key components involved in foaming, including surfactants, hydrophobic particles, and gas bubbles ($N_2$ production in the present study). These components were evaluated in the next three sections, together with foaming potential. Comparisons were made on a raining day and a dry day to see what may cause the foaming difference.

### 3.3.3.2    Nitrogen Gas Production

An initial explanation for periodic reduced foaming was that there may have been less intense anoxic zone nitrogen gas ($N_2$) production during raining days. Therefore, the possible production of $N_2$ by denitrification was estimated through nitrogen balances over the anoxic zone. The

experiments were conducted on two different days: a dry day with a typical foam production of 6.5 kg on September 16, 2014, and a raining day with reduced foam production (2.4 kg) on October 2, 2014 (Table 3.6). On both days, the influent and two internal re-circulation flow rates were all controlled at 3.7 L/min, and mixed liquor samples were taken from each zone for $NO_X$-N analysis at the SRT = 25 days train. The sampling interval was two hours over a total sampling period of 12 hours. Mass balance calculations were based on Figure 2.19 and Equation (2.8) in Chapter 2. The results showed that on the low foam wet day, 40.9 g $N_2$ gas was estimated to have been produced during the 12 hour period, which was greater than the estimated 31.5 g produced on the high foam dry day (Table 3.6). This excludes reduced gas production as the cause that reduces foam formation on wet days.

**Table 3.6 Summarized results from foaming study**

| Parameter | High foam dry days (September 14 & 16, 2014) | Low foam wet days (October 1 & 2, 2014) |
|---|---|---|
| $N_2$ gas production (anoxic zone) | 31.5 g/12 hr [a] | 40.9 g/12 hr |
| Surface tension of anoxic zone liquid (millinewton/ meter) | 65.8 ± 1.23 [b] grab samples, n = 6 [c] | 67.3 ± 1.19 grab samples, n = 4 |
| Relative hydrophobicity of anoxic zone ML [d] | 0.643 ± 0.029 n = 6 | 0.566 ± 0.008 n = 4 |
| Relative foam volume of anoxic zone ML, Vrel [e] | 1.36 ± 0.05 n = 7 | 1.14 ± 0.05 n = 6 |
| Sample temperature ($^0$C) | 20.3 ± 1.1 | 18.7 ± 0.3 |
| Sample pH | 7.07 ± 0.07 | 7.32 ± 0.02 |

Notes: (a) Sampling interval was 2 hrs, for a total of 12 hrs; (b) mean ± one standard deviation; (c) grab samples were taken every two hours, and each grab sample was split into 3 subsamples for measurements; (d) calculated using Equation (3.1); and (e) calculated using Equation (3.2).

### 3.3.3.3    Surface Tension

Surfactant is one of three components in the "flotation mechanism". The presence of surfactants is indicated by the reduced surface tension of the ML liquid phase, and low surface tension is essential to prevent liquid drainage from the gas bubble walls, therefore stabilizing foam (Petrovski et al., 2011). Samples for surface tension measurement were taken on a dry day (September 14, 2014) and a wet day (October 1, 2014). The foam productions on these two days were 6.1 and 3.1 kg, respectively. Table 3.6 shows that measured average surface tensions of the liquids derived from anoxic zone ML were 65.8 and 67.3 millinewton/ meter for the dry and wet days, respectively. Since these two sets of data were not naturally paired, a paired t-test was not suitable for confirming if the difference was significant. Instead, two-sample t-tests were used since both sets of data follow a normal distribution as indicated by the Anderson-Darling test (see Appendix B). Based on the two-sample t-tests, we could not conclude that the difference in surface tension between a dry and wet day was significant at a 95 % confidence level ($p = 0.092$, Appendix B.3). Consequently, surface tension was not considered to be a significant factor leading to the foaming difference.

### 3.3.3.4    Hydrophobicity and Foaming Potential

The existence of hydrophobic particles can be evaluated by assessing the hydrophobicity of ML. Hydrophobicity measurements were conducted on the same two days (one dry and one wet) on which the surface tension was assessed. Foaming potential was measured on the same two days when the samples were taken to assess nitrogen gas production. Table 3.6 compares the measured hydrophobicity and foaming potential values from both the dry day and a wet day. The

average relative hydrophobicitiy was 0.643 for the dry day and 0.566 for the wet day. A two-sample t-test confirmed that the hydrophobicity of the anoxic zone mixed liquor was significantly higher on the dry day than on the wet day ($p = 0.001$, Appendix B.3). Foaming potential was evaluated by the relative volume of foam (Vrel) produced by the Alka-Seltzer method. The measured Vrel was also significantly higher on the dry than on the wet day, based on the two-sample t-test ($p = 0.000$, Appendix B.3).

The Alka-Seltzer method is known to be influenced by temperature (and pH probably), so a few samples from the wet day were also adjusted by water bath and acid to bring these samples to the same temperature and pH as the samples from the dry day (Table 3.6). The adjusted samples did not show obvious changes in foaming potential, probably because the differences were minor. A difference in TSS concentration may also influence the foaming potential; however, since the TSS concentration was not immediately available (needs drying overnight), TSS adjustment was not made. Fortunately, the results obtained after the experiments showed that the average TSS concentrations were close, being $4,704 \pm 86$ and $4,565 \pm 45$ mg/L on the two experimental days.

Based on the experiments, it seems that decreased hydrophobicity was responsible for the reduced foam formation on raining days. The observed relationship between foaming and hydrophobicity was in agreement with findings by Khan et al. (1991). The subsequent question is "what in rain water resulted in the reduced hydrophobicity?" One possible contributor could be the bentonite clay that was excavated and flushed from construction sites into the sewer while raining. During the present study, there was considerable construction work on the UBC campus. In fact, bentonite was added successfully in a few research studies to reduce foaming through

modification of the surface chemistry of cells or biomass (Stratton et al., 2002; Kocianova et al., 1992).

### 3.3.3.5    Comments on the Modified Methods

In the present study, two methods of measuring surface tension and hydrophobicity were modified based on literature review and practical consideration. Many different methods have been reported in the literature but standard methods are not available. For example, to measure the hydrophobicity of ML, most of the methods in the literature were modified from Rosenburg et al. (1980). However, many of them were not modified correctly, as discussed by Rosenburg (2006). In some research, distilled water was mistakenly used to replace PUM solution, or fresh n-hexadecane was not used. The two methods used in the present study were modified after such lessons have been learned from the literature. They have proven to be reproducible, as the coefficients of variation (COV), calculated from the measurements of three split samples in a same grab sample, were less than 10 %, 8 %, and 2 % for hydrophobicity, foaming potential, and surface tension tests, respectively.

A foaming study was conducted to determine why rain precipitation reduced foam generation rate. Correlation between rain precipitation and UBC campus sewage flow rate suggested that rain infiltration into the south campus sewer occurred. However, no significant correlations were found between foam generation rate and several parameters that might be influenced by rain precipitation. These parameters included influent temperature and COD, pH, and air humidity. A comparison study showed that the reduced hydrophobicity of the anoxic zone mixed liquor was responsible for reduced foaming generation rate on a low-foam, wet day.

116

**3.4    Conclusions and Engineering Significance**

Foam formed from the MEBPR process represents an excellent resource for phosphorus recovery due to its high phosphorus concentration. This Chapter focused on fully characterizing foam as a resource and its formation in the MEBPR process. The following conclusions were reached.

- At all three SRTs, TP concentration was significantly higher in the anoxic zone foam than in the corresponding aerobic zone ML. The increments were about two times for SRT = 60 days and three times for 25 days. Increasing SRT from 25 to 40 days significantly increased TP concentrations in foam. No significant difference in TP concentration was observed between 40 and 60 days.

- In general, foam formed in the anoxic zone was significantly different from the underlying anoxic ML in terms of VSS/TSS, TP/TSS, and TKN/TSS at SRT = 60 days. Specifically, the VSS/TSS and TKN/TSS ratios were higher and the TP/TSS ratio was lower. This indicates that foaming is a selective process. The average foam TSS concentration was 38 or 33 g TSS/ kg wet foam when wet foam production was greater than or less than 7 kg wet foam day, respectively. The average foam VSS/TSS was found to be $0.85 \pm 0.04$.

- The concentrations of soluble components ($PO_4$-P, $NH_4$-N, NOx-N) were significantly different in the anoxic zone foam than in the underlying anoxic zone mixed liquor. The differences were believed to result from different environments in which the foam and mixed liquor resided.

- Based on fractional factorial experiments, we could not conclude that any of three controllable operating parameters was a significant factor for foaming within its

117

examined range, i.e., 25 to 40 days for SRT, 1 to 2 mg/L for DO, and 0.75 to 1.0 for aerobic recycle ratio (ARR). However, SRT exhibited a positive relationship to foam generation, while both DO and ARR were negative factors.

- Based on time series of foam generation data, a paired t-test confirmed that the foam generation rate was significantly greater at SRT = 60 days than at 25 days, with median values of 11.3 and 4.9 kg wet foam/ day (2.1 and 0.9 kg/m$^3$ wastewater treated), respectively.

- Rain precipitation strongly influenced foam generation. A correlation between rain precipitation and the UBC south campus sewage flow rate suggested that rain water likely infiltrated into the sewage, and the reduced hydrophobicity was responsible for reduced foaming potential and foam generation rate.

- Methods were modified for hydrophobicity measurement and surface tension test. Both methods were reproducible and easy to use.

Utilizing foam as a resource for phosphorus recovery represents an innovative solution to the foaming problem, which becomes more severe in a membrane bioreactor operated at a long SRT. However, foam exists as a separate phase from the mixed liquor. To incorporate the foam into the operation of an MEBPR process (e.g., to control SRT) or to utilize it for the subsequent phosphorus extraction, the foam needs to be fully characterized. This study, for the first time, established a database for the foam at three different SRTs. These data were obtained from a plant treating real sewage and therefore, should find practical uses. The correlations developed between the foam and mixed liquor (either anoxic or anaerobic zone) enable foam characteristics to be estimated from those of the mixed liquor. Such estimations can save extra analytical work

118

in WWTPs, or be useful for process modeling. The modified methods for hydrophobicity measurement and surface tension also provided reference for other researchers working in the similar areas.

# Chapter 4: Evaluation of Methods To Extract Phosphorus From Activated Sludge Mixed Liquor And Foam From An MEBPR Process

## 4.1   Introduction

Recovering phosphorus, as struvite, requires phosphorus in the form of orthophosphate ($PO_4^{3-}$), as shown in Equation (1.1) of Chapter 1. However, most of the phosphorus in the aerobic zone mixed liquor of an MEBPR process is stored by the phosphorus-accumulating organisms (PAOs) in the form of polyphosphates (poly-P) (Chapter 1, Section 1.2.1.1). Two other forms are organic phosphorus and orthophosphate. The sum of these three forms is called total phosphorus (TP). This Chapter therefore investigates the technologies to convert TP in foam and aerobic zone mixed liquor (ML) to orthophosphate.

Anaerobic P-release through microbial activity is the conventional method, and the mechanism is well understood (Chapter 1, Section 1.2.1.1).  Practically, it is used in the Phostrip process (Grady et al., 2011) and the WASSTRIP process marketed by Ostara Nutrient Recovery Technologies Inc. However, the orthophosphate extraction efficiency, i.e., the ratio of $PO_4$-P released to initial TP, has rarely been reported. Srinivas (2006) reported about 50 % release efficiency with a retention time of nearly 30 hours using anoxic zone ML from the UBC pilot plant. Monti et al. (2007) conducted batch tests to determine phosphorus release and uptake kinetics using aerobic zone ML from the UBC pilot plant, using a two-hour anaerobic P-release period. They reported that the maximum P-release rates ranged from 5 to 30 mg P/ g VSS•h and

the P/ VFA ratios were 0.5−0.6 g P/ g COD. Both of these studies utilized mixed liquor obtained from an MEBPR process operated at some typical, relatively short SRTs (20 or 12 days). In summary, anaerobic P-release is a simple technology to use, but only limited research work has been conducted on its kinetics and on how much orthophosphate can be released maximally within what time period, particularly for a sludge with high TSS and TP concentrations.

Microwave-based hydrogen peroxide advanced oxidation process (MW-$H_2O_2$ AOP) is a relatively new technology that is used for sludge disintegration. Its utilization so far is limited to bench or pilot scales. When utilized to extract $PO_4^{3-}$ from foam samples, the MW-$H_2O_2$ AOP can achieve its maximum extraction efficiency at temperatures of 160−180 ℃, $H_2O_2$ 0.5−1.0 volume %, and pH 2−3 (More et al., 2015; Lo et al., 2010). A higher TSS concentration of the foam sample and a higher extraction efficiency required harsher conditions. MW-$H_2O_2$ AOP also releases some $NH_4^+$-N (< 220 mg/L), VFAs, and large amounts of metals (More et al., 2015). One drawback of MW-$H_2O_2$ AOP is that it needs a very low pH to achieve the maximum extraction efficiency, and during subsequent struvite crystallization, the pH needs to be increased to about 7.2−7.8 (Donald Manivic, Professor at UBC, personal communication). Since anaerobic P-release can convert poly-P into $PO_4^{3-}$, and MW-$H_2O_2$ AOP (without pH lowering) can oxidize organic phosphate into $PO_4^{3-}$, it was interesting to see if a combination of these two technologies could extract the same amount of $PO_4$-P as MW-$H_2O_2$ AOP with a lowered pH. In addition, More et al. (2015) and Lo et al. (2010) only focused on treating foam with MW-$H_2O_2$ AOP. It is helpful to extend their work to mixed liquor, because when foam is not sufficiently generated, aerobic zone ML needs to be wasted for SRT control and then utilized as a resource for phosphorus recovery.

121

Anaerobic digestion is conventionally designed to remove colloidal COD attached to wasted biomass; therefore, its ability to release $PO_4^{3-}$ is not normally an important consideration. However, the reported average $PO_4$-P concentrations in the centrates from two WWTPs in Metro Vancouver (British Columbia) were between 76−149 mg/L (Chapter 1, Section 1.2.2.1), which should represent a small portion of the TP (although no such TP concentration data are available). Since microbial cells break up under anaerobic digestion, release of poly-P from the cells is also expected. Therefore, changes in digestion conditions may increase the $PO_4^{3-}$ concentrations. Using low pH anaerobic digestion at pH < 5.7, Latif et al. (2005) reported a 57 % greater $PO_4$-P concentration compared to that released at neutral pH conditions (7−7.7). In general, the ability of anaerobic digestion to extract $PO_4$-P and $NH_4$-N has not been studied systematically. Anaerobic digestion seems to be the only process that can produce large amounts of $NH_4^+$, one of the three components required for struvite crystallization. It would be interesting to see how we can improve the $PO_4^{3-}$ concentration from the same digestion process. Another attractive feature of anaerobic digestion is the production of methane, which can be recovered as energy.

The major objective of this part of the study was to evaluate these three technologies for $PO_4$-P and $NH_4$-N extraction from both foam and mixed liquor. Some combinations of these technologies were examined to see if improved extraction efficiency could be achieved without lowering pH. Settling and dewatering characteristics of such treated samples were also examined. The knowledge obtained from this study was subsequently used to propose a new system for the recovery of phosphorus as struvite.

122

## 4.2 Materials and Methods

### 4.2.1 MW-H$_2$O$_2$ AOP Treatment

MW-H$_2$O$_2$ AOP treatment was performed on aerobic zone ML, and a mixture of aerobic zone ML and foam (50 %: 50 %) taken from the MEBPR pilot plant during operation with SRT = 60 days. In this study, the same bench-scale microwave equipment (frequency 2,450 MHz, Figure 4.1a) and experimental conditions were used as described in More et al. (2015), so that the results obtained here can be compared directly with their results. Specifically, these conditions were temperature = 180 $^0$C, H$_2$O$_2$ = 0.5 volume %, holding time = 15 minutes, and pH = 3 adjusted with acid (H$_2$SO$_4$). These conditions gave reasonably high PO$_4$-P extraction but required moderate H$_2$O$_2$ addition and pH adjustment. The microwave equipment had 12 containers and each could hold up to 30 mL of sample, so the total treatment capacity in one run was 360 mL. Into each of 30 mL samples, about 0.51 mL of 30 % H$_2$O$_2$ stock solution (density 1.11 g/mL) was added.
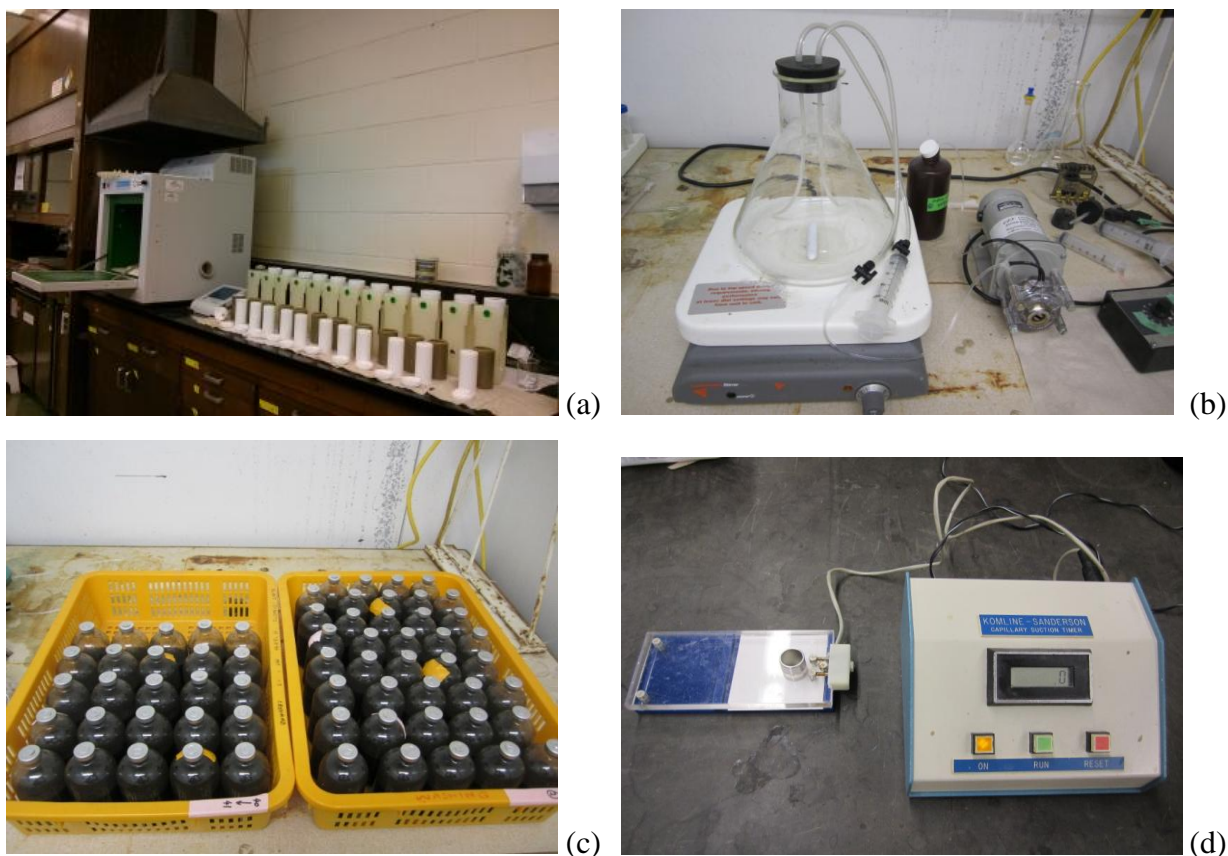
**Figure 4.1 (a) MW-H$_2$O$_2$ AOP apparatus; (b) anaerobic P-release batch test apparatus; (c) anaerobic digestion serum bottles; and (d) CST instrument.**

### 4.2.2    Anaerobic P-release

Anaerobic P-release was conducted by putting 2.8 L aerobic zone ML in a 3 L Erlenmeyer flask as a reactor (Figure 4.1b). N$_2$ gas was sparged for 15 minutes to remove DO, then the flask was sealed tightly and left (at room temperature) for 2−3 hours with gentle mixing to remove any NO$_X$ residual. Before adding sodium acetate trihydrate (CH$_3$COONa·3H$_2$O), samples of reactor contents were taken to measure initial NO$_X$-N, PO$_4$-P, and VFA concentrations. Acetate stock solution was added using three different feed modes. As shown in Table 4.1, batch tests 1 and 2 (BT1 and BT2) used a continuous feed. Using BT1 as an example, the acetate stock solution was

made by dissolving 10.194 grams of sodium acetate trihydrate in 400 mL distilled water. At the

end of the test, the remaining volume of the stock solution was measured, and the stock solution

added was then calculated to be 308 mL. Based on the experimental time, a flow rate of stock

solution was calculated to be 1.14 mL/min. The actual concentration of the stock solution was

analyzed to be 11,804 mg/L acetate, so that the quantity of acetate added could be calculated

based on the volume of stock used. BT3 utilized a semi-continuous feed mode. First, 6 grams of

sodium acetate trihydrate was dissolved in 30 mL distilled water, then 25 mL of this stock

solution was added into the reactor at four different times, i.e., 6 mL at the beginning, 6 mL at 30

minutes, 9 mL at 60 minutes, and 4 mL at 150 minutes. The remaining 5 mL was used for

analyzing the concentration of the stock solution. For BT4, all 25 mL of the stock solution was

added at the beginning.

**Table 4.1 Addition of acetate for anaerobic P-release**

| Feed mode | Continuous | | Semi-continuous | One time |
|---|---|---|---|---|
| Parameter | BT1 [a] | BT2 | BT3 | BT4 |
| Sample size (L) | 2.8 | 2.8 | 2.8 | 2.8 |
| Sodium acetate trihydrate (g) | 10.194 | 7.646 | 6 | 6 |
| /  H$_2$O (mL) | / 400 | / 400 | / 30 | / 30 |
| Measured stock acetate conc. (mg/L) | 11,804 | 8,919 | 77,306 | 93,381 |
| Stock added (mL) | 308 | 371 | 6(0) [b]; 6(30); 9(60); 4(150) | 25 one time |
| Flow rate (mL/min) | 1.14 [c] | 1.37 | | |

Notes: (a) BT—batch test; (b) 6 mL stock solution added at 0 min; (c) calculated by stock

solution added divided by experimental time.

125

Once acetate had been added to the reactor, 25 mL samples were taken by a syringe every 10 minutes over the first 30 minutes, then every 15 minutes for the next one hour, and every 30 minutes thereafter until at least 180 minutes. The initial frequent sampling was used to determine maximum specific $PO_4$-P release rate, which was calculated for the first 45 minutes of the experiment using linear regression analysis, in a similar manner to that used by Monti et al. (2007). A few more prolonged sampling times were sometimes used at, for example, 510 minutes (8.5 hours) and 1,290 minutes (21.5 hours) to determine the maximum $PO_4$-P concentration that might be achieved. Once taken, samples were immediately centrifuged at 8,000 RCF for 5 minutes, followed by glass fiber (Ø2.5cm, 1.2 µm) and 0.45 µm membrane filtration. The filtrate was then split into different vials, preserved by 5 % $H_3PO_4$ for VFA and phenol mercuric acetate for $PO_4$-P samples. Due to the small calibration range (0−25 mg/L), the $PO_4$-P samples needed to be diluted to 1/25 before analysis.

### 4.2.3 Anaerobic Digestion

Anaerobic digestion was assessed using 150 mL serum bottles (Figure 4.1c). A total of 64 bottles was used, which comprised of eight groups with each group having eight replicates (Table 4.2). These experiments were designed to examine the digestion effects on raw anoxic zone foam and aerobic zone ML from the MEBPR operating at an SRT = 60 days, as well as the foam and ML with some different pre-treatments. Due to the large number of bottles involved, the digestion was conducted in a temperature-controlled room at 35 $^0$C, and all bottles were manually shaken two times each day, in the morning and afternoon. For foam samples (Groups 2 and 4), an aliquot of 5 mL was used as feed that was mixed with 95 mL anaerobic digestion inoculum

obtained from the Lulu Island WWTP, Richmond, BC. Such a sample size gave an organic

loading of approximately 1.7 g-VSS/L (Yi, 2012). Accordingly, for assays with ML (Groups 1,

3, and 5), 12 mL samples were used. In addition, 8 mL of a mixture of foam and ML (50 % : 50

%, volume) was used in Group 6. Groups 7 and 8 used the same inoculum but in different

amounts (95 and 88 mL), as the controls for foam and ML samples, respectively. Each bottle was

first purged with $N_2$ gas to remove oxygen then sealed tightly with a rubber septum using a

crimper.

**Table 4.2 Groups and materials for anaerobic digestion**

| Group 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| ML | Foam | ML + P-rel. | Foam + MW | ML + P-rel. + MW | Foam + ML | Inoculum 1 | Inoculum 2 |

Notes: (1) Inoculum 1 and 2 were same but with different amounts (95 mL in 1, 88 mL in 2); (2) "ML + P-rel."—ML treated with anaerobic phosphorus release; "Foam + MW"—foam treated with MW-$H_2O_2$ AOP; "ML + P-rel. + MW"—ML treated first with anaerobic phosphorus release then with MW-$H_2O_2$ AOP. "Foam + ML"—mixture of foam and ML.

**Sample Pre-treatment**. MW-$H_2O_2$ AOP treatment of "Foam" and "ML+P-release" samples was

conducted in the same manner described in Section 4.2.1, except without pH adjustment (Table

4.2, Groups 4 and 6). The treatment was finished on the same day as anaerobic digestion was

started. The anaerobic P-release treatment of "ML" sample (Table 4.2, Group 3) started one day

before and lasted about 22 hours. Procedures were the same as described in Section 4.2.2 for

BT4.

127

**Characterization of Biogas and Other Parameters**. On each day, biogas production was measured in each bottle and was then released. Biogas measurement was conducted using a manometer (Fisher Scientific, USA) and an attached needle. Biogas composition was measured three times (days 3, 11, and 21) during the digestion using a Fisher-Hamilton Gas Partitioner. All the feed materials (including those pre-treated) were characterized (TP, TSS, etc.) before digestion started. On the 7th, 14th, and 21st days, one to three bottles from each group were opened and analyzed for $PO_4$-P and $NH_4$-N. To do this, an aliquot of 30 mL sample was centrifuged at 14,000 RCF for 8 minutes (from start), followed by glass fiber (Ø2.5 cm, 1.2 µm) and 0.45 µm membrane filtration. Because of the high analyte concentrations, samples were diluted to 1/25 for $PO_4$-P analysis and to 1/50 for $NH_4$-N. The digestion experiment lasted 2 months, until biogas production ceased. All the remaining bottles were opened at the end, and $PO_4$-P, $NH_4$-N, and TCOD were analyzed.

**Measurements at Lower pHs**. At the working pH (~7.3) struvite precipitation may occur during the digestion due to coexistence of high concentrations of $PO_4$-P, $NH_4$-N, and $Mg^{2+}$. To determine the amounts of $PO_4$-P and $NH_4$-N that could be extracted by the anaerobic digestion, concentrations of $PO_4$-P, $NH_4$-N, and $Mg^{2+}$ were also measured at pH $\leq 5.5$. The value of 5.5 was determined by using the computer program PHREEQC and by setting $PO_4$-P, $NH_4$-N, and $Mg^{2+}$ at their possible maximum concentrations. In other words, when the pH was lowered to $\leq$ 5.5, no struvite precipitation should occur. To adjust pH, each digested sample (~ 40 mL) was acidified with 20 % $H_2SO_4$ followed by 15-minute mixing. The rest of the procedures were the same as described above.

### 4.2.4 Dewatering and Settling Tests

Capillary suction time (CST) was measured to evaluate dewatering characteristics of different samples. In this study, a capillary suction timer (Komline-Sanderson Engineering Corporation, Peapack, New Jersey, USA) was used (Figure 4.1d). The instrument includes digital timer, a paper support block, and stainless-steel reservoir with an inner diameter of 18 mm and a height of 25 mm. The settling ability of MW-treated samples was evaluated by a modified sludge volume index (MSVI), calculated as

$$\text{MSVI, mL/g} = \text{settled sludge volume, mL/100 mL} \,/\, \text{TSS of sludge, g/100 mL} \qquad (4.1)$$

The standard SVI test uses a 1 L graduated cylinder and lasts 30 minutes (Grady et al., 2011). However, since the microwave oven used in the present study had a small treatment capacity of 360 mL per run (Section 4.2.1), More et al. (2015) modified the tested by using a 100 mL graduated cylinder and a 60-minute time span, and the same method was adopted in the present study.  However, since the wall effects resulting from the use a 100 mL cylinder for sludge settling tests can be different from that of a 1 L cylinder, the results obtained from the present study may not be easy to compare directly to other results from a standard test.

### 4.2.5 Chemical Analysis

Mixed liquor and foam were characterized based on the same methods reported in Chapters 2 and 3. VFA and magnesium were analyzed according to standard methods (APHA et al., 2005). VFAs were measured using an HP 6890 Series GC system, and magnesium was measured on using a flame atomic absorption spectrometer, SpectrAA 220/FS, Varian. A stock solution of 20

g/L $La^{3+}$ solution, from $LaCl_3$ or $La(NO_3)_3.6H_2O$, was used to eliminate chemical interference for magnesium measurement.

### 4.3    Results and Discussion

### 4.3.1        MW-$H_2O_2$ AOP Treatment

The results of MW-treated "ML and "Foam + ML" " samples are given in Table 4.3, where they are compared with the foam results reported by More et al. (2015). These data show comparable $PO_4$-P extraction efficiencies for "ML" and "Foam and ML" samples with $86 \pm 3$ % and $89 \pm 4$ %, respectively. Extraction efficiency is defined here by the ratio of released $PO_4$-P concentration to initial TP concentration (i.e., $PO_4$-P/ TP). Results for "Foam A" of More et al. (2015) were obtained under the same operating conditions as those used in the present study. Although the "Foam A" sample resulted in a lower extraction efficiency (67 %) than for the "ML" and "Foam + ML" samples, the final $PO_4$-P was higher than the final concentrations of the other two, all based on a fixed sample volume (30 mL). In other words, MW-$H_2O_2$ treatment of foam alone may be more economically favorable because of its higher initial TP concentration and lower water content (i.e., higher TSS). When normalized to their initial TSS concentrations, the specific $PO_4$-P extraction efficiencies of these three samples ranged from 0.036 to 0.031 mg P/ mg TSS (Table 4.3). A higher efficiency (> 90 %) was observed for "Foam B" with even lower pH of 2 and a higher $H_2O_2$ addition (1.0 volume %). Consequently, the resulting specific $PO_4$-P extraction (0.048 mg P/ mg TSS) was significantly higher than the others.

