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Conceptual system for sustainable and next-generation wastewater resource recovery facilities

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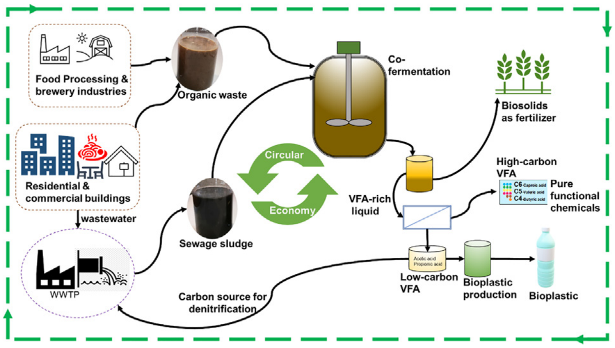
HIGHLIGHTS

- A system for waste resource recovery facility is envisaged to extract bioproducts.
- Anaerobic treatment of mainstream wastewater is proposed to produce biogas.
- VFA is produced as a platform chemical from sludge and external organic waste.
- VFA is used for denitrification, PHA production, or recovered as one-type VFA.
- Qualitative environmental sustainability assessment depicts a positive outlook.

GRAPHICAL ABSTRACT



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ABSTRACT

Shifting the concept of municipal wastewater treatment to recover resources is one of the key factors contributing to a sustainable society. A novel concept based on research is proposed to recover four main bio-based products from municipal wastewater while reaching the necessary regulatory standards. The main resource recovery units of the proposed system include upflow anaerobic sludge blanket reactor for the recovery of biogas (as product 1) from mainstream municipal wastewater after primary sedimentation. Sewage sludge is co-fermented with external organic waste such as food waste for volatile fatty acids (VFAs) production as precursors for other bio-based production. A portion of the VFA mixture (product 2) is used as carbon sources in the denitrification step of the nitrification/denitrification process as an alternative for nitrogen removal. The other alternative for nitrogen removal is the partial nitrification/anammx process. The VFA mixture is separated with nanofiltration/reverse osmosis membrane technology into low-carbon VFAs and high-carbon VFAs. Polyhydroxyalkanoate (as product 3) is produced from the low-carbon VFAs. Using membrane contactor-based processes and ion-exchange techniques, high-carbon VFAs are

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Abbreviations: AD, anaerobic digestion; AnAOB, anammox bacteria; AOB, ammonia-oxidizing bacteria; C/N, carbon/nitrogen ratio; COD, chemical oxygen demand; EGSB, expanded granular sludge blanket; HRT, hydraulic retention time; IFAS, integrated fixed-film activated sludge; LCA, life cycle assessment; MF, microfiltration; MMC, mixed microbial culture; N/DN, nitrification and denitrification; NF, nanofiltration; NOB, nitrite-oxidizing bacteria; PDMS, polydimethylsiloxane; PHA, polyhydroxyalkanoate; PN/A, partial nitritation/anammox; PTFE, polytetrafluoroethylene; PV, pervaporation; RO, reverse osmosis; SBR, sequencing batch reactor; TDDA, tridodecylamine; TOA, trioctylamine; TSS, total suspended solids; UASB, upflow anaerobic sludge blanket; UF, ultrafiltration; VFA, volatile fatty acid; VPMC, vapor permeation membrane contactor; WWTP, wastewater treatment plant.

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recovered as one-type VFA (pure VFA) and in ester forms (product 4). The nutrient-rich fermented and dewatered biosolid is applied as a fertilizer. The proposed units are seen as individual resource recovery systems as well as a concept of an integrated system. A qualitative environmental assessment of the proposed resource recovery units confirms the positive environmental impacts of the proposed system.

1. Setting the scene

The ultimate aim of wastewater treatment is to remove contaminants before discharging the water into the environment to safeguard the natural ecosystem and public health. Hence, the principal focus of wastewater treatment plants (WWTPs) is to meet national and international effluent quality standards. In view of this, WWTPs are typically designed to meet certain requirements often using destructive means to remove substances that may pose threat to the environment, without any major resource-efficient considerations (Ahmetović et al., 2014). Globally, it costs an amount of US$ 0.35 to 2.92 (€0.3–2.5) for collecting and treating a cubic meter of wastewater (KPMG International, 2017). Energy accounts for about 25–40 % of these operating costs, with energy consumption ranging between approximately 0.3–2.1 kWh/m^3 of treated wastewater (Panepinto et al., 2016).

In recent times there have been efforts to transition into a fossil-free society due to the alarming adverse effects of petroleum-based products on the climate. To achieve this, WWTPs ought to be shifted from energy-consuming to energy-producing entities. Therefore, there is a need to implement innovative technologies to produce energy and functional materials through a bio-based approach from sustainable sources. Biogas, nutrients (phosphorus and nitrogen), polyhydroxyalkanoates (PHA), cellulose fiber, volatile fatty acids (VFAs), heat, and metals are some of the resources that can be recovered from wastewater (Kehrein et al., 2020). Until now, biogas is the main resource that is usually recovered from WWTPs through anaerobic digestion (AD) of sewage sludge from the WWTPs. The AD process includes a cascade of reactions with intermediate products such as VFAs with higher values. VFAs are short-chain carboxylic acids such as acetic, propionic, butyric, and caproic acids. VFA recovery from wastewater can be coupled with the recovery of nutrients and metals such as phosphorus (Crutchik et al., 2018) and nickel (Molaey et al., 2021), respectively. Moreover, VFA can be used to replace conventional fossil-based carbon sources such as methanol to optimize enhanced biological phosphorus removal processes of WWTPs (Qi et al., 2021). Other applications of VFAs include the production of PHA, hydrogen, bioelectricity, and biodiesel (Atasoy et al., 2018).

Resource recovery from WWTPs contributes to environmental sustainability, which relates to the UN Sustainable Development Goals particularly goals 6, 7, 11, and 12. This leads to clean water and affordable energy production, contributing to a sustainable society, and reducing the consumption of fossil-based materials. Because of this, regional bodies and nations are making the effort to reduce the overreliance on petrochemicals and fossil fuels through a switch to the usage of bioproducts. Examples of policies put in place to obtain a sustainable society include the EU CO_2 emission trading system (European Union, 2020), market mechanisms on fossil fuels (Gavrilescu and Chisti, 2005), and the new Roadmap for the Global Energy Sector for Net Zero by 2050 (International Energy Agency, 2021). Next-generation carbon-neutral technologies are needed to turn the inherent resources in wastewater into new bio-based products and not only methane to create zero-waste approaches for a closed loop in the circular economy model.

In recent times, several technological solutions have been investigated by researchers to shift WWTPs to resource recovery facilities. While these technologies present the needed solutions, their implementations in the already existing and new WWTPs have been very slow (Kehrein et al., 2020). These resource recovery solutions are often presented in isolation without clear suggestions as to how to integrate them into the design of the WWTPs. Thus, there are only a few studies on an integrated approach to shifting WWTPs to resource recovery facilities (Chrispim et al., 2020). Given this, the current study aimed to conceptualize an integrated system based on researched technological solutions to shift WWTPs to resource recovery facilities. A self-sufficient resource recovery system that will close the material loop for wastewater treatment plants and produce valuable bio-based products is proposed. The current study proposed individual resource recovery systems as well as a concept of integrated systems. Therefore, different components can be adapted depending on the need and possibilities of the WWTP under question.

2. Methodology

This article is based on experience and knowledge over the last years on the development of innovative technologies for wastewater treatment with a focus on resource recovery. The research works of authors and support by literature from other sources are presented. Based on the results of previous studies, this study proposes a new design of a conceptual recovery system for wastewater. The study focuses on the mainstream treatment of municipal wastewater through direct anaerobic treatment and nutrient removal processes as well as side-stream fermentation of sewage sludge and external organic waste to produce VFA as a platform chemical for other bioprocesses. Moreover, a qualitative sustainability assessment of the proposed system is done. The environmental analysis is done for each major component of the system.

3. A recommended approach to next-generation wastewater resource recovery facilities

The proposed wastewater resource recovery system combines the anaerobic treatment of mainstream wastewater and the co-fermentation of sewage sludge with external organic waste like food waste (Fig. 1). The process leads to material recycling within the system. The direct anaerobic treatment of pre-settled wastewater will convert dissolved organics to biogas (product 1) using upflow anaerobic sludge blanket (UASB) reactor which can be used within the facility for heating. Part of the mixed VFAs (product 2) produced from the co-fermentation can be used in place of traditional carbon sources such as methanol and acetic acid for denitrification. Membrane separation technique is proposed to be employed to separate the remaining missed VFAs into high-carbon VFAs (4C-6C) with higher market value and low-carbon VFAs (2C-3C). Low-carbon VFAs may be used in post-stream bioprocess like PHA production (product 3). High-carbon VFAs can be further separated and purified to produce market-ready pure (one-type) VFAs (product 4).

3.1. Preliminary and Primary treatment

The preliminary treatment stage involves conventional processes. This includes screens that consist of bars with spaces for removing large materials which may find themselves in the wastewater. In the grit chamber, solids such as sand, gravel, eggshells, cinders, and coffee are settled out of the wastewater and removed. Screens and grit chamber are necessary to prevent damage to pumps caused by abrasion and operational difficulties in the primary clarifier and other steps of the wastewater treatment system (Muralikrishna and Manickam, 2017). However, this is still an opportunity to improve the pretreatment stage to recover value-added products.

