Fermentation of Sludge for Phosphorus Recovery

by

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ABSTRACT

Controlled struvite precipitation is thought to be the most promising way to recover phosphorus in a useable form. Fluidized bed struvite precipitation processes successfully remove up to 90% of incoming phosphorus at dissolved phosphorus concentrations of 70 mg/L or higher with sufficient magnesium. Therefore attaining high dissolved phosphorus concentration in the influent stream to the struvite precipitation process is key to high phosphorus recovery rates.

Typical feed streams to struvite precipitation processes are anaerobically digested sludge supernatant or dewatering filtrate/centrate. While these liquid streams are high in dissolved phosphorus, they typically contain only 35% of the phosphorus removed from wastewater in biological phosphorus removal (BPR) treatment plants. Much of the removed phosphorus is locked in the sludge or lost as phosphate scaling on pipes and sludge handling equipment downstream of anaerobic digestion.

While many energy intensive processes have been developed to solubilize phosphorus from the sludge stream either before or after digestion, they remain at the bench or pilot scale due to high operational costs per mass of recovered phosphorus. These processes use heat, chemicals, and physical processes to solubilize phosphorus from sludge. At full scale, the technique that is most widely employed to increase orthophosphate concentrations in the sludge stream prior to digestion utilizes the phosphorus release mechanism of phosphorus accumulating organisms (PAO) in BPR sludge. The PAO in the sludge release stored polyphosphates and take up VFA resulting in approximately 25 - 30% of the total phosphorus in the sludge released as orthophosphate at the cost of a nearly equivalent mass of VFA as COD. Since sufficient VFA are vital for maintaining effective biological phosphorus removal and denitrification in the mainstream processes, consumption of VFA for phosphorus release in the side stream can reduce the efficiency of the main stream process.

Short term fermentation of un-digested sludge was explored as a means of increasing the dissolved phosphorus in the sludge and simultaneously producing VFA; thus, increasing the amount of phosphorus available for recovery from sludge with minimal energy input while producing VFA that can be recycled to the wastewater treatment process to enhance BPR. Fermentation of primary sludge (PS), waste activated sludge (WAS), and co-thickened sludge (PS and WAS) showed significant phosphorus solubilization and VFA production at 2 – 4 days of fermentation. Factors found to affect phosphorus solubilization rates from sludge were sludge type, fermentation time, total phosphorus in sludge, and pH. WAS fermentation solubilized the most phosphorus per mass of volatile solids (VS) followed by co-fermented or co-thickened sludge. PS fermentation producing the most VFA per mass VS fermented while WAS produced the least. Overall, co-fermented sludge resulted in the best combination of phosphorus release and VFA production. After 4 days of fermentation, co-fermented sludge contained 48% of TP as dissolved phosphorus, and produced 1624 mg l^{-1} of VFA-COD which corresponds to a VFA-COD yield per mass of volatile solids of 0.139 mg per mg VS applied. In terms of total sludge management, co-fermentation resulted in greater overall VFA production and phosphorus solubilization than individual sludge fermentation.

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1. Introduction

Phosphorus is a valuable resource that can be recovered and recycled from wastewater. With mineral phosphorus resources diminishing worldwide, consideration has been given to the feasibility of recovering phosphate from wastewater (Durrant, et al. 1999; Stratful et al., 2004). The understanding of phosphorus as a finite resource has led to a focus on phosphorus management throughout the global phosphorus cycle; primarily in agriculture where the majority of mined phosphorus is used, but also in related industries such as wastewater treatment (where much of the phosphorus from agricultural products is deposited). At the same time, the widespread use of phosphorus in agricultural and consumer products since the mid-20th century has led to increased phosphorus deposition in water bodies causing accelerated eutrophication (Knud-Hansen, 1994). These combined drivers have increased the value of phosphorus; while the eutrophic impact of phosphorus-rich effluent on receiving waters has led to extensive research on phosphorus removal and recovery techniques in wastewater treatment (De-Bashan & Bashan, 2004).

The main mechanisms for phosphorus removal in wastewater treatment are through chemical precipitation or biological uptake. By transferring the influent phosphorus in wastewater to the sludge fraction, both phosphorus removal techniques are able to remove over 90% of the total influent phosphorus load and concentrate it into the sludge stream (Metcalf & Eddy, 2003).

Existing phosphorus recovery techniques focus on the more concentrated streams in wastewater treatment such as the sludge stream, centrate stream, or ash. Recovery processes involve initial solubilization of the phosphorus before controlled recovery often as a crystal such as struvite or calcium phosphate or as a less refined product such as phosphorus rich slag. Phosphate crystals such as struvite can be used directly as a fertilizer, the calcium phosphate and phosphorus rich slag can be further refined in existing phosphate processing facilities.

1.1. FORM AND USE OF PHOSPHORUS -

Phosphorus is an essential element for all life. As the main component of ATP (adenosine triphosphate), phosphorus plays a major part in the energy transfer of all known organisms. Phosphorus is also a vital component of DNA, RNA, proteins, lipids, bones, and all cell membranes (phospholipids).

Phosphorus is the eleventh most abundant element in the earth’s crust. Elemental phosphorus can exist in two major forms – white and red phosphorus – however phosphorus is highly reactive and is therefore never found in its elemental form in nature. Most of the phosphorus on earth is bound in soil as inorganic mineral phosphates. Apatite (calcium phosphate) is the preferred source of phosphorus for the phosphate mining industry, with high quality apatite sources containing 30-40% P_2O_5 (13-17% P).

The most common use for phosphorus compounds is for fertilizer. Other uses include pesticides, nerve gases, batteries, soaps/detergents, food additives, bone china and matches. Of the approximately 220 million tons of phosphate rock mined per year worldwide, 90% is utilized in the fertilizer industry (Cordell et al., 2009).

As the human population increases, our increasing need for food is leading to a greater dependence on inorganic phosphorus fertilizers. Figure 1 shows the increase in worldwide phosphorus production since the 1800s with the global population growth curve for the same interval. Of the total global phosphorus production, approximately 2.5 Mt/year is obtained from organic sources most of which is from manure, with only a fraction of a percent from human excreta or guano (Cordell et al.,2009).

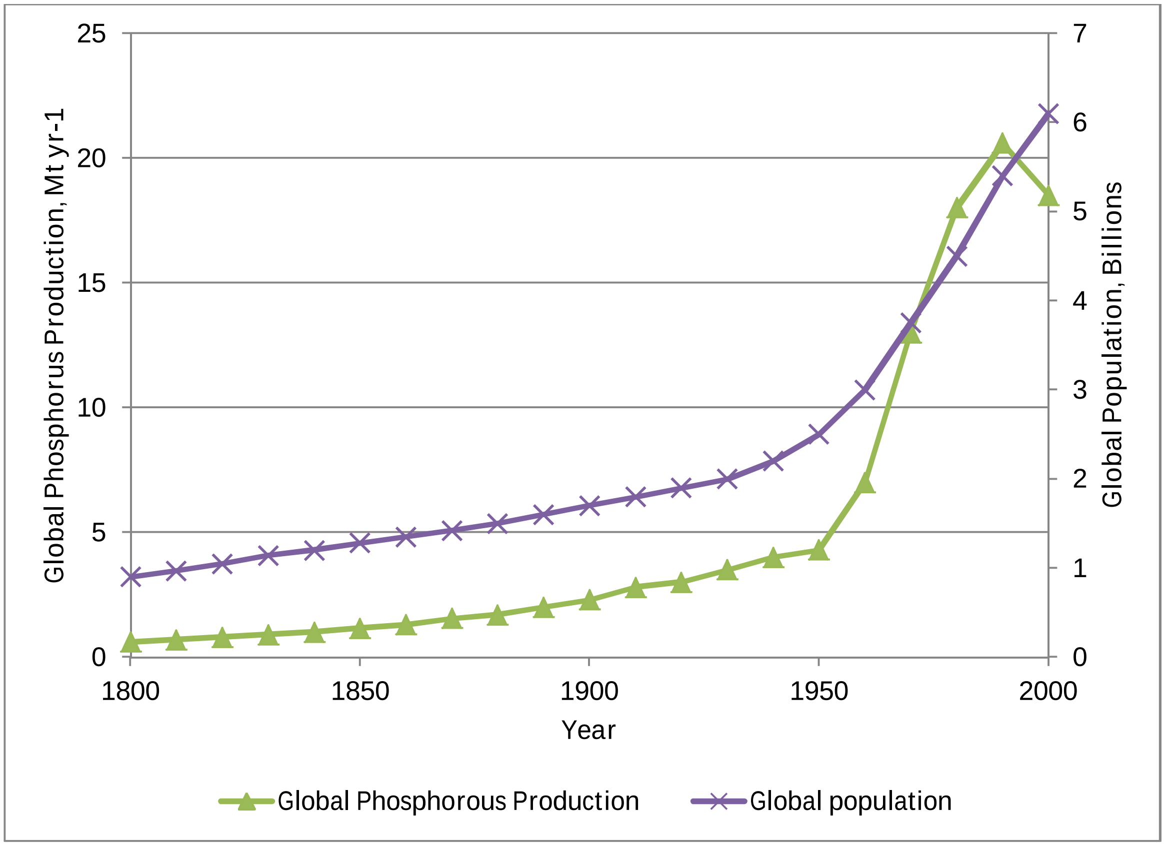

Figure 1: Correlation between Global Phosphorus Production and Global Population (calculations based on data from Cordell et al., 2009)

The vast majority of phosphorus is produced from mined phosphate rock which is a non-renewable resource. The largest reserves of high quality phosphate rock occur in Morocco, USA, and China, however these reserves will be depleted in 100-200 years (Jasinski, 2013). Meanwhile the constantly increasing population will result in a proportionate increase in phosphate demand for food production. A phosphate supply and demand model developed by Mohr and Evans (2013) which includes the phosphorus production from over 80 countries, indicates that global demand for phosphates will outpace supply as soon as 2030 or as late as 2250 depending on technical, environmental, and political factors.

As the demand for phosphorus increases the value of phosphorus will increase, leading to the exploration of alternative phosphorus sources that are currently uneconomical. For example, large phosphate rich rock deposits have been detected in the continental shelves of the Atlantic and Pacific Oceans (Jasinski, 2013). Current technology makes accessing these deposits too expensive, however as deep water mining technology is improved, and cost of phosphorus increases, these reserves will become economically feasible. Another important source of phosphorus will be the recycling and recovery of phosphorus from wastewater.

1.2. INCREASED PHOSPHORUS USE AND EUTROPHICATION -

Natural mobilization of phosphorus into the environment relies on the slow weathering of sedimentary rock, while low solubility of phosphates and their rapid transformation to insoluble forms make the element commonly the growth-limiting nutrient, particularly in aquatic ecosystems (Smil, 2000). However, due to heavy phosphorus mining and use in inorganic fertilizers since the mid-20th century, increased soil erosion and runoff from fields, and discharges of urban and industrial wastes the global mobilization of phosphorus was roughly triple compared to its natural flows by the beginning of the 21st century (Cordell et al.,2009; Smil, 2000).

This increased P mobilization is primarily driven by the need to keep up with the fertilizer demand required to produce food for the growing population. According to a number of global phosphorus mass balance models, approximately 85% of mined phosphate rock is converted into fertilizer and used in the agricultural industry for food production, (Van Vuuren 2010; Liu et al. 2008; Cordell et al., 2009). In 2012, global phosphorus fertilizer consumption was 18.3 Mt as phosphorus (Jasinski 2013). Although crops use the applied phosphorus with relatively high efficiency, inefficient fertilizer application techniques and soil management practices allow loss of the nutrient from arable land (Smil, 2000). Of the total phosphorus mass added to the global cropland per year from mined phosphate rock, between 30% - 50% of it is lost surface waters via runoff and erosion, or discharged to surface waters from point sources such as industrial, agricultural, or municipal waste treatment systems leading to accelerated eutrophication (Van Vuuren 2010; Cordell et al., 2009; Liu et al., 2008).

1.2.1. Eutrophication:

Eutrophication is the process of nutrient enrichment of a lake. Over time, influent streams to a lake can deposit nutrients such as carbon, nitrogen and phosphorus. Given certain conditions, the nutrient content of a lake may increase, making it more productive in both plant and animal matter. Over tens of thousands of years, the lake may gradually fill up with organic material, turning into a swamp and eventually dry land. This natural process may be significantly accelerated if the input of nutrients to a freshwater body outpaces the rate of removal of these nutrients (Smil, 2000).

Of the three main nutrients necessary for production of living matter – carbon, nitrogen and phosphorus – only phosphorus cannot be volatilized from a water body. Research at the experimental lakes area (Schindler et al., 2008) showed that, in typical freshwater environments, phosphorus is the limiting nutrient (as opposed to nitrogen) in cyanobacteria blooms, which characterize accelerated eutrophication of freshwater environments. Excessive growth of cyanobacteria can have many deleterious effects on a lake environment; if used for drinking water, blooms can block intake and filter components and typically cause taste and odour issues (Knud-Hansen, 1994). Sunlight cannot penetrate the thick mat of algae on the top of the water, causing loss of plant life below the bloom. After the bloom of algae dies and settles to the bottom of the lake, it decomposes, robbing the deep-water environment of dissolved oxygen leading to fish kills and potentially destroying deep-water fisheries. Toxins, such as microcystins produced by cyanobacteria can kill both fish and aquatic plants and can pose a risk to human health (Boyer, 2008). Aesthetically, recreational use of eutrophic waters suffers because green “slimy” water is typically not enjoyable to swim in; mats of decomposing algae along beaches presents health and odour issues; and, one is also more likely to get "swimmer's itch" from swimming in eutrophic waters (Knud-Hansen, 1994).