**Table 4.3 Summary of MW treatment results (results of foam A and B from More et al. (2010))**

| Sample source | ML | Foam+ ML (1:1 by volume) | Foam A[1] | Foam B[2] |
|---|---|---|---|---|
| *Phosphate Extraction* | | | | |
| Initial TP (mg/L) | $669 \pm 16$ | $943 \pm 31$ | 1,730 | 1,670 |
| TSS (mg/L) | 16,130 | 24,510 | 37,168 | 31,719 |
| VSS (mg/L) | 12,860 | 21,510 | 28,648 | 27,254 |
| Released $PO_4$-P (mg/L) | $578 \pm 21$ | $842 \pm 42$ | 1,160 | 1,520 |
| Extraction efficiency (%)[3] | $86 \pm 3$ | $89 \pm 4$ | 67 | 91 |
| Specific $PO_4$-P extraction (mg P/mg TSS) | 0.036 | 0.034 | 0.031 | 0.048 |
| *Settling and Dewatering (after MW treatment)* | | | | |
| MSVI (mL/g)[4] | 12 | 7 | 8 | |
| CST (seconds)[5] | $12.2 \pm 0.4$ | $13.8 \pm 2.1$ | 18.9 | |

Notes: (1) Conditions: pH = 3; $H_2O_2$ = 0.5 volume %; (2) conditions: pH = 2; $H_2O_2$ = 1.0 volume %; (3) = released $PO_4$-P concentration/ initial TP concentration. (4) tests with a 100-mL graduated cylinder for 60 minutes; calculated using Equation (4.1); and (5) CST before MW = $366.4 \pm 34.9$ s.

The above discussion shows that, if MW-$H_2O_2$ AOP is used to extract orthophosphate, foam is a better source than the aerobic zone ML because foam contains less water and higher TP concentration; this make the treatment more cost-effective. On the other hand, to achieve more than 90 % extraction from the highly concentrated foam, very harsh conditions are required, e.g., pH = 2 and $H_2O_2$ addition of 1.0 volume %.

One of the most important considerations in AOP is the dose of oxidant applied. In the current study, the $H_2O_2$ dose was calculated to be 0.35 and 0.23 g $H_2O_2$/ g TSS for the treatment of

mixed liquor (ML) and a mixture of Foam + ML (1:1 by volume), respectively, based on their TSS concentrations given in Table 4.3.

It is difficult to find literature reports of another AOP process that has been studied for nutrient release; therefore, direct comparison of the dose was not be possible. Many studies have used ozone oxidation to reduce sludge yield, and the reported ozone dosages were 0.05 to 0.5 g/g TS (Parez-Elvira et al., 2006). Based on this reported range, the $H_2O_2$ dose used in the present study appears to be typical. It should be noted that Saktaywin et al. ( 2005) studied sludge reduction and phosphorus recovery using ozone oxidation, and they observed that increasing ozone doses (up to 0.187 g/g SS) did not increase the $PO_4$-P concentration but only the acid-hydrolyzable phosphorus. For the MW-$H_2O_2$ AOP, increasing $H_2O_2$ dose alone also did not improve $PO_4$-P release. Other studies have shown that the combination of $H_2O_2$ dose and MW heating temperature was the second significant factor, while the temperature was the dominating factor to influence orthophosphorus release (More et al, 2015, Wong et al., 2007).

### 4.3.2    Anaerobic P-release

A total of four batch tests were conducted for anaerobic P-release. Three of them (BT1 to BT3) utilized aerobic zone ML from the MEBPR process operating at SRT = 60 days, and the fourth one (BT4) used a mixture of foam and influent wastewater because the foam alone was too thick to mix well. BT1 and BT2 were duplicate runs with continuous acetate feed. BT3 used a semi-continuous feed mode with acetate being added at four times. For BT4, all acetate was added one time at the beginning of test. In a full-scale application, it is more practical to use continuous or semi-continuous feeding of acetate to avoid a sudden decrease of pH when a large quantity of

acetic acid is added, or a sharp increase in $Na^+$ concentration when sodium acetate is used. The one-time-addition method guarantees that excess acetate is present at the beginning of the test, but it may cause inhibition. It seems that the semi-continuous feed mode is the best way to determine the maximum $PO_4$-P release rate, as long as the first feeding introduces sufficient acetate.
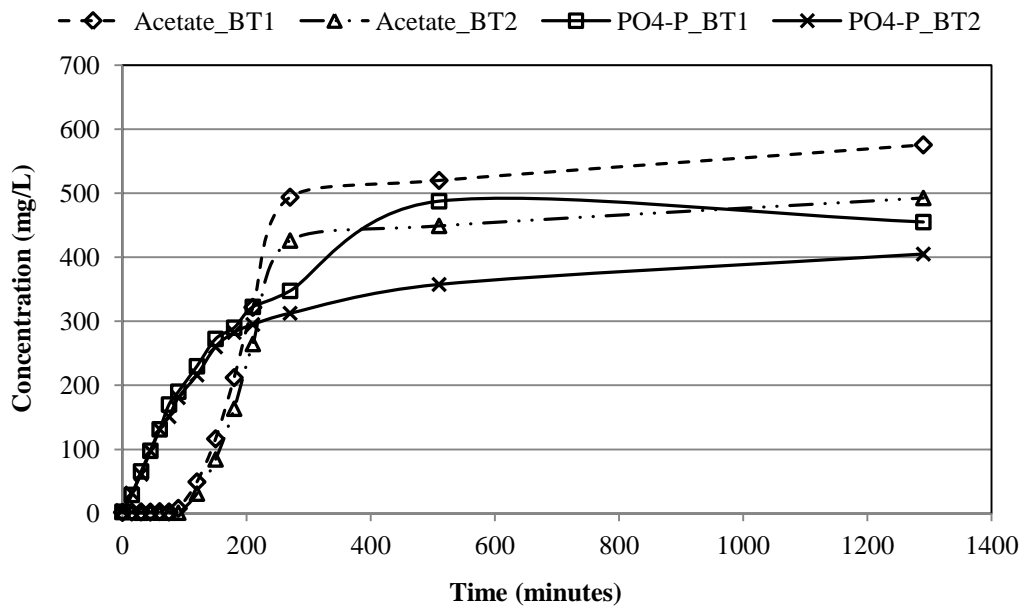


(a)
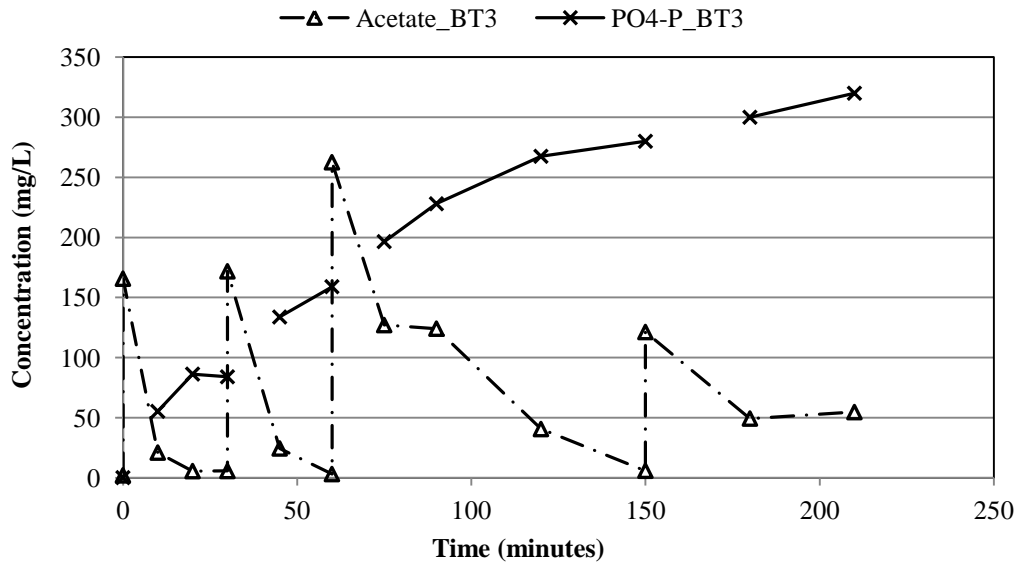
**(b)**
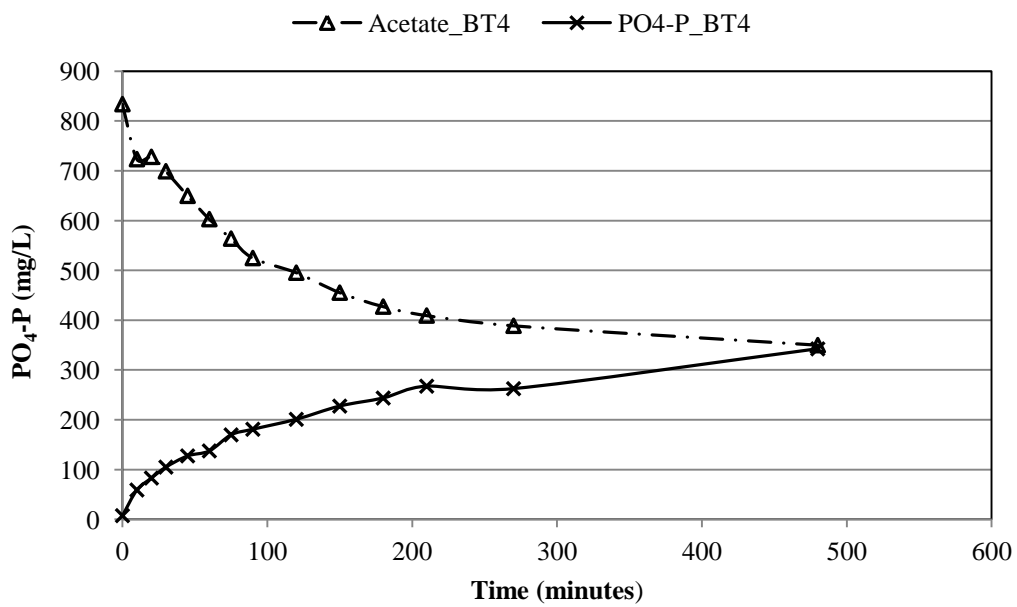


(c)

**Figure 4.2 Results of four batch tests. (a) BT1 and BT2 (duplicate) with continuous acetate feed; (b) BT3 with semi-continuous feed of acetate; and (c) BT4 with one time addition of acetate at the beginning.**

**PO$_4$-P Release Efficiency**. Figure 4.2 shows the P-release profiles and the concentrations of acetate for all four batch tests. In test BT1, PO$_4$-P concentration of 455 mg/L was achieved after 1,290 minutes (21.5 hours). A higher concentration (488 mg/L) was measured at t = 510 minutes (8.5 hours). Unfortunately, no replicate samples were analyzed to cross-check this result. BT2 was a duplicate test to BT1 and exhibited a slightly lower PO$_4$-P concentration of 405 mg/L at 21.5 hours. The averaged result from BT1 and BT2 was comparable at 8.5 hours (423 mg/L) with that at 21.5 hours (430 mg/L). This suggested that a reaction time of 8.5 hours might be more practical in application. The experimental times for BT3 and BT4 were shorter, consequently a PO$_4$-P concentration of 320 mg/L was observed at 3.5 hours in BT3, and 343 mg/L at 8 hours in BT4 (also a lower initial TP concentration). Table 4.4 summarizes the four batch test results. It shows that PO$_4$-P extraction efficiencies ranged from 42 % to 60 %, with higher efficiencies obtained at longer release times.

Comparing the released PO$_4$-P/VSS ratios after eight hours between BT2 and BT4 (Table 4.4) suggested that microorganisms in foam were active, at least for the PAOs, because the ratio in the latter (0.023) was only slightly lower than that in the former (about 0.028). In addition, Hall et al (2011) confirmed that that calculated similarity of the microbial communities in anoxic zone foam and the underlying ML was approximately 80 %. They also observed that the anoxic foam was active for phosphorus release, although the specific phosphorus-release activity was lower than that of aerobic zone mixed liquor biomass.

**Table 4.4 Summary of P-release batch tests**

| Batch test | BT1 | BT2 | BT3 | BT4 |
|---|---|---|---|---|
| Sample source | ML | ML | ML | Foam + influent (1:1 by volume) |
| Initial TP (mg/L) | 756 | 756 | 756 | 645 |
| TSS (mg/L) | 16,050 | 16,050 | 16,520 | 18,188 |
| VSS (mg/L) | 12,850 | 12,850 | 13,070 | 14,888 |
| TP/VSS | 0.059 | 0.059 | 0.058 | 0.043 |
| Released $PO_4$-P (mg/L) | 455 (21.5 hrs) | 405 (21.5 hrs) | 320 (3.5 hrs) | 343 (8 hrs) |
| Extraction efficiency (%) [1] | 60 | 53 | 42 | 53 |
| g $PO_4$-P /g acetate | 0.46 | 0.45 | | |
| Specific max. P-release rate (mg P/g VSS h) | 10 | 10 | 14 | 13 |

Notes: 1) Defined by released $PO_4$-P concentration/ initial TP concentration.

It is interesting to assess the composition of TP in mixed liquor to see how much orthophosphate could be released theoretically. Using BT1 and BT2 as an example, from Table 4.4, the ratio of TP to VSS (TP/ VSS) is 5.9 % (756/ 12,850). Qasim (1999) estimated the ratio of non-releasable P to TVSS in the mixed liquor as 2.3 %, based on the chemical formula $C_{60}H_{87}O_{23}N_{12}P$ for mixed mass growth. Subtracting 2.3 % from 5.9 % estimates that the ratio of releasable forms of P constitute (i.e., poly-P and ortho-P) to VSS would be about 3.6 %. This gives a maximum releasable P of 463 mg/L (3.6 % $\times$ 12,850), which accounts for 61 % of the TP. Based on this calculation, it appears that BT1 almost reached the maximum theoretical P release, after 21 hours of incubation.

**Maximum PO$_4$-P Release Rate**. The maximum release rates were found to be 10, 10, 14, and

13 mg P/g VSS•h in the four batch tests (Table 4.4), respectively. BT1 and BT2 showed a

smaller specific maximum P-release rate than the other two, because of the continuous feed

mode of acetate applied. In both BT1 and BT2, excess acetate was not detectable until around 90

minutes (Figure 4.2a). The specific maximum P-release rates were comparable for BT3 and BT4

(14 and 13 mg P/g VSS•h). Excess acetate was present at all times in both BT3 and BT4,

although at some points in BT3 the acetate concentrations were low (5.5 and 5.6 mg/L) (Figure

4.2b). In BT4, with all the acetate added at the beginning, a relatively low release was observed,

probably due to mass transfer limitations, because BT4 had the highest TSS concentration.

Consequently, the value of 14 mg P/g VSS•h from BT3 should be a better representation of the P

release rate for the aerobic zone ML. Monti et al. (2007) reported a range of 5−30 mg P/g VSS•h.

This value of 14 mg P/g VSS•h was slightly lower than their average.


**P/ VFA Ratio**. The ratios of g PO$_4$-P released/ g VFA consumed are consistent from BT1 and

BT2, with 0.45−0.46 g P/g acetate, or 0.42−0.43 g P/g COD. These numbers are lower than those

reported by Monti et al. (2007), which were 0.5 and 0.6 g P/g COD for pilot-scale and batch

tests, respectively. Kuba et al. (1997) reported 0.22−0.40 g P/g COD and Rabinowitz and

Oldham (1986) reported 0.85 g P/g COD. The estimated values here were within the literature

range.


In summary, the efficiency of the anaerobic P-release method is highly dependent on the

releasable phosphorus contained in the aerobic zone ML and the batch reaction time allowed. In

this research, the maximum efficiency of orthophosphate release was calculated to be about 61

%, and a reaction time of 8.5 hours would be required. This method is not suitable for foam, since foam is very concentrated and mass transfer of acetate into the PAOs can become limiting.

### 4.3.3 Anaerobic Digestion

Raw and pre-treated ML and foam samples were analyzed before anaerobic digestion, so that the results could be compared with those obtained after digestion to determine the effect of anaerobic digestion. The sample analyses, pretreatment procedures, and sample abbreviations are explained in Section 4.2.3. The results are given in Table 4.5. In general, the results of "ML" and "ML + P-rel." (i.e., ML treated with anaerobic P-release, Table 4.2) samples here were consistent with those previously reported in the anaerobic P-release study (Section 4.3.2), except that the ML used here contained a higher TP concentration (845 vs 756 mg/L). The extraction efficiency of anaerobic P-release was calculated to be 56 % (475/ 848), which was similar to the average efficiency of the BT1 and BT2 batch tests in Table 4.4. The results from "Foam" and "Foam + MW" samples were similar to those reported by More et al. (2015) and are shown in Table 4.3. The MW pre-treatment of foam achieved 63 % (1,130/ 1,785) extraction efficiency, only slightly lower than the 67 % reported by More et al. (2015) at pH = 3 (Table 4.3). It should be noted that the value of 63 % was achieved without adding any acid. MW pre-treatment was able to decrease foam pH from an initial value of 6.92 to 4.27, without acid addition.

**Table 4.5 Characterization of initial materials utilized for anaerobic digestion assays**

| Group | 1 | 2 | 3 | 4 | 5 | 6 | 7&8 |
|---|---|---|---|---|---|---|---|
| Samples | ML | Foam | ML + P-rel. | Foam + MW | ML + P-rel.+ MW | Foam + ML[*] | Inoculum |
| pH | 7.15 | 6.92 | 6.66 | 4.27 | 6.04 | - | 7.36 |
| $PO_4$-P (mg/L) | 0.09 | 72 | 475 | 1,130 | 467 | 36 | 159 |
| NOx-N (mg/L) | 2.32 | 0.36 | 0 | 2.69 | 2.84 | 1.34 | 0.29 |
| $NH_4$-N (mg/L) | 1.13 | 15.9 | 30.5 | 179 | 69.3 | 8.5 | 1,035 |
| TP (mg/L) | 845 | 1,701 | 848 | 1,785 | 872 | 1,273 | 393 |
| TKN (mg/L) | 1,333 | 3,100 | 1,333 | 3,517 | 1,400 | 2,217 | 1,859 |
| TSS (mg/L) | 18,040 | 40,500 | 17,610 | 21,470 | 12,490 | 29,270 | 15,040 |
| VSS (mg/L) | 14,220 | 34,020 | 13,840 | 17,410 | 9,960 | 24,120 | 11,220 |
| VS (mg/L) | 14,660 | 35,072 | 14,268 | 35,072 | 14,268 | 24,866 | 11,567 |
| TCOD (mg/L) | 15,733 | 37,139 | 14,367 | 37,139 | 14,367 | 26,436 | 14,078 |
| SCOD (mg/L) | 49 | 84 | - | 381 | 8,456 | 67 | 631 |
| $Mg^{2+}$ (mg/L) | 1.48 | 5.25 | 97.54 | 264 | 79.5 | 3.37 | 0.77 |
| CST (seconds) | 366 | N/A | 289 | 35.4 | 877 | - | - |

* all data for "Foam + ML" are averages of Foam and ML.

Theoretically, the sample "ML + P-rel. + MW", i.e., mixed liquor pre-treated by anaerobic P-release and MW-$H_2O_2$ AOP in sequence, was expected to release more $PO_4$-P than the "ML + P-rel." sample, because MW-$H_2O_2$ AO is capable of oxidizing organic phosphorus into $PO_4$-P which cannot be achieved by anaerobic P-release. However, the observed $PO_4$-P concentration (467 mg/L) was not significant different from that of "ML + P-rel." sample (475 mg/L). One explanation is that MW treatment could have released more $PO_4$-P, but this $PO_4$-P was then precipitated. MW-$H_2O_2$ AOP treatment of foam is known to release $NH_4^+$ and metals (e.g., $Mg^{2+}$, $Ca^{2+}$) in addition to $PO_4^{3-}$ (More et al., 2015). The measured, significantly higher CST of the

"ML + P-rel. + MW" sample than that of the "ML + P-rel." sample (877 vs 289 seconds, Table 4.5) could be caused by precipitate (e.g., struvite) blocking the pores of filter paper.

### 4.3.3.1    Extraction of $PO_4$-P and $NH_4$-N at Digestion pHs

Figures 4.3 shows the concentrations of $PO_4$-P at the end of the anaerobic digestion assays. These were the concentrations calculated after subtracting the contributions of inoculum (controls), therefore only six groups are shown in the Figure 4.3. As an example, the measured average $PO_4$-P concentrations of the bottle contents in Group 1 (12 mL + 88 mL inoculum) and Group 8 (inoculum only, 88 mL) at the end of digestion were $180 \pm 4$ mg/L, and $154 \pm 3$ mg/L, respectively (Figure 4.4).  The $PO_4$-P concentration released after digestion for Group 1, therefore, was calculated as:

$$[(180 \text{ mg/L} \times 0.1 \text{ L}) - (154 \text{ mg/L} \times 0.088 \text{ L})]/ 0.012 \text{ L} = 371 \text{ mg/L}$$

The $PO_4$-P concentrations from the other digestion groups were calculated in a similar way, but based on their respective sample volume used for digestion, i.e., 12 mL for Groups 1, 3, and 5 (ML samples), 5 mL for Groups 2 and 4 (foam samples), and 8 mL for Group 6 (mixture of ML and foam).
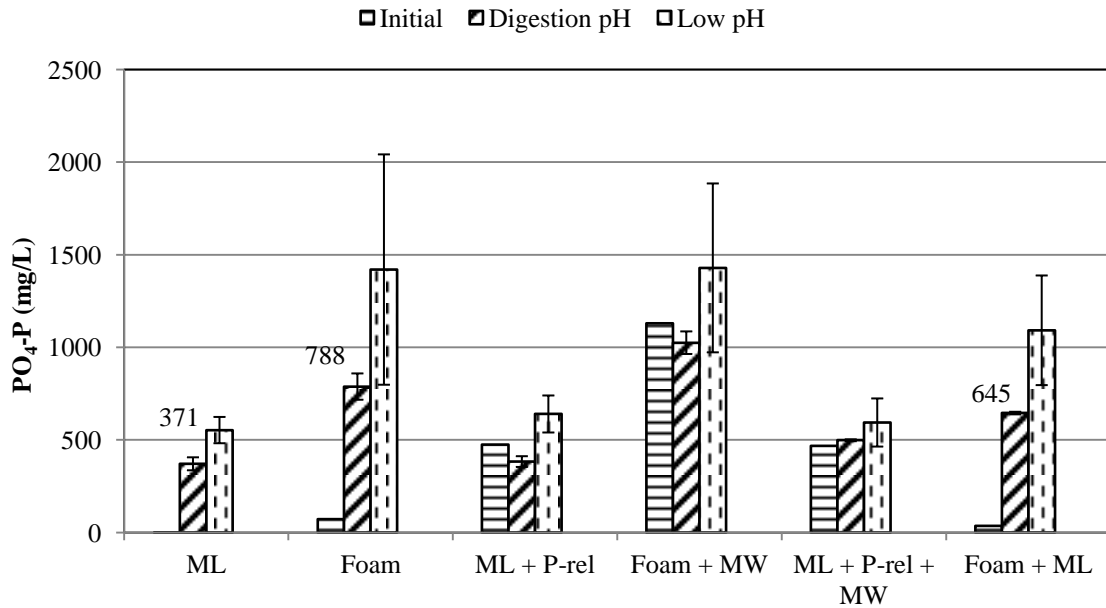
**Figure 4.3 Concentration of PO₄-P from different sample groups at the end of digestion. Digestion pH—pH without adjustment; low pH—pH adjusted to ≤ 5.5 after digestion. Error bar represents one standard deviation.**
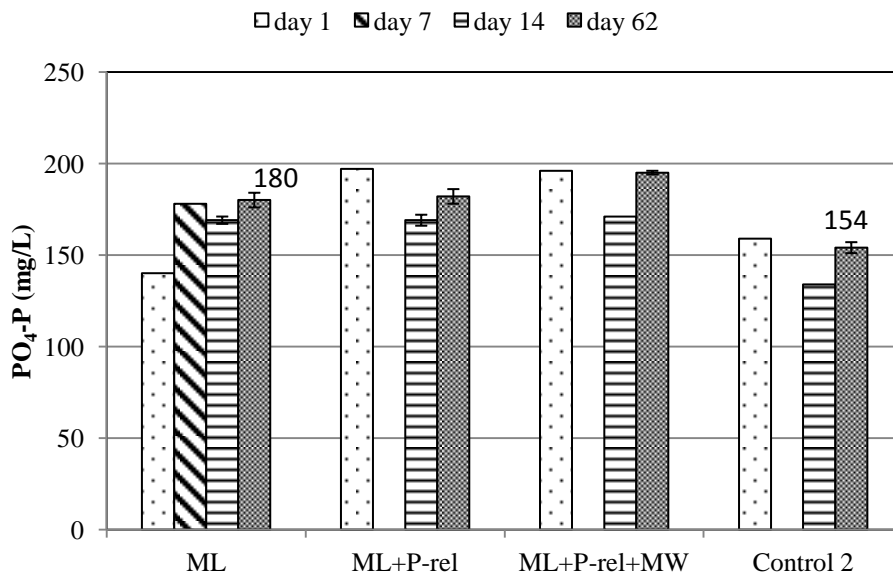


**Figure 4.4 Extraction of PO₄-P from different ML-related groups and their control. Error bar represent one standard deviation.**

Figure 4.3 shows that both raw "Foam" and "ML" samples were able to release significant quantities of $PO_4$-P through anaerobic digestion, with 788 mg/L for foam and 371 mg/L from ML. The difference was attributed to their initial TP concentrations (1,701 vs 845 mg/L, Table 4.5). The "Foam + ML" sample showed 645 mg/L $PO_4$-P, similar to the average of values from "Foam" and "ML" samples. When normalized to their initial TP concentrations, "Foam" and "ML" samples exhibited comparable $PO_4$-P release efficiencies (46 % vs 44 %). On the contrary, no obvious increases in $PO_4$-P concentration were observed from pre-treated ML or foam samples.

The $NH_4$-N concentrations were assessed in a similar way to those for $PO_4$-P. Different from $PO_4$-P, Figure 4.5 shows that $NH_4$-N concentration had increased significantly by the end of digestion in each group. Foam had the potential to release 1,379 mg/L $NH_4$-N, and aerobic zone ML was able to release 401 mg/L $NH_4$-N, which were equivalent to release efficiencies of 44 % and 30 %, respectively, based on the initial TKN concentrations (Table 4.5). Pretreatment of foam and ML samples by either MW-$H_2O_2$ AOP or anaerobic P-release, generally reduced the $NH_4$-N concentrations generated by anaerobic digestion.
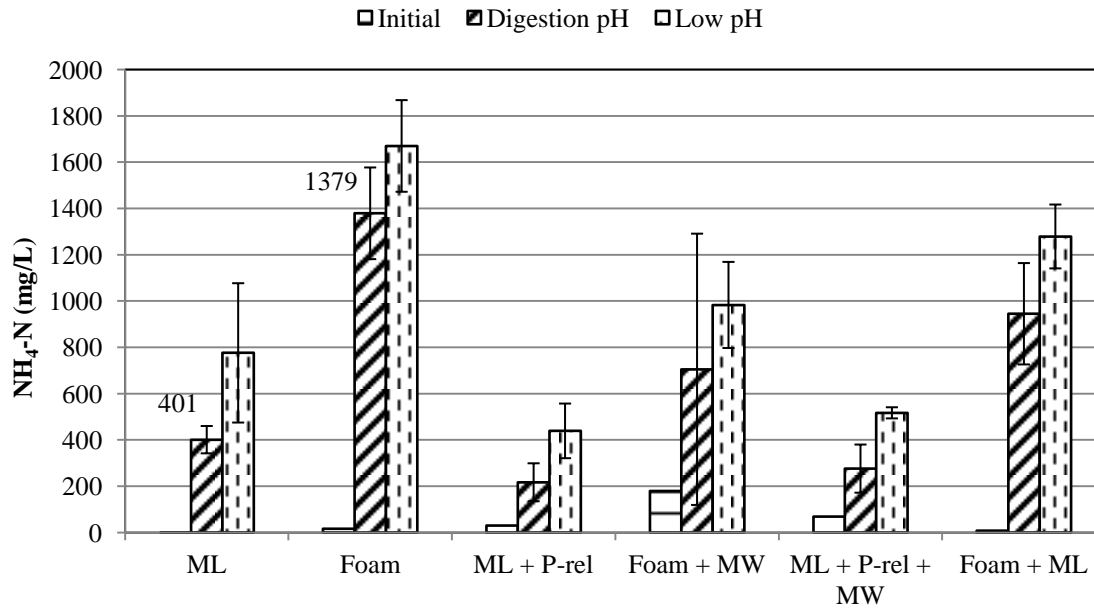
**Figure 4.5 Extraction of NH$_4$-N from different groups at the end of digestion. Digestion pH—pH without adjustment; low pH—pH adjusted to ≤ 5.5. Error bar represents one standard deviation.**

The concentrations of PO$_4$-P and NH$_4$-N released by the anaerobic digestion are summarized in Table 4.6. The concentrations in Table 4.6 were based on a unit volume of original ML and foam samples after subtracting the contribution from inoculum. Comparing Tables 4.5 and 4.6 reveals that anaerobic digestion could produce about 10-times higher NH$_4$-N concentrations than the other methods, for example, MW-H$_2$O$_2$ AOP (1,379 vs 179 mg/L, for foam) or anaerobic P-release (401 vs 30.5 mg/L, for ML). Consequently, anaerobic digestion may be a necessary component for producing sufficient NH$_4^+$ for struvite crystallization.