Chemical-enhanced primary sedimentation is needed to remove phosphorus and particulate chemical oxygen demand (COD) from wastewater before the water enters the UASB reactors. Phosphorus removal by

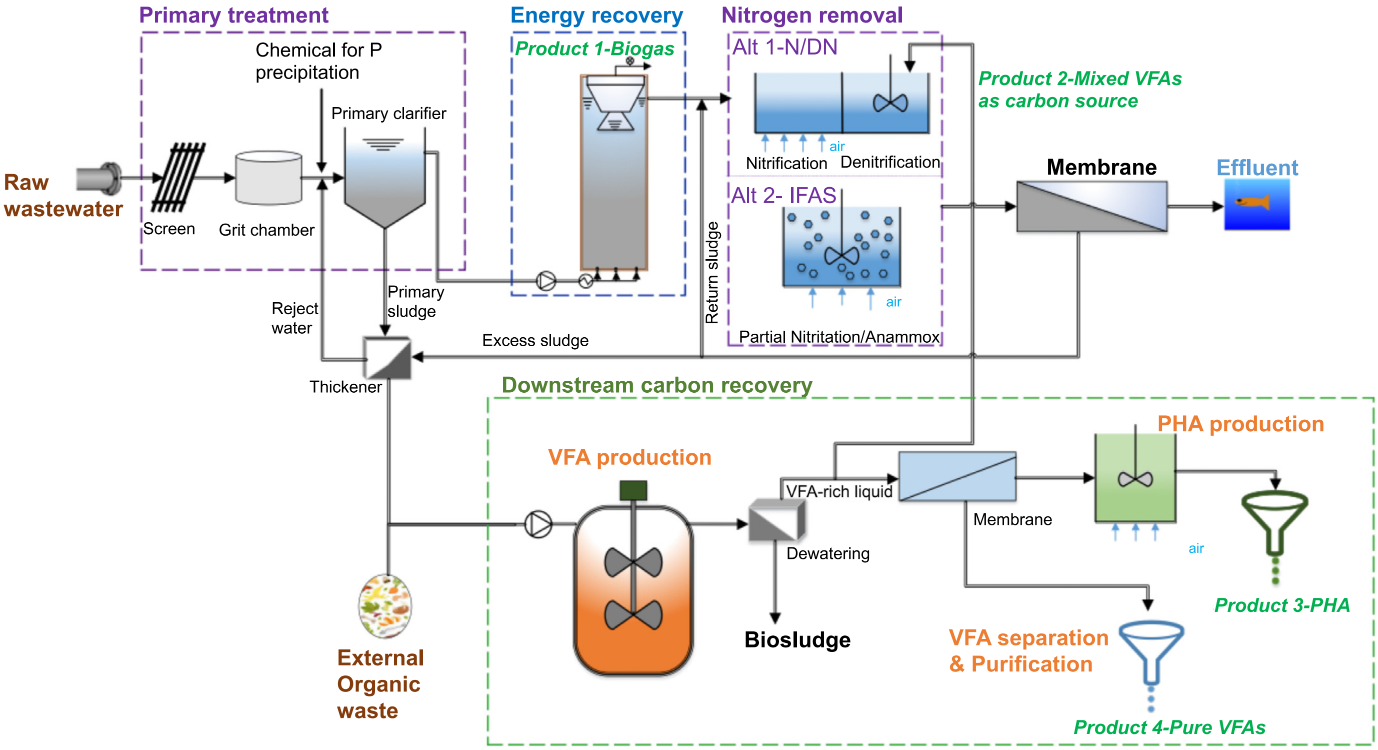

Fig. 1. Schematic of the conceptual next-generation wastewater resource recovery facility (Alt is alternative; IFAS is integrated fixed-film activated sludge).

chemical precipitation is proposed in the conceptual design. This involves the addition of metal salts (usually ferric or aluminum salt) to effluent before the primary clarifier. Chemical precipitation is one of the most common P-removal options because of its ability to help WWTPs comply with stringent effluent standards (Bunce et al., 2018). In the EU for instance, the standards for total phosphorus are 2 mg/L and 1 mg/L for WWTPs with 10,000–100,000 PE and >100,000 PE, respectively. This is even stricter in some countries like Sweden where the standard is as low as 0.5 mg/L (Preisner et al., 2020). The captured P will be in the primary sludge which presents an opportunity for phosphorus recovery. When the sludge is fermented for VFA and other bioproducts recovery, the biosolid which will be rich in phosphorus can be used as fertilizer.

A major component of the WWTP is a primary clarifier where the wastewater's physical sedimentation process occurs. Most of the suspended solids (up to 98 % of total suspended solids (TSS)) are removed from the wastewater during chemically-enhanced primary sedimentation (Ansari and Farzadkia, 2022). This is because chemicals for the precipitation of P, also remove colloidal solids in the primary clarifier. In some cases, fine-mesh sieves are used in place of the primary clarifier to recover cellulosic primary sludge (Ghasimi et al., 2016). The recovered cellulose can be used as adhesion binders for asphalts, as raw material for paper products and to produce bioproducts (Crutchik et al., 2018). However, this may not be an option if chemical phosphorus removal is being considered. Primary sludge with high content of organic matter is the main source for further handling to produce bioproducts and recover other chemicals such as phosphorus and heavy metal.

3.2. Biogas recovery (product 1) through direct anaerobic treatment

Conventional activated sludge system for handling municipal wastewater usually needs aeration which is energy-intensive and increases immensely the cost of operation. During the activated sludge process, organic matter in the wastewater is converted into carbon dioxide which increases the carbon footprints of WWTPs. Treating mainstream municipal wastewater anaerobically is a more sustainable alternative that can reduce energy consumption by WWTPs while producing energy which could lead to net positive energy systems.

High-rate processes such as UASB and expanded granular sludge blanket (EGSB) can be used for direct anaerobic treatment of municipal wastewater. In UASB and EGSB reactors, the influent wastewater passes through the bottom and flows upwards to the outlet. Anaerobic granule-based reactors use hydrodynamics of the system which is based on the upward flow rate and gravity to form a suspended sludge blanket with enriched anaerobic microorganisms in granule form. The microorganisms mineralize the organic matter in the wastewater under anaerobic conditions to produce biogas. Such reactors usually contain a three-phase separator which is placed in the upper part of the reactor to separate the mixture of water, suspended granules, and biogas (Lettinga and Hulshoff Pol, 1991).

High-rate granule-based technologies including UASB show higher performance due to the efficiency of the anaerobic granules in the mineralization of substrates in wastewater. Some of the characteristics of granule-based anaerobic systems that make them advantageous for directly treating wastewater include the good settling characteristics of the anaerobic granules which prevent biomass washout (Kiran et al., 2016). Moreover, the mixing resulting from the produced gas bubbles and influent flow is adequate to provide enough contact between the substrates and microorganisms without the need for any mechanical mixing (Subramanyam and Mishra, 2013; Wu et al., 2015). Due to the nature of the granular sludge and the distribution of microorganisms within the granule, granule-based anaerobic reactors could operate under harsh conditions such as oscillation in influent concentration, temperature, pH as well as high salinity (Kobayashi et al., 2018; Sudmalis et al., 2018). High-rate anaerobic reactors such as UASB and EGSB have been demonstrated to be successful in treating different kinds of wastewaters and are usually used for treating high-strength wastewater such as food industry wastewater. The treatment of low-strength wastewaters such as municipal wastewater with the UASB process is often found in regions with warmer climates where the temperature of the wastewater can be relatively higher. However, in temperate regions, due to lower temperatures of the wastewater especially in the winter times, the use of UASB for treatment of low-strength municipal wastewater is not popular, mainly due to low efficiency. Nonetheless, in recent times, the interest in employing anaerobic granule-based reactors for the treatment of low-strength wastewater, particularly municipal wastewater under sub-mesophilic conditions has gradually increased (Owusu-Agyeman et al., 2021b, 2019; Serrano León et al., 2018). There have been some suggestions to modify UASB to increase its efficiency at sub-mesophilic temperatures and to remove emerging contaminants such as micropollutants. Such modifications include coupling the UASB reactor with a digester and with a membrane (Faria et al., 2020; Petropoulos et al., 2019; Zhang et al., 2018). However, it has been shown that while such modifications may give slightly better performance, they could result in significantly increasing the cost of treating wastewater and the complexity of the design and making the UASB system a net negative energy system (Petropoulos et al., 2019). It is therefore necessary to understand the microbial dynamics of the granular sludge and how operation parameters influence the system in order to find ways to increase the efficiency of the UASB system under slow operating temperatures.