1.2.2. Wastewater Treatment and Eutrophication:

Globally, it is estimated that humans excrete approximately 3 Mt of phosphorus per year (Van Vuuren 2010); half of which is generated in areas not serviced by wastewater collection systems and is therefore recycled more or less directly to land (Liu et al., 2008). Thus, wastewater collection systems around the world transport approximately 1.5 Mt of human excreted phosphorus to wastewater treatment plants each year (Cordell et al., 2009). Adding the phosphorus from detergent use and industrial effluent puts total annual wastewater phosphorus content at approximately 3 Mt. Although the total amount of phosphorus in wastewater is much smaller compared to mass of phosphorus transported by agricultural land erosion and runoff – estimated at 19.3 Mt per year (Liu et al., 2008) over pre-industrialized erosion rates (Smil, 2000) – the eutrophic impact of phosphorus discharged by wastewater treatment plants is significant.

In the US and Canada in the middle of the last century nearly 10,000 lakes were showing signs of accelerated eutrophication (ReVelle and ReVelle 1988). Many lakes experienced algal blooms so severe, whole fish populations were wiped out. In lake Erie, one of the Great Lakes in North America, the approximately 9,000 kg/d of phosphorus entering the lake – primarily from municipal and industrial sources – at the end of the 1960's resulted in a 6,700 km^2 area of the lake with no oxygen within three metres of the bottom (Beeton 1971).

As a result of the rapid degradation of lake environments, legislation was introduced to limit the amount of phosphorus discharged by WWTPs. Initial efforts looked at reducing phosphorus inputs to WWTPs – focusing on soaps and detergents which contributed significantly to wastewater phosphorus concentrations. In the North America in the late 1960's it was estimated that 50% of the phosphorus in municipal wastewater came from soaps and detergents, which could be nearly 20%, phosphorus by dry weight (Knud-Hansen 1994). Canada's response to the problem with eutrophication was to pass the Canada Water Act in 1970, which mandated an immediate reduction to 8.7% phosphorus in laundry detergent, with a further reduction to 2.2% phosphorus by the end of 1971 (Conservation and Natural Resources Sub-committee, 1972). Modern Canadian legislation has since amended the regulations down to 0.5% elemental phosphorus by weight in household detergents and cleaners and 2.2% elemental phosphorus by weight in commercial detergents and cleaners (Canadian Environmental Protection Act, 1999).

Legislative efforts and public awareness campaigns have slowed the rate of eutrophication of freshwater lakes, however significant damage has already been done to many freshwater ecosystems (Knud-Hansen, 1994). Decreasing raw wastewater phosphorus levels was successful at limiting the amount of phosphorus discharged to surface water bodies by wastewater treatment plants, however for many impacted lakes and rivers further reduction in phosphorus concentrations was necessary – thus phosphorus removal processes were developed for full scale implementation in WWTPs worldwide.

1.3. PHOSPHORUS REMOVAL FROM WASTEWATER

There are two main methods for removing phosphorus from wastewater during the treatment process: by chemical precipitation or by biological uptake of phosphorus. Both methods transfer orthophosphate from the liquid phase to the solid phase, where final removal of phosphorus from wastewater occurs by filtration/sedimentation. Thus phosphorus removal processes prevent discharge of phosphorus in treated effluent (liquid phase) by trapping it in the sludge (solid phase).

1.3.1. Phosphorus Removal by Chemical Precipitation:

Soluble phosphorus readily reacts with metal ions to produce insoluble metal phosphates. Metal salts of typically aluminum or iron are dosed into the treatment train at various points to react with orthophosphate, in order to create the insoluble metal phosphates that can be subsequently removed by sedimentation, filtration, or other solids separation techniques. Due to the relatively simple and effective nature of this method for phosphorus removal, it is the most widely practiced method of phosphorus removal in wastewater treatment. Dosage of metal salts can be tailored to the specific wastewater type and can be applied in conjunction with any treatment method from wastewater stabilization ponds to tertiary physical or biological treatment systems.

The most significant factors that influence how effective chemical precipitation is for removing phosphorus from wastewater are: the pH of the wastewater, the mass of chemical applied, mixing conditions and dosing point in the treatment process (Neethling and Gu, 2006; Metcalf & Eddy, 2003). There is not one best point of application in a treatment train to achieve phosphorus removal by chemical precipitation. Dosing point depends on the treatment process, wastewater characteristics, and level of phosphorus removal that is required.

The main drawback to removal of phosphorus by chemical precipitation is the increased sludge production. Typical dosing rates for phosphorus removal by metal salts is 2 – 5 times the stoichiometric requirement depending on the level of phosphorus removal required. Much of the added metal salt is converted into metal hydroxides, especially when lower effluent phosphorus concentrations are required (below 0.5 mg L^{-1}) (USEPA 2010). For minimum sludge production (10-40% increase in total plant sludge mass) WWTPs typically dose metal salts after the final clarifier in a tertiary treatment process. When adding metal salts earlier in the treatment process such as to the primary clarifier or the secondary treatment process, overall sludge production can be expected to increase by 60-70% and 35-45% by mass respectively (USEPA 2010). Metal salts have other drawbacks such as decreasing sludge dewaterability, interfering with nitrification, and promoting corrosion in sludge handling due to the high content of inorganic salts in the sludge (USEPA 2010).

1.3.2. Biological Phosphorus Removal (BPR):

Biological phosphorus removal has been studied in depth since the 1960s when high phosphorus concentration in activated sludge was observed in a municipal wastewater treatment plant in San Antonio TX (Vacker 1967). At first, the biological phosphorus removal mechanism was termed “luxury uptake” and was generally treated as a “black box” process by engineers. However, the theory of phosphorus removal was eventually refined to through cooperation between engineers, microbiologists, and chemists. Barnard (2006) presented a concise review of the historical development of BPR technology.

It is generally understood that groups of bacteria, collectively called phosphorus accumulating organisms (PAO), will store large amounts of phosphorus in their cellular mass as polyphosphate given the right environmental conditions (Barnard, 1976; McLaren, 1976; He and McMahon, 2011). PAO bacteria accumulate phosphorus within the cellular mass when exposed to alternating anaerobic and aerobic conditions. In the anaerobic zone, when soluble carbon is present, PAOs discharge adenosine triphosphate (ATP) to obtain energy required to uptake the soluble carbon which is stored as polyhydroxyalkanoate (PHA) in the cell. In the aerobic zone, respiration allows metabolism of stored carbon, which provides energy for cell growth and glycogen replenishment. PAOs also use the energy produced by metabolism of the stored carbon to uptake dissolved phosphorus (orthophosphate) and store it as polyphosphate. In fact, PAOs are found to uptake significantly more phosphorus than what was initially discharged in the anaerobic zone (Barnard 1976). When these PAOs are removed from the treatment train in the aerobic state, the stored polyphosphate is removed and concentrated into sludge stream; resulting in an effective phosphorus removal strategy that does not require chemical addition to the main-stream process.

The actual microbiology of the PAO bacteria is still being researched. Currently, the group '*Candidatus* Accumulibacter' is considered responsible for the biological phosphorus removal mechanism however, no confirmed PAO exhibiting all of the characteristics observed during the EBPR process has been successfully cultivated in isolation (He and McMahon, 2011). Instead, in-situ analytical techniques such as fluorescent in situ hybridization (FISH) have been used to confirm the abundance of the Accumulibacter in lab scale reactors worldwide (Oehmen et al., 2007) and in full scale EBPR treatment plants (Zilies et al., 2002).

Increasing understanding of the BPR mechanism revealed that concentrations of soluble carbon in the anaerobic zone significantly influence overall phosphorus uptake by the PAOs in the aerobic zone (Rabinowitz and Oldham, 1985; Danesh & Oleszkiewicz 1997). Volatile fatty acids (VFA), especially acetic and propionic acid, were found to be the ideal soluble carbon source for PAOs; promoting high phosphate discharge and carbon uptake in the anaerobic zone followed by increased phosphorus uptake in the aerobic zone (Fuhs & Chen 1975). Barnard (2006), showed that 7-9 mg/L VFA are required for removal of 1 mg/L of P. In some places, influent wastewater contains sufficient concentrations of readily biodegradable carbon (rbCOD) that quickly converts to VFA in the anaerobic zone and provides sufficient substrate for phosphorus removal and accumulation inside the bacterial cells. However, in many places this is not the case and addition of rbCOD (as methanol typically) that can be fermented easily into VFA in the anaerobic zone is required. Alternatively VFA can be produced from sidestream sludge fermentation and recycled directly into the anaerobic zone to provide the necessary substrate for phosphorus removal. This process of VFA production by sludge fermentation is explained in further detail in the following section.

1.3.2.1. Production of VFA for BPR by Sludge Fermentation:

Due to the high cost of methanol addition for BPR, alternative methods for soluble carbon production have been explored. Acid fermentation of sludge is a well-established method of solubilizing the organic carbon in the sludge with specific design criteria developed from common sludge treatment processes such as two stage anaerobic digestion.

Acid fermentation of sludge can be considered to consist of two main steps; hydrolysis and acidogenesis. Primary sludge (PS), made up of a variety of organics, is readily putrescible and undergoes hydrolysis at a much quicker rate than secondary sludge (WAS). WAS is primarily made up of bacterial cells which are protected from lysis (cellular breakdown) by a cell wall. The hydrolysis rates of WAS are dependent on how quickly the cell wall can be ruptured. In acidogenesis a group of fermentative bacteria called acidogens convert hydrolyzed organics into VFA. This conversion is the major process in acid fermentation; the most common types of VFA produced being acetic and propionic acid (Batstone, et al. 2002).

Due to the relative ease of fermenting PS as opposed to WAS, the fermentation of primary sludge was established as a cost-effective method of producing VFA for wastewater treatment plants (Pittman et al., 1992; Banister and Pretorius, 1998). Various fermentation schemes have been developed for the production of VFA with yields from PS fermentation in the range of 120 -200 mg VFA-COD/g COD (Rabinowitz et al., 2011). Implementation of primary fermenters in BPR wastewater treatment plants in western Canada has shown primary sludge fermentation can provide sufficient additional VFA for full phosphorus removal in weak wastewaters (Banister and Pretorius, 1998; Rabinowitz and Oldham, 1985).

It has also been shown that PS fermentation results are highly variable between plants and even within the same plant as the influent wastewater changes seasonally (Barnard, 2006). Interest has turned toward fermenting WAS, as a more stable source of VFA and one that is indigenous to the WWTP. WAS fermentation alone shows VFA yields in the order of 150 mg VFA-COD g COD^{-1} (Yuan and Oleszkiewicz, 2010) but takes longer time due to the more stable structure of WAS than PS.

A potential drawback of WAS fermentation for the production of VFA is the concurrent release of nutrients contained within the cell. Tremblay, et al. (2005) and Yuan et al. (2010) found significant phosphorus release and NH_3 production occurred during WAS fermentation for VFA production. This phosphorus release is attributed to the secondary release mechanism of the PAO's in the RAS and the lysing of bacterial cells. Ammonia production during fermentation occurs due to the anaerobic metabolism of proteins in the sludge (Rabinowitz, et al. 2011). It has been shown by McIntosh & Oleszkiewicz (1997) that the nutrients contained in such a fermented biomass supernatant may actually offset the benefits of VFA produced. Therefore in order to benefit from the VFA produced during WAS fermentation, removal or recovery of nutrients from the fermented sludge liquor is required prior to returning it to the anaerobic zone.

Removal of phosphorus from wastewater is becoming a common requirement in developed countries due to concerns over the accelerated eutrophication of fresh water bodies. Since BPR is a more economical process for phosphorus removal from wastewater, the complexity of operation effectively limits BPR application to medium and large WWTPs. Smaller wastewater plants, with smaller operating budgets and less access to highly trained operators, typically utilize the simpler to implement method of chemical addition to meet phosphorus removal requirements. As such, the majority of phosphorus removal in North America is still accomplished through chemical addition. This generates chemically bound phosphorus sludge which is typically landfilled, thus losing the potential for phosphorus recycling.

1.4. PHOSPHORUS RECOVERY FROM WASTEWATER

Phosphorus is a valuable resource that can be recovered and recycled from wastewater. With mineral phosphorus resources diminishing worldwide, consideration has been given to the feasibility of recovering phosphate from wastewater (Durrant, et al. 1999; Stratful et al., 2004). Development of a phosphorus recovery process for a WWTP is typically driven by the need to:

- Reduce or eliminate the problems associated with phosphate scaling on WWTP piping and equipment (Ohlinger et al., 1999);
- Remove phosphorus to conform to strict discharge limits imposed because of their role in eutrophication (Munch and Barr, 2001); and/or,
- Recover phosphorus in a form that is suitable for recycling or reuse within the fertilizer industry (Liberti et al., 2001).

1.4.1. Phosphate Scaling:

For many wastewater treatment plants the spontaneous precipitation of insoluble phosphate products results in significant scaling downstream of the sludge digestion process, clogging pipes, pumps and dewatering equipment. The 1,740 MLD Hyperion WWTP serving Los Angeles CA was one of the first reported cases of significant struvite scaling (Borgerding, 1972). Acid washing and mechanical descaling are required to remove phosphate deposits; an expensive operation due to both the labour costs and process down time associated with equipment descaling. Since dissolved phosphorus concentration in the sludge stream increases significantly during anaerobic digestion, dosing metal salts into the digester to precipitate the solubilized phosphorus is a common practice; however this makes phosphorus recovery impossible (Donnert & Salecker, 1999). Alternatively, methods for recovering phosphorus from sludge before digestion have been explored in order to avoid encrustation issues. Since undigested sludge primarily contains phosphorus in particulate form, recovery methods require an initial step to solubilize the P. These techniques are discussed further in Section 1.5.

1.4.2. Reducing the Eutrophic Impact of Sludge:

A common solution to phosphate scaling in wastewater treatment plants is to dose metal salts such as alum or ferric chloride into the anaerobic digester and/or downstream of sludge digestion, prior to dewatering (Buchanan et al., 1994). Metal salt addition locks phosphorus as a metal phosphate in sludge preventing unwanted nutrient recycling to the WW treatment process via sidestream return flows (i.e. sludge dewatering centrate). Nutrient loading to mainstream processes from return side streams can be significant and must be avoided in highly sensitive areas where phosphorus discharge limits are stringent.