143

**Table 4.6 Final PO$_4$-P and NH$_4$-N concentrations after anaerobic digestion**

| Group | Sample | PO$_4$-P concentration (mg/L sample) | | NH$_4$-N concentration (mg/L sample) | |
|---|---|---|---|---|---|
| | | At digestion pHs | At low pHs ($\leq 5.5$) | At digestion pHs | At low pHs ($\leq 5.5$) |
| 1 | ML | $371 \pm 35$ | $553 \pm 71$ | $401 \pm 59$ | $776 \pm 301$ |
| 2 | Foam | $788 \pm 71$ | $1,080 \pm 141$ | $1,379 \pm 198$ | $1,670 \pm 198$ |
| 3 | ML + P-release | $383 \pm 29$ | $640 \pm 100$ | $217 \pm 82$ | $439 \pm 118$ |
| 4 | Foam + MW | $1,025 \pm 61$ | $1,429 \pm 456$ | $705 \pm 586$ | $983 \pm 186$ |
| 5 | ML + P-release + MW | $498 \pm 5$ | $594 \pm 130$ | $276 \pm 104$ | $517 \pm 24$ |
| 6 | Foam + ML | $645 \pm 7$ | $842 \pm 124$ | $945 \pm 219$ | $1,279 \pm 138$ |

Notes: PO$_4$-P and NH$_4$-N concentrations were the net concentrations from foam, ML, or their mixture samples after subtracting contributions from the control (inoculum).


**Table 4.7 PO$_4$-P and NH$_4$-N extraction efficiency from anaerobic digestion (AD) and pH lowering after AD.**

| Group | Sample | PO$_4$-P extraction efficiency (%) | | | NH$_4$-N extraction efficiency (%) | | |
|---|---|---|---|---|---|---|---|
| | | Before AD | After AD | After pH lowered | Before AD | After AD | After pH lowered |
| 1 | ML | 0 [a] | $44 \pm 4$ [b] | $65 \pm 8$ [c] | 0 | $30 \pm 4$ | $58 \pm 23$ |
| 2 | Foam | 4 | $46 \pm 4$ | $64 \pm 8$ | 1 | $44 \pm 6$ | $54 \pm 6$ |
| 3 | ML + P-release | 56 | $45 \pm 3$ | $76 \pm 12$ | 2 | $16 \pm 6$ | $33 \pm 9$ |
| 4 | Foam + MW | 63 | $57 \pm 4$ | $84 \pm 27$ | 5 | $23 \pm 9$ | $32 \pm 6$ |
| 5 | ML + P-release + MW | 54 | $59 \pm 1$ | $70 \pm 15$ | 5 | $21 \pm 8$ | $39 \pm 2$ |
| 6 | Foam + ML | 3 | $51 \pm 1$ | $66 \pm 10$ | 0 | $43 \pm 10$ | $58 \pm 6$ |

Notes: all the extraction efficiencies were based on initial TP (or TKN) given in Table 4.5, and calculated as PO$_4$-P/TP (or NH$_4$-N/TKN). (a) PO$_4$-P is given in Table 4.5; (b) and (c) PO$_4$-P values are given in Table 4.6.

### 4.3.3.2　Extraction of PO₄-P and NH₄-N at Low pHs

The observed extraction efficiencies (%) of $PO_4$-P and $NH_4$-N are given in Table 4.7. The reduced $PO_4$-P extraction efficiencies for two samples from the digestion (Groups 3 and 4) led to the hypothesis that chemical precipitation of phosphate had occurred. The possibility existed for formation of struvite because of the co-existence of high concentrations of $PO_4^{3-}$, $NH_4^+$, and $Mg^{2+}$. To test the hypothesis, the contents of each serum bottle was split into two portions at the end of anaerobic digestion. One portion was used to measure the concentrations of these three constituents directly (under digestion pHs), and the other was acidified to a lower pH of ≤ 5.5, mixed for 15 minutes, and then analyzed for $PO_4^{3-}$, $NH_4^+$, and $Mg^{2+}$ concentrations. The method used to specify this pH 5.5 was introduced in Section 4.2.3. Below pH 5.5, struvite was not expected to form. Comparing the concentrations under digestion and low pHs would have suggested how much struvite had been re-solubilized back into solution. The concentrations of $PO_4$-P and $NH_4$-N observed at the low pHs, therefore, represented the achievable concentrations when struvite precipitation did not occur (e.g. at low pHs), or $PO_4^{3-}$, $NH_4^+$, and $Mg^{2+}$ did not co-exist at normal pHs.

Table 4.7 shows that the extraction efficiencies were 64−65% for ML and foam under lower pHs. These efficiencies were comparable to the theoretical maximum estimated for the anaerobic P-release approach (61%, Section 4.3.2). This suggested that all of the polyphosphate portion of TP was likely hydrolyzed to $PO_4$-P at the low pHs, and the remaining phosphorus was in the form of organically-bound phosphate, which needs a strong oxidant to convert it into $PO_4$-P.

Table 4.7 also demonstrates that, at low pHs, extraction efficiencies increased 11 % (Group 5) to 31 % (Group 3) for $PO_4$-P, and 9 % (Group 4) to 28 % (Group 1) for $NH_4$-N. By comparison, Latif et al. (2015) reported a 57 % increase in $PO_4$-P release by an anaerobic digestion conducted at some low pHs ($< 5.7$), and Bi et al. (2012) reported an increase of 25 %. When comparing the results from both digestion and low pHs side-by-side in Table 4.8, the following is apparent. (1) In all cases, concentrations of $PO_4$-P, $NH_4$-N, and $Mg^{2+}$ increased significantly, which indicates that solubilization of precipitated struvite indeed occurred. (2) The molar concentrations of $Mg^{2+}$ released by acidification were consistently lower than those of $PO_4^{3-}$-P and $NH_4^{+}$-N, which indicates there were other sources of $PO_4$-P that were subject to acidification. If not, it would be expected that the increased molar concentrations of all three constituents would be the same based on Equation (1.1) in Chapter 1. The other potential sources could be unhydrolyzed polyphosphates at a neutral pH, or other phosphate precipitate. For example, Latif et al. (2015) observed partial solubilization of precipitated calcium phosphates from their low-pH anaerobic digestion.

It can be concluded that anaerobic digestion is a necessary component of a system that would release phosphorus for recovery as struvite. It cannot be replaced by any other method of providing sufficient $NH_4^{+}$. When anaerobic digestion was also used as a method to extract orthophosphate from foam or aerobic sludge, lowering pH to $\leq 5.5$ after digestion significantly improved the $PO_4$-P release efficiency (11−31 %). The resulting high efficiency from ML (65%) suggested that all the polyphosphate portion of TP was converted to soluble $PO_4^{3-}$ at the low pHs applied. Compared to the low pH anaerobic digestion reported by Latif et al. (2015), this post-

digestion low pH approach avoided problems such as reduced methane production potential and potential inhibition of digestion.

**Table 4.8 Increased molar concentrations of $PO_4$-P, $NH_4$-N, and $Mg^{2+}$ after lowering pH to ≤ 5.5 from digestion pHs.**

| Group | pH | $PO_4$-P (mg/L) | Δ mmol/L | $NH_4$-N (mg/L) | Δ mmol/L | $Mg^{2+}$ (mg/L) | Δ mmol/L |
|---|---|---|---|---|---|---|---|
| 1 | 7.28/5.43 | 191/354 [a] | 5.3 [b] | 1,266/1,302 | 2.6 | 12.48/68.63 | 2.3 |
|  | 7.29/5.48 | 169/342 | 5.6 | 1,256/1,353 | 6.9 | 9.34/66.06 | 2.4 |
|  |  |  | 5.4 ± 0.2 [c] |  | 4.8 ± 3.1 |  | 2.4 ± 0.0 |
| 2 | 7.26/5.45 | 186/363 | 5.7 | 1,340/1,417 | 5.5 | 4.02/81.18 | 3.2 |
|  | 7.34/5.45 | 181/353 | 5.5 | 1,354/1,403 | 3.5 | 7.14/72.04 | 2.7 |
|  |  |  | 5.6 ± 0.1 |  | 4.5 ± 1.4 |  | 3.0 ± 0.4 |
| 3 | 7.30/5.49 | 179/285 | 3.4 | 1,232/1,277 | 3.2 | 7.59/59.37 | 2.2 |
|  | 7.28/5.50 | 184/267 | 2.7 | 1,246/1,297 | 3.6 | 7.54/44.02 | 1.5 |
|  |  |  | 3.0 ± 0.5 |  | 3.4 ± 0.3 |  | 1.8 ± 0.5 |
| 4 | 7.38/5.48 | 196/315 | 3.8 | 1,318/1,382 | 4.6 | 1.01/67.08 | 2.8 |
|  | 7.32/5.45 | 192/314 | 3.9 | 1,282/1,365 | 5.9 | 0.72/66.29 | 2.7 |
|  | 7.30/5.47 | 198/275 | 2.5 | 1,340/1,380 | 2.9 | 0.75/54.63 | 2.2 |
|  |  |  | 3.4 ± 0.8 |  | 4.5 ± 1.5 |  | 2.6 ± 0.3 |
| 5 | 7.34/5.35 | 195/289 | 3.0 | 1,258/1,298 | 2.9 | 0.84/62.31 | 2.6 |
|  | 7.29/5.41 | 196/263 | 2.2 | 1,233/1,293 | 4.3 | 0.69/46.71 | 1.9 |
|  | 7.28/5.49 | 195/261 | 2.1 | 1,247/1,298 | 3.6 | 0.62/22.02 | 0.9 |
|  |  |  | 2.4 ± 0.5 |  | 3.6 ± 0.7 |  | 1.8 ± 0.8 |
| 7 (control) | 7.37/5.44 | 152/274 | 3.9 | 1,344/1,398 | 3.9 | 8.82/53.59 | 1.9 |
|  | 7.36/5.47 | 146/233 | 2.8 | 1,344/1,413 | 4.9 | 8.87/50.70 | 1.7 |
|  | 7.34/5.46 | 157/219 | 2.0 | 1,348/1,378 | 2.1 | 6.26/47.51 | 1.7 |
|  |  |  | 2.9 ± 1.0 |  | 3.6 + 1.4 |  | 1.8 ± 0.1 |

Notes: two or three serum bottles were used for each group. (a) Concentrations of the mixture in serum bottle at digestion and low pHs after anaerobic digestion; (b) calculated by [(354−191) mg P/L] / (31 g P/mol); (c) average ± one standard deviation.

### 4.3.3.3   Biogas Production and Composition

Biogas production is an extra benefit of the anaerobic digestion method and, therefore, was closely monitored during the study. Biogas mainly consists of methane ($CH_4$) and carbon dioxide ($CO_2$). The cumulative biogas production is shown in Figures 4.6 and 4.7 for foam and ML, respectively. Data for the other substrates are given in Appendix A, Figures A17−A20. To plot these figures, a daily, average biogas production was calculated from all the serum bottles in one group, and these daily values were then accumulated over the entire digestion time. Figure 4.6 shows that an average of 278 mL biogas was measured from group 2 samples, which contained 95 mL inoculum (control) and 5 mL of foam. Subtracting 216 mL biogas from the control left 66 mL biogas produced by the 5 mL foam, equivalent to 13.2 mL biogas/ mL foam. In a similar way, a production of 5.1 mL biogas/ mL mixed liquor was calculated from Figure 4.7. The ML sample showed much lower biogas production than the foam, due to its lower suspended solids concentration. However, if based on their initial VS concentrations (Table 4.5), the specific gas productions were actually close with 0.38 L/g VS added for foam and 0.35 L/g VS added for ML.
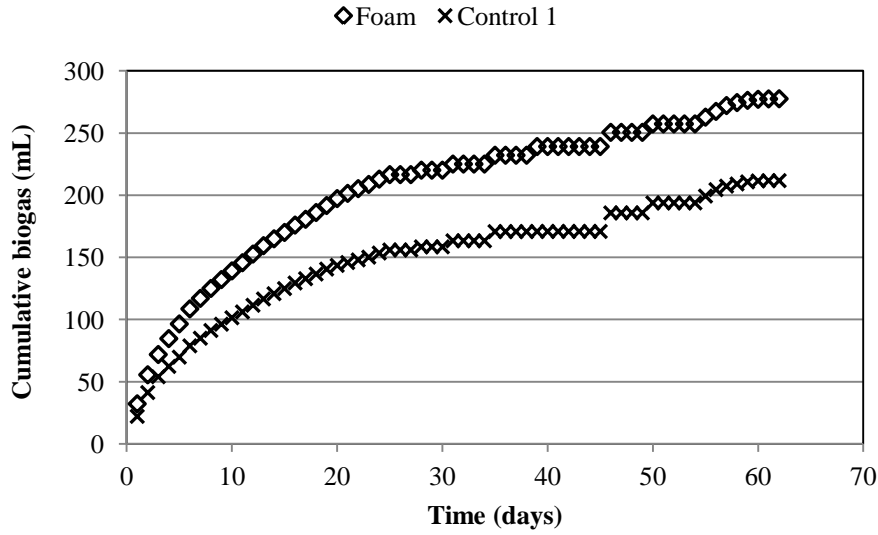
**Figure 4.6 Cumulative biogas production from foam sample (Group 2), calculated on daily averaged biogas production from all serum bottles in one group.**
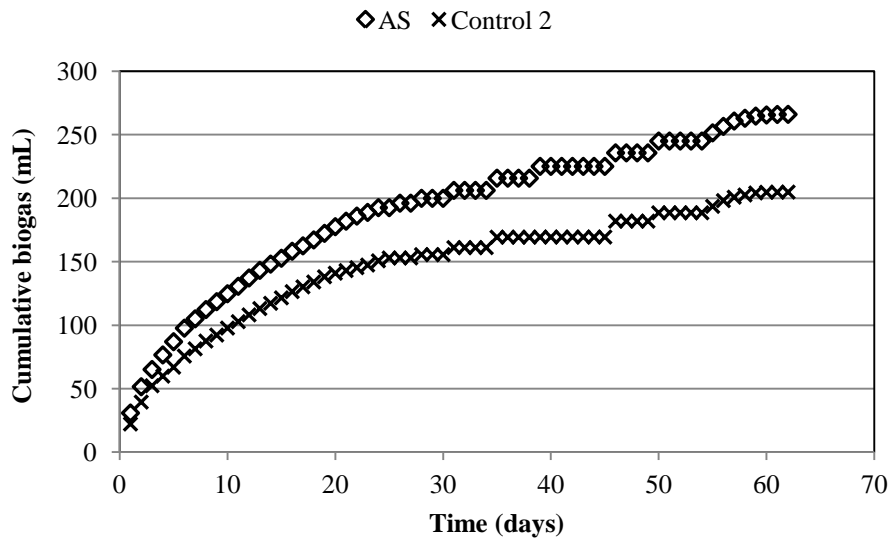


**Figure 4.7 Accumulative biogas production from mixed liquor (Group 1), calculated on daily averaged biogas production from all serum bottles in one group**

The biogas production results from the other group tests are given in Table 4.9. It is clear that

MW pre-treatment significantly increased biogas production by 32 % for foam samples and 43 %

149

for ML samples, pretreated with anaerobic P-release. Yi (2012) reported a 12 % increase in biogas production from MW-$H_2O_2$ pretreatment of a thickened secondary sludge. The lower increase percent might be attributed to the lower temperature (80 ℃) used by Yi (2012) for the MW pretreatment. Figures 4.6 and 4.7 show that about 80 % of the biogas was produced the first 30 days of digestion, and it required about 62 days for the substrates to be digested completely. The relatively long digestion time was thought to be due to the absence of constant mixing. If an incubator with auto-shaking had been available, the digestion could have been completed within 40 to 45 days (Yi, 2012).

**Table 4.9 Biogas production for different substrate materials**

| Group | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Sample | ML | Foam | ML + P-rel. | Foam + MW | ML + P-rel. + MW | Foam + ML |
| Biogas mL / mL sample | 5.1 | 13.2 | 4.9 | 17.4 | 7.0 | 8.2 |
| Biogas L/g sample VS added | 0.35 | 0.38 | 0.34 | 0.50 | 0.49 | 0.33 |
| $CH_4$ mL/ mL sample | 3.8 | 9.0 | 3.8 | 9.0 | 4.1 | 6.2 |
| $CH_4$ L/g sample VS added | 0.26 | 0.26 | 0.26 | 0.26 | 0.29 | 0.25 |

 Notes: see Table 4.5 for VS values.

Biogas produced by anaerobic digestion was mixture of methane ($CH_4$) and carbon dioxide ($CO_2$), with traces of oxygen ($O_2$) and nitrogen ($N_2$). The trace of $O_2$ is believed to come from air that entered the needle during collection of the sample and injection into the gas chromatograph. The $N_2$ was the residual from that used to purge the serum bottles to remove $O_2$ at the beginning

of the anaerobic digestion batch test. The composition of biogas was measured on days 3, 11, and 21. Table 4.10 shows that, except for the two controls (groups 7 and 8), the combined volume of $CO_2$ and $CH_4$ (i.e., biogas) from all other groups reached 72 % or more of the total volume on day 3, 90 % on day 11, and 95 % on day 21. The percentage of $CH_4$ then reached a stable level of 61–63 % for groups 1 to 6. These data were consistent with those reported by Yi (2012). To estimate methane production for each sample, an averaged methane concentration (%) was first calculated within each of four periods (e.g., day 1 to 3, day 4 to 11), then multiplied by the cumulative volume of biogas produced over the same period. The sum of all four periods gave the total methane produced. The results for net biogas and methane production per unit volume of substrate sample are shown in Table 4.9. Interestingly, the methane production remained the same for the foam samples with and without MW treatment. It seemed that MW-$H_2O_2$ AOP produced only more $CO_2$.

**Table 4.10 Biogas compositions at three sampling days**

| Group | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| *Day 3* | | | | | | |
| $CO_2$ (%) | 27.3±0.8 | 26.5±0.2 | 25.4±0.2 | 29.8±0.3 | 28.7±0.1 | 31.5±0.2 |
| $CH_4$ (%) | 47.2±2.6 | 49.8±0.1 | 46.6±1.5 | 48.8±0.1 | 51.2±1.1 | 54.6±0.5 |
| total | 74.5 | 76.3 | 72.0 | 78.6 | 79.9 | 86.1 |
| *Day 11* | | | | | | |
| $CO_2$ (%) | 34.8±1.1 | 34.9±0.3 | 32.6±1.4 | 36.8±1.1 | 35±0.0 | 32.4±0.4 |
| $CH_4$ (%) | 56.7±1.0 | 57.7±0.3 | 57.4±2.8 | 56.4±0.9 | 58.7±0.8 | 58.7±1.4 |
| total | 91.5 | 92.6 | 90.0 | 93.2 | 93.7 | 91.1 |
| *Day 21* | | | | | | |
| $CO_2$ (%) | 34.4 | 34.2 | 32.7 | 37.6 | 36.7 | 34.4 |
| $CH_4$ (%) | 60.9 | 62.7 | 62.8 | 60.4 | 59.6 | 60.5 |
| total | 95.3 | 96.9 | 95.5 | 98.0 | 96.3 | 94.9 |

#### 4.3.3.4    COD Stabilization

The amount of COD stabilized is a typical characteristic used to evaluate the performance of an anaerobic digestion system. In full-scale anaerobic digestion operated in the continuous feed mode, the COD reduction is typically between 30−40 % at an SRT of about 50 days, if the feed is 100 % waste ML with initial BOD = 3.9 g/L (Grady et al., 2011). Table 4.11 shows the results obtained in the present study through direct COD measurements before and after batch digestion.

**Table 4.11 COD stabilization of each sample**

| Group | Unit | 1 | 2 | 3 | 4 | 5 | 6 | 7 & 8 |
|---|---|---|---|---|---|---|---|---|
| Sample size | mL | 12 | 5 | 12 | 5 | 12 | 8 | |
| Initial COD | mL/g | 15,733 | 37,139 | 14,367 | 37,139 | 14,367 | 26,436 | |
| COD added | mg | 189 [a] | 186 | 172 | 186 | 172 | 211 | |
| COD after digestion (mixture) | mg/L | 10,964 ± 225 | 11,720 ± 170 | 10,669 ± 194 | 10,961 ± 406 | 10,238 ± 267 | 11,571 ± 259 | 11,513 ± 335 |
| COD left | mg | 83 [b] | 78 | 54 | 2 | 11 | 98 | |
| COD reduced | mg | 106 | 108 | 118 | 184 | 161 | 113 | |
| Stabilization | (%) | 56 | 58 | 69 | 99 | 94 | 54 | |

Notes: (a) COD added = sample size × initial COD concentration (from Table 4.5); (b) COD left = COD after digestion × 0.1 L − 11,513 × (0.1 − sample size) L; (c) stabilization = COD reduced / COD added.

The COD reduction in the batch testing was 56−58 % for untreated foam and aerobic zone ML, significantly higher than the full-scale values reported by Grady et al. (2011). Two MW-pretreated samples showed 94–99 % COD reduction, which were surprisingly high, particularly the result of the Group 4 foam sample. No COD reduction of close to 90 % has been reported from the anaerobic digestion of pretreated waste sludge (Carrère et al., 2010). Yi (2012) reported

a COD reduction of 81 % for thickened mixed liquor that was pre-treated by MW at a lower temperature of 80 ℃. The very high COD reduction observed in the present study is probably attributable to the heterogeneous nature of foam, which was evidenced by a high standard deviation (406 mg/L) of the COD measured after digestion, associated with the Group 4 samples. It seems that no one else has ever studied anaerobic digestion of foam with or without pretreatment, and the result observed here may need further verification.

### 4.3.4    Settling and Dewatering Tests

Solids-liquid separation is a necessary step for all WWTPs and it is often assessed by column settling tests and dewatering tests. Because of its high concentration of TSS, ML from SRT = 60 days operation did not settle in a 1-L cylinder, at least within the standard 30 minute test. However, MW-treated ML and foam settled very well in a modified test that used a 100 mL graduated cylinder (Table 4.3). This test was modified by More et al. (2015) due to that fact that each run of the MW oven used could only treat a maximum of 360 mL sample. Capillary suction time (CST) tests showed that aerobic zone ML had an average CST of 366 seconds. The same ML after anaerobic P-release (ML+ P-rel.) exhibited a slightly better dewatering potential (289 seconds), probably due to the lower pH associated with treatment (Table 4.5). Surprisingly, further MW treatment of the "ML+P-rel." sample significantly increased the CST to 877 seconds.

The high CST value was consistent with the observation that the "ML + P-rel. + MW" sample was difficult to filter for the measurement of TSS concentration. A possible explanation is that struvite (and probably other) precipitation occurred during MW treatment (without adding acid)

153

due to the presence of high concentration $PO_4$-P, $NH_4$-N, and $Mg^{2+}$. As a result, the struvite precipitate made the filtration/ dewatering very difficult. This same thing did not happen to the MW-treated foam, probably because the latter sample had a lower pH (4.27, see Table 4.5) that may have prevented the struvite precipitation from occurring. In general, microwave treatment significantly improved the settling and dewatering characteristics for both foam and aerobic zone ML. On the contrary, anaerobic digestion tended to degrade the dewatering characteristics of samples. The observed CSTs of samples after digestion ranged from 521 to 815 seconds.

## 4.4   Conclusions and Engineering Significance

This Chapter compared the potential for extracting $PO_4$-P and $NH_4$-N from foam and aerobic zone ML using three technologies: anaerobic P-release, MW-$H_2O_2$ AOP, and anaerobic digestion. The following conclusions were reached.

- Anaerobic P-release was a simple and non-destructive (to microbes) technology. Within 8.5 hours, it released up to 60 % of the TP from aerobic zone ML obtained from a 60 day SRT process, a value that was close to the theoretical maximum. The P/ VFA ratio was found to be 0.45−0.46 g P/g acetate. However, this technology appeared not to be suitable for the foam due to mass transfer limitations caused by the high suspended solids concentration of foam. Anaerobic P-release could also release a large amount of $Mg^{2+}$, but little $NH_4$-N.

- MW-$H_2O_2$ AOP was able to release 86 % of the TP as $PO_4$-P from the aerobic zone ML with the conditions of T = 180 ºC, pH = 3, and $H_2O_2$ = 0.5 volume %. An extraction

efficiency of 89 % was observed with a mixed sample of foam and aerobic zone ML

(volume 1:1) under the same treatment conditions.

- Anaerobic digestion released 44 % and 46 % of the TP as $PO_4$-P from aerobic zone ML

  and foam, respectively, under digestion pHs. Lowering the pH of digested material to $\leq$

  5.5 increased these two values to 65 % and 64 %, which were believed to be the

  polyphosphate portion of the initial TP. The increased anaerobic P-release was believed

  to result from dissolution of struvite precipitate and other forms of precipitated

  phosphorus.

- Anaerobic digestion released an average of 30 % and 44 % of TKN as $NH_4$-N from

  aerobic zone ML and  foam, respectively, under digestion pHs, and 58 % and 54 % when

  the pH was lowered to $\leq$ 5.5. Anaerobic digestion showed to be the only technology that

  could generate sufficient $NH_4$-N to support struvite crystallization.

- Anaerobic digestion produced methane gas. The methane production was found to be

  0.25 to 0.29 $CH_4$ L/g sample VS. The COD reduced by anaerobic digestion ranged from

  94−99 % for two MW pre-treated samples and from 54−69 % for the other substrates.

- Several treatment alternatives were assessed to maximize $PO_4$-P extraction without

  lowering the pH. MW-$H_2O_2$ AOP did not increase the $PO_4$-P concentration from the

  sample pretreated with anaerobic P-release. Anaerobic digestion also had little impact on

  the $PO_4$-P release from any samples that had received pretreatment by either MW-$H_2O_2$

  AOP or MW-$H_2O_2$ AOP, or both, unless the pH was lowered. However, anaerobic

  digestion significantly increased the final $NH_4$-N concentration from all examined

  substrates, at both normal and reduced pHs.

- Dewatering and settling tests showed that MW-$H_2O_2$ AOP significantly improved dewatering and settling characteristics of all the samples except for the ML sample pretreated by anaerobic P-release. On the contrary, anaerobic digestion worsened the dewatering characteristics.

- The advantages and disadvantages of these three P-release methods are summarized in Table 4.12.

The present study examined multiple options to extract $PO_4$-P from foam and aerobic zone mixed liquor. In particular, this study demonstrated that anaerobic digestion was able to extract as much $PO_4$-P as the anaerobic P-release method, with a pH adjustment (to $\leq 5.5$) after digestion. This approach could fully utilize the ability of anaerobic digestion to generate $NH_4$, as well as to extract considerable $PO_4$-P from both foam and aerobic zone mixed liquor (64−65 % of TP). This might be more cost-effective than a process that uses an anaerobic P-release process to extract $PO_4$-P and an anaerobic digester to generate $NH_4$ separately. Alternatively, the struvite precipitate may be utilized as seed material for struvite crystallization, if they can be effectively separated from other solids. To extract more $PO_4$-P, the MW-$H_2O_2$ AOP can be used after anaerobic digestion to oxidize the organically-bound phosphate. In this case, a reduced pH (to 3 or 2) is not needed, making the MW-$H_2O_2$ AOP more practical.

**Table 4.12 Comparison of MW-H$_2$O$_2$ AOP, anaerobic P-release, and anaerobic digestion**

| Methods | Advantages | Disadvantages |
|---|---|---|
| Anaerobic P-release | • Simple<br>• Non-destructive to microorganisms | • Consumes acetate: 0.45−0.46 g P/g acetate<br>• Medium PO$_4$-P extraction efficiency (53−60 %) within 8.5 hours under batch conditions |
| MW-H$_2$O$_2$ AOP | • Highest PO$_4$-P extraction: 63 % (no acid) to 91 % (pH = 2)<br>• Extraction of NH$_4$-N, Mg$^{2+}$, VFA, etc.<br>• Much improved settling and dewatering characteristics | • Needs specialized MW unit: pressurized<br>• Consumes H$_2$O$_2$: 0.5−1.0 volume %<br>• Needs lower pH (2 or 3) to extract more PO$_4$-P; later need to increase pH back to 7.2−7.8 for struvite crystallization |
| Anaerobic digestion | • Only way to produce large concentrations of NH$_4$-N<br>• Can produce methane: about 0.26 CH$_4$ L/g sample VS | • Releases lowest proportion of PO$_4$-P from foam and ML: 44−46 % at digestion pHs<br>• Long operation time<br>• Poor settling and dewatering characteristics |

# Chapter 5: Operational Costs Of A Conceptual Full-Scale MEBPR Plant Operating At Different SRTs

## 5.1 Introduction

Membrane bioreactors (MBRs) are increasing in application today in both municipal and industrial wastewater treatment (Judd, 2011) due to their advantages of excellent effluent quality, flexible operation, and a small footprint, with the first one being the major driving force (van Nieuwenhuijzen et al., 2008). For the second advantage (i.e., flexible operation), disagreement exists on whether or not MBRs should be operated at a long solids retention time (SRT), although there is no upper SRT limit that applies to MBRs except for the α-factor restriction. On one hand, long SRTs reduce sludge yields (Chapter 2, Section 2.3.3.2); on the other hand, a long SRT will decrease oxygen transfer efficiency, therefore consuming more energy. A long SRT may also potentially increase membrane fouling rate and phosphorus concentration in the effluent of MEBPR plants, but these two problems were not observed from the UBC pilot plant operating at SRT = 60 days (Chapter 2, Sections 2.3.2 and 2.3.4). Therefore, this Chapter focuses on how the operational costs of an MEBPR plant might be influenced by long SRT operation.

In general, the main obstacle to MBR applications is their higher capital and operational costs relative to those incurred with conventional activated sludge processes (CASPs) which use a secondary clarifier to separate liquid from suspended solids. For MBRs, the major capital costs are related to membrane module installation and replacement, and significant operational costs include those for membrane aeration (scouring), permeate pumping, chemical cleaning of membranes in addition to biological aeration (reaction), and sludge handling (treatment and

disposal). While the first three operational costs are exclusively associated with MBRs, and the last two costs are shared with CASPs.

A long SRT often results in increased mixed liquor suspended solids (MLSS) concentrations when the MBR volume is fixed. Higher MLSS concentrations reduce the α-factor (oxygen transfer correction factor for waste water), therefore increasing biological aeration power requirements. In addition to the MLSS concentration, the α-factor is also influenced by other parameters like organic loading rates, surfactant concentrations, and air flow rates (Cornel et al., 2003). Consequently, reported α values vary widely among different research groups (Krampe and Krauth, 2003; Germain, 2004; Günder, 2001; Muller et al., 1995). More information is given in Chapter 1, Section 1.2.3.