3.2.1. How feasible is it under sub-mesophilic temperatures?

The structure of the anaerobic granule sludge is an important factor that can determine the performance of the UASB system. There is a direct link between the structure of the anaerobic granules and their microbial community (Owusu-Agyeman et al., 2019). It was found in our recent study involving two pilot-scale UASB systems each with a working volume of 2.5 m^3 that the acetoclastic archaeal family *Methanosaetaceae* was more dominant in anaerobic sludge with bigger granules and multi-layered internal structure than in anaerobic sludge with smaller granules whose internal structures were not layered. The microbial population dynamics and the physiological structure might have contributed to the instability in the biogas production obtained at an operating temperature of 20 °C from the UASB reactor with a smaller granule size distribution (J. Wu et al., 2016). It is therefore necessary to ensure an effective sludge granulation stage during the start-up to have a robust granule-based anaerobic system (Xu et al., 2018). There has been a success in using microbial communities from soils and sediments in a low-temperature environment as inoculum for anaerobic treatment of low-strength wastewater at temperatures between 4 and 15 °C (Petropoulos et al., 2019, 2017). These developments reiterate the point that high-rate anaerobic granule-based systems are capable to replace conventional activated sludge systems for the treatment of mainstream municipal wastewater with comparative performance in terms of organic matter removal efficiency whereby energy is also produced.

The main bottleneck of treating municipal wastewater anaerobically at low temperatures is the low rates of hydrolysis which usually leads to the accumulation of particulates in the reactor. Therefore, usually, high hydraulic retention time (HRT) is needed to guarantee sufficient treatment efficiency. It was shown that low hydrolysis rates were obtained at HRTs lower than 10 h for municipal wastewater-fed UASB reactors operated under psychrophilic conditions (17–19 °C) (Serrano León et al., 2018). It could therefore be necessary to have chemically enhanced primary sedimentation before the granule-based anaerobic treatment to reduce the influent particulate matter. In the current concept where there exist distinct routes to recover organic carbon, having a primary sedimentation stage before the UASB reactor will ensure that the UASB can run efficiently with relatively lower HRT. In view of this, another study with the aforementioned UASB reactors was carried out to ascertain the implication of operating parameters on UASB performance. The COD removal efficiency of up to 85 % was obtained at an HRT of 5 h and operating temperature of 20 °C with effluent COD as low as 27 mg/L (Owusu-Agyeman et al., 2021b). This is much lower than the discharge limit set by the Council of the European Communities (91/271/EEC) for urban wastewater treatment plants (EEC, 1991). Other studies have also shown that the use of the UASB process for treating municipal wastewater under sub-mesophilic conditions could achieve satisfactory treatment efficiency. In a recent study, a COD removal efficiency of 79.3 % was attained at an HRT of 7.68 h and an operating temperature of 15 °C (Petropoulos et al., 2019).

Biogas recovery is one major aspect of direct anaerobic treatment of municipal wastewater. Besides saving energy by not aerating the system, biogas can be an additional resource for the wastewater treatment plant. In our study, a biogas production of 0.91 to 1.07 m^3/day was achieved for each reactor. It is known that one cubic of biogas is equivalent to 6 kWh of heat energy and 2 kWh of electric energy (Svenskt Gastekniskt Center AB, 2012) and therefore such an amount of energy can be produced from the biogas produced daily. The question is, can the granule-based anaerobic system be a self-energy sufficient system especially when operated at low temperatures for low-strength wastewater like municipal wastewater? The COD concentration of the mainstream municipal wastewater may not be adequate to produce the required amount of biogas to heat the UASB reactor to the mesophilic temperature range. Nonetheless, it has been shown in a study that, UASB treating low-strength domestic wastewater can be a positive energy system with a net positive energy of 0.04 kWh for a cubic of wastewater treated (Petropoulos et al., 2019). These results, therefore, give a promising outcome for the anaerobic granule-based system to be used to treat municipal wastewater at low temperatures and low hydraulic retention time which are comparable with the conventional waste-activated sludge system. When used for the treatment of high-strength municipal wastewater such as blackwater from a separate sewer system, the anaerobic granule-based system can produce even more energy. Nonetheless, using UASB instead of an activated sludge system will significantly reduce the cost of aeration. Under psychrophilic or sub-mesophilic conditions, recovery of methane is more difficult because it is dissolved in the liquid phase. Methane's solubility increases with decreasing temperature. It has been reported that dissolved methane could account for 40–50 % of methane generated in anaerobic treatment systems under sub-mesophilic temperatures (Smith et al., 2013). The issue of dissolved methane at sub-mesophilic temperatures can be mitigated by implementing dissolved methane techniques such as degassing membranes which can remove up to 98 % of dissolved methane (Stazi and Tomei, 2021). This will address the issue of greenhouse gas emissions and increase the recovered energy.

One challenge that can arise from directly treating municipal wastewater anaerobically at sub-mesophilic temperatures can be the high particulate matter that can build up in the reactor (Lettinga et al., 2001). This can be mitigated in the proposed system because of the use of a primary clarifier. Another challenge that could come up is a high concentration of sulphate which could lead to the production of hydrogen sulphide. This reduces the performance of the reactor the produced hydrogen sulphide could lead to the corrosion of metallic pipes. The issue of sulphate and hydrogen sulphide can be mitigated by recirculating the effluent of the nitrification tank to the UASB reactor to be used as a nitrate source for desulphurization (Bayrakdar et al., 2016). There may be no need for an additional denitrification tank as it can also serve as the denitrification unit by recirculating the effluent of the nitrification tank to the UASB reactor. However, the volume of the UASB reactor may need to be slightly larger. The effluent of UASB needs to be further treated to meet guidelines for not only nitrogen but also phosphorus and suspended solids. Nitrogen is removed by nitrification/denitrification or partial nitritation/anammox. Phosphorus is removed by chemical precipitation while the suggested membrane system will remove suspended particles.

3.3. Waste-derived VFA production

3.3.1. VFA production process

The AD is one of the most widely applied and approved technologies for wastewater and sludge treatment for more than a century because of its unique features: net energy production, sludge usage as fertilizer, less waste sludge production, treatment of hazardous chemicals and pathogens (Náthia-Neves et al., 2018). In recent times, AD technology has been developed to recover other valuable bio-based products aside from biogas. Notable among the emerging products from AD are the carboxylate platform chemicals (Bhatt et al., 2020).

There are four main stages involved in the AD process: (1) hydrolysis: where complex compounds in the wastewater are converted to simple compounds; (2) acidogenesis stage where VFAs, alcohols, etc. are formed (3) acetogenesis: H_2 and CO_2, as well as acetic acid, are formed from the products of stage 1 and 2; (4) methanogenesis: methane and CO_2 are formed from the products of other stages (Manchala et al., 2017). Thus, VFAs are formed at the acidogenesis and acetogenesis stages. The most common VFAs are acetic acid, propionic acid, butyric acid, valeric acid, and caproic acid (Lee et al., 2014). VFAs are used in many application areas such as chemical, food processing, and medical applications (Atasoy et al., 2018). Acetic acid is used in plastic, food processing, paints, and coating industries (Vidra and Németh, 2018). Propionic acid is used in the agricultural industry for animal feed, herbicides, and plasticizers production as well as in the pharmaceutical, food processing, cosmetic and chemical industries (Bhatia and Yang, 2017). Butyric acid is also utilized in the pharmaceutical, food and beverage, textile, and chemical industries (Dwidar et al., 2012). Furthermore, another valuable VFA is caproic acid, which is used directly as a feed additive, plant growth promoter, antimicrobial and raw material for lubricants, paint additives, and pharmaceuticals production (Cavalcante et al., 2017).

The market demand for VFAs is increasing and consequently, global production is also increasing. For instance, 9 million tons of acetic acid were produced in 2020 with projected production of about 12 million in 2026 (Expert Market Research, 2022). Additionally, the global production of caproic acid is projected to grow at a compound annual growth rate of roughly 5.6 % and will reach 252.8 million USD in 2027, from 172.5 million USD in 2027 (Research and Markets, 2022). However, currently, a large quantity of VFAs in the market (>90 %) are synthesized with petrochemicals (Agnihotri et al., 2022). Nonetheless, the interest in bio-based VFA production has been considerably increasing in the last decade. Bio-based VFA can be produced from many different waste streams. There have been several studies on microbial VFA production to address the bottleneck of limited production yield and challenges on the separation and purification of the end products, which strongly limits the potential industrial development of the current bio-based VFA production (Aghapour Aktij et al., 2020; Atasoy et al., 2018; Karp et al., 2018; Zhu et al., 2021). Numerous studies have been conducted to overcome these challenges by optimizing operational and environmental conditions, applying several pre-treatment methods, and using different strategies (e.g. bioaugmentation) to enhance the microbial community (Atasoy and Cetecioglu, 2021, 2020; Owusu-Agyeman et al., 2021a).