Unfortunately, phosphorus bound in chemical sludge is also considered to be unavailable for plant uptake where sludge is land applied (De-Bashan & Bashan, 2004; Rigby 2013) and is unavailable for recovery except through sludge mono-incineration and chemical recovery of phosphorus from the sludge ash. This process is still highly experimental with only a few full scale installations around the world (Kabbe 2013). In sensitive watersheds, where eutrophication threatens receiving water bodies, land application of sludge with high phosphorus content may be discouraged. For example in Winnipeg MB, Canada, phosphorus application limits are proposed for land application of sludge which could limit sludge application rates to approximately 1/10th of current rates (Oleszkiewicz, 2004). At these low application rates, it will be uneconomical to continue with land application and the sludge will be landfilled – wasting a valuable resource. Recovery of phosphorus from the sludge stream (prior to metal salt addition) would prevent the loss of nutrients caused by landfilling phosphorus rich sludge, provide a revenue source to the WWTP in terms of the phosphate product, and enable the continuation of sludge application to land and associated nutrient recycling.

1.4.3. Recovery of Phosphorus in a Useable Form:

In wastewater treatment phosphorus is removed from wastewater by conversion of the soluble phosphate ions into a solid; most commonly as an insoluble metal salt precipitate, or as a microbial mass in an activated sludge. Due to concerns over heavy metal and other contaminant loading to cropland, land application of sludge is being phased out or sludge quality requirements are being made more stringent in many jurisdictions (Milieu Ltd., 2008).

Stabilized biosolids may contain contaminants, both organic such as dioxins and furans) and inorganic (most commonly minerals and heavy metals). Most municipal sewage systems accept some amount of industrial waste which contributes organic and inorganic pollutants to the wastewater and ultimately the sludge stream. In addition, various products used in the home such as cleaners, detergents, fragrances, medications, and personal care products contain organic compounds that are considered pollutants. Many of these organic pollutants enter and leave WWTPs unaltered or incompletely removed and subsequently have been identified in the environment (Kinney, et al., 2006) while other inorganic compounds, such as heavy metals, are actually concentrated in the sludge. It has been shown in numerous reports (Evans, 2012; Singh & Agrawal, 2008; Kinney, et al., 2006; Sanchez-Monedero, et al., 2004) that contaminant accumulation in soils amended with biosolids does occur.

In a 2010 study by the National Biosolids Partnership in the US, participants focused substantially on the persistence of public perception of health issues regarding sludge application to land. These in turn have driven local and state regulatory and policy actions limiting sludge management options including land application bans and the introduction of more restrictive management practices such as fence line setbacks and incorporation requirements (WEF, 2011). Therefore techniques to recover phosphorus from wastewater in a truly sustainable way must focus on producing a clean phosphorus product.

Successful phosphorus recovery techniques must economically produce a product rich in phosphorus. Additionally the product should be easily transported and stored, relatively free of contaminants such as heavy metals, and should be suitable for use directly as a fertilizer or recycled into the phosphate production industry. As such, most phosphorus recovery processes recover phosphorus as a crystal, either:

- Struvite – directly useable as slow phosphorus release fertilizer; or,
- Calcium Phosphate – recycled into phosphate rock industry.

1.4.3.1. Struvite

Controlled struvite precipitation is thought to be the most promising way to recover phosphorus in a useable form (Jaffer, et al. 2002). Indeed, in North America, the most widely used full-scale phosphorus recovery technology utilizes the struvite crystallization process. Struvite is an orthorhombic crystal made up of magnesium (Mg^{2+}), ammonium (NH_4^+) and phosphate (PO_4^{3+}) ions in a 1:1:1 molar ratio. Another name for struvite is magnesium ammonium phosphate hexahydrate, which can be abbreviated to MAP – not to be confused mono-ammonium phosphate, a conventional phosphate fertilizer. Struvite forms spontaneously in liquids with high concentrations of constituent ions. Although various experimental values for the solubility constant for struvite have been developed (Rahaman, et al., 2006), it is clear that struvite solubility decreases with an increase in pH; thus lower saturation values are necessary for precipitation of the crystal.

Struvite precipitation processes for phosphorus recovery utilize phosphorus rich liquid streams from sludge treatment such as dewatering centrate of digested sludge. After anaerobic digestion, the sludge contains high levels of ammonium and phosphate ions along with considerable magnesium. Adjustment of the pH will initiate struvite precipitation however magnesium addition to the process ensures that it is not magnesium limited. Optimum pH for struvite precipitation is 8.5 or higher but struvite precipitation processes for phosphorus recovery can operate at lower pH to limit the amount of chemicals required for pH adjustment (Britton, et al., 2005).

There are numerous benefits to recovering phosphorus as struvite. As discussed previously, the actual precipitation of struvite requires relatively low inputs of energy and chemicals. Research has shown (Battistoni, et al., 2000) that struvite produced from wastewater or sludge side streams is low in heavy metals and other pollutants, and that the nutrients are in plant available form, making struvite suitable for direct agricultural use as a slow release fertilizer. Finally, struvite crystals can be dried and packaged, simplifying transportation and distribution of the product.

1.4.3.2. Calcium Phosphate

Calcium phosphate is another crystalline product of phosphorus recovery processes. Calcium phosphate ($Ca_3(PO_4)_2$) can be precipitated directly from calcium and phosphorus rich solutions however its amorphous form makes recovery of the product difficult. Seeding a reactor with crystals or pellets of sand or calcium silicate helps to induce precipitation of calcium phosphate at lower saturation levels and makes recovery of the product more feasible (Cornel & Schaum, 2009). The extremely low solubility of calcium phosphate makes it impractical to be used as a fertilizer directly. Instead, calcium phosphate recovered from WWTPs, which is the same basic chemical makeup as mined phosphate rock, can be recycled to the phosphate industry as a secondary material (Schipper, 2001).

1.5. PHOSPHORUS RECOVERY PROCESSES OVERVIEW

Currently, the vast majority of phosphorus recovery techniques focus on recovery of phosphorus as struvite, due to the many benefits of the product as discussed in Section 1.4.3.1. While phosphorus recovery techniques can be applied to recover phosphorus directly from wastewater, the sheer volume of liquid requiring treatment, and the low concentration of phosphorus typically found in wastewater (5-10 mg/L) makes this unfeasible. Efficient recovery of phosphorus from wastewater depends on maximizing phosphorus removal from the wastewater stream and solubilizing the phosphorus in a concentrated stream to facilitate crystallization of phosphate minerals. BPR wastewater treatment typically concentrates up to 90-95% of the incoming phosphorus into the sludge stream making subsequent phosphorus recovery from sludge and related side streams much more feasible. Typical sludge volume produced at a WWTP is between 1 – 5% of the wastewater volume.

Following removal of phosphorus from wastewater by BPR, the phosphorus that has been concentrated in the sludge stream is primarily in particulate form. To recover the phosphorus in sludge, most processes somehow solubilize the phosphorus and then recover it by either struvite of calcium phosphate crystallization. In fact, the majority of phosphorus recovery processes can be considered phosphorus solubilization processes with a crystallization step at the end.

Various reviews on phosphorus recovery methods have been performed (Morse, et al. 1998; De-Bashan & Bashan, 2004; Dichtl et al., 2007; Schick, et al. 2009; Nieminen, 2010; Kabbe, 2013). Typically the different phosphorus recovery methods are divided into groups based on the wastewater/sludge stream that the process is applied to, namely; solid streams, ash, and liquid streams.

Alternatively they can grouped by the methods employed to solubilize P, such as; wet chemical methods, acid leaching, struvite/calcium phosphate crystallization, etc. For the purpose of this overview, the techniques will be grouped based on phosphorus solubilization methods.

1.5.1. Biological methods: Anaerobic digestion and WAS-P release mechanism

The earliest examples of phosphorus recovery as a recyclable product were calcium phosphate and struvite precipitation processes from secondary effluent or liquid side streams. DHV Crystallactor, developed in the Netherlands in the late 1970's was a phosphorus recovery technology that precipitated calcium phosphate on seed material (usually sand) from secondary effluent or liquid side streams such as centrate. The DHV Crystallactor was implemented successfully at full scale and produces calcium phosphate that can be recycled back into the phosphate industry (DHV Consulting Engineers, 1991). Similar early technologies CSIR™, Kurita™, Phosnix™, etc. (Morse, et al. 1998) produced either calcium phosphate or struvite by crystallizing the dissolved phosphorus from secondary effluent or liquid side streams. These early phosphorus recovery processes which were essentially phosphorus crystallization technologies, form the basis for nearly all the phosphorus recovery process development that followed.

The phosphorus crystallization process is limited in that only dissolved phosphorus can be recovered. Therefore processes to increase the dissolved phosphorus concentrations will increase the amount of phosphorus available for recovery by crystallization methods. Anaerobic digestion significantly increases the dissolved phosphorus concentration in the liquid fraction of sludge by lysing and hydrolyzing the bacterial cells contained in the sludge. Digester supernatant or digested sludge dewatering centrate, that contain dissolved phosphorus concentrations of 150 mg/L, are therefore better feed streams for crystallization processes than secondary effluent. Ostara ™ (Britton, 2009) and Air-Prex ™ (Heinzmann, 2009) are two modern phosphorus recovery processes that are in full-scale operation and use post anaerobic digestion sludge streams for phosphorus recovery by struvite crystallization (Kabbe, 2013).

Significant struvite scale formation on plant piping and equipment can occur after anaerobic digestion as was discussed in Section 1.4.1. To mitigate this problem, processes such as PhoStrip™ and WASSTRIP™ utilize the phosphorus release mechanism of PAO to achieve high dissolved phosphorus concentrations in sludge side streams before digestion (Schauer, et al., 2009). Both processes store BPR sludge (RAS in PhoStrip; WAS in WASSTRIP) for a short time in anaerobic conditions and in the presence of VFA. This anaerobic storage phase induces phosphorus release by the PAO community in the sludge and can increase dissolved phosphorus concentrations to 35% of the total phosphorus in the sludge (Schauer, et al., 2009); enabling phosphorus recovery by the crystallization processes. WASSTRIP™ is associated with OSTARA and the phosphorus rich liquid stream produced from the biological release is mixed with the post anaerobic digestion centrate stream to maximize phosphorus recovery. PhoStrip™ is technically a phosphorus removal process and was not developed as a phosphorus recovery process although it does bind phosphorus as calcium phosphate and can be implemented in front of crystallization processes (such as DHV Crystalactor™) to increase phosphorus recovery (DHV Consulting Engineers, 1991).

To date, crystallization methods with biological phosphorus release are the only phosphorus recovery methods that are economical at full scale. Modern, full-scale phosphorus recovery processes such as OSTARA™ can recover up to 90% of the dissolved phosphorus input to the reactor; efficiency increases with dissolved phosphorus concentrations (Britton, et al., 2005).

1.5.2. Chemical Based Phosphorus Solubilization –Phosphorus Recovery from Sludge Solids

Another group of phosphorus recovery techniques from sludge employ heat and/or chemical methods to solubilize the bound phosphorus in sludge, producing a phosphorus rich liquid stream. This phosphorus rich liquid stream is then typically subject to crystallization technologies to recover phosphorus as struvite or calcium phosphate. Acid leaching, alkaline leaching, thermal treatment, chemical oxidation, or wet oxidation are methods employed to dissolve most of the sludge constituents by cell destruction (lysis) and hydrolysis. These processes can solubilize over 90% of the phosphorus contained in the sludge, however other sludge components such as heavy metals, are solubilized as well. Thus additional steps are required to purify the resulting liquid stream until phosphorus can be recovered without significant contamination.

Table 1: Chemical Phosphorus Solubilization Processes

Process Name	Solids Stream	Description	Full Scale Installation	References
Seaborne/Gifhorne	Digested sludge	Acid leaching of phosphorus – amorphous phosphorus precipitate with magnesium	Gifhorne WWTP, Germany	(Müller, et al. 2006) (Nieminen 2010)
Mephrec	Dried Sludge	High temp (2000^{o}C) metallurgical process – phosphorus rich slag product	Nürnberg Germany	(Kabbe 2013)
KREPRO	Sludge	acid leaching, thermal hydrolysis, precipitation as ferric phosphate	Helsingborg, Sweden	(Dichtl, et al. 2007)
KEMIKOND	Digested Sludge	acid leaching and oxidation, precipitation as ferric phosphate, conditioning and dewatering	Keppala, Sweden	(Dichtl, et al. 2007)
Aqua-Reci	Sludge	Wet oxidation, alkaline treatment, $CaPO_4$ precipitate	No full scale installation	(Stendahl & Jäfverström 2004)
LOPROX/PHOXNAN	Sludge	Wet oxidation, liquid separation, nano-filtration for phosphorus recovery	No full scale installation	(Dichtl, et al. 2007)

Table 1 shows many of the phosphorus recovery processes for solids streams have only a single installation or have not been implemented at full scale. The cost of chemical addition, pH manipulation, or energy for thermal treatment make many of these processes not feasible at current market value of phosphorus/phosphate fertilizers (Nieminen, 2010). The benefit of these recovery methods is that nearly all the sludge bound phosphorus is recoverable – only the fraction of phosphorus that is not biologically removed during wastewater treatment (typically <10%) would not be recoverable.

1.5.3. Phosphorus Leaching - Recovery of Phosphorus from Ash

Ash phase recovery of phosphorus is a separate group of processes that use chemical leaching to potentially recover all of the incoming phosphorus to a wastewater treatment plant. It is important to note that currently, recovery of phosphorus from sewage sludge ash is only possible when the ash is incinerated alone (mono-incineration) and not combusted with other material such as municipal solid waste (Petzet & Cornel, 2013). Multi-step phosphorus leaching processes can solubilize 99% of the phosphorus in the sludge ash (Petzet & Cornel, 2013). Leaching the phosphorus from ash with acids or bases also solubilizes high concentrations of heavy metals present in the ash. Therefore additional steps have to be taken to purify the leachate so that contamination of the recovered phosphorus is avoided (Nieminen, 2010). Once a relatively contaminant free liquid fraction of phosphorus is produced, phosphate crystallization techniques can be utilized to produce struvite or calcium phosphate from the orthophosphate. Because sludge is often co-incinerated and due to the high cost of energy and chemicals required for nutrient recovery from sewage sludge ash, these processes are not widely implemented at full-scale (Kabbe, 2013).

