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Critical Review

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Capture - Ferment - Upgrade: A three-step approach for the valorization of sewage organics as commodities

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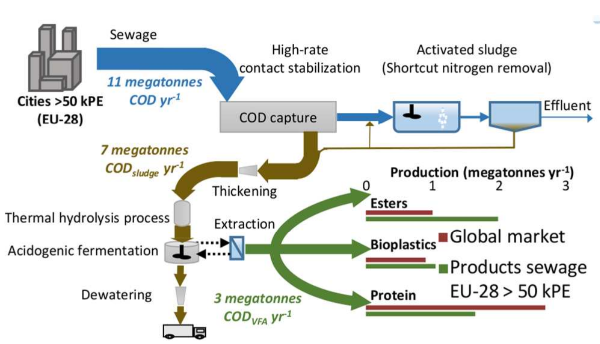
Abstract

This critical review outlines a roadmap for the conversion of chemical oxygen demand (COD) contained in sewage to commodities based on three-steps: capture COD as sludge, ferment it to volatile fatty acids (VFA), and upgrade VFA to products. The article analyzes the state-of-the-art of this three-step approach and discusses the bottlenecks and challenges. The potential of this approach is illustrated for the European Union's 28 member states (EU-28) through Monte Carlo simulations. High-rate contact stabilization captures the highest amount of COD (66-86 gCOD person equivalent^{-1} day^{-1} in 60% of the iterations). Combined with thermal hydrolysis, this would lead to a VFA-yield of 23-44 gCOD person equivalent^{-1} day^{-1}. Upgrading VFA generated by the EU-28 would allow, in 60% of the simulations, for a yearly production of 0.2-2.0 megatonnes of esters, 0.7-1.4 megatonnes of polyhydroxyalkanoates or 0.6-2.2 megatonnes of microbial protein substituting, respectively, 20-273%, 70-140% or 21-72% of their global counterparts (*i.e.*. petrochemical-based esters, bioplastics or fishmeal). From these flows, we conclude that sewage holds a strong potential as biorefinery feedstock, although research is needed to enhance capture, fermentation and upgrading efficiencies. These developments need to be supported by economic/environmental analyses and policies that incentivize a more sustainable management of our resources.

TOC/ Abstract art



Keywords

High-rate contact stabilization; Chemically enhanced primary treatment; High-rate activated sludge; Anaerobic fermentation; Carboxylate platform; High-pressure thermal hydrolysis pretreatment; Esterification; Ethyl acetate; Butyl acetate; Polyhydroxyalkanoates; Single-cell protein; Purple non-sulfur bacteria; Resource recovery;

1. Introduction

The European union (EU) adopted a bio-economy strategy which sets course towards a sustainable society that relies on "the production of renewable biological resources and the conversion of these resources and waste streams into value-added products, such as food, feed, bio-based products as well as bio-energy".[1] One resource that could be exploited in this context is the organic matter contained in sewage, which is commonly measured as chemical oxygen demand (COD). The sewage treatment works of the 28 member states that constitute the EU-28 receive about 25 megatonnes of COD (130 g COD population equivalent $(PE)^{-1}$ d^{-1} and 503 million PE in EU-28). Roughly 8.4 megatonnes is dissipated as CO_2 via the activated sludge process and a relatively minor fraction of this COD is channeled to biogas as a renewable energy source. In 2014, about 17% of the incoming COD was valorized as biogas, which accounted for about 9% of the total biogas production in Europe.[2] In the last decade, several routes have emerged to convert COD-contained in wastewater to marketable commodities, including esters,[3] plastics,[4] feed,[5] alginate and cellulose.[6] The value of these products, such as polyhydroxyalkanoates (PHA), a precursor for bioplastics, can be up to 4 times higher than that of methane (€1.2 kg^{-1} COD_{PHA} *vs.* €0.14-0.26 kg^{-1} COD_{CH4}).[7]