3.3.2. The practicality of VFA production from municipal waste streams

It is shown in our current study that primary sewage sludge can be a good substrate for VFA production. Moreover, it is shown that the fermentation of sewage sludge with other organic waste (including food waste) significantly improved VFA production yield and changed the composition of VFA into more valuable products (Owusu-Agyeman et al., 2020). The study revealed that the addition of 25 % (in terms of COD) of external organic wastes to primary sludge increased the VFA yield by about 20 % with an increase in the proportion of longer carbon-chain VFAs (particularly valeric and caproic acids). The practice of co-fermentation enhances waste-based bioproduction and waste management, simultaneously. Fermentation of sewage sludge and other organic wastes like food waste is therefore proposed in the current conceptual system. Moreover, it was seen in our study that the operation strategies can influence the VFA yield and composition. It was found that while batch reactors resulted in VFA with acetic acid as the dominant acid type, a reactor operated in a semi-continuous mode produced a VFA mixture dominated by caproic acid at the same operating pH of 5. Changes in pH can significantly influence VFA production and composition. In our current study where 3 parallel reactors were operated under different pH conditions, it was found that reactors operated at pH 5 and with no pH control achieved maximum VFA productions of 17 (Owusu-Agyeman et al., 2020) and 25 g COD/L (Owusu-Agyeman et al., 2023). However, the reactor operated at a pH of 10 achieved maximum VFA production of 30 g COD/L (Owusu-Agyeman et al., 2022). The effect of pH was not on VFA yield only but also on the VFA composition. VFAs produced by reactors operated at pH 5 and with no pH control had similar compositions and were dominated by caproic acid (≈ 50 %) (Owusu-Agyeman et al., 2023, 2020). The similarity in the VFA composition was explained by the fact that the pH of the no pH control reactor was in the range of 5.0–5.7 (Owusu-Agyeman et al., 2023). The higher caproic acid content in the VFA is a positive development because caproic acid is known to be produced mainly through an upstream process of chain elongation using short-chain VFA including acetic acid via β-oxidation with reductive agents such as ethanol, methanol, and lactic acid (Agler et al., 2012; Wu et al., 2018). However, the VFA produced by the reactor operated at pH 10 composed of about 70 % acetic acid. Moreover, the operating pH influenced the long-term operation of the reactors in that, unlike the pH 5 and no pH control reactors, the VFA production of the reactor operated at pH 10 reduced drastically to about 10.0 g COD/L after day 121st day of operation due to high alkalinity (9.9 g $CaCO_3$) and sodium inhibition due to dosing of NaOH for pH adjustment. The study on the hand showed the resilience of the VFA production system because reducing the pH from 10 to 9 led to a restoration of total VFA production ranging between 27 and 32 g COD/L (Owusu-Agyeman et al., 2022).

Other studies have also shown that the production of VFA from sewage sludge and other organic waste can be a sustainable resource recovery option. In a full-scale application, sludge fermentation was operated at alkaline pH of 10–11 to produce VFAs to be used as external carbon sources for enhancing biological nutrient removal in a WWTP (Liu et al., 2018). It was shown that a VFAs yield of 261.32 mg COD/g VSS was achieved. More importantly, the study concluded that VFA production presented a greater economic advantage than the biogas production process with net profits of 9.12 and 3.71 USD/m^3 sludge, respectively (Liu et al., 2018). Another study of co-fermentation of sewage sludge and food waste with no external control of pH resulted in a maximum VFA yield of 867.42 mg COD/g VS (Q.-L. Wu et al., 2016). Moreover, it is opined that VFA recovery from WWTPs can be done in conjunction with other products such as phosphorus. It has been estimated that coupling VFA production from primary sludge with phosphorus recovery will raise the potential market value of 0.46 €/capita·year to about 1.95 €/capita·year. Thus, the amount of 2.9 kg COD/capita·year of VFA is 3.0 m^3/capita·year of methane and 0.15 kg/capita·year of struvite can be produced from a global average of 13–15 kg TSS/capita·year of cellulosic primary sludge (Crutchik et al., 2018). Besides VFAs, organic waste streams can be used as feedstock for the production of other value-added bioproducts including single-cell animal/fish feed, bioethanol, and lactic acid (Ahmad et al., 2020; Manyuchi et al., 2018; Pawar et al., 2020).

One major bottleneck of waste-derived VFA production with mixed microbial cultures (MMCs) is the production of VFA mixture with different compositions (Atasoy et al., 2018). As has been proposed in the conceptual design, VFA separation into pure products will be employed. Nonetheless, there has been success in increasing the dominancy of one acid type from mixed culture production through bioaugmentation. It has been shown that bioaugmentation of an MMC reactor with *Clostridium butyricum* resulted in an increase in butyric acid production from 260 mgCOD/L to 2889 mgCOD/L (Atasoy and Cetecioglu, 2020). While in that study dairy industry wastewater was used, the result is an interesting one and could be applied to municipal waste streams since MMCs were involved in both cases. These encouraging results from our studies and other studies over the world give a promising impression that the VFA production which is part of the current proposed conceptual system is feasible. Fig. 2 illustrates the various product pathways of VFA within the system.

3.4. Nitrogen removal

3.4.1. Nitrification and denitrification (N/DN)-alternative I

Advanced biological treatment is often carried out in municipal WWTPs with nutrient release limit requirements for the removal of nitrogen and phosphorus. Access to readily degradable organic material is crucial to process efficiency and performance. Conventional nitrogen removal technology is based on nitrification and denitrification processes, where ammonium is converted into nitrate in the nitrification step and nitrate into

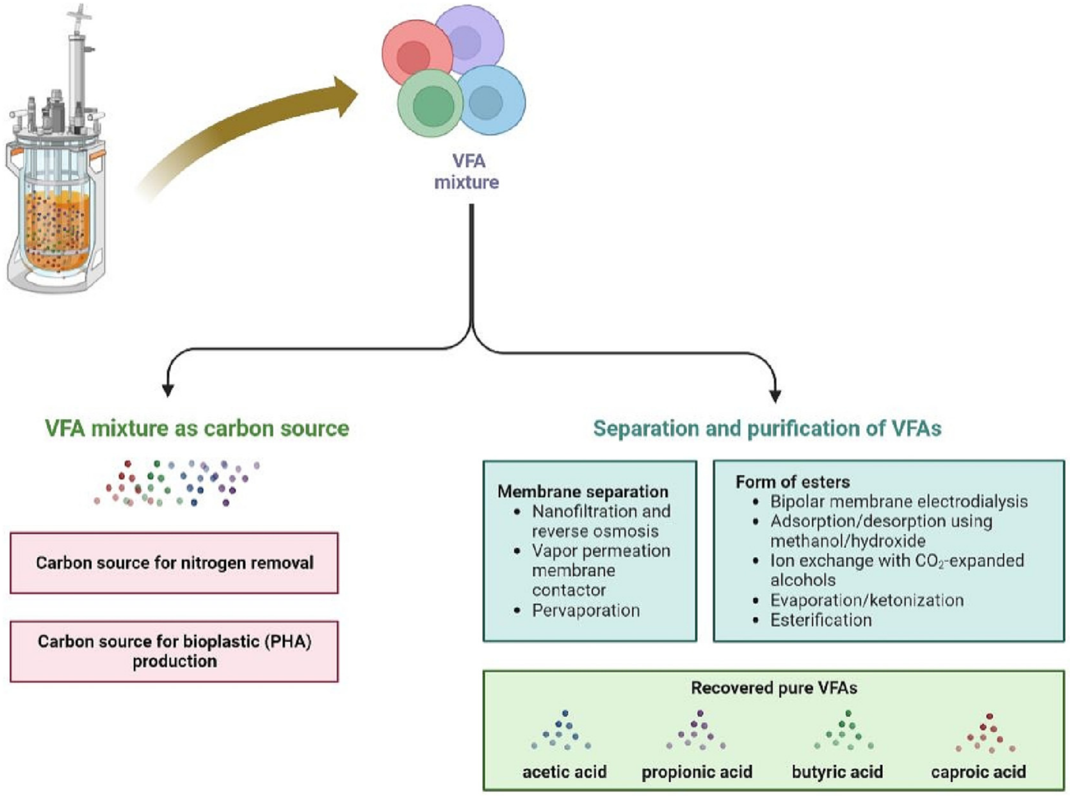

Fig. 2. Schematic illustration showing the various bioproducts from VFAs.

nitrogen gas in the denitrification step. The denitrification step usually requires a carbon source as an electron donor. Often municipal wastewater has an insufficient carbon/nitrogen (C/N) ratio and/or the carbon is not easily degradable. Therefore, organic carbon from external sources is often added to facilitate the denitrification process. Methanol, ethanol, and acetic acid are some of the common conventional external carbon sources used in municipal WWTPs for denitrification (Cherchi et al., 2009). The use of external carbon sources increases treatment costs and leads to a higher carbon footprint because they are often fossil-based (MacDonald, 1990; Yerushalmi et al., 2013). VFAs from the fermentation of sewage sludge and other organic wastes are easily assimilated and present an opportunity to be used as carbon sources for denitrification within the WWTPs to close the loop. Although the N/DN process is an established process with a proven record for removing nitrogen from wastewater, it requires energy for aeration in the nitrification process and an external carbon source for the denitrification process.

3.4.2. The use of VFA as a carbon source (product 2)

The VFAs produced from municipal waste streams have been tested for efficiency as carbon sources for denitrification and compared with commercial acetate and commercial methanol. Using the VFAs as carbon sources for denitrification resulted in a higher denitrification rate than commercial methanol and acetate. The fermentation effluents obtained specific denitrification rates of 14–16 mg NO_x-N/(g VSS·h), while the specific denitrification rate for acetate was 10 ± 1 mg NO_x-N/(g VSS·h) (Owusu-Agyeman, 2022). It was observed that there was no significant difference between the denitrification obtained by the acetic acid-dominated VFA and caproic acid-dominated VFA. This shows that the VFA composition does not influence the denitrification rate. Methanol achieved a specific denitrification rate of 5 ± 1 mg NO_x-N/(g VSS·h), i.e., the specific denitrification rate for the VFA-rich liquids was almost 3 times higher than for methanol (Owusu-Agyeman et al., 2020). Methanol achieved the lowest denitrification rate because methanol can be used directly by only methanol-assimilating bacteria while acetate and VFA-rich liquids are readily biodegradable. It was observed that there was no significant difference between the denitrification rate obtained by using the acetic acid-dominated VFA and caproic acid-dominated VFA as carbon sources. This shows that the VFA composition does not influence the denitrification rate. Moreover, using the VFAs as carbon sources for the denitrification of nitrified UASB effluent in a continuous mode of operation resulted in nitrate removal of up to 98 % efficiency (Owusu-Agyeman et al., 2023).