Table 2: Leaching Processes for Phosphorus Recovery from Ash

Process Name	Leaching Method	Description	Full Scale Installation	References
THERMPHOS	Acid	P recovery from Al-sludge- acid leaching, CSH based phosphorus recovery	No full scale installation	(Kabbe 2013)
Ash-Dec	Acid	P recovery from sludge ash – high temp thermo chemical treatment – produces K, Mg phosphates	Koenigs Wusterhausen Germany	(Kabbe, 2013)
PASH	Acid	Liquid-liquid extraction removes iron and HM – CaPO4 or struvite precip.	No full scale installation	(Montag et al., 2009)
Bio-Con	Acid	Purify leachate with ion-exchange resin columns – produces H2PO4	No full scale installation	(Nieminen 2010)
Nano-filtration	Acid	Ion-exchange membrane filters out HM – struvite precipitation	No full scale installation	(Dichtl, et al. 2007)

1.6. SUMMARY AND OBJECTIVES

Full-scale phosphorus recovery techniques from wastewater treatment plants currently focus on struvite or calcium phosphate precipitation of phosphorus. For these crystallization processes, a liquid stream high in dissolved phosphorus concentrations is essential. Recovery efficiencies of over 90% are reported for struvite precipitation processes when fed with liquid streams containing over 70 mg l^{-1} of dissolved phosphorus (Britton, et al., 2005).

The most commonly used feed streams for struvite precipitation processes are post-anaerobic digestion streams such as digester supernatant or dewatering centrate. However, recovering phosphorus after digestion allows the potential for struvite scaling on digestion and dewatering equipment and piping. Phosphorus recovery before anaerobic digestion will limit this scaling problem and will minimize chemical use associated with limiting struvite scaling. Additionally, recovery of phosphorus before anaerobic digestion will improve overall phosphorus recovery rates by avoiding losses of recoverable phosphorus due to scaling and chemical precipitation.

Recovery of phosphorus before anaerobic digestion by struvite precipitation requires solubilization of phosphorus in the sludge. Many techniques for phosphorus solubilization have been explored, including biological release, acid leaching, alkaline leaching, thermal treatment, ultrasound, sludge freezing, microwave, or some combination of these (Koster and Londong, 2005; Liao et al., 2005). However, due to the cost of chemicals and high energy input, only biological release methods based on phosphorus release and VFA consumption are successfully employed.

The goal of this work is to explore sludge fermentation as a low energy input method for phosphorus solubilization to facilitate recovery of phosphorus from wastewater sludge before anaerobic digestion. Measureable objectives used to determine whether sludge fermentation is an effective technique for pre-digestion phosphorus solubilization from sludge include:

- Solubilization of >100 mg P/L to maximize recovery efficiencies in conventional struvite precipitation processes;
- Short term (1 - 4 day) fermentation to minimize volume requirements for the process;
- Production of VFA from the fermentation process (as opposed to consumption of VFA in PAO release mechanism based processes); and,
- Exploration of the effect of co-fermentation on phosphorus solubilization and VFA production.

2. Materials and Methods

2.1. SLUDGE TYPES USED IN FERMENTATION EXPERIMENTS

2.1.1. *Co-thickened Sludge*

Co-thickened sludge was collected from the underflow of the primary clarifier/thickeners from two wastewater treatment plants in Winnipeg, Manitoba; the North End Water Pollution Control Centre (NEWPCC) and South End Water Pollution Control Centre (SEWPCC). Both plants operate as carbon only removal facilities using the high purity oxygen activated sludge (HPOAS) process. At both facilities, waste activated sludge (WAS) is co-thickened with primary solids (PS) and the produced mixed sludge is fed into an anaerobic digestion process. Information from plant staff indicate that the mixing ratio of PS and WAS in the co-thickeners is approximately 1:1 by volume. Average characteristics of the co-thickened sludge from the NEWPCC and SEWPCC are shown in Table 3.

Table 3: Initial characteristics of co-thickened sludge used in semi-continuous fermentation tests – from the NEWPCC and SEWPCC, Winnipeg Manitoba

	NEWPCC	**SEWPCC**
pH	6.10	5.86
TS, g l^{-1}	35.8	33.1
VS, g l^{-1}	25.0(70% of TS)	26.7(81% of TS)
COD, g l^{-1}	42.5	48.5
TP, mg l^{-1}	397	351
PO_4-P, mg l^{-1}	61 (15% of TP)	113 (32% of TP)
TP/VS, mg g^{-1}	15.9	13.1

2.1.2. Primary Sludge (PS)

WAS and PS are co-thickened in the primary clarifiers. In order to obtain primary sludge only, raw influent wastewater from the SEWPCC was collected immediately after the de-gritting chamber and allowed to settle for 3 hours. After decanting, the remaining sludge was collected and allowed to settle again for 45 minutes. After the second decanting, the remaining primary sludge was used in the fermentation experiments. Characteristics of the primary sludge produced by this method are shown in Table 4.

2.1.3. Waste Activated Sludge (WAS)

WAS was collected from the return sludge line at the SEWPCC. Characteristics of the waste activated sludge are shown in Table 4.

2.1.4. Combined PS+WAS

Combined sludge used in the batch fermentation experiments was a 1:1 mixture by volume of WAS and PS (collected as described above). The 1:1 mixing ratio was selected to mimic the mixing ratio of sludge in the NEWPCC and SEWPCC co-thickening clarifiers. Based on the characteristics of the WAS and PS used to produce this mixed sludge, the ratio of volatile solids in the combined sludge was approximately 70:30 PS to WAS. Initial characteristics of the combined sludge were almost an average of the WAS and PS characteristics as shown in Table 4.

Table 4: Initial characteristics of sludge collected from the SEWPCC used in concurrent fermentation trials

	PS	**WAS**	**WAS+PS**
pH	7.06	6.78	6.90
TS, g l^{-1}	17.1	8.8	13.0
VS, g l^{-1}	13.6 (80% of TS)	7.3 (83% of TS)	10.2 (79% of TS)
COD, g l^{-1}	23.1	11.5	15.0
TP, mg l^{-1}	93	199	156
PO_4-P, mg l^{-1}	5.6	19.4	22.4
TP/VS, mg g^{-1}	6.8	27.3	15.3

2.2. FERMENTATION TESTS

2.2.1. *Batch Fermentation*

Batch sludge fermentation was conducted in 5 L plastic vessels. Vertical impeller mixers provided constant mixing. Sludge was added to the fermenters and stirred constantly for the duration of the fermentation experiments. Batch fermentation tests were performed for 4 or 5 days. Temperatures were ambient room temperature, approximately 21^{o}C. The fermenters were covered during fermentation and were only uncovered briefly during sampling. The reactors were operated under complete mix conditions and the pH was monitored but not controlled. During the batch fermentation tests an initial volume of 4 L of sludge was added to each reactor and was sampled at the same time daily to maintain consistency. Total volume of the fermenting sludge was typically 4 L and daily sample volume from each reactor was approximately 60 ml.

In the concurrent batch fermentation tests three types of sludge were fermented concurrently to compare phosphorus solubilization and VFA production during fermentation: WAS, PS, and a mixture of both PS and WAS. Triplicate fermentation trials were performed for each sludge type (total of 9 tests).

2.2.1. Semi-continuous Fermentation

In the semi-continuous fermentation tests an initial 4 L of sludge was added to the 5 L reactors at the beginning of the experiment. A sampling-wasting-feeding cycle was performed daily for each reactor. Sampling occurred directly from the reactor and not from the wasted fraction of sludge in order to obtain well-mixed samples. Following sampling, the desired amount of sludge was wasted and then replaced with fresh sludge to maintain a 2 day or 3 day HRT in the fermenter. The semi-continuous fermenters were stirred constantly for the duration of the fermentation experiments conducted at room temperature; approximately 21^{o}C. The fermenters were covered during fermentation and were only uncovered briefly during sampling and feeding. The reactors were operated under complete mix conditions and the pH was not controlled. Semi-continuous fermentation tests of the co-thickened sludge were carried out for two and four weeks for SEWPCC and NEWPCC respectively.

During some of the semi-continuous fermentation tests, sludge was harvested from the wastewater treatment plant every two days and kept in refrigerated storage at 4^oC, between daily feeding cycles. A brief study was undertaken to determine if a significant P release occurred during the storage time by measuring the change in characteristics of the sludge during the 2 days of storage. Results indicated 4% ± 2% change in the dissolved P concentration in the sludge and 8% ± 3% change in VFA concentration during the refrigerated storage phase.

2.3. MEASUREMENTS AND ANALYSIS

Total solids (TS) and Volatile Solids (VS) measurements were performed according to Standard Methods (APHA, 1998). Hach COD digestion vials were used to measure COD. Dissolved orthophosphate was measured using a Lachat Instrument Quik Chem 8500, following the Quik Chem orthophosphate method 10-115-01-1-O. The analysis of VFA composition was conducted by means of a Varian CP-3800 Gas Chromatograph using a flame ionization detector (FID) and HP-FFAP capillary column (inner diameter of 0.25mm and length of 25m). Samples for VFA analysis were prepared by centrifugation of the fermented liquor at 10000 RPM for 10 minutes followed by filtration through a 0.2μm filter. VFA concentration was converted to COD concentration by using the following conversion factors: 1.07 for acetic acid, 1.51 for propionic acid, 1.82 for butyric and isobutyric acid, 2.04 for valeric and isovaleric acid, 2.21 for caproic and iso-caproic acid and 2.34 for heptanoic acid.

3. Results and Discussion

3.1. PHOSPHORUS SOLUBILIZATION

3.1.1. Batch Fermentation Tests – Co-thickened Sludge

Initial experiments of short term batch fermentation of co-thickened sludge from the NEWPCC were conducted to evaluate the potential for P release from fermenting sludge. Although results varied significantly (Figure 2), it was shown that after 2 days of fermentation, concentrations of soluble phosphorus above 100 mg l^{-1} could be achieved.

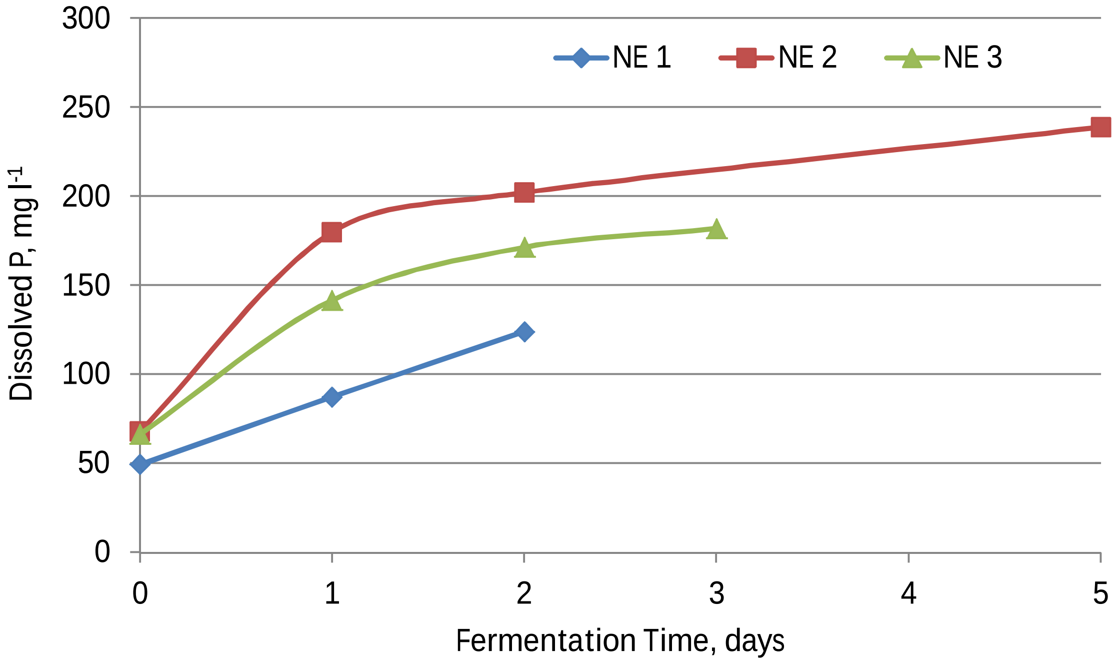

Figure 2: Soluble phosphorus in batch fermentation of co-thickened sludge - NEWPCC

A plot of the soluble phosphorus concentration as a percent of total phosphorus (TP) in the sludge showed that the first fermentation trial, which had the lowest actual concentration of soluble phosphorus after two days of fermentation, actually released the highest fraction of the TP contained in the sludge; 57% of TP. The second trial had twice the concentration of soluble phosphorus than the first trial after one day of fermentation. However, trials 1 and 2 were insignificantly different in terms of percent of TP released after one day as shown in Figure 3. These observations show that the amount of soluble phosphorus released during fermentation is dependent on the amount of total phosphorus in the sludge.

