Novel Nutrient Recovery Process from Wastewater Treatment Plants

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Abstract

Small scale wastewater treatment plants (WWTPs) tend to have low efficiencies of nutrient recapture, especially of phosphorus (P). Phosphorus removal performed by biological accumulation steps is directly opposed to the hydrolytic nature of anaerobic digestion. The use of both processes in WWTPs results in a high load of nutrients in the digestate, which can be problematic during long-term operation of the plant and can increase nutrient loading into the hydrologic systems where they discharge. This research focused on the development of an integrated system to allow for the efficient release of phosphorus from thickened sludge and its subsequent recapture. Through the implementation of a two-stage anaerobic digestion, the effluent can be digested and subsequently be treated in intermediate reactors for solid separation and nutrient recapture. This system was scaled up into a pilot plant model with a continuous stirred tank reactor (CSTR) thermophilic fermenter, a sequencing batch reactor for P precipitation, and an upflow anaerobic sludge blanket (UASB) digester to model large-scale municipal wastewater treatment. This system has the capacity of producing a low-odor low-organic load liquid effluent, as well as value-added commodities such as biogas and high-purity P-bearing minerals. However, further optimization and scaling need to be performed to establish a completely continuous and economically feasible system.

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Chapter 1

Phosphorus Recovery from Municipal Wastewater Treatment Plants: Overview of the technological advances, implementation challenges, and costs

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Abstract

Phosphorus (P) plays a key role in the production of food for the world's growing population, yet the dissipative application of P fertilizers in agriculture impairs our watersheds and compromises our future food security. Hence, phosphorus recapture technologies have emerged as a way to enhance wastewater treatment processes with the intent of closing the loop of P use. This work provides a comprehensive review of the different methods that have been developed for phosphorus recapture and their potential implementation in medium and small-scale wastewater treatment plants. The paper focuses on the existing methods for P removal from wastewater, as well as the systems that are used to retrieve phosphorus as a commercially viable product. Various P recovery systems were compared to identify parameters worthy of optimization as well as potential improvements to make the process more economical and environmentally friendly.

Phosphorus in wastewater represents a significant resource that could be tapped into to reduce the reliance on mineral P fertilizers. Many promising technologies have been compiled, but to facilitate the adoption of phosphorus recycling into municipally operated facilities it is necessary to improve removal efficiency and final product quality so that the monetary investment gets justified. This work shows mainstream P-recovery technologies established up to now. The P recovery efficiency is a key parameter that needs to be balanced with the operation complexity and the process stability, therefore reliability of the system should be the first design criterion. Other relevant factors and operational parameters, such as scale and costs are also reported and discussed.

Introduction

Phosphorus (P) is a key element for the correct development and growth of all living organisms. P is a component of many macromolecules and energetic intermediaries of metabolism, such as ATP (adenosine triphosphate). Therefore, phosphorus is essential for proper biological functions. Although phosphorus is an abundant element on our planet, it is estimated that 5.7 billion hectares of farmland globally have deficient phosphorus levels (Solangi et al., 2023). This low phosphorus environment has been shown to reduce the energy metabolism in plants and negatively impact food productivity (Sinclair & Vadez, 2002). To maintain increased crop yields, fertilization with phosphorus (P) and nitrogen (N) is necessary in nutrient-deficient environments. Important crops like potatoes and corn rely on fertilization to meet market demands (Hopkins & Hansen, 2019). The adoption of non-organic fertilizers has greatly enhanced agricultural production. This in turn, has generated a reliance on phosphorus fertilizer to keep up with the ever-growing world population's demand for food (Tan et al., 2005).

Currently, most phosphorus supplementation occurs via the application of mineral-P fertilizers. These fertilizers are obtained from the mining of phosphate ore deposits. It is estimated that in 2020, 223 Mt (megatons) of phosphate rock were produced, and that number is expected to continue to increase (Amar et al., 2022). The phosphate ore is mined and refined to obtain P-concentrated products, commonly called P-rock fertilizer (Geissler et al., 2018). The mining and enrichment process produces many byproducts that are disposed of without strict regulation and constitute a significant source of pollution (Kroiss et al., 2011). There is no consensus on the lifetime of the P-rock reservoirs, but it is estimated the deposits could last anywhere from 120 years to more than 600 years (EFMA, 2000; Schröder et al., 2011). Either way, problems relating to the quality and supply of phosphorus minerals have highlighted that the current supply chain is fragile.

Now, deposits with lower P composition are used as higher quality ore is exhausted. The lower-quality deposits also contain higher concentrations of heavy metals such as cadmium and uranium (Kratz & Schnug, 2006; Roberts, 2014). Because of this, many countries have set limits on heavy metal content in fertilizers, which translates into increased processing for fertilizer producers (Rashmi et al., 2020).

The uneven geographical distribution of P reservoirs makes regions without domestic supply susceptible to shortages. An example of this is the 2008 phosphorus price peak, Figure 1.1, which occurred when export tariffs and disruptions in shipping resulted in an 800% increase in the price of P-rock fertilizers (Cordell & White, 2014). These fluctuations primarily affect low-income farmers in developing countries. Resource depletion and volatility in the commodity market make the future supply of P fertilizers uncertain. Hence, it's important to establish proper methods to manage and legislate regarding this resource and ensure P security (Cordell & White, 2015).

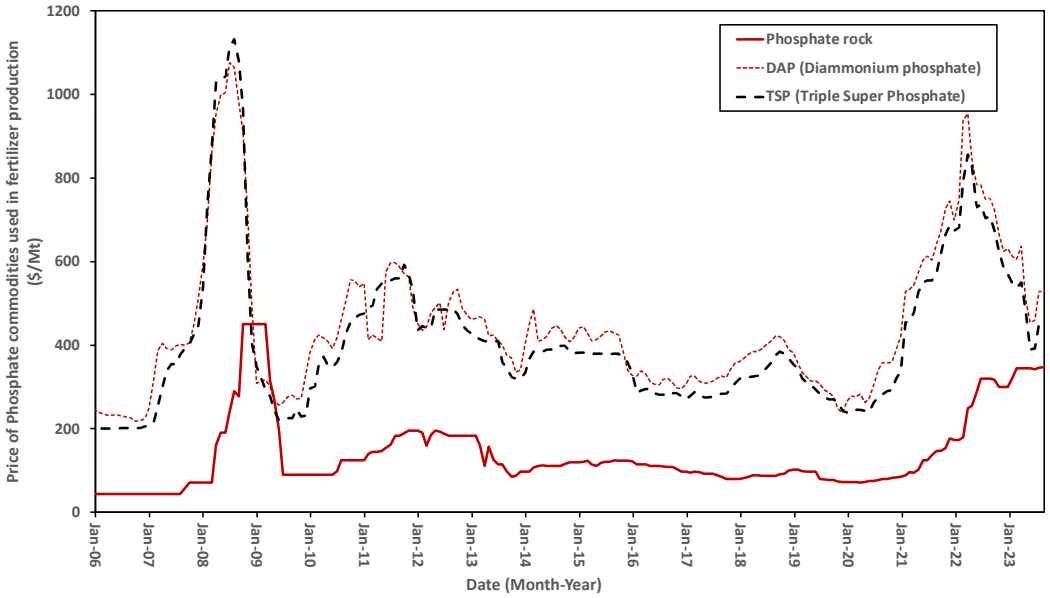

Figure 1-1 Monthly Price of phosphate raw materials used in fertilizers (US$ ton^{-1}), high volatility in commodity prices is associated with trade issues between producer countries and buyer countries. (data obtained from Commodity Markets, World Bank)

Phosphorus is used on farmland as a highly concentrated fertilizer applied to the soil surface; consequently, the elements wash away most of this phosphorus. The current production systems are highly inefficient, as only one-fifth of the total P applied as fertilizer gets eaten as food (Schröder et al., 2011). Continuous application of P-fertilizers in farmlands disrupts the natural P cycle. The unused P also accumulates in agricultural soil and aquatic sediments as legacy phosphorus (Brownlie et al., 2021). P release occurs through several pathways: agricultural losses due to erosion and runoff, direct release from the P-fertilizer production, wastewater treatment plant discharge, and other forms of urban runoff (Ownby et al., 2021).

The washed-off P accumulates in terrestrial and aquatic ecosystems, impacting shallow groundwater quality and watershed P concentrations (Cerven et al., 2021). As many water bodies are naturally low in nutrients (oligotrophic), increases in P create an over-enriched environment (eutrophic), which increases proliferation of microorganisms like algae and cyanobacteria. Eutrophic watersheds are associated with low dissolved oxygen, increased toxin concentrations, fish kills, and overall biodiversity reduction (Hwang, 2020). The demand of water and food resources has resulted in a push to move into a circular phosphorus economy. Circular P economy consists of recapturing P from the endpoints of the production chain (mining, food, runoff, and municipal wastes) and reusing it. The recaptured P can then be processed and reapplied to the land to continue food production. P recycling must be widely implemented to ensure phosphorus security and the quality of hydrological resources. A great percentage of the washed-off phosphorus ends up in water systems, both natural and man-made. Between 1 and 5 Mt of phosphorus are estimated to be embedded in the wastewater produced globally in a year (Mateo-Sagasta et al., 2015). Most of this P is precipitated into the sewage sludge or removed separately to comply with the strict regulations regarding phosphorus content in WWTP effluent.

Sewage sludge is already used as a soil amendment because of its high nutritional content (organic matter, P, N). This is especially true in developed countries with advanced waste treatment processes; for example, about 39% of all sludge produced in the European Union is recycled into agriculture (Lamastra et al., 2018). However, there are growing concerns regarding the presence of recalcitrant pollutants in the sludge, which include microplastics, heavy metals, and per-fluorinated substances (Liu et al., 2021) Because of this, several countries have strictly regulated the use of sewage sludge in agriculture without additional processing and has pushed the development of other sludge disposal methods, such as incineration (over 40% of EU sludge is disposed of this way) (Hudcová et al., 2019).

Developing countries have a lower adoption of sewage sludge in agriculture due to the lack of infrastructure and poorly developed treatment plants. Nonetheless, farmers sometimes use sanitary runoff as a soil amendment despite the problems that the persistent and bioaccumulating pollutants present in the sludge may produce (Pozzebon & Seifert, 2023). Circumstances in developed and emergent countries are very different concerning the management wastewater, but there is a clear need in both cases for processes that can extract phosphorus in efficient and practical ways.

The United States has great potential for phosphorus recapture as the yearly production of municipal sewage sludge in the US is more than 6.5 million dry tons, and 90% of all P that passes through the WWTP system ends up in these biosolids (Venkatesan et al., 2015; Witek-Krowiak et al., 2022). The untapped phosphorus resource in wastewater can be exploited to close the nutrient cycle, ensuring food security in the country for years to come. This work focuses on the different ways in which P can be recaptured from centralized wastewater treatment facilities. The comparison of current phosphorus extraction technologies from wastewater sludge and the development of a novel sludge treatment process for a more efficient nutrient recapture.

Phosphorus applied to farmland, its fate and effects

Phosphorus application to farmland has greatly increased during the past century, with peak applications in the late 1980s, when almost 17000 Mt were used worldwide (Russell, 1998). Back then, it was widely thought that phosphorus applied to arable land was immobile and hence, did not pose any risk of transfer (Haygarth & Jarvis, 1999). It is now known that P fertilization represents an important point source of phosphorus pollution to the environment. Hart et al., determined that surface and subsurface runoff from areas recently fertilized with P-amendments had roughly 4.5 times greater total phosphorus content and 6 times greater dissolved phosphorus content than non-treated fields (Hart & Quin, 2004). While these losses are insignificant to agricultural yields, this small amount of displaced runoff can seriously affect surface waters. P concentrations higher than 0.03 mg/L in a lake can stimulate excessive growth of phytoplankton populations, rendering the lake eutrophic (EPA, 2000). Eutrophication is associated with increased proliferation of algal biomass, harmful fluctuations in pH and dissolved oxygen, and increased mortality in fish and aquatic invertebrates (Rathore et al., 2016; Arend et al., 2011).

Even as phosphorus became more controlled, the P runoff into large watersheds like Lake Erie has not registered the same reductions. Powers et al. have determined that this is due to the accumulation of legacy phosphorus in the soil, which is not accessible for plant uptake but can be mobilized into the watershed (Powers et al., 2016). The flow of phosphorus into the hydrosphere is a pressing matter that continues to represent a threat to water quality all over the world, as the United Nations Environment Program estimates that about 40% of lakes and water reservoirs in the world are affected by eutrophication (Yang, 2008). As agricultural runoff represents a significant source of P that occurs in concentrations too low for conventional wastewater treatments, governmental authorities have resorted to even stricter effluent limits in established WWTPs, in

conjunction with better P-fertilizer management practices, to reduce the impact of P accumulation (Altamira-Algarra et al., 2022). Hence, agricultural nutrient loading into the hydrosphere increases the treatment load of wastewater treatment facilities, which also deals with stormwater runoff and industrial and municipal sewage to decrease point source phosphorus pollution (Yang & Toor, 2018). As lower P effluents become more strictly regulated, the recovery of nutrients from the WWTPs could shift from an option to an outright requirement.

Phosphorus removal in wastewater treatment plants (WWTPs)

Since wastewater has a high concentration of bioavailable phosphorus, it also possesses a great capacity for reducing water quality and promoting eutrophication if not treated properly. However, this abundance of phosphorus makes wastewater and its sludge byproduct ideal substrates for nutrient recapture. It is essential to develop better P-retrieval processes to ensure the sustainability of our water and food systems. As regulations for P release into the hydrosphere continue to tighten, the adoption of more effective P removal technologies becomes necessary, especially in areas with output into important water reservoirs. Areas like estuaries, deltas, lakes, and rivers are especially sensitive to increases in dissolved P; the excess P produces algal blooms, reduces dissolved oxygen, and limits biodiversity overall (Correll, 1998).

Municipalities with a direct flow of nutrients into large water reservoirs are perfect examples of increased regulation, such as the binational Great Lakes Water Quality Agreement, enacted by Canadian and American authorities to reduce the phosphorus load entering the Lake Erie basin by 40% (EPA, 2012). As regulations become more stringent, it is crucial to adopt processes that allow for P recapture from waste streams. Further research and development in this area will help to close the loop in the nutrient flow of our current dissipative system.

Wastewater treatment process

Wastewater treatment involves a series of physical, chemical, and biological processes that separate solid components and organics from the wastewater and ensure that the resulting water output complies with the levels of polluting agents, pathogens, and nutrients established in the local regulation. A diagram of the conventional wastewater treatment is shown in Figure 1.2, which additionally illustrates common steps where P removal occurs. The diagram shows a WWTP that includes preliminary screening, a grit chamber for large particle sedimentation, and primary, secondary, and tertiary water treatment (Alley, 2007). All WWTP setups include primary and secondary treatment as the main steps for managing water quality, but additional steps may be added depending on water composition, regulation, funding, or operation capacity (Tebbutt, 1998).

There are numerous ways in which WWTPs can set up and sequence their treatment processes, depending on the final requirements of the plant's treated effluents. Monitoring the effluents is required to ensure the proper removal and control of the waste.

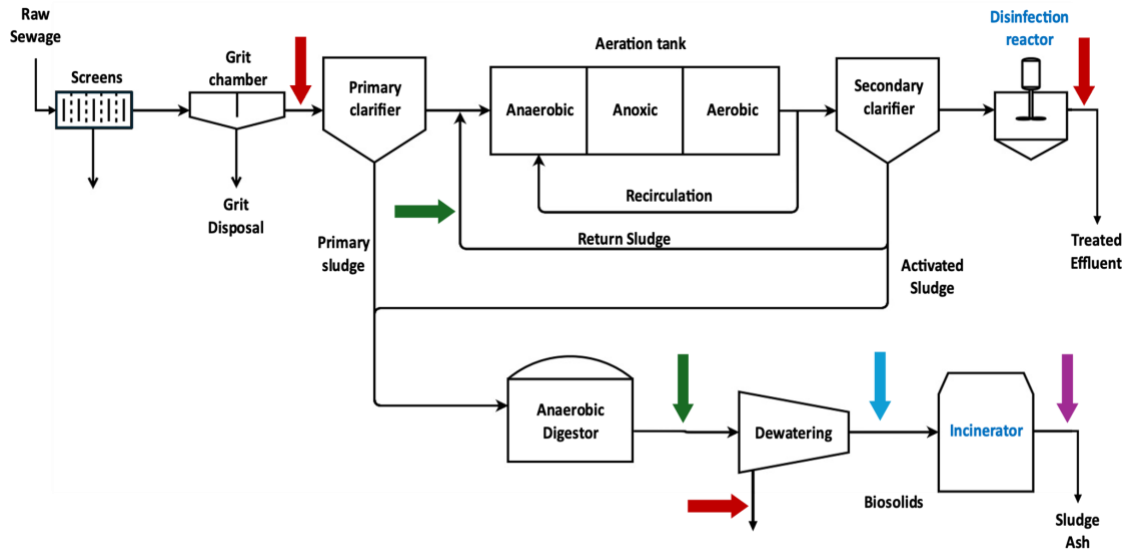

Figure 1-2 Wastewater treatment process diagram, blue font indicates steps that are optional. The arrows indicate the side streams where phosphorus recovery can occur, the aqueous phase (red), sludge fraction(green), dewatered solids (teal), and in the sludge ash (purple)(adapted from Alley, 2007)

All the main steps of wastewater treatment are described below.

- Preliminary Treatment: This step mainly refers to the removal of large solid components in the wastewater inflow, including wood, glass, rock, and plastic. These large solids can damage the pumps and other equipment in the plants and disrupt the hydraulic flows within the piping. In addition, large clumps of fat, grit, and organic matter may also be removed in this step. Preliminary treatments can range from metal grids and bar screens to sand chambers that settle dense debris.

- Primary Treatment: This process is designed to remove small, suspended solids and scum using a two-step system that consists of aeration and sedimentation. Air is pumped into aeration chambers where the bubbling effect in the liquid separates the heavy grit into the bottom and the less dense fats into the top. The floating material is then skimmed using water jets and the solids are scraped to obtain an effluent that is concentrated in primary clarifiers. The primary clarifiers further settle out any remaining dense materials. All the separated components will be mixed again to obtain a concentrated effluent called primary sludge. During this process, a large portion of the suspended solids from the inlet are removed, resulting in a decrease in several of the monitored parameters of wastewater. About 25-50% of the biochemical oxygen demand (BOD) is removed from the incoming water, as 50-70% of total suspended solids (SS) and 65% of the grease in raw sewage (Sonune & Ghate, 2004). While a portion of the organic phosphorus in the wastewater is removed in the primary treatment, most of the dissolved and colloidal organics will remain in the primary effluent, which must be further treated to reduce overall nutrients.

- Secondary Treatment: It consists of biological operations that further reduce the organic load in the wastewater. Because primary treatment cannot by itself accomplish the required organic load in the water, microorganism communities are used to eat up the dissolved and suspended organics that are still present in the primary effluent. By modulating conditions in a controlled environment, microorganisms can be induced to consume the organic matter, producing biogas which contains carbon dioxide as a main component. By changing the rate of oxygenation and feeding, stable populations of microorganisms can develop to maximize nutrient and solids reduction. While trickling filters are still used, most secondary treatment processes consist of activated sludge (AS) tanks. Both methods use microorganisms to consume the excess nutrients, but AS tanks have a higher conversion rate and lower residence times. In these systems, the wastewater is aerated to increase dissolved oxygen (DO) concentration and then mixed with sludge containing a high population of microorganisms. This mixture is agitated in the aeration tank for an extended period to maximize organics degradation after which it is again separated in a different settling tank (Rezai & Allahkarami, 2021). To obtain a successful AS process, it is necessary to exploit the flocculent nature of the microbial biomass. The flocs produced by the microorganism communities must be efficient in the adsorption of dissolved organic matter and quickly separate from the liquid effluent in the sedimentation tank. The sludge that is separated in the settling tank is called activated sludge and can be used for the treatment of more primary effluent, while the excess sludge is discarded as waste-activated sludge (WAS). This process can remove more than 85% of the remaining organic matter in the wastewater (EPA, 1998).

- Tertiary Treatment: This term encompasses any additional processes that the treated water is subjected to before being released into the environment. The most common is chlorination which is a sanitization step to eliminate pathogenic bacteria and to reduce odors. Other disinfection systems can be used, such as ozone or UV light systems. Additionally, other processes can be implemented if there is a specific requirement for the water that is treated, additional filtrations, reverse osmosis or more biochemical treatment can occur.

- Sludge Processing: All the produced sludge and scum need to be treated properly, and because of the intense processing requirements, sludge-handling costs are usually the decisive factors in WWTP design and operation (Qasim, 2017). Sludge has a high concentration of organics and microorganisms, so it must be treated to reduce the total volume and destroy pathogenic agents within. This can be problematic because of the sludge's heterogeneous properties; usually, sludge will have solids content between 0.5% and 3%. However, additional dewatering steps can be used to increase the solids concentration before further treatment. The main process for sludge treatment is anaerobic digestion, which utilizes other microbial agents to degrade the organic components. The anaerobic digestion of the sludge results in volume reduction, pathogen destruction, and biogas production (Demirbas et al., 2017).

As it has been established here, WWTPs aim to minimize the environmental impact of municipal waste and sewage, reducing the overall organics released into receiving water bodies. Recapturing phosphorus is one of the main innovation drivers to maximize the benefit and economic feasibility of the treatment plant operation. However, this requires the collaboration of government entities to fund and push for the implementation of these technologies.

Wastewater phosphorus removal

Wastewater treatment facilities use several phosphorus removal methods to control the P effluent released to the hydrosphere. The EPA Clean Water Act (CWA 502, 33 U.SC §1251) has established guidelines for the monitoring and regulation of water discharge, and many states have enacted their local regulations regarding P effluents per this directive. In Minnesota (MPCA Permit 42000) and Wisconsin (DNR NR217), a general P limit effluent of 1 mg/L is mandated for all publicly operated and privately managed wastewater treatment facilities in their respective municipalities. However, plants that discharge into areas of great ecological importance might have their own regulations, further reducing the allowed P effluent. As new environmental regulations continue to restrict the discharge of P loads from WWTPs, modifications to current P removal methods will have to be enacted to maintain compliance (MPCA, 2009; WDNR, 2011).

Phosphorus from the sewage influent needs to be physically removed from the water portion. The mechanical treatments used in the first steps of wastewater treatment can separate large non-soluble materials that may contain P. These particles end up in the primary sludge portion, which accounts for total phosphorus (TP) removal of around 15% (Kroiss et al., 2011).

The vast majority of the bioavailable phosphorus is still present in the liquid portion, either as suspended minuscule solids in a colloidal sol or incorporated into a solution. Many processes have been developed to remove the P in the liquid. However, these can be broadly categorized as chemical and biological. Additionally, complex physical processes can also be used, exploiting microscale structures and filters to separate the P. Despite the efficiency of these methods, the high costs and complex operations required result in much lower adoption rates (Leo et al., 2011).

Phosphorus speciation in wastewater

To properly treat the P content of the wastewater influent, it is necessary to know the different chemical species in which phosphorus is present. The majority of the phosphorus comes from human excreta, food waste, and to a minor extent household cleaning products. Still, smaller contributions from soil, animal manure, and industrial and agricultural waste may find their way into the WWTP treatment grid. Phosphorus as an element is highly reactive and if bioavailable, it is quickly incorporated into biological organisms. Hence, P is rarely found in free elemental form in the environment. That is also the case in wastewater, where most of the phosphorus is integrated into the organic mass or in the form of the inorganic oxidized molecule called orthophosphate. Generally, the P present in the wastewater can be classified as inorganic P (orthophosphate), polyphosphates, and organic molecules containing P (Azam et al., 2019). Figure 1.3. shows some of the polyphosphates that are present in wastewater.

Organic P can be found in the form of proteins, nucleic acids, phospholipids, and phytic acid among many other compounds. The processes used in WWTPs are capable of releasing most of the P bound to these molecules through microbial metabolism which hydrolyzes the present macro molecules and generates smaller constituents, the most important of which is the inorganic P form orthophosphate.

It is also necessary to highlight that the different processes used for wastewater treatment can also affect the P portion of each of these categories, biological treatment favors the accumulation of phosphorus in biomass, which will incorporate P into organic molecules.

On the other hand, chemical treatments immobilize P into inorganic salts so mineral forms of the nutrient will be more prevalent. Effective P removal approaches require the removal of all types of phosphorus so usually a combination of treatment steps is used.

All the particulate phosphorus, which is not incorporated into solutions or colloidal suspension, is removed during the sedimentation steps in the WWTP (Dueñas et al., 2003). This means that the phosphorus that needs to be addressed in consequential P removal steps is the soluble forms, mainly the phosphates. However, the addition of chemical coagulants and biological steps within the treatment plant can transform the present orthophosphate in the solution into other P-containing molecules, so it is important to consider side reactions.

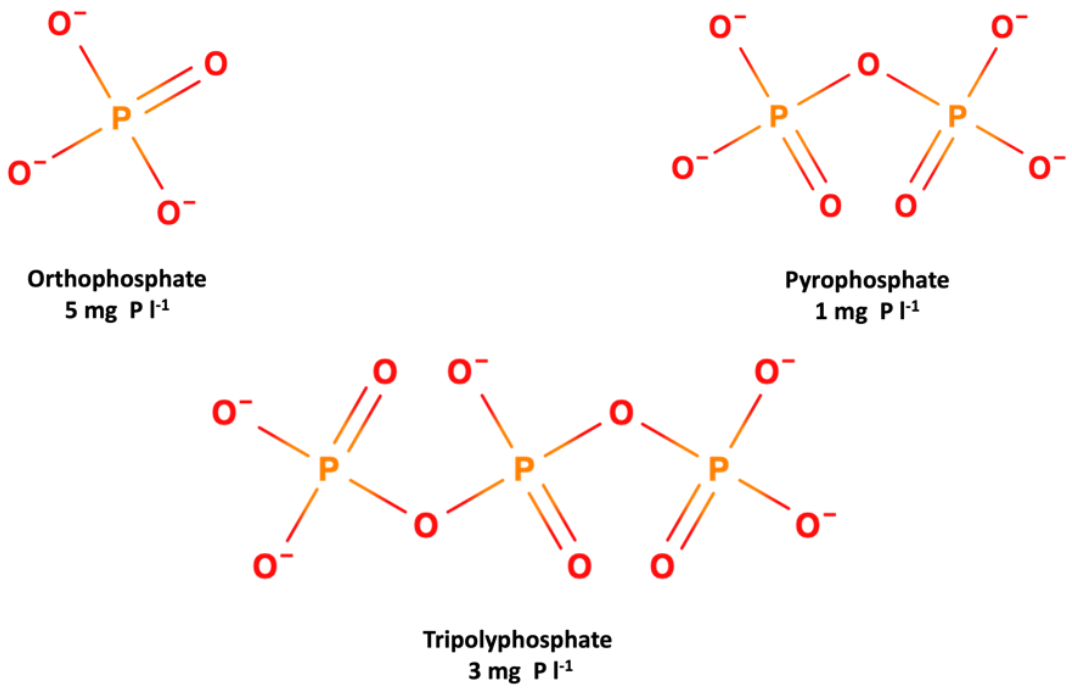

Figure 1-3 Phosphate forms and their approximate concentrations in typical raw domestic sewage (data obtained from Jenkins et al., 1971)

Yu et al. indicate that phosphorus in sludge obtained after biological processes of P removal contains mostly polyphosphates with a composition of 30-80%, while the phosphorus present in primary sludge is primarily inorganic P (83-89%), which consists mainly of the precipitate formed by metal salt dosing (Yu et al., 2021). Particulate phosphorous is completely removed in the system, phosphorus removal approaches should focus on the solubilized P in the primary phosphate form $[PO_4]^{3-}$, which consistently occurs in every step of the treatment. To maximize removal based on phosphate properties, polyphosphates and organic forms of P should be transformed into ortho-P.

Chemical phosphorus removal

Chemical P removal is widely implemented in plants across the world because it is a reliable and relatively simple way of controlling the phosphorus concentration in the treated effluent. The main method used is chemical precipitation, where metal salts are added to the solution and pH is modulated to favor the crystallization of P-containing minerals. The negatively charged orthophosphate ions $[PO_4]^{3-}$ that are dissolved in the solution interact with trivalent metal ions supplied by the added metal salt. The orthophosphate complexes into compounds with lower solubility which prompts the crystallization and precipitation of these compounds to the bottom of the tanks.

After the phosphate is converted into solid particulate, it can be removed from the sedimentation tanks with pumping or physical removal mechanisms. The diverted slurry can be disposed of as part of the solids generated in the treatment process. Many ions form precipitating compounds with phosphate, but calcium, aluminum, and iron salts are most used for wastewater treatment purposes. These metals form strong complexes with phosphorus in the mid to high range of pH, facilitating their addition in several wastewater treatment steps (Kroiss et al., 2011).

In order of implementation, the most used inorganic coagulants are ferric chloride ($FeCl_3$), ferric sulfate ($Fe_2(SO_4)_3$), and aluminum sulfate ($Al_2(SO_4)_3$) (Jiang & Graham, 1998). The main precipitation reactions are compiled in Table 1.1. Since there are many compounds present in the treated effluent solution, many chemical interactions are present during the crystallization process. The complexity of the composition of ions in solution makes modeling the reactions inconvenient. Therefore, the wastewater is treated as a solution that only contains orthophosphate to simplify the reactions that are involved in crystallization. However, the presence of other ions in the solution can hinder P precipitation so control and monitoring of the overall effluent is always required.

Table 1-1 Phosphorus precipitation reactions of metals used in wastewater treatment (Deng & Dhar, 2023; Shih & Yan, 2016; Tchobanoglous et al., 2003)

Metal	Basic Reaction	Precipitates	pH
Ca^{2+}	$3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2 \downarrow$ $4Ca^{+2} + H^+ + 3PO_4^{3-} + 3H_2O \rightarrow Ca_4H(PO_4)_3{\cdot}3H_2O \downarrow$	Calcium phosphates, $CaCO_3$	>9
Fe^{2+}	$3Fe^{2+} + 2H_2PO_4^- \rightarrow Fe(PO_4)_2 \downarrow + 4H^+$ $Fe^{2+} \rightarrow Fe^{3+} + e^-$ $Fe^{3+} + H_nPO_4^{(3-n)-} \rightarrow FePO_4 \downarrow + nH^+$	$Fe_3(PO_4)_2$, $Fe_x(OH)_y(PO_4)_z$, $Fe(OH)_2$, $Fe(OH)_3$	6-8.5
Fe^{3+}	$Fe^{3+} + H_nPO_4^{(3-n)-} \rightarrow FePO_4 \downarrow + nH^+$	$Fe_x(OH)_y(PO_4)_z$, $Fe(OH)_3$	6-8.5
Al^{3+}	$Al^{3+} + H_nPO_4^{(3-n)-} \rightarrow AlPO_4 \downarrow + nH$	$AlPO_4$, $AL(OH)_3$	>6
Mg^{2+}	$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow NH_4MgPO_4{\cdot}6H_2O \downarrow$	$MgNH_4PO_4$, $Mg(OH)_2$	>10

Pure reagents are rarely used during the precipitation process, because of the high cost associated with higher-purity compounds. These reagents produce better quality products and are easier to dose, however, alternative materials that are byproducts of other industries are much cheaper and can achieve similar results.

Lime can be used as a cheap source of calcium salts and it is a widespread material used for phosphorus removal, however, the heterogeneous composition of lime results in the formation of diverse calcium phosphates (CPs) which include amorphous calcium phosphate (ACP, $Ca_3(PO_4)_2 \cdot nH_2O$), octacalcium phosphate (OCP, $Ca_8H_2(PO_4)_6 \cdot 5H_2O$), dicalcium phosphate dihydrate (DCPD, $CaHPO_4 \cdot 2H_2O$), and hydroxyapatite (HAp, $Ca_5(PO_4)_3OH$). Handling difficulties complicate the process design and there is a high sludge production associated with lime, which makes calcium utilization harder (Clark et al., 1997; Vasenko & Qu, 2019).