The results showed that valuable carbon sources can be recovered from municipal wastewater treatment plants through anaerobic treatment of primary sludge and external organic waste. This technology can contribute to optimal resource recycling and sustainable wastewater treatment in the future. The challenge now is the VFA-rich liquid usually contained phosphorus and nitrogen which may add to the total nutrients and lead to missing the guideline values. Nonetheless, a study using VFA-rich liquid as a carbon source for biological nutrient removal from municipal wastewater resulted in total phosphorus and nitrogen efficiencies of 89.65 % and 94.39 %, respectively (Liu et al., 2018). These results led to treated wastewater with nutrient concentrations that met the discharging standards.

3.4.3. Partial nitritation/anammox (PN/A)-alternative II

The partial nitritation/anammox (PN/A) is a cost-effective nitrogen removal process that requires low energy and no additional carbon. The PN/A process is often applied to treat high ammonium wastewater such as landfill leachate, reject water, and anaerobic digester effluent. The technology that is based on autotrophic deammonification consists of two processes: partial nitritation (where half of the ammonium is converted into nitrite) and anammox (where nitrite reacts with ammonium into nitrogen gas).

An increasing number of full-scale applications of the Anammox process for nitrogen removal from reject water (high temperatures of 30 °C and high ammonium concentrations) showed that for wastewaters with a low C/N ratio, energy requirements can be substantially lowered, compared to the traditional nitrification/denitrification process (Lackner et al., 2014). Moreover, emissions of CO_2 and N_2O are lowered. However, applying the PN/A technology for nitrogen removal from mainstream wastewater with low temperatures and low ammonium concentrations is still a challenge. The use of the PN/A process for mainstream nitrogen removal will allow the WWTPs to recover organic carbon present in wastewater rather than using it in the nitrogen removal process. In this new proposed system, the UASB technology is used to recover organic carbon from mainstream wastewater before applying the PN/A process for nitrogen removal from the UASB effluent with a low COD/N ratio.

The mainstream PN/A process is operated in different reactor configurations. These include sequencing batch reactors, moving bed biofilm reactors, integrated fixed-film sludge (IFAS) reactors, and plug flow or fully mixed continuous flow systems. The IFAS configuration that couples suspended sludge (responsible for partial nitritation) and moving bed biofilm (responsible for anammox) has been found to perform better than the moving bed biofilm reactor because IFAS ensures an efficient PN/A process (Malovanyy et al., 2015). An IFAS system helps to suppress nitrite-oxidizing bacteria activity while ensuring substantial growth of ammonium oxidizing bacteria (AOB) to promote partial nitritation step and consequently increase anammox bacterial activity (Persson et al., 2017; Trojanowicz et al., 2021).

There have been studies on coupling IFAS with UASB for mainstream nitrogen removal on a pilot scale at low temperatures in recent years with promising results (Malovanyy et al., 2015; Pedrouso et al., 2019; Trojanowicz et al., 2021). A sufficient nitrogen removal efficiency of up to 73 % has been achieved for the UASB-IFAS systems (Pedrouso et al., 2019). Thus, the application of the new process configuration with separate stages for organic carbon and nitrogen removal will result in improved nitrogen elimination and increased biogas production. This new solution will lead toward resource-effective WWTPs in the future.

3.5. PHA (product 3) production from waste-derived VFAs

One attractive application of waste-derived VFAs is their bioconversion into PHAs. PHAs are biocompatible and biodegradable polyesters and have similar characteristics to conventional petrochemical-derived plastics, they are deemed a viable green alternative. More than 300 bacterial and archaeal species have been identified as PHA producers. These species accumulate PHAs intracellularly as energy and carbon storage under environmental stress conditions such as nitrogen starvation.

The main barrier to commercial PHA production is its cost, which is 3–6 times higher than petroleum-derived plastics (Khatami et al., 2020). PHA production cost can be potentially reduced by 19 % using MMCs (Gurieff and Lant, 2007). Moreover, the use of waste streams as carbon sources is proposed as a plausible solution to reduce the cost of PHA production (Khatami et al., 2020). Production of PHAs using VFAs has traditionally been known as a 3-step process (Fig. 3), involving 1) production of VFAs through fermentation, 2) enrichment of the MMC with high PHA-storing species through feast and famine regimes 3) PHA accumulation (Valentino et al., 2017). PHAs have a wide application area including packaging, medical, chemicals, food industry, and membranes (Chen, 2009). However, the high costs of their extraction and recovery impose limitations on their cost competitiveness. Therefore, finding other applications for the PHAs without extraction is contemplated.

In this context, PHA production using VFA-rich effluents from the fermentation of municipal waste streams has been studied. When MMCs were used together with VFA-rich effluents to produce PHAs, a positive selection of PHA producers was observed (Perez-Zabaleta et al., 2021). After 50 days of enrichment in sequencing batch reactors, the biomass of PHA content of around 20 % w/w and a yield of 0.08 g PHA/g VFA was attained. None of the VFAs present in the effluents accumulated in the medium and all were consumed eventually. The growth rates were around 0.1 h^{-1}, a competitive growth rate for the MMCs, showing that the VFA effluents were not toxic to the cells. The cultivation broth was only supplemented with a minimal and inexpensive salt medium by virtue of VFA effluents containing other essential nutrients such as nitrogen and phosphorous that can be used by the microorganisms. Another positive aspect of the VFA-rich effluents as carbon sources for PHA was the carbon/nitrogen ratio. The ammonium contents in the VFA-rich effluents were around 0.5–1.0 g/L NH_4^+. These concentrations allow using the VFAs effluents as the only feed-nutrient in the PHA accumulation step (fed-batch cultivations), where the nitrogen should be limited to boost PHA production by reducing cell growth and the carbon source (VFA) should be high during the whole cultivation. A competitive PHA production was obtained, reaching a PHA content of 43.5 % w/w during fed-batch cultivation using VFA-rich effluent with acetic acid as the dominant acid type. VFA-rich effluent dominated by caproic acid gave a higher concentration of biomass (3 times) resulting in higher amounts of PHA per liter of cultivation broth (3.3 g PHA/L) (Perez-Zabaleta et al., 2021).

The study also revealed that VFA composition plays a crucial role in the selection of microorganisms as well as in the composition and production of PHA (Perez-Zabaleta et al., 2021). The acetic acid-dominated effluent resulted in a PHA with a higher content of (*R*)-3-hydroxyvalerate (5.2 % w/w) than the caproic acid-dominated effluent (2.9 % w/w) due to the percentage of VFAs with even and an odd number of carbons. The acetic acid-dominated effluent had 19.7 % of VFAs with an odd number of carbons composed mainly of propionic acid (15.7 %) and isovaleric acid (3.8 %). Conversely, the VFA-rich effluent with caproic acid as the dominant acid had only 6.5 % of isovaleric acid, a fatty acid with lower consumption rates than propionic acid. Other studies using the VFAs from the organic fraction of municipal solid waste and sewage sludge on a pilot scale obtained similar PHA contents of 51 % w/w PHA(Moretto et al., 2020) and 48 % w/w PHA (Valentino et al., 2020).

Moreover, pure microbial cultures also have exhibited the ability to consume the aforementioned waste-derived VFAs and accumulate PHA without growth inhibition. Two bacterial species, *Cupriavidus necator* and *Burkholderia cepacia* successfully accumulated PHA using the VFA-rich effluent with PHA production of up to 78 % and 55 % of cell dry weight, respectively (Khatami et al., 2022). The copolymer was made up of mainly (*R*)-3-hydroxybutyrate (97–99 %) and (*R*)-3-hydroxyvalerate (1–3 %). The obtained PHA yields were comparable to the results obtained when simple sugars were used as a carbon source. Co-cultivation of these bacterial strains gave higher (*R*)-3-hydroxyvalerate content (an increase of 21 %) of the PHA. Prior to utilization in PHA production, the VFA-enriched effluent may undergo a pretreatment step to eliminate any solid

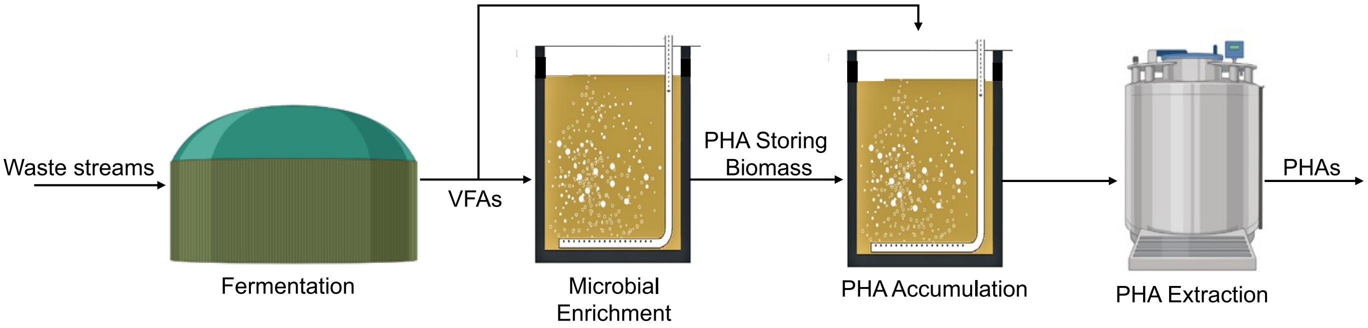

Fig. 3. Polyhydroxyalkanoates (PHA) production process using waste-derived VFAs.

or impurity content that may disrupt the PHA production process. In the above studies, the fermentation liquids were filtered with 200 μm bag filters (Perez-Zabaleta et al., 2021) and 0.2 μm filters (Khatami et al., 2022) for the MMC and pure culture experiments respectively. In these studies, the substrate composition with respect to the ratio of carbon/nitrogen was optimal and no further pretreatment of the VFA-rich effluent was needed.