Membrane aeration, or membrane air scouring demand, is often represented by a specific aeration demand (SADm, $Nm^3/m^2 \cdot h$) which is based on membrane area. Typically SADm is a design criterion, either determined by pilot study or from manufacturer guidelines (Judd, 2011). Empirical pilot data between $0.25-0.54$ $Nm^3/m^2 \cdot h$ have been reported for GE ZeeWeed membranes, and an average of $0.30$ $Nm^3/m^2 \cdot h$ was reported for hollow fibre (HF) membranes in full-scale installations (Judd, 2011). The membrane aeration requirement ranges from $30-50$ % of the total air demand, and is expected to decrease as new membranes and aeration systems are developed (Yoon, 2015). On the other hand, air used for membrane scouring may partially compensate for the oxygen required for biological reactions when the membranes are inside the aeration tank, or even when a separate membrane tank is used but biomass is recycled from the membrane tank to the aeration tank. The amount of this contribution can be determined by

oxygen mass balance calculations or modelling (Judd, 2011). Yoon (2015) reported that the air used for membrane scouring could compensate for 10−30 % of biological reaction air demand, and Giesen et al. (2008) reported the lower end (10 %) from separate membrane and aeration tanks.

Data on sludge handling costs are much less available, as these vary with sludge handling methods. Reported costs varied from Euro €43 per ton dry solids (tonDS$^{-1}$) that covers chemicals, labor, treatment and disposal, to €259 tonDS$^{-1}$ (Stensel and Strand, 2004) that accounts for collection, thickening, digestion, dewatering, reuse, but not including haulage (Verrecht et al., 2010; Maere, 2012). These costs were equivalent to Canadian dollars CAD $71 to 425 per tonne DS (1 € = 1.49 CAD$, 1 ton = 0.91 tonne). Permeate pumping is a requirement specifically related to MBRs, but its energy cost is relatively small compared to the biological aeration, membrane aeration, and sludge handling costs, especially for an immersed MBR because the trans-membrane pressure (TMP) is very low (Henze et al., 2008). Chemical costs for membrane cleaning will depend on the cleaning protocols, particularly the cleaning frequency, which can be membrane type- and/or treatment plant-dependent.

Previous Chapters have demonstrated that operating an MEBPR plant at SRTs as high as 40 or 60 days is technically feasible. For a new technology to be industrialized, economic consideration is a key factor to influence the final decision. Therefore, the main objective of this Chapter is to estimate operational costs for a conceptual full-scale MEBPR plant to be operated at long SRTs of 40 and 60 days, and to compare these to costs at the typical 25 day SRT. Although a long SRT with increased MLSS concentration helps to reduce bioreactor footprint

and therefore, capital costs, the major impacts of long SRT operation are on the system operational costs. For this reason, the main focus of the present study was on operational costs, and the capital costs were only slightly discussed. The major costs considered here were biological air demand, membrane air scouring demand, pumping energy (permeate and sludge recycle), mixing, sludge handling, and chemical costs, but labour costs were excluded. A comparison between MBRs between CASPs is also briefly discussed.

## 5.2   Materials and Methods

Based on the literature review, several criteria can be used for the economic analysis of the conceptual full-scale plant. These include a typical membrane flux value of 20 liters per square meter per hour (LMH) (Verrecht et al., 2010; Judd, 2011); averaged SADm for full-scale plants of 0.30 $Nm^3/(m^2 \cdot h)$; and energy consumption of 0.025 $kWh/Nm^3$ for air supply, determined by Verrecht et al. (2010) from a full-scale plant; α-factor was measured by Sandberg and Hall (2016) using mixed liquor from the UBC MEBPR plant. Pumping energy was calculated based on the UBC pilot plant, which can be scaled up linearly because the pumping energy constituted a small portion of the total energy consumed in the entire plant. Due to the importance and variation of α-factor, sludge handling costs, and SADm, a sensitivity analysis was performed on these three parameters.

The process oxygen requirement can be calculated based on Metcalf & Eddy (2003).

$$AOTR = Q(S_O\text{-}S) - 1.42\ P_{X,VSS} + 4.33Q(NO_X) \tag{5.1}$$

$$AOTR = SOTR\left(\frac{\beta C_{S,T,H} - C_L}{C_{S,20}}\right)(1.024^{T-20})(\alpha)(F) \tag{5.2}$$

where   AOTR = actual oxygen transfer rate under field conditions, g $O_2$/h,

SOTR = standard oxygen transfer rate in tap water at 20 $^{0}$C, and zero dissolved oxygen, g O$_2$/h,

Q = influent flow rate of 5,328 L/day was used,

S$_O$ = COD concentration in influent including external acetate, (292 + 29 ) mg/L,

S = COD concentration in effluent. An average of 28 mg/L was used,

P$_{X,VSS}$ = Sludge wasting rate, g VSS/day. See Table 5.1,

NOx = NOx-N concentration in effluent, mg/L. Concentrations used were 15.8, 12.7, 10.1 mg/L for SRT = 25, 40, and 60 days, respectively,

β = salinity-surface tension correction factor, typically 0.95 to 0.98. Average 0.97 was used.

Cs$_{,T,H}$ = average dissolved oxygen saturation concentration in clean water in aeration tank at temperature T and altitude H, mg/L. A value of 9.2 mg/L was used

C$_L$ = operating oxygen concentration of 1.0 mg/L was used.

Cs$_{,20}$ = dissolved oxygen saturation concentration in clean water at 20 $^{0}$C and 1 atm, mg/L. A concentration of 9.17 mg/L was used.

α = oxygen transfer correction factor for waste water. See Table 5.1.

F = fouling factor, typically 0.65 to 0.9. An average of 0.78 was used.

The air flow rate can also be calculated based on Metcalf & Eddy (2003).

$$\text{Air flowrate, m}^3/\text{min} = \frac{\text{SOTR kg/h}}{[(E)\left(60\frac{\text{min}}{\text{h}}\right)(O_2 \text{ in air, kg/m}^3)]} \quad (5.3)$$

where E = standard oxygen transfer efficiency (SOTE) of air diffuser system for clean water, %, depth dependent.

O$_2$ in air, kg O$_2$/m$^3$ air = (density of air ρa, kg/m$^3$) × (O$_2$ weight % in air).

Density of air ρa, kg/m$^3$ = PM/ RT.

where   P = atmospheric pressure (sea level 1.01325 × 10$^5$), N/m$^2$,

M = molecular weight of air = 28.97 kg/kg-mole,

R = universal gas constant = 8,314 N.m/kg-mole.K,

T = temperature, K (Kelvin) = (273.15+ $^0$C)

O$_2$ weight % in air = 23.18 % in dry air at 0 $^0$C and 1.0 atmosphere.

Depending on the depth of submergence, transfer efficiencies of 5 % to 8 % may be attained with non-porous diffusers, and 15 % to 25 % with fine-pore diffusers (Metcalf & Eddy, 2003).

## 5.3    Results and Discussion

### 5.3.1        Energy Demand

The energy costs considered consist of air demands for biological reactions and membrane scouring, permeate pumping, sludge recirculation pumping, and mixing. Each of these is discussed below.

### 5.3.1.1    Oxygen Demand for Biological Reactions

To calculate oxygen demand for biological reactions, the sludge production rate needs to be determined first. The sludge production at the UBC MEBPR plant can be calculated using observed yields at different SRTs and the averaged amount of COD removed. Chapter 2 reported

the observed yields of 0.3, 0.27, and 0.25 g VSS/ g COD for SRT = 25, 40, and 60 days,

respectively. With the averaged influent TCOD of 292 mg/L, external acetate addition of 29 mg

COD/L, effluent COD of 28 mg/L, and influent flow rate of 5,328 L/d, the average mass of COD

removed was calculated to be 1,561 g/d. This results in observed sludge wasting rates (Px,vss) of

468, 421, and 390  g VSS/ d for the three SRTs, as shown in Table 5.1.

AOTR, SOTR and air flow rate were calculated and the results are also given in Table 5.1. The

values of α-factor were obtained from Sandberg and Hall (2016) as shown in Figure 5.1. These

values were determined on a pilot-scale column contactor, or by using aerobic zone mixed liquor

from the UBC MEBPR plant, and they are generally lower than those reported in the literature

(see Figure 5.1). Only the value determined at MLSS = 16 mg/L (i.e., 0.1) was close to that

reported by Germain (2004). The air flow rate was estimated at a temperature of 16 $^0$C (an

average operating temperature for the UBC pilot plant) and assuming that the SOTE of the

diffuser was 20 %, an average value for fine-pore diffusers according to Metcalf & Eddy (2003).

**Table 5.1 Estimated sludge wasting rate and biological oxygen demands at different SRTs**

| SRT (d) | Aerobic MLSS (g/L) | α value[a] | Px, $_{VSS}$ (g VSS/d) | Px, $_{TSS}$ (g TSS/d) | AOTR (g/d) | SOTR (g/d) | Air flow (Nm$^3$/d)[b] |
|---|---|---|---|---|---|---|---|
| 25 | 8 | 0.35 | 468 | 571 | 1,266 | 5,899 | 104 |
| 40 | 10 | 0.25 | 421 | 526 | 1,263 | 8,243 | 145 |
| 60 | 16 | 0.10 | 390 | 459 | 1,261 | 20,572 | 362 |

Notes: a) Data from Sandberg and Hall (2016); and b) data calculated at sea level (standard

atmosphere) and temperature of 16 $^0$C (an average aerobic zone temperature for the UBC pilot

plant), and assuming SOTE of diffuser is 20 % for clean water (Equation 5.3).
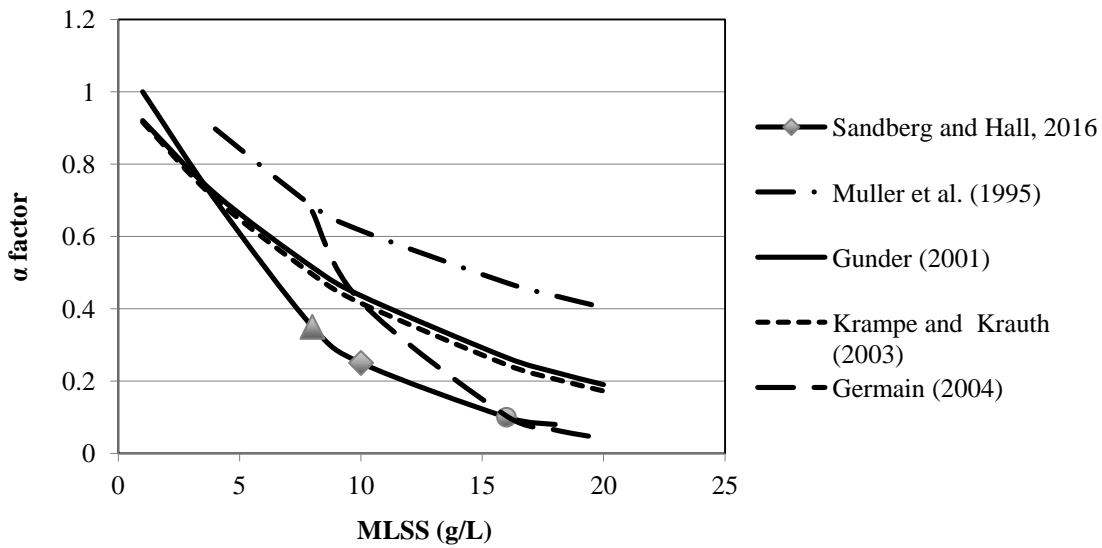
**Figure 5.1 α-factor at different MLSS concentrations (adapted from Judd, 2011 and Sandberg and Hall, 2016).**

It can be seen that the AOTRs are similar for the three SRTs, but the SOTRs increase sharply from SRT = 40 days to 60 days due to the increased MLSS concentration and decreased α values (Figure 5.2). From the literature, it seems that the maximum MLSS concentration in MBRs should be kept no higher than 10−15 g/L (Germain et al., 2007). Above 15 g/L, air demand increases significantly, and the reduced sludge production (and handling costs) did not offset the increased costs related to air demand. Using a value of 0.025 kWh/Nm$^3$, energy consumption for SRT = 25, 40, and 60 days was calculated to be 2.6, 3.6, and 9.1 kWh/d, respectively.
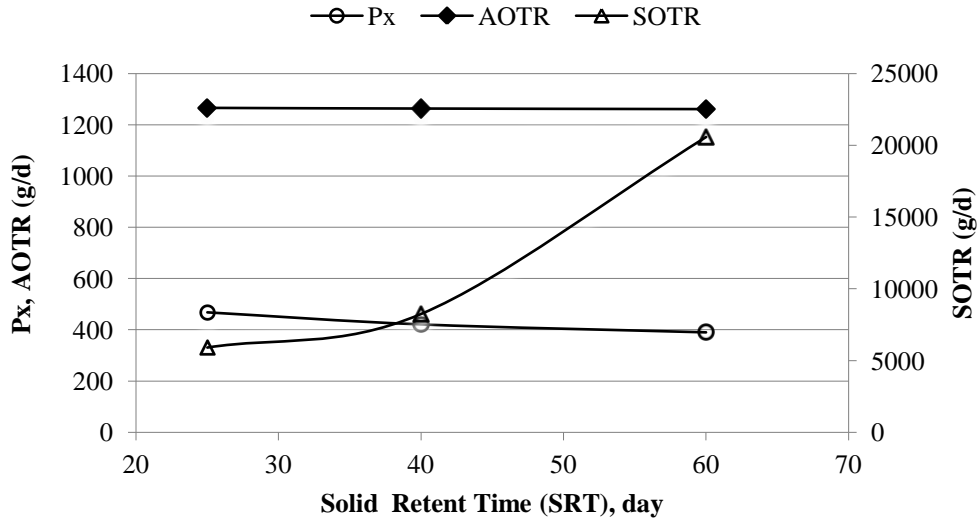
**Figure 5.2 Sludge wasting rate and oxygen transfer rate.**

### 5.3.1.2 Air Demand for Membrane Scouring

During the entire experimental period, the UBC MEBPR pilot plant was operated with a constant

membrane flux of about 10 LMH (Chapter 2, Section 2.2). This small flux, however, is not

suitable for a modern full-scale MBR. Instead, a typical flux of 20 LMH has been reported in the

literature (Verrecht et al., 2010; Judd, 2011). When this value is used, the membrane area

required to treat a wastewater flow rate of 5,328 L/d is 11 $m^2$. Using the SADm of 0.30

$Nm^3/(m^2 \cdot h)$ for full-scale plants, the air flow rate needs to be 79 $Nm^3/d$ (= 0.30 × 11 × 24). The

energy demand is estimated to be 79 $Nm^3/d$ × 0.025 $kWh/Nm^3$ = 2.0 kWh/d. The value of 0.025

$kWh/Nm^3$ was obtained from Judd (2011) and Verrecht et al. (2010).

### 5.3.1.3 Permeate and Recirculation Pumping

Pumping energy is required mainly for permeate pumping and mixed liquor (ML) recirculation,

i.e., anoxic and aerobic zone ML recycle. While the former is only related to MBRs, the latter is

166

common for all biological nutrient removal (BNR) processes including both MBRs and CASPs.

Important factors affecting the energy for permeate pumping include TMP, flux, and the operating protocol applied (continuous or on/off modes). Trussell et al. (2007) reported that increasing MLSS concentration reduced the permeability of a membrane, and it can be expected that permeate pumping will consume more energy at a higher MLSS concentration if the same flux is maintained. However, for MBRs with immersed HF membrane modules, the TMP is usually very low, and as a result, the permeate pumping energy requirement is correspondingly small and constitutes a relatively small portion of the total energy cost when compared with sludge handling, and biological and membrane scouring aeration requirements. Consequently, the permeate pumping energy was considered to be the same for all three SRTs. By comparison, ML recirculation between tanks exerts a greater energy demand, in particular when denitrification and/or phosphorus removal is required (Henze et al., 2008), as in this study with the UBC pilot plant. In general, the pumping energy can be calculated using the following equation (Yoon, 2015):

$$P_0 = \left| \frac{\Delta P}{\rho g} + \frac{v_L^2}{2g} + \Delta h \right| \frac{\rho g Q_L}{\varepsilon_P \varepsilon_M} \qquad (5.4)$$

Where $P_0$ = power consumption of pump (W),

$\Delta P$ = differential pressure between pump inlet and outlet (Pa),

$\rho$ = liquid density (kg/m$^3$),

g = gravity acceleration (9.8 m/s$^2$),

$V_L$ = liquid velocity in pump outlet (m/s),

$\Delta h$ = vertical height difference between water intake level and discharge pipe exit (m),

$Q_L$ = liquid flow rate (m$^3$/s),

$\epsilon_P$ = pump efficiency (-), and

$\epsilon_M$ = motor efficiency (-).

In practical situations, the velocity head, $V_L^2/2g$, is negligible compared to the pressure head, and therefore can be removed from the equation. Pump efficiencies ranging from 35 % to 70 % have been reported under field conditions, for flow rates frequently changed with on and off modes (Kaya et al., 2008). Because of the relatively small contribution from these pumping energy costs, the calculation was simplified by considering only the first term for permeate pumping and the third term for ML recirculation.

Consequently, permeate and ML recirculation pumping energy was calculated as follows.

$$Wp = (\Delta Pm \times Qp)/\eta \qquad (5.5)$$

$$Ws = (\Delta h\rho gQs)/\eta \qquad (5.6)$$

Where Wp = power consumption for permeate pumping (W),

Ws = power consumption for ML recirculation pumping (W),

$\Delta Pm$ = average TMP (Pa),

Qp = permeate flow rate ($m^3/s$),

Qs = internally recycled activated sludge ($m^3/s$), and

$\eta = (\epsilon_P * \epsilon_M)$, combined efficiency of pump and motor

Other terms are defined in Equation (5.4)

For the UBC MEBPR plant, an average $\Delta Pm$ at all SRTs was $(3+16)/2 = 9.5$ in Hg = 32,171 Pa,

$Q_p = Q_s = 3.7$ L/min. $= 6.17 \times 10^{-5}$ m$^3$/s, lift height of ML recirculation $\Delta h = 1.7$ m, ML density $\rho$

$= 1,400$ kg/m$^3$ (Qasim, 1999), g = 9.8 m$^2$/s, and assumed $\eta = 40$ % (Henze et al., 2008).

$$Wp = (32,171 \times 6.17 \times 10^{-5})/ 0.4 = 5.0 \text{ W} = 0.005 \text{ kW} = 0.120 \text{ kWh for one day}$$

$$Ws = (1.7 \times 1,400 \times 9.8 \times 6.17 \times 10^{-5})/ 0.4 = 3.6 \text{ W} = 0.0036 \text{ kW} = 0.086 \text{ kWh for one day}$$

The aerobic and anoxic recycle circuits have the same $Q_s$ and $\Delta h$, therefore the same $W_s$.

Verrecht et al. (2010) estimated the energy of ML recirculation using a factor of 0.016 kWh/m$^3$

ML pumped for a full-scale plant. Using the same factor for the UBC pilot plant results in 0.085

kWh/d (= 0.016 kWh/ m$^3$ ML pumped $\times$ 5,328 m$^3$/d), which is very close to the value calculated

above (0.086 kWh/d). In total, ML recirculation accounts for $2 \times 0.086 = 0.172$ kWh/ d with

both anoxic and aerobic recycle ratios being 1:1 (see Chapter 2). Of course, a greater energy

input would be needed with higher ML recycle ratios. In the present study, the energy required

for permeate pumping and ML recirculation was comparable, and the total required pumping

energy was considered to be the same for all three SRTs (25, 40, and 60 days), at about 0.29

kWh/d.

### 5.3.1.4   Mixing Energy

The mixing power requirement can be calculated by using 8 W/ m$^3$ anoxic tank volume (Metcalf

and Eddy, 2003; Verrecht et al., 2010). For the UBC pilot plant, this assumption resulted in a

daily mixing energy requirement of

$$(8 \text{ Wm}^{-3}) \times (2.228 \text{ m}^3 \times 0.28) \times (24 \text{ hr/d }) / 1,000 \text{ W/kW} = 0.12 \text{ kWh/d}$$

where 2.228 m$^3$ is the total volume of three zones of the UBC pilot plant, and 0.28 is the volume ratio of the anoxic zone.

Similarly, the mixing energy was calculated as 0.05 kWh/d for the anaerobic zone based on its volume ratio of 0.11. Therefore, the total mixing energy requirement is 0.17 kWh/d.

### 5.3.1.5    Breakdown of Energy Demand

Sections 5.3.1.1 to 5.3.1.4 show the energy demands for biological aeration, membrane aeration, permeate pumping, ML recirculation pumping, and ML mixing. Among them, the biological aeration requirements were different, being 2.6, 3.6, and 9.1 kWh/day for SRT = 25, 40, and 60 days, respectively. Other energy demands remained the same at the three SRTs, being 2.0, 0.12, 0.17, and 0.17 kWh/day for membrane aeration, permeate pumping, ML recirculation pumping, and ML mixing. It should be noted that these data were based on the treatment capacity of 5,328 L/ day of the UBC pilot plant. To roughly estimate the operational costs of a full-scale MBR plant operating at an SRT range of 25 to 60 days, these data must be linearly scaled up based on the actual treatment capacity of the full-scale plant.

The breakdown of the estimated energy consumption is given in Figure 5.3 for SRTs of 25, 40, and 60 days. For SRT = 25 days, both biological (52 %) and membrane aeration (40 %) requirements are in the typical ranges reported in the literature. For example, Yoon (2015) reported that the membrane aeration requirement typically ranged from 30−50 % of the total air demand. In the present study, the combined biological and membrane aeration at SRT = 25 days accounts for 92% of the total energy demand, while energy costs for permeate pumping, ML

170

recirculation pumping, and ML mixing are comparable and each is less than 4 % of the total. The total energy cost was calculated to be 5.0 kWh/day, or 0.94 kWh/m$^3$ permeate based on the treatment capacity 5,328 L/day.

For SRT = 60 days, the biological aeration requirement increases to 79 % of the total energy cost of 11.5 kWh/day or 2.1 kWh/m$^3$ permeate. Although a 60 day SRT significantly increases the biological air demand, the total energy per unit permeate is still in the typical range of 0.5−2.5 kWh/m$^3$ for large-scale MBRs (van Nieuwenhuijzen et al., 2008).

In summary, the total energy requirements are comparable with SRTs = 25 and 40 days (0.94 vs 1.1 kWh/m$^3$), but operation at SRT = 60 days more than doubles the energy requirements, due mainly to the sharp increase in biological aeration demand.
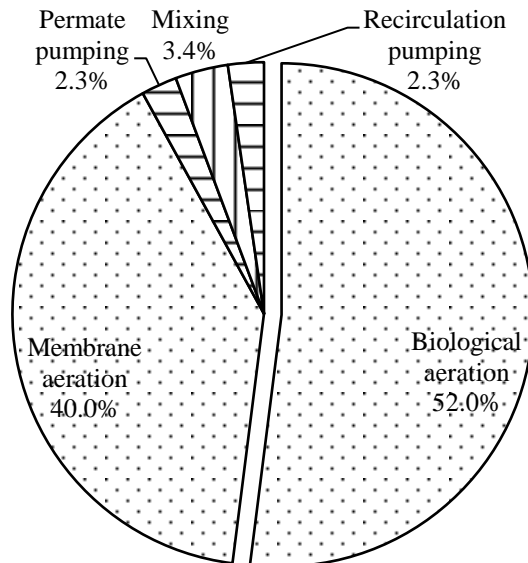


(a)
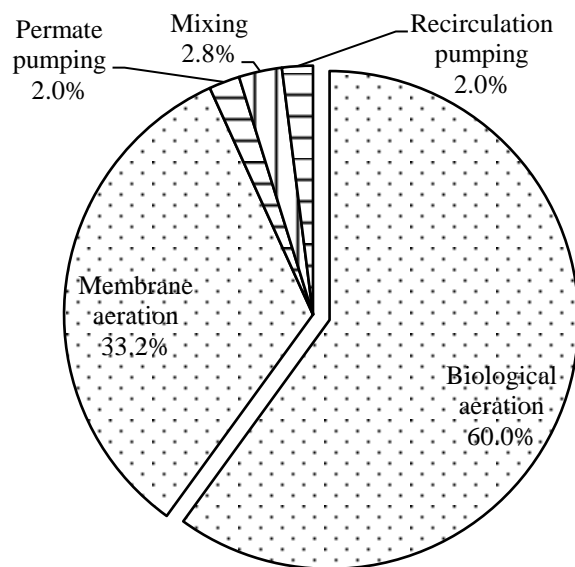
(b)
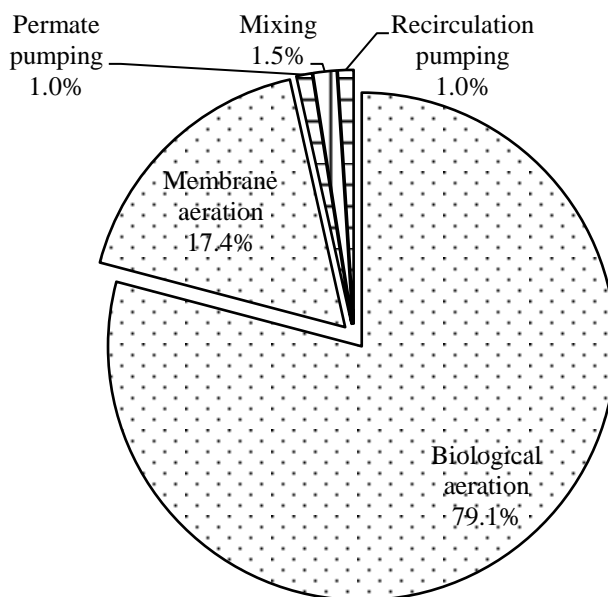


(c)

**Figure 5.3 Energy requirement breakdown of the conceptual full-scale plant (a) SRT = 25 days, total energy: 0.94 kWh/m³ permeate; (b) SRT = 40 days, total energy: 1.1 kWh/m³ permeate; (c) SRT = 60 days, total energy: 2.1 kWh/m³ permeate.**

172

### 5.3.2 Costs for Sludge Handling and Disposal

The quantity of waste sludge can be represented by the daily wasted dry suspended solids $P_{X,TSS}$, which was calculated by Px,vss/ (VSS/TSS). VSS/TSS values of 0.82, 0.80, and 0.85 were used for SRT = 25 days, 40, and 60 days (see Chapter 2, Table 2.7), respectively, depending on whether the major waste source was aerobic zone mixed liquor (25 days), or anoxic zone foam (60 days), or a mixture of both (40 days). The results are given in Table 5.1, which shows that the longer SRTs of 40 and 60 days reduce $P_{X,TSS}$ by 8 % and 20 % relative to the $P_{X,TSS}$ at SRT = 25 days, respectively. To estimate the handling and disposal costs in 2016, an annual inflation rate of 2 % was used based on CAD \$425 per tonne DS in 2004 (i.e., €259 tonDS$^{-1}$, see Section 5.1). The 2 % was estimated from the chemical engineering plant cost index from 2006 to 2014, which averaged 1.9 %, and the CAD \$425 per tonne DS is a conservative value, representing a complete treatment and disposal of the sludge. The calculation results in CAD \$540 per tonne DS for 2016 (= $425 \times 1.02^{12}$). The assumed sludge handling methods included thickening, anaerobic digestion, dewatering, and final disposal, but did not include transportation costs.

### 5.3.3 Chemicals for Membrane Cleaning

According to the chemical cleaning protocol given by Judd (2011), membranes need to be cleaned in place (CIP) weekly with 500 ppm NaOCl and 2000 ppm citric acid, and out of place (COP) twice per year with 1000 ppm NaOCl and 2000 ppm citric acid. This suggested COP frequency matches well with the practice at the UBC pilot plant. Based on this protocol, Verrecht et al. (2010) estimated the chemical costs to be 2.5 % of total operational costs.

### 5.3.4 Comparison of Major Operational Costs

To compare the major operating costs at different SRTs, only the costs for sludge handling, biological aeration, and membrane scouring aeration were considered. Among these, differences only exist for the first two in the present study. Costs related to pumping, mixing, and chemicals are not presented because they were relatively small. Their combined costs account for 8 %, 7 %, and 6 % of total operational costs for SRT = 25, 40, and 60 days, respectively. To calculate the costs, a unit energy cost of CAD $ 0.0825/ kWh and a sludge handling cost of CAD $540 per tonne DS were used. Figure 5.4 shows that the total major costs were CAD $ 0.69, 0.75, and 1.16, respectively for SRT = 25, 40, and 60 days, respectively. Since these costs were based on the treatment capacity of the UBC MEBPR pilot plant (i.e., 5,328 $m^3$/d), they were equivalent to CAD $ 0.13, 0.14, and 0.22/ $m^3$ permeate. Because all major costing parameters were selected based on full-scale values, the costs of the conceptual full-scale MEBPR plant can be scaled up linearly using these values. The costs were comparable between operations at SRT = 25 and 40 days, but at SRT = 60 days, the cost is about 70 % higher than that at 25 days, due to the significantly increased SOTR (and air flow) for biological aeration (Table 5.1).

It can be concluded, that when operational costs are considered, an MLSS of more than 15 g/L (and very low α-factor) should be avoided. However, a long SRT (e.g., 60 days) with a high MLSS concentration helps to reduce bioreactor size, therefore saving capital costs. In addition, a longer SRT produces less waste sludge, which also reduces the sizes of downstream reactors and storage tanks required for waste sludge treatment. Finally, when phosphorus recovery is considered, an MEBPR plant operated at a long SRT can produce mixed liquor (and foam) with a high TP concentration, which makes phosphorus recovery more cost-effective.