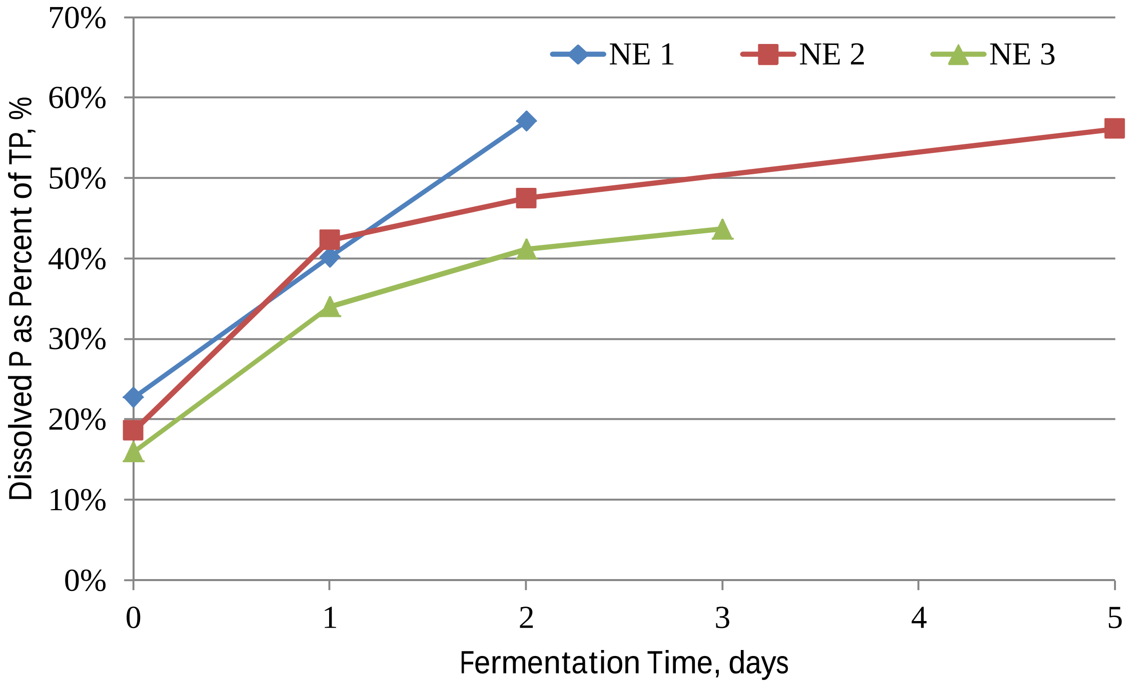

Figure 3: Soluble phosphorus as percent total phosphorus in batch fermentation of co-thickened sludge - NEWPCC

Figure 4 plots the pH in the batch fermentation reactors over time. From an initial pH of approximately 6.14, the pH decreased with fermentation time in each trial. However, the rate of pH decrease differed between fermentation trials so that after two days of fermentation, the pH in the fermenters ranged from 5.59 to 6.01

for trials 1 and 3 respectively. In pH controlled fermentation experiments of WAS, Chen, et al. (2007), found that a lower pH in the fermenters corresponded with higher phosphorus solublization within a pH range of 4 to 12. In the batch fermentation experiments of NEWPCC co-thickened sludge trial 1 had the lowest pH after two days of fermentation and trial 3 had the highest pH. At the same time, trial 1 had the highest phosphorus solubilization as a percent of TP while trial 3 had the lowest; 57% and 41% respectively. Trial 2 had a similar drop in pH after five days of fermentation (5.66) as trial 1 had at two days. This pH drop corresponded to a similar phosphorus solubilization of 56% of TP for trial 2 at five days fermentation compared to 57% of TP at two days fermentation for trial 1. Therefore, decreased pH in the fermenter corresonded to increased phosphorus solubility in these uncontrolled pH experiments, confirming the observations of Chen, et al. (2007) in controlled pH experiments.

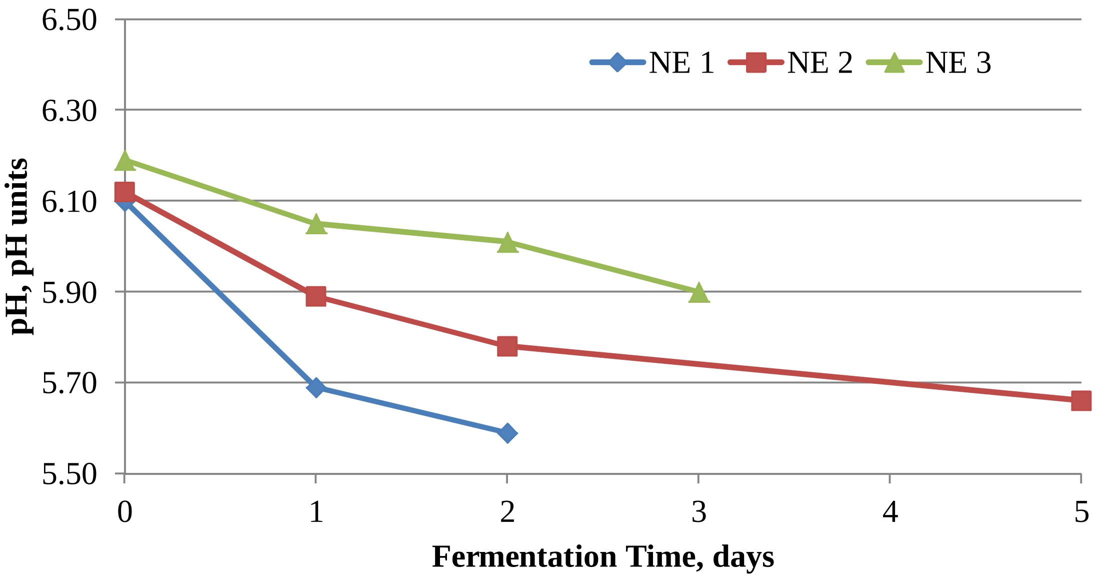

Figure 4: Plot of pH in batch fermentation of co-thickened sludge - NEWPCC

3.1.2. Semi-continuous Fermentation Tests – Co-thickened Sludge

Semi-continuous fermentation of co-thickened sludge from the NEWPCC was carried out to mimic results of the fermentation process in a large scale continuous fermentation installation and to establish a more continuous process that might serve to reduce the effect of sludge variability on the phosphorus solubilization results. Results from a four week trial of semi-continuous fermentation of co-thickened sludge from the NEWPCC are shown in Figure 5. The reactor was completely mixed and the hydraulic retention time was two days. Details of reactor operation are found in Section 2.2.1. A two day HRT was selected based on the results of the batch fermentation tests which demonstrated that the most significant increase in dissolved phosphorus concentration occurred in the first two days of fermentation.

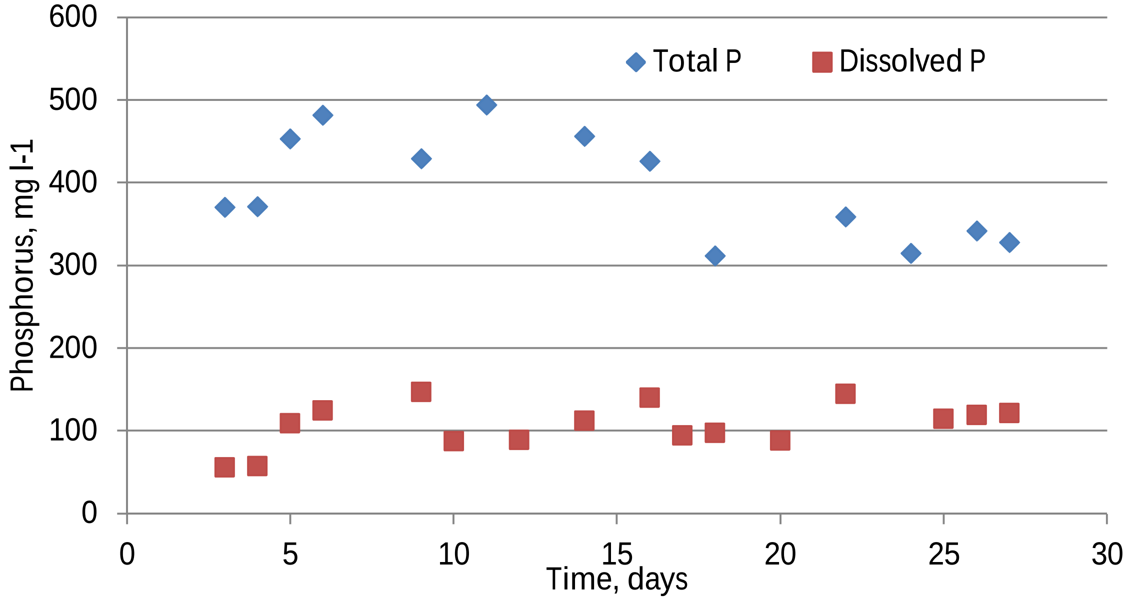

Figure 5: Phosphorus in semi-continuous fermentation of co-thickened sludge - NEWPCC Trial 1

Total phosphorus and soluble phosphorus still varied over time but on average the total phosphorus of the sludge in the fermenter was 397 mg l^{-1} and soluble phosphorus concentration averaged 113 mg l^{-1}. The soluble phosphorus concentration corresponded to approximately 28% of TP, which was lower than results from batch test fermentation after two days but still surpassed the objective of 100 mg $l^{-}1$ of soluble phosphorus. The lower phosphorus solubilization in the semi-continuous fermentation test could be due to the fact that there was only one wasting/feeding cycle per day so at any given time, half of the sludge in the fermenter was only fermenting for one day. The pH in the fermenter averaged 5.56 over the four weeks of operation.

A second trial of semi-continuous fermentation of NEWPCC was performed. Two semi-continuous fermenters were operated simultaneously; one with a two day HRT and one with a three day HRT. Results are shown in Figure 6. Total phosphorus of the sludge was 386 mg l^{-1} which was comparable to the first trial. Soluble phosphorus averaged 135 mg l^{-1} in the two day HRT fermenter and 144 mg l^{-1} in the three day HRT fermenter. In terms of percent of TP solubilized, the two day and three day HRT fermenters were very similar on average, with 35% and 37% of TP solubilized respectively. The pH in the two day HRT fermenter averaged 5.43 and the pH in the three day HRT fermenter averaged 5.28.

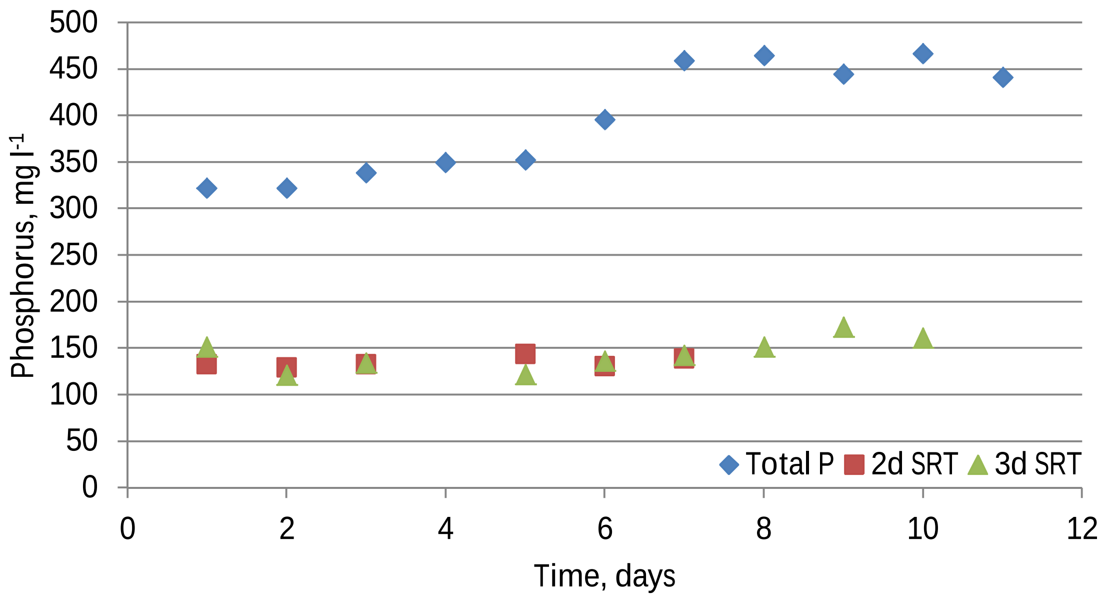

Figure 6: Phosphorus in semi-continuous fermentation of co-thickened sludge - NEWPCC Trial 2

The second trial of semi-continuous fermentation had better phosphorus solubilization results than the first but was still lower than the phosphorus solubilization results in the batch tests. The pH in the two day HRT fermenter of the second semi-continuous fermentation trial was lower than in the first trial which corresponded to increased phosphorus solubilization. The pH of the three day HRT fermenter was lower still than the two day HRT fermenter in the second trial but this corresponded to only a small increase in the percentage of TP solubilization. This could be explained by the short operation of the two day HRT fermenter in the second trial. The two day fermenter was only operated for seven days while the three day HRT fermenter was operated for eleven days. It can be seen in Figure 6 that the TP in the sludge increases significantly around day six. Therefore, this increase did not significantly impact the average TP concentration calculated in the two day HRT trial but did increase the average TP of the three day HRT fermenter. It can be seen that the last half of the data points for soluble phosphorus in the three day HRT fermenter indicate a rising trend in soluble phosphorus that mirror the total phosphorus increase but at a time lag of about one HRT. If this experiment was continued for a longer time it is likely that a more significant increase in soluble phosphorus would have been observed in the three day HRT fermenter.