The current PHA yields from MMCs can be improved through the manipulation of the bacterial structure of the MMC. Bioaugmentation strategies of these pure culture strains can further enrich the mixed microbial communities with potent PHA producers and enhance the VFA conversion into biopolymers. These results are promising as the integration of PHA production in the current municipal wastewater treatment plants will be a contributing factor toward the development of a bioeconomy.

3.6. Pure VFA (product 4) through separation and purification

After dewatering the fermented sludge, the VFA-rich supernatant still contained suspended particles, microorganisms, residual sugars, proteins, colloids, or pigments that could interfere with the downstream membrane separation process. Microfiltration (MF) and ultrafiltration (UF) are used for clarification of fermentation broth by removing these particles to enhance the downstream separation process (Aghapour Aktij et al., 2020). This pre-treatment step is seen as the first step of the VFA recovery process. In a study, a pilot-scale UF unit with a tubular mono-channel ceramic membrane of 300 kD and a surface area of 220 cm^2 was used to recover the VFA-rich liquid from the solids of a fermented organic waste (Garcia-Aguirre et al., 2019). The UF permeate had a VFA concentration of 12.3–26.6 g COD/L. In another study, two MF membranes with pore sizes of 0.45 μm and 3 μm and three UF membranes of molecular weight cut-offs of 3.5, 10 and 50 kDa were tested for removing particles from fermented effluent (Jänisch et al., 2019). Results showed that both MF and UF membranes are completely permeable to the VFAs and UF membranes. Thus, both MF and UF can be used as pre-treatment steps for other separation processes.

3.6.1. VFA mixture separation with nanofiltration/reverse osmosis

Various studies discussed above have shown that fermented effluents produced from waste streams contain a mixture of VFAs. The concept of the proposed approach is to separate the VFAs into low-carbon VFAs (C2-C3; acetic acid, propionic acid) and high-carbon VFAs (C4-C6; butyric acid, valeric acid, caproic acid). Pretreated VFA-rich liquid can be treated using low-pressure reverse osmosis (RO) and nanofiltration (NF) membranes with well-defined properties such as pore diameter and membrane surface charge to separate the VFAs. The principle is that low-carbon VFAs such as acetic acid have lower molecular weights and therefore are expected to easily permeate through the NF/RO membranes while other longer carbon-chain VFAs such as caproic acids are retained. In a study with NF/RO membranes, it was found that acetic acid could pass through the NF and RO membranes while other acids could be enriched in the retentate (Jänisch et al., 2019). Acetic acid (low market value) dominated VFAs are equally good for denitrification and bioplastic production within the WWTPs, there is the need to separate the VFAs into low-value organic acids and high-value organic acids.

3.6.2. Recovery of VFAs in the form of esters

An efficient separation and purification process is crucial to improve the implementation of VFAs as raw materials for industrial production. The main requirements for the industrial implementation of bioproducts are obtaining high-purity end products (>99.5 %), high recovery (>90 %) and low chemicals and energy consumption. Producing esters from the VFA is seen as one of the promising ways to obtain pure (one-type) VFAs. The main challenges are caused by the pH of the mixed-culture fermentation and the presence of other impurities such as proteins, amino acids, inorganic salts, and others. The pH of an anaerobic fermentation with MMCs critical because it determines the dominant microorganisms and the production route (Liu et al., 2012). The fermentation pH could have a direct impact on the consequent separation of the VFAs because the VFAs are fully dissociated at a pH above their pK_a. The traditional recovery at pH above the pK_a consumes high energy and produces salt-waste as a by-product (López-Garzón and Straathof, 2014). The challenges are their low concentration (2–20 g/L), high solubility in aqueous solution, low participation coefficient (especially for VFAs <C4), and high boiling point (making evaporation of water an expensive step) (Cabrera-Rodriguez, 2018).

Some technologies have been developed for the purification of VFAs in ester forms. These include electrodialysis combined with the formation of ester (Xu et al., 2015); bipolar membrane electrodialysis; adsorption/desorption using methanol/hydroxide (Wang et al., 2011); ion exchange adsorption and desorption with CO_2-expanded alcohols (Fernando-Foncillas et al., 2021) and evaporation/ketonization or esterification. The main challenge remains in obtaining high purity and selectivity; reducing cost and designing a stable production process to make products for the bulk chemicals market (<5 €/kg). High selectivity and concentration have been obtained using ion-exchange adsorption and desorption with CO_2 expanded alcohols for medium-chain fatty acids. It has been reported that an increase in concentrations of 14.6 and 20.7 was obtained for hexanoate and heptanoate using this technique (Fernando-Foncillas et al., 2021). The integration of this recovery and purification step can allow for the implementation of these solutions on a global scale.

3.6.3. Separation of mixed VFAs using vapor permeation membrane contactor

The waste-derived VFAs in the fermentation liquid can also be separated and purified by membrane-based processes (Alloul et al., 2018; Yesil et al., 2021a). Vapor permeation membrane contactor (VPMC) is a recently studied membrane-based process, which enables VFA separation with a transport mechanism driven by a concentration gradient or partial pressure difference (Aydin et al., 2018; Tugtas, 2014; Yesil et al., 2021a). In VPMC systems, air-filled or extractant-filled membranes separate two aqueous (feed and permeate) phases (Aydin et al., 2018; Han et al., 2005). Although VPMC systems use microporous hydrophobic membranes like in the MF process, the processes are different. Unlike MF, there is no convective flow through VPMC membrane pores, and the system is not pressurized, and it does not separate solutes based on the mechanism of size exclusion (Aydin et al., 2018; Tugtas, 2014). VFAs in the feed solution would be transported across the membrane and received by a permeate solution until concentration or partial pressure equilibrium (no driving force) has been reached at both sides in isothermal batch operations (Aydin et al., 2018). To create a constant driving force, equilibrium conditions should be prevented by converting unionized forms of VFAs (e.g., acetic acid) to their ionized forms (e.g., acetate) at the permeate phase through a reaction with an alkaline solution (e.g., sodium hydroxide (NaOH)) (Aydin et al., 2018; Yesil et al., 2014). Consequently, the partial pressure of VFAs on the acidic feed side of the membrane will be higher than on the alkaline permeate side, creating a constant concentration gradient and preventing VFAs' back diffusion (Tugtas, 2014; Yesil et al., 2014). There have been studies on the application of VPMC systems for the separation of VFA mixture.

In a study by Yesil et al. (2021a), the transport of a mixture of VFAs through a Polytetrafluoroethylene (PTFE) membrane (0.45 μm air-filled pores) was assessed in a VPMC system at varying temperatures (21–38 °C) and concentrations of NaOH (0.5 N and 1.0 N). It was revealed that a temperature of 38 °C and 1.0 N NaOH were the optimal conditions for capturing VFAs. Under these conditions, the highest fluxes for acetic acid, propionic acid, butyric acid, valeric acid, and caproic acids were approximately 18.2, 19.3, 6.8, 6.6, and 5.3 $g/m^2.h$, respectively (Yesil et al., 2021a). Similarly, another study determined the VFA separation performance of a PTFE membrane (0.2 μm air-filled pores) at 38 °C with 0.5 N NaOH and a synthetic VFA mixture with individual VFA concentration of 1250 mg/L (Aydin et al., 2018). The study achieved recovery efficiencies of acetic acid, propionic acid, butyric acid, valeric acid, and caproic acid of 54 %, 64 %, 69 %, 72 %, and 74 %, respectively. When the membrane pores were filled with trioctylamine (TOA) (PTFE membrane with extractant-filled pores), recovery generally increased with efficiencies of

34 %, 85 %, 98 %, 99 %, and 99 %, respectively. The extraction capacity of TOA is related to the hydrophobicity and acidity of the VFAs. Acetic acid is the least hydrophobic among other VFAs and therefore attained the lowest recovery efficiency with TOA-impregnated membrane. Although TOA was not very selective toward acetic acid and a low separation factor was observed (0.74), an increase in chain length of the VFAs increased separation factor values of 7.05, 171.2, and >1250 separation factors for propionic acid, butyric acid, and valeric-caproic acids, respectively due to the increase in strength of ion-pair complex with TOA (Aydin et al., 2018). Moreover, the increase in the alkyl chain length of the VFAs increases the hydrophobicity of the acid (Yesil et al., 2014). Accordingly, higher recovery efficiencies were observed for higher-order VFAs via the use of either air-filled or extractant-filled membranes. Nevertheless, the PTFE membrane with air-filled pores gave poor selectivity of all the individual VFAs, while the extractant-filled PTFE membrane resulted in higher selectivity for valeric acid and caproic acid (Aydin et al., 2018).