Aluminum salts are highly effective at P precipitation but are significantly more costly than calcium ones. Even when less purified sources of aluminum, like alum, are used; aluminum salts are still considerably more costly than calcium and iron ones. Furthermore, aluminum is widely recognized as a pollutant that interferes with aquatic organisms' osmoregulation and may pose a risk to humans, therefore strict monitoring is required when using Al salts (Rosseland et al., 1990).

Iron salts are less efficient at precipitating phosphorus from solution but are relatively cheap. Thus, iron salts are the most adopted method of precipitation. Moreover, iron salts may be used in the WWTP systems as a method of dealing with sulfides, which have other detrimental effects such as odors and corrosion. Concurrent management of both P and sulfides is not widely used but can be implemented as a way of saving additional steps in the final treatment process. Ferrous and ferric chlorides can be used as the precipitating salts, which require a specific process

design to allow for the oxidation of the Fe^{+2} into Fe^{+3} if the goal is to capture phosphorus, or the reduction of the iron ions for the precipitation of sulfides (Gutierrez et al., 2010).

Regardless of the metal salt that is selected for the P precipitation, plant operation still requires a lot of monitoring regarding dosage and P removal efficiencies. Because both the reagents and the substrate treated are complex mixtures of components, it is difficult to establish a determinate mechanism of precipitation. Nonetheless, complexation, adsorption, and coagulation/flocculation seem to be the main drivers of the precipitation of P (Szabó et al., 2008). However, it is hard to establish adequate standards of dosage given all the factors that play a part in precipitation, which is why the industry routinely practices overdosing to ensure adequate P removal. "Safe dosing" may ensure proper P removal, but it also significantly raises overhead material costs and increases sludge production, which are both detrimental to overall plant operation. Plus, it is important to evaluate the placement of the salt precipitation step, because the additional slurry created can hamper the dewaterability of the sludge effluent or it can negatively affect the nitrification conditions of the activated sludge process (Xie et al., 2005).

When the recapture aspect of the phosphorus removal is considered, the use of conventional Fe and Al metal salts becomes less attractive given that many of the precipitates formed have very low quality as fertilizers because of the low P solubilization they have (Melia et al., 2017; Yeoman et al., 1988). Soils treated with chemically precipitated sludge that comes from iron and aluminum treatments have low P solubilization in normal agricultural conditions (Kyle & McClintock, 1995). This low phosphorus bioavailability makes this sludge less marketable as an alternative to conventional fertilizers. On the other hand, calcium and magnesium precipitation has gained much more popularity as these metals form minerals with much higher bioavailability, which makes them attractive products for agricultural use.

Biological phosphorus removal

Biological phosphorus removal processes are very attractive nutrient control methods because they usually do not require the addition of chemical reagents, which reduces the economic requirements of the system. Additionally, these processes have the potential for the revalorization of the nutrients captured from the wastewater, especially the P.

Biological P removal uses microorganisms' metabolic capabilities to promote biomass increases in microorganism communities. As the bacteria grow, they consume the nutrients in the environment, immobilizing the P from the effluent. In normal activated sludge systems, microorganisms remove phosphorus as they use it as a nutrient for growth.

Phosphorus uptake by microorganism growth is necessary for any activated sludge system, so a portion of the P content in the wastewater will always be immobilized. The P removal depends on the plant's overall organics load and the population equivalent treated. Population equivalent (PE) is the average organic load in a sewage system per inhabitant, and standard PE is 120 g of chemical oxygen demand (COD) per day. P removal achieved by normal microbial growth in a sludge system can be up to 1 g P/ PE*day (Kroiss et al., 2011). However, it is necessary to have other P-removal systems, given that wastewater has a continuous supply of excess phosphorus. Enhanced biological phosphorus removal (EBPR) is used to increase the amount of P removed, and this employs specific microorganisms capable of luxury phosphorus uptake. These organisms, known as phosphorus accumulating organisms (PAO), can store phosphorus in quantities much larger than the ones required for biomass growth.

PAOs have the capacity to accumulate P even in conditions where it is found in excess within their environment (Oehmen et al., 2007). This phenomenon was first observed in India in 1959, where researchers found that alternating conditions of oxygenation could induce some microorganisms to accumulate P via biological processes that could be disrupted by high temperatures (Srinath et al., 1959).

The mechanism for phosphorus accumulation is now well-defined and consists of the alternation of anaerobic and aerobic. In the former stage, high concentrations of bioavailable organics are degraded via a process that hydrolyzes complex molecules into simpler ones like volatile fatty acids (VFAs) which are then quickly consumed. This process releases phosphates into the solution which can then be consumed by the microorganisms in the second phase. This latter phase occurs in aerobic or anoxic (no oxygen but other electron acceptors are present) conditions. The change into an aerobic environment induces the rapid consumption of phosphate in solution.

Hence, EBPR relies on phosphorus-accumulating metabolisms that involve the anaerobic hydrolysis and aerobic synthesis of polyphosphates within the cellular structure of PAOs. This does not happen in isolation as other energy-storing molecules are accumulated and consumed during those processes. Examples of these molecules are intracellular carbon polymers like glycogen and polyhydroxyalkanoates (PHAs) (Long et al., 2021). Overall, in this process, more phosphorus is absorbed by the microorganisms than what is released from the hydrolysis of organics. This enhanced phosphorus removal process results in a total reduction of phosphates in the water effluent and in the enrichment of the activated sludge with that same P, this is shown in Figure 1.4.

Very low phosphorus concentrations can be achieved when the sludge is circulated through chambers with alternating anaerobic and aerobic conditions. Hence, this operation process is widely adopted because it can manage the phosphorus in the water effluent reliably and consistently, below

the 0.5 mg-P/L threshold (Hesselmann et al., 1999; McMahon et al., 2002). The enriched sludge produced during the aerobic phase of the treatment is usually recirculated back to the initial EBPR chamber to serve as a seed inoculum for the microorganisms, however, excess sludge is removed to maintain the volumetric balance of the operation. This phosphate-rich sludge can contain phosphorus in a range of 0.05-0.1 mg-P/mg-SS depending on the system operation, which makes it a prime raw material for the extraction of phosphorus (Dorofeev et al., 2020).

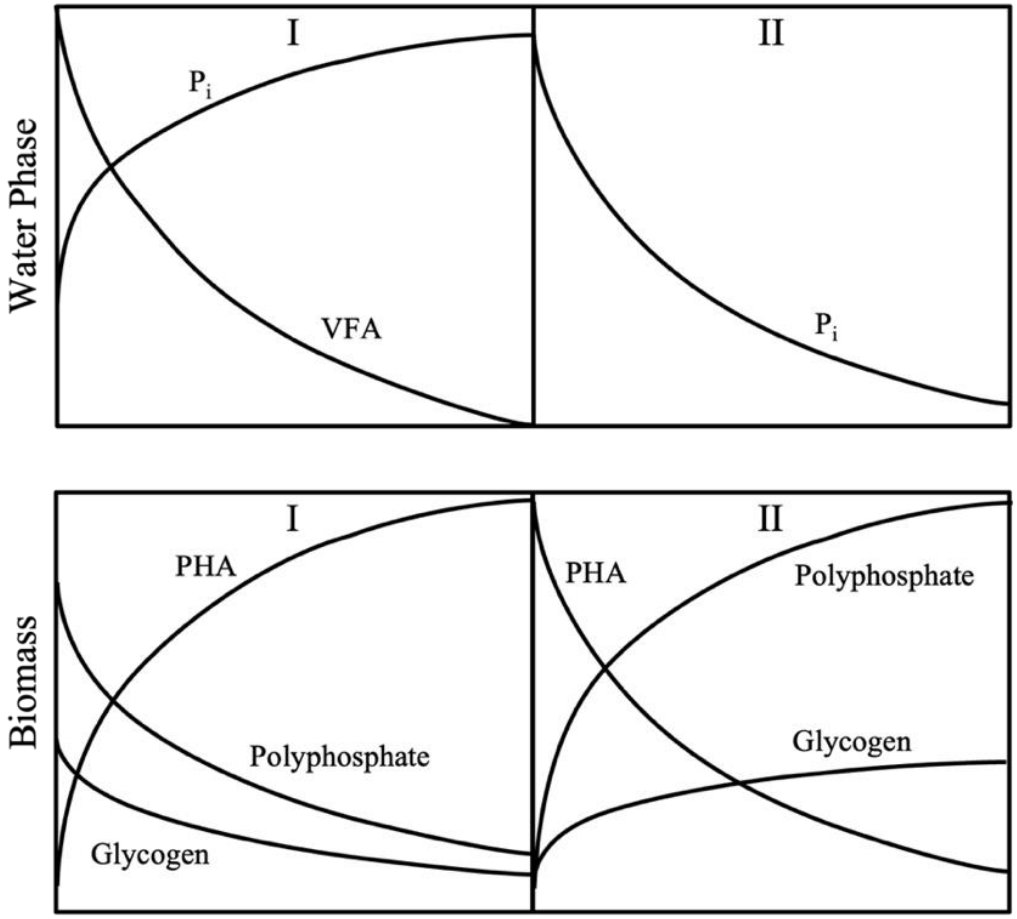

Figure 1-4 General cycle of enhanced biological phosphorus removal. The concentrations of orthophosphate (P_i) and volatile fatty acids (VFAs) in the wastewater and the intracellular content of polyhydroxyalkanoates (PHA), polyphosphate, and glycogen vary depending on the oxygenation of the environment: Anaerobic Chambers (I) or Aerobic Chambers (II) (adapted from Dorofeev et al., 2020).

Alternative Phosphorus Removal Technologies

While chemical precipitation and EBPR are the most widely adopted methods of phosphorus removal, other technologies have been developed to address these same issues. Removal technologies usually take advantage of the chemical properties of phosphorus in solution to separate it from the liquid portion. A list of the different mechanisms that have been developed as other P treatment methods can be found below.

- Chemical Sorption: These methods mainly consist of allowing the flow of wastewater through a large porous structure that contains reactive components on its surface, such as calcium and iron minerals. The removal capacity in these systems is dependent on the material used and on the lifetime of the filter. The P-capture mechanism is like the one used for chemical precipitation, but the accumulation of the P-bearing minerals occurs within the same filter (Drizo et al., 2006). The filter materials usually have a pH over 9 and work by releasing metal cations into the water phase that can precipitate into phosphate-containing minerals on the filter surface. These systems are attractive for very small-scale operations and can use low-cost materials such as metallurgical slags, lime, or calcium silicates. Absorbent filters can also achieve P removal rates of over 95% but require more attention in the operation and the periodical replacement of the filters (Gustafsson et al., 2008).

- Simultaneous Nitrogen and Phosphorus removal: Biological systems with specific conditions can be used to remove N and P in the same growth process by utilizing the anammox pathway followed by partial denitrification and denitrifying dephosphatation. This means that a reactor with anaerobic conditions can induce

microorganisms to use ammonium ions as electron acceptors to directly produce nitrogen gas; afterwards, P is removed with the excess NO^{3-} as the electron acceptor via precipitation. While this process hasn't been applied on a large scale because of operational instability, small experiments show good potential for both N and P removals (>90%) (Ji et al., 2020).

- Ion Exchange: Most phosphorus in wastewater is present as the inorganic form orthophosphate (PO_4^{3-}), which at normal operating pH (≥7) is present mainly in the form of the divalent cation (HPO_4^{2-}). This cation has a higher affinity for transition metal cations. If the cations are immobilized into polymeric structures, they can act as ion exchangers where phosphate can be immobilized reversibly (Zhao & Sengupta, 1998). The ion exchange method employs polymers that contain many of these cations to selectively capture phosphate into the surface of a filter. Once the filter P removal capacity is depleted, it can be treated with a regenerating solution to release all the captured phosphate and restore the removal properties of the system. These systems can achieve P removal rates of 90% with short contact times and may have the added advantage of nutrient recycling capabilities (Seo et al., 2013). However, these resins are costly and require intermittent backflush to regenerate the exchange sites; this in turn, makes adoption of the technology unlikely given the large monetary investment required for its operation (Martin et al., 2009)

- Filtration: Depending on the size of the membrane used this can refer to reverse osmosis (RO), ultrafiltration, or nanofiltration. These membranes are efficient at separating ions and organic molecules of small size. Nanofiltration membranes (~1 nm pore size), for example, can achieve a slight charge because of the dissociation

of functional groups and the absorption of charged molecules. Hence it is possible for these membranes to electively reject multivalent anions such as (PO_4^{3-}) (Leo et al., 2011). Ultrafiltration (up to 100 nm pore size) has lower energy requirements but does not have an ionic selectivity so it requires additional modifications to the surface to improve adsorption (Koh et al., 2020). All membrane filtration technologies require high inputs of pressure and energy as well as backwash upkeep to maintain working conditions.

- Algal P removal: These biological methods use primarily algae and cyanobacteria as the agents that accumulate phosphorus. There are well-established systems that use *Chlorella sp*. and *Scenedesmus sp*. as microorganisms that can grow quickly in wastewater. Algal treatments can occur both in suspension or in the form of biofilms and are attractive because of the low energy requirements (Bunce et al., 2018). These systems can achieve very high P removal rates in different conditions (up to 97%) and have the potential for increased valorization of the algal biomass (Sukačová et al., 2015). Still, there are operational restrictions associated with this type of system, such as strict light and temperature requirements, poor settling properties, and NH_3 growth inhibition (de Godos et al., 2009).

While all these systems can potentially remove phosphorus in WWTPs, the adoption rates in wastewater treatment plants are very low, given the monetary investment required to adapt large-scale facilities designed to work with more conventional methods. Consequently, there is a very clear barrier of entry for these systems, where the return on investment needs to be high enough to warrant the substitution of the currently used methods.

Phosphorus management in sewage sludge

Sludge is an unavoidable byproduct that results from the wastewater treatment process, it contains most of the solids and organics from the sewage influent. The main sources of sludge are the primary settling tank, the settling material from chemical phosphorus removal, and the excess sludge removed from the biological treatment chamber. While the term sludge refers to all the waste streams that branch out from any of the clarification tanks in the WWTP, the properties and composition of each vary according to the source and specific treatment that occurs in that tank. Still, because most of the P removal treatments assimilate the phosphate molecules into the immobile solid portion, more than 90% of the phosphorus load in the wastewater is incorporated into the sludge (Desmidt et al., 2015). This rich composition of the sewage sludge makes it a very good source of nutrients for agricultural practice. Furthermore, the organic matter present in the sludge can be further processed to obtain biogas, which is why wastewater sludge is also considered an alternative source of renewable energy.

In WWTP systems, sludge is dewatered to allow easier processing, but this can also significantly add to the plant's operation costs. Figure 1.5 shows a diagram of the different approaches WWTPs can take to process sludge. The water content in unprocessed sludge can range from 97 to 99%, so the removal of this excess is critical for its further treatment; if it is not removed, this will add weight and mass for transport or drying (Nazari et al., 2018). Conventional thickening processes such as drums and gravity belts press the excess liquid out of the mixture. Once the sludge is thickened, it can undergo volume reduction and organics removal; anaerobic digestion (AD) is the most widely implemented process. AD is used as a waste management practice, but it also allows for energy recovery as biogas. Alternatively, technologies like hydrothermal treatment can be used to extract bio-oils from the sludge (Catallo & Comeaux, 2008). Both byproducts are

energy-rich and can be used as fuels to supply the energy grid. Finally, the solids left after these treatments can be disposed of, but they still contain a very high concentration of nutrients.

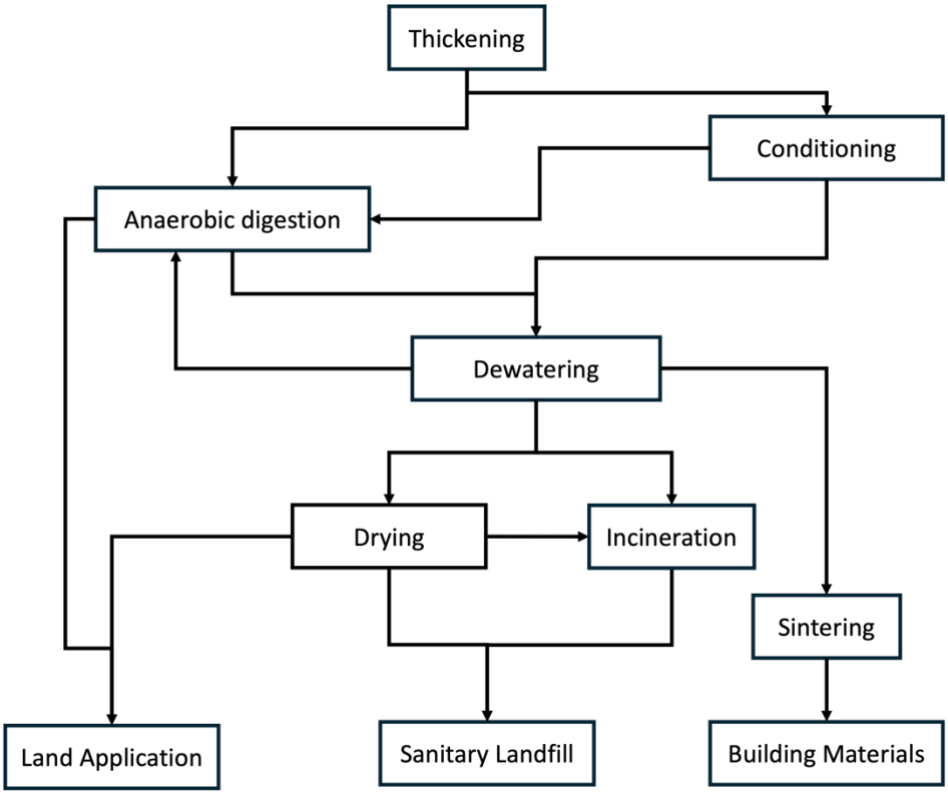

Figure 1-5 Sludge processing routes commonly used for treatment and disposal (adapted from Yang et al., 2015).

The simplest way of utilizing all the nutrients recaptured in the sludge is its direct application into farmland as a fertilizer, but this is significantly limited given the concerns of pollutants present in this product. Wastewater sludge is a sink for many pollutants and substances of concern because the waste streams concentrate heavy metals, antibiotics, hormone disruptors, bacteria, and parasites that enter the municipal water system.

Additionally, there are reports of gastrointestinal distress and other effects that reduce the quality of life associated with the use of sewage sludge in communities close to the application sites (Lowman et al., 2013).

Because of the concerns associated with sludge application, there are strict pollutant thresholds for sludge land application both in the US (EPA reg. 40 C.F.R. Part 503) and the EU (86/278/EEC), and this greatly impairs the total adoption of sludge as an amendment in agriculture. Still, 61% of the produced sludge in North America is used for land application (Kroiss et al., 2011). Therefore, other methods of nutrient recovery can be used to avoid the drawbacks associated with the direct use of sewage sludge.

In addition to land application, other conventional methods of managing sludge waste are landfill disposal and incineration. However, the push for a closed loop of nutritional flows does not traditionally mesh well with conventional waste disposal, even when incinerated to reduce its biological impact. One modification to this is using the sludge ashes as a source of nutrients for land applications. Incineration is viewed as a simple way of managing waste because it destroys the organic compounds and pathogens while reducing the overall volume by up to 90% (Chen & Yan, 2012). In addition, the ashes obtained from the incineration process contain a high fraction of phosphorus, ranging between 4% and 9% of its total dry weight. This occurs because phosphorus does not form any stable gaseous compounds and, hence, does not volatilize into the air (Franz, 2008).

Sewage sludge incineration ashes can, therefore, be considered a moderately rich source of phosphorus. They could replace mineral ores used in agricultural fertilizers, given that both raw materials need to be processed to increase the concentration of P (Kasina et al., 2020). Adopting sewage sludge derivatives as a source of phosphorus could fulfill the goal of having a closed-loop

nutrient system. Furthermore, the widespread availability of sewage sludge will help its adoption as a nutrient source. Creating additional infrastructure to accomplish nutrient recapture seems costly, but it is important to consider that WWTP nutrient recapture could potentially offset the costs of P-bearing mineral extraction, especially when the rising mining, processing, and transportation expenses of P-rock fertilizers are considered.

Phosphorus recovery

As aforementioned, there is a pressing need to address the way that phosphorus is treated in municipal facilities. There are issues of water eutrophication and P insecurity that can be minimized when appropriate treatment systems are used in WWTPs. And, while it is true that many conventional approaches of P removal used in wastewater facilities can reduce the P concentration under the established thresholds, the byproducts of these treatments (e.g., chemical precipitation) are usually disposed of in landfills. This is also the case for a big portion of the biosolids produced from EBPR.

The US produced 3.79 million dry metric tons of sewage sludge in 2022, of which only 56% was used in land application (EPA, 2023). Therefore, the field of phosphorus recovery is attracting considerable interest, because it comprises both the P removal and the creation of value fertilizers. The main driver of this approach is the fact that high levels of phosphorus end up in WWTPs from both biological and agricultural. However, due to the large volumes of wastewater that are treated in the facilities, a combination of treatments needs to be used to immobilize and concentrate the phosphorus into a product that has a P content similar to other P sources in the market. Still, it is worth noting that with the reduced quality of mineral P ores, even low-content P products will become attractive in the future if they come from renewable sources.

Phosphorus recovery systems

The design of P recovery processes is very complex because it requires the use of combinations of biological, chemical, and physical steps to maximize phosphorus recapture and obtain a product that has satisfying characteristics for its use. Several processes in the market have been implemented on a large scale for the recovery of wastewater P. Phosphorus recovery focuses on producing valuable P-containing materials rather than water treatment, therefore it can treat the liquid portion, the sludge portion, or a slurry mix of both. This gives much more flexibility to the process design as it allows for the treatment step to be placed on different points of the WWTP layout. All current processes in the market focus on the generation of inorganic minerals as a final product. This is mainly because of regulations that restrict the composition and application of biosolids into the land, and the ease of handling and characterization that are associated with mineral products.

The commercial processes for P recovery that are available in the market are collected below in Table 1.2. While other authors provide more detailed comparisons of the techno-economical aspects of these processes (Egle et al., 2015, 2016), this list serves as a good frame of reference to understand how these processes have different units of operation to obtain P-bearing minerals. The recovery step can occur on the wastewater itself or in the sludge produced by its treatment, therefore it is useful for the description of the processes to categorize them as treating the wastewater, the sludge, or sludge ashes. Regardless of the mechanism used for P retrieval, successful processes must be able to handle the variable concentration of P in the inflow, as well as have the capacity to immobilize the maximum amount of phosphorus while minimizing pollutants in the final product. The listed systems all employ thoroughly studied principles of phosphorus recapture that reliably manage to produce P minerals, mainly crystallization, and

precipitation. Development of processes that use these methods benefit from using infrastructure that is easily retrofitted and adapted to systems already in use in WWTPs. Sludge ash processes have the added benefit of removing the vast majority of organic pollutants that end up in municipal facilities, but the energy input required for the furnace operation can increase costs quickly.

While innovation in novel P recapture processes could result in more economically feasible processes, the reality is that implementation of new recapture mechanisms into existing municipal facilities requires a large investment in technology and skilled labor. Therefore, it is also beneficial to study the available processes comprising different setups in their units of operation to facilitate their adoption. Retrofitting the P recapture technologies in the form of modification of layouts and order of treatment can help reduce the initial development cost. Hence with process engineering, it can be possible to implement new systems with higher efficiencies and ease of operation. This is of utmost importance to ensure the adoption of recovery technologies, because there is little incentive and funding to improve the current working WWTP processes, which are approached with the perspective of waste management and not the production of a valuable resource.

Complex plant management and costly operation spending can make even an efficient process unfeasible for its use on a larger scale, which happened to the Thermphos company that went bankrupt in 2012 while trying to market its sewage ash process (Egle et al., 2016; Schipper et al., 2004). This failed P recycling venture has caused administrative and political issues given the high cost of maintaining the abandoned plant and the risk the accumulated waste poses to the population (Ministerie van Sociale Zaken en Werkgelegenheid, 2015). Therefore, in the development process of novel treatment systems, close collaboration with private and public entities is required to ensure the proper distribution of waste, products, and funds. This is necessary for the longevity and effective operation of the waste treatment facility.

Table 1-2 Phosphorus recovery processes that are available for large-scale use

Process	Recovery Fraction	Reactor Type	Process Description	P recovery	Ref.
AirPrex®	Digested Sludge	Cylindrical Aeration Column	Crystallization occurs directly on sludge stream, upwards aeration strips CO_2 within the sludge and increases pH in the mixing zone of the reactor, $MgCl_2$ is added to the reaction to precipitate P as struvite, this occurs on the external precipitation cylinder where settled struvite is removed.	80-90% from effluent	(Heinzmann & Engel, 2006)
Ostara Pearl®	Dewatered Sludge Supernatant	Fluidized bed Reactor	Controlled chemical crystallization occurs in the fluidized bed reactor as the liquid protiom is recirculated in addition to $MgCl_2$ and NaOH to allow the formation of Struvite. This process achieves the formation of a larger struvite pellet product by the consequential size separation that occurs in the column.	85-90% from effluent	(Britton et al., 2009)
STRUVIA®	Dewatered Sludge Supernatant	CSTR with lamella separator	The rejected water obtained from dewatering the sludge is fed to a CSTR, rapid mixing is achieved in the chamber where pH is controlled with chemical bases, additionally magnesium salts are added to initiate struvite precipitation. A lamellar settler within the tank separates the struvite grains from the treated effluent. The formed material can then be pumped to a draining facility for drying.	60% Overall	(Veolia, 2015)
Stuttgart process	Sewage Sludge	Sequential CSTR, Filtration, and CSTR	This process consists of three separate steps, first an acidic leaching step to mobilize the chemically precipitated phosphate with H_2SO_4, following a filter press separation and finally a precipitation reactor where precipitation and agglomeration take place using MgO and NaOH. The precipitate is separated by a filter press or sieving.	50% Overall	(Meyer et al., 2019)
Gifhorn Process®	Sewage Sludge	Digestor and stripper reactor	The large-scale process used consists of an acidic nutrient extraction unit and a precipitation unit that performs both a struvite precipitation step as well as an ammonia stripping process. Control of the Iron leaching that can occur because of the acidic treatment is necessary for the correct operation of the ammonia stripping step as well as to increase the quality of the struvite precipitate.	35-50% Overall	(Esemen, 2012)

Process	RECOVERY FRACTION	REACTOR TYPE	PROCESS DESCRIPTION	P RECOVERY	REF.
PRISA	Sewage Sludge	Dewatering Belt, Filtration Step and Precipitation CSTR	In this process the EBPR effluent is dewatered before the anaerobic treatment of the solids, this way the Phosphorus that is already dissolved int the aqueous phase cannot be reintegrated into the organic matter in the anaerobic digestor. This is mixed with the effluent from the other thickening steps. The Phosphate rich effluent is then filtered to remove organic particulate and the effluent is treated using MgO and Lime to precipitate Struvite in a stirred tank reactor.	90% from effluent	(Montag, 2008)
ExtraPhos®	Anaerobic effluent	Pressurized plug reactor, centrifuge and CSTR	This process performs an acid leaching step using pressurized CO_2 to lower pH and release metal bound phosphorus, after the treatment coagulants are added to remove solids through filtration. Finally, a quick degassing step is used to recover the solubilized CO_2 which is recaptured to use in other treatments and the liquid effluent is treated with lime to precipitate calcium diphosphate.	70-80% from Effluent	(Schnee & Opitz, 2018)
FIX-Phos	Anaerobic Effluent	CSTR	Calciumsilicate hydrate is added to a conventional Anaerobic digestion reactor setup. The particles act as nucleation seeds for the formation of calcium phosphate which can precipitate with the sludge. This method is attractive because it reduces the dewatering step of the sludge without negatively affecting biogas production.	20-30% Overall	(Petzet & Cornel, 2012)
DHV Crystalactor®	Anaerobic effluent	Fluidized Bed Reactor	The full effluent produced in the EBPR step is treated in a fluidized bed reactor. First a carbonate stripping step occurs to reduce inhibition. Filter Sand is used as seed material in the reactor and the addition of $Ca(OH)_2$ solution facilitates the precipitation of Calcium phosphate in the sand grains. The sand is harvested and exchanged for new seed in intervals.	70-80% from effluent	(Cornel & Schaum, 2009)
PHOSPAQ®	Anaerobic effluent, rejection water	Aerated CSTR	Uses a side stream of the sewage sludge to produce the reaction zone. pH in the reactor increases because of CO_2 stripping to a range of 8.0 to 8.5, MgO is added to precipitate P in the form of struvite. Separation Occurs at the bottom of the tank and with the aid of a screw press.	80% from effluent	(Driessen et al., 2009)

Process	RECOVERY FRACTION	REACTOR TYPE	PROCESS DESCRIPTION	P RECOVERY	REF.
NuReSys®	Anaerobic effluent, rejection water	Two CSTR system	Two continuous reactors are connected where the first reactor acts as an aerator to strip CO_2 and lower pH, in the second reactor $MgCL_2$ and a NaOH solution are added to initiate struvite crystallization at a controlled pH of 8.5. Harvesting is done by intermittent purging.	85% from effluent	(Moerman et al., 2009)
PHOXNAN®	Anaerobic Sludge	Batch Reactor, Two Filtration Units, precipitation	A Batch reactor is used to treat sewage sludge by using low-pressure wet oxidation, which occurs at elevated temperatures in presence of pure oxygen and acidic conditions. The effluent from the reactor is then filtered through a ultrafiltration system to remove particulate matter and a nano filtration system to remove interfering ions. Finally, precipitation occurs.	54% Overall	(Blöcher et al., 2012)
Aqua Reci®	Sludge ash, digested sludge	Batch Reactor	This Harvesting Method can be used to recover P from conventional sludge ash or from residues resulting from supercritical water oxidation of the sludge. After the process leaching of the phosphorus can be achieved with HCl or with NaOH. Base leaching is more selective to P over heavy metals but is less efficient than acid. Final precipitation is achieved with Calcium dosing to obtain calcium phosphates.	>90% from ash	(Levlin, 2007)
AshDec®	Sludge ash	Furnace	AshDec uses a conventional incineration process to remove all organic pollutants from the sewage sludge solids. This ash still contains heavy metal compounds, so a second thermochemical step is performed. Chlorine salts are mixed with the ashes and exposed to temps above 1000°C. At this temperature Zn, Cu, Hg, Pb react with the salts and gasify. The final product contains P in diverse mineral phases such as stanfieldite	>90% from ash	(Hermann & Schaaf, 2018)
EcoPhos®	Sludge Ash	Batch Reactor	Ashes and low-grade P-minerals are purified by HCl digestion of the ashes, with the addition of $CaCO_3$. This solubilizes the P which can be precipitated in the form of dicalcium phosphate after a liquid-solid separation step. The resulting minerals are dicalcium phosphate and gypsum, additionally the HCl can be reused.	>90% from ash	(Takhim et al., 2019)

Discussions

The P removal technologies that have been developed over the years have varying degrees of effectiveness and technical difficulty in achieving compliant levels of P in wastewater-treated effluent. However, to effectively recover the P in forms that can be reinserted into the food systems it is required to carefully tailor the processes used to allow for the immobilization of P into products that have good P release for plant absorption. Hence, a combination of technologies is used, some of which focus on maximizing the removal of P from the solution and others that can properly concentrate and purify the nutrient for its use as an agricultural resource.

Phosphorus removal from wastewater is a crucial step for the overall P recovery goal, and systems need to be studied to increase the transfer of P in the aqueous phase to the sludge portion. The P-enriched liquid slurry is therefore the most efficient side stream product on which to perform the phosphorus recovery steps. P transfer into side streams can be obtained by hybrid techniques, membrane processes, or EBPR, but because of its low cost and more mature development, EBPR systems can easily be implemented to achieve high P incorporation into microbial biomass that can be readily separated from the wastewater. Different treatments can be applied to the sludge to extract and recover P. However, the bioavailability of the final P products needs to be considered, which is why some filtration and chemical absorption technologies cannot be included in the recovery systems, especially the ones that use iron ions for P immobilization.