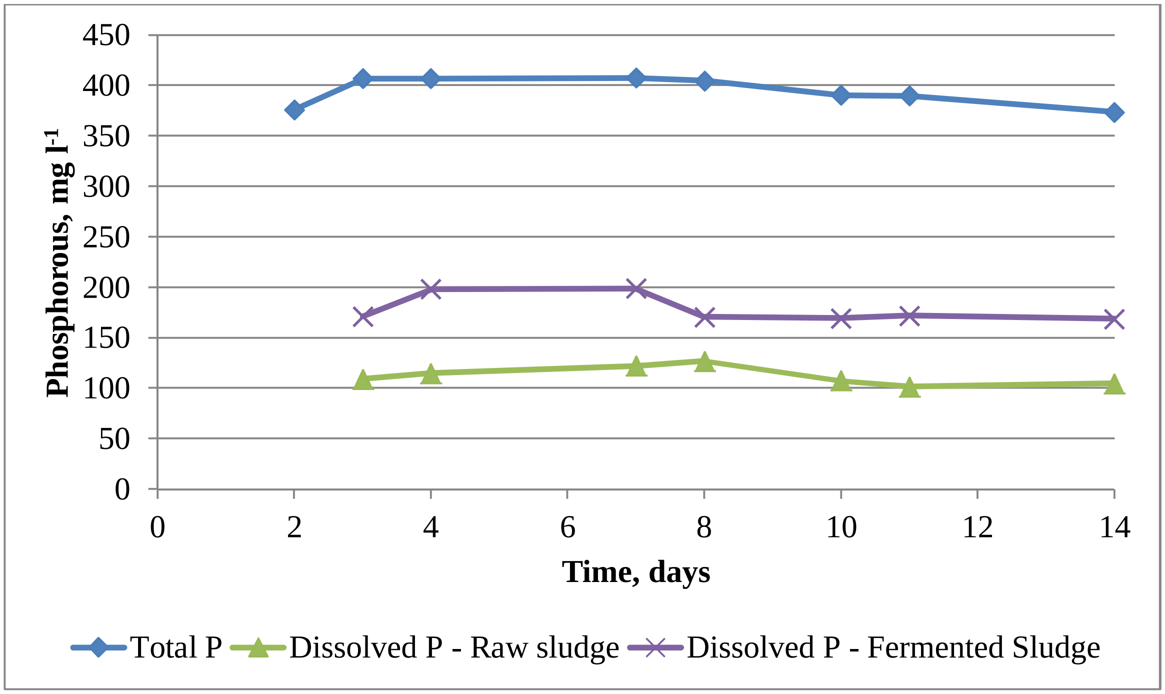

Figure 7: Phosphorus in semi-continuous fermentation of co-thickened sludge - SEWPCC

Co-thickened sludge from the SEWPCC was also fermented in a semi-continuous fermenter operating with a two day HRT. Results of the two week trial are shown in Figure 7. Prior to feeding the sludge to the reactor, soluble phosphorus of the feed sludge was measured in addition to total phosphorus and soluble phosphorus in the fermenter. On average, the SEWPCC co-thickened sludge contained an initial dissolved phosphorus concentration of 112 mg l^{-1}, corresponding to 32% of TP already dissolved in the co-thickened sludge. In the two day HRT semi-continuous fermenter, soluble phosphorus concentrations averaged 178 mg l^{-1} corresponding to 51% of TP. The pH of the feed sludge averaged 5.86 and pH in the fermenter was 5.51.

A comparison of the initial characteristics of the NEWPCC and SEWPCC co-thickened sludge shows that the concentrations of total P for both co-thickened sludges were similar; on average 397 mg l^{-1} and 351 mg l^{-1} respectively. However, the percentage of total phosphorus that was soluble after two days of semi-continuous fermentation differed significantly; 28-35% of TP and 51% of TP respectively for NEWPCC (Trials 1 &2) and SEWPCC co-thickened sludge. The significantly higher dissolved phosphorus concentration in the SEWPCC sludge after 2 days of fermentation corresponded to higher initial concentration of dissolved phosphorus in the co-thickened sludge as sampled from the primary clarifier/thickener at the plant. On average, the SEWPCC co-thickened sludge contained an initial dissolved phosphorus concentration of 112 mg l^{-1}, corresponding to 32% of TP already dissolved in the co-thickened sludge. The NEWPCC sludge initially contained only 61 mg l^{-1} of dissolved phosphorus, corresponding to 15% of TP. The change in soluble phosphorus (ΔP_{sol}) in the semi-continuous fermenters for both the NEWPCC and SEWPCC co-thickened sludge was very similar; ΔP_{sol} of 13-20% of TP for NEWPCC and ΔP_{sol} of 19% of TP for SEWPCC co-thickened sludge. This indicates that the rate of P solubilization is approximately constant over the short fermentation times (1-4 days) in these experiments.

The elevated initial concentration of dissolved phosphorus in the SEWPCC co-thickened sludge may be due to increased fermentation occurring in the primary clarifier/thickeners at the SEWPCC compared to the NEWPCC. Although the clarifiers at the NEWPCC and SEWPCC are operated in a similar way with respect to hydraulic and solids retention times, the actual clarifier/thickener tank shapes differ. At the SEWPCC the clarifier/thickeners are long rectangular tanks while the NEWPCC clarifier/thickeners are round. The round tanks are typically more efficient and effective at solids collection and removal while the long rectangular tanks may have dead zones where sludge can build up and begin to ferment. This built-up sludge may cause a seeding effect in the co-thickened sludge blanket. Seeding with partially fermented sludge has been found to increase sludge fermentation (Banister and Pretorius, 1998) possibly leading to the elevated dissolved phosphorus concentrations found in the SEWPCC co-thickened sludge. The low pH of the co-thickened sludge (5.86) from the SEWPCC clarifiers further indicates that fermentation is occurring in the clarifiers.

3.1.3. Concurrent Batch Fermentation Tests

Concurrent batch fermentation of fresh primary sludge (PS) alone, waste activated sludge (WAS) alone, and combined PS and WAS was performed to explore the difference in phosphorus solubilization for each sludge type during fermentation and to explore if the effect of cofermentation on phosphorus solubilization.

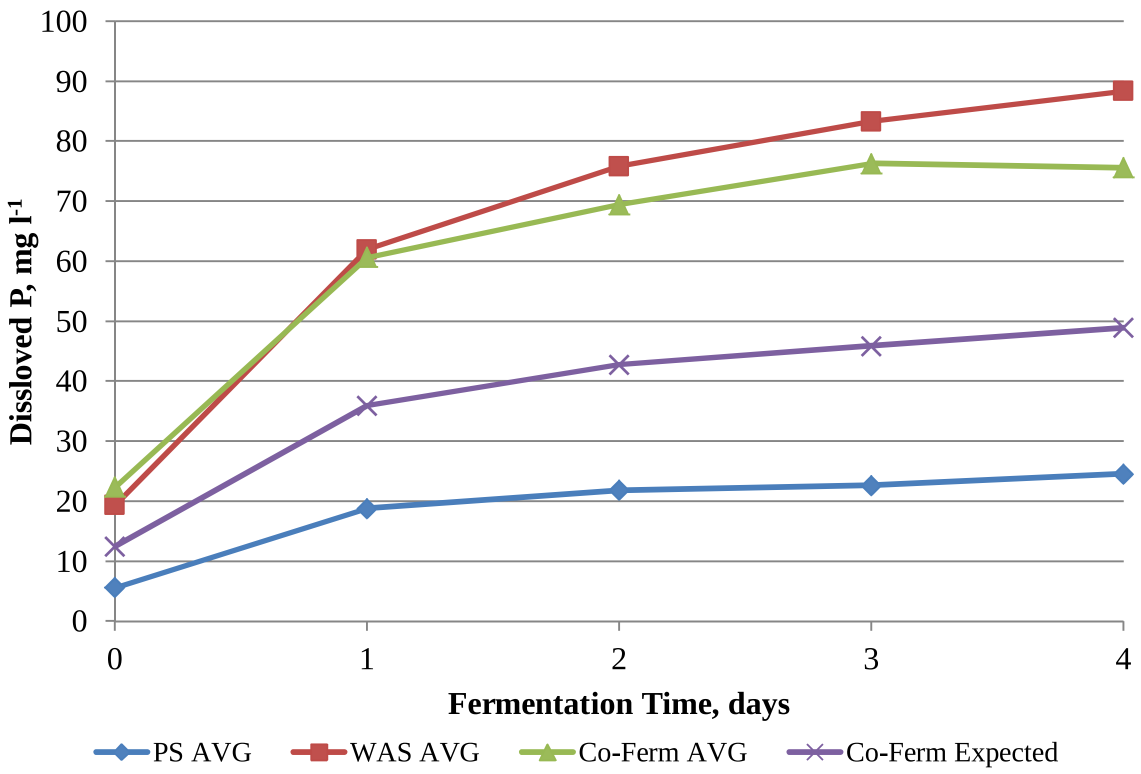

Figure 8: Phosphorus release in concurrent batch fermentation - Average of 3 trials

Batch fermentation of PS, WAS, and combined (WAS and PS) sludge showed that dissolved phosphorus concentrations increased with time for all sludge types as shown in Figure 8; which was expected based on comparable sludge fermentation experiments (Koster and Londong, 2005; Schauer et al., 2009; Yuan et al., 2010).

Fermentation of WAS alone produced the highest overall concentration of soluble phosphorus; after 4 days of fermentation 69 mg l^{-1} of phosphorus was solubilized resulting in a concentration of 88.4 mg l^{-1} of dissolved phosphorus. Fermentation of primary sludge alone showed lower phosphorus solubilization; 18.9 mg l^{-1} of phosphorus was solubilized after 4 days of fermentation increasing the initial soluble phosphorus concentration of 5.6 mg l^{-1} to 24.5 mg l^{-1}. Co-fermentation of WAS and PS solubilized 53.2 mg l^{-1} of phosphorus, resulting in a total of 75.6 mg l^{-1} of dissolved phosphorus in the sludge.

As discussed in Section 2.1.4, the combined sludge is a 1:1 mixture of PS and WAS by volume, but 70:30 mixture by mass of volatile solids (VS). Since phosphorus solubilization in fermenting sludge is caused by the hydrolysis of the volatile solids in sludge it was expected that the combined sludge would act more similarly to PS than WAS in terms of phosphorus release. A weighted average of the phosphorus solubilization of PS and WAS only fermentation was plotted (in purple) with the actual results of the concurrent fermentation to compare the expected solubilization from combined sludge fermentation with the observed solubilization. It can be seen in Figures 8, and 9 that the actual phosphorus solubilization exceeds the expected solubilization based on individual PS and WAS fermentation performance. Compared to the weighted average of WAS and PS solubilization as shown in Figure 8, combined sludge fermentation resulted in 61% greater soluble phosphorus concentrations after two days of fermentation.

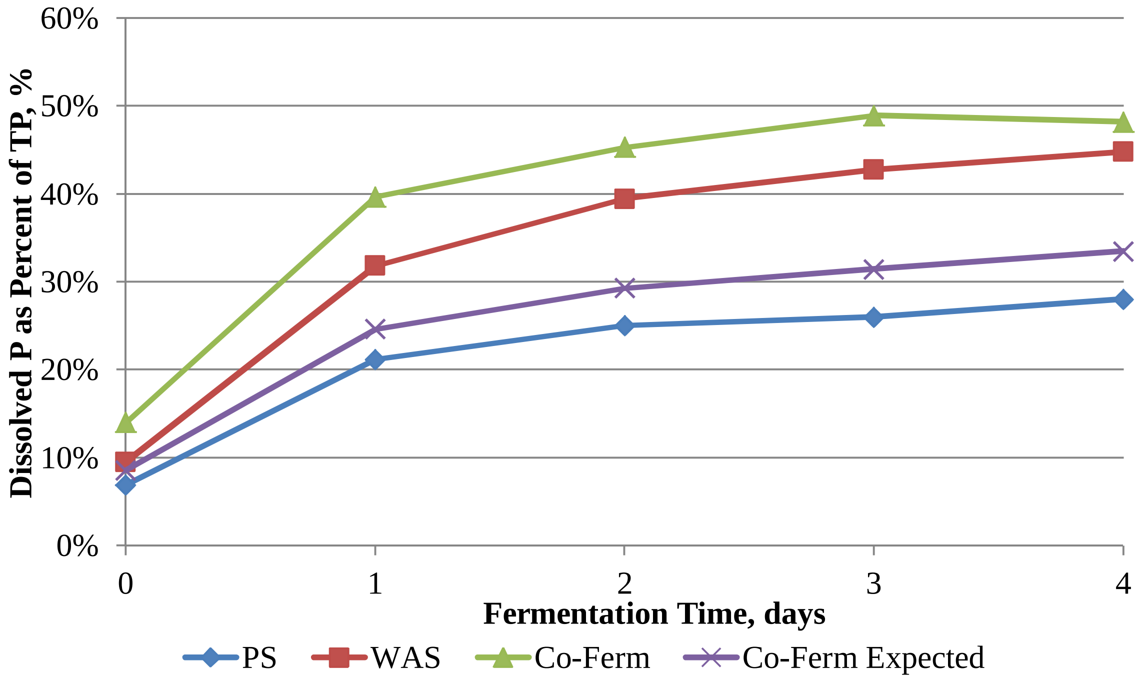

Figure 9: Soluble phosphorus as percent of total phosphorus in concurrent batch fermentation - Average of 3 trials

Since WAS had the highest concentration of total phosphorus and PS had the lowest concentration, it was expected that phosphorus solubilization would be highest from WAS fermentation and lowest from PS fermentation. In this series of experiments, the total phosphorus concentration of the WAS, on average, was 214% higher than in the PS. To account for this difference in TP concentration, dissolved phosphorus concentration was expressed as a percent of total phosphorus as shown in Figure 9. WAS fermentation still resulted in better phosphorus solubilization than PS; after 4 days of fermentation 45% of TP was present as soluble phosphorus in WAS while only 28% of TP was present as soluble phosphorus in PS. The combined sludge fermentation solubilized 34% of total phosphorus in the sludge, which resulted in a final dissolved phosphorus concentration equal to 48% of TP in the sludge after four days of fermentation.

The latter exceeded the percentage of total phosphorus that was solubilized in the WAS-only fermentation.

Fermentation of the freshly combined sludge resulted in similar percent of TP solubilized after two days of fermentation compared to the batch fermentation of NEWPCC co-thickened sludge and much higher increase compared semi-continuous fermentation experiments of co-thickened sludge as shown in Table 5. These results indicate that the rate of phosphorus solubilization appears to be constant over the short time period examined in these experiments. Batch fermentation appears to result in a higher phosphorus solubilization than semi-continuous fermentation, however this may be due to experimental methodology as discussed in section 3.1.2. “Freshness” of sludge did not appear to impact phosphorus solubilization rates as was suspected at the outset of the concurrent batch fermentation experiments. Finally, the difference in total solids concentration between the combined sludge and co-thickened sludge also did not appear to affect the phosphorus solubilization rate. These observations lead to the conclusion that within a wide range of sludge types, fermentation of combined sludge can be expected to increase soluble phosphorus concentrations by 20-30% of total phosphorus concentration.