Volatile fatty acids (VFA) with 1 to 5 carbon atoms, are the central building-block in the generation of esters, plastics and feed. They are produced during acidogenic fermentation of a plethora of COD-rich substrates, including wastewater streams.[7-9] To date, the conversion of COD-rich aqueous streams into VFA has focused mainly on industrial waste and sidestreams, such as potato starch wastewater,[10] paper mills,[11] fruit juice wastewater,[12] sugar cane molasses,[13] thin stillage,[14] and yeast fermentation beer.[15] These are usually characterized by COD concentrations > 4000 mg COD L^{-1} of easily fermentable COD.[16] In contrast, the variation in flow, complexity and low COD concentrations of sewage (usually ranging between 250-800 mg COD L^{-1})[17] hinders further processing of the VFA into products and, especially, their cost-effective recovery.[18] However, a number of emerging scientific and technological developments may enable the use of sewage COD as a resource for the production of valuable commodities.[3-5] These come together in a ‘three-step approach’ that comprises the capture of COD as sludge, conversion to VFA and subsequent upgrading into commodities. This critical review sets out to describe the state-of-the-art of this three-step approach and critically evaluate its remaining challenges. This is followed by an assessment of the potential market volume and value of the three products, which takes into account technological uncertainty. Finally, the roadmap to a successful sewage-to-commodities value chain is discussed and conclusions are drawn.

2. Technologies to valorize sewage organics in three steps

The key elements of the proposed three-step approach for sewage COD valorization are depicted in Figure 1. The first step ‘capture’ aims to capture a maximal amount of COD as sludge. The second step ‘ferment’ targets to refine the sludge organics and maximize their conversion to VFA through acidogenic fermentation, optionally following sludge pretreatment. The third step ‘upgrade’ aims to synthesize commodities from VFA. In the following subsection each step will be discussed in detail.

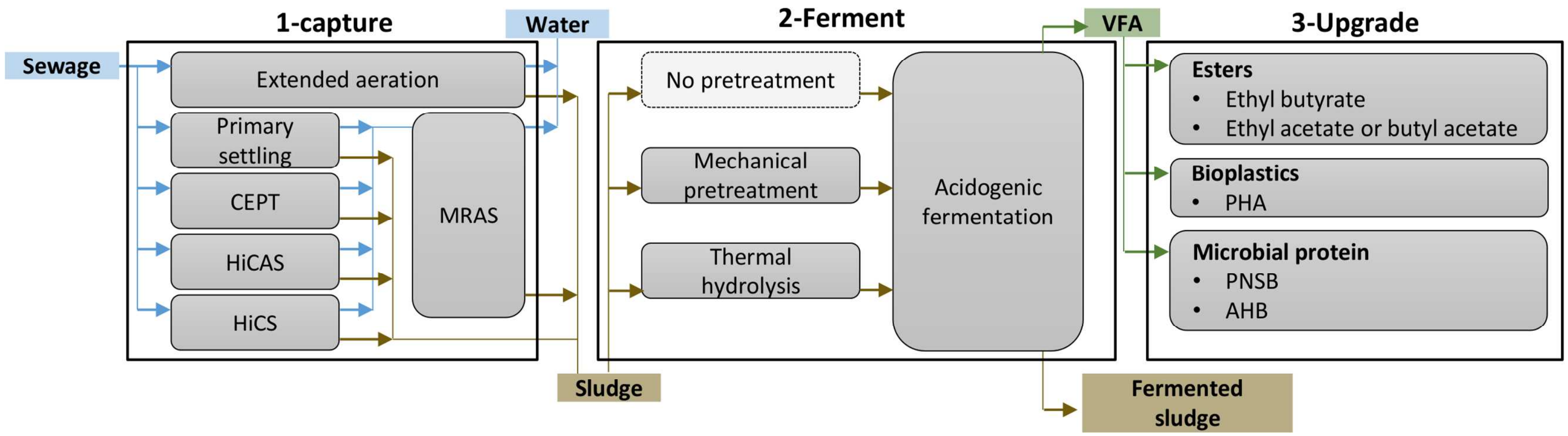


Figure 1 An overview of the key technologies considered to capture, ferment and upgrade sewage organics to commodities. All technologies are further described and discussed in the following subsections. Activated sludge as polishing stage with a sludge retention time of 15 days. CEPT: chemically enhanced primary treatment, HiCAS: high-rate conventional activated sludge, HiCS: high-rate contact stabilization, VFA: volatile fatty acid; PHA: polyhydroxyalkanoates; PNSB: purple non-sulfur bacteria; AHB: aerobic heterotrophic bacteria

2.1. Capture COD as sludge.

COD-capture technologies rely on a combination of physical, chemical and/or biological processes that captures dissolved, colloidal and particulate COD as sludge. Four key technologies are primary settling, chemically enhanced primary treatment (CEPT), high-rate conventional activated sludge (HiCAS) also known as the A-stage from the *Adsorptions-Belebungsverfahren,* Adsorption-Biooxidation or A-B process, and high-rate contact stabilization (HiCS).