Many of the current P removal systems on the market use a combination of steps to maximize phosphorus interaction with the compound used for its immobilization. Hence, it seems that processes that focus on the treatment of wastewater sludge have higher recovery efficiencies than the ones that focus on the retrieval of phosphorus in line with the traditional wastewater

treatment process. This can be attributed to the flexibility that is allowed when treating side streams. Because there is no longer a risk of disrupting the quality of the treated water, the conditions to which the sludge is subjected can be optimized to remove a higher quantity of P. Sludge-focused treatments also work on a more concentrated material which facilitates mass transfer and overall control of conditions. When considering process design, a more concentrated material also requires smaller reactors which can reduce some of the initial cost, while the rheology of a more concentrated effluent may additionally increase the energetic demand for pumping and agitation. Still, considering the composition of the produced sludge is of utmost importance because different P species will behave in different ways when subjected to the same thermochemical or biological treatments. Separating between primary sludge and EBPR sludge can be a potential opportunity to extract the phosphorus present in them in different settling tanks or the same tank that has different flow inputs.

The P recovery processes that have been presented in this work mostly focus on the precipitation of P-bearing minerals from different wastewater treatment streams, which is adopted mainly because chemical precipitation is a mature technology that gives good results even when the conditions of the treated effluent vary. To obtain a high-quality precipitate, the suspended solid content should be minimized. This is why many of the systems include solids separation steps, such as belt presses and continuous centrifuges, such as the case of the NureSys, PHOSPAQ and OstaraPearl systems. Solids separation steps are usually required during conventional WWTP sludge processing so there is a potential to alter the currently used process in a plant to add the phosphorus recapture system. The use of equipment and materials that are already in use in conventional WWTPs is very attractive as it minimizes the overhead cost of implementing P recovery systems. The final composition of the product requires the removal of the organic fraction up to the colloidal solids that are not removed by conventional separation steps (belt presses and

centrifuges) therefore the application of polymers to the dewatering steps may be of value for P recapture goals. Another major issue when precipitating P-bearing minerals is the presence of competitive ions in the solution. When considering the struvite or the CaPs precipitation systems the two main disruptors of precipitation are carbonate (CO_3^{2-}) and iron ions ($Fe^{2+/3+}$). Both types of ions are present in large quantities in wastewater, the former because of the coagulation processes used in many WWTPs and the latter because of the organic matter decomposition and water hardness (Dudziak & Kudlek, 2019). The presence of other metals in the solution can induce precipitation in the form of low-bioavailability minerals, while the buffering capacities of carbonate can significantly increase the need for acids or bases for pH control. Additionally, the precipitation of other minerals in the crystallization step can reduce the overall P content of the final product, a parameter that is crucial for alternative P marketability.

Systems like the Stuttgart, Grifhorn, and ExtraPhos, include an acidic leaching step to increase the phosphorus available for precipitation and reduce the interference created by metal ions. Others, like PHOXNAN, use complex filtration systems to selectively sort for phosphate ions in the effluent solution. The reliance on processes that require more extreme pH conditions can be problematic as that can increase the overall use of chemical materials because neutralization is often required before the final disposal.

Processes that utilize CO_2 stripping as the main pH regulator have more potential for application because they do not require the additional chemical input or do so in much smaller quantities. In addition to acids and bases, the use of metal salts for the precipitation represents a high percentage of the total facility expenditures, because pure compounds are costly consumable materials. Therefore, the use of lower-quality chemicals (like slaked lime) could be adopted, with the consideration that this will also reduce the final P concentration of the obtained product and

consequently its market value. Phosphorus recovery technologies that utilize sludge ash as a P source have very high extraction rates where high-purity products can be obtained. When acids are used for the leaching process as in EcoPhos, it is possible to recycle and repurify the reagents to create a loop reducing significantly the cost of consumables. Other systems like AshDec use ionic donors to volatilize heavy metals to obtain a purified phosphate product, so the use of reagents would be like other technologies that use metal salts.

Finally, concerns regarding the energetic input required to operate large-scale furnaces could hinder the adoption of ash recovery technologies in small-scale WWTPs as well as in places where biosolids burning is not adopted. Because in the US incineration of biosolids represents only 16% of the total biosolids disposal, adoption of ash P recovery technologies is not a feasible solution to implement nationwide. Economic and energetic analysis must then be performed to determine what are the best conditions to suit each treatment plant, as variations in nutrient input, environmental conditions, and plant size and location can favor the use of one system over another. The adoption of P recovery processes is necessary for the compliance with P-security directives, but in order for that to happen P recovery systems will need to achieve high P recovery efficiency with low economic and labor input. It should be observed that the expression of P recapture efficiency is not standardized as some authors presented the P recapture from the treated portion while others presented the P recapture of the overall plant by calculating mass balances. The latter is therefore a more significant figure as it illustrates the immobilization of total P that goes through the WWTP. While most of the P does end up in the sludge fraction, optimizing the separation steps and P removal steps can help breach the gap of lost P flows into disposed or released fractions.

Conclusions

The reliance on P-based fertilizers for the productivity of our food systems has created an unstable market for the extraction of P-rich minerals, therefore a shift towards renewable nutrient resources is necessary to ensure P security for future generations. Wastewater is a rich source of phosphorus and other nutrients, which is why P recapture technologies have attracted so much interest. An efficient treatment of wastewater with the included P recovery could reduce the reliance of developed economies on mineral P fertilizers.

The adoption of P recovery technologies in WWTPs will allow for this paradigm shift. Hence, continuous development and optimization of the P recapture technologies are needed to reduce the cost of the treatments and increase the financial benefit obtained from the final products. In addition, the widespread application of these technologies will require the conscientization of the overall population to support and subsidize the additional expenses for the adaptation of the plants. Government subsidizing and support are necessary to establish these technologies, which can be promoted by discussing the economic aspect of nutrient recovery. Furthermore, the reduced dependence on geopolitically unstable commodities like P-rock and the environmental benefits that would be associated with the P recovery system can be considered. However, that requires additional studies that can properly illustrate the overall socioeconomic impact of the implementation of P-recovery.

The parameters that are used for the evaluation of the appropriate P-recovery technology are varied and location-dependent. Overall, though, reduced complexity and cost, as well as increased P recaptured efficiency will be favored in most cases. Technologies with simpler reactors and process layouts represent lower initial investments for municipal facilities and may be more

readily adopted than systems that require more complex infrastructure and maintenance. As discharge standards become more stringent, more sophisticated wastewater treatments will be required. This represents a unique opportunity to incorporate recovery technologies into WWTPs. It is evident that the solutions should be studied on a case-by-case basis so that the appropriate technology is selected. Other aspects of the wastewater treatment process need to be considered as well, such as greenhouse gas emissions and energy requirements.

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Chapter 2

Effect of Fermentation Conditions on solubilization of Phosphorus and Organic Compounds in Anaerobic Digestion

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Abstract

Small-scale wastewater treatment plants tend to have low efficiencies of phosphorus recapture, which occurs given the opposition of the recapture mechanisms employed in enhanced biological phosphorus removal and the degradation that occurs in anaerobic digestion. This research focused on the determination of ideal conditions of fermentation in an anaerobic digestor to maximize available soluble phosphorus for its recapture with a chemical precipitation step. The effect of sludge pretreatments, fermentation time, fermentation temperature, and volatile solids loading rate on nutrient solubilization was evaluated. The use of thermophilic conditions aided in the phosphorus solubilization in the digestate by an additional 9% over the phosphorus solubilized in the mesophilic conditions. The pretreatments and loading rate did not affect phosphorus solubilization. After a solids separation process on the AD digestate, the resulting supernatant is a good substrate to perform phosphorus precipitation on; jar test assays achieved phosphorus removal of up to 97%. The liquid portion of digestate that was obtained after the P-recovery treatment demonstrated high digestibility in a high rate upflow anaerobic sludge blanket (UASB) digester, achieving a 77% COD reduction.

Introduction

Phosphorus is a relatively abundant nutrient present in domestic wastewater, and its discharge into the hydrosphere is associated with adverse environmental effects such as eutrophication (Correll, 1998). Wastewater treatment plants (WWTPs) operate to remove the P present in the wastewater and to reduce the overall impact of the produced municipal effluent. Waste management and nutrient recovery are two essential aspects considered when operating municipal wastewater treatment facilities. The former is the primary goal of centralized sewage treatment, as it ensures the elimination of pathogens, pollutants, and overall organics from water released into the hydrosphere. The latter is a recent addition that seeks to align conventional waste treatments with sustainability and value extraction goals. There is a high potential for the recapture of phosphorus from wastewater, as it is estimated that more than 16% of the annually mined phosphorus ends up in sewage (Cordell et al., 2009). Recapture of the P present in wastewater is especially relevant as other sources of phosphorus become scarcer because of overexploitation.

During the wastewater treatment process, more than 90% of the P that enters the treatment facility is immobilized into the sludge fraction (Witek-Krowiak et al., 2022; Zhou et al., 2017). If we consider that somewhere between 1 and 5 megatons of phosphorus end up in wastewater globally every year, the sludge produced in WWTPs that recaptures most of that P is a good material for performing phosphorus extraction (Mateo-Sagasta et al., 2015). The sludge that is created can be categorized as primary sludge obtained from settleable solids that are removed from raw wastewater in clarification tanks and secondary sludge (waste activated sludge), which is discharged from the enhanced biological phosphorus removal (EBPR) system overflow (Xi et al., 2023). In both cases, only a portion of the phosphorus will be present as soluble phosphate, which is the P species that can be readily recaptured through precipitation.

Phosphorus in sludge can be bound to solids as a product of the EBPR system in the form of polyphosphates, in the microbial mass in the form of organic molecules, or as inorganic P bound to mineral ions (Jardin & Pöpel, 1994). The P contained in the sludge is accessible for nutrient recovery systems focused on sustainability and circularity, so it is necessary to understand how this P is embedded into the sludge to facilitate its release and subsequent recapture.

Many phosphorus recapture technologies focus on the precipitation of P by the addition of metal salts. This process is well documented and readily implemented, as it only requires solid-liquid separation, pH regulation, and chemical dosing. The controlled precipitation of specific minerals like struvite (NH_4MgPO_4) and brushite ($CaHPO_4$) is desired, as these materials can be used as slow-release fertilizers in agricultural settings (Le Corre et al., 2009). While the use of chemical precipitation processes for phosphorus recapture is very promising, the overall phosphorus recovery efficiency tends to be low as a significant portion of the phosphorus is lost in the solid stream during dewatering, some authors estimate that the lost P could account for 80% of the total phosphorus in WWTPs (Latif et al., 2017).

To increase the phosphorus available as soluble P in the sludge, it is necessary to destroy the sludge structure and hydrolyze the organic molecules that contain the element. Anaerobic digestion (AD) is a technology used for waste management and is commonly used to treat the sludge obtained from WWTPs. AD is a process of decomposition of organic matter in an environment devoid of oxygen. In AD, microbial organisms degrade organic materials and produce biogas. The AD process is widely adopted given several advantages over other forms of waste treatment: there is a reduction in overall biomass volume, it is successful in treating wastes with high water content, it is effective at pathogen destruction, and the produced emissions consist mainly of methane and CO_2 (Mata-Alvarez, 2002; Nag et al., 2019; Sahlström, 2003).

The biogas produced during the AD process can be collected and used as an alternative fuel, given the energetic potential of components like methane and hydrogen. The obtained biogas can then be purified to substitute fossil natural gas. The additional income that could be obtained from capturing and processing this gas is relevant, as it can help offset the costs of more expensive processes in the WWTP. According to Murray (2017), the wastewater treatment infrastructure could produce up to 0.1% of the US's current annual energy consumption at a cost comparable to that of natural gas (Murray et al., 2017).

AD is a complex process that degrades organic matter to produce biogas. It is modeled by identifying four main steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Fig. 2.1).

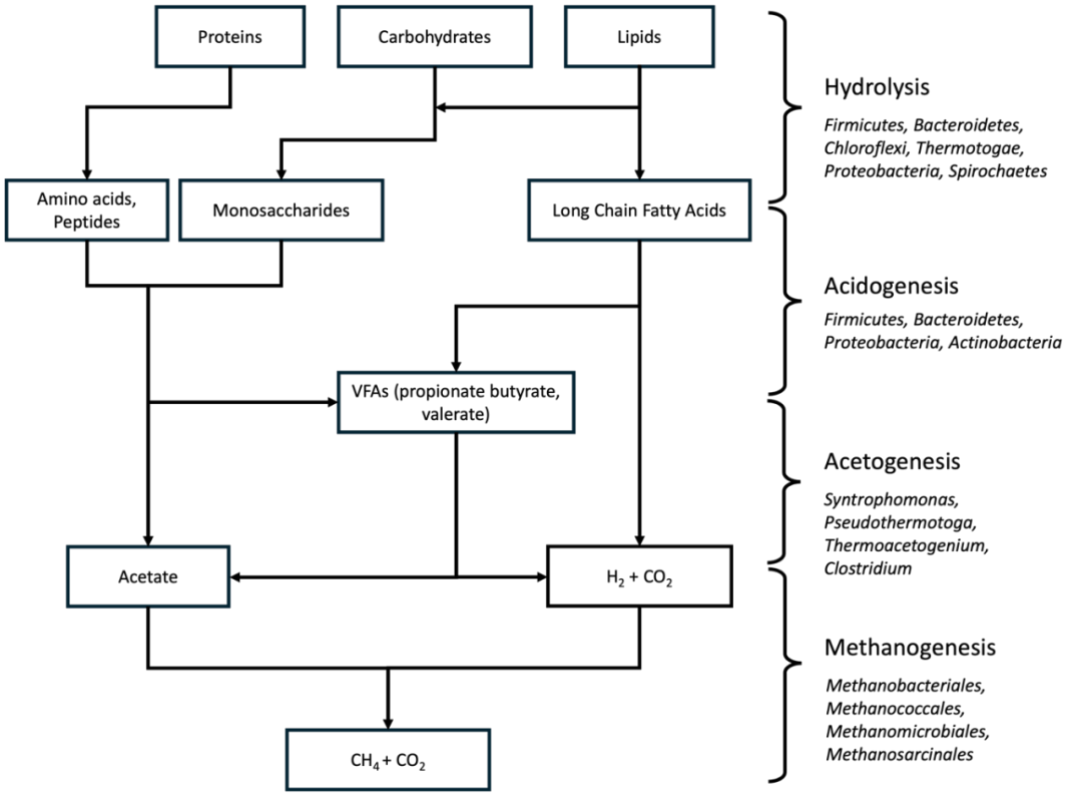

Figure 2-1 Diagram of the anaerobic digestion process, each step is indicated alongside the taxa that are associated with it (adapted from Nguyen et al., 2019).

The hydrolysis step is a biochemical process that occurs extracellularly. Hydrolytic bacteria produce enzymes that can degrade soluble and non-soluble organic compounds of high molecular weight, increasing the availability of organics in solution. In this step, inert particulate matter can also disintegrate. The acidogenic step is performed by fermentative bacteria that consume the monomeric molecules produced by hydrolysis (monosaccharides and amino acids). The organisms involved use the monomers as final electron acceptors for their respiratory processes and generate products such as volatile fatty acids (VFAs), alcohols, CO_2, and H_2. Acetogenesis is the phase in which organic acids (VFAs and long-chain fatty acids) are metabolized into acetate, CO_2, and H_2. Some methanogenic microbes partially utilize the hydrogen produced during acetogenesis to produce methane. The acetate is finally metabolized by acetoclastic microbes to produce methane and CO_2 (Batstone et al., 2002; Mata-Alvarez, 2002).

During AD, many of the compounds present in the biomass solubilize back into the liquid portion. This is the case with phosphorus-rich sludge produced during wastewater treatment. Researchers have found varying degrees of nutrient solubilization with AD, with reports of experiments where the P release was up to 80% of the total immobilized phosphorus within the sludge. In contrast, other studies place that figure closer to 40% (Jardin & Pöpel, 1994; Mavinic et al., 1998). Nonetheless, the increase in soluble phosphorus in the digestate can produce operational problems, such as mineral deposits that require constant maintenance.

In addition, fluctuation in biomass composition and mineral ion concentrations can result in highly variable soluble P fractions (Mazzini et al., 2020). By improving the solubilization step of the total P contained in the sludge, the AD process could increase the fraction available for precipitation recovery. The literature that focuses on the solubilization of P from AD effluents is limited. Some previous studies used pretreatments such as acid digestion, ultrasonic degradation,

and thermal degradation to increase methane yields in the digesters but the effect of these treatments on overall phosphorus availability has been seldomly discussed (Pérez-Elvira et al., 2009; Wang et al., 2016).

It is necessary to remark that while EBPR and AD systems are beneficial and widely employed in wastewater treatment facilities, these processes affect each other in a detrimental fashion. The biomass accumulation of EBPR systems can reduce the final sludge's dewaterability, increasing processing demands and energetic footprint (Shimp et al., 2013).

Additionally, the processing of the phosphate-rich EBPR sludge through AD can cause the precipitation of P-minerals that can clog piping and accumulate in reactors. P-minerals encrusted in the equipment increase the operation and maintenance cost of the plant by reducing reactor efficiency, increasing pumping requirements, and making it necessary to replace components (Achilleos et al., 2022; Fattah & Chowdhury, 2015). The P released from the sludge in anaerobic digesters needs to be addressed to reduce the costly maintenance. On the other hand, the AD process can interfere with P removal technologies by increasing the presence of soluble P species in the latter stages of the WWTP, requiring additional treatment to comply with P release regulations. The chemical precipitation of phosphorus is hindered by the presence of suspended solids, and the mixing required to achieve crystallization is especially energy-consuming when performed on highly viscous sludge (Achilleos et al., 2022).

It is hypothesized that by modifying how sludge is handled after its separation from the aqueous portion, it will be possible to address the low P recovery and low dewaterability observed in conventional EBPR-AD processes. Separating the AD process into two reactors will allow for the solubilization of phosphorus in the first thermophilic acid digester. The effluent of the first reactor can be subjected to solid separation, and the nutrient-rich supernatant will allow for further P

precipitation and biogas generation in further reactors (Figure 2.2). The system is hypothesized to be capable of achieving biogas production rates and solids consistent with those observed in conventional AD systems , while allowing for phosphorus recapture technologies.

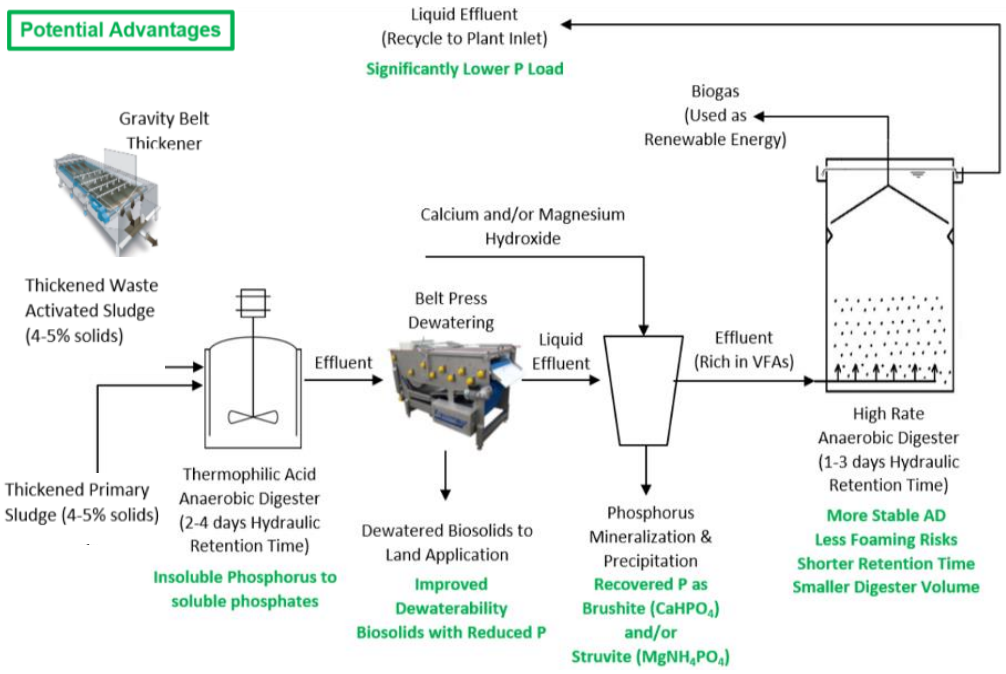

Figure 2-2 Proposed Process that integrates thermophilic acid AD, P-Recovery, and high-rate AD

This chapter focuses on the determination of the viability of the proposed process. By establishing ideal fermentation conditions for the solubilization of the phosphorus present in primary sludge and waste activated sludge. Batch tests of different temperature setups, loading rates, and hydraulic retention times were conducted. Moreover, three pretreatment methods were evaluated concerning their P solubilizing capacity. An increase in degradation rate respective to overall volatile solids (VS) is hypothesized to allow for higher P solubilization.

Hence, pretreatment conditions that can produce significant changes in the molecular structure of organic matter will increase the P fraction in solution. Additionally, temperature and fermentation time increases are expected to result in higher P solubilization, as both would increase the degradation of the overall organic where phosphorus can be embedded. Acid pretreatments are also expected to maintain a lower pH, increasing the $[PO_4]^{3-}$ solubility in contrast to its complexation with metal ions in solution. Finally, using the optimized fermentation conditions will allow the separation of a liquid fraction with a high soluble nutrient concentration. This supernatant is expected to be appropriate for metal salts P precipitation and further digestion.

Materials and Methods

Sample collection and culture maintenance

All the wastewater treatment plant effluents were collected from a public facility in the Twin Cities Metropolitan Area, Minnesota, United States. Thickened primary sludge (TPS) was collected from the waste sampling spouts connected to the primary clarifier. Thickened waste activated sludge (TWAS) was collected from the gravity belt thickener unit. The digested sludge (DS) was collected from a mesophilic anaerobic digester that processes mixed TPS and TWAS. All the samples collected were stored at 4 °C for a maximum of 3 months from sampling. The DS was used as inoculum for a continuous thermophilic reactor operated throughout the fermentation experiments. Before inoculationtion, the DS was supplemented with 10 g/L of amorphous cellulose to reactivate the microbial community, and it was allowed to degas for 7 days at 37 °C.Table 2.1 presents the properties of the initial effluents that were sampled.

Table 2-1 Properties of the effluents sampled.

	Thickened Primary Sludge (TPS)	**Thickened Waste Activated Sludge (TWAS)**	**Digested Sludge (DS)**
TS (%)	5.51 ± 0.10	7.10 ± 0.21	2.56 ± 0.02
VS (%)	4.83 ± 0.11	5.39 ± 0.15	1.67 ± 0.04
VS/TS (%)	87.6 ± 3.9	75.9 ± 5.21	65.2 ± 3.2
TDS (%)	0.41 ± 0.02	0.56 ± 0.08	0.93 ± 0.05
TSS (%)	5.04 ± 0.03	6.65 ± 0.06	1.63 ± 0.05
Initial pH	5.83	6.76	7.12
Total COD (mg/L)	50,935 ± 2586	81,692 ± 4269	18,000 ± 82
Soluble COD (mg/L)	8,069 ± 787	4249 ± 439	6157 ± 24
Total P (mg P/L)	624 ± 32	2106 ± 328	659 ± 43
Sol P (mg PO_4^{3-}-P/L)	216 ± 16	1013 ± 65	153 ± 10
TAN (mg/L)	283 ± 32	358 ± 12	959 ± 39

Experimental design of batch anaerobic digestion

The AD test used for the determination of fermentation conditions was a modified version of the closed vessel batch test used for biochemical methane potential (BMP) determination (Angelidaki et al., 2009). Serum vials of 100 ml capacity were used as the vessels for fermentation. A total working volume of 60 ml was used to allow headspace for gas accumulation. The fermentation time, the temperature and other fermentation conditions were modified depending on the experimental run, as described below in Table 2.2. To simulate an initial hydraulic retention time of 3 days, the primary experiments used an inoculum-feed ratio of 2 to 1 (wet-mass based).

The fermentation substrates used were TPS, TWAS, a mixed slurry of 1:1 (TPS:TWAS, wet-mass based) hereon called MIX 50/50, and a diluted sample of TWAS with a mixing ratio 1:1

(Deionized water:TWAS, wet-mass based). The diluted sample of TWAS was used to simulate the properties of unthickened waste activated sludge (WAS) so it was referred to as such during the experiments. Blank samples contained 60 ml of inoculum and no feed to achieve the final volume. However, gas production and nutrient release accounted for this difference by a factor of 2/3. Before sealing the vessels, the initial pH of the substrate-inoculum mixture was registered, and the oxygen in the containers was purged using pressurized nitrogen to maintain anaerobic conditions. After feed addition and nitrogen purging, the vessels were sealed and placed in temperature-controlled water baths in mesophilic conditions (37 °C) and thermophilic conditions (45 °C and 55 °C). The samples were analyzed before and after fermentation to determine the overall change in composition. The overall change in each treatment and the change corresponding only to feedstock degradation were evaluated for discussion of results. Comparison within the treatment occurred by subtracting the final composition of the control inoculum from each treatment's gas and nutrient release values. All groups were operated in triplicates, to allow for statistical analysis.

Table 2-2. Experimental conditions evaluated, the variable condition is underlined for each run.

	Run 1	**Run 2**	**Run 3**	**Run 4**	**Run 5**
Feed	1:1 Mix	TPS, TWAS, 1:1 Mix	TPS, TWAS, 1:1 Mix	TPS, TWAS, 1:1 Mix	TWAS
Temperature	55 °C	55 °C	55 °C	55 °C, 45 °C	55 °C
Dilutions	1x	1x	1x	1x	1, 2, 3, 5, 7x
Pretreatment	Heat, Acid, Acid + Heat	Heat, Acid, Acid + Heat	None	None	None
Ferm. Time	3 days	3 days	2, 3, 6 days	3 days	3 days

Pretreatment methods

Both TPS and TWAS were pretreated to assess changes in nutrient release after treatment and fermentation. For the thermal pretreatment, the samples were subjected to regulated temperatures of 100 °C in a jacketed oven with an exposure time of 60 minutes. Acid pretreatment of the samples consisted of the addition of hydrochloric acid at a 4 N concentration and mixing of the sludge until the sample's pH reached 4. The pH of 4 was selected to not interfere with orthophosphate dissociation, as other authors used a final pH of 2, but phosphate as phosphoric acid has a pKa of 2.2 (Devlin et al., 2011). The samples stayed under agitation for 12 hours before use. Finally, a combined treatment of thermal and acidic pretreatment was also used.

Jar testing for phosphorus precipitation

A modified version of Clark and Stephenson's jar test (1999) was used to establish ideal chemical dosage and precipitation conditions. The fermented sludge samples were centrifuged at 5000 rpm for 10 minutes to separate the larger settleable solids from the liquid supernatant. The obtained supernatant was tested for total phosphorus content and then aliquoted in 50 ml portions to precipitation vessels of 100 ml capacity. The addition of both calcium chloride and magnesium chloride was tested. These were added proportionately to the phosphorus concentration in molar ratios of 1:1, 1.2:1, and 1.5:1 (P:Metal). Afterwards, NaOH solution of 10 N was added to obtain a final pH of 8 for calcium and 10 for magnesium tests. After pH control, the solutions were flash mixed at 400 rpms for 1 min, followed by 30 minutes of slow mixing and 45 minutes of precipitation time (Clark & Stephenson, 1999). The supernatant solution was tested for total phosphorus content and was used for cation analysis through ion chromatography.

Digestate liquid fraction's digestibility and potential for biogas production

The supernatant obtained from the different fermentations was fed to an up-flow anaerobic sludge blanket (UASB) reactor to evaluate its performance in a high-rate digester. The UASB reactor was seeded with granular sludge sourced from a UASB digestor that treats lignocellulosic material from a private agricultural feed company (Marshall, Minnesota). The UASB reactor had two pump systems for continuous recirculation and feeding. The reactor was fed with 400 ml of supernatant per day, as it had a working volume of 1.2 L and hence an effective HRT of 3 days. VFA analyses were performed before and after exiting the digester to corroborate the digestibility of the separated liquid, as well as determinations of gas production and composition.

Analytical methods

Substrate degradation was monitored by measuring biogas production over time; the amount of gas production was measured using a 12 ml syringe for excess gas removal. The vials were agitated before the gas collection to allow for the release of entrapped bubbles in the sludge. Biogas composition was determined on a micro gas chromatograph (micro-GC, Agilent 490, USA) equipped with a thermal conductivity detector (TCD) and two columns of molecular sieve 5 A (MS5A) and PoraPLOT U (PPU). After fermentation, the vials were opened, and the samples were stored for nutrient analysis at 4°C. The blanks' overall gas production and nutrient release were measured and subtracted from the feed treatments to account for baseline production.

Wastewater characterization was performed on all samples to determine total and soluble organics, phosphorus, and ammonia nitrogen (NH3-N) fractions. The samples were centrifuged to separate the soluble fraction, and the supernatant was filtered through a 0.45 µm syringe filter to obtain the liquid reject containing the soluble fraction (APHA, 2005). Chemical oxygen demand

(COD, total, and soluble) was measured as an indicator of solubilized organics. COD was determined with colorimetric methods on a spectrophotometer (DR5000, Hach, USA) using standard APHA methodology.

Total phosphorus (tP) and soluble phosphorus (sP) were determined using ascorbic acid colorimetric measurements with Hach commercial vials (TNTplus 845, Hach, USA). Total ammonia nitrogen and soluble ammonia nitrogen were analyzed using the salicylate colorimetric method of commercial kits (TNTplus 833, Hach, USA). Total solids (TS) and volatile solids (VS) were measured using sequential drying steps as established in EPA's method 1684 for solids determination (EPA, 2001) Total dissolved solids (TDS), and total suspended solids (TSS) were determined according to EPA's method 160-(1-2) that uses a filtration separation and drying process (EPA,). A handheld P100 pH meter (Cole Palmer, USA) was used for pH measurements.

VFA analysis was done using a high-performance liquid chromatography system (HPLC, Infinity 1200, Agilent, USA) with a refractive index detector and an Aminex HPX-87H column (Bio-Rad, USA). Ion concentrations of magnesium, calcium, and phosphate were determined on an ion chromatography system (ICS) (Dionex, Thermo Fisher Scientific, USA).

Statistical analysis

Statistical analysis was performed using JMP lab software. Preliminary comparisons of variance equality were performed to establish ANOVA validity. A one-way analysis of variance (ANOVA) was used to compare treatments and conditions; if variances were unequal, Welch's test was performed to compare mean values. A significance of $\alpha=0.05$ was used in all tests to assess the mean difference. When required, comparisons between individual treatments or comparisons from before and after treatment were performed using a T-test or a Tukey Range test. Additionally,

least squares regressions and mechanistic growth modeling were used to establish relationships for sample dilutions (former) and fermentation time (latter). Moreover, for graphical descriptions, all figures contain error bars depicting the standard errors of the experiment replicates.

Results and Discussion

Effects of pretreatment on sludge feedstocks

To determine if pretreatments would achieve higher nutrient solubilization, it was necessary to establish the effects of the processes on their own on undigested sludge. The sludge samples were characterized, and all values measured in this experiment are compiled in Table 4.1 of the appendix. Figure 2.3 shows that the use of thermal and acid pretreatments has a significant effect on nutrient solubilization.

A one-way ANOVA analysis was used to compare the effect of pretreatments on sludge nutrient composition. Dissolved solids increased significantly in all the tested groups compared to the untreated samples ($p<0.001$) for both TPS and TWAS. On the other hand, only the TWAS samples had a significant reduction in NH3-N content after pretreatment. The treated sludge showed a drop of 28-45% in soluble NH3-N. This is likely due to the volatility of ammonia and its conjugated compounds. Donovan et al. (1983) estimated that NH_3 volatilization was most active during the first 3 hours of the exposure of sludge to air, and ammonia loss was increased with high pH and temperatures (Donovan & Logan, 1983).