In the literature, there are different studies investigating the separation of mixed VFAs from real fermentation broths or other VFA-containing waste streams. In one study with a TOA-filled PTFE membrane, VFA separation from three VFA-rich effluents (fermentation broth, chicken manure and landfill leachates) was assessed at 38 °C (Aydin et al., 2018). Separation efficiencies of individual VFAs were high (45–100 %) for both fermentation broth and landfill leachate. Whereas the VFA separation efficiency from chicken manure digestate was the lowest (4–76 %). The relatively lower performance obtained by the VFA-rich effluent from chicken manure was attributed to the presence of ions in the chicken manure digestate that can form complexes with TOA and a higher concentration of suspended solids that formed cake on the membrane surface. In another study of a hybrid anaerobic fermentation/VPMC system operated for 53 days at 35 °C with 1.0 N NaOH as the alkaline permeate solution, there was an enhancement of the VFA production efficiency (Yesil et al., 2021a). The hybrid system resulted in separation efficiencies of 57.0 %, 56.0 %, 61.9 %, 48.1 %, and 57.4 % for acetic acid, propionic acid, butyric acid, valeric acid, and caproic acid, respectively. The continuous removal of VFAs from the fermentation reactor decreased the effect of VFA accumulation and inhibition enhancing the VFA production by 42 %.

3.6.4. Separation of mixed VFAs with pervaporation

Pervaporation (PV) is another membrane-based technique that is recently being used for VFA separation (Zhu et al., 2021). In a PV system, mass transport of VFAs across a membrane is realized through the pressure difference at the feed and permeate sides of the membrane. There are four main stages of the PV process: (1) the desorption of VFA from feed liquid, (2) sorption of the VFA into the PV membrane, (3) diffusion of VFA via the PV membrane, and (4) desorption into the permeate vapor phase (Yesil et al., 2020). Similar to the VPMC systems, both air-filled and extractant-filled porous membranes are used to separate VFAs from fermentation broths. Moreover, composite membranes with dense active and porous support layers can also be used for VFA separation via the PV process.

In a recent study, pervaporation separation of mixed VFAs was investigated using a PTFE membrane with air in pores, a PTFE membrane with pores filled with tridodecylamine, and a PTFE/silicon rubber composite membrane (Yesil et al., 2020). The VFA mixture was a synthetic solution that contained 2 g/L each of acetic acid, propionic acid, butyric acid, valeric acid, and caproic acids. It was reported that higher operational temperatures resulted in enhanced VFA separation performance for the air-filled PTFE membrane. This result was attributed to increased driving force as the vapor pressure of VFAs at the feed phase increased with the increase of temperature while permeate phase remained almost constant (Yesil et al., 2020). As opposed to the air-filled PTFE membrane, an increase of temperature from 21 °C to 35 °C improved VFA separation of the extractant-filled PTFE membrane while the further increase of temperature to 55 °C diminished its performance due to higher coextraction of water along with individual VFAs. Moreover, when the operating temperature was either 21 °C or 35 °C, the impregnation of the PTFE membrane with TDDA resulted in enhanced separation efficiencies for all studied VFAs as tertiary amine extractants (e.g. TDDA) can lead to increased membrane affinity toward VFAs by forming strong acid–amine complexes. Another membrane type assessed in the study was composite silicone rubber/PTFE membrane (Polydimethylsiloxane (PDMS)/PTFE membrane). It was reported that the separation performance of composite membranes decreased with the increase of membrane thickness as the only mechanism for mass transport is diffusion in composite membranes. In a PV system, the energy required to separate acetic acid from a synthetic VFA mixture at 21 °C was reported as 2.6 kWh/kg (Yesil et al., 2020).

There is no quantitative comparison between the different VFA recovery and purification techniques in terms of economic and environmental impacts. Nonetheless, each of the separation and purification techniques has its advantages and disadvantages. For instance, some of the advantages of VPMC and pervaporation techniques include net zero GHG emissions and the possibility of additional energy and water recovery. On the other hand, there are disadvantages such as low separation efficiency at low VFA concentrations, low selectivity for low carbon number VFAs such as acetic acids, pH adjustment requirement, and the need to replenish/regenerate permeate solution. Moreover, while recovering of VFAs in ester form can yield a market-ready product with higher purity, there is the challenge of low selectivity for short-chain VFAs and relatively high cost. The NF/RO processes tend to be used for the separation of VFAs from other compounds in the fermentation liquid or for concentrating the VFAs in the fermentation liquor. With the different retention mechanisms, the NF/RO membranes can be used to separate the VFA mixture. Using NF/RO membranes for concentrating VFAs may also lead to unwanted compound concentration. The issues of higher energy demand and membrane fouling are some of the disadvantages of the NF/RO technique. With these, it is clear that many factors and criteria need to be considered in choosing the appropriate technique for VFA separation and purification. Table 1 summarizes the different bioproducts that are recovered from the proposed system with their possible production efficiencies.

4. Sustainability analysis of the system

The main aim of a WWTP is to increase the quality of the treated water to a degree that it can be discharged to a receiving water body. Therefore, we can assume that the quality of the treated water does not change in the transition from WWTPs to wastewater resource recovery facilities, but the variety, quality, and amount of the recovered resources are aimed to be higher. We can suggest that the avoided burdens will be higher. From a life cycle assessment (LCA) perspective when a system has multiple products, either the environmental burdens sourced from the system are allocated between the products or the system is extended to include the environmental benefits of the produced co-products. The co-products replace the production otherwise, and therefore the burdens supposed to

Table 1
A summary of the bioproducts and production efficiency of the proposed system.

Product no.	Bioproduct	Type of stream	Production efficiency	Reference
1	Biogas	Mainstream wastewater	Net energy: 0.04 kWh/m^3	(Petropoulos et al., 2019)
2	VFA mixture as carbon source	Sewage sludge and external organic waste	Up to 32 g/L	(Owusu-Agyeman et al., 2022)
3	PHA	VFA-rich effluent	Up to 78 % cell dry weight	(Khatami et al., 2022)
4	Pure one type VFA	VFA-rich effluent	- Up to 99 % recovery - >20 times higher value VFAs	(Aydin et al., 2018) (Fernando-Foncillas et al., 2021)

originate from the production will be avoided. The avoided production might be for the same product or a product functionally equivalent. In this conceptual system, the main product is the treatment of wastewater, and the co-products are biogas, VFA-rich effluent, purified VFAs, PHA, and biosolids (Fig. 4). From an LCA perspective, the energy and material consumption during the construction and operation and even decommissioning of a WWTP are important as the avoided burdens provided by co-products. However, in this conceptual study, the proposed system is not evaluated as a quantitative case study where the results would highly depend on the energy mix of the region, but the possibilities realized with the additional resource recovery routes are investigated.

In this conceptual system, the wastewater is directed to a UASB reactor after primary treatment and the biogas is generated directly from the wastewater. Although from a technical point of view, this difference would affect the amount of biogas generation, the avoided burdens per unit of biogas would not change. Therefore, evaluating research results of biogas generation using other waste streams is a close approximation to understanding the possible benefits of biogas generation as an energy recovery process. The avoided burdens of biogas generation would vary depending on the replaced function. The generated biogas can be (1) used in vehicles after upgrading, as a replacement for diesel or (2) combusted to produce heat and/or electricity. If it is consumed as vehicle fuel, it will avoid the burdens stemming from diesel production and if it is used for energy generation the avoided burdens will depend on the alternative energy source.

In conventional WWTPs, sludge is treated with anaerobic digesters and heat generated from the combustion of generated biogas can be used internally to keep the digesters` temperature at mesophilic conditions. A study has shown that one-third of the generated biogas can be used to heat the digesters (Hospido et al., 2004). In the proposed system, biogas is generated in the UASB reactor.

In the conceptual system, VFAs are produced via the fermentation of wastewater sludge and external organic waste. While a part of VFA-rich effluent is directly for denitrification instead of methanol (and other carbon sources), a part of VFA-rich effluent is used to produce pure VFAs by separation and purification processes and replace fossil-based VFA production, and the rest is used for PHA production which can be used as bioplastic after further processing and replace fossil-based plastic.

Using the fermentation liquid in the denitrification process avoids the production of its replacement. Methanol, acetate, and fossil-based and renewable ethanol are commonly used carbon sources. It was reported that 1 kg VFA content in a VFA-rich effluent replaces approximately 1 kg methanol (Elginoz et al., 2020). When this VFA-rich effluent is produced as a co-product of a food waste treatment system which is comprised of a hygenization container, a fermenter, and a centrifuge, it decreases the total impact of the treatment system considerably, varying from 10 to 55 % of the impact category results (Elginoz et al., 2020). In our recent study (Cetecioglu et al., 2020), the usage of different carbon sources (fossil-based methanol, renewable methanol, renewable ethanol, and waste-derived VFA) in the denitrification process were compared based on their global warming potentials. The results revealed that usage of the waste-derived VFA was the most environmentally friendly from an LCA perspective while the fossil-based methanol was the worst option (Cetecioglu et al., 2020). These results suggest that the usage of waste-derived VFAs internally in the WWTP provides considerable improvement in decreasing environmental burdens.