2.1.1. Process description.

In primary settling, the velocity of water flow is reduced to minimize the drag force of particles, thereby enabling the settling of suspended solid by gravitational force. In this manner COD can be captured at efficiencies between 0.28-0.44 g COD_{sludge} g^{-1} COD_{fed}.[17] Chemically enhanced primary treatment (CEPT) combines the physical settling of primary sedimentation with enhanced chemical aggregation/coagulation. Chemical agents, *e.g.* coagulants containing Fe^{3+} or Al^{3+}, and flocculants, such as organic polymers, are added producing a more settleable sludge with capturing efficiencies of about 0.50-0.60 g COD_{sludge} g^{-1} COD_{fed}.[19] These physical-chemical processes can efficiently remove the particulate COD fraction (about 80% of captured COD is particulate), but capture low-to-no dissolved COD (primary settling *ca.* 0 g COD_{sludge} g^{-1} COD_{fed}; CEPT 0.20-0.25 g COD_{sludge} g^{-1} COD_{fed} due to the adsorption of organics onto metal hydroxide precipitates).[20]

In the biological HiCAS system, the influent wastewater is mixed under aerobic conditions with return sludge at high food-to-microorganism ratios between 2-10 g biodegradable COD per gram volatile suspended solids (VSS) per day.[21,22] The hydraulic retention time (HRT) is very short (< 30 min) and the sludge retention time (SRT) is only several hours to 2 days,[17,22] resulting in a high sludge yield, and COD-capture efficiencies of 0.35-0.54 g COD_{sludge} g^{-1} COD_{fed}.[23] The produced aerobic sludge is then separated by gravity settling.[23]

Recently, Meerburg, et al. [23,24] proposed the HiCS system, a high-rate variant of the contact stabilization system.[25] This process combines the high sludge-specific loading rates and the short SRT of a conventional HiCAS system with the principle of aerobic sludge stabilization followed by adsorption of influent organics. When the return sludge is aerated in the stabilization phase, biomass growth on adsorbed and stored substrates is promoted. Subsequently, the sludge is mixed with influent during a non-aerated contact phase, to allow storage and adsorption of fresh substrates. This alternating system creates a feast-famine regime where sorption and storage are interchanged with biomass growth. Based on lab-scale results, the COD-capture efficiency of the HiCS process can be up to 0.50-0.64 g COD_{sludge} g^{-1} COD_{fed}.[23] In terms of capturing dissolved COD, HiCS and also HiCAS have higher dissolved COD removal efficiencies of respectively 0.17-0.43 g COD_{sludge} g^{-1} COD_{fed}[23] and 0.17-0.34 g COD_{sludge} g^{-1} COD_{fed}[20] compared to physical-chemical system (Figure 2).

After capturing the COD and separating the COD-containing sludge from the sewage, sludge should be further thickened to ensure a compact fermenter. The final dry weight concentration of the understream of a settler will be roughly 2-3%, through thickening this should be increased to a dry weight of 4-6%. Thickeners are a well-established technology with good efficiencies (solids recovery 85-99%),[17] and little-to-no COD loss.

2.1.2. Comparison and challenges.

From an overall process perspective, realization of high COD-capture efficiencies is only relevant if this is coupled to a high anaerobic biodegradability of the COD, since this will determine the potential VFA production. CEPT sludge has a comparatively low biogas yield because organics in the sludge are less accessible and/or less reactive to the microorganisms due to the association of the organics with the coagulant in the sludge floc (Figure 2).[26] Evidence shows that the dosing of a cationic polyelectrolyte at >15 g kg^{-1} dry solids, decreased the methane production by up to 38%, likely due to the formation of larger flocs, thereby resisting efficient mass transfer within the sludge flocs.[27] However, this effect may be dependent on the type of chemical, as no such effect could be observed for anionic and non-ionic flocculants.[27] Flocculants may hamper VFA production in a similar manner, although to the authors' knowledge this is yet to be proven. In comparison to the physical-chemical capturing technologies, HiCAS and HiCS, produce highly biodegradable sludge (Figure 2). Batch tests for the biomethanisation potential have shown that the "young" biomass resulting from a short SRT is highly biodegradable under anaerobic conditions (specific methane yields > 1 g COD_{CH4} g^{-1} total suspended solids:TSS *vs.* 0.5 g COD_{CH4} g^{-1} TSS for conventional activated sludge).[23,28,29]