The solubilization of P and organics associated with COD was also determined, as shown in Figure 2.4. The ANOVA revealed a significant increase in the soluble COD of the thermal and

the conjugated acid and thermal treatments of the TWAS (242% and 258%, respectively) and the TPS (42 and 24%, respectively), indicating that the degradation of the biomass structure is more associated with the physical treatment rather than the addition of a corrosive agent.

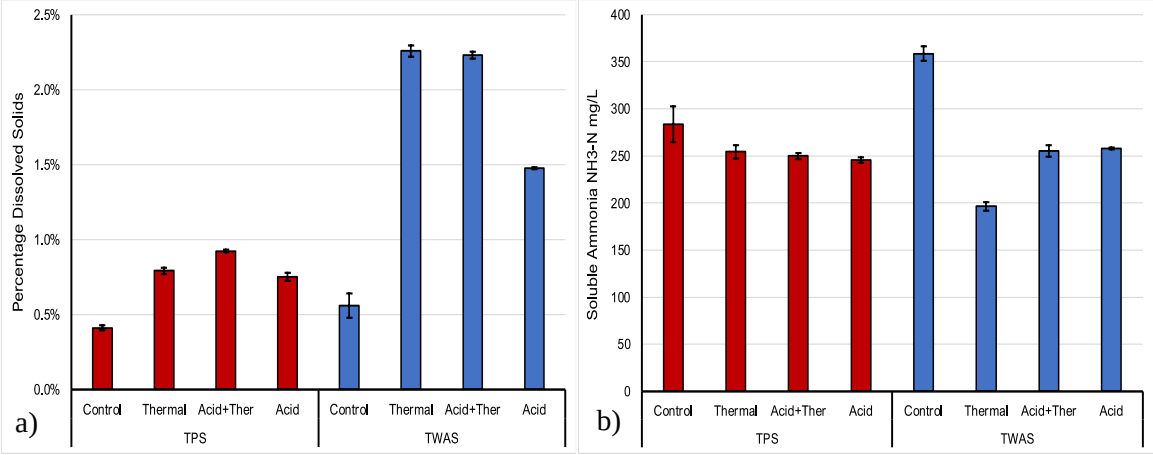

Figure 2-3 Comparison of dissolved solids (a) and soluble NH3-N (b) amongst untreated and pretreated feedstocks TWAS and TPS.

A higher dosage of HCl or the use of a stronger acid could potentially increase COD solubilization. Devlin et al. (2011) reported an increase in overall soluble COD and protein solubilization that was significant, but this required a dosage of 8.75 ml/kg wet sludge of 37% HCl to achieve this at pH 2 (Devlin et al., 2011). Still, it may not be feasible for WWTPs to use different reagents, as they can inflate overhead operation costs and increase post-processing requirements.

Regarding phosphorus solubilization, it was determined that all the pretreatments had a significant impact on the portion of phosphorus in solution in TWAS, as phosphorus associated with the microbial biomass was released during cell degradation processes. The thermal, acid, and combined treatments could solubilize a large portion of the total P in the TWAS with increases of 48%, 55%, and 56%, respectively. Differences between treatments were not statistically significant ($p>0.05$), indicating that any of these pretreatments can achieve similar amount of solubilization when applied to raw untreated TWAS. This effect could be attributed to the destruction of the PAOs in all pretreatment cases, after which other more resilient strains can hydrolyze the accumulated phosphorus biomolecules. Pretreatments did not increase P solubilization on TPS, and in the case of thermal and combined treatments, there was a small reduction in soluble P from the untreated sludge (-13% and -19%, respectively).

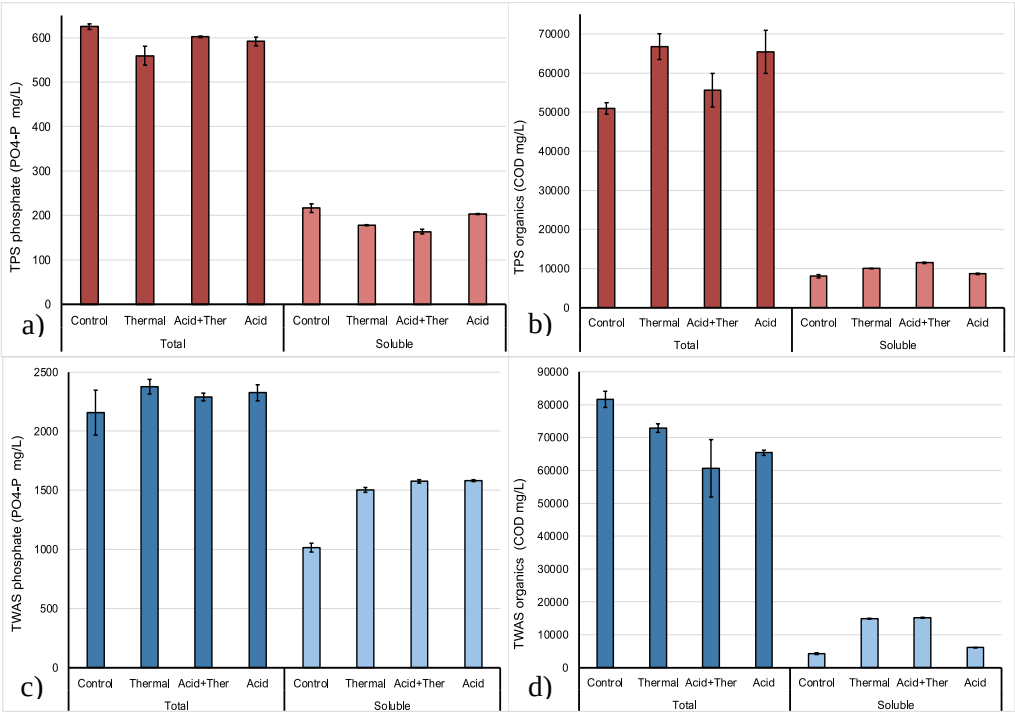

Figure 2-4 Changes in total and soluble form nutrients in the feedstocks after pretreatment. a) Phosphorus species in TPS, b) COD species in TPS, c) Phosphorus species in TWAS, b) COD species in TWAS.

Because TPS is not subjected to conditions conducive to phosphorus accumulation, the destruction of some of the bacterial cells present will not release additional P-bearing polymers. Yuan et al. (2012) postulated that high organics destruction or feed reconcentration could aid in further P solubilization (Yuan et al., 2012). In contrast, the TWAS consists of a matrix of large biomolecules produced by microbial consortia during EBPR. Consequently, the cleavage of these macromolecular compounds by physical or chemical action will facilitate their degradation by microbial metabolism. Both thermal and pH fluctuations can compromise cell structure, releasing cytosolic material into the solution. The macromolecules used for energy accumulation in PAOs, such as polyphosphates, can then be hydrolyzed into smaller components, increasing the overall soluble phosphorus concentration.

It should also be noted that variances in nutrient compositions were expected because of the heterogeneous nature of the untreated sludges used. This is especially evident in the quantification of total P and COD content because the analyses required serial dilution, and the high-solid content and polymeric substances suspended in the sludge did not allow for a homogenous solution. These two measurements consistently showed the most variation throughout the experimentation.

Optimization of fermentation conditions for Phosphorus solubilization

The overall results of the five optimization runs are collected in Table 2-3, which describe the experimental variables that were changed in each fermentation. Several authors report on improving biogas production in AD with pretreatments, but there is no data regarding phosphorus solubilization (Aboulfoth et al., 2015; Gonzalez et al., 2020; Li et al., 2019). Therefore, initial fermentation runs focused on overall nutrient solubilization.

Table 2-3 Fermentation optimization runs reasoning, variable conditions, results, and findings.

	Run 1	**Run 2**	**Run 3**	**Run 4**	**Run 5**
Evaluated Variable	Pretreatments	Separate feed, pretreatments	Fermentation times	Fermentation Temperature	Substrate dilution
Reasoning	Pretreatments reported to increase hydrolysis and solubilization of organics (Aboulfoth et al., 2015)	More thorough analysis of individual feed degradation	AD batch fermentation data regarding solubilization of P lacking	No direct comparison of AD batch fermentation temperature on P release	Previous run hinted at a better solubilization proportion at lower VS loadings
Nutrient release	Only NH_4 release significantly reduced by pretreatments	Only NH_4 release significantly reduced by pretreatments in TWAS	No significant change in P and COD release after 3d, NH_4 peak 3d	No change in COD, NH_4 release reduced, and significant increase in P solubilization in thermophilic AD,	All nutrient solubilization behaved in a linear fashion regarding VS loading
Biogas production	Pretreatments significantly reduce CO_2 production. Highest VFA accumulation in untreated feed	Pretreatments significantly reduce CO_2 production. Highest VFAs in untreated feed, more in TWAS	Highest biogas production at 6d. VFA accumulation with TPS highest at 2d, and at 3d with TWAS	Mesophilic AD produces more biogas, but H_2 production doesn't increase. VFAs are significantly higher in thermophilic AD	Non-linear behavior of gas production, ideal VS dosing occurs at 2.5x dilution
Full Data	Table 4.2	Table 4.3	Table 4.4	Table 4.5	Table 4.6

The results of the co-digestion of feedstocks did not show a significant effect of pretreatments on P solubilization ($p>0.05$). This indicates that thermal or acid pretreatments of the feedstock sludge did not contribute to improved overall phosphorus solubilization after AD. Anaerobic digestion is a very complex process that achieves a thorough breakdown of the organic biomass contained in the feed; these results suggest that the hydrolysis achieved by the microbial consortia in the digester can degrade the available polyphosphate in the influent biomass without preliminary degradation. To account for differences in composition, the experiment was repeated with separate sludges, and the same results were observed. No significant change in phosphorus solubilization was measured in the pretreated feedstocks ($p>0.005$).

In all the fermentation runs performed, the variable with the greatest impact on P solubilization concentrations was feedstock composition, which is to be expected as TWAS has an overall higher concentration of solids, organics, and phosphorus. Other combinations of feedstock ratios and dilutions were also tested to consider process configurations different from using belt-thickened sludge.

Afterward, experimentation to determine ideal retention times were performed. Previous studies have reported on the effects of hydraulic retention times on overall VFAs and ammonia concentration (Banerjee, 1997). Nonetheless, there is a lack of reported data from batch testing AD on the solubilization of the phosphorus fraction regarding essential operational aspects such as temperature and fermentation time. Still, many papers have been published regarding the effects of alternating anaerobic conditions for the enrichment of PAOs, in which, after the switch to an anaerobic environment, the accumulated phosphorus is quickly released again (Coats et al., 2011).

The fermentation time experimentation helped identify that while AD by itself still does not achieve 100% solubilization of the total phosphorus present in the sludge, the process can

achieve the depolymerization of a vast majority of the available polyphosphates in the sludge. This can be achieved in 3 days, after which the increase in solubilization of COD and P is negligible. These fermentation conditions achieved total phosphorus solubilization greater than 65% with a 3-day digestion period. This value is higher than the overall recapture efficiency reported by Veolia of 60%, while the prepared sludge still requires further processing to achieve an overall recapture value, this amount of P solubilization could achieve the same efficiency as the Struvia process with a 91% P recapture efficiency in the precipitation step (Veolia, 2015). Additional fermentation days up to 6-day fermentation do not appear to have an extra effect on P solubilization.

Subsequently, fermentation temperature tests were performed to determine the effect on phosphorus solubilization. Temperature had a significant effect ($p=0.0027$) in phosphorus solubilization, as on average, the thermophilic digestate had 9% higher soluble phosphorus concentrations. This was also closely related to the final pH of the digestate, which was lower by a small but significant amount with an average pH of 5.64 (S.D ±0.06). This value is very close to the ideal P solubilization pH of 5.5 reported by Stutzenstein for hydrothermally treated AD digestate (Stutzenstein, 2018).

Finally, VS loading fermentations were performed to determine if a lower organic load could increase the phosphorus solubilized per gram of volatile solids. It was determined that the P solubilization behaved in a linear fashion, and hence, loading did not play a role in overall P solubilization. It was determined that a thermophilic fermentation with a hydraulic retention time of three days and no pretreatment would be the most conducive to phosphorus solubilization of the TWAS substrate. The thermophilic conditions showed a higher concentration of VFAS, which are assumed to aid in the P solubilization. While a higher concentration of VFAs can provide more intermediates for methane production, increased accumulation of VFAs also causes inhibition of methanogenesis and effectively halts biogas production (Al-Sulaimi et al., 2022).

The system proposed in this dissertation intends to reduce the need for constant monitoring of the operational stability of the thermophilic fermenter by maximizing VFAs accumulation, so methanogenesis is not desired in the first reactor. The methanogenesis was inhibited in all our experimentations by an accumulation of VFAs, but digestate effluents high in readily metabolized organics were obtained. This can be attributed to the acidification of the substrate, which may help inhibit methanogenic archaea and solubilize the phosphorus. The thermophilic acid fermentation successfully inhibited the methanogenic pathways as all vials lacked methane in the biogas produced. While there was only a small significant change in pH among the treatments, P solubilization did increase in the lower pH vials.

The conditions with increased solubilization are inferred to increase the metabolic activity of the microbial consortia in the sludge, which helps in greater degradation and allowing for a pH reduction. This facilitates the hydrolysis of polyphosphates, as these biopolymers are the main contributors to total P in TWAS. However, a significant portion of other mineral precipitates are also carried into the wastewater system. Many of these compounds, such as fluorapatite ($Ca_{10}(PO_4)_6F$), tricalcium phosphate ($Ca_3(PO_4)_2$), and vivianite ($Fe_3(PO_4)_2 \bullet 8\ H_2O$), have very low solubility products (>-24 Kps), making them practically insoluble in water or requiring very low pH to effectively dissociate into soluble ions (Miretzky & Fernandez-Cirelli, 2008).

Goldstein reported the action of solubilization of inorganic mineral-P by gram-negative bacteria and proposed that mechanisms of action include the direct oxidation of the mineral by secretion of acidic protons that directly attack the structure (Goldstein, 1995). However, this direct interaction is less feasible in a moving liquid medium with far more accessible phosphorus sources and readily oxidizable organic matter. So it is suspected that increases in P solubilization by the metabolic pressure of increase growth, which depletes the bioavailable P and increasing the use of alternative metabolic pathways (Barber, 2016; Wang et al., 2016).

Thermophilic digestion of pretreated feedstocks

Run 1 of the fermentation optimization process consisted of evaluating the effect of thermal and acid pretreatments on overall nutrient solubilization. Table 4.2 of the appendix presents all values obtained from the fermentation of the pretreated feedstocks. Despite the increase in soluble phosphorus observed in the pretreated TWAS over untreated TWAS before the digestion, there was no statistical significance in the soluble phosphorus concentration of the digested effluents. Moreover, there was no statistical difference in the concentration of the digested sludge regarding COD or solids composition (VS, TS, TDS, TSS).

Figure 2.5 depicts the concentrations of soluble nutrients in the sludge effluents before and after digestion. Only NH3-N concentrations were significantly lower in all the pretreated effluents. The decreases in soluble NH3-N from the combined, acid, and thermal treatments were 15%, 14%, and 8%, respectively. This result agrees with the reduction in soluble NH3-N found in the analysis of undigested but pretreated sludges, as ammonia is a volatile compound that evaporates. If a significant portion of that ammonia is lost during pretreatment, even the degradation of nitrogen-containing biomolecules will not replenish the ammonia present in the untreated sample.

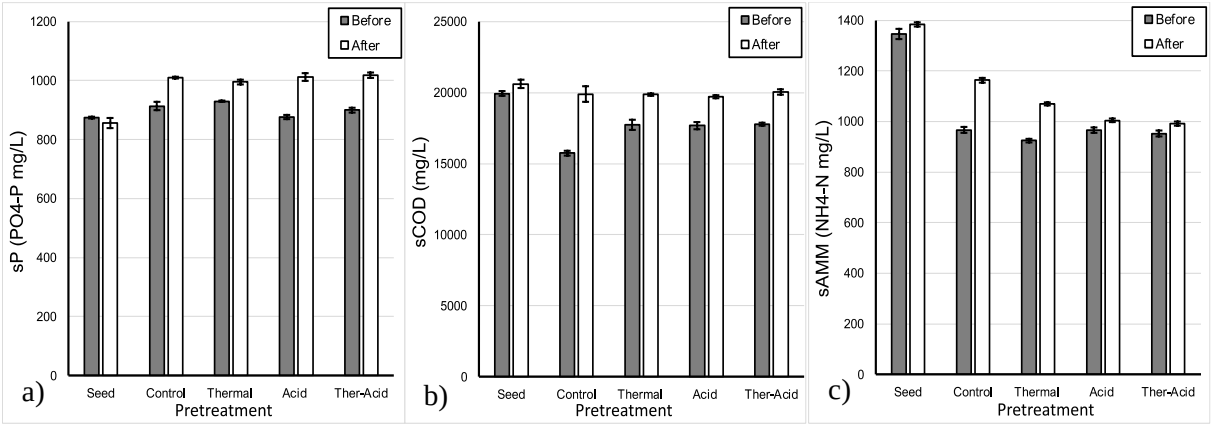

Figure 2-5 Changes in soluble nutrients in the fermentation effluents after thermophilic AD, all experiments used pretreated mixed feedstocks. a) Phosphorus species, b) COD species in TPS, and c) Ammonia species in TWAS.

The lack of variability between the experimental treatments can be explained by the homogenizing contribution of the seed sludge used as inoculum. To resemble a 3-day hydraulic retention time (HRT) in a continuous reactor, 2:1 seed-to-feed ratios were used. Therefore, the nutrient contribution of the seed amounted to most of what was measured in the digested effluent.

The inoculum has already undergone AD; hence, a second fermentation process does not significantly affect its composition. This allowed for arithmetical treatment to eliminate the influence of the nutrients supplied by the seed inoculum. Analysis performed on the nutrients corresponding to the feedstock contributions confirmed that a significant difference was found only on soluble NH3-N ($p<0.001$). When the NH3-N from the seed was not accounted for, the reduction in soluble NH3-N from acid, combined, and thermal treatments were 66%, 72%, and 40%, respectively, compared with the untreated feedstock.

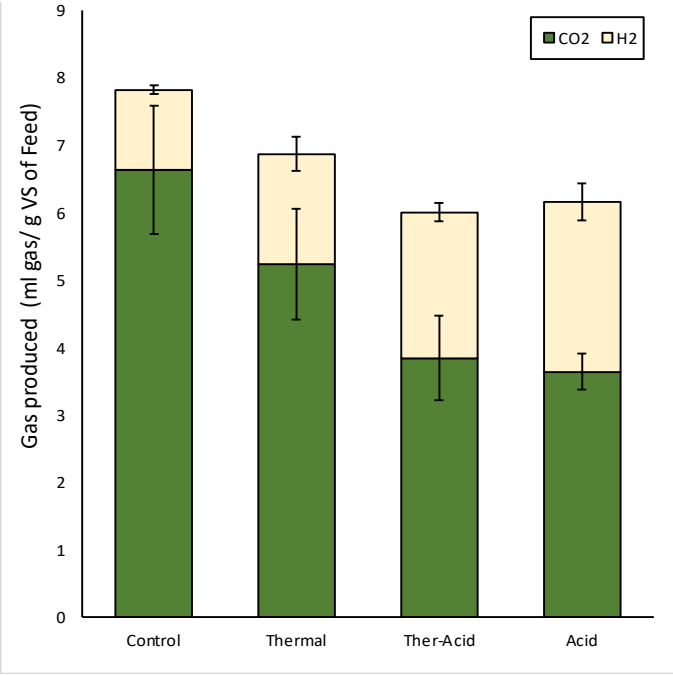

Figure 2-6 Gas production during thermophilic AD by pretreated feedstocks. All production was normalized to ml of gas at STP generated per g of volatile solids added from the feed.

Overall, the difference in biogas volumes between the treatments was not statistically significant. However, the composition of the produced biogas varied according to the pretreatments (Figure 2.6). Both the acid pretreatment and the combined thermal-acid pretreatment had a higher production of H_2 and a lower production of CO_2 in comparison to the untreated control. Given the different composition of TPS and TWAS, the incorporation of WWTP streams into a single digestion reactor resulted in an effluent with lower solids and total phosphorus than that of TWAS alone. To determine if the effect of the pretreatments was different on each substrate, the fermentation experiment was repeated using TPS and TWAS as single feedstock sources. The final values obtained from this fermentation experiment are listed in Table 4.3 of the appendix.

The separate fermentations presented significant solubilization between feedstock treatments (Use of only TWAS or TPS). This was expected given that TWAS has higher concentrations of total P, total COD, and VS, exceeding TPS by 237%, 60%, and 11%, respectively. Nevertheless, one-way ANOVA analysis of the separate feed did not find statistically significant differences between treatments regarding sCOD and sP solubilization ($p>0.05$). This was repeated for the nutrients only associated with the feedstock degradation, and the results were still insignificant. The only nutrient solubilization metric that was significant, was that regarding soluble NH3-N between pretreated and untreated TWAS. Again, the pretreatment negatively affected overall NH3-N solubilization ($p<0.002$). This suggests that the bulk of the ammonia supplied to the fermentation media comes from the nitrogen compounds present in the TWAS and that the pretreatment increases the evaporation of these compounds. Graphs of solubilization comparison are not included here but are attached to the appendix (Figures 4.1-2).

These results imply that thermal or acid pretreatments of the feedstock sludge did not contribute to an improved overall nutrient solubilization after AD. AD is a very complex process that achieves a thorough breakdown of the organic biomass contained in the feed; these results

suggest that the hydrolysis achieved by the microbial consortia in the digester can degrade the available polyphosphate in the influent biomass without preliminary degradation. The biogas production was also evaluated. One-way ANOVA testing of the TPS-fed fermentations indicated a greater overall biogas production in the untreated feed ($p<0.05$). Additionally, a significantly higher hydrogen production was found in the thermal and the combined pretreated fermentations over the control (48% and 28% respectively, $p<0.002$).

The TWAS-fed fermentations were also evaluated. The acid pretreatment showed a significant increase in H_2 production (11% increase, $p<0.003$). Also, as small decrease in H_2 production was found for the other thermal and combined pretreatments (16% and 20%, respectively). The VFAs of the digestates were analyzed to further elucidate the mechanisms of nutrient solubilization within the AD system. Figure 2.7 shows VFA concentration in samples. ANOVA testing of the final VFA concentrations showed a significant difference between the control and all pretreatments. The VFA concentrations after pretreatments were lower for the thermal, acid, and combined pretreatments by (-9%, -18%, and -29%, respectively) compared to the control. This suggests acid and thermal pretreatments did not provide an additional VFAs.

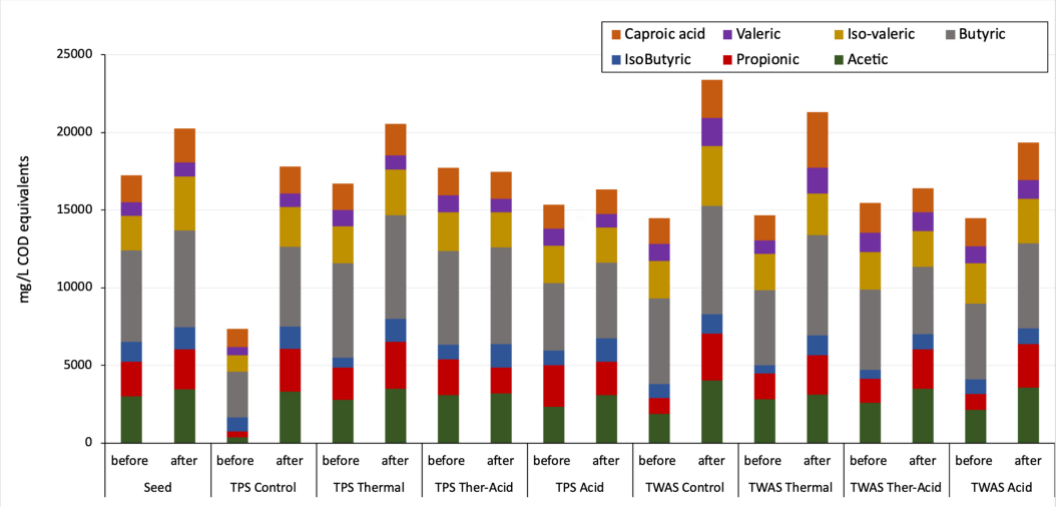

Figure 2-7 Volatile fatty acid profile of sludge before and after AD fed with separate pretreated sludge.

Nutrient release at different fermentation times

Fermentation experiments were performed with the three previously evaluated feedstock in thermophilic conditions but with different fermentation times. Full fermentation values and gas production are presented in Table 4.3 and Figure 4.3. Figure 2.8 presents the changes in soluble nutrient concentrations of several batches of thermophilic AD of TWAS, TPS, and coculture of both.

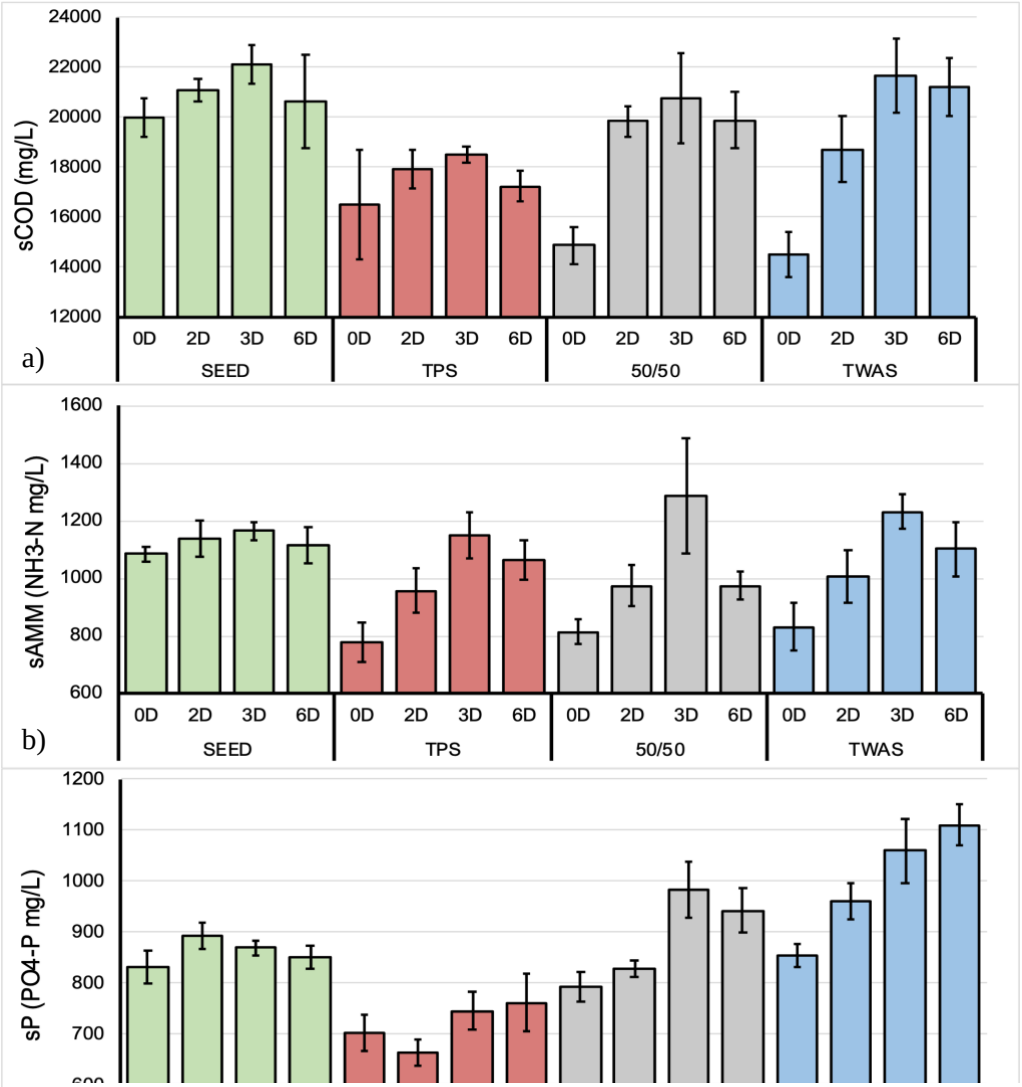

Figure 2-8 Changes in soluble nutrient concentration with varying thermophilic anaerobic digestion fermentation times. a) COD changes in the fermentation effluents, b) changes in soluble ammonia concentration, c) soluble phosphorus change at different fermentation times.

Maharaj et al. report maximum NH3-N generation at 60 hours in a mesophilic system (I. Maharaj & Elefsiniotis, 2001). This is similar to what was determined in this fermentation, where maximum ammonia solubilization was achieved at three days (72 hours). As NH3-N indicates protein degradation in anaerobic conditions, increasing fermentation time without additional feeding could force facultative protein metabolizers after sugars are depleted.

Because the interruption of methane production is not desired in conventional AD, little information is available on the overall solubilization of COD in thermophilic acid AD. Kaosol et al. found that the highest degree of COD removal was achieved with a 10-day retention time for co-digestion of wastewater with palm oil cake (Lerdrattranataywee & Kaosol, 2015); this would indicate that a longer HRT can dissolve a greater percentage of organic matter. However, product inhibition would probably occur because the smaller molecules would accumulate in the solution without efficient biogas production. On the other hand, Maharaj reported the accumulation of VFAs in an AD system treating primary sludge, where the highest VFAs concentration in a steady-state continuous stirred tank reactor (CSTR) was achieved at an HRT of 30 hours (I. Maharaj & Elefsiniotis, 2001). Figure 2.9 shows the VFAs profile obtained after 0, 2, 3, and 6 days of fermentation of the different feedstocks. For the TPS-fed and Mixed (50/50) fermentations coincide with Maharaj's time frame for maximum VFAs accumulation, while TWAs has a peak at 72 hours.

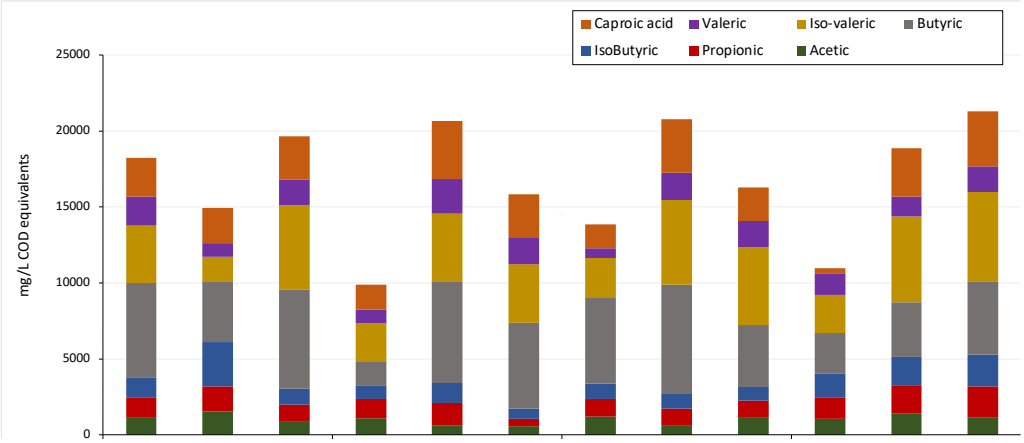

Figure 2-9 Volatile fatty acid profile of sludge before and after AD fed with separate pretreated sludge.

As VFAs concentration is closely related to sCOD concentration, given that soluble organics (COD) are metabolized to more basic compounds (VFAs), Maharaj posited that a comparison of the two can help determine if hydrolysis or acetogenesis is the rate-limiting step (I. J. Maharaj, 1999). As concentrations of sCOD and the COD equivalents of VFAs are very close together, it can be inferred that hydrolysis is the rate-limiting step. Hence, a more complex feedstock will require a longer fermentation time to achieve VFAs accumulation; this mirrors the results seen in Figure 2.9. In all the conditions gas production increased with fermentation time, as organics continue to degrade as the reaction time of the feedstock grows. Nonetheless usually the costs incurred in increasing HRT have diminishing returns to the potential extra gas produced (Ozgun et al., 2021).