Table 5: Comparison of change in % of TP as soluble P

Sludge Type	Soluble P as % TP		Increase in soluble P as % TP
	Day 0	Day 2	
Combined Sludge Batch	14%	45%	+31%
Co-thickened Batch NEWPCC	19%	49	+30%
Co-thickened Semi-continuous SEWPCC	32%	51%	+19%
Co-thickened Semi-continuous NEWPCC	15%	28-35%	+15-20%

In the three fermentation trials of combined sludge, the initial concentration of dissolved phosphorus was found to be significantly higher than an average of the dissolved phosphorus concentrations of the PS and WAS (Table 5). The initial measurement of dissolved phosphorus was taken within minutes of mixing the PS and WAS indicating that a rapid solubilization of phosphorus occurred upon mixing the sludge. In BNR sludge, a rapid increase in dissolved phosphorus has been observed to occur as the PAO bacteria release stored phosphorus in order to uptake VFA, however the sludge in this experiment was from a non-BNR wastewater plant which was not expected to contain PAO in the active biomass. The rapid initial increase in dissolved phosphorus that occurred upon mixing the PS and WAS indicated that there may be micro-organisms that act in a similar manner as PAO bacteria within the non-BNR biomass used in these experiments.

It can be seen that over 4 days the fermentation of combined sludge solubilized more phosphorus than what was theoretically expected. It appears that by co-fermenting primary and waste activated sludge, a synergistic affect is realized that improves solubilization of phosphorus beyond what is expected based on individual sludge fermentation results. This synergistic effect of co-fermentation agrees with the results from Yuan et al. (2010) who found that co-fermentation of sludge enhanced not only nutrient release (NH_4-N and PO_4-P) but also improved VFA production from the fermented sludge.

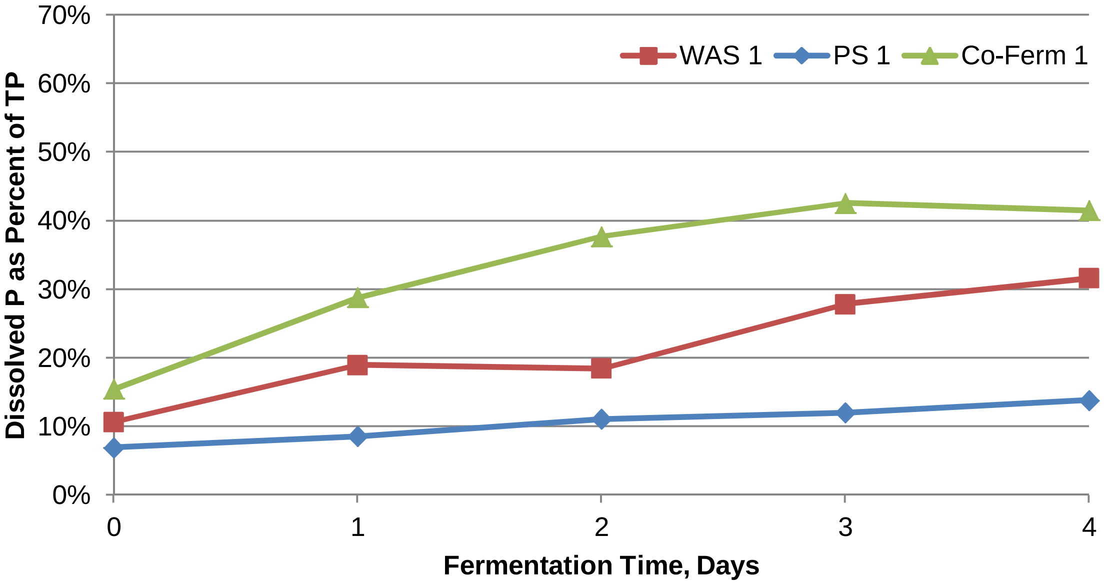

Figure 10 shows the phosphorus solubilization of the first concurrent fermentation trial in terms of percent of TP solubilized. After four days of fermentation, combined sludge contained 41% of TP as soluble phosphorus while WAS had 32% and PS had 14% of TP as soluble phosphorus. The results of the second concurrent fermentation trial (Figure 12) show increased phosphorus solubilization for all sludge types; 62%, 60% and 37% of TP as soluble P for combined sludge, WAS, and PS respectively. Comparing the pH in the fermenters for both trials (Figure 11 and Figure 13) reveals that the improvement in phosphorus solubilization in the second trial corresponds to decreased final pH for all sludge types.

The hydrolysis of cellular mass in the WAS releases significant alkalinity that buffers pH change and led to increased pH in the WAS fermenters over the four day fermentation time explored in these experiments. Conversely, primary sludge does not appear to contain as much buffering capacity and the pH was observed to drop more significantly during fermentation. The pH in the combined sludge fermenter appeared to generally follow the same pattern as WAS in the first trial but was still lower than the WAS fermenter. In the second trial, the pH dropped significantly, following the pattern of pH in the PS fermenter. Based on previous observations that lower pH corresponds to increased phosphorus solubilization, it is likely that the improvement in phosphorus solubilization realized from combined sludge fermentation is due to the lower pH in the fermenter probably caused by the PS fraction in the combined sludge.

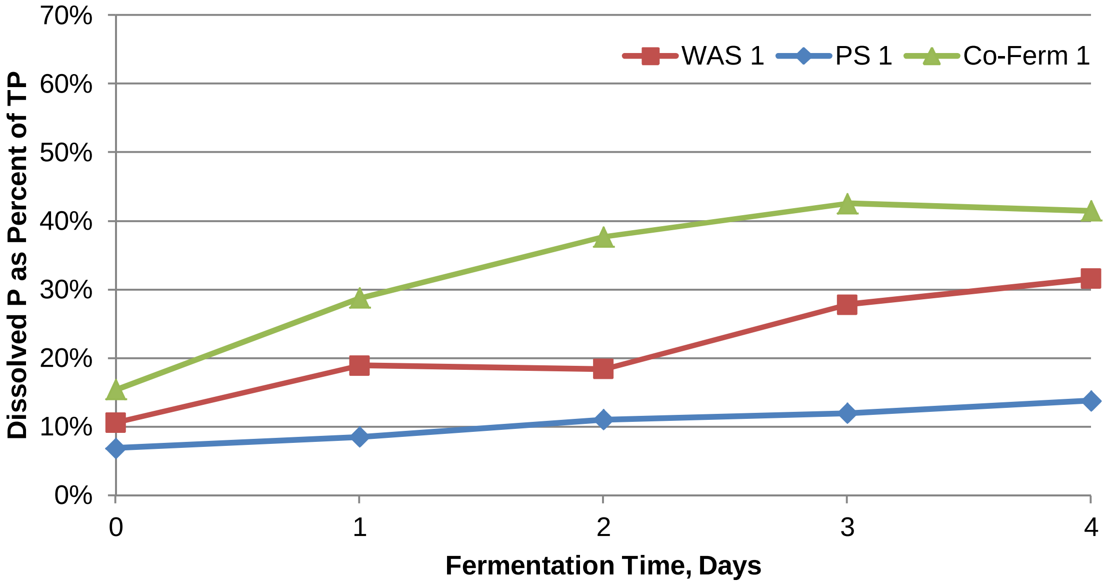

Figure 10: Soluble phosphorus as a percent of total phosphorus in concurrent batch fermentation – Trial 1

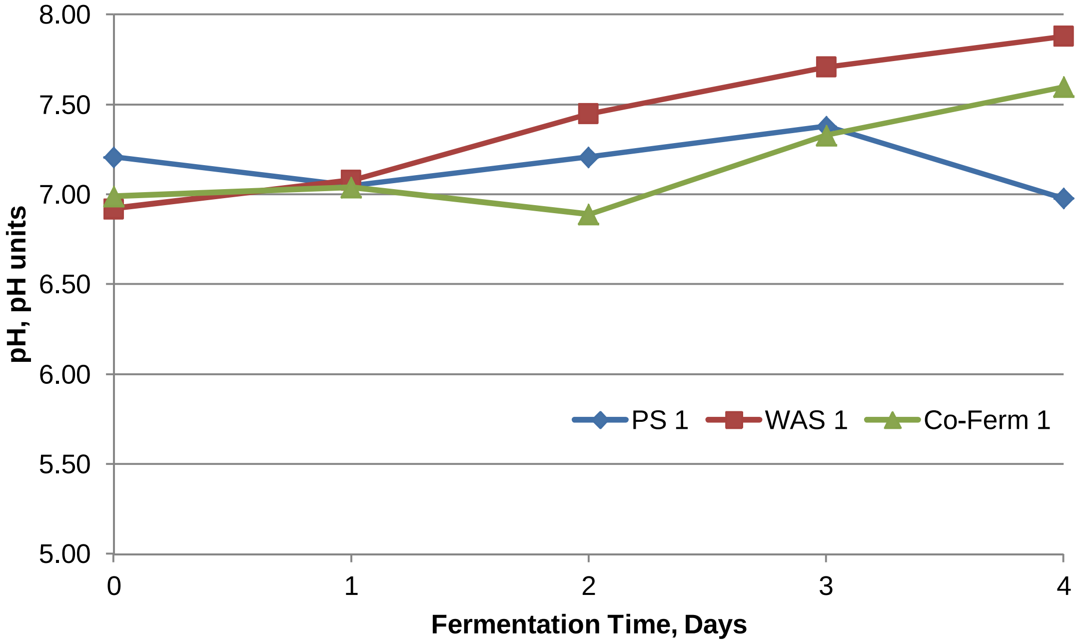

Figure 11: Plot of pH in concurrent batch fermentation - Trial 1

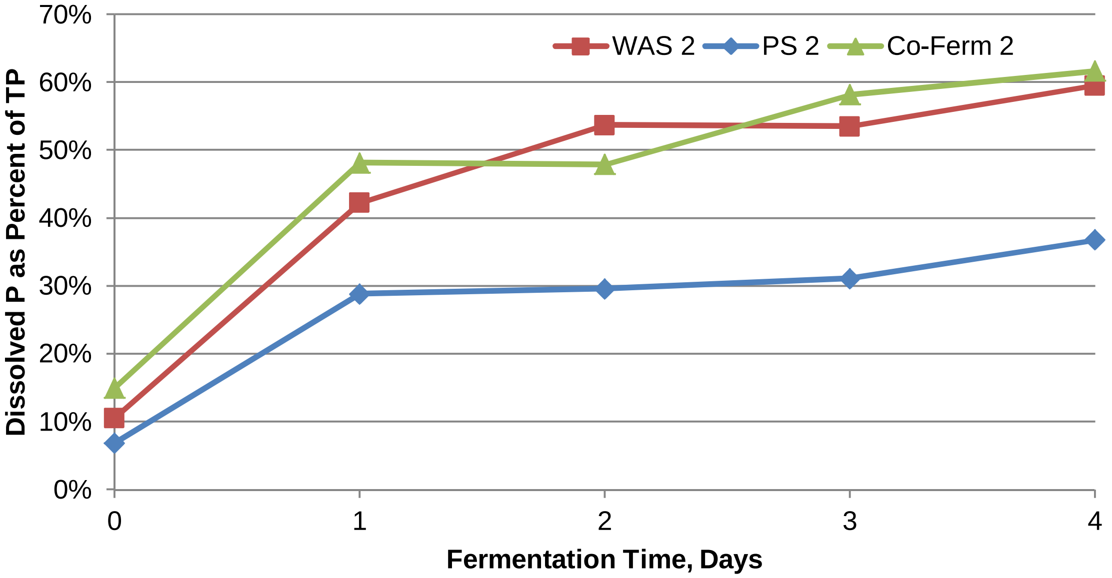

Figure 12: Soluble phosphorus as a percent of total phosphorus in concurrent batch fermentation - Trial 2

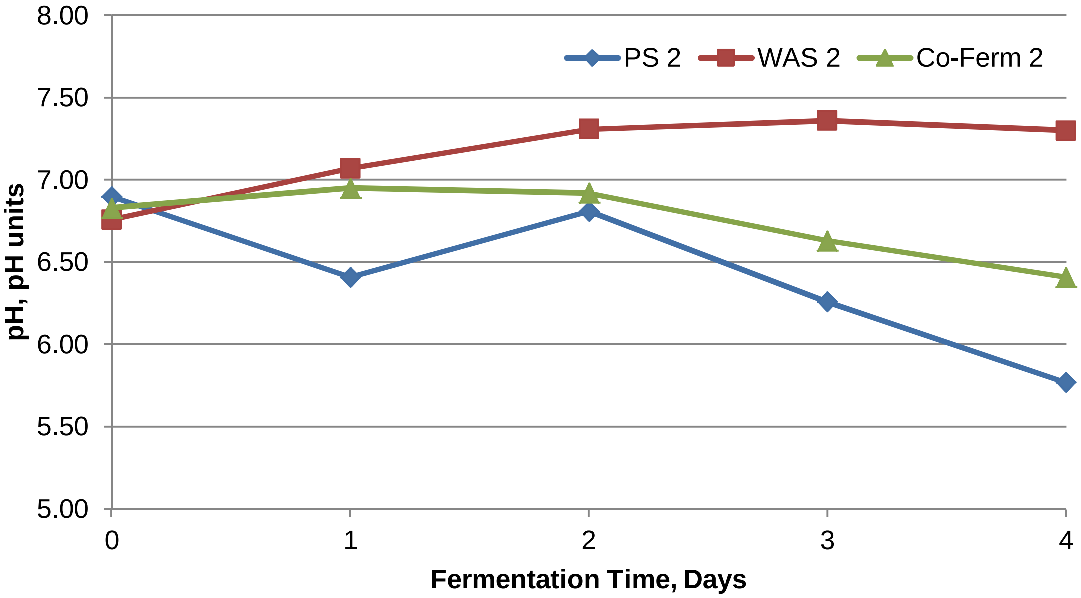

Figure 13: Plot of pH in concurrent batch fermentation - Trial 2

3.2. VFA PRODUCTION

Production of VFA increased with fermentation time for WAS, PS, and combined sludge fermentation. Since primary sludge is made up of a variety of organics, which are readily fermentable and undergo hydrolysis at a much quicker rate than the bacterial cells in WAS, the VFA production from PS is typically higher than from WAS during fermentation. In the batch fermentation experiments PS fermentation demonstrated the highest production of VFA of 1666 mg l^{-1} expressed as VFA-COD. VFA-COD production from combined sludge fermentation produced 1624 mg l^{-1} while from WAS fermentation, only 352 mg l^{-1} of VFA-COD was produced after 4 days.