174
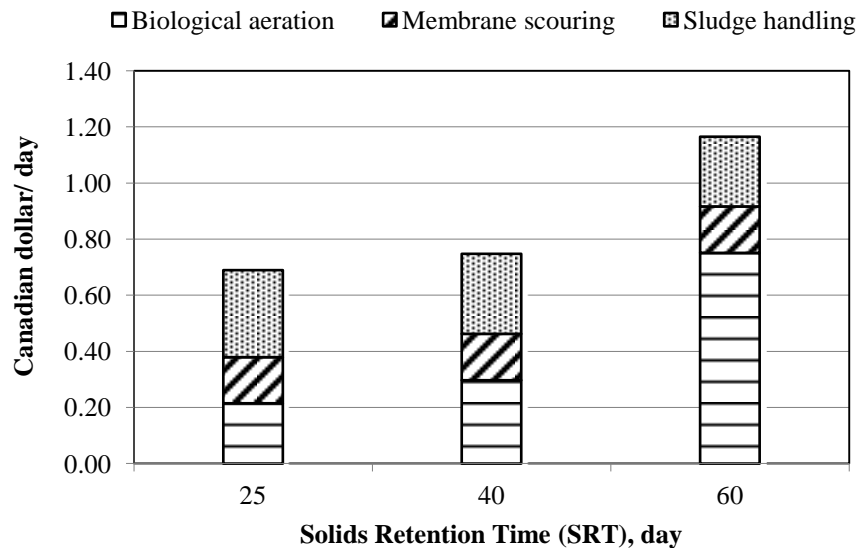
**Figure 5.4 Comparison of major operational costs at different SRTs, based on the capacity of the UBC MEBPR plant, 5,328 L/day.**

### 5.3.5　　Sensitivity Analysis

A sensitivity analysis was conducted to determine the response of the operational cost estimates to changes in each contributing parameter. The three most important parameters were identified as being the α-factor for biological air demand, the membrane aeration parameter SADm, and the sludge handling cost per unit tonne of dry solids. The sensitivities to changes in these three parameters are given in Figure 5.5. Because the reported α values varied widely (e.g., 0.1 to 0.5 for 16 g/L, a 400 % increase, Figure 5.1), the sensitivity analysis for α covers a wider range than the other two parameters. The figure shows that α-factor is the most significant parameter affecting the major operational costs, particularly at the lower end of the range assessed. When the other two parameters are held constant, the α value needs to be about 200 % higher (i.e., 0.3)

in order to make the cost at 60 days comparable to that at 25 days (0.69 CAD/day). The sludge handling cost and membrane SADm exert very similar, but less significant, impacts.
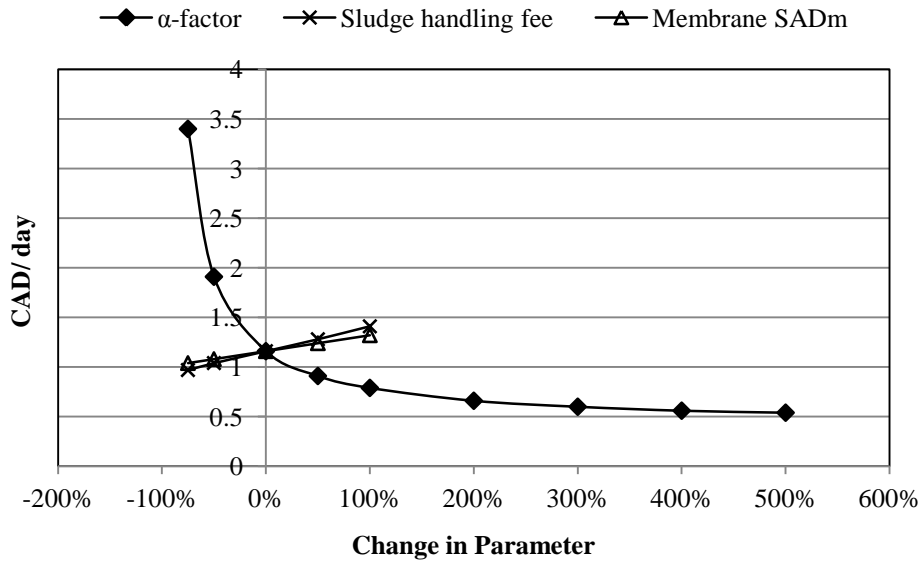


**Figure 5.5 Sensitivity analysis for SRT = 60 days, based on the capacity of the UBC MEBPR plant, 5,328 L/day.**

### 5.3.6    MBRs Versus CASPs

In previous sections, major operational costs were compared for a conceptual full-scale MEBPR plant operated at different SRTs, based on the combined data from the UBC pilot plant and the literature. van Nieuwenhuijzen et al. (2008) reported that the energy costs of large-scale MBRs can be up to twice those of CASPs. In addition, there are other costs specifically associated with MBRs, which include chemical costs for membrane cleaning and membrane replacement (therefore re-investment) after a theoretical life time of 13 years (Brepols et al. (2010). Buffer tanks and pretreatment are also often required (Verrecht et al., 2010; Judd, 2011). As such,

MBRs are still more expensive than the CASPs. As mentioned previously, the major driver for MBRs is the high effluent quality. Therefore, MBRs should be compared with systems that achieve the same effluent quality, not just CASPs. In applications requiring a high effluent quality, CASPs need to be considered in combination with tertiary treatment, for example, sand filtration and probably disinfection. Brepols et al. (2010) reported that the investment costs of MBR plants actually could be lower than the costs of comparable CASPs utilizing tertiary treatment, to meet the same stringent discharge criteria.

## 5.4    Conclusions

Operating costs for an MEBPR process were calculated based on the UBC pilot-scale plant, with a treatment capacity of 5,328 L/day. The costs consisted of three parts: energy requirements, sludge handling costs, and chemical costs. The energy cost was further split into requirements for membrane aeration, biological reaction aeration, and others (pumping and mixing). During the calculations, a few parameters related to membrane aeration (membrane flux, SADm, and energy consumption for air supply) were set to typical values from full-scale applications, so that the calculated results were relevant to the conceptual full-scale plant. Biological aeration requirements were strongly influenced by the α-factor, which was determined at the UBC pilot plant. Since the observed α-factor was smaller than most of the values reported in the literature, the calculated biological reaction aeration requirements were rather conservative, and therefore, could be safely scaled up. The energy requirements for pumping and mixing were relatively small ($\leq$ 8% of the total energy required in all three SRTs); consequently, they could be considered collectively and scaled up linearly. Sludge handling costs were estimated based on

177

Euro € tonDS[-1] from the literature for full-scale applications. Finally, the chemical costs were estimated to be 2.5 % of the total operating costs.

The energy requirements for operating the UBC pilot plant at SRT = 25, 40, and 60 days were estimated to be 0.94, 1.1, and 2.1 kWh/m$^3$ of permeate produced. All of these were within the reported range of 0.5−2.5 kWh/m$^3$ permeate for full-scale MBRs. Therefore, it is practical to operate at a long SRT = 60 days, although the cost is about 70 % higher than the cost with SRT = 25 days, and about 3 to 4 times that of a conventional activated sludge plant. The major operational costs, including sludge handling, biological and membrane aeration, were estimated to be CAD $ 0.13, 0.14, and 0.22/ m$^3$ permeate. These values can be linearly scaled up based on the treatment capacity of a conceptual full-scale MEBPR plant. Additional 10 % may be considered to include the pumping, mixing, and chemical costs. Labour has been excluded from these calculated operating costs. A sensitivity analysis suggested that the α value has the most significant impact on the total energy costs, particularly at high MLSS concentrations (e.g., >15 g/L). From the viewpoint of economics only, MBRs are only comparable to CASPs when stringent effluent quality is mandated. A long SRT of 60 days is economically feasible only when an extra benefit is recognized in term of phosphorus recovery.

# Chapter 6: Proposed Systems For Phosphorus Recovery

## 6.1    Introduction

Previous Chapters have demonstrated that operation with SRT = 60 days is technically practical

and economically feasible. In addition, different technologies were assessed to extract

phosphorus (as orthophosphate) from anoxic zone foam and aerobic zone mixed liquor. These

technologies included MW-$H_2O_2$ AOP, anaerobic P-release, and anaerobic digestion. Since

struvite crystallization is a proven technology for full-scale applications, every component is

available to configure an integrated system for phosphorus recovery. There are many process

options, depending on which method is used to extract phosphorus. Two systems are proposed

here, and in each system, the MEBPR process is intended to operate at SRT = 60 days.

## 6.2    System without MW-$H_2O_2$ AOP

Figure 6.1 is the simplest configuration with intermediate phosphorus recovery. In this system,

wasted foam and aerobic zone mixed liquor are fed directly into an anaerobic digester. Although

this is similar to the first generation process that Ostara Nutrient Recovery Technologies Inc.

used to recover phosphorus as struvite, there are two major differences. One is that the system

proposed here uses an MEBPR process with a long SRT = 60 days. This produces aerobic zone

mixed liquor (ML) and anoxic zone foam with very high TP concentrations. The other difference

is that the pH would be lowered to about 5.5 after anaerobic digestion to significantly increase

the $PO_4$-P concentration, i.e., 21 % and 18 % for aerobic zone mixed liquor and foam,

respectively (Chapter 4, Table 4.7). However, there would be a penalty for this extra gain

because later, in a struvite crystallizer, the pH needs to be raised to 7.2─7.8 (Donald Mavinic,

179

Professor at UBC, personal communication), depending on, for example, the concentrations of other constituents. Chapter 5 demonstrated that anaerobic digestion could achieve $PO_4$-P extraction of 44−46 % of TP for aerobic zone ML and foam samples (Table 4.6). The efficiency was 40 % for the inoculum obtained from the Lulu Island WWTP with a $PO_4$-P concentration of 159 mg/L and TP concentration of 393 mg/L (Table 4.5).
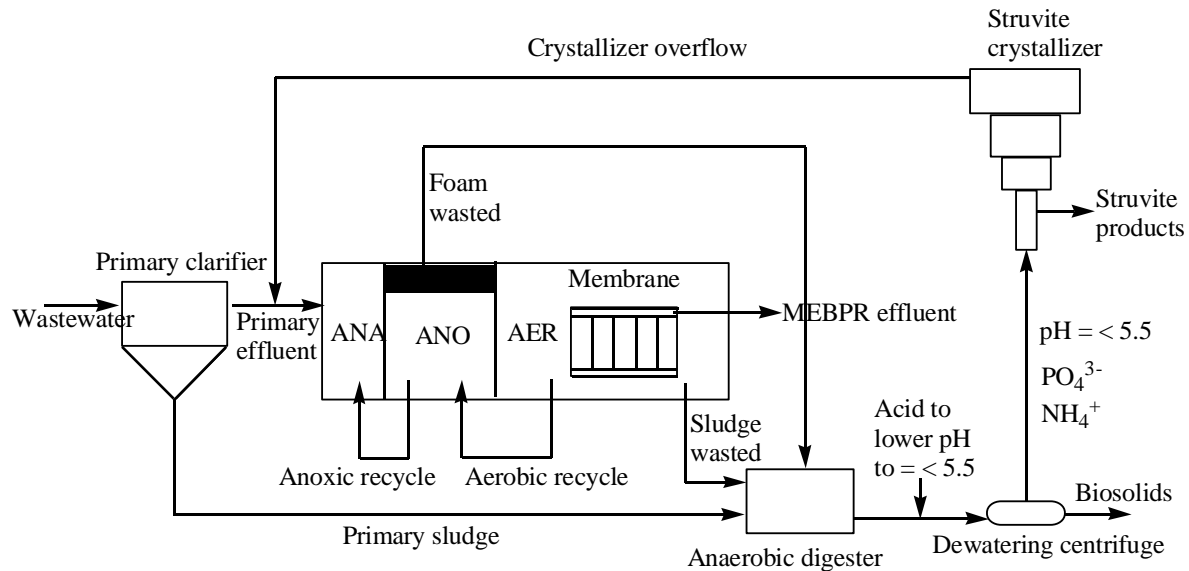


**Figure 6.1 Proposed system to recover phosphorus as struvite from an MEBPR process without MW-H$_2$O$_2$ AOP. Biosolids need to be disposed of or further treated.**

As a second generation process, Ostara uses a process called WASSTRIP, in which an anaerobic P-release unit is added before an anaerobic digester, to extract more phosphorus (Figure 6.2). As shown in Table 4.4 (Chapter 4), the maximum orthophosphate that could be extracted was found to be about 60 %, using anaerobic P-release. Therefore, by adding the anaerobic P-release, the WASSTRIP process could achieve a comparable $PO_4$-P extraction efficiency to that of the proposed system in Figure 6.1 (64 % at reduced pH, Table 4.7). However, the WASSTRIP process needs an extra anaerobic reactor and thickening centrifuge, and consumes about 2.2 g

180

acetate /g P released. One advantage of the process is that the digester size can be smaller than

that in Figure 6.1, due to the upstream sludge thickening.
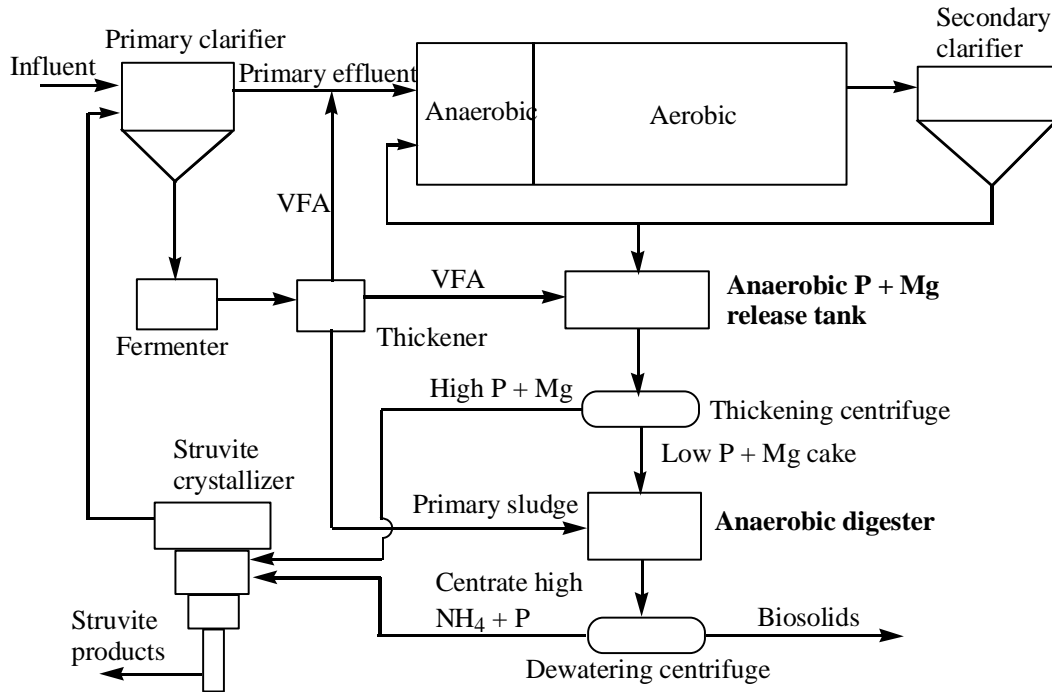


**Figure 6.2 Schematic representation of WASSTRIP process (Source: Ostara Nutrient Recovery Technologies Inc.).**

To better understand the proposed system shown in Figure 6.1, two scenarios were examined. In

case 1, all the waste biomass was assumed to be foam. The foam wasting may be achieved by so-

called "classifying selectors" (Parker et al., 2003). Experiments at SRT = 60 days showed that

the average suspended solids wasting rate would be 459 g TSS/ day for SRT control (Table 5.1).

By using TSS, TP, and TKN concentrations in foam from Table 4.5, the amount of wet foam to

be wasted was 11.3 kg/ day (TSS concentration 4.05 %), and the calculated the P:N ratio is about

1:3.7, as shown in Table 6.1. The centrate to the struvite crystallizer after anaerobic digestion

would contain about 1,080 mg/L $PO_4$-P and 1,670 mg/L $NH_4$-N (Table 4.6). The $PO_4$-P

concentration is thus 4.5 times what achievable by the WASSTRIP process, assuming that the

same waste sludge (TP 393 mg/L) produced by the Lulu Island WWTP is used in the

WASSTRIP process, and that an extraction efficiency of 60 % would result from the anaerobic

P-release. The increases are attributed to the MEBPR process, the long SRT, and the use of foam

as the phosphorus source.

**Table 6.1 Sample calculations when only foam is wasted for system in Figure 6.1**

| PO$_4$-P release | | NH$_4$- N release | |
|---|---|---|---|
| TP concentration in foam (mg/kg) | 1,829 [a] | TKN concentration in foam (mg/kg) | 3,333 [a] |
| TP in foam waste (g/d) | 21 | TKN in foam waste (g/d) | 40 |
| Extraction % (after pH lowered) | 64 [b] | Extraction % | 54 [b] |
| PO$_4$-P (g/d) | 13 | NH$_4$-N (g/d) | 22 |
| Molar number of P (mole/d) | 0.42 | Molar number of N (mole/d) | 1.57 |
| **P/ N molar ratio**: 0.42/ 1.57 = 1: 3.7 | | | |

Notes: (a) calculated from foam density 0.93 g/mL and TP or TKN concentrations in Table
4.5; and (b) value from Table 4.6 with low pH.

In case 2, all waste sludge was assumed to be aerobic zone mixed liquor, and the average data

from pseudo-steady state were used. The average TSS concentration in the aerobic zone ML was

$15,926 \pm 613$ mg/L (Section 2.3.3.1). Therefore, the waste sludge volume was calculated to be

29 L/day, based on the suspended solids wasting rate 459 g TSS/ day. The average TP and TKN

concentrations in aerobic zone ML were $676 \pm 56$ mg/L (Section 2.3.3.1) and $1,192 \pm 81$ mg/L

(n = 24), respectively. The calculated P:N ratio is about 1:3.4 (Table 6.2). The centrate to the

struvite crystallizer, after anaerobic digestion, would contain about 439 mg/L $PO_4$-P and 691 mg/L $NH_4$-N. In both case 1 and case 2, $NH_4^+$ would still be in excess, but both P:N ratios are much higher than the two (1:16 and 1:22) found in the typical centrates of two WWTPs in Metro Vancouver, as mentioned in Chapter 2. In both cases, the performances are comparable, except that case 1 requires a smaller anaerobic digester.

Compared to WWTPs using a conventional, non-EBPR process, the significant improvement of the P:N ratio in the proposed system means not only recovering significantly more phosphorus (due to higher TP/TSS) and corresponding $NH_4$, the higher P:N also means less $NH_4$ needs further treatment. When the P:N molar ratio is close to the ideal, less ammonia will be in the returned overflow. This helps to lower the costs incurred to remove ammonia in the MEBPR, since it is cheaper to remove ammonia through struvite precipitation than biological nitrification plus denitrification (Rob Simm, Stantec Inc., personal communication).

**Table 6.2 Sample calculations when only aerobic zone mixed liquor (ML) is wasted for system in Figure 6.1 (SRT = 60 days)**

| PO$_4$-P release | | NH$_4$- N release | |
|---|---|---|---|
| TP concentration in aerobic zone ML (mg/L) | 676 | TKN concentration in aerobic zone ML (mg/L) | 1,192 |
| TP in ML waste (g/d) | 20 | TKN in ML waste (g/d) | 35 |
| Extraction % (after pH lowered) | 65 [a] | Extraction % (after pH lowered) | 58 [a] |
| PO$_4$-P (g/d) | 13 | NH$_4$-N (g/d) | 20 |
| Molar number of P ( mole/d) | 0.42 | Molar number of N (mole/d) | 1.43 |
| PO$_4$-P conc. in centrate (mg/L) | 439 | NH$_4$-N conc. in centrate (mg/L) | 691 |
| **P/ N molar ratio**: 0.45/ 1.43 = 1: 3.4 | | | |

Notes: (a) value from Table 4.6 with low pH.

Chapter 5 showed that the energy cost at 60 days was 2.1 kWh/m$^3$ permeate, which was 120 %

higher than that at SRT of 25 days (0.94 kWh/m$^3$ permeate). This higher energy cost might be

offset by cost reductions resulting from a few additional considerations.

(1) Reduced sludge handling costs at SRT = 60 days. When sludge handling costs were included,

the operational cost at SRT = 60 days was only 70 % higher than that at SRT = 25 days.

(2) Reduced recycle of ammonium in struvitre crystallizer overflow to the MEBPR process.

Providing a slightly better P:N ratio in the feed to the struvite crystallizer (1:3.4 in Table 6.2),

when compared to the P:N ratio (1:4) at SRT= 25 days (Table 6.3). The calculations in Table 6.3

were based on the following data. At SRT =25 days, the daily waste solids Px,$_{TSS}$ was 571 g/d

(Table 5.1), and the average TSS concentration in the aerobic zone ML at pseudo-steady state

was 8,115 ± 587 mg/L (sample size n = 32). Therefore, the waste sludge volume was calculated

to be 70 L/day. The average TP and TKN concentrations in aerobic zone ML were 302 ± 48

mg/L (Section 2.3.3.1) and 620 ± 48 mg/L (n = 40).

It can be seen that the daily recovered phosphorus was similar (14 vs 13 g/d) at both SRT = 25

and 60 days, and this can be understood from the P mass balance. Because the TP loading in the

MEBPR influent was the same for both runs, and TP in the effluent was similar, therefore the

wasted P should be similar at both SRTs. The higher P:N ratio at 60 days mainly resulted from a

reduction in the amount of NH$_4$-N released in the centrate. (i.e., 20 g/d) that would serve as the

feed to a struvite crystallizer. Therefore, at SRT=25 days, more $NH_4$-N would be left in the crystallizer overflow, requiring further energy-intensive treatment.

**Table 6.3 Sample calculations when only aerobic zone ML is wasted at SRT = 25 days**

| PO₄-P release | | NH₄- N release | |
|---|---|---|---|
| TP concentration in aerobic zone ML (mg/L) | 302 | TKN concentration in aerobic zone ML (mg/L) | 620 |
| TP in ML waste (g/d) | 21 | TKN in ML waste (g/d) | 43 |
| Extraction % (after pH lowered) | 65 [a] | Extraction % (after pH lowered) | 58 [a] |
| PO₄-P (g/d) | 14 | NH₄-N (g/d) | 25 |
| Molar number of P ( mole/d) | 0.45 | Molar number of N (mole/d) | 1.8 |
| PO₄-P conc. in centrate (mg/L) | 196 [b] | NH₄-N conc. in centrate (mg/L) | 360 |
| **P/ N molar ratio**: 0.45/ 2.3 = 1: 4 | | | |

Notes: ( a) value from Table 4.7 with low pH. (b) = 302 mg/L $\times$ 65 %

(3) Reduced volume of daily sludge waste. At SRT = 60 days, the volume of daily waste sludge was calculated to be 29 L/day, compared to 70 L/day at SRT = 25 days. The reduced sludge volume should help to reduce sludge pumping costs and the size of storage tanks and reactors (e.g., anaerobic digester).

(4) At SRT = 60 days, the estimated PO₄-P concentration in centrate was more than twice that at SRT = 25 days, as shown in Table 6.4. It is not clear how the increased PO₄-P would influence crystallization efficiency and/or struvite crystal size, but the higher concentration product at SRT = 60 days should help to decrease the pH required for the crystallization. This would reduce the costs of chemicals used to adjust the pH for struvite crystallization.

**Table 6.4 Summary of PO$_4$-P and NH$_4$-N concentrations in centrate**

| System | PO$_4$-P in centrate (mg/L) | NH$_4$-N in centrate (mg/L) | Concentration product [c] | P:N molar ratio |
|---|---|---|---|---|
| MEBRP, SRT = 25 days | 196 [a] | 360 [a] | 70,560 | 1:4 |
| MEBRP, SRT = 60 days | 439 [b] | 691[b] | 303,349 | 1:3.4 |
| Local WWTP1, conventional non-EBPR | 149 | 1,057 | 157,493 | 1:16 |
| Local WWTP2, conventional non-EBPR | 76 | 757 | 57,532 | 1:22 |

Notes: (a) see Table 6.2; (b) see Table 6.3; (c) = PO$_4$-P in centrate (mg/L) $\times$ NH$_4$-N in centrate (mg/L).

In summary, the proposed system may be best recommended to WWTPs that are required to recover phosphorus and that currently have membrane bioreactors (MBRs) or will install membrane ultrafiltration to achieve a high effluent quality.

## 6.3 System with MW-H$_2$O$_2$ AOP

Anaerobic digestion is able to extract up to 64−65 % of the TP in aerobic zone ML or foam as PO$_4$-P. The PO$_4$-P is believed to come mainly from polyphosphate. The remaining 35 % of the total phosphorus is probably in the form of organically-bound phosphate. To oxidize this organic-P into PO$_4$-P, MW-H$_2$O$_2$ AOP can be employed in the system after anaerobic digestion, as shown in Figure 6.3. In this way, the MW-H$_2$O$_2$ AOP acts as a finishing step and can be operated more flexibly.

MW-$H_2O_2$ AOP has the potential to extract > 90 % of TP in foam as $PO_4$-P. However, there are a few drawbacks related to this technology. First, to date, no full-scale MW ovens have been developed that can be operated under pressure to reach a temperature of 180 ℃. Therefore, it is not practical to use MW-$H_2O_2$ AOP as the principal process to extract $PO_4$-P. Second, only at pH = 2, can significantly more $PO_4$-P be extracted, when compared to the system proposed in Figure 6.1. However, the need for a downstream pH increase from 2 to 7.2−7.8 prior to struvite crystallization is very significant and probably too expensive to implement. Third, MW-$H_2O_2$ AOP will also solubilize COD, suspended solids, and metals. How these components will affect the struvite crystallization is unknown. Considering these drawbacks, it is more practical to place the MW-$H_2O_2$ AOP after anaerobic digestion as a finishing step, rather than putting it before the digestion as the major process to extract $PO_4$-P. In the former case, MW-$H_2O_2$ AOP can be operated without lowering the pH, because its major function is to oxidize organically bound phosphorus to $PO_4$-P. As a finishing step, MW-$H_2O_2$ AOP can be adopted more flexibly (e.g., in a batch mode), or whenever justified.
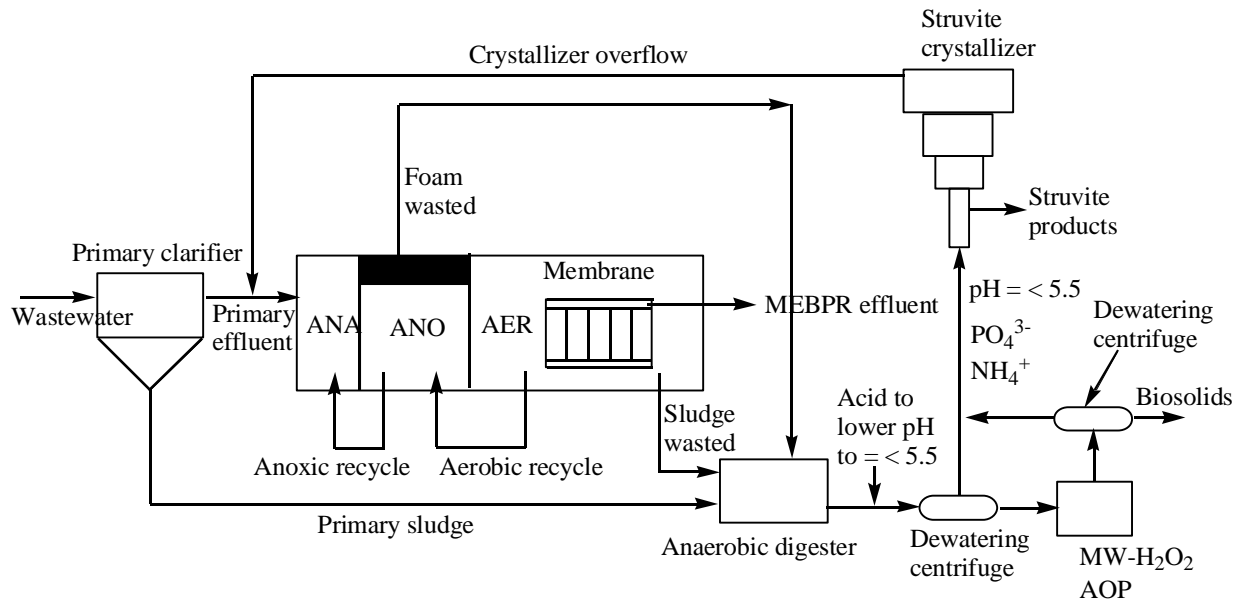
**Figure 6.3 Proposed system to recover phosphorus as struvite from an MEBPR process with MW-H$_2$O$_2$ AOP. Biosolids need to be disposed of or further treated.**

## 6.4 Conclusions

The above discussions suggest that the system in Figure 6.1 might be the best option so far, because it is the simplest one with a reasonably high phosphorus recovery. This system is also practical if the MEBPR process operating at SRT = 60 days can be upgraded to a full-scale application. The system with MW-H$_2$O$_2$ AOP adds a possibility to recover more than 65 % of incoming phosphorus, but this system strongly depends on the economic feasibility of employing the MW-H$_2$O$_2$ AOP.

# Chapter 7: Conclusions

## 7.1 Conclusions of this Dissertation

- An MEBPR pilot plant was successfully operated at three increasingly long SRTs to increase TP concentrations in mixed liquor so that phosphorus recovery could be made more cost-effective. Operations at two longer SRTs (i.e., 40 and 60 days) achieved comparable COD (91−92 %) and phosphorus (95−96 %) removal efficiencies to those of the control SRT = 25 days. The total nitrogen removal was increased from 61 % to 69 % and then 75 % when SRT was increased from 25 to 40 and 60 days.

- Although paired t-tests showed that at SRT = 60 days, the effluent average TP and $PO_4$-P concentrations were significantly higher than those at SRT = 25 days, all these values were so low that the differences did not affect phosphorus removal in practical terms. At SRT = 60 days, the median effluent TP and $PO_4$-P concentrations were 0.03 and 0.13 mg/L, respectively. The 95th percentile concentrations were 0.09 and 0.51 mg/L, respectively.

- Paired t-tests confirmed that the effluent $NO_X$-N, $NH_4$-N, and TN concentrations were significantly lower at SRT = 60 days than at 25 days. The effluent COD concentrations were comparable for both 60 and 25 days SRT operation.

- The average TP concentrations of aerobic zone ML were 302, 475, and 676 mg/L for SRT = 25, 40, and 60 day, respectively. The TP concentration at 60 days was 220 % of that at 25 days.