While the experimental design employed for this work does not allow for continuous monitoring of the soluble phosphorus concentration, the results can be used to model the behavior of phosphorus solubilization within a batch thermophilic anaerobic digester. Even widely used modeling programs specialized in wastewater treatment, like BioWin 6.0, have difficulties predicting phosphorus speciation and its release in anaerobic digesters with high VFAs concentrations (Vineyard et al., 2024). However, the model presented in Figure 2.10 has the potential to help as a baseline for further approximations. The JMP mechanistic growth model was used to model solubilization curves of different AD broths to account for the use of different feedstocks. The fit of the model was satisfactory as it maintained an overall R^2 of 0.904.

The mechanistic growth model can describe processes of uptake and development in living organisms. Given that phosphorus release is dependent on PAO cell lysis, which is also associated with anaerobic biomass growth, this model was selected as being representative of the underlying mechanism.

Using the mechanistic model, it was possible to establish theoretical asymptotes of maximum solubilization for the fermentation of TWAS, TPS and a 50/50 mix of the two. The asymptote values obtained were 1246, 667, and 1026 mg PO_4-P/L, respectively. When evaluated in comparison with the total phosphorus content in the broth it was determined that the asymptotic values corresponded to 70%, 59%, and 72% of total phosphorus solubilization, respectively.

T-testing of the model values did not find a statistically significant difference in phosphorus concentration between a 3-day fermentation and a 6-day fermentation. This would indicate that by the third day of fermentation the readily available material for solubilization has already been metabolized. The mean values of the soluble phosphate in the digestate of three-day thermophilic AD correspond to an overall phosphorus solubilization of 67%, 65%, and 66% for treatments fed with 50/50 mix, TPS, and TWAS, respectively. These values agree with values of total phosphorus solubilization reported in other thermophilic CSTR systems, such as the Struvia Process, which has a total phosphorus recapture efficiency of 60% (Veolia, 2015).

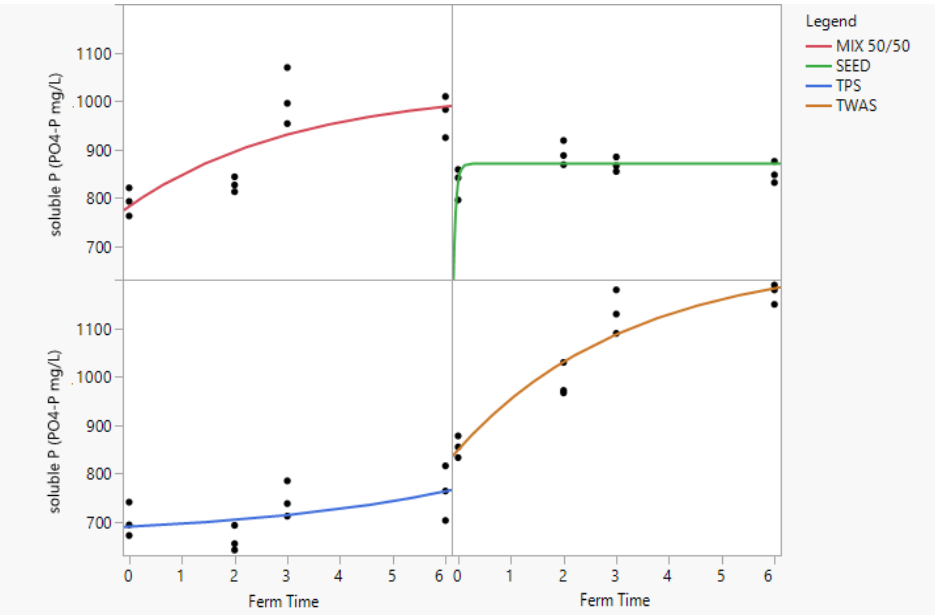

Figure 2-10 Mechanistic growth model used to fit solubilization patterns of phosphorus in thermophilic AD. The overall fit has an R2 of 0.904, generating estimated asymptotes of maximum achievable solubilization.

Temperature-dependent digestion of wastewater sludge

Nutrient solubilization was compared between 45 ºC and 55 ºC during AD, the full values obtained from the experimental run are listed in Table 4.5 in the appendix. Figure 2.11 depicts the concentration of soluble nutrients in 3-day AD carried at different temperatures. One-way ANOVA determined that temperature significantly affected soluble NH3-N, with higher-temperature fermentations exhibiting a mean 10% reduction in soluble NH3-N content ($p=0.0014$). This correlates to the tendency of ammonia to volatilize at higher temperatures and higher water concentrations (Ryan & Keeney, 1975). The ANOVA analyses also revealed differences in COD between temperatures that were only statistically significant for the 50/50 WAS fed treatment with a 5% reduction ($p=0.005$). Hence, it can be inferred that thermophilic fermentation could result in a very slight reduction in organics solubilization.

The tests determined that temperature statistically impacted soluble phosphorus concentration in the digestate ($p=0.0027$). Further analysis of the temperature effect in P solubilization indicated that the mean soluble phosphorus concentrations at 55 ºC increased by 9% compared to that at 45 ºC. Hydrolysis is sped up in these higher-temperature conditions, accumulating VFAs as methanogenesis becomes the rate-limiting step. It is inferred that increasing VFA concentration may aid in P solubilization. Turner et al. posited that the solubilization of immobilized P in wet soils could be mainly caused by the action of diester phosphatases produced by microorganisms like *E. coli*, which have an optimum temperature range of 30-60 ºC (Mazorra et al., 2002; Turner et al., 2002). The higher temperatures could effectively increase microbial mechanisms that could release non-soluble P. Additionally, thermophilic digestate had a significantly ($p<0.003$) lower pH with an average of 5.64 compared to a pH of 5.93 on the mesophilic digestate. This approaches, the ideal pH for phosphorus solubilization of 5.5, reported by Stutzenstein for thermally treated digestate (Stutzenstein et al., 2018).

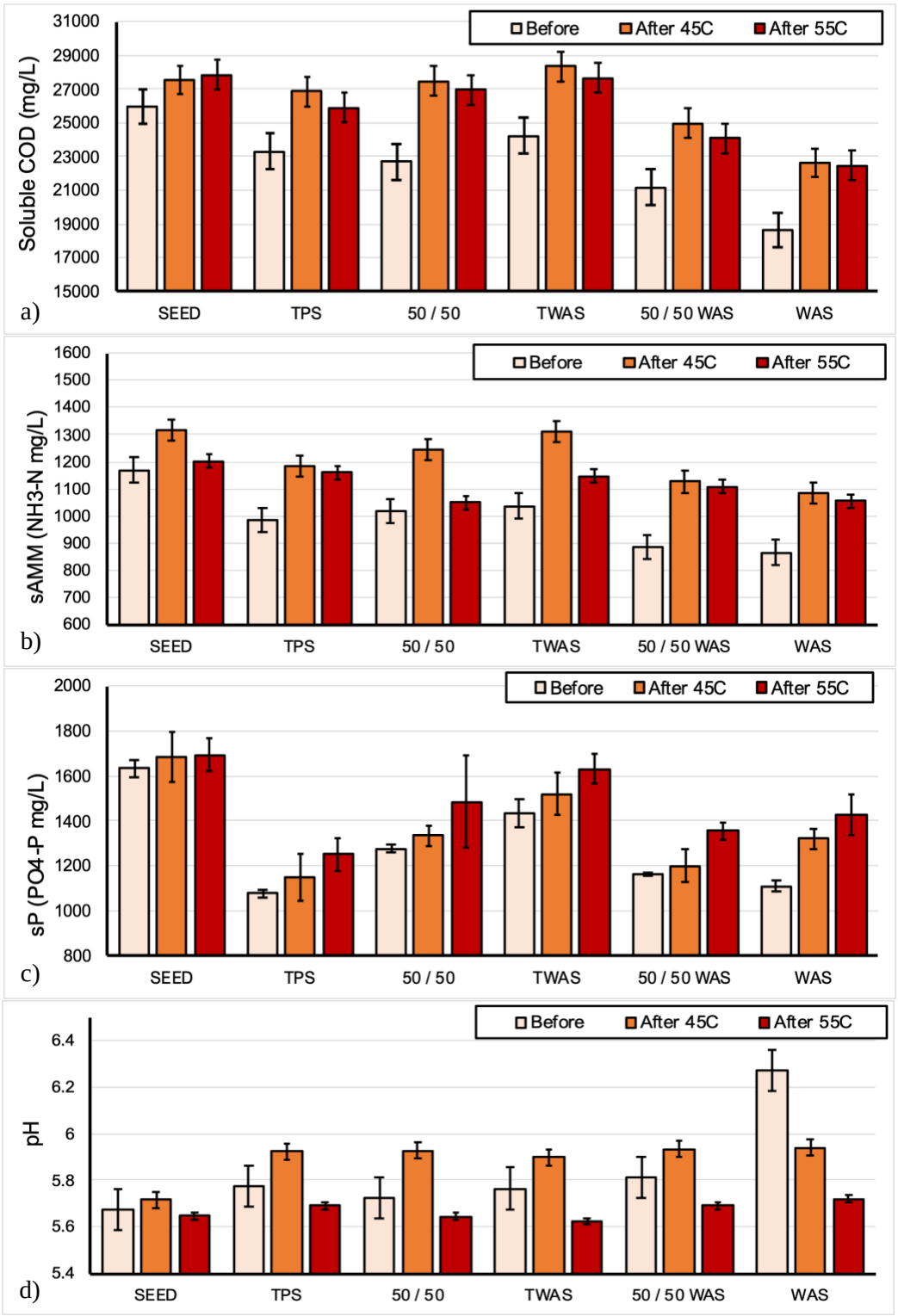

Figure 2-11 Nutrient Solubilization after anaerobic digestions in mesophilic conditions and thermophilic conditions. These correspond to a) COD concentration changes, b) ammonia solubilization, c) soluble phosphorus solubilization, and d) pH changes before and after fermentation.

Figure 2.12 displays the soluble P results associated with feedstock degradation. Two trends appear: the source of the feed is essential because its composition will directly impact the final concentration of nutrients, and slightly higher solubilization can be achieved with thermophilic AD. Given the increase in scale produced by the factor of VS, the high variance presented in these values does not give statistically significant differences between different treatment temperatures.

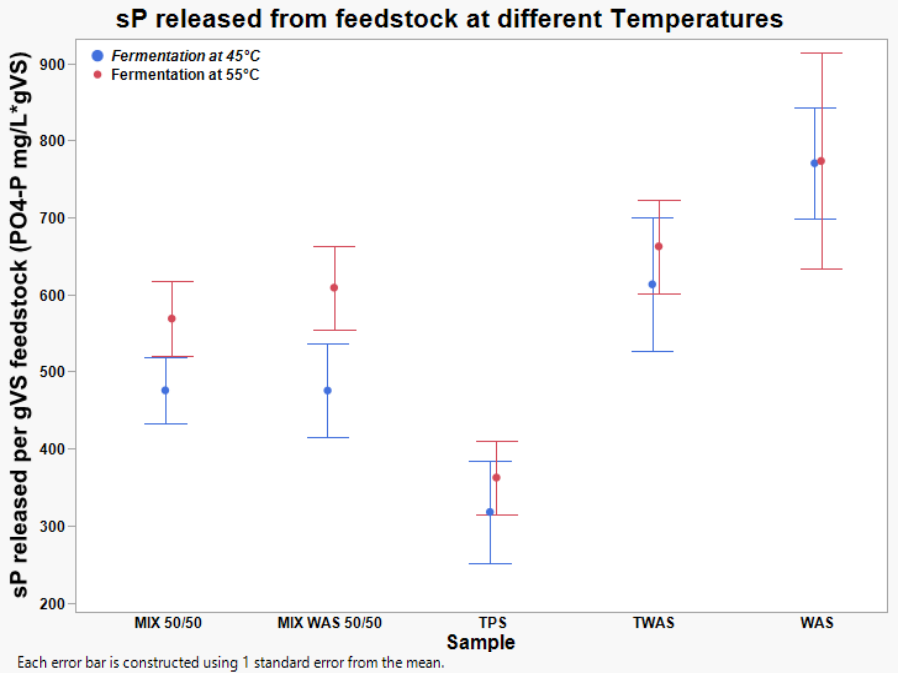

Figure 2-12 Phosphorus released per gram of volatile solids fed from the feedstocks into an anaerobic digestion system with thermophilic and mesophilic conditions

Figure 2.13 shows the gas production results. It is very clear that the lower temperature system (45 ºC) had a significantly higher production of biogas, with additional CO_2 productions of 66%, 120%, 170%, 91%, and 100% for TWAS, TPS, 50/50 MIX, 50/50 WAS mix, and WAS, respectively, this is expected as VFAs accumulation is associated with decreased methane yield (Wu et al., 2022). Interestingly, hydrogen production differences were not significant ($p>0.05$) for

any treatment other than 50/50 WAS (p=0.03), which had a 130% increase in the thermophilic treatment.

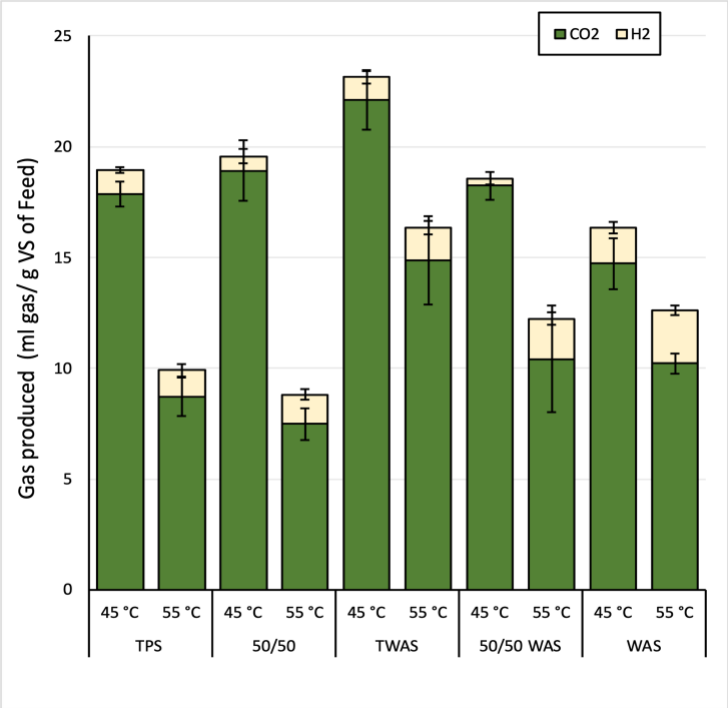

Figure 2-13 Gas production in different temperature conditions for an anaerobic digestion system. All production was normalized to ml of gas at STP generated per g of volatile solids added from the feed.

Effect of feedstock dilution on nutrient release in thermophilic AD

Nutrient solubilization was evaluated with different VS loading rates. The full fermentation data is compiled in Table 4.6 of the appendix. All the solubilization measurements displayed a similar trend of concentration reduction with the lower-strength feed because using lower-strength sludge resulted in the dilution of the whole solution, including the inoculum. Figure 2.14 shows the effect of the fermentation on each of the nutrients studied, and it additionally shows the values of the nutrient solubilization corresponding to the feedstock portion. It was hypothesized that a reduction in organic loading would increase the potential solubilization of the P and COD because

it would allow for a more thorough degradation of the polymeric matrix of the material supplied. The solubilization values per gram of VS in the feed were used for curve fitting. While an array of linear and non-linear models was used, a simple linear model was found to describe solubilization most appropriately. The linear fit exhibited the lowest value of Arcsine-logarithmic calibration curve (AlCc) residuals differing by 2.4 with the next best-fit model (exponential 2P). Burnham et al. stated that a difference of 2 points or more in AlCc values implies substantial empirical support for the model with lower AlCc (Burnham & Anderson, 2004).

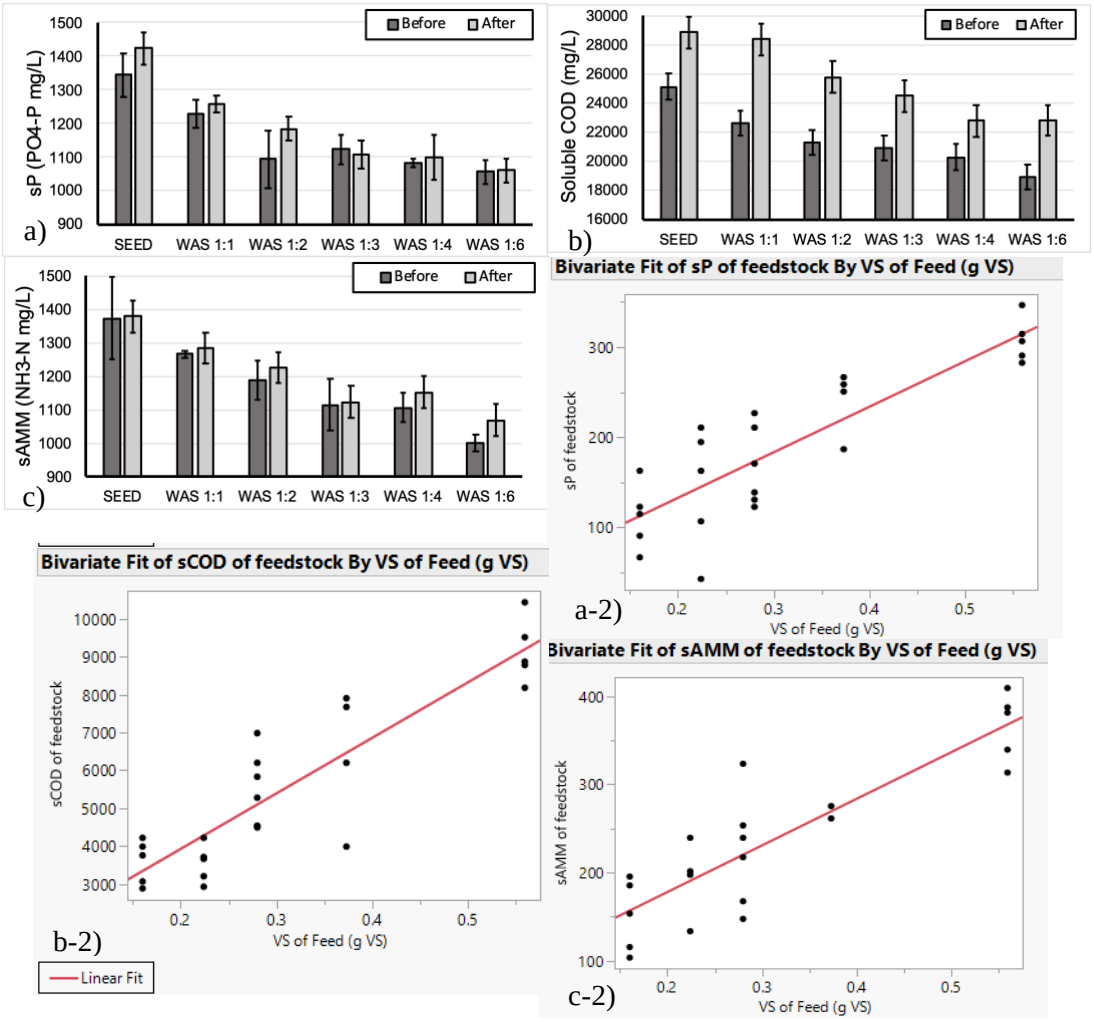

Figure 2-14 Nutrient Solubilization according to volatile solids content of feed, after thermophilic AD and least squares regressions. These correspond to a) phosphorus solubilization, b) COD concentration changes, and c) ammonia solubilization.

Given that the linear model was the one that described solubilization of COD, P, and ammonia better, it can be inferred that solubilization is not improved with a lower organic load. However, when designing the final process other aspects like pumping and mixing efficiency could make a good argument for a more diluted loading. Additionally, the operational stability of the system should also be considered, as organic loading stress can generate process instability (Wu et al., 2022).

In contrast with nutrient solubilization, organic loading influenced CO_2 gas production as seen in Figure 2.15. Further curve fitting revealed that a cubical model could describe the gas production behavior properly with a production maximum peak around a dosage of 0.21 gVS per digester, which would correspond to a 2.5x dilution (TWAS 1:1.5 H_2O ratio). Hydrogen production followed a linear trend. However, the low production and small volumes produced high variability that did not allow for any statistically significant fitting.

This experiment indicates that nutrient solubilization cannot be improved by dilution of the feed, while gas production does have a specific ideal range for production.

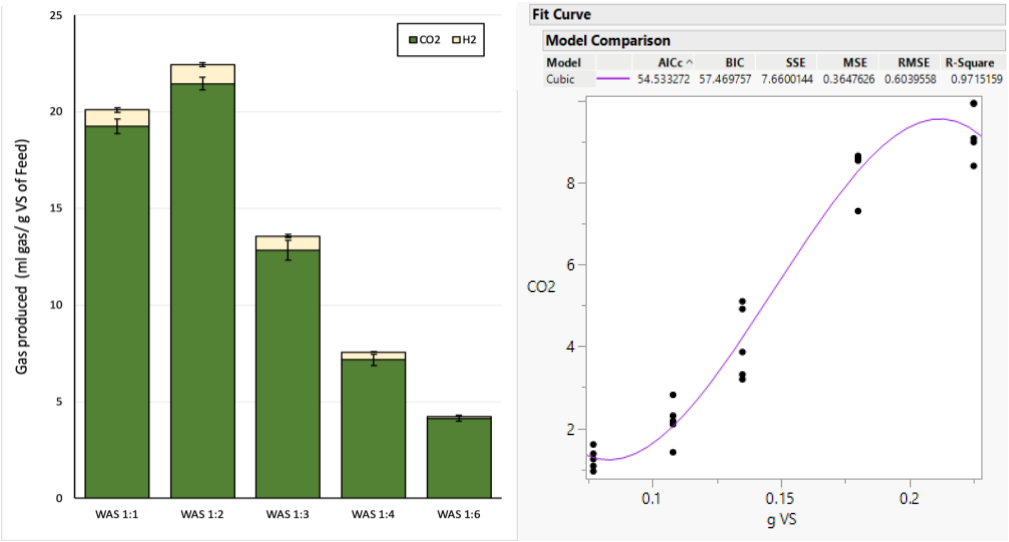

Figure 2-15 Gas production in anaerobic digestion system fed with varying strength TWAS. Curve fitting of CO_2 production with different loading rates of grams of volatile solids of TWAS.

Optimization of phosphorus precipitation conditions

Once the conditions for P solubilization were determined, the capacity for phosphorus precipitation by chemical precipitation of the obtained supernatant was evaluated. Figure 2.16 presents the phosphorus removal efficiency of different precipitation treatments, as well as the concentrations of several ions in the solution. All the calcium-dosed samples had pH control up to 8, and the magnesium-supplemented tests were adjusted to pH 10; both processes were performed with a sodium hydroxide solution (10 M). Both Ca and Mg can be used for the precipitation of phosphorus in liquid wastewater, but studies have shown that for magnesium precipitation to be effective, a higher dose than stoichiometric should be used, with Lorick et al. suggesting that molar ratios as high as 4:1 (Mg:P) could be beneficial in high strength wastewater (Lorick et al., 2020).

All treatments significantly differed from the negative control and the pH-adjusted one, which still showed a 20% phosphorus reduction. With calcium dosing, there was no statistical difference between the dosing ratios (1:1, 1.2:1, and 1:1.5), with sP removal efficiencies of 96%, 94%, and 96%, respectively. For magnesium dosing, the three different treatments had statistically significant differences, with removal rates of 87%, 93%, and 98% for the dosing ratios of 1:1, 1.2:1, and 1:1.5, respectively. These results agree with studies published by Li et al., which found P removal efficiencies in the range of 90-98% when using dosing ratios of 1 to 1.8 of Mg to P (L. Li, Pang, et al., 2019). This confirms that the high-nutrient liquid fraction obtained from the thermophilic AD is a good substrate for phosphorus precipitation via chemical dosing of calcium or magnesium chlorides. Further optimization could be performed to facilitate precipitation and retrieval of the produced P-minerals, as Ye et al. suggested diluting the obtained supernatant to a lower P concentration before Mg dosing to favor the growth of larger crystals (Ye et al., 2014).

Other researchers suggested MgO as a better dosing agent that facilitated struvite precipitation with a lower dosing of 1:1 MgO when compared to MgCl (Stolzenburg et al., 2015).

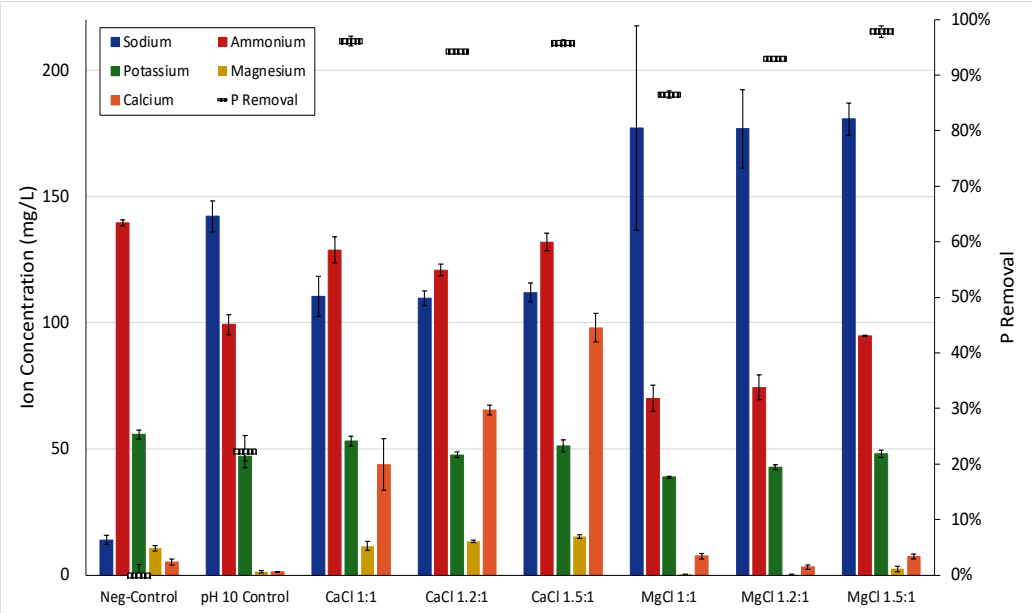

Figure 2-16 Cation content in different precipitation jar tests that used liquid supernatant of anaerobic digestion. Striped bars represent achieved phosphorus removal after treatment.

Digestibility of nutrient-rich liquid digestate in high-rate AD

The digestibility of the high-nutrient liquid fraction was tested after the phosphorus precipitation treatment, as this supernatant still maintained a high concentration of dissolved VFAs. The UASB reactor used for this purpose (shown in Figure 2.17) was initially set up with granular sludge from an industrial corn digestor and fed with a glucose solution of 3 g/L to acclimate the inoculum. The day of the reactor shifting to use only high-nutrient supernatant was treated as the first day of operation. The UASB reactor reached consistent treatment efficiency around day 10 of operation; the average COD concentration of the influent was 23630 ± 2975 mg/L. Figure 2.23 presents the average gas production by volume and the pH registered for the effluent collected.

Figure 2-17 Up flow anaerobic sludge blanket reactor setup

Gas production in the reactor increased with ongoing operation time until it reached a plateau beginning around day 30. On day 37, a disruption in the process can be seen after a pumping hose plugged and leaked into the reactor. This caused a disruption in gas production and pH, after which the reactor was not restored. Additionally, the produced gas composition was analyzed in samples collected on days 5, 10, 20, and 30. These are shown in Figure 2.18.

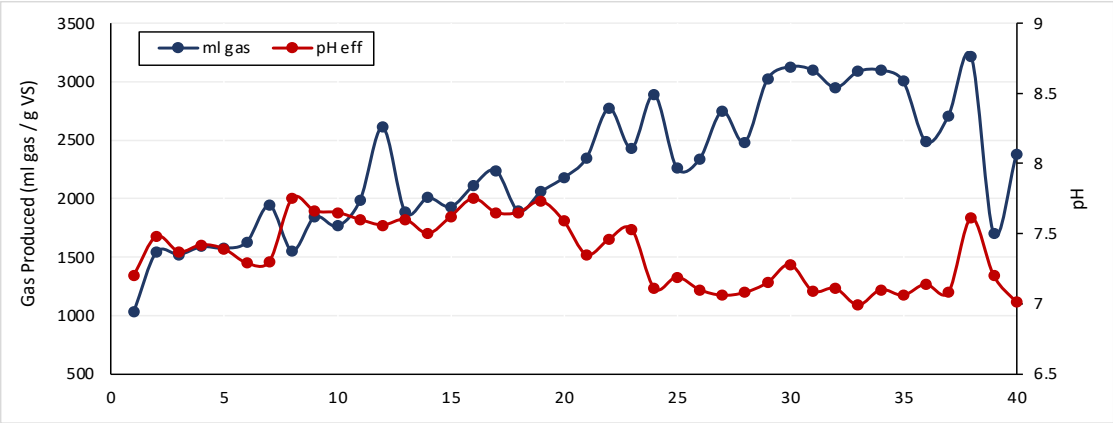

Figure 2-18 Gas production in different temperature conditions for an anaerobic digestion system. All production was normalized to ml of gas at STP generated per g of volatile solids added from the feed

The composition of the biogas produced in the UASB has a starkly different composition to that of the biogas produced during the thermophilic acid AD tests. As in the second digester the intent is to completely metabolize all the solubilized organics (mostly in the form of VFAs) from the first fermentation. As can be seen in Figure 2.19, even when the reactor had not reached process stability (day 5), the production of methane was very significant with an overall composition ranging from 79% to 82% by day 30. These results placed the biogas production on the high range of the reported composition of raw biogas (50-75%) (Y. Li, Alaimo, et al., 2019). This suggests that the high VFAs of the liquid fraction can be readily metabolized into methane within a high-rate UASB reactor.

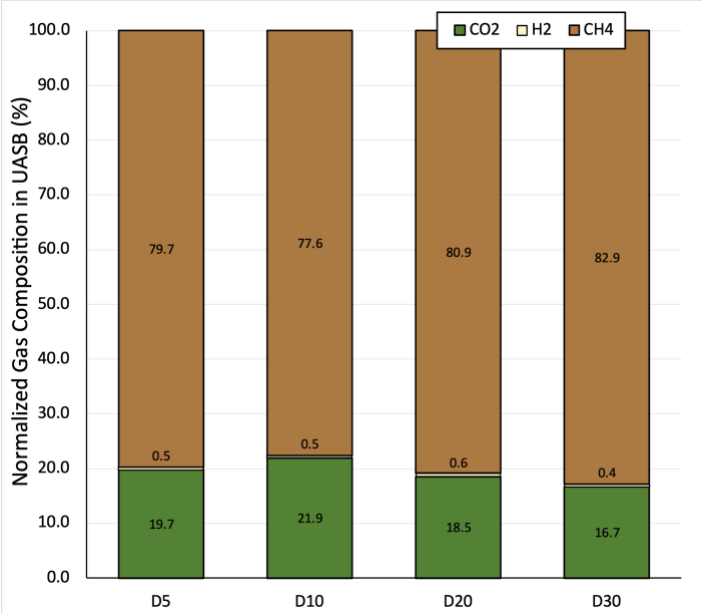

Figure 2-19 Gas composition of biogas sampled from UASB fed with VFA-rich liquid portion obtained from thermophilic AD.

To corroborate the reduction of the organic fraction in the liquid fed to the UASB, further analysis of the VFAs profile was performed on the influent and effluent of the reactor. Figure 2.20 illustrates the reduction of COD equivalents attributed to each VFA.

The process on day 10 did not achieve the same reduction observed on latter measurement, which coincides with the reduced gas produced at the beginning of the operational period of the reactor. COD reduction on day 10 was 39%, which was further improved to 71% and 77% on days 20 and 30, respectively. While this is a good performance metric overall for water treatment, other researchers reported COD removal efficiencies closer to 86% in conventional mixed wastewater systems (Dutta et al., 2018). On the other hand, Sperling et al. reported COD removal efficiencies of 69% to 84% in medium strength (14000 mg/L COD) wastewater (Von Sperling et al., 2001). Longer operation times and continuous feeding of the system could help improve the obtained results; additionally, some variation can be expected as these are single-point observations.