Downstream separation and purification processes are needed to use waste-based VFAs as feedstock instead of their fossil-based counterparts. There was a study of caproic acid production from food waste and recovery by downstream processes (Chen et al., 2017). According to the results, while the production of 1 kg caproic acid causes 5 kg CO_2-eq emission, downstream processes cause 3.5 kg CO_2-eq emission. It was suggested that direct usage of VFA-rich effluent in microbial oils production after a microfiltration step might have better environmental performance in comparison to energy-intensive separation processes (Gálvez-Martos et al., 2021). However, further research is needed to determine the environmental burdens of VFA separation and purification processes and their contribution to the total environmental impact of VFA recovery.

Integrating PHA production processes into WWTPs has been investigated using LCA in several studies. After comparing five WWTP configurations, it was suggested that better environmental performance can be

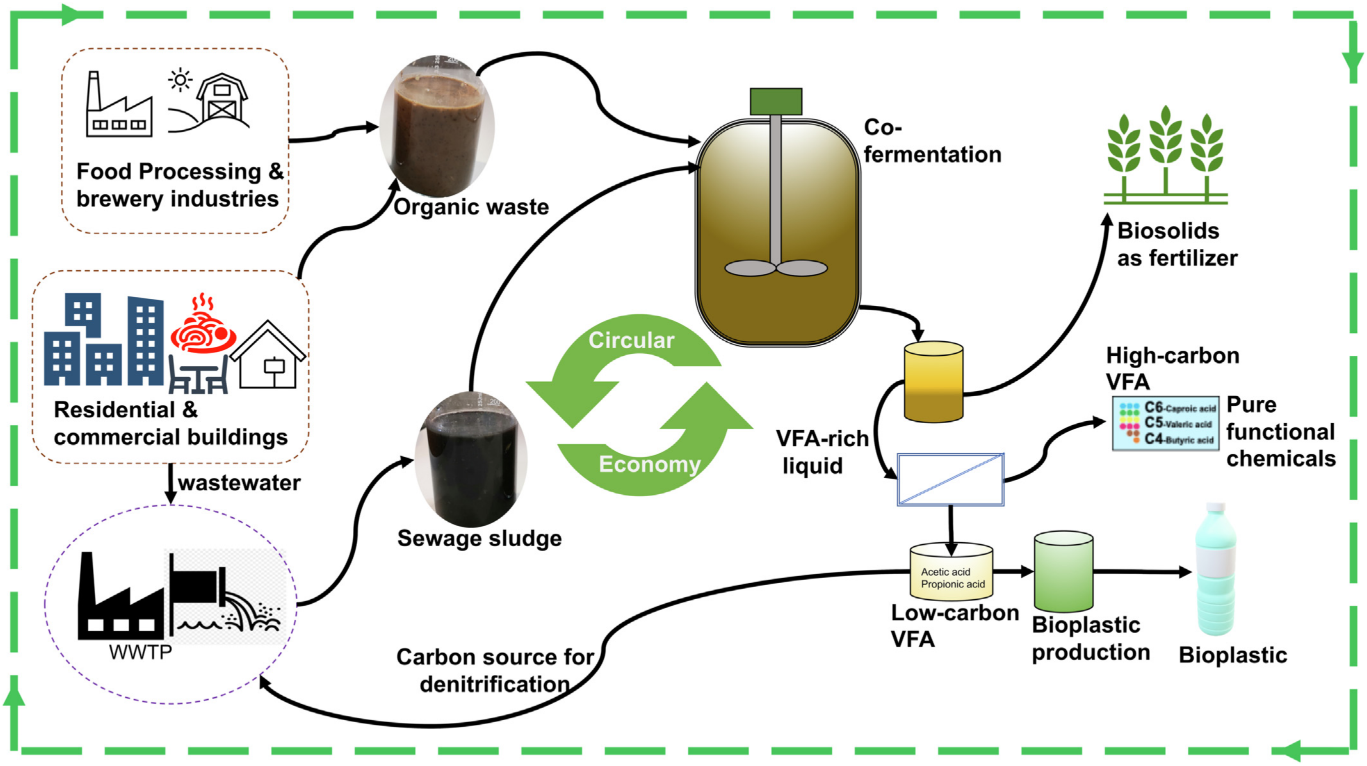

Fig. 4. A scheme of a circular economy concept for the proposed system.

achieved by integrating PHA-rich biomass production into a WWTP in comparison with a conventional reference case (Morgan-Sagastume et al., 2016). In the conventional case, electricity and heat are generated from biogas using a combined heat and electricity plant, the generated electricity replaces grid electricity and heat replaces thermal energy from natural gas combustion. In the PHA production alternatives, PHA-rich biomass substitutes for PHA by pure-culture fermentation. The substitution affects the results to an important extent, but the most important result of the study is even without the substitution PHA production cases environmentally perform better than the conventional case. Environmental burdens arise mainly from downstream processes in mix-culture PHA production (Gurieff and Lant, 2007). Since downstream recovery processes affect the total environmental performance, a study compared three downstream processes based on alkali, surfactant-hypochlorite, and solvent treatment (Fernandez-Dacosta et al., 2019). It was revealed that alkali treatment performs best in terms of environment and economy, however, produced biopolymers still cannot compete with their fossil-based counterparts economically.

The biosolids generated in the fermenter can be considered as co-products or by-products according to their usage which is related to the regulations of the country where the WWTP is located. If biosolids are allowed to be used in agriculture, they avoid the burdens of equivalent fertilizer production. On the other hand, the heavy metal content of the biosolids becomes problematic when biosolids are applied to agricultural land. Nonetheless, it has been shown in one of our studies that alkaline fermentation can produce biosolids that are suitable for agricultural use with a low level of heavy metals with low bioavailability (Yesil et al., 2021b). Another issue is the continuous production of biosolids and limited time (spring and autumn) for application to agricultural areas (Hospido et al., 2004). Another option for disposal of the biosolids is co-incineration with waste which provides energy recovery. A comparison of agricultural application and co-incineration showed that agricultural application is worse than co-incineration. In the agricultural application case of transporting the biosolids, the energy consumption for pasteurization, and the release of acidifying substances and heavy metals into the soil overcome the profit gained by avoiding fertilizer production (Lundin et al., 2004).

Beyond the environmental benefits, the proposed system is economically beneficial. A study revealed that adding UASB to an existing WWTP of conventional activated sludge treating municipal wastewater under psychrophilic conditions can lead to a positive economic gain of 526 € per day with a payback time of only 3–4 years (Cecconet et al., 2022). Moreover, studies have shown that the VFA production platform is economically feasible. A full-scale study of VFA production from sewage sludge and its application for biological nutrient removal resulted in a net gain of 9.13 $\$/m^3$ of sludge (Liu et al., 2018). In our current study, it was shown that without the cost of separation and purification, VFA production from sewage sludge and external organic waste can result in a positive net profit of 9.8–14.7 €/m^3 of waste (Owusu-Agyeman et al., 2023). Furthermore, a more comprehensive techno-economic study has shown that a high-purity (>98 %) propionic acid can be produced from WWTPs with a net profit of 2.4 $/kg of propionic acid (Veluswamy et al., 2021). The favourable outcomes from those studies indicate that the conceptual system is both environmentally and economically promising.

5. Conclusion

The paper proposes a new concept to shift municipal wastewater treatment to resource biorefineries where various bio-based products can be recovered while achieving the primary aim of removing the contaminants. The proposed system includes chemical-enhanced pretreatment to remove phosphorus and particulate organic matter before the wastewater is treated anaerobically using UASB. UASB can produce net energy of 0.04 kWh/m^3 of treated municipal wastewater. Furthermore, the nitrogen is removed by two main alternatives; conventional nitrification/denitrification process and partial nitritation anammox system before the wastewater is passed through a membrane and discharged. Ultimately, the sewage sludge treatment system is used together with external organic waste to produce VFA (32 g COD/L) as a platform chemical for other bio-based products like PHA (up to 78 % dry cell weight). Besides, the produced VFA is further separated and purified to pure VFAs (one-type) using membranes (up to 99 % recovery) and ion exchange techniques (>20 times higher concentration of higher value VFAs). The produced biorefinery concept will result in four main products: biogas, VFA-mixture as carbon source, PHA, and pure VFAs. The nature of the proposed system makes it possible to implement only some components. Moreover, the concept can be integrated into existing WWTPs. Environmental analysis of the system gives a positive outlook.

CRediT authorship contribution statement

Isaac Owusu-Agyeman: Conceptualization, methodology, writing-original draft, review & editing, visualization. **Elzbieta Plaza**: Conceptualization, validation, writing-review & editing, supervision. **Nilay Elginöz**: Validation, writing-review & editing. **Merve Atasoy**: Writing-original draft, validation. **Mariel Perez-Zabaleta**: Original draft & editing. **Carlos Cabrera-Rodríguez**: Writing-original draft, validation. **Kasra Khatami**: Original draft & editing. **Hatice Yesil**: Writing-original draft. **Evren Tugtas**: Validation, writing-original draft, review & editing, supervision. **Baris Calli**: Validation, writing-review & editing, supervision. **Zeynep Cetecioglu**: Conceptualization, resources, validation, writing-review & editing, supervision.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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