- Phosphorus mass balance calculations suggested that at SRT = 60 days, 78 % and 15 % of incoming TP was wasted with foam and aerobic zone ML, respectively. These values

were 52 % and 34 % at SRT = 40 days, and 30 % and 65 % at 25 days. This indicated

that the foam was the major phosphorus-carrying source at SRT = 60 days. The

phosphorus mass balances also showed that the combined errors from all the sources

were within ± 5.5 % for SRTs of 25 and 60 days,

- Nitrogen mass balance calculations showed that the unaccounted-for nitrogen removal

  was 22 %, 70 %, and 64 % of the incoming TN in influent wastewater at SRT = 25, 40,

  and 60 days, respectively. The unaccounted-for nitrogen removal was concluded to result

  from simultaneous nitrification and denitrification due to the low DO set point and the

  high TSS concentrations in the aerobic zone.

- Observed biomass yields were found to be 0.30, 027, and 0.25 g VSS/ g COD removed

  for SRT = 25, 40, and 60 day, respectively. Different from values reported by other

  researchers, these yields were calculated including foam in the solids inventory. The

  observed yield was reduced by 17 % at SRT = 60 days compared to that at 25 days;

  meanwhile the waste biomass volume was reduced by 68 % due to the fact that foam with

  a higher TSS concentration was the  major waste source at 60 days.

- Experiments showed that chemical cleaning frequencies of membranes were comparable

  for all three SRTs, with average service times of six to seven months. This proved that

  higher TSS concentration does not necessarily increase membrane fouling rate.

- Foam was characterized during operations at the three different SRTs. The median foam

  generation rates were 4.9, 7.8, and 11.3 kg wet foam/day (0.9, 1.5, and 2.1 $kg/m^3$

  wastewater treated) for SRT = 25, 40, and 60 days. A paired t-test confirmed that the

  foam generation rate was significantly higher at 60 days than at 25 days.

- It was found that rain precipitation events strongly influenced the foam generation rate at the UBC MEBPR pilot plant. An intermediate Pearson correlation suggested that rain water infiltrated the sewer from which influent wastewater was taken. A comparison study confirmed that reduced hydrophobicity of anoxic zone ML, associated with rainfall, likely reduced foaming potential and foam generation.

- The average foam TP concentrations were 1,060, 1,324, and 1,375 mg/L for SRT = 25, 40, and 60 days, respectively. The foam TP concentration at 60 days was comparable to that at 40 days, but both were significantly higher than the TP concentration at 25 days. When compared to the TP concentrations of respective aerobic zone ML, the foam TP concentrations were 350 %, 280 %, and 200 % as high for SRT = 25, 40, and 60 days, respectively, suggesting that TP partitioning between the foam and mixed liquor was different at different SRTs .

- The average TSS concentrations were found to be 33 g/ kg foam  when wet foam mass was ≤ 7 kg/day, and 38 g/ kg foam when the wet foam mass was > 7 kg/day.

- Paired t-tests confirmed that, at SRT = 60 days, the anoxic foam TP/TSS was significantly lower than the TP/TSS of underlying anoxic zone ML. On the contrary, the anoxic foam VSS/TSS and TKN/TSS ratios were significantly higher, and there was no significant difference for the COD/TSS. The higher VSS/TSS and lower TP/TSS suggested that foaming is a selective process, and PAOs tend to preferentially remain in the ML at this long SRT.

- Three operating variables—SRT, aerobic zone DO, and aerobic recycle ratio—were examined for their impacts on foam generation through factorial experiments, because they were controllable and relevant to foaming. From these experiments, we could not

191

conclude that any of these variables exhibited a significant effect within it examined range (SRT 25 to 40 days, DO 1 to 2 mg/L, and aerobic recycle ratio 0.75 to 1). However, the experiments suggested that SRT exhibited a positive relationship to foam generation, and aerobic zone DO and recycle ratio were negatively related to foam generation.

- Extraction of $PO_4$-P from aerobic zone ML and foam was evaluated on anaerobic P-release, MW-$H_2O_2$ AOP, and anaerobic digestion. All of the ML and foam samples were obtained from the UBC MEBPR pilot plant operating at SRT = 60 days. TP concentrations in these samples were high, ranging from 680−845 mg/L for the ML samples and about 1,700 mg//L for the foam samples. The anaerobic-P release could extract about 60 % of the TP after 8.5 hours, an efficiency that was close to the theoretical maximum. The P/ VFA ratio was found to be 0.42−043 g P/g COD. The anaerobic P-release method is best applied to ML, because the foam was too thick to avoid mass transfer limitations.

- The MW-$H_2O_2$ AOP treatment exhibited 85−87 % extraction efficiencies for the aerobic zone ML and a mixture of foam and aerobic zone ML (volume 1:1) under conditions of 180 ℃, pH = 3, and $H_2O_2$ = 0 .5 volume %. The MW-$H_2O_2$ AOP is more cost-effective to treat foam because foam contains less water.

- Anaerobic digestion achieved 44−46 % $PO_4$-P extraction efficiency at normal digestion pHs (7.28−7.38). When the pHs of digested samples were subsequently lowered to ≤ 5.5, the resulting overall $PO_4$-P extraction efficiencies increased to 64−65 % of the initial TP. Significant increases in $NH_4$-N and $Mg^{2+}$ concentrations concurrently suggested that solubilization of struvite precipitate occurred at the reduced pH.

192

- Anaerobic digestion produced 0.25−0.29 L methane per gram added VS of foam or aerobic zone ML. Anaerobic digestion also reduced COD by 54−69 %. For the samples pretreated with MW-$H_2O_2$ AOP, the COD reduction reached more than 90 %.

- Although MW-$H_2O_2$ AOP could produce some released $NH_4$-N, anaerobic digestion was the only technology that could produce sufficient $NH_4$-N to crystallize all the released $PO_4$-P into struvite. Therefore, anaerobic digestion becomes a necessary component in the proposed system for phosphorus recovery.

- MW-$H_2O_2$ AOP treatment significantly improved the settling and dewatering properties of ML and foam samples except for the ML samples that were pretreated by anaerobic P-release. In general, anaerobic digestion worsened the settling and dewatering characteristics of ML and foam.

- Biological aeration (for reaction) and membrane aeration (for scouring) comprised 92.0 %, 93.2 %, and 96.5 % of the total energy requirements for SRT = 25, 40, and 60 days, respectively. The energy required for biological aeration increased from 52.0 % at 25 days to 79.1 % at 60 days.

- Energy requirements were estimated to be 0.94, 1.1, and 2.1 kWh/$m^3$ of permeate produced for SRT = 25, 40, and 60 days, respectively. All these values were within the reported range of 0.5−2.5 kWh/$m^3$ permeate for full-scale MBRs, suggesting that it could be economically feasible to apply these SRTs in practice.

- Operational costs of a conceptual full-scale MEBPR plant were evaluated at three different SRTs of 25, 40, and 60 days. Biological aeration (for reaction), membrane aeration (for scouring), and sludge handling and disposal comprised the major operational costs, totaling CAD $ 0.13, 0.14, and 0.22 /$m^3$ permeate, respectively.

- A sensitivity analysis was conducted on three major parameters, the α-factor for biological aeration, the specific aeration demand (SADm) for membrane scouring, and the sludge handling and disposal cost per unit tonne of dry solids. The analysis showed that α-factor was the most significant parameter affecting operational costs.

- From the viewpoints of economics only, MBRs are only comparable to conventional activated sludge processes (CASPs) when stringent effluent quality is mandated, and a long SRT of 60 days is economically feasible when an extra benefit is recognized from phosphorus recovery.

- Two integrated systems were proposed to recover phosphorus as struvite. Utilizing an MEBPR process operating at SRT = 60 days, these systems could potentially recover 60 % of the incoming TP without an MW-$H_2O_2$ AOP, and more than 80 % when an MW-$H_2O_2$ AOP is added.

## 7.2   Contributions of this Dissertation

This research has made several significant and novel contributions.

- A long-SRT operation was previously believed to compromise phosphorus removal efficiency, resulting in elevated effluent phosphorus concentrations. The present study demonstrated  that operation of an MEBPR process at SRT = 60 days could achieve similar phosphorus removal efficiencies to those reported at SRT = 25 days, when the influent VFA/TP ratio, DO concentration in aerobic zone, and aerobic recycle ratio are carefully controlled.

- Common practice does not included foam in the estimation of suspended solids inventory, therefore excluding foam from process SRT control calculations. The present study demonstrates that foam should be included because it is an active component of the MEBPR process. This research also showed how the process SRT could be controlled by wasting of foam (and mixed liquor).

- Foaming in wastewater treatment bioreactors has long been an operational nuisance. the present study research demonstrated how the foam, after being wasted from the process for SRT control, could be utilized as an alternative resource for phosphorus recovery. Foam was characterized at three different SRTs (25, 40, and 60 days) and its properties are now better understood.

- Current phosphorus recovery systems use anaerobic digester centrate as the feed to a struvite crystallizer, and the P:N molar ratios in the centrate from non-EBPR processes can be very low (e.g., 1:16, 1:22). The present research proposes a new system that could improve the P:N ratio to about 1:4 in the centrate. By incorporating an MEBPR process operating at SRT = 60 days, this system could also produce high quality effluent and generate less waste sludge.

## 7.3    Strengths and Limitations of the Research

The majority of this research was completed on a MEBPR pilot plant that treated real domestic wastewater, at a capacity of about 5,300 L/d for a total operating time of 15 months. In this context, the data obtained from the study are considered to be more relevant to full-scale application, than data obtained from batch or small pilot-scale studies. All the batch tests

195

associated with $PO_4$-P extraction (Chapter 4) used mixed liquor and foam generated from the pilot plant, so the characteristics of these samples were also considered to be representative of those generated from a full-scale WWTP. Overall, the results and knowledge obtained in this study provided valuable information to improve real engineering practices.

There are a few limitations for this research. First, for the systems in Figure 6.1, the crystallizer overflow is proposed to recycle back to the mainstream MEBPR. This recycle is desirable since currently, the crystallizer recovers about 90–95 % of $PO_4^{3-}$ in the feed. There is still some $PO_4^{3-}$ in the overflow, and the overflow also needs to be disposed of. However, during the time the research was conducted, there was no pilot-scale crystallizer with the capacity that matched the capacity of the UBC MEBPR process. Consequently, it was impossible to test how this recycled overflow would influence the mainstream MEBPR process. Second, due to limited time for the entire research, treatment of primary sludge was not assessed. Primary sludge could be either co-digested with the secondary sludge and foam as proposed in Figure 6.1, or fermented separately to provide VFA for the MEBPR process, or both, as proposed in the WASSTRIP process (Figure 6.2).

## 7.4   Future Work

To complete the systems in Figures 6.1 and 6.3, some further studies are needed.

- To pilot test how the effluent of a struvite crystallizer will affect the MEBPR process, if the effluent is returned to the MEBPR process.
- To test the feasibility of co-digestion with primary sludge and wasted ML and foam.
- To incorporate MW-$H_2O_2$ AOP and test the system (Figure 6.3) at a pilot scale, once the

microwave oven is available.

A few interesting phenomena were observed during this research and need further investigation.

- The first one is the unaccounted-for N removal (60−70 % of total TN removal) at the two longer SRTs (40 and 60 days), for which SND was considered as the cause. This needs to be verified and research might be conducted on how to control/ manage the SND.

- The second one was the stable membrane TMP at SRT = 60 days for four months, in spite of high TSS in the aerobic zone. Is this a random event or is there something related to foaming?

- The third one is about reduced foaming during rainy days. The question of why rain reduces foaming is still not fully answered. This phenomenon has never been reported before and may be associated with some parameters not commonly studied such as Zeta potential, pH, and viscosity. Although fully understanding the foaming mechanisms remains as a research interest, in practice, some measures can be adopted to promote foam against the rain impact; for example, better storm water management to reduce infiltration into the sewer, better design of plant configuration (e.g., proper location of mixer blade), using a equalization tank to store foam, and further increasing SRT.

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# Appendices
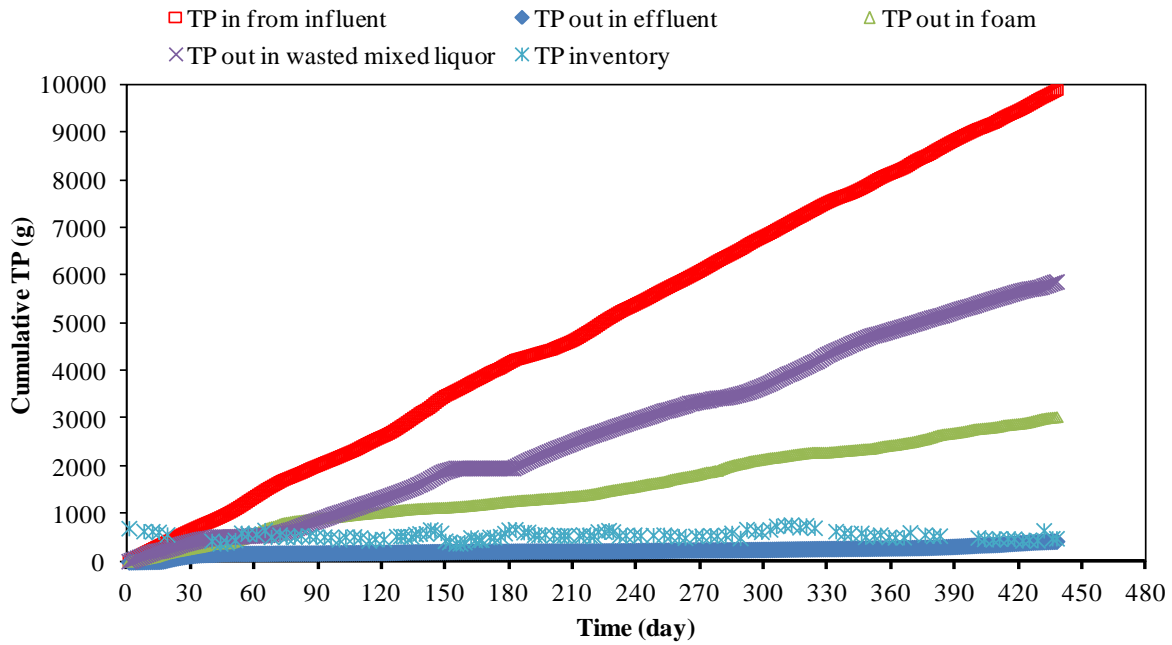
## Appendix A  Additional Figures and Tables



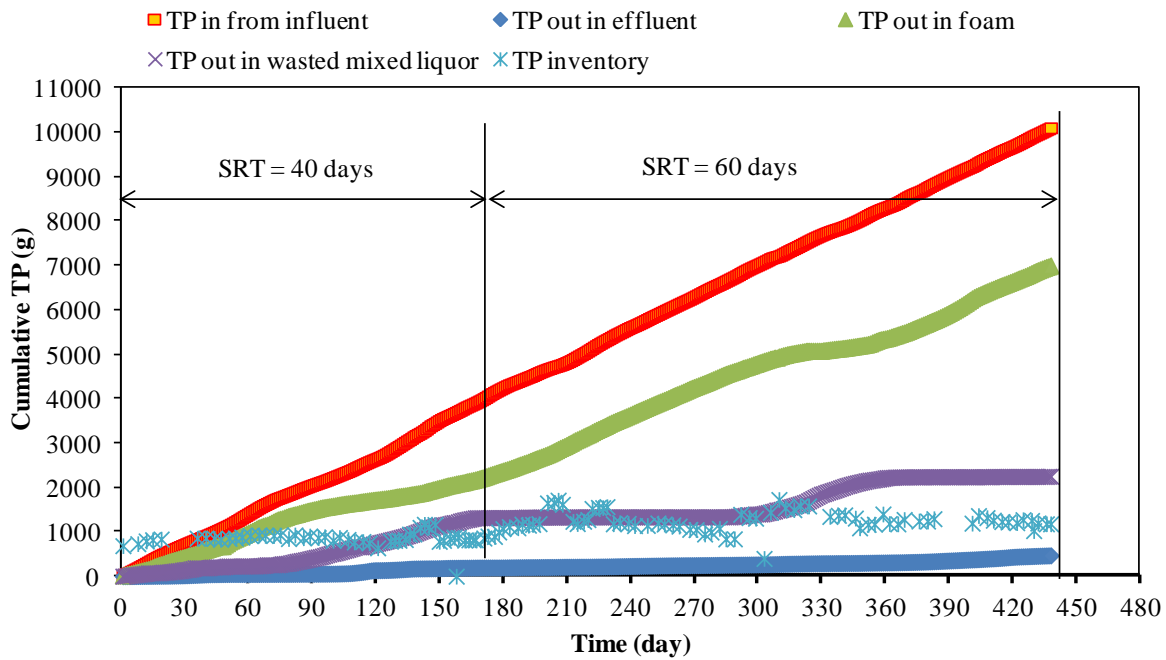**Figure A1 Cumulative TP mass flows for phosphorus balance at SRT = 25 days.**



**Figure A2 Cumulative TP mass flows for phosphorus balance at SRT=40 days and 60 days.**
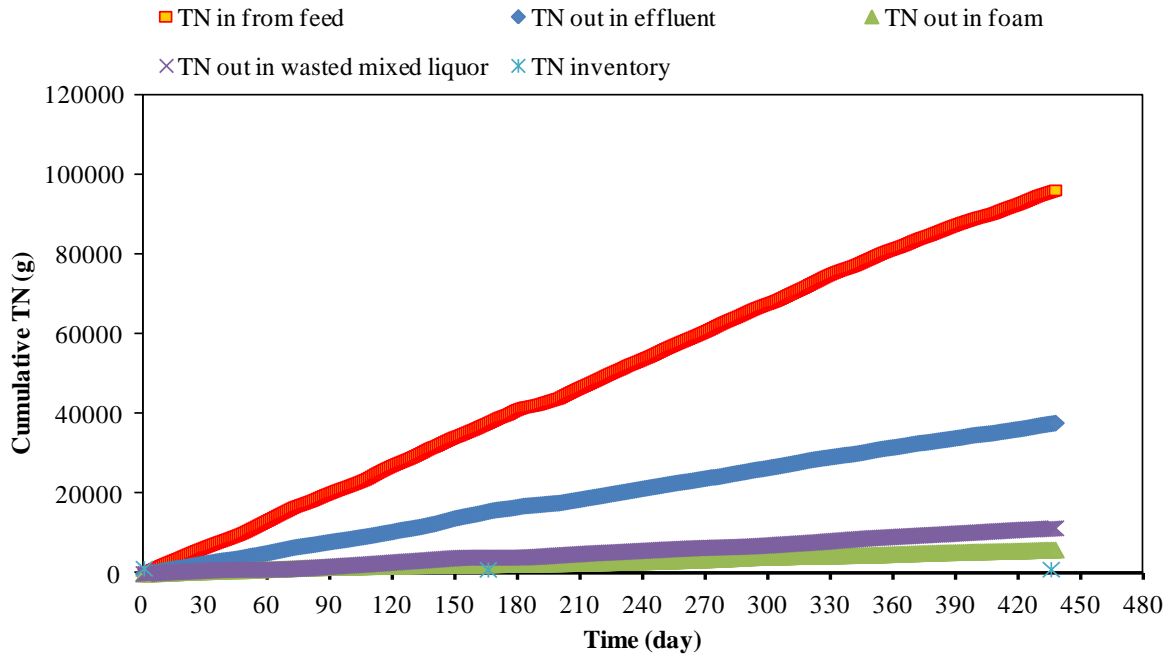
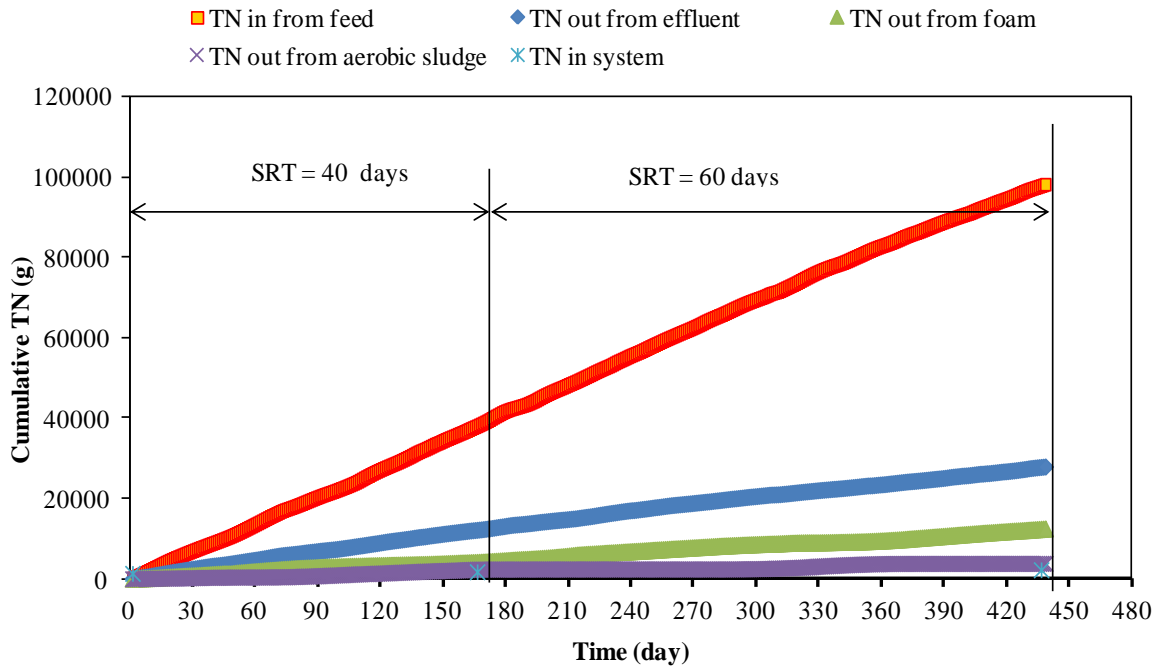**Figure A3 Cumulative TN mass flows for nitrogen balance over entire system at SRT = 25 days.**



**Figure A4 Cumulative TN mass flows for nitrogen balance over entire system at SRT = 40 days and 60 days.**
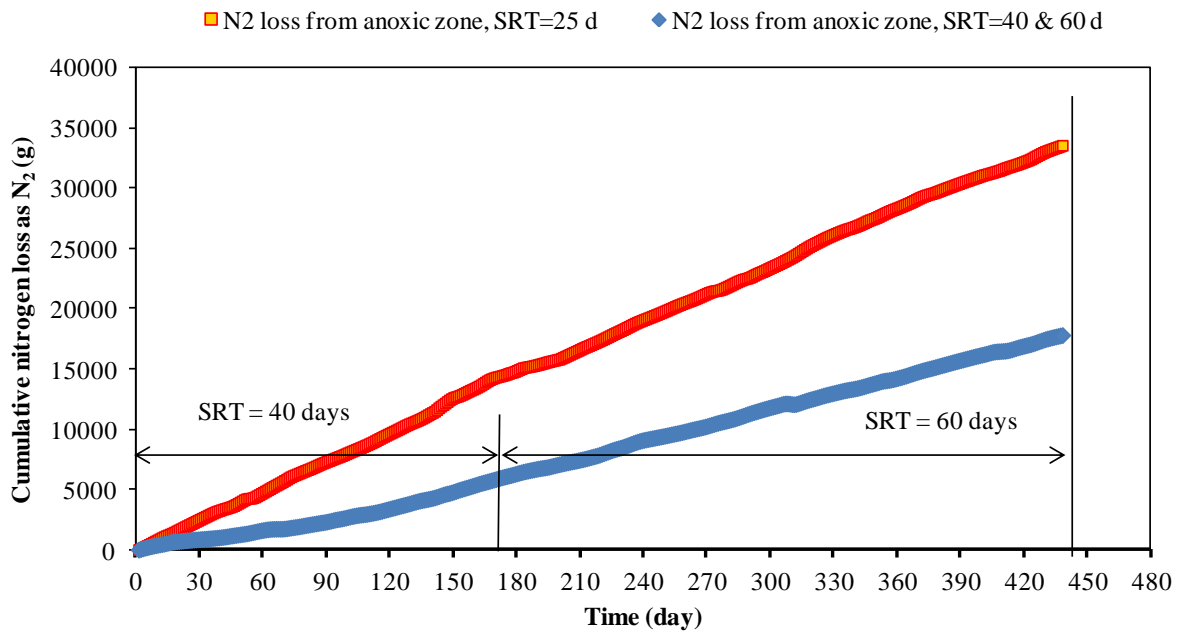
**Figure A5 Cumulative nitrogen removal as N$_2$ for NOx-N mass balance over anoxic reactors at three SRTs.**
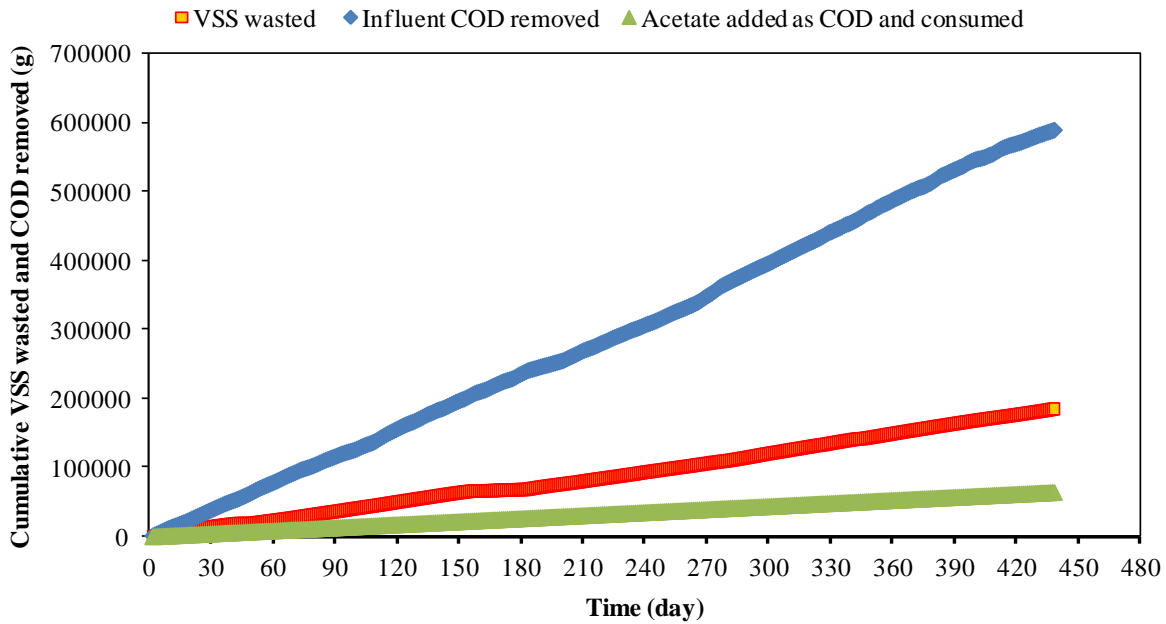


**Figure A6 Cumulative VSS increased and COD removed at SRT = 25 days.**
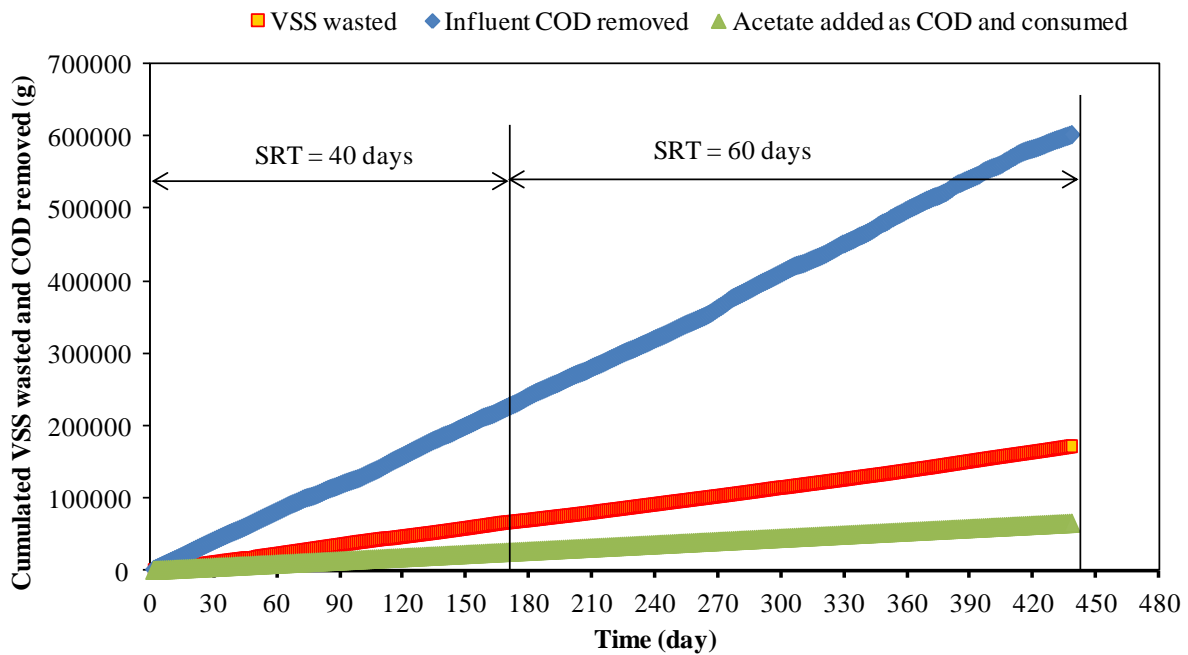
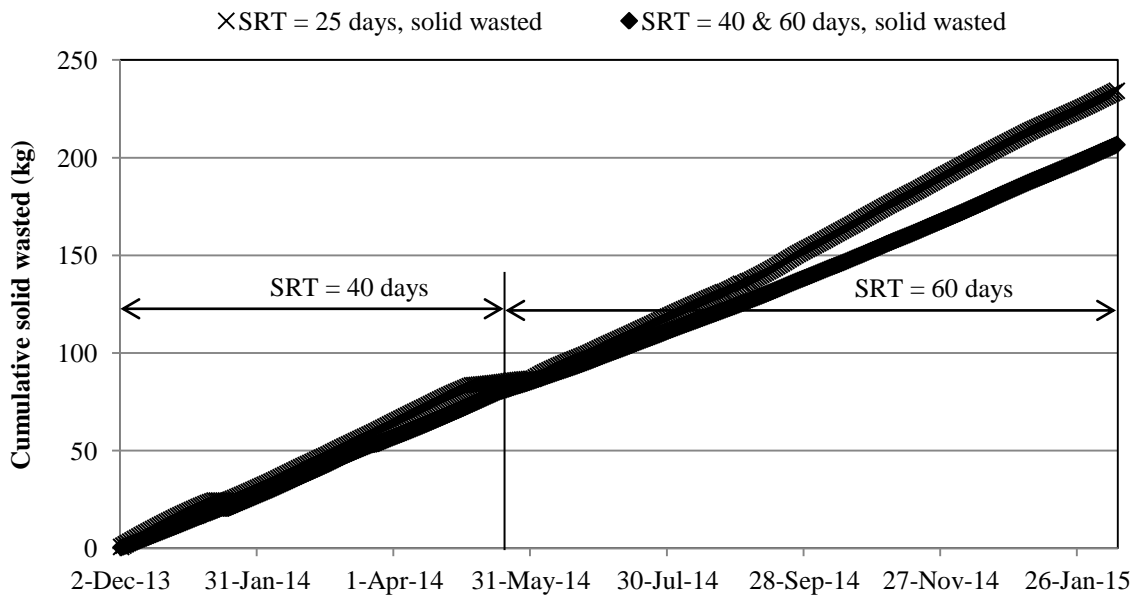**Figure A7 Cumulative VSS increased and COD removed at SRT=40 and 60 days.**