Still, the capacity of the UASB system to reduce COD from high-strength digested supernatant was proven with COD removal efficiencies of up to 77%, even after the liquid separated from the digestate was subjected to a phosphorus precipitation process.

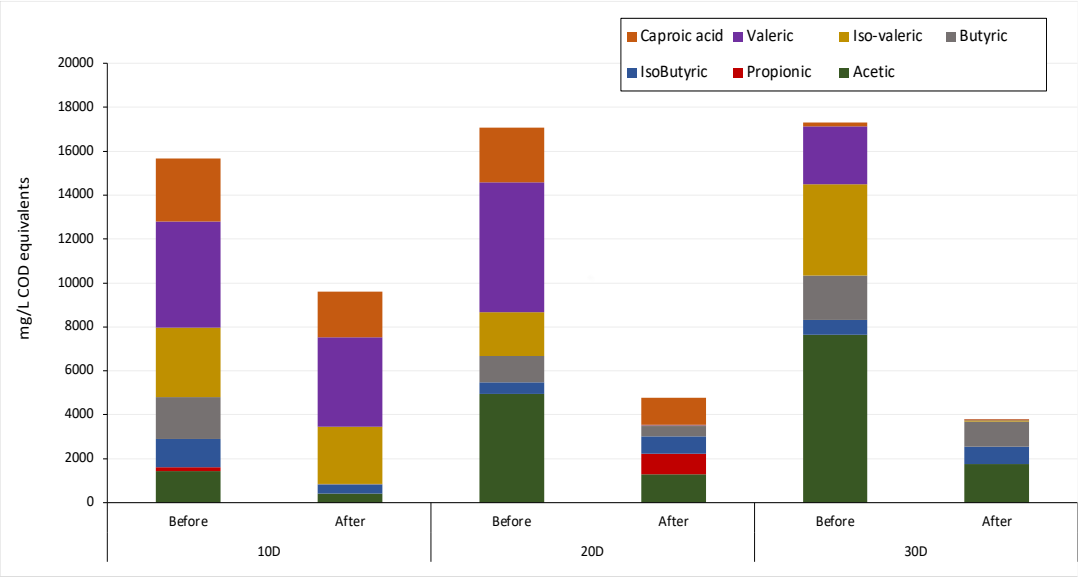

Figure 2-20 Volatile fatty acid profile of high nutrient liquid fed to the UASB bioreactor and the resulting reactor effluent.

Full process viability

The results of this work indicate that the separation of the AD process is a viable method of nutrient solubilization, after which a separation step can produce a supernatant rich in soluble organics, ammonia, and soluble phosphorus that can be processed through a phosphorus precipitation step and further digested to generate biogas. This process can utilize the infrastructure used for conventional AD while recapturing the phosphorus that is present in the sludge.

While AD by itself does not represent a technology for P recovery, the wide adoption of anaerobic digesters in WWTPs eases the implementation of P recovery from the digestate. AD is a mature technology with significant optimization of processes in terms of design, build, and operation. Nowadays, many plants have high biogas yield performance, with some achieving methane content higher than 60% in biogas (Al-Wahaibi et al., 2020). However, biogas is considered a low-value product, and AD systems are usually only economically feasible with the help of governmental subsidies. Hence, optimizing nutrient release for its subsequent recapture is attractive, if not necessary, as the revenue obtained from selling the produced minerals could help subsidize the overall plant operation. The implementation of the two-reactor process could facilitate overall sludge treatment, but further testing and scalability assessments are required.

Conclusions

The use of pretreatments in TPS and TWAS did not increase the nutrient solubilization capabilities of the thermophilic acid AD process for phosphorus, ammonia, or COD in comparison to the untreated controls. This was observed both for the co-digestion and separate digestion of the sludge feedstocks. Fermentation time of the AD process was found to significantly impact nutrient solubilization of phosphorus and COD, with a mechanistic growth relationship. Changes in nutrient solubilization between 3 and 6-day fermentation were negligible. Thermophilic fermentation conditions (55 ºC) for the AD process were beneficial for phosphorus solubilization, with an average 9% increase in solubilized phosphorus compared to the AD at 45 ºC. However, thermophilic conditions did not improve COD solubilization and decreased soluble NH3-N concentration in the digestate. The VS loading rate of TWAS in the anaerobic digester had a linear relationship with the concentration of phosphorus and other nutrients released from the substrate, indicating that reducing the loading rate did not increase nutrient solubilization per gram of VS from the feed. Additionally, the potential for phosphorus recapture from the digested liquid fraction was determined with a soluble P removal of 97% with the most efficient treatment (magnesium dosage at a Mg:P molar ratio of 1.5:1). Finally, the digestion capability of the MgCl treated effluent was established in a UASB system, achieving a 77% COD removal and producing high methane concentration biogas (88%). Further experimentation on scalability and process optimization is required.

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Chapter 3

Application of a three-stage wastewater treatment process for phosphorus recovery: A pilot-scale study

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Abstract

The anaerobic digestion (AD) and enhanced biological phosphorus removal (EBPR) technologies that are used in wastewater treatment facilities have opposing catabolic and anabolic mechanisms. These affect each other and can generate operational issues that impact nutrient removal performance and increase overhead costs. A pilot plant optimization study was conducted to determine the phosphorus (P) solubilization capacity of the separate reactors with different digestion conditions (thermophilic-acid and high-rate mesophilic). Additionally, phosphorus recovery was evaluated after the solid separation step. Overall P solubilization was capable of 59% was achieved and a total 50% phosphorus recovery in the form of P-bearing mineral solids. The overall system was also capable of methane production, even when the overall yield was 31% lower than the yield achieved by conventional WWTP treatment. Further optimization is required to achieve higher methane production and phosphorus recapture.

Introduction

Phosphorus (P) is an essential for the correct development and growth of all living organisms. Hence, P is usually supplemented to crops in all large-scale agricultural practices. Most of the phosphorus used in fertilizers is derived from rock phosphate, which is a geographically limited natural resource that is susceptible to supply disruptions and depletion (Kroiss et al., 2011). As the mineral deposits exploited for P-rock get depleted, the costs associated with the extraction and refinement of poor-quality ore will increase and jeopardize future supply (Schröder et al., 2011). In addition to its importance in agriculture, this macronutrient is relatively abundant in domestic wastewater, where it behaves as a pollutant. Excessive P discharge into the hydrosphere is associated with adverse environmental effects such as eutrophication (Correll, 1998). Large runoff water systems like the Great Lakes and the Gulf of Mexico are especially vulnerable as nutrients accumulate in these bodies of water.

In the Midwest, both Minnesota (MPCA Permit 42000) and Wisconsin (DNR NR217) have established a general P limit effluents that are regulated and monitored through their own pollution control agencies. The Minnesota pollution control agency (MPCA), issues permits that range from 14 to 0.5 mg P/L, with the majority of the wastewater treatment facilities having issued limits of 1 mg/L (MPCA, 2009). To comply with the P effluent limits, wastewater treatment plants of large capacity often employ enhanced biological P removal (EBPR). In addition to EBPR, the majority of plants use anaerobic digestion (AD) treatments to reduce sludge volume and overall organics (Sahlström, 2003). Figure 3.1 depicts the conventional process of EBPR sludge processing and some of the issues that arise when dealing with highly putrescible and P-rich material.EBPR is a widely adopted technology that employs the luxury phosphorus uptake mechanisms of phosphorus accumulating organisms (PAOs) to reduce the available soluble phosphate in the water effluent.

Well-managed EBPR can reliably achieve effluents with P concentrations lower than the 0.5 mg-P/L recommended threshold (McMahon et al., 2002). During EBPR, more than 90% of the P entering the treatment facility is immobilized into the sludge fraction, primarily in polyphosphates (Jardin & Pöpel, 1994). When the excess sludge is treated in an AD system, the polyphosphate accumulated in the PAO biomass will be hydrolyzed and released as soluble phosphate (PO_4^{-3}).

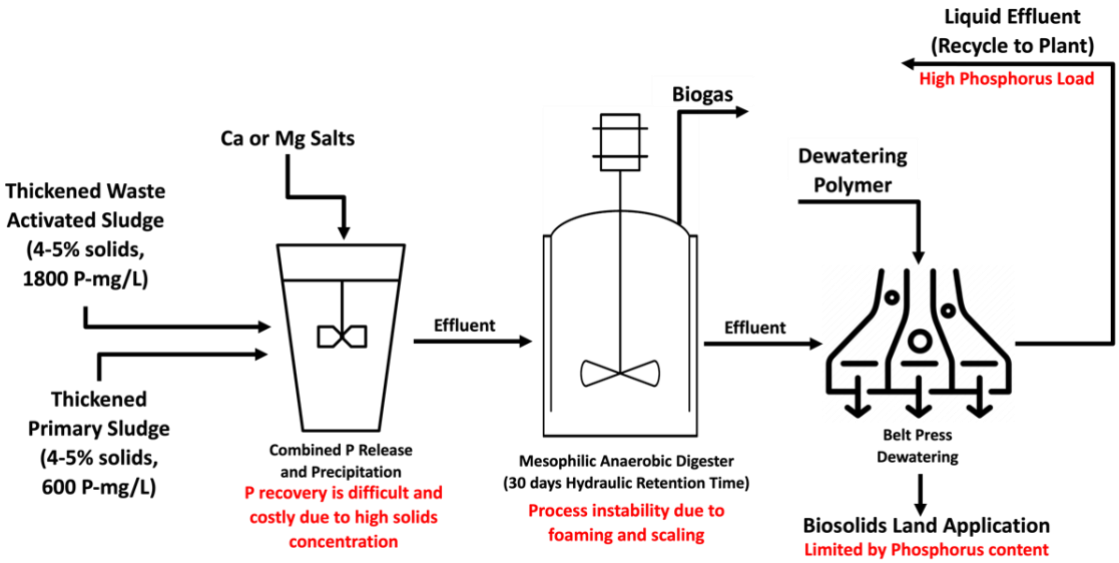

Figure 3-1Conventional sludge processing protocol and issues associated with it (Ross, 2013; Stratful et al., 2004).

The AD and EBPR technologies have opposing catabolic and anabolic mechanisms that affect each other and can generate operational issues that impact nutrient removal performance and increase overhead costs. EBPR systems increase overall mass growth and the associated production of extracellular polymeric substances, which, combined with a change in phosphorus species, can reduce the final sludge's dewaterability (Shimp et al., 2013). Additionally, the processing of the phosphate-rich sludge through AD can cause the precipitation of P-minerals creating fouling and clogging in the equipment. The AD process resolubilizes a great amount of P that usually is recycled into the plant, as this recycled stream can represent over 50% of the total plant load, the

recycling stream can significantly increase the amount of material used for chemical dosing in the system to maintain the operational stability (Ross, 2013). The chemical precipitation of phosphorus is also hindered by the presence of suspended solids, so implementing this technology is feasible in only some WWTPs (Achilleos et al., 2022). In previous work, the fermentation parameters for increased P release in AD systems were studied. It was found that a thermophilic acid process could increase soluble phosphorus by up to 9% compared to the mesophilic system. These conditions, combined with a modification of the overall sludge treatment process, are promising for the controlled recapture of Phosphate minerals.

For a novel process to be fully implemented in a real-scale WWTP, there needs to be previous proof of concept of the system in smaller pilots. As the initial economic investment required to fit new systems into a municipal plant is very high, determinations of treatment efficiency and compliance with regulatory ordinances are required. Moreover, small bench-scale operations are not always replicable in large systems. Reaction kinetics, thermodynamics, and fluid dynamics change in larger reactors as surface contact, mass transfer, and agitation are greatly reduced (Blancho et al., 2024). Therefore, it is very important to develop a scale-up plan that will allow the replication of laboratory results into a pilot-scale operation.

It is hypothesized that separating the anaerobic digestion into two reactors (thermophilic-acid and high-rate) will allow for maximum P-solubilization in the larger pilot, as it was observed in the bench-scale. The effluent of the first reactor can be subjected to solid separation while managing the reported low dewaterability. Finally, the nutrient-rich supernatant with low solids concentration will allow for the efficient recapture of P without hindering overall biogas generation. Accordingly, addressing the low P recovery and low dewaterability observed in conventional EBPR-AD processes in the continuously operated pilot will be possible.

Materials and Methods

Sample collection and culture maintenance

The Thickened Waste-activated Sludge (TWAS) used as feedstock during the experimental pilot plant's operation was collected from a public facility in the Twin Cities Metropolitan Area, Minnesota, United States. The sludge was scooped into storage receptacles from the belt thickener unit's exit conveyor belt. All the samples collected were stored at 4 °C for a maximum of 2 months from sampling.

The effluent of the small continuous thermophilic reactor, which operated throughout the whole experimentation phase of this work, was used as inoculum for the larger pilot-scale system. Given the system's six-month continuous operation, sampling had to be repeated thrice to retrieve enough substrate for the pilot plant to operate at full capacity. Table 3.1 presents the properties of the three TWAS effluents sampled alongside the whey permeate used as a supplemental carbon source in the trial. The whey permeate used as a fermentation amendment for the AD reactor in this project was obtained from a dairy processing plant in St. Paul, Minnesota.

Description of the pilot plant

The schematic that is shown in Figure 3.2 illustrates the array of processes and reactors that were used to treat the sewage sludge. The collected TWAS was diluted with the same volume of water to obtain half-strength TWAS. This was performed to improve the rheology of the sludge, reducing the stress exerted on the pumps and mixers. Operational details of the individual units are listed in Table 3.2.

Table 3-1 Properties of the effluents sampled.

	TWAS (11/22/2022)	TWAS (02/27/23)	TWAS (04/19/23)	TWAS (07/10/23)	Whey Permeate
TS (%)	6.66 ± 0.15	8.05 ± 0.17	6.56 ± 0.06	5.83 ± 0.06	18.00 ± 1.07
VS (%)	4.68 ± 0.10	6.05 ± 0.16	5.04 ± 0.03	4.44 ± 0.05	15.87 ± 0.59
VS/TS (%)	70.27 ± 2.41	75.15 ± 2.77	76.87 ± 0.84	76.08 ± 0.95	84.3 ± 4.95
TDS (%)	0.58 ± 0.08	0.71 ± 0.16	0.51 ± 0.04	0.53 ± 0.05	4.05 ± 0.08
TSS (%)	6.33 ± 0.18	7.37 ± 0.10	6.11 ± 0.10	5.36 ± 0.04	0.13 ± 0.03
Initial pH	6.81	6.83	6.72	6.91	5.3
Total COD (mg/L)	69267 ± 2647	104319 ± 5885	92507 ± 3224	70350 ± 3652	192871 ± 7263
Sol COD (mg/L)	4751 ± 227	7908 ± 715	5035 ± 316	4368 ± 162	157316 ± 3986
Total P (mg P/L)	2373 ± 83	3793 ± 320	2880 ± 243	2467 ± 227	2126 ± 91
Sol P (mg PO_4^{3-}-P/L)	1060 ± 52	1513± 110	1153 ± 61	1024 ± 53	1910 ±57
TAN (mg/L)	376 ± 23	583 ± 29	406 ± 36	391 ± 14	133 ± 15

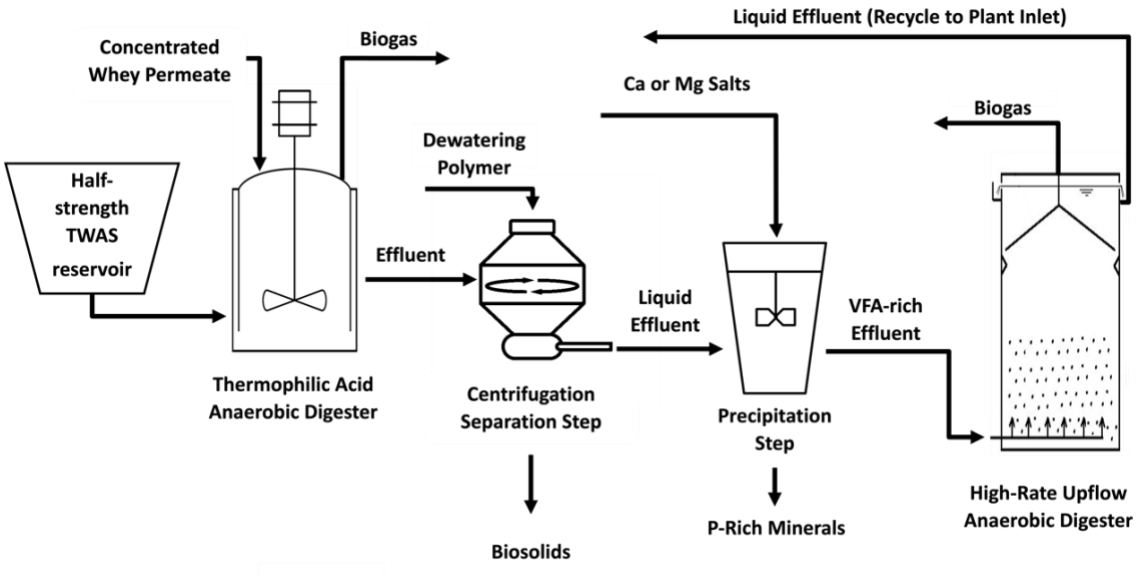

Figure 3-2 Schematic of pilot plant that integrates thermophilic-acid AD, P-Recovery, and high-rate AD

Table 3-2 Operational Parameters of pilot plant units.

	Thermophilic CSTR	**Centrifuge Dewatering**	**P precipitation**	**High-rate UASB**
Flow Rate (mL/day)	4232	3000	1500	1500
Feed Events (Cycles/day)	8	1	0.5	40
Volume per cycle (mL)	529	3000	3000	38
Feed	Half-strength TWAS, whey permeate	CSTR effluent, dewatering polymer	Separated Liquid, CaCl, MgCl, NaOH	P-treated Liquid Effluent
Agitation system	3 stacked disc turbine impeller	-	Paddle impeller	Pumping (290 ml/min)
On/Off agitation time (min)	25/5	-	10/30	Continuous
Operation Temperature	55 °C	Room	Room	37 °C

Pilot trial and evaluation of full process feasibility against WWTP

The wastewater treatment pilot was conducted continuously for 6 months (180 days) to determine overall process stability, scalability, and nutrient recapture efficiency. The pilot system build is depicted in Figure 3.3.

During the pilot trial, effluent samples were collected daily from the CSTR and UASB reactors. The samples were analyzed for pH, phosphorus, ammonia, COD, solids composition (TS and VS), and extracellular polymeric substances (EPS). Gas production was also monitored daily in both reactors. Moreover, metallic ion concentrations, VFA profiles, and biogas compositions were examined periodically to better describe the overall process. Data generated during the trial operation was compared directly with the partner wastewater treatment plant's historical data log for operation, nutrient removal, and overall mass balance.

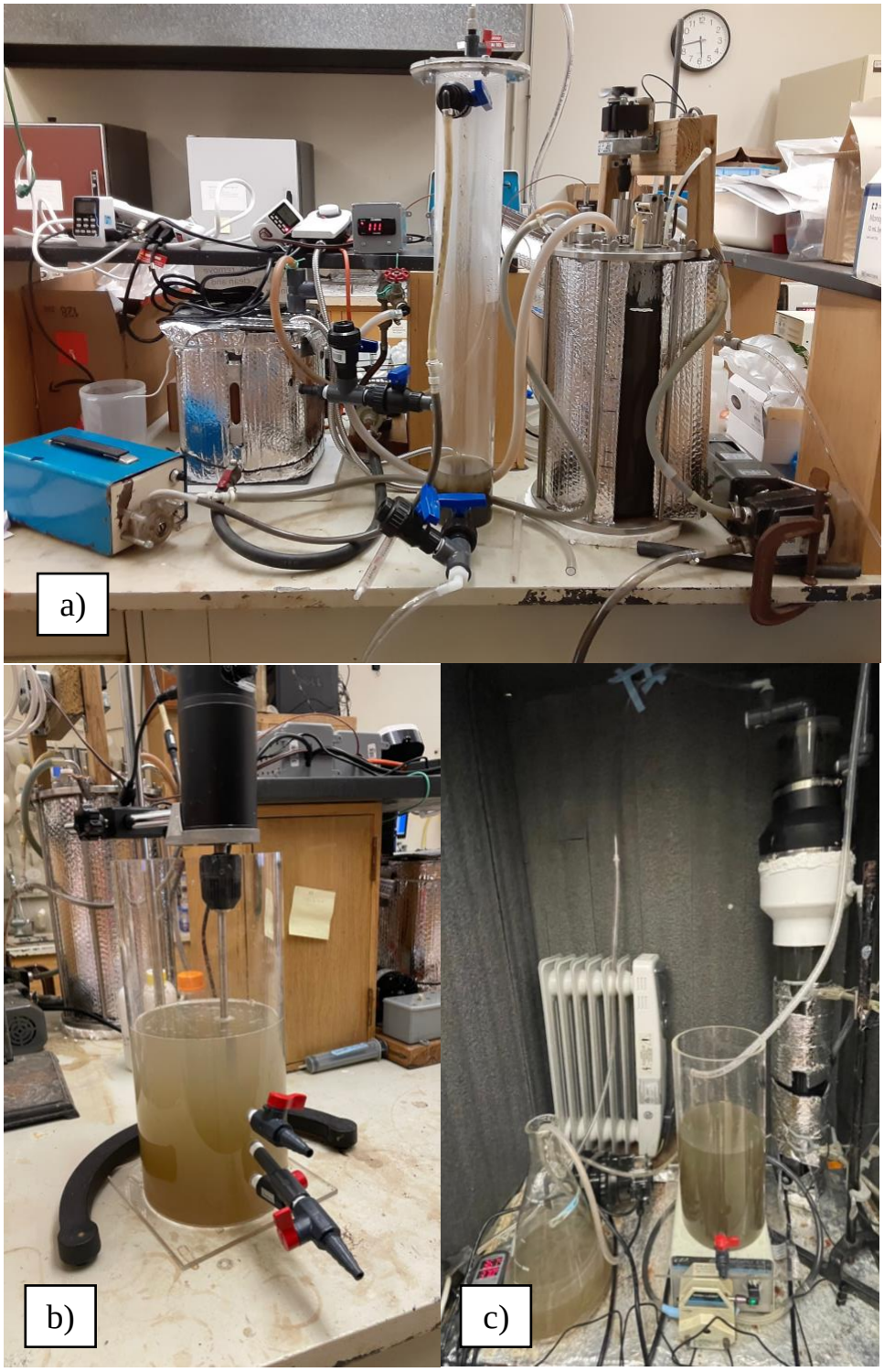

Figure 3-3 Images of the a) CSTR system b) P-precipitation system and c) UASB system that comprised the pilot plant.

Continuous stirred-tank reactor

The diluted TWAS (1:1 volume) was pumped into the continuous stirred-tank (CSTR) reactor with a peristaltic pump that automatically fed the system every 3 hours for a total of 8 cycles per day (4.2 L/day). The feeding pump would activate 5 minutes after the operation of the effluent pump, the effluent pump ran beforehand to displace the same amount of volume into an effluent reservoir. The final hydraulic retention time of the CSTR was three days, and its dimensions were 15.3 L total fermenter volume and 12.7 L working volume. Additionally, whey permeate was used to amend the organics profile of the digestor and lower the pH; this permeate was added at a rate of 60 mL/day, increasing digestible sugars in the reactor and overall COD in the reactor by 11,572 mg COD/day. The CSTR and the effluent reservoir had gas lock systems to escape produced gas into a turbine volumeter that recorded total gas production.

Solids separation centrifugation step

Daily operation of the dewatering step was required to allow for the storage of newly displaced digestate. This portion of the pilot operation was not automated, as small-scale continuous dewatering systems were unavailable. The pH and volume of the digestate effluent were measured and recorded.

A digestate sample was stored separately for further characterization and analysis. The remaining three liters of the digestate were thoroughly mixed with Clarifloc® dewatering polymer at an operation dosage of 50 lbs/ton (polymer: sludge dry weight). The polymer amended sludge was centrifuged in a benchtop centrifuge (Allegra X-15R) in a swing bucket rotor at 3900 RPMs for 7 minutes. The solids were sampled and analyzed while the supernatant continued the treatment process.

Phosphorus precipitation step

The high-nutrient liquid fraction obtained from the solid separation step was subjected to a phosphorus recapture process. The liquid's phosphorus content was determined using commercial colorimetric assays to establish magnesium dosage. A magnesium chloride ($MgCl_2$) or calcium chloride ($CaCl_2$) solution was added to the liquid digestate to achieve a molar ratio of 1.2:1 (metal:P). Afterward, the pH of the solution was adjusted to 8 with a sodium hydroxide solution 10N, and the liquid fraction was agitated for 10 minutes at 200 rpm to allow the precipitation reaction to take place. The crystals were allowed to decant for an additional 30 minutes, after which the supernatant was separated and transferred into the feed reservoir of the up-flow anaerobic sludge blanket reactor.

Upflow anaerobic sludge blanket reactor

The P-treated liquid fraction was fed to an up-flow anaerobic sludge blanket reactor (UASB). The UASB reactor was seeded with granular sludge sourced from a UASB digestor that treats lignocellulosic material from a private agricultural feed company (Marshall, Minnesota). The UASB reactor had two pump systems: continuous recirculation and feeding. The reactor had a working volume of 4.8 L and was fed 1.6 L daily, with an effective HRT of 3 days. To corroborate the change of composition of the effluents and feeds, a VFA analysis was performed before and after exiting the digestor. Additionally, total gas production and composition were determined normalized by grams of VS fed into the reactor.

Analytical methods

Sludge degradation was monitored by measuring biogas production on the CSTR system and the UASB reactor; each reactor had a volumeter recording gas production. The produced gas was sampled to establish the reactor's gas composition. All the digestate samples collected were subjected to wastewater characterization analysis to measure total and soluble fractions of organics, phosphorus, and ammonium-bound nitrogen (N-NH3). The soluble fraction was obtained by spinning the samples down in a centrifuge and filtering the supernatant through a 0.45 µm syringe filter to obtain the liquid reject containing the soluble fraction (APHA, 2005).

Total COD and soluble COD (Chemical oxygen demand) were quantified with colorimetric methods (Hach 8000 COD HR+) in a spectrophotometer (Hach DR5000) using standard APHA methodology. Total phosphorus (tP) and soluble phosphorus (sP) was analyzed using Hach commercial vials (TNT 845, Hach, Loveland, Co), which employ the ascorbic acid colorimetric method. Total ammonium nitrogen and soluble ammonium nitrogen were analyzed using the salicylate colorimetric method of commercial kits (TNTplus 833, Hach, Loveland, Co). The composition of total solids, volatile solids, suspended solids, and dissolved solids (TS,VS,TSS,TDS) were analyzed according to EPA's method 1684 and method 160-(1-2) for solids determination (EPA, 2001; EPA, 1999). A handheld P100 pHmeter (Cole Palmer, USA) was used for pH measurements.

The concentration of extracellular polymeric substances (EPS) was determined using the Lowry method to determine protein concentration; the measurement was performed sequential extraction samples to determine soluble EPS, lightly bound EPS, and tightly bound EPS. This was achieved through sequential saline extraction, as described by Zhen (Zhen et al., 2013).

Volatile fatty acid (VFAs) profiles were analyzed using high-performance liquid chromatography in a 1260 infinity HPLC system (Agilent Technologies, USA) with an Aminex HPX-87H Column. Gas composition was determined using gas chromatography analysis performed in a 490 Micro gas chromatographer fitted with a J&W durabond FFAP column (Agilent Technologies, USA). Magnesium, calcium, and phosphate concentrations were determined by Ion Exchange chromatography in a Dionex Aquion Chromatography system (Thermo Fisher, USA).

Statistical Analysis

To determine overall removal and solubilization values in the pilot plant, the daily values were used to calculate means and confidence intervals to a confidence of 95%. When required, a one-way analysis of variance (ANOVA) and T-tests were used to compare treatments. A significance of α=0.05 was used in all tests to assess the mean difference. All the statistical analyses were performed using JMP lab software. Additionally, several equations were used to determine flow-mass balances and operational parameters required for the process analysis. These equations, their use, and their authors are compiled in Table 3.3

Table 3-3 Operation formulas for WWTP process.

Parameter	Formula	Legend	Reference
Volatile solids reduction (Van Kleeck)	$VK = \frac{VS_f - VS_e}{VS_f - (VS_f VS_e)}$	VS_f -volatile solids in feed; VS_e – VS in effluent	(Switzenbaum et al., 2003)
Volatile solids reduction (Mass Balance)	$VSR = \frac{TS_f VS_f - TS_e VS_e}{(TS_f VS_f)}$	TS_f -total solids in the feed; TS_e – TS in the effluent	(Resek et al., 2023)

Results and Discussions

Nutrient monitoring over 180 days of operation

As the reactor was initially inoculated with a half-strength digestate obtained from the smaller continuous reactor, the first days of operation consisted of rapid organics accumulation. This was associated with a sharp decrease in pH within the digestor. The fluctuation in pH and soluble nutrients during the 180 days of the pilot plant operation is shown in Figure 3-4. The reactor achieved process stability after 10 days of operation, in which the nutrient solubilization and solids reduction within the reactor were maintained relatively constant. It should also be noted that given the overall length of the operation run, the sludge feedstock had to be replenished from the WWTP on four different occasions. The variability associated with using raw untreated feed is to be expected, as environmental conditions and sludge composition fluctuate throughout the year. Consequently, changes in feed samples resulted in starkly different organic and phosphorus content, affecting the effluent's overall nutrient concentrations. Sludge treatment processes must be robust enough to deal with the variation in influent composition and maintain adequate treatment.

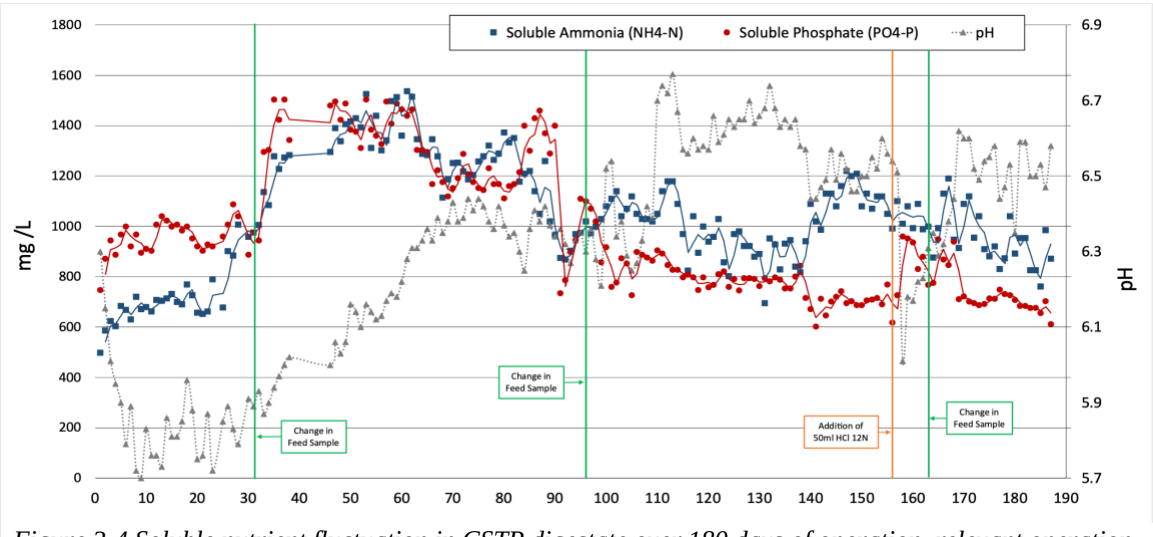

Figure 3-4 Soluble nutrient fluctuation in CSTR digestate over 180 days of operation, relevant operation events are also shown.