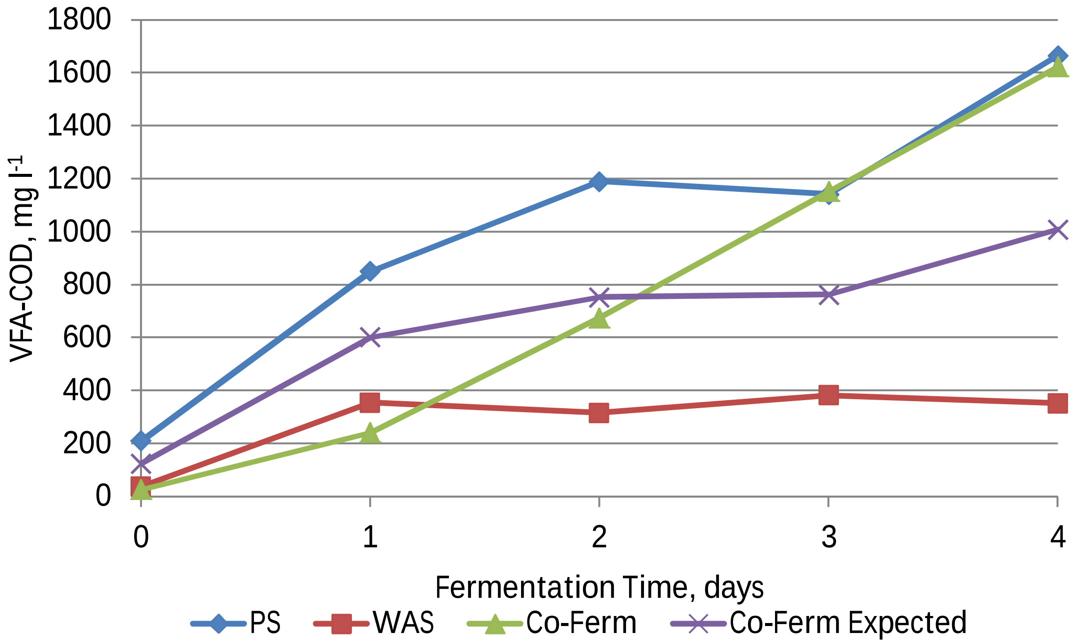

Figure 14: VFA concentration in concurrent batch fermentation

Combined sludge fermentation produced the most VFA-COD per mass of volatile solids; 0.139 mg per mg VS applied after 4 days of fermentation (Figure 14). The expected VFA production for combined sludge fermentation was calculated in the same way as for phosphorus solubilization; as a weighted average of the individual VFA production of PS and WAS only fermentation. The combined sludge produced 67.5% more VFA after 4 days of fermentation than expected given the VFA production from individual sludge fermentation and the mass ratio of volatile solids in the combined sludge.

The improvement in VFA production from combined sludge over what was expected based on the individual sludge performance may have been due to the presence of WAS microorganisms in the combined sludge having the ability to break down PS solids. Conversely, there are few microorganisms in PS that would be specialized to break down WAS cells. Therefore because the combined sludge was 70% PS by mass, the WAS portion served as inoculum for the sludge, and after a lag phase of approximately one day as shown in Figure 15, the degradation of the sludge increased rapidly, evidenced by the rapid increase in VFA-COD concentration in the reactor.

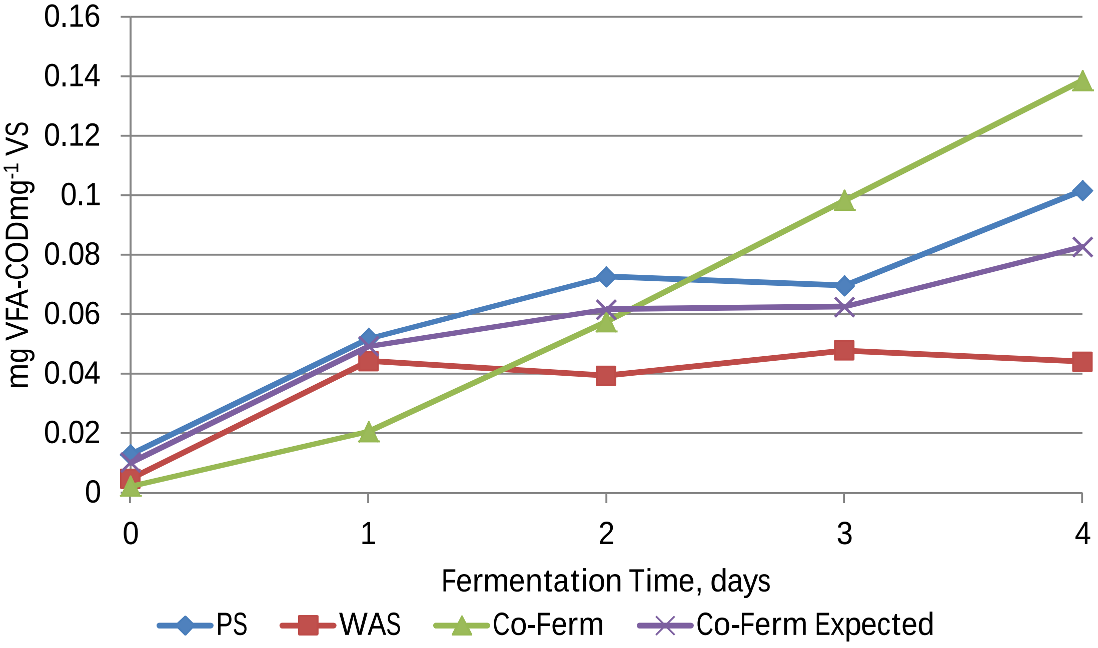

Figure 15: VFA production per mass of volatile solids in concurrent batch fermentation

VFA production was also measured during the semi-continuous fermentation of co-thickened sludge, operating with a 2d HRT. On average, the semi-continuous fermentation of SEWPCC sludge had a specific rate of VFA-COD production of 0.203 mg per mg VS applied while the NEWPCC sludge had a rate of 0.371 mg per mg VS applied. In comparable sludge fermentation experiments (Uscik and Heinze, 2008; Yuan, 2011) combined sludge fermentation had VFA-COD yields of 0.114 mg per mg VS applied and 0.061 mg per mg COD applied. An extensive summary of sludge fermentation produced by WERF (Rabinowitz et al., 2011) found that primary sludge fermentation typically has VFA-COD yield ranging from 0.05 – 0.3 mg per mg VS applied and approximately 0.09 mg per mg VS applied in WAS fermentation. Thus it can be seen that the yields found in the combined sludge batch fermentation and semi-continuous co-thickened sludge fermentation experiments are comparable to the higher end of the reported results for primary sludge fermentation.

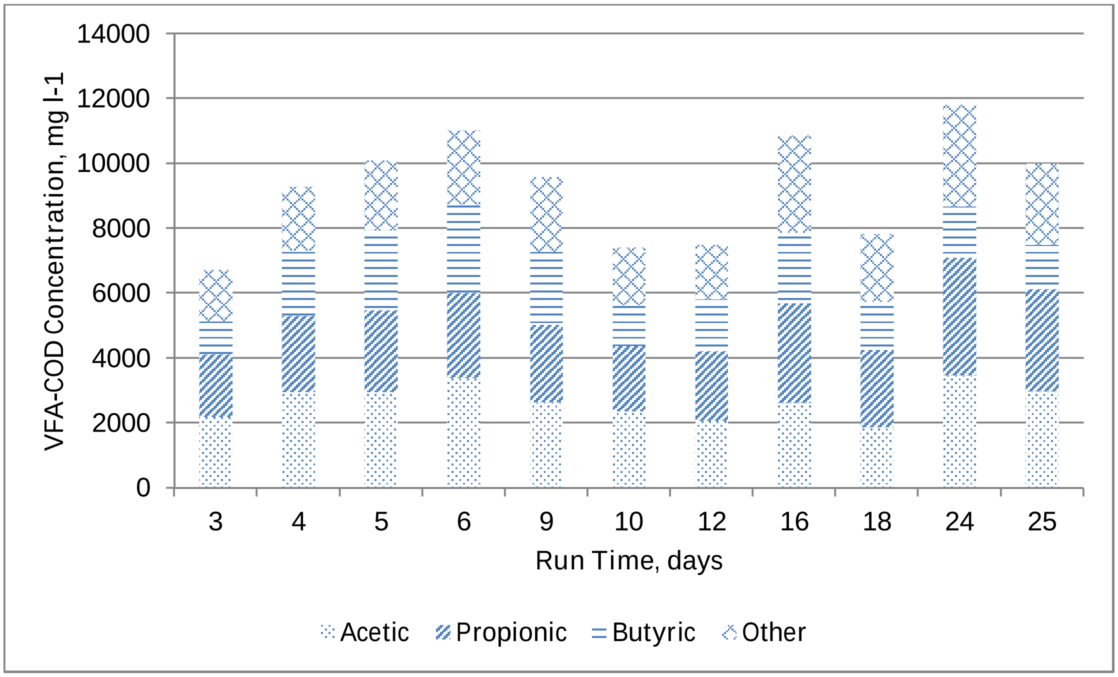

Figure 16: VFA concentration as COD in semi-continuous fermentation of NEWPCC co-thickened sludge (2d HRT)

Figure 16 shows the VFA production during the month-long operation of the semi-continuous fermenter fed co-thickened sludge from NEWPCC. Acetic and propionic acids made up 29% and 28% respectively of the VFA produced from the sludge fermentation. Almost 20% of the VFA produced was butyric acid and the remainder was a combination of longer chain acids; mainly iso-valeric and valeric acids.

4. Conclusions and Engineering Significance

Sludge fermentation was explored as a means for phosphorus solubilization to facilitate recovery of phosphorus as struvite. Current phosphorus solubilization methods utilize high energy processes to hydrolyze sludge solids, utilize anaerobically digested sludge, and/or rely on the phosphorus release mechanism of PAO in biological phosphorus removal (BPR) sludge. The latter method is only suitable for use on sludge from enhanced biological nutrient removal processes and the phosphorus release mechanism consumes VFA which is an important carbon source for the biological nutrient removal processes in the wastewater treatment process. Sludge fermentation was explored as a low energy input method that produces high concentrations of soluble phosphorus and VFA suitable for recovery, before anaerobic digestion to reducing phosphate scaling in downstream piping.

Batch and semi-continuous fermentation experiments were carried out with primary sludge (PS), waste activated sludge (WAS), combined PS and WAS, and co-thickened sludge from non-EBPR treatment plants in Winnipeg, Manitoba. Phosphorus solubilization and volatile fatty acids (VFA) production from the sludge fermentation of plants was explored. Based on conventional processes that recover phosphorus by struvite precipitation an objective of 100 mg l^{-1} of soluble phosphorus was set which corresponds to phosphorus concentrations high enough for over 95% recovery as struvite.

Short term fermentation of co-thickened sludge from conventional wastewater treatment plants (high purity oxygen activated sludge) was sufficient to produce soluble phosphorus concentrations in excess of 100 mg l^{-1} and VFA concentrations comparable to conventional PS fermentation. Semi-continuous fermentation (2 day HRT) of the co-thickened sludge resulted in soluble phosphorus concentrations of 113 mg l^{-1} and 178 mg l^{-1} respectively from the NEWPCC and SEWPCC, corresponding to 29% and 51% respectively of total phosphorus as soluble phosphorus in the co-thickened sludge. VFA production during semi-continuous fermentation varied between the two sludge sources. The NEWPCC semi-continuous fermenter contained 9278 mg l^{-1} VFA-COD on average, corresponding to 0.371 mg per mg VS applied. The SEWPCC semi-continuous fermenter contained 5419 mg l^{-1} VFA-COD on average, corresponding to 0.203 mg per mg VS applied.

Batch fermentation of PS and WAS alone was compared with batch fermentation of a 1:1 combination of PS and WAS by volume. This mixing ratio corresponded to the mixing ratio of the co-thickened sludge used in the previous experiments. After four days of fermentation the PS fermenter contained 24.5 mg l^{-1} of soluble phosphorus and 1666 mg l^{-1} of VFA as VFA-COD while the WAS fermenter contained 88.4 mg l^{-1} of soluble phosphorus and 352 mg l^{-1} of VFA as VFA-COD. After four days, the co-fermenting WAS and PS contained 75.6 mg l^{-1} of soluble phosphorus and 1624 mg l^{-1} of VFA as VFA-COD. The batch test fermentation experiments showed that fermentation of PS alone results in the highest concentrations of VFA-COD while fermentation of WAS alone results in the highest concentrations of soluble phosphorus. However, combined fermentation of WAS and PS produced elevated VFA-COD and soluble phosphorus concentrations simultaneously. In fact, co-fermentation of WAS with PS produced significantly higher dissolved phosphorus and VFA-COD concentrations than what was expected based on individual sludge fermentation performance; resulting in greater overall VFA production and phosphorus solubilization than fermentation of individual sludges. In the batch fermentation tests it was found that co-fermentation resulted in 67.5% more VFA production and 60.5% more phosphorus solubilization than separately fermenting the equivalent mass of sludge.

Thus co-fermentation of primary and waste activated sludge can be used to generate VFA and facilitate phosphorus recovery. Co-fermenting sludge improves phosphorus recovery by producing high concentrations of dissolved phosphorus. In these experiments, 30-50% of total phosphorus in the co-fermenting sludge was solubilized within two days of fermentation which can be recovered before digestion using conventional struvite precipitation techniques. Co-fermentation of sludge shows the potential to:

- Facilitate recovery of phosphorus from conventional WWTP sludge;
- Reduce the problems associated with phosphate scaling on WWTP piping and equipment and thereby maximize the potentially recoverable phosphorus by allowing for phosphorus recovery before digestion;

- Facilitate removal of phosphorus from sidestream and recycle streams (RAS and centrate);
- Allow for recovery of phosphorus as struvite which is suitable for direct reuse within the fertilizer industry;
- Improve biological nutrient removal processes by generating significant quantities of VFA in the order of 0.14 – 0.37 mg VFA-COD per mg VS applied; and,
- Provide a sustainable way of managing both sludge streams in a single process – limiting infrastructure requirements.

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