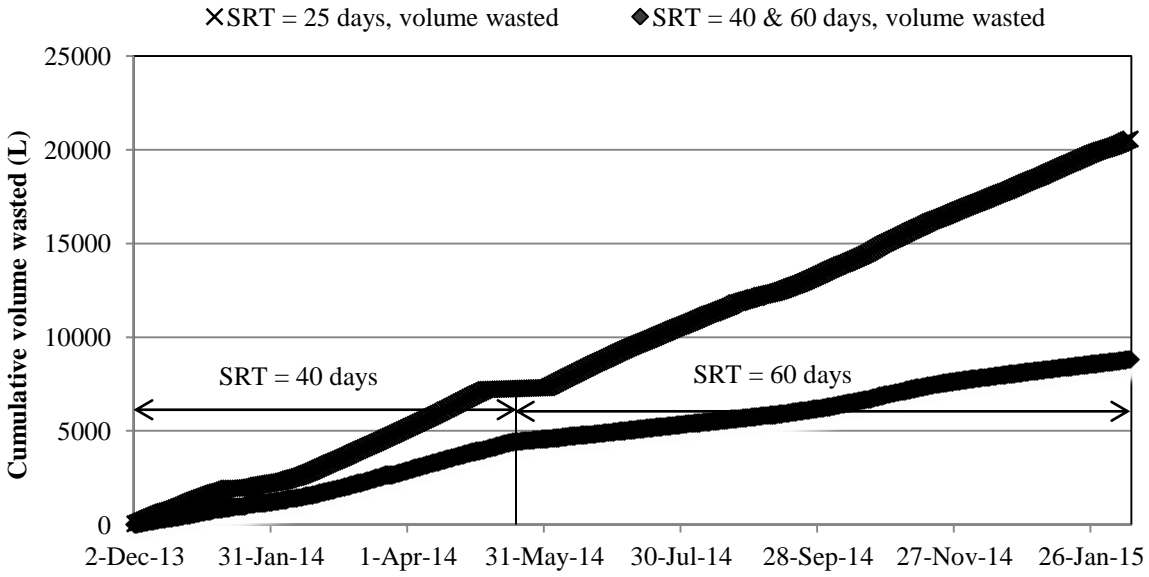**Figure A8 Cumulative dry solids wasted in foam and aerobic zone mixed liquor.**

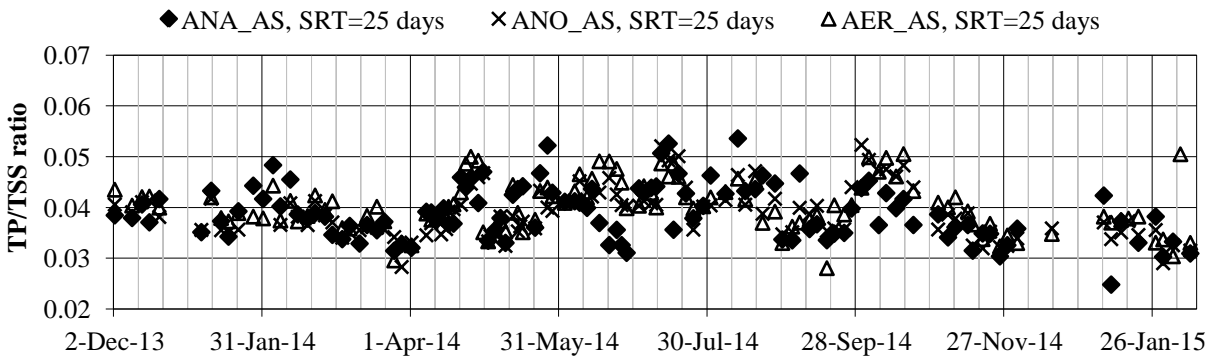**Figure A9 Cumulative volume of wasted foam and aerobic zone mixed liquor.**



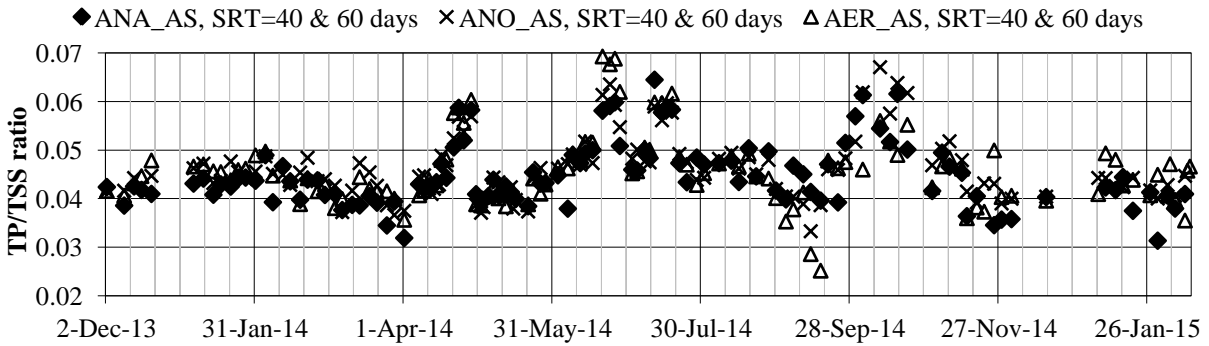**Figure A10 TP/TSS ratios of mixed liquor in each zone at SRT = 25 days.**



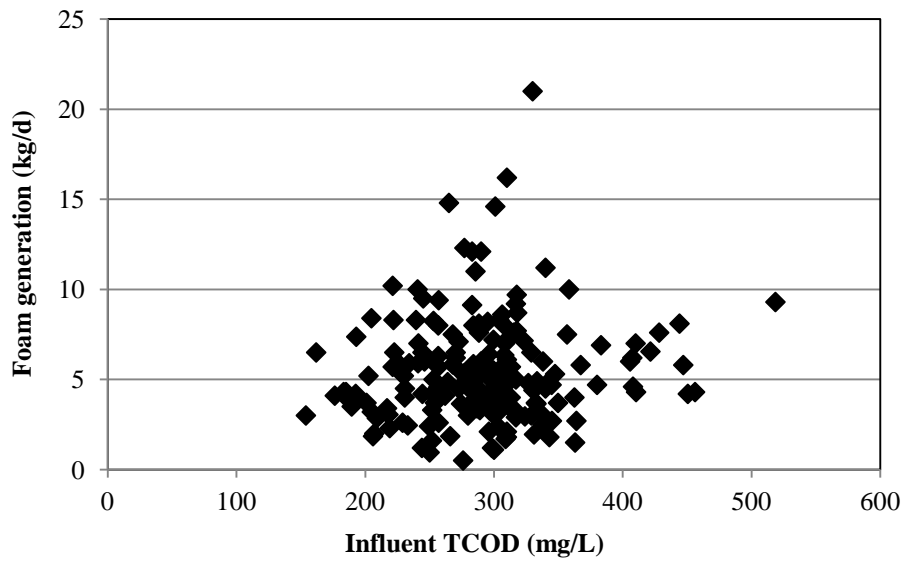**Figure A11 TP/TSS ratios of mixed liquor in each zone at SRT = 40 and 60 days.**

213

**Figure A12 Correlation between foam generation and influent TCOD.**
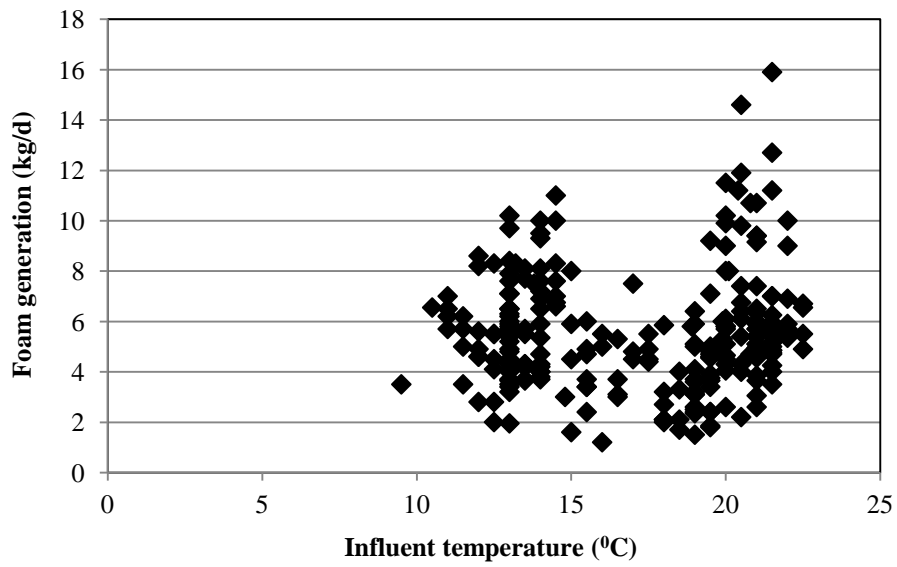


**Figure A13 Correlation between foam generation and influent temperature.**
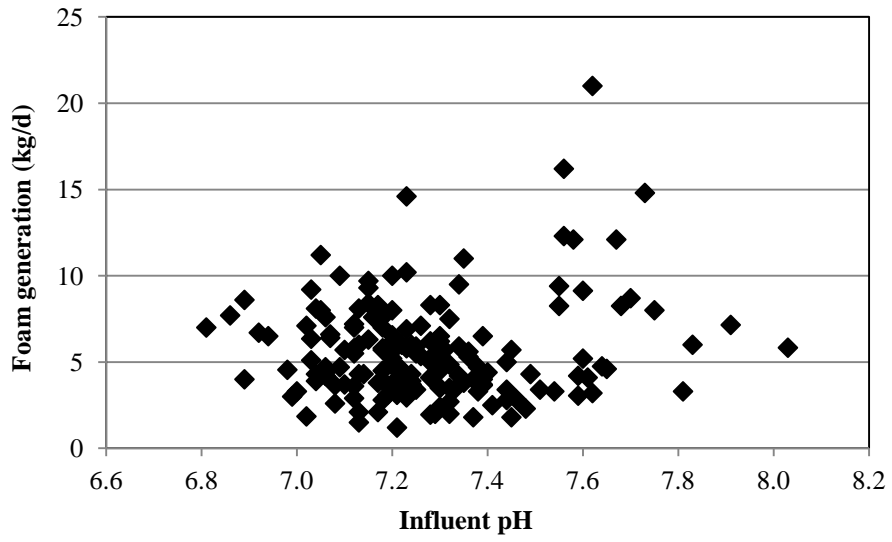
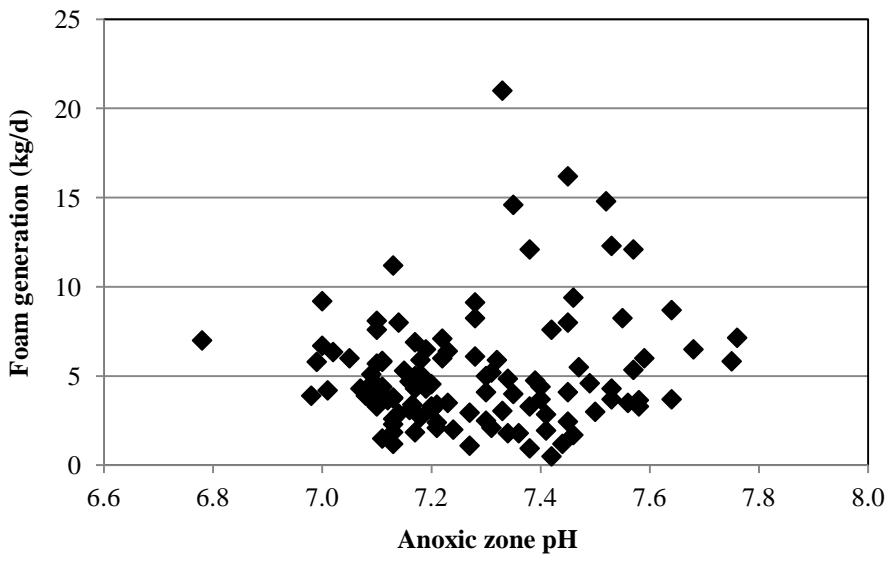**Figure A14 Correlation between foam generation and influent pH.**



**Figure A15 Correlation between foam generation and anoxic zone pH.**
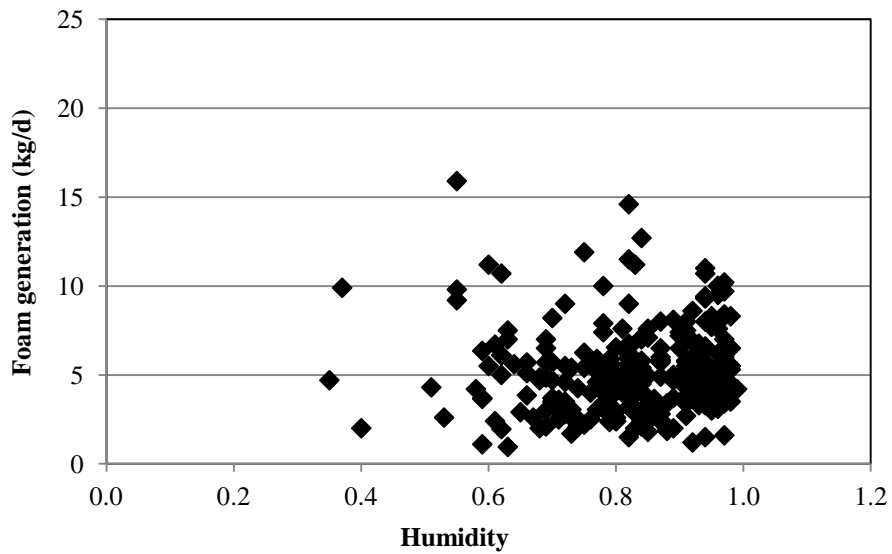
**Figure A16 Correlation between foam generation and atmospheric humidity.**



**Figure A17 Cumulative biogas production from "ML + P-release" sample (Group 3), calculated over daily averaged biogas production from all serum bottles in one group.**

**Figure A18 Cumulative biogas production from "Foam + MW" sample (Group 4), calculated over daily averaged biogas production from all serum bottles in one group.**



**Figure A19 Cumulative biogas production from "ML + P-release + MW" sample (Group 5), calculated over daily averaged biogas production from all serum bottles in one group.**

217

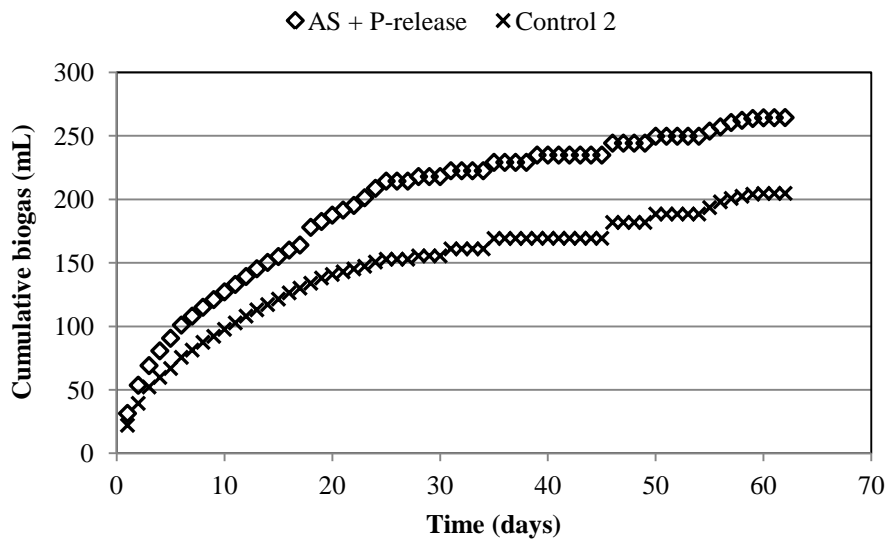**Figure A20 Cumulative biogas production from "ML + Foam" sample (Group 6), calculated over daily averaged biogas production from all serum bottles in one group.**

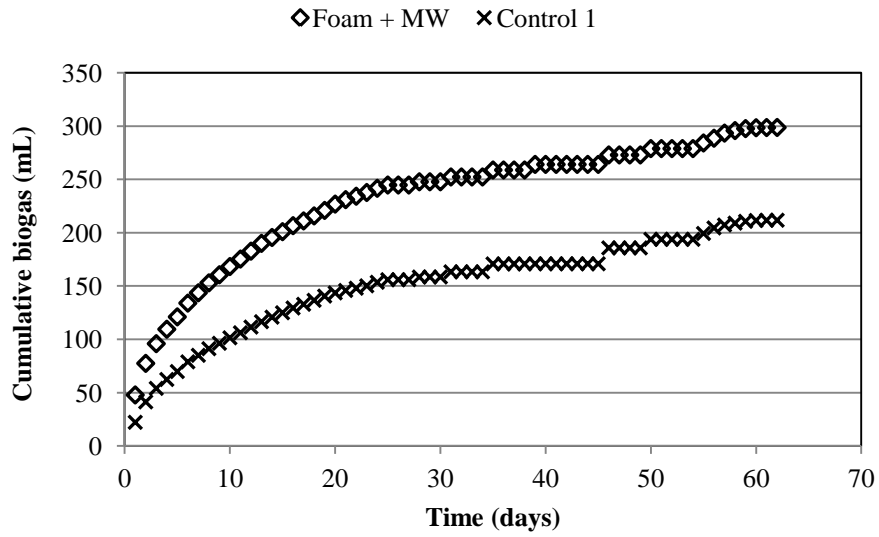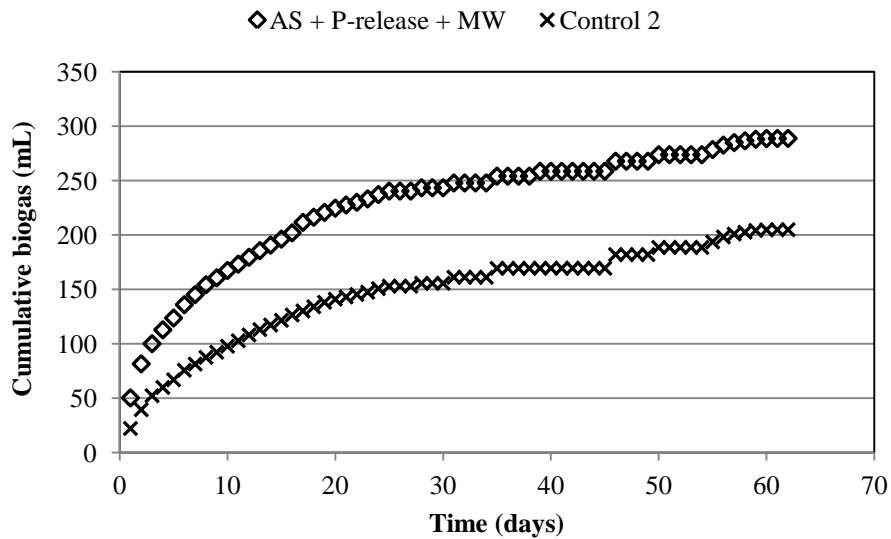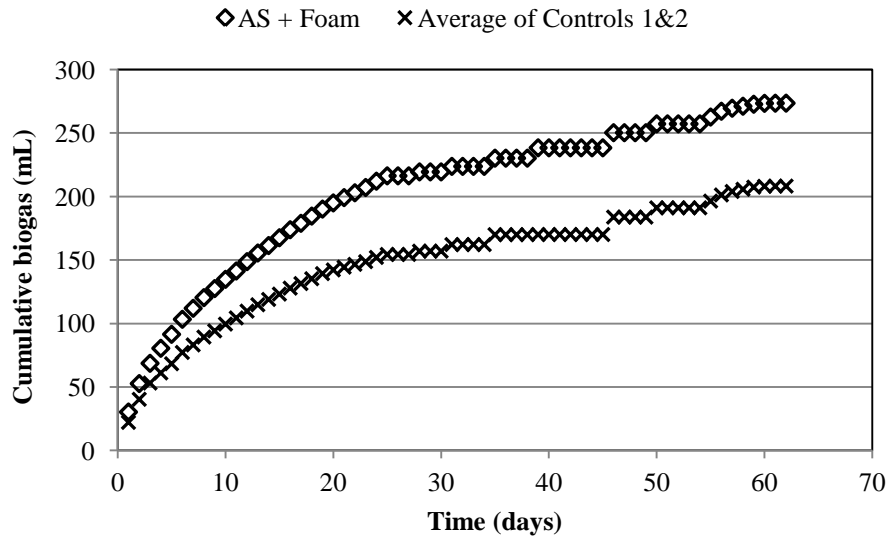**Table A1 Phosphorus mass balance components at SRT of 25 and 60 days for 271 days operation. The low- and high-end foam TSS values defined by the 95 % CIs were used for calculations**

| Cumulative mass flows | SRT = 25 days | | SRT = 60 days | |
|---|---|---|---|---|
| | TSS = 31.8 | 34.6 g/kg foam | TSS = 37.5 | 39.3 g/kg foam |
| $TP_{INF}$, g | 6,026 | 6,026 | 6,205 | 6,205 |
| $TP_{FOAM}$, g | 1,725 (29 %) [c] | 1863 (31 %) | 4,766 (77 %) | 4970 (80 %) |
| $TP_{AS}$, g | 3,913 (65 %) | 3,913 (65 %) | 936 (15 %) | 936 (15 %) |
| $TP_{EFF}$, g | 215 (4 %) | 215 (4 %) | 276 (4 %) | 276 (4 %) |
| $\Delta TP$ in system, g | 32 | 32 | 360 | 360 |
| Balance [a], g | 141 | 3 | -133 | -337 |
| Error, % [b] | 2.3 | 0.05 | -2.1 | -5.4 |

Notes: (a) balance is equal to the right-hand side of Equation (2.5); (b) error was calculated by balance / $TP_{INF}$; and c) percentages were based on $TP_{INF}$.

**Table A2 Nitrogen mass balance at SRT of 25 and 60 days for 271 days operation. The low- and high-end foam TSS values defined by the 95 % CIs were used for calculations**

| Cumulative mass flows | SRT = 25 days | | SRT = 60 days | |
|---|---|---|---|---|
| | TSS = 31.8 | 34.6 g/kg foam | TSS = 37.5 | 39.3 g/kg foam |
| $TN_{INF}$, g | 58,152 | 58,152 | 59,872 | 59,872 |
| $TN_{FOAM}$, g | 3,489 | 3,765 | 8,922 | 9,302 |
| $TN_{AS}$, g | 7,359 | 7,359 | 1,440 | 1,440 |
| $TN_{EFF}$, g | 22,088 | 22,088 | 15,700 | 15,700 |
| $\Delta TN$ in system, g | 42 | 42 | 493 | 493 |
| Total $N_2$ removed from system [a], g | 24,957 | 24,898 | 33,317 | 32,937 |
| $N_2$ removed from anoxic zone, g | 19,445 | 19,445 | 12,097 | 12,097 |
| Unaccounted-for N removal [b] | 22 % | 22 % | 64 % | 63 % |

Note: (a) Calculated based on Equation (2.7); (b) = (total removal − removal from anoxic zone)/ total removal.

**Table A3 Results of four fractional factorial experiments**

| | | Mass | Density | VSS/TSS (%) | | TSS | | TP | | TKN | | TCOD | | PO$_4$-P (mg/L) | | NO$_X$-N (mg/L) | | NH$_4$-N (mg/L) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exp. | Day | Foam (kg) | Foam (g/mL) | Foam | ML | Foam (%) | ML (mg/L) | Foam (mg/kg) | ML (mg/L) | Foam (mg/kg) | ML (mg/L) | Foam (g/kg) | ML (mg/L) | Foam | ML | Foam | ML | Foam | ML |
| 1 | 1 | 3.4 | 0.94 | 0.74 | 0.8 | 2.62 | 4150 | 954 ± 73 | 155 ± 8 | 2009 ± 88 | 318 ± 18 | 27.8 | 5.01 | n/a | 7.48 | n/a | 0.46 | n/a | 17.1 |
| | 2 | 2.9 | 0.903 | 0.71 | 0.78 | 3.16 | 4120 | 922 ± 24 | 143 ± 1 | 2007 ± 33 | 326 ± 7 | 40.9 | 5.34 | 6.53 | 3.3 | 3.83 | 0.3 | 6.49 | 16.6 |
| | 3 | 2.9 | 0.878 | 0.83 | 0.84 | 3.02 | 3930 | 913 ± 22 | 150 ± 1 | 1980 ± 12 | 326 ± 1 | 38.0 | 4.92 | 7.09 | 8.8 | 3.29 | 0.4 | 8.08 | 19.5 |
| | 4 | 3.7 | 0.897 | 0.92 | 0.83 | 2.73 | 4140 | 923 ± 66 | 148 ± 12 | 2144 ± 87 | 333 ± 11 | 35.4 | 4.71 | 30.44 | 1.22 | 3.44 | 0.3 | 11.8 | 18.1 |
| 2 | 1 | 4.5 | 0.974 | 0.83 | 0.82 | 3.11 | 3750 | 930 ± 15 | 125 | 2243 ± 44 | 297 | 30.0 | n/a | 4.34 | 10.8 | 0.64 | 0.17 | 18.5 | 16.9 |
| | 2 | 3.2 | 0.951 | 0.83 | 0.81 | 3.13 | 2850 | 893 ± 23 | 98 ± 3 | 1886 ± 254 | 242 ± 7 | 35.5 | 2.98 | 4.78 | 10.35 | 0.63 | 0.63 | 18.1 | 23.9 |
| | 3 | 2.8 | 0.963 | 0.86 | n/a | 3.29 | 2700 | 1106 ± 53 | 98 | 2676 ± 134 | 240 | 31.7 | 2.63 | 54.55 | 15.8 | 0.75 | 0.63 | 22.8 | 26 |
| | 4 | 3.6 | 0.963 | 0.81 | 0.82 | 2.98 | 3170 | 1132 ± 6 | 118 | 2701 ± 60 | 277 | 36.6 | 3.8 | 55.5 | 14.7 | 0.79 | 0.06 | 26.55 | 18.4 |
| 3 | 1 | 4.6 | 0.914 | 0.79 | 0.77 | 3.1 | 7300 | 1223 ± 24 | 299 ± 1 | 2480 ± 98 | 585 ± 8 | 36.0 | 8.97 | 5.65 | 1.3 | 3.25 | 1.4 | 4.43 | 9.66 |
| | 2 | 4.7 | 0.891 | 0.68 | 0.78 | 3.56 | 7190 | 1212 ± 20 | 302 ± 9 | 2437 ± 37 | 555 ± 33 | 41.8 | 8.08 | 3.61 | 0.19 | 3.91 | 0.33 | 3.54 | 8.47 |
| | 3 | 4.5 | 0.891 | 0.84 | 0.81 | 3.47 | 7220 | 1308 ± 166 | 311 ± 11 | 2155 ± 106 | 529 ± 29 | 37.8 | 8.19 | 3.46 | 2.48 | 4.26 | 2.17 | 3.86 | 10.6 |
| | 4 | 5.1 | 0.888 | 0.87 | 0.81 | 3.37 | 7390 | 1277 ± 77 | 317 ± 15 | 2346 ± 123 | 612 ± 52 | 37.4 | 8.78 | 4.48 | 0.24 | 3.41 | 0.85 | 4.08 | 8.64 |
| 4 | 1 | 10.1 | 0.974 | 0.78 | 0.76 | 4.06 | 7980 | 1407 ± 29 | 296 | 2674 ± 160 | 578 | 38.0 | n/a | 6.61 | 4.71 | 0.63 | 0.04 | 11.4 | 10.1 |
| | 2 | 8.7 | 0.969 | 0.8 | 0.76 | 3.91 | 8050 | 1329 ± 38 | 308 ± 8 | 2429 ± 184 | 595 ± 32 | 41.2 | 8.06 | 5 | 3.93 | 0.64 | 0.64 | 9.66 | 10.25 |
| | 3 | 6.4 | 0.952 | 0.89 | n/a | 3.39 | 7720 | 1398 ± 47 | 293 | 2842 ± 119 | 609 | 35.0 | 8.06 | 32.35 | 5.96 | 1.16 | 0.63 | 6.33 | 9.24 |
| | 4 | 7.0 | 0.963 | 0.83 | 0.78 | 3.32 | 7850 | 1436 ± 37 | 312 | 2958 ± 93 | 614 | 43.8 | 7.94 | 36.75 | 4.44 | 0.94 | 0.09 | 7.93 | 7.52 |

Notes: foam — anoxic zone foam; ML — anoxic zone mixed liquor.