Changes in the feedstock used for the pilot operation occurred on days 31, 97, and 162. The larger organic load in the reactor caused a gradual increase in the pH following day 31. Even when the substrate feed into the system was again changed into a lower P and VS concentration feed, the pH did not decrease to the optimal <6.00 range expected in the operation. Feeding a sample with lower organics content into the reactor was incapable of reestablishing the low pH, even after several weeks of operation in these conditions. Therefore, a high dose of hydrochloric acid was added on day 156 to try to change the microbial consortia in the reactor into something more conducive to higher acid accumulation.

Even after the HCl dosage, the bioreactor's pH quickly increased again, indicating that the system was no longer stable at more acidic conditions. Hori et al. indicate that the microbial community structure within a thermophilic reactor is highly dependent on pH, which allows for the proliferation of hydrogenotrophic methanogens (Hori et al., 2006). While this was experienced at the beginning of the reactor operation, the change in organics loading may have caused a redistribution of microbial populations that did not favor VFA accumulation. In addition, the high buffering capacity of the influent did not facilitate pH reduction. Further experimentation is required to determine process stability in the system or methods of pH control that do not require continuous acid addition.

Process stability, COD and solids reduction in CSTR during pilot plant operation

The solids content of the effluent and influent were monitored during the operation of the CSTR thermophilic acid system. The total and volatile solids values are shown in Figure 3.5. The total solids and volatile solids in the system was lower in the effluent than in the feed, indicating

that effective organics degradation was occurring. The bioreactor was initially inoculated with digestate from a smaller, continuously operated CSTR, treating the same feedstock. The reactor was initiated with 50% digestate and 50% water, which created a highly dilute effluent during the first days of operation.

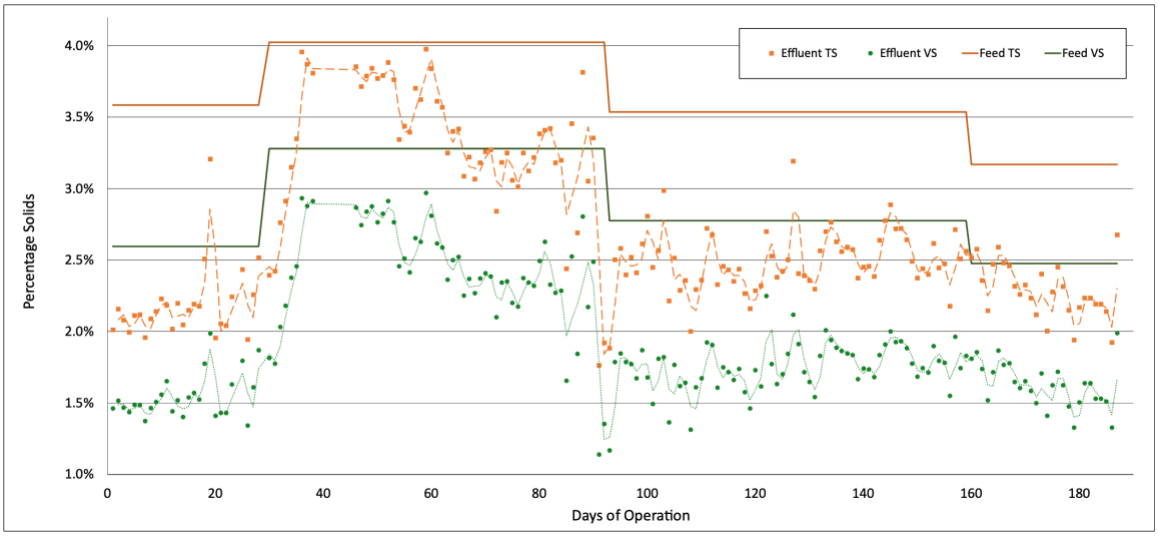

Figure 3-5 Total solids and volatile solids comparison between feed and effluent in thermophilic-acid reactor.

Figure 3.6-a shows overall solids reduction in the reactor's effluent. This is relevant as in a stirred tank reactor, minimal grit deposition should occur. The separation of heavier solid components would indicate settling and improper mixing in the reactor. Still, a small portion of the fixed solids is also degraded during AD so it is not uncommon to see a slight contribution to total solids reduction from the non-volatile portion (Switzenbaum et al., 2003). During the initial operation of the reactor the solids content in the digestor was lower than that of the feed, hence the feedstock ended up being diluted during the first stretch of the CSTR operation. This is shown as a greater portion of total solids is removed until day 30 in comparison with the rest of the days. During the first operation, the reactor experienced mixing issues as a solid foamy plug formed at the top of the working volume. This also resulted in the excessive retention of solids, during this

time, solids reduction attributed to grit deposition averaged at 10% (S.D. ±0.3%) of the total reduction. After day 31, an additional impeller was installed in the reactor that allowed for the agitation of the uppermost portion of the reactor's working volume. After this modification, proper mixing was achieved in the reactor, as it demonstrated in Figure 3.6-a as most of the solids reduction is attributed to the VS portion. After operation day 31 the mean fixed solids reduction was 1.3% (S.D. ±2.6%).

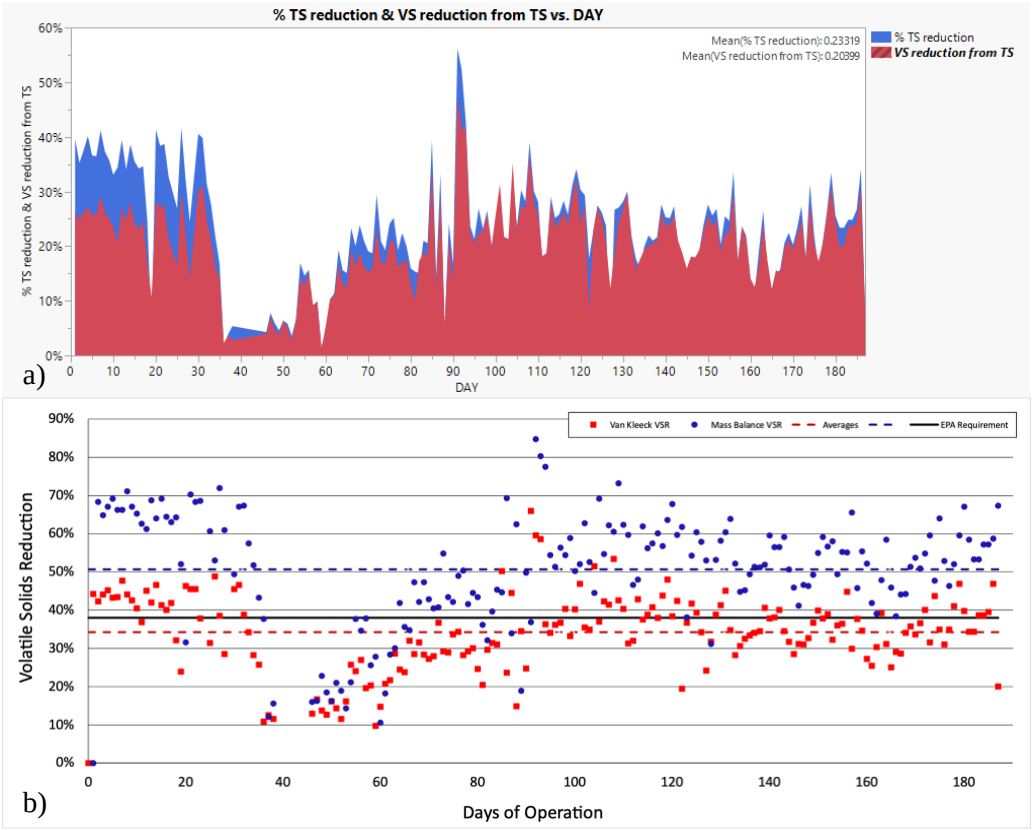

Figure 3-6 a) Total Solids reduction during reactor operation and b) Volatile solids reduction.

The EPA has specific regulations for the treatment of wastewater sludge with the intention of vector attraction reduction, as per the federal regulations code (EPA, 2003). To comply with these requirements, the reduction of the volatile solids fraction (VSR) in an AD process needs to be higher than 38% (Resek et al., 2023).

The VSR value of the reactor was calculated using the Van Kleeck equation, which is used as a conservative measurement of overall VSR. This parameter achieved an average reduction of 34% (S.D. ±10%). It should be noted that the values are negatively affected by the initial adaptation period after the first feedstock change, where the VS reduction decreased drastically to the lowest value of 12% VSR. The approximate mass balance equation also calculated a more descriptive VSR value with a mean value of 51% (S.D. ±15%).

The mass balance equation yields values above the VSR threshold designated by EPA, which means that this process alone would be an acceptable treatment for the wasted sludge. Switzenbaum has described the disparity found when using the two different formulas.

Figure 3-7 a)Total COD and soluble COD comparison between feed and effluent in the thermophilic-acid reactor, b)COD reduction and solubilization over CSTR operation.

Because the Van Kleeck equation assumes the retention of all the fixed solids, it commonly underestimates total VSR when fixed solid reduction occurs (Switzenbaum et al., 2003). During the CSTR operation, the mean fixed solids reduction was 17% (S.D. ±12%), hence the large difference between values. Another important operational aspect is overall COD reduction. Figure 3.7-a illustrates the overall fluctuation of total and soluble COD in the effluent of the reactor. It should be noted that variation in overall sludge structure made total COD measurements highly variable. Therefore, some measurements obtained for total COD were higher than those of the input feed, which does not hold in the mass balance. Figure 3.7-b shows the values of COD reduction and the percentage of COD solubilized from the feedstock.

COD reduction reports vary significantly depending on the system and retention time, Steiniger et al. determined a COD reduction of 63% in thermophilic reactors (53ºC) treating TPS and TWAS mixture for a 20d HRT (Steiniger et al., 2023). On the other hand, Sillero et al. evaluated the thermophilic anaerobic digestion of a mix of sewage sludge, wine pressings, and poultry manure at an HRT of 3d. They obtained a tCOD reduction of 35%(Sillero et al., 2023), similar to the 29% value obtained in this work. Still the mean COD reduction in the CSTR in addition to the increased COD solubilization give a value of 49% if we expect the full reduction of the soluble COD portion, while that is probably not feasible, an increase in overall COD reduction is expected after the second digestion process.

The thermophilic trials illustrated that the half-strength TWAS fed reactor could be operated efficiently at volumetric loading rates of 11 g COD/L/day at a HRT of 3d. The process achieved a volatile solids removal averaging 51% and a COD removal of 29% throughout the trial peri. Additionally, further solubilization of 20% total COD was achieved, which is intended to be further reduced and converted to methane in the second reactor.

These values are acceptable for the operation of an municipal anaerobic digestor in accordance to EPA volatile solids reduction requirements. However, the increase in loading rate produced by the change in feedstock created a process instability that reduced VS and COD reduction while also increasing the pH over the intended range. The pH increase registered after the change in feedstock could not be controlled afterwards indicating that the conditions need to be optimized to favor a drop in pH.

Phosphorus Solubilization in thermophilic Acid CSTR

The phosphorus solubilization was also evaluated during the operation of the CSTR, and Figure 3.8 presents the fraction of total and soluble phosphorus in the system during the 180 days of operation.

Figure 3-8 Total P and soluble P comparison between feed and effluent in thermophilic-acid reactor.

As phosphorus does not readily volatilize in the anaerobic digestor, given that it doesn't form stable gaseous compounds (Roels & Verstraete, 2001), the system has only one input and output. Therefore, all phosphorus that enters the system should also exit it.

Slight variations in its composition are expected, given the heterogeneous nature of the sludge, which can be seen in Figure 3.8. The focus of the work is on the distribution of this phosphorus in soluble and non-soluble fractions. The average P solubilization over the whole period of operation was 59% (S.D. ±10%). This value is 47.5% higher than the solubilization reported by Popel et al. on mesophilic AD digestion of TWAS at an HRT of 20 days, which was 40% of the total P (Jardin & Pöpel, 1994).

However, in addition to the temporal and feed variation in the reactor, the other parameter intended to be controlled was the working pH within the CSTR. However, issues associated with the process instability and mass transfer at the beginning of the operation time irreversibly disrupted the system's pH. Because of this it was also possible to model phosphorus solubilization in regard to pH. This is shown in Figure 3.9 which pools reading by feedstock sample and pH to better understand the CSTR operation.

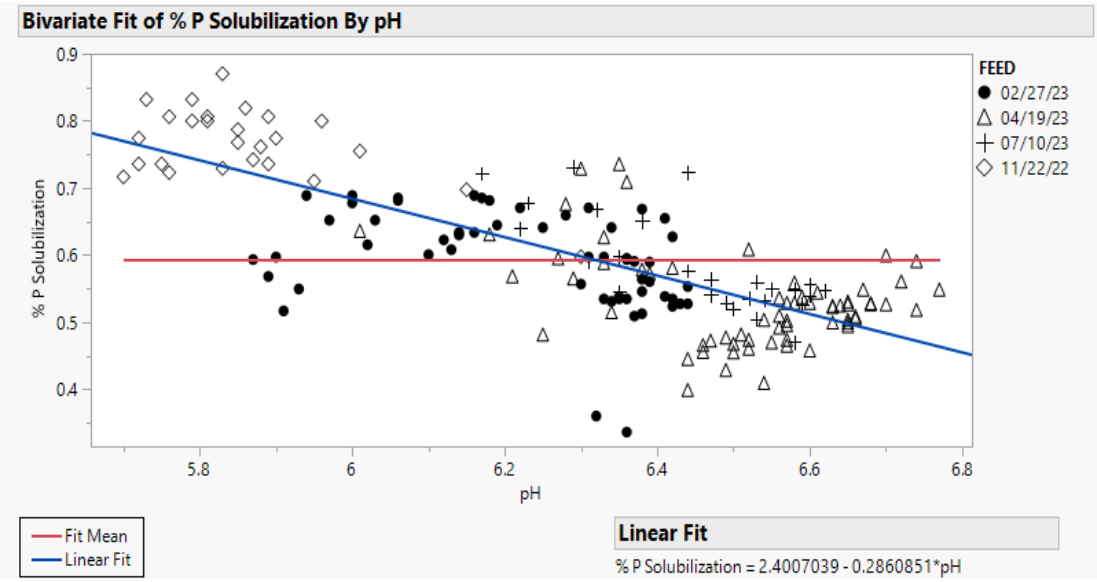

Figure 3-9 Linear fit of P solubilization regarding pH variations in the CSTR reactor

Summary statistical analysis indicated that the pH and the phosphorus solubilization had a significant correlation of -0.82 ($p<0.0001$). The linear fit indicated that higher P solubilization was achieved in the thermophilic acid CSTR, according to the equation shown in Figure 3.9. The R^2 of the fit was 0.599, which is to be expected given the high variability of the total and soluble P measurements. The increased solubilization at lower pH follows data reported by Latif et al. The author indicates that the highest phosphorus solubilization (75%) in anaerobic digestion of WAS is achieved at a pH of 5.2 (Latif et al., 2017). This study was performed in mesophilic conditions aided by hydrochloric acid dosing to achieve the desired pH. This effect of increased solubilization can be attributed to the solubilization of certain mineral fractions ($Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$) that contain phosphates and start to dissociate at pHs 5.5 and 6, respectively (Luyckx et al., 2021).

In the operation period of days 5-30, before the process instability, the reactor averaged a solubilization efficiency of 76%(S.D. ±5%) with a mean pH of 5.82 (S.D. ±0.13). This indicates that the same amount of P solubilization can be achieved at a higher pH in half-strength TWAS-fed reactor thermophilic conditions at an HRT of 3d. The stable process achieved a P solubilization of 76% at a pH of 5.82, and the overall process achieved 59% solubilization at an average pH of 6.32 (S.D. ±0.24).

Solid separation of thermophilic acid digestate during pilot operation

During the pilot plant operation, the extracellular polymeric substance content of the sludge was determined and used to monitor dewaterability in the reactor. Figure 3.5-a depicts the changes in EPS concentration over the full operation time. After the first feedstock shift, the total EPS content increased until it almost doubled, from an average concentration of 2.3 g/l (S.D. ±0.5) to a mean of 3.7 g/L (S.D. ±0.4). Additionally, the graph shows the overall liquid recovery from the solids separation step, which used centrifugation and Clarifloc polymer dosage. Several authors

report a negative effect of EPS concentration on sludge dewaterability (Lei et al., 2007; Sam et al., 2022). This occurs because of the properties of the complex polymeric matrix that is formed by these substances that increase floc adhesion, volume capillarity, and hydrophobic interactions (Liu & Fang, 2003). Therefore, an increase in the overall EPS concentration would proportionally increase the polymer dosage requirement for successful dewaterability (Novak et al., 2003)

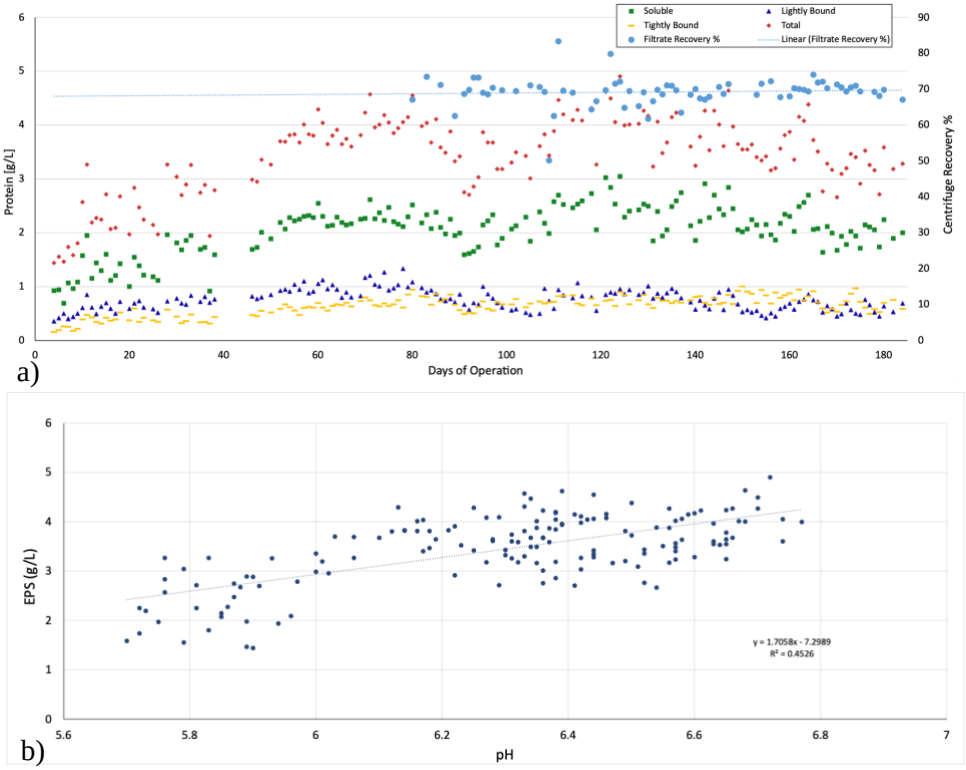

Figure 3-10 a)EPS content and liquid recovery from thermophilic-acid digestate over 6 months of operation. b) EPS content vs pH plot.

There was also a strong correlation between the EPS concentration and the pH of the effluent (0.713, p=0.008). Zheng et al. report that variations in sludge pH affect the surface characteristics of the EPS and that less extractable protein is available at lower pHs (Zheng et al., 2007). Additionally, Jyoti et al. infer that bacterial cells growing at lower pH reduce EPS secretions due to acid stress (Jyoti et al., 2024).

These two phenomena combined would indicate that at lower pH, there is less EPS production and that the absorption capacities of these EPS would be hindered. This is relevant for the increase in sludge dewaterability in WWTP processing systems.

During the pilot's operation run, the liquid recovery had a mean value of 69% (S.D. ±4%). The remaining solid cake had an average composition of 7.6% (S.D. ±0.6%) TS and 6.1% (S.D. ±0.3%) VS. To determine if recovery efficiency had a relationship to EPS content, bivariate fit analysis of the data was performed. The fit is shown in Figure 3.11. The Pilot's solids separation method found no relationship between EPS content and dewatering efficiency.

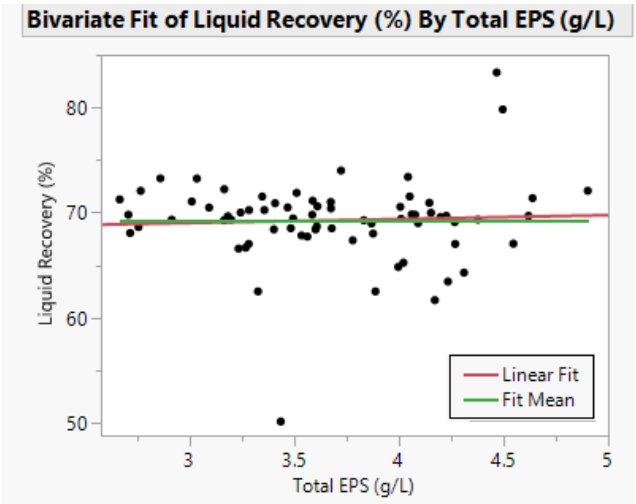

Figure 3-11 Linear fit comparison of liquid recovery and EPS content.

It's noteworthy to indicate that the established pilot operation used the same polymer loading dose as the municipal wastewater treatment facility (50 lb. polymer/ ton-TS). Novak et al. indicate that for a 3-day HRT WAS anaerobic digestion effluent, the polymer requirement for efficient dewaterability is around 20 lb/ton (Novak et al., 2003). This suggests that the plant uses an engineering safety factor of 2.5 and that, effectively, the overdosing of the polymer did not allow for the determination of dewatering variations regarding the EPS content.

Phosphorus recovery from the liquid fraction of thermophilic-acid digestate

Following the solids separation step, the centrifugation produced a high-nutrient supernatant that contained a significant portion of the solubilized nutrients. This effluent was first subjected to P-precipitation using metal salts. The phosphorus recovery efficiency was registered and compiled in Figure 3.12, alongside the pH values of the adjusted liquid. During the operation of the P-precipitation step, the average P recapture efficiency was 84.6% (S.D. ±4.8%) of the total phosphorus present in the liquid digestate. This result is in agreement with other recapture efficiencies published in the literature. Karabegovic et al. report that the P recapture process from wastewater has 80% efficiency, and the authors of this paper used a working pH of 9.2. A comparative study by Lorick et al. found that the efficiency removal increases when the dosing agent molar ratio and the treatment pH increase, which mirrors the results presented in the previous chapter. Nonetheless, these parameters alone are incapable of modeling removal efficiency (Lorick et al., 2020). The synergistic effects of feedstock composition, reactor configuration, and processing methods produce high variability in the crystallization observed. Hence, the parameters of each unique process need to be optimized for the conditions of that specific reactor. The results of the batch jar testing were significantly higher than the pilot efficiencies (93% removal); this indicates that further experimentation would be required to determine ideal precipitation dosing in the semicontinuous large-scale system. While higher alkalinity (over pH 10) could result in better P removal, additional processing of the basic solution makes optimization a process of managing costs and benefits (Li et al., 2019). Still, the P precipitation operation of the large-scale batch-reactor process for P recapture could efficiently treat high-P liquid digestate. The process achieved a P recovery averaging 84.6%.

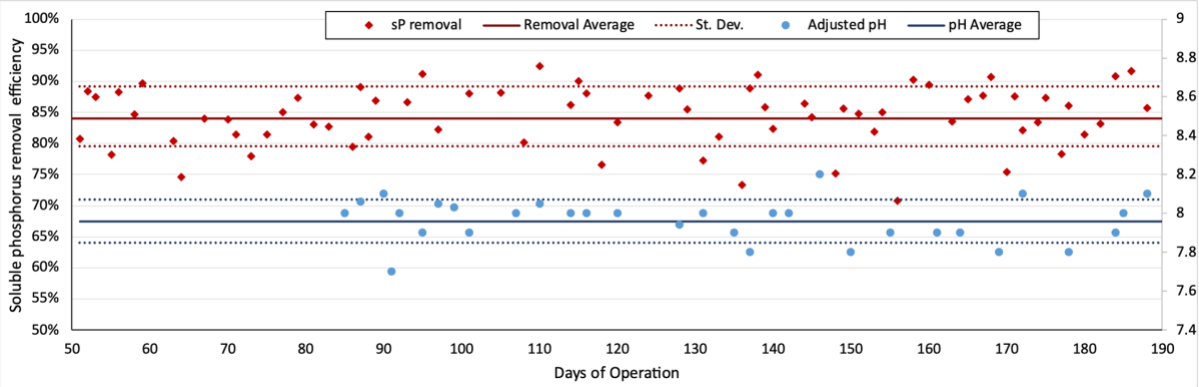

Figure 3-12 Phosphorus recapture and final pH obtained in liquid fraction of high-nutrient digestate.

Organics Removal efficiency from P-treated liquid fraction in a high-rate anaerobic digestor

To determine the overall removal of the solubilized COD in the P-treated liquid digestate, the daily values of effluents and influents were recorded (Figure 3.13). Additionally, the values of COD removal efficiency are also shown. After an equilibration period of 15 days, the UASB reactor efficiently removed the COD at an average of 88% (S.D. ±3%) on an average organic load of 7.8g COD/L*day (S.D. ±2). VFA reduction was also evaluated, Figure 4.5 in appendix, which was determined to have a mean 78%(S.D. ±7%) reduction.

There are no comprehensive reports on the COD reduction of the center obtained from fermented TWAS, as setups that treat only full sewage influents or greywater influents are usually studied. Mahmoud et al. determined a sCOD reduction of 77% on a UASB treating full sewage wastewater, which also contains a high fraction of non-soluble COD (Mahmoud et al., 2004). Bogte et al. studied the COD removal of a UASB reactor that treated greywater and low solids concentration blackwater with a 4-day HRT. The authors achieved a maximum COD removal of 80% (Bogte et al., 1993). While none of these comparisons are equivalent to the process or

feedstock used in this project, they are a good indicator of overall COD removal efficiencies in wastewater feedstocks.

On the other hand, other low solids wastewater treatments have much higher COD removal rates. Han et al., who treated food waste fermentation wastewater in a UASB report a COD removal efficiency of 96% at a loading rate of 12.9g COD/L*day (Han et al., 2005). It's worth mentioning that overall removal efficiencies are highly dependent on the feedstock composition, as more complex samples achieve lower COD reductions.

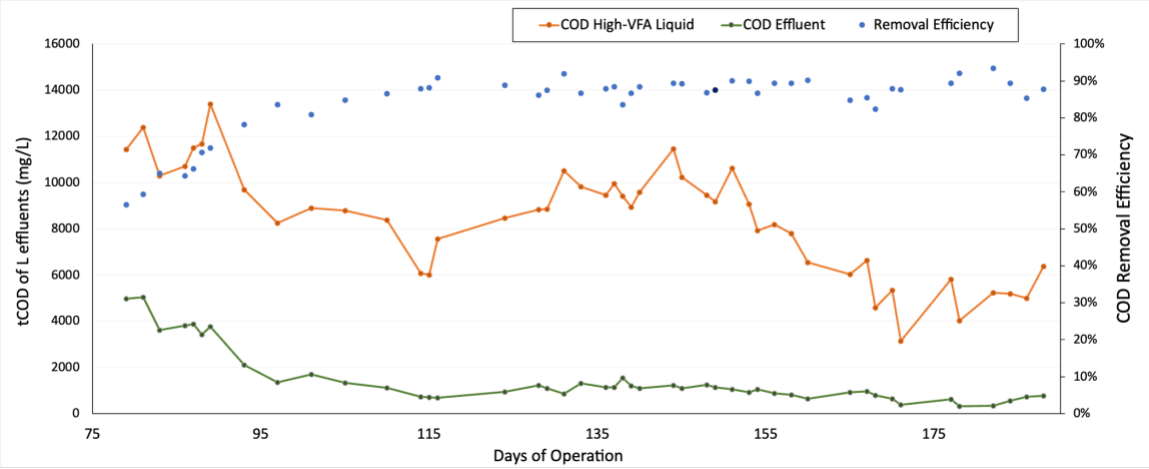

Figure 3-13 Operation parameters of UASB reactor: Overall COD reduction, feed and effluent total COD concentrations.

https://meet.google.com/tra-yepf-zqs

Additionally, the gas production of the UASB reactor was monitored, and its values and composition are shown in Figure 3.14. The UASB reactor achieved a specific methane yield of 0.22 L-CH_4/g-COD (S.D. ±0.08). The theoretical methane yield per gram of COD is 0.35L, as described by Heidrich, meaning that the overall conversion process achieved was 62% (Heidrich et al., 2011). Finally the biogas composition, after the stabilization period, averaged 74% CH_4 (S.D. ±5%).

The operation of the high-rate UASB reactor demonstrated an efficient treatment of P-treated liquid centrate. The reactor was capable of 88% COD removal at loading rates of 7.8 g COD/L/day and at an HRT of 3d. after the change in feedstock could not be controlled afterwards indicating that the conditions need to be optimized to favor a drop in pH.

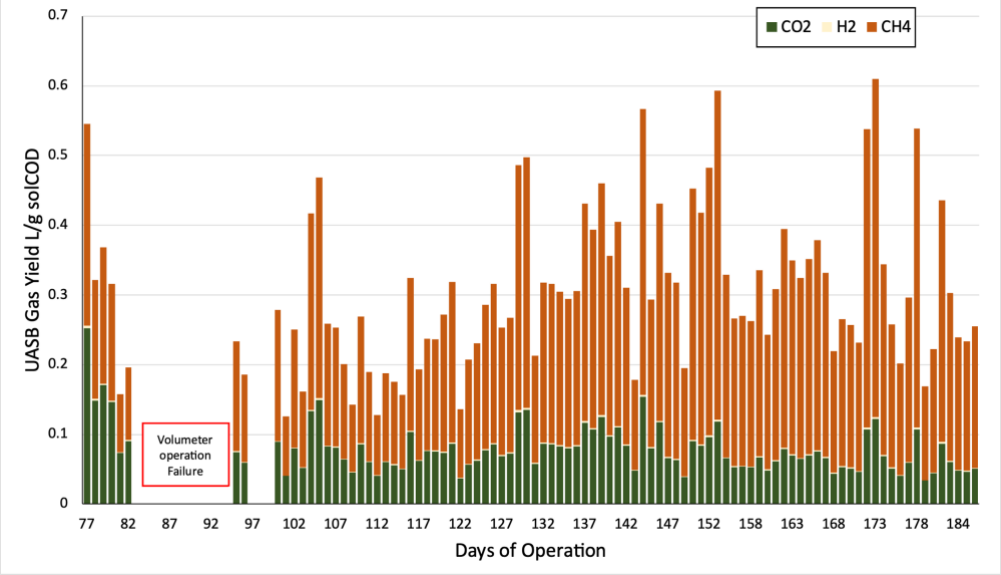

Figure 3-14 Daily biogas yield and composition in a high-rate UASB digestor during reactors operation.

Mass Balances: comparison of the process with conventional WWTP solids processing and other P recapture systems.

The performance of novel phosphorus recapture pilot plant was regularly monitored in terms of its overall biomass input and output. The characteristics of the feed influent, gas production and solids production are detailed in Table 3.4. The overall performance of the system was good as the combined action of all the units of operation could treat the half-strength TWAS and reducing its volatile solids content, while solubilizing nutrients required for the precipitation of struvite or other P-containing minerals. Phosphorus was efficiently solubilized in the thermophilic acid reactor

without the need of concentrated acids for pH regulation. Whey permeate added as an amendment, increased the concentration of fermentable sugars and aiding in the production of VFAs. This combination of food byproducts and fermentation conditions could solubilize an average of 59% (S.D. ±10%) of the total phosphorus available in the influent feed. The subsequent P recovery steps could immobilize the majority of the phosphorus solubilized to achieve a final overall recovery of 50% (S.D. ±9%).