# Appendix B  Statistical Analysis

## B.1    Normality tests of PO$_4$-P, TP, COD concentrations in effluent, TSS in foam at three SRTs by Anderson-Darling test

Note: A P-value <0.05 suggests the population does not follow a normal distribution.
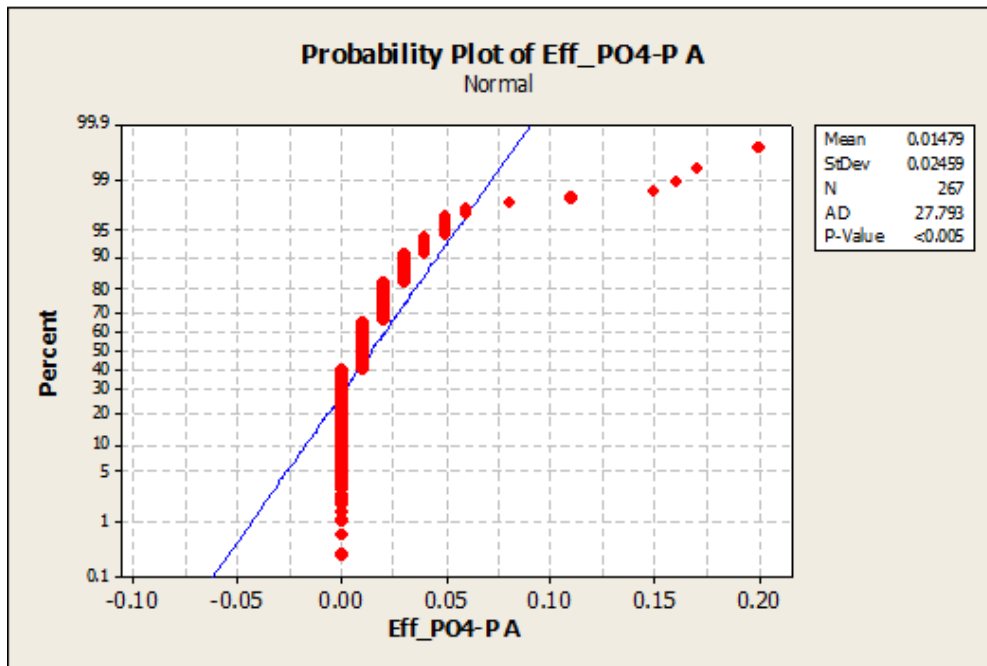


**Figure B1 Normality test for effluent PO$_4$-P concentrations at SRT=25 days (May 18, 2014 to Feb. 12, 2015)**
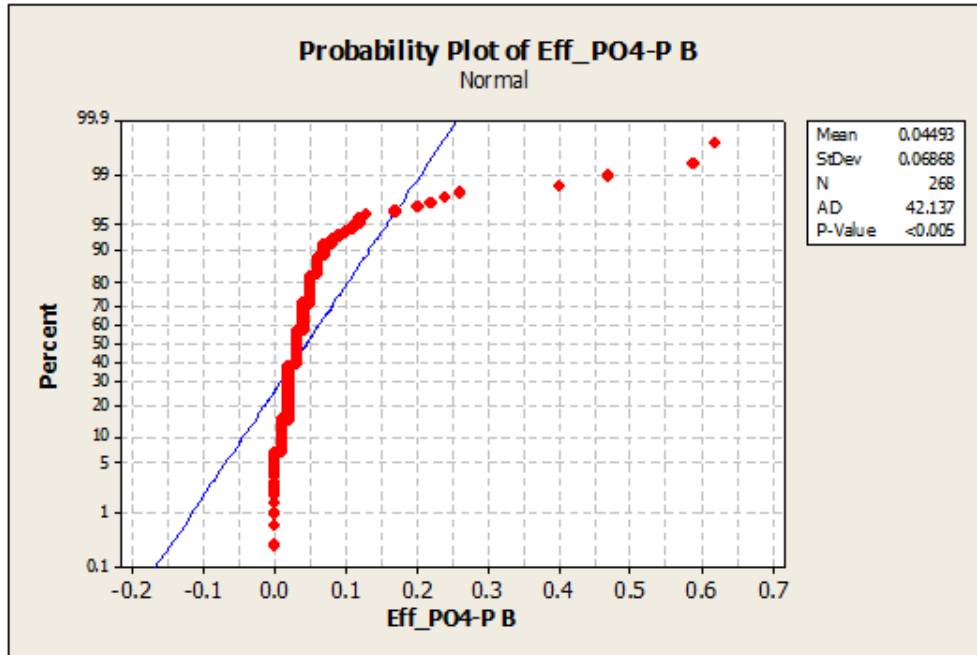
**Figure B2 Normality test for effluent PO₄-P concentrations at SRT=60 days (May 18, 2014 to Feb. 12, 2015)**



**Figure B3 Normality test for effluent TP concentrations at SRT=25 days (May 18, 2014 to Feb. 12, 2015)**
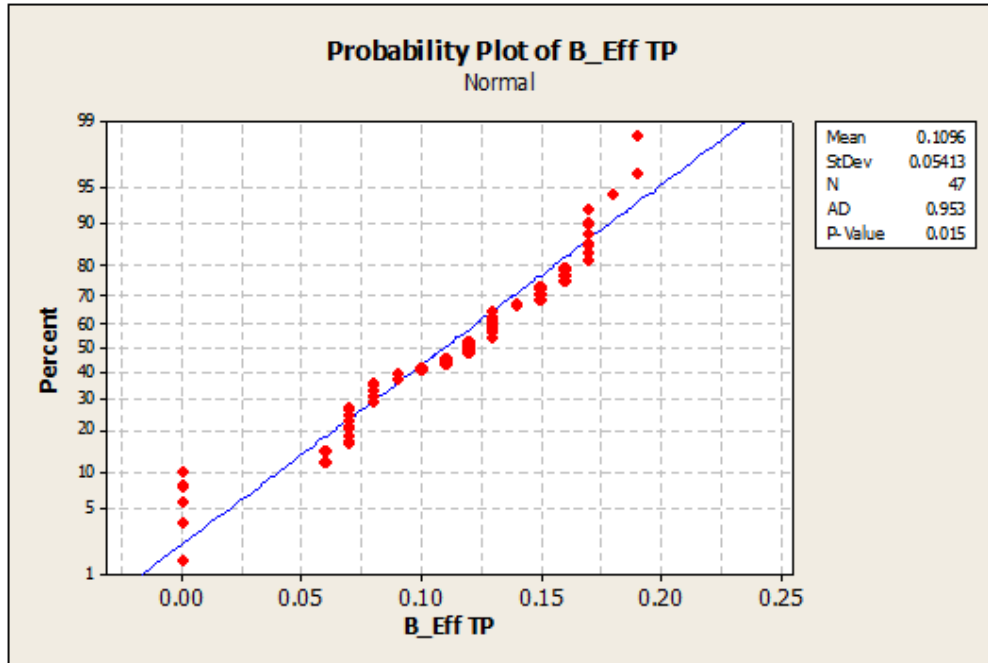
**Figure B4 Normality test for effluent TP concentrations at SRT=60 days (May 18, 2014 to Feb. 12, 2015)**
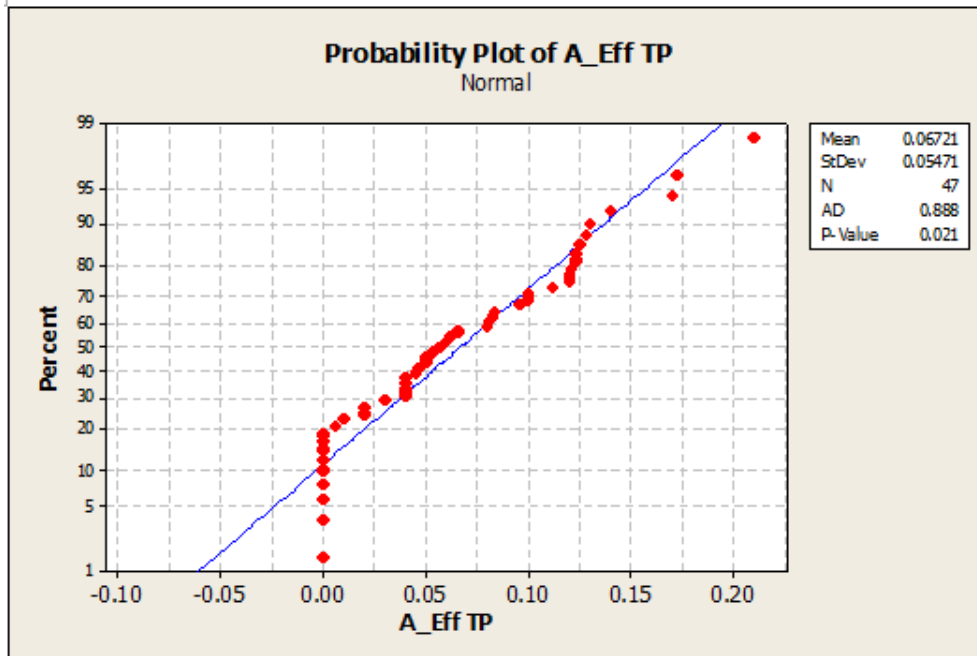


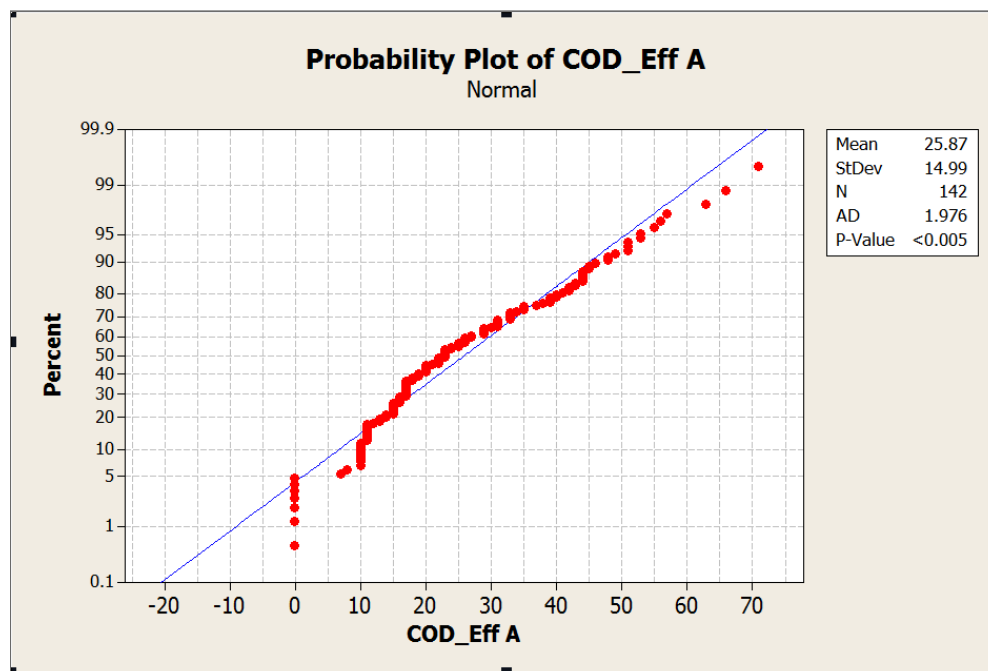**Figure B5 Normality test for effluent COD concentrations at SRT=25 days.**
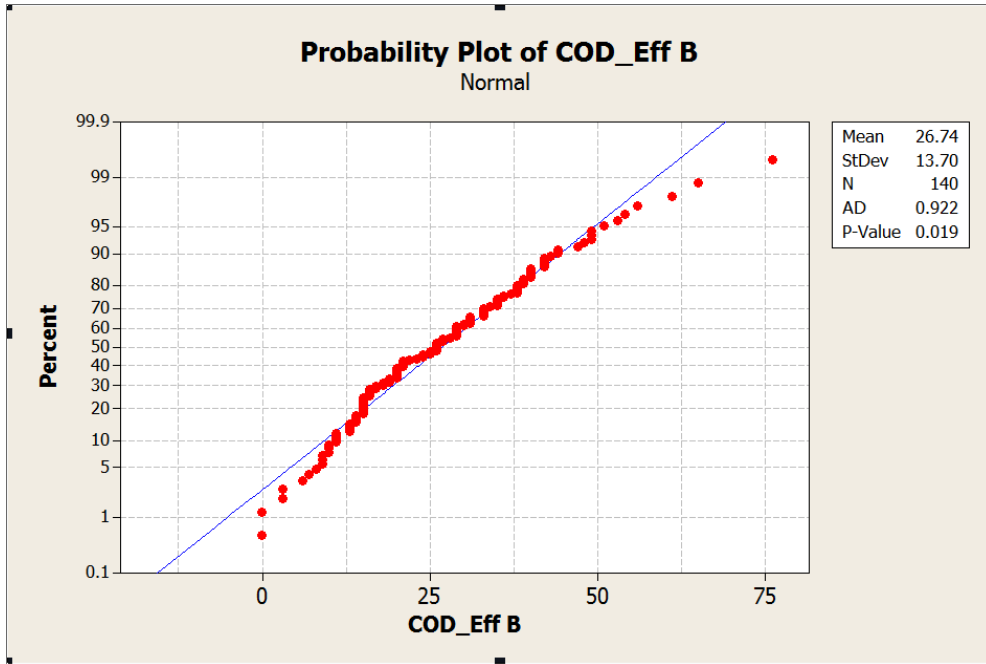
**Figure B6 Normality test for effluent COD concentrations at SRT=40 and 60 days.**
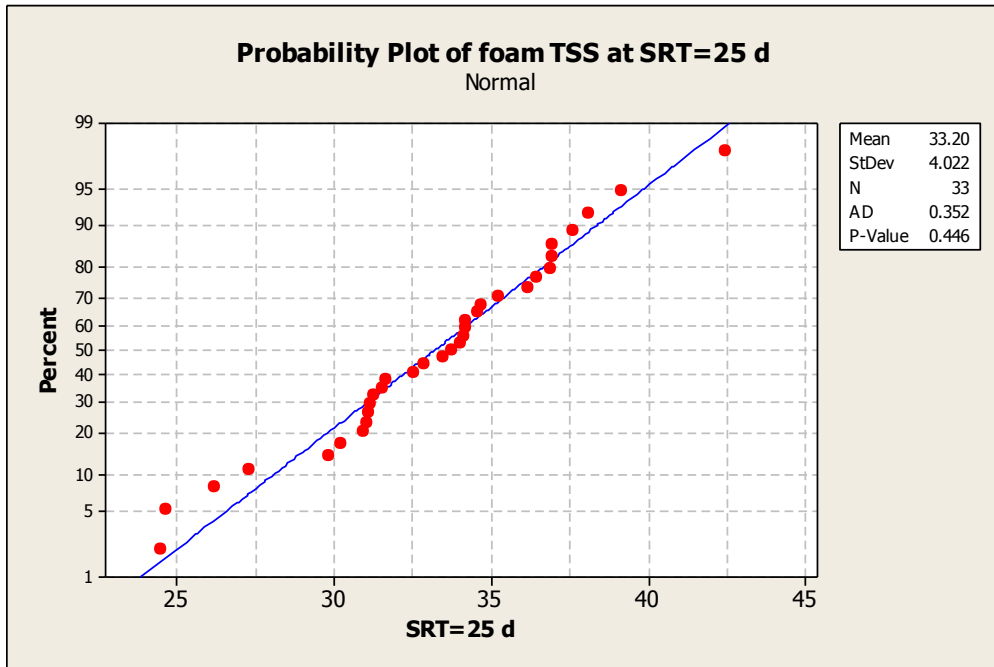


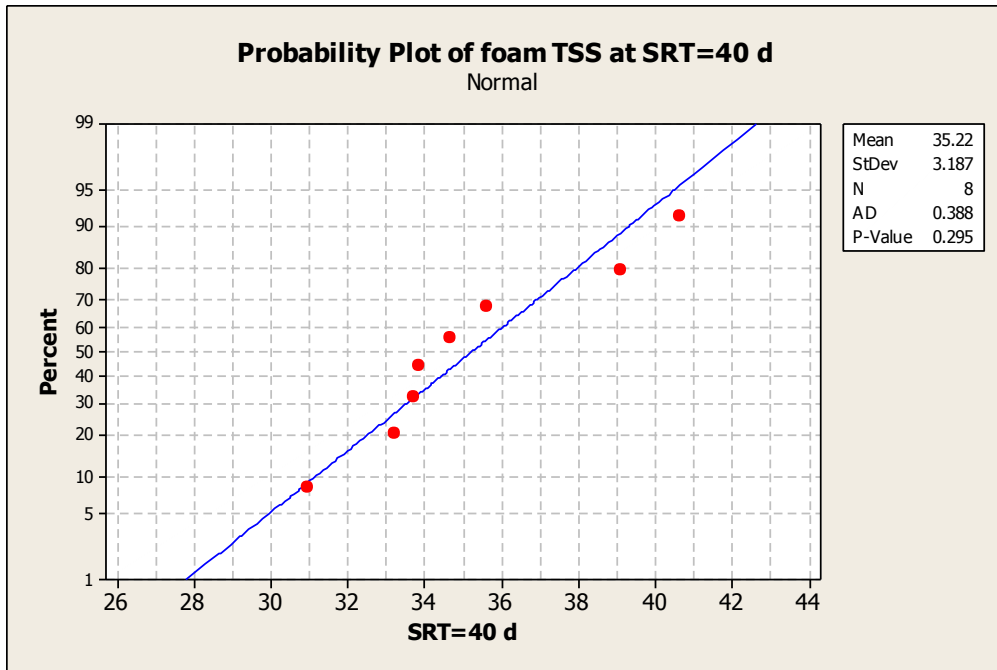**Figure B7 Normality test for foam TSS concentrations at SRT=25 days.**

**Figure B8 Normality test for foam TSS concentrations at SRT=40 days.**
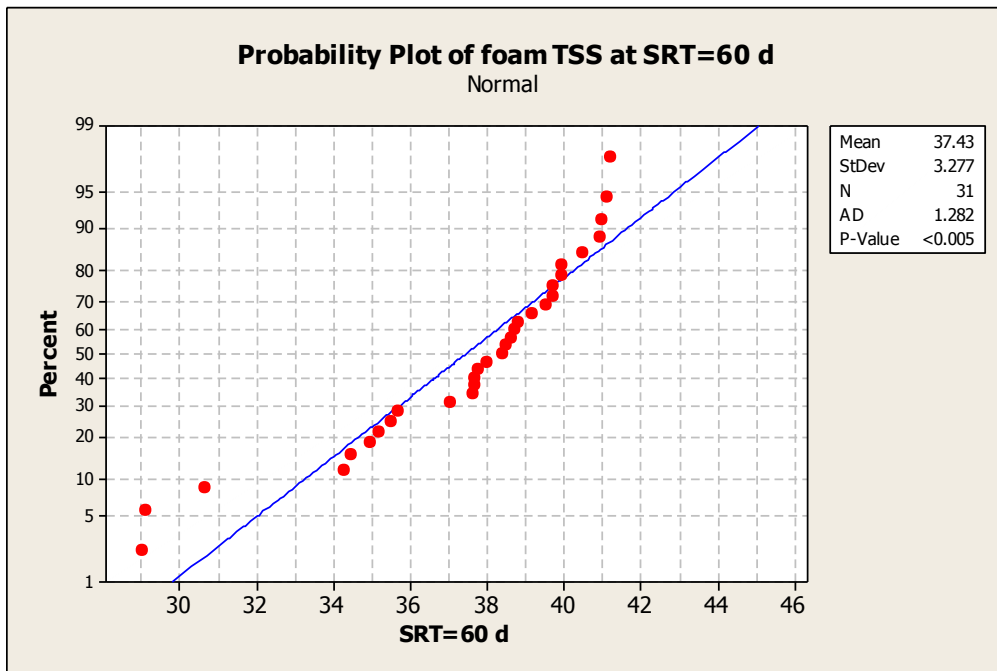


**Figure B9 Normality test for foam TSS concentrations at SRT=60 days.**

## B.2    Paired t-tests

Note: If 95% CI does not include zero, it suggests that mean difference is significant

(1) Paired t-tests for effluent concentrations between SRT = 25 and 60 days

## Paired T-Test and CI: effluent TP_25 days, TP_60 days

```
Paired T for TP_25 - TP_60

                 N      Mean     StDev    SE Mean
TP_25           74   0.138014  0.158972  0.018480
TP_60           74   0.179014  0.159830  0.018580
Difference      74  -0.041000  0.085493  0.009938


95% CI for mean difference: (-0.060807, -0.021193)
T-Test of mean difference = 0 (vs not = 0): T-Value = -4.13  P-Value = 0.000
```

## Paired T-Test and CI: effluent PO$_4$-P_25 days, PO$_4$-P_60 days

```
Paired T for PO4-P_25 - PO4-P_60

                   N      Mean     StDev    SE Mean
PO4-P_25          267   0.012434  0.014211  0.000870
PO4-P_60          267   0.042397  0.065748  0.004024
Difference        267  -0.029963  0.066714  0.004083


95% CI for mean difference: (-0.038001, -0.021924)
T-Test of mean difference = 0 (vs not = 0): T-Value = -7.34  P-Value = 0.000
```

## Paired T-Test and CI: effluent TN_25 days, TN_60 days

```
Paired T for TN_25 - TN_60

               N     Mean    StDev   SE Mean
TN_25         70   16.0609  2.5032   0.2992
TN_60         70   11.0247  2.7806   0.3323
Difference    70    5.03614  3.33527  0.39864


95% CI for mean difference: (4.24088, 5.83141)
T-Test of mean difference = 0 (vs not = 0): T-Value = 12.63  P-Value = 0.000
```

**Paired T-Test and CI: effluent NOx-N_25 days, NOx-N_60 days**

```
Paired T for NO3-N_25 - NO3-N_60

              N     Mean    StDev   SE Mean
NOx-N_25    271  15.1149   2.5269   0.1535
NOx-N_60    271  10.3546   2.3741   0.1442
Difference  271  4.76033  2.90460   0.17644


95% CI for mean difference: (4.41295, 5.10771)
T-Test of mean difference = 0 (vs not = 0): T-Value = 26.98  P-Value = 0.000
```

**Paired T-Test and CI: effluent NH₄-N_25 days, NH₄-N_60 days**

```
Paired T for NH4-N_25 - NH4-N_60

              N       Mean     StDev   SE Mean
NH₄-N_25    268  0.301642  1.276123  0.077952
NH₄-N_60    268  0.060299  0.327376  0.019998
Difference  268  0.241343  1.314773  0.080313


95% CI for mean difference: (0.083217, 0.399470)
T-Test of mean difference = 0 (vs not = 0): T-Value = 3.01  P-Value = 0.003
```

**Paired T-Test and CI: effluent COD_25 days, COD_60 days**

```
Paired T for COD_25 - COD_60

              N       Mean      StDev    SE Mean
COD_25      144   25.9444    14.9633     1.2469
COD_60      144   26.5278    13.5688     1.1307
Difference  144  -0.583333  16.379887  1.364991


95% CI for mean difference: (-3.281500, 2.114833)
T-Test of mean difference = 0 (vs not = 0): T-Value = -0.43  P-Value = 0.670
```

(2) Paired t-test for TP/TSS ratios between anoxic foam and activated sludge

**Paired T-Test and CI: A_Ax_foam (anoxic foam, SRT=25 days), A_Ax_ML (Anoxic zone mixed liquor, SRT=25 days);  Dec. 02, 2013 to Feb. 12, 2015.**

```
Paired T for A_Ax_foam - A_Ax_ML

              N       Mean     StDev   SE Mean
A_Ax_foam    24  0.032442  0.003771  0.000770
A_Ax_ML      24  0.037679  0.005202  0.001062
Difference   24  -0.005238 0.005488  0.001120
```

```
95% CI for mean difference: (-0.007555, -0.002920)
T-Test of mean difference = 0 (vs not = 0): T-Value = -4.68  P-Value = 0.000
```

**Paired T-Test and CI: B_Ax_foam (anoxic foam, SRT=40 days), B_Ax_ML (Anoxic zone mixed liquor, SRT=25 days);  Dec. 02, 2013 to May 17, 2014.**

```
Paired T for B_Ax_foam - B_Ax_ML

            N      Mean     StDev   SE Mean
B_Ax_foam   8   0.037775  0.003452  0.001221
B_Ax_ML     8   0.040263  0.002326  0.000822
Difference  8  -0.002487  0.004119  0.001456


95% CI for mean difference: (-0.005931, 0.000956)
T-Test of mean difference = 0 (vs not = 0): T-Value = -1.71  P-Value = 0.131
```

**Paired T-Test and CI: B_foam (anoxic foam, SRT=60 days), B_Ax_ML (Anoxic zone mixed liquor, SRT=60 days); May 18, 2014 to Feb. 12, 2015.**

```
Paired T for B_foam - B_ML

            N      Mean     StDev   SE Mean
B_foam     18   0.043422  0.008549  0.002015
B_Ax_ML    18   0.050556  0.008359  0.001970
Difference 18  -0.007133  0.008458  0.001994


95% CI for mean difference: (-0.011339, -0.002927)
T-Test of mean difference = 0 (vs not = 0): T-Value = -3.58  P-Value = 0.002
```

**Paired T-Test and CI: B_foam (anoxic foam, SRT=60 days), B_An_ML (Anaerobic zone mixed liquor, SRT=60 days); May 18, 2014 to Feb. 12, 2015.**

```
Paired T for B_foam - B_An_ML

            N      Mean     StDev   SE Mean
B_foam     18   0.043422  0.008549  0.002015
B_An_ML    18   0.047172  0.009053  0.002134
Difference 18  -0.003750  0.008309  0.001958


95% CI for mean difference: (-0.007882, 0.000382)
T-Test of mean difference = 0 (vs not = 0): T-Value = -1.91  P-Value = 0.073
```

<u>(3) Paired t-test for TKN/TSS ratios between anoxic foam and activated sludge</u>

**Paired T-Test and CI: A_Ax_foam (anoxic foam, SRT=25 days), A_Ax_ML (Anoxic zone mixed liquor, SRT=25 days);  Dec. 02, 2013 to Feb. 12, 2015.**

```
Paired T for A_Ax_foam - A_Ax_ML

             N      Mean     StDev   SE Mean
A_Ax_foam   23   0.078074  0.015157  0.003160
A_Ax_ML     23   0.078896  0.007615  0.001588
Difference  23  -0.000822  0.016009  0.003338


95% CI for mean difference: (-0.007744, 0.006101)
T-Test of mean difference = 0 (vs not = 0): T-Value = -0.25  P-Value = 0.808
```

**Paired T-Test and CI: B_Ax_foam (anoxic foam, SRT=40 days), B_Ax_ML (Anoxic zone mixed liquor, SRT=40 days);  Dec. 02, 2013 to May 17, 2014.**

```
Paired T for B_Ax_foam - B_Ax_ML

             N      Mean     StDev   SE Mean
B_Ax_foam   8   0.072650  0.010333  0.003653
B_Ax_ML     8   0.077100  0.003639  0.001287
Difference  8  -0.004450  0.008808  0.003114


95% CI for mean difference: (-0.011814, 0.002914)
T-Test of mean difference = 0 (vs not = 0): T-Value = -1.43  P-Value = 0.196
```

**Paired T-Test and CI: B_Foam (anoxic foam, SRT=60 days), B_Ax_ML (Anoxic zone mixed liquor, SRT=60 days); May 18, 2014 to Feb. 12, 2015.**

```
Paired T for B_Foam - B_Ax_ML

             N      Mean     StDev   SE Mean
B_Foam     17  0.085594  0.020441  0.004958
B_Ax_ML    17  0.070100  0.011136  0.002701
Difference 17  0.015494  0.022516  0.005461


95% CI for mean difference: (0.003918, 0.027071)
T-Test of mean difference = 0 (vs not = 0): T-Value = 2.84  P-Value = 0.012
```

**(4)** Paired t-tests for foam production rate between SRT = 25 and 60 days

## Paired T-Test and CI: Foam production rate, at SRT = 25 days and 60 days

```
Paired T for 25 days - 60 days

               N      Mean     StDev   SE Mean
25 days       174    4.8897    2.2273   0.1689
60 days       174   13.4540    9.0176   0.6836
Difference    174   -8.56437  8.74141  0.66268


95% CI for mean difference: (-9.87236, -7.25638)
T-Test of mean difference = 0 (vs not = 0): T-Value = -12.92  P-Value = 0.000
```

## B.3    Two-sample t-tests

Note: If 95% CI does not include zero, it suggests that mean difference is significant

## Two-Sample T-Test and CI: Surface tension_1 (samples from the dry day), Surface tension_2 (samples from the wet day)

```
Two-sample T for Surface tension_1 vs Surface tension_2

                    N    Mean   StDev  SE Mean
Surface tension_1   6   65.75    1.22     0.50
Surface tension_2   4   67.30    1.18     0.59


Difference = mu (Surf tens_1) - mu (Surf ten_2)
Estimate for difference:  -1.55000
95% CI for difference:  (-3.44511, 0.34511)
T-Test of difference = 0 (vs not =): T-Value = -2.00  P-Value = 0.092  DF = 6
```

## Two-Sample T-Test and CI: foaming potential_1 (samples from the dry day), foaming potential_2 (samples from the wet day)

```
Two-sample T for

                     N     Mean    StDev  SE Mean
foaming potential_1  7   1.3614   0.0521    0.020
foaming potential_2  6   1.1417   0.0496    0.020


Difference = mu (hydrop_1) - mu (hyrop_2)
Estimate for difference:  0.219762
95% CI for difference:  (0.156851, 0.282673)
T-Test of difference = 0 (vs not =): T-Value = 7.78  P-Value = 0.000  DF = 10
```

## Two-Sample T-Test and CI: hydrophobicity_1 (samples from the dry day), hyrophobicity_2 (samples from the wet day)

```
Two-sample T for hydrophobicity_1 vs hyrophobicity_2

                    N     Mean    StDev  SE Mean
Hydrophobicity_1    6   0.6435   0.0290    0.012
Hydrophobicity_2    4  0.56575  0.00818   0.0041


Difference = mu (Hydrop_1) - mu (Hydrop_2)
Estimate for difference:  0.077750
95% CI for difference:  (0.047060, 0.108440)
T-Test of difference = 0 (vs not =): T-Value = 6.20  P-Value = 0.001  DF = 6
```