Table 3-4 Calculated flows for the full capacity process operation of the Pilot system. Standard deviations are in parenthesis

Unit of Operations	**Thermophilic CSTR**	**Centrifuge Dewatering**	**P precipitation**	**High-rate UASB**
Flow Rate (mL/day)	4232	4232	2920 (204)	2814 (73)
Solid Exit Rate (g/day)	-	1340 (78)	38 (12)	-
Loading Rate (g VS/day)	123 (13)	-	-	33 (5)
Loading Rate (g COD/day)	246 (30)	-	-	82 (21)
Methane Production (L/day)	7 (13)	-	-	17 (9)
Gas CH_4 Comp	44% (3%)	-	-	75% (6%)
P Solubilization/Recovery	59% (10%)	99% (2%)	85%(5%)	-

To properly compare the solids reduction efficiency and gas production parameters of the pilot with the conventional WWT plant, all inputs and outputs were normalized to production by g VS, and the volatile solids reduction (VSR) equation were applied. These values, alongside the T-test comparisons between systems, are summarized in Table 3.5.

The comparison between digestion efficiency of the bench scale and the plot systems indicate that the same amount of volatile solids reduction was achieved, while the P solubilization

and P recapture values achieved in the small scale (66% and 63% respectively) could not be replicated in the larger pilot. This can be attributed at the low operational stability of the process that did not allow the pH regulation below 5.8 as intended.

Table 3-5 Operation Parameters comparison between pilot and conventional WWTP process, bench-scale experiments parameters are also shown. Standard deviation in parentheses

Unit of Operations	Pilot Plant	Conventional WWTP	Benchscale Testing	Pilot and plant comparison (t-Test)
VSR (Van Kleeck)	37% (2%)	43% (3%)	35%(1%)	Sign. Diff. ($p<0.0001$)
VSR (Approximate Mass Balance)	60% (3%)	60% (5%)	57%(2%)	No Sign. Diff.
P solubilization	59% (10%)	-	66% (5%)	-
P recapture	50% (9%)	-	63% (3%)	-
Gas Production (L-biogas/g-VS)	0.28 (0.13)	0.47 (0.23)	0.33 (0.17)	Sign. Diff. ($p<0.0001$)
Total CH_4 Comp	63% (24%)	55% (3%)	78%(9%)	Sign. Diff. ($p<0.0001$)

As the fixed solids reduction in the thermophilic system was significant (17% S.D. ±12%), the Van Kleeck equation effectively underestimated the VSR. Hence, there is a statistically significant difference between VSR values obtained by this equation. VSR values calculated using the approximate balances equations where not statistically different. As the approximate balance equation is considered a more rigorous evaluation of the performance, it can be determined that either system can achieve the same amount of organic mass degradation and can comply with the EPA norms regarding solids destruction (EPA, 2003). In the partner WWTP, the P concentration of the plants influent is managed using ferric chloride ($FeCl_3$) which is disposed of via landfills.

Therefore, the achieved 49.3% P-recapture represents a very significant improvement regarding nutrient recovery in the plant. Regarding methane production the overall biogas yield of the pilot system was significantly lower than that of the WWTP ($p<0.0001$), with a decrease of 41% overall biogas yield in comparison to the conventional system. However, the methane production in the pilot system was increased by 15% ($p=0.0053$). When determining overall CH_4 production per gram of VS, the WWTP achieved a methane yield of 0.258 mL-CH_4/g-VS and the pilot converted 0.178 mL-CH_4/g-VS; meaning the pilot had a 32% decrease in methane production.

There are some caveats with the methane production evaluation as both the reactors in the pilot (CSTR and UASB) and the large-scale digestor had highly variable reading of daily gas production. In the three readings, standard deviations were over 50% of the mean values indicating a wide or non-normal distribution. Additionally, several operational issues occurred that prevented the reading of the produced biogas in the pilot reactors. This may have reduced the overall production registered in the CSTR and UASB, as gas leaks and clogged piping occurred often. As the results of the months long operation now indicate, a reduction in overall gas production in the proposed system, but further studies with more rigorous control of leakages and obstructions would be beneficial to further elucidate gas productivity. Still as the proposed system has no difference in overall solids destruction and the added recovery of P-minerals, the benefit of operating this setup could offset the losses in methane production.

The phosphorus recapture values obtained in during the operation of the pilot were used to compare P recovery of the pilot plant, with other systems. It should be emphasized that authors studying phosphorus recapture sometimes only report on soluble phosphorus recapture rather than overall recapture efficiency. Regarding, the immobilization of the soluble P fraction, the centrifugation process and sequential metal-salts struvite precipitation achieved P removal

comparable to that of other large-scale systems (85% ±5% removal). The Ostara pearl system has a phosphorus recapture from liquid portion of 60-81% (Britton et al., 2009; Garcia-Belinchón et al., 2013). Airlift reactors are reported to have a phosphate recovery efficiency of 85-90% (Stumpf et al., 2009). Hence it can be inferred that the dosing process has little room for optimization.

The overall recovery rate of Phosphorus is highly dependent on the degree of P solubilization in the AD step. The overall P recapture achieved in this pilot trial was 50%, which is lower to that of other reported systems. The KEPRO system is capable of 60-70% total phosphorus recapture (Hultman, 1999); while the Stuttgart process is capable of 60-67% phosphorus recapture (Antakyali et al., 2013). However, both processes use acid supplementation (HCl and H_2SO_4, respectively) to reduce the pH of the sludge below 4 during the AD. The added use of Acids would increase the demand for a base reagent during the precipitation step, increasing total overhead costs.

Conclusions

The results of this pilot trial illustrated that the CSTR was capable of appropriate solids and organics treatment, achieving 60% VSR. During this operation step an average of 59% of the total phosphorus was solubilized with the potential for higher solubilization with appropriate operation control. The P-recovery system be used to treat raw thickened waste activated sludge to produce P-bearing mineral solids. The solid separation was successful, achieving consistent dewatering with 69% liquid recovery. The operations of both the pilot plant units were stable even at a higher pH than planned (6.2±0.2 pH) and the performances for P recapture were excellent (85%±5%). The overall system was also capable of methane production, even when the overall yield was 31% lower than the yield achieved by conventional WWTP treatment. Separating the anaerobic digestion into two reactors increased P-solubilization and achieved an overall P recapture of 50%.

Conclusions and Future Work

The continuous operation of the pilot system reactor experiment demonstrated capability for satisfactory organics and solids reduction. Additionally, the system could recover 50% percent of total influent P, without the addition of acids for pH regulation. However, the system requires more experimentation to increase P recapture efficiencies and improve operation stability. Further tests to control pH and VFA concentrations in the CSTR reactors are required. The potential for improvement in the pilot system presented in this work is detailed in Figure 3.15. At the beginning of the pilots' operation (1-34 d), solubilization of the total P averaged 75% which would indicate a potential for overall recovery of up to 65% without acid supplementation. Further studies into the operation stability of the CSTR element are required to optimize phosphorus solubilization in the pilot scale. Precipitation trials using non-reagents grade metal salts would also need to be performed to establish ideal dosing ratios for the slag used for the precipitation. Finally, studies into the implementation of alternate dewatering systems, such as belt presses could be done to create a fully continuous system that could operate non-stop. The P-recapture system would benefit from a techno economic analysis to determine the overall cost of fitting the processing units into a large-scale WWTP while taking into consideration the energy input, operation, and maintenance.

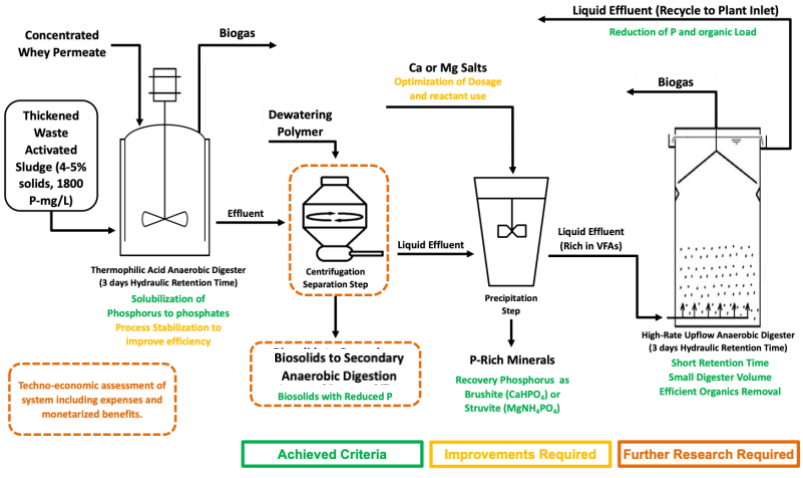

Figure 3-15 Achieved process metrics and future improvements.

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Chapter 4 Appendix

Table 4-1 Pretreatments on different feedstocks

TPS						TWAS					
		P	COD	SE P	SE CO			P	COD	SE P	SE CO
Total	Control	625	50936	6	1493	Total	Control	2157	81692	190	2465
	Thermal	559	66774	21	3288		Thermal	2375	72872	61	1315
	Acid+Ther	602	55614	2	4321		Acid+Ther	2290	60677	33	8786
	Acid	592	65394	10	5542		Acid	2325	65394	69	814
Soluble	Control	216	8070	9	455	Soluble	Control	1013	4250	38	253
	Thermal	178	10014	1	85		Thermal	1504	14846	20	122
	Acid+Ther	164	11487	5	178		Acid+Ther	1576	15203	13	132
	Acid	204	8702	1	178		Acid	1582	6079	8	47

Table 4-2 Separate Feeds Different Pretreatments

TWAS trial		TS		VS		TDS		TSS		sP (PO_4-P mg/L)		sCOD (mg/L)		sAMM (NH_3-N mg/L)	
		Avg.	S.D	Avg.	S.D	Avg.	S.D	Avg.	S.D	Avg.	S.D	Avg.	S.D	Avg.	S.D
SEED	Before	5.96%	0.06%	4.39%	0.04%	1.35%	0.06%	4.62%	0.04%	1034	75	704	4	18501	281
	After	6.16%	0.05%	4.66%	0.03%	1.50%	0.05%	4.66%	0.08%	1087	25	671	24	20334	659
CONTROL	Before	6.09%	0.03%	4.54%	0.04%	1.20%	0.07%	4.89%	0.07%	762	14	1029	28	13393	217
	After	6.06%	0.10%	4.53%	0.06%	1.85%	0.12%	4.21%	0.17%	1004	49	944	48	20878	632
THERMAL	Before	6.27%	0.08%	4.68%	0.05%	1.70%	0.03%	4.57%	0.06%	852	20	1060	10	17565	507
	After	5.95%	0.19%	4.47%	0.13%	1.86%	0.05%	4.09%	0.23%	1030	46	866	68	21615	506
THER-ACID	Before	6.10%	0.03%	4.57%	0.02%	1.59%	0.07%	4.50%	0.07%	787	27	1047	6	16284	166
	After	5.80%	0.11%	4.37%	0.08%	1.90%	0.02%	3.90%	0.11%	917	70	1103	152	20380	61
ACID	Before	6.16%	0.05%	4.59%	0.06%	1.32%	0.00%	4.84%	0.06%	830	37	1043	6	14505	304
	After	5.93%	0.08%	4.46%	0.06%	1.86%	0.04%	4.06%	0.11%	989	37	1020	165	20464	1423

TPS trial		TS		VS		TDS		TSS		sP (PO_4-P mg/L)		sCOD (mg/L)		sAMM (NH_3-N mg/L)	
		Avg.	S.D	Avg.	S.D	Avg.	S.D	Avg.	S.D	Avg.	S.D	Avg.	S.D	Avg.	S.D
SEED	Before	6.08%	0.10%	4.54%	0.09%	0.99%	0.09%	5.09%	0.09%	1034	75	704	4	18501	281
	After	6.25%	0.07%	4.66%	0.06%	2.03%	0.02%	4.23%	0.09%	1197	29	735	98	20587	681
CONTROL	Before	5.83%	0.04%	4.53%	0.02%	0.81%	0.03%	5.02%	0.13%	802	50	487	17	12971	3774
	After	6.05%	0.08%	4.75%	0.07%	1.78%	0.15%	4.27%	0.20%	979	23	614	63	18838	453
THERMAL	Before	5.93%	0.05%	4.64%	0.04%	0.92%	0.02%	5.01%	0.03%	859	17	580	72	16783	452
	After	6.10%	0.06%	4.81%	0.06%	1.63%	0.02%	4.47%	0.07%	949	14	634	20	17764	706
THER-ACID	Before	5.80%	0.05%	4.54%	0.05%	0.84%	0.07%	4.96%	0.09%	788	31	512	48	15448	414
	After	6.03%	0.02%	4.73%	0.02%	1.63%	0.02%	4.39%	0.03%	903	19	686	21	17373	1117
ACID	Before	5.79%	0.03%	4.49%	0.04%	0.82%	0.06%	4.97%	0.07%	905	5	693	6	15295	526
	After	6.08%	0.10%	4.54%	0.09%	0.99%	0.09%	5.09%	0.09%	1034	75	704	4	18501	281

Table 4-3 Different Fermentation Times, Evaluation

	Ferm Days	TS (%)		VS (%)		TDS (%)		TSS (%)		pH		VFA		sAMM		sP		sCOD	
		Avg.	S.D	Avg.	S.D	Avg.	S.D	Avg.	S.D	Avg.	S.D	Avg.	S.D	Avg.	S.D	Avg.	S.D	Avg.	S.D
Seed	0	5.3	0.03	4.02	0.01	1.10	0.08	4.19	0.09	5.71	0.02	6093	339	1087	25	832	33	19989	783
	2	5.9	0.11	4.38	0.02	1.19	0.04	4.73	0.12	5.65	0.10	6260	104	1140	61	892	25	21094	470
	3	6.1	0.20	4.33	0.18	0.86	0.01	5.22	0.19	5.63	0.03	6013	225	1167	32	869	15	22122	766
	6	6.2	0.40	4.43	0.31	1.54	0.03	4.66	0.37	5.63	0.01	5640	207	1117	60	852	22	20649	1885
TPS	0	5.3	0.04	4.09	0.06	1.54	0.08	3.70	0.09	5.83	0.03	4867	155	780	68	702	35	16492	2191
	2	5.6	0.06	4.41	0.05	0.83	0.01	4.81	0.05	5.87	0.02	5250	89	959	76	663	27	17903	772
	3	5.6	0.04	4.38	0.03	1.16	0.02	4.44	0.05	5.91	0.01	5343	343	1150	79	745	37	18486	322
	6	5.5	0.03	4.26	0.03	1.04	0.03	4.44	0.00	6.01	0.03	5147	210	1064	69	761	57	17244	633
50/50 mix	0	5.4	0.04	4.18	0.04	1.75	0.03	3.67	0.06	5.87	0.01	4373	278	814	44	792	29	14866	716
	2	5.8	0.07	4.38	0.06	0.89	0.01	4.87	0.08	5.95	0.01	5247	156	976	73	828	16	19836	613
	3	5.9	0.15	4.50	0.13	1.54	0.03	4.38	0.12	5.95	0.02	5420	272	1290	200	983	53	20787	1801
	6	5.6	0.32	4.21	0.25	1.02	0.05	4.54	0.36	5.97	0.04	5993	376	975	48	943	44	19867	1130
TWAS	0	5.8	0.04	4.32	0.03	2.00	0.05	3.82	0.07	5.94	0.02	4780	217	833	84	855	23	14513	881
	2	5.9	0.07	4.37	0.05	0.96	0.03	4.96	0.08	5.87	0.02	5593	206	1008	89	960	36	18716	1315
	3	6.0	0.06	4.38	0.04	1.54	0.02	4.43	0.07	5.91	0.03	6007	290	1233	59	1060	62	21661	1496
	6	5.7	0.11	4.12	0.14	1.09	0.14	4.60	0.04	5.92	0.03	6263	309	1103	95	1110	40	21201	1158

Table 4-4 Different Temperature Fermentations

		TS		VS		pH		sAMM (NH_3-N mg/L)		sP (PO_4-P mg/L)		sCOD (mg/L)	
		Avg.	S.D	Avg.	S.D	Avg.	S.D	Avg.	S.D	Avg.	S.D	Avg.	S.D
Seed	Before	5.69%	0.01%	4.20%	0.01%	5.68	0.01	1170	52	1634	68	25941	1106
	After 45C	5.01%	0.16%	3.52%	0.12%	5.72	0.07	1318	59	1687	194	27537	1470
	After 55C	5.24%	0.12%	3.74%	0.09%	5.65	0.06	1201	17	1693	127	27828	966
TPS	Before	5.05%	0.02%	3.87%	0.03%	5.78	0.01	986	36	1078	30	23318	390
	After 45C	4.50%	0.03%	3.31%	0.03%	5.92	0.01	1185	20	1150	106	26862	230
	After 55C	4.62%	0.21%	3.43%	0.16%	5.69	0.05	1161	198	1251	75	25895	678
50/50	Before	5.36%	0.03%	3.98%	0.01%	5.73	0.01	1017	25	1278	35	22674	716
	After 45C	4.66%	0.02%	3.34%	0.00%	5.93	0.02	1243	46	1333	74	27475	1000
	After 55C	4.94%	0.10%	3.63%	0.10%	5.64	0.06	1050	38	1486	83	26954	322
TWAS	Before	5.08%	0.02%	3.13%	0.02%	5.77	0.02	1037	51	1435	109	24239	390
	After 45C	4.31%	0.10%	3.57%	0.09%	5.90	0.03	1311	50	1520	161	28365	759
	After 55C	5.11%	0.10%	3.63%	0.08%	5.62	0.05	1146	32	1632	113	27675	253
50/50 WAS	Before	4.68%	0.01%	3.48%	0.00%	5.82	0.01	887	21	1162	10	21178	423
	After 45C	4.13%	0.03%	2.92%	0.09%	5.93	0.02	1126	13	1200	75	24990	575
	After 55C	4.17%	0.02%	3.02%	0.03%	5.69	0.06	1108	58	1356	68	24070	186
WAS	Before	3.74%	0.04%	2.16%	0.02%	6.27	0.01	866	15	1110	45	18647	618
	After 45C	4.01%	0.09%	2.85%	0.08%	5.94	0.02	1086	1	1320	75	22628	401
	After 55C	3.79%	0.01%	2.83%	0.30%	5.72	0.03	1055	78	1428	160	22459	266

Table 4-5 Different Dilution Fermentations

		TS		VS		pH		sAMM		sP		sCOD	
		Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.
SEED	Before	5.86%	0.15%	4.19%	0.44%	5.65	0.08	1373	122	1344	63	25128	950
	After	6.31%	0.30%	4.83%	0.62%	5.68	0.05	1378	47	1424	49	28856	1287
WAS 1:1	Before	5.29%	0.11%	3.76%	0.26%	6.04	0.04	1266	11	1229	40	22628	858
	After	5.04%	0.14%	3.68%	0.14%	5.85	0.03	1285	39	1258	25	28390	566
WAS 1:2	Before	4.81%	0.14%	3.60%	0.15%	6.18	0.03	1189	57	1093	86	21309	1577
	After	4.63%	0.10%	3.43%	0.09%	5.93	0.02	1226	26	1184	34	25785	716
WAS 1:3	Before	4.52%	0.05%	3.22%	0.11%	6.27	0.03	1114	76	1123	45	20940	759
	After	4.49%	0.24%	3.29%	0.19%	6.00	0.05	1124	46	1107	43	24505	575
WAS 1:4	Before	4.29%	0.12%	3.12%	0.08%	6.27	0.05	1105	44	1083	12	20281	497
	After	4.15%	0.20%	3.07%	0.09%	6.04	0.04	1152	38	1099	66	22784	1018
WAS 1:6	Before	4.15%	0.10%	3.06%	0.08%	6.33	0.07	1001	24	1056	37	18900	582
	After	4.07%	0.09%	2.93%	0.13%	6.09	0.03	1069	41	1061	36	22821	377

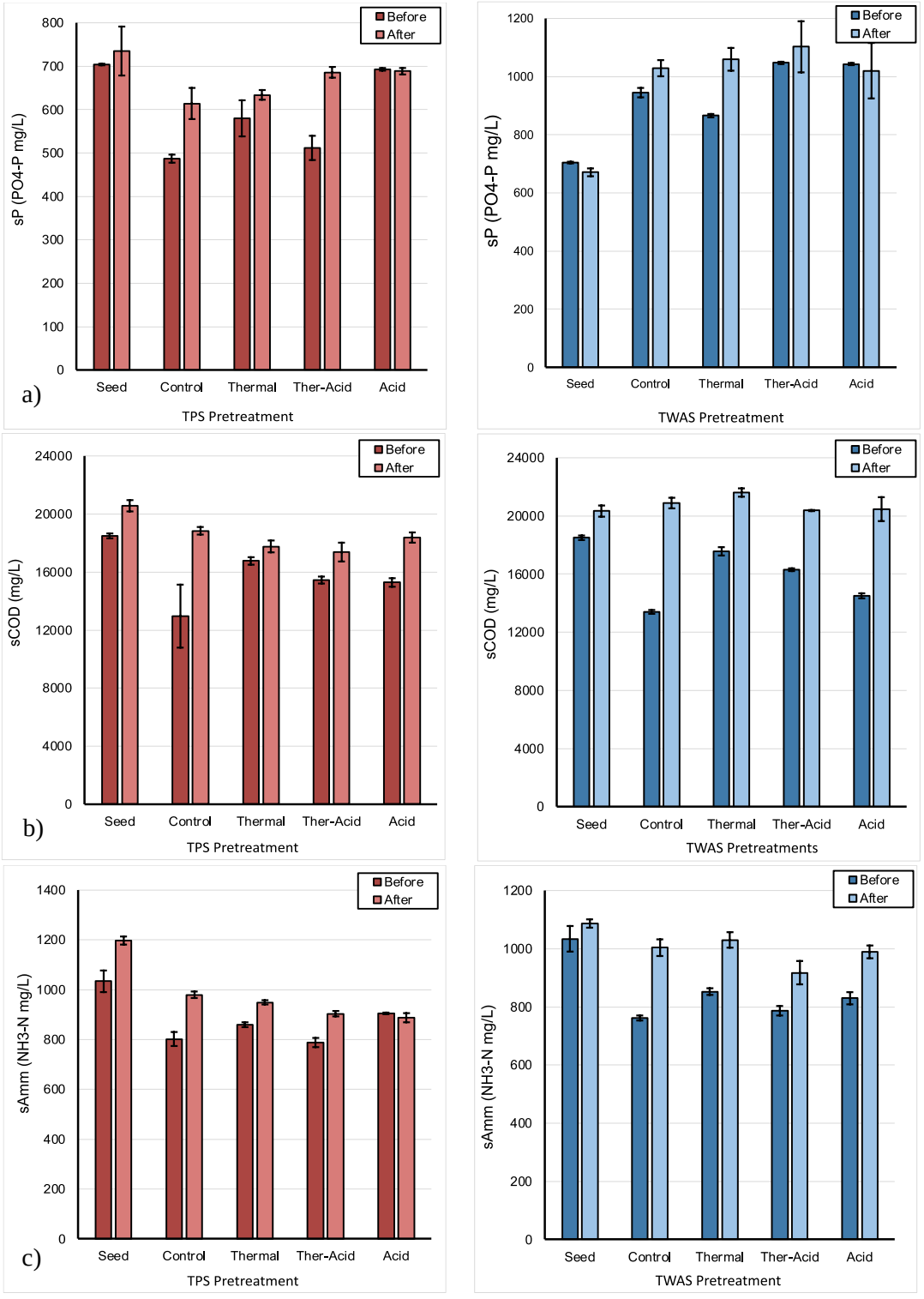

Figure 4-1 Nutrient Solubilization after thermophilic AD of separated feedstocks subjected to different pretreatments. Red graphs correspond to TPS, and blue graphs correspond to TWAS fermentations. a) Phosphorus solubilization, b) COD changes, and c) ammonia solubilization.

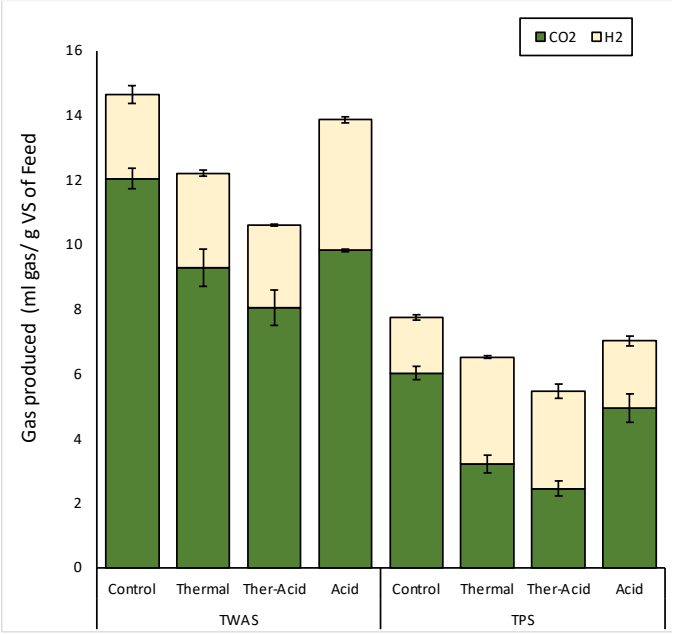

Figure 4-3 Gas production during thermophilic AD of separated pretreated feedstocks. All production was normalized to ml of gas at STP generated per g of volatile solids added from the feed.

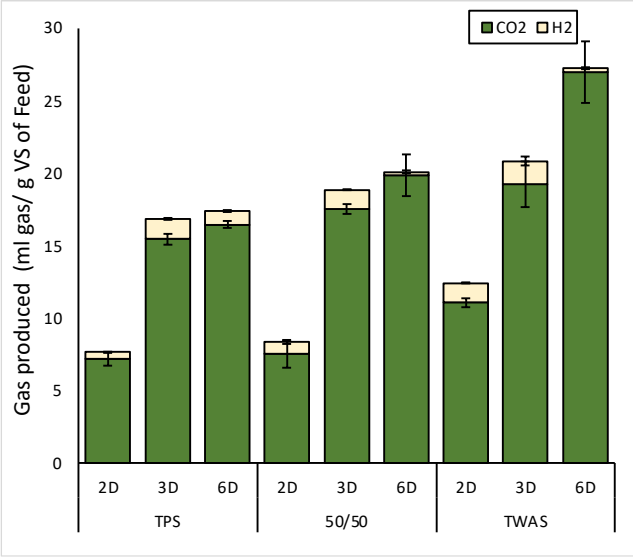

Figure 4-2 Gas production after different durations of thermophilic AD. All production was normalized to ml of gas at STP generated per g of volatile solids added from the feed.

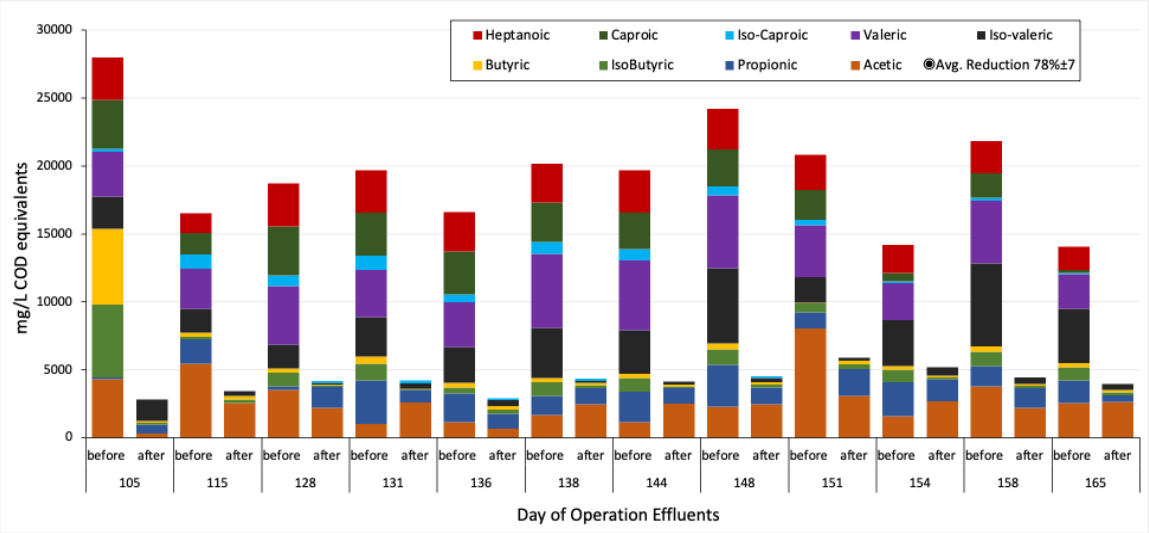

Figure 4-4 VFA composition change in liquid fraction of digestate, before and after high-rate digestion.

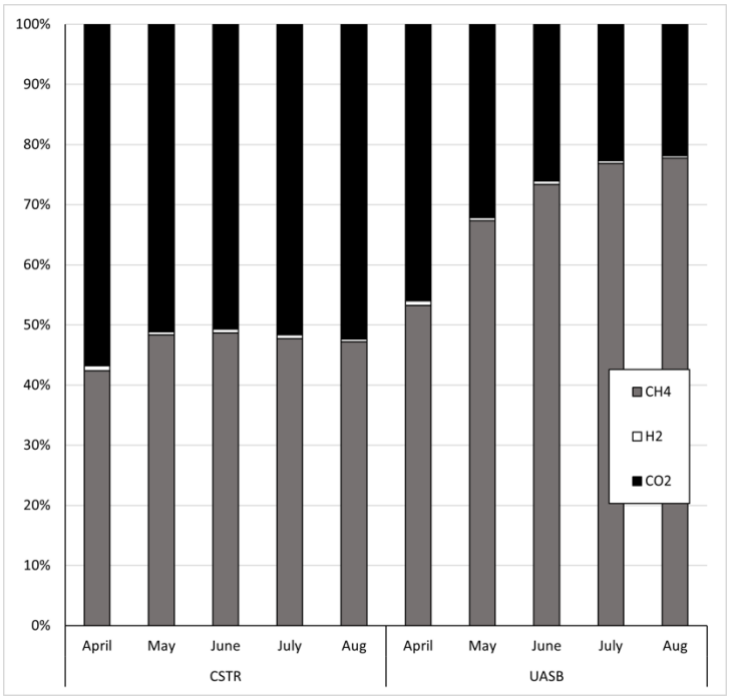

Figure 4-5 Average monthly gas compositions in each reactor.

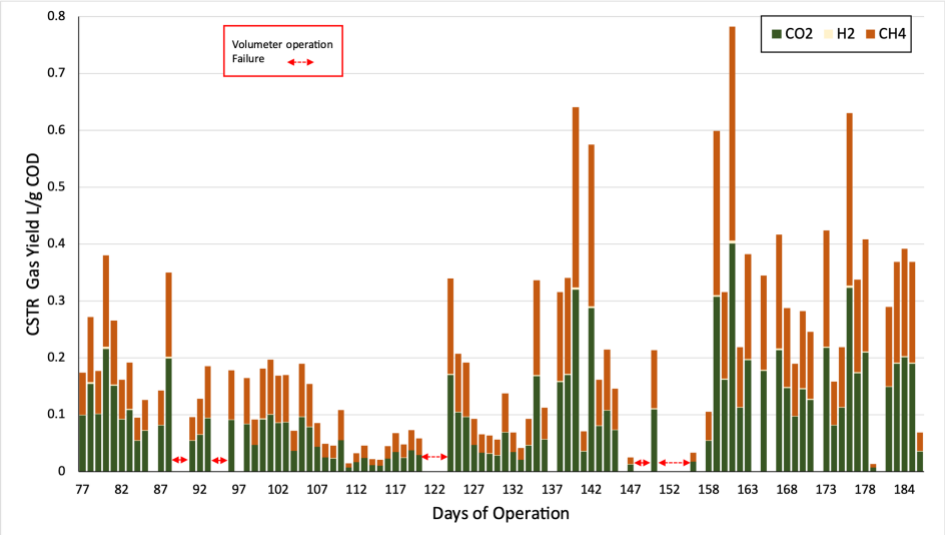

Figure 4-6 Daily biogas yield and composition in a thermophilic-acid CSTR digestor during systems' operation.