Biological COD-capturing technologies have, however, one key disadvantage; the settleability of the sludge produced is low, making sludge separation and capture challenging. HiCS and HiCAS are operated at a high feed-to-microorganism ratio, which combined with low aeration intensity and short SRT, results in formation of pinpoint aggregates that do not settle well.[20] Rahman, et al. [30] compared the sludge volume index (measure for settleability) for HiCAS and HiCS sludge, which were respectively 1434 mL g^{-1} TSS and 167-582 mL g^{-1} TSS. While HiCS sludge had much better settling properties than HiCAS, its values were still above 150 mL g^{-1} TSS, the threshold above which sludge is considered to have poor settling properties.[17] Several approaches have been proposed to circumvent poor settling, including: membrane filtration,[31] dissolved air flotation,[32] or CEPT[19] combined with HiCAS.

Primary settling and CEPT are well-established technologies and standard in most conventional activated sludge systems (technology readiness level Supporting Information S6).[17] About 58 HiCAS systems have been identified worldwide, treating sewage or a combination of industrial and domestic wastewater.[20] On the contrary, the HiCS system has only been tested at 454-L pilot-scale (Washington, DC, USA).[30] To be applied at full-scale, some technological challenges still need to be overcome. Future research should focus on improving colloidal and dissolved COD recovery efficiencies, and on minimizing aeration and volume[33] requirements in comparison with HiCAS. Additionally, a meaningful control parameter and an associated control strategy should be developed, so that HiCS systems are not operated on pre-defined fixed settings, but rather can be controlled based on the dynamic behavior of incoming sewage and plant needs (*e.g.* varying influent composition, stricter effluent requirements, fluctuations in HRT due to rain).

2.2. Ferment sludge to VFA.

2.2.1. Process description.

The anaerobic conversion of complex COD to biogas is carried out by a mixed community and requires four steps, namely hydrolysis, acidogenesis, acetogenesis and methanogenesis.[34] If methanogenic activity is suppressed, VFA can accumulate in the broth,[7] in a process that we term acidogenic fermentation, encompassing the first two abovementioned steps. These fermentation processes have different pathways, yielding a mixture of VFA, CO_2 and H_2.[35]

To date, research has mainly focused on the acidogenic fermentation of primary and secondary sludge[36-38], and process development has brought the technology up to TRL 6-7 (1.2m^3 BIOVAP pilot plant treating primary sludge, PHARIO project)[4] with VFA yields around 0.25 g VFA g^{-1} VSS and VFA concentrations in the fermentate in the order of 8-10 g COD L^{-1}.[39] Such VFA yields, around 0.22 g COD_{VFA} g^{-1} COD_{fed}, are consistent with those reported in other lab- and pilot-scale experiments studying acidogenic fermentation of primary and secondary sludge.[40] There are fewer studies on the acidogenic fermentation of HiCAS sludge, available results indicate VFA yields around 0.21 g COD_{VFA} g^{-1} COD_{sludge}.[41] To the best of the author's knowledge acidogenic fermentation of HiCS sludge is yet to be tested, although the anaerobic digestion of HiCS sludge yields around 0.3-0.5 L_{biogas} g^{-1} total solids.[20] One can expect that VFA yields from HiCS sludge should be comparable, if not higher, to those of other sludge given its higher biogas yields (*cf.* activated sludge 0.2 L_{biogas} g^{-1} total solids).[20]

Hydrolysis (*i.e.* solubilizing of particulate COD and breakdown of polymers into monomers) is the rate limiting step in sludge anaerobic digestion/acidogenic fermentation. The utilization of sludge pretreatment steps to increase biogas production has long been explored for anaerobic digestion using mechanical, thermal, chemical, biological and hybrid methods, and few are already applied at full-scale.[42]

High-pressure thermal hydrolysis is the most mature pretreatment technology, applied at full-scale in anaerobic digestion (*e.g.* Cambi THP™, Exelys™, Digelis™, among others) to increase biogas yields and minimize waste sludge. In this treatment, sludge is exposed to temperatures of 130-180°C and pressures of 6-12 bar to lyse cells and solubilize organics, which enhance the final biogas production in anaerobic digestion by 30-65%[43,44] and the net energy production by *ca.* 20%.[45] The acidogenic fermentation of thermal pretreated sludge showed a five-fold increase in the VFA yields (up to 0.46 g COD_{VFA} g^{-1} COD_{fed}), reaching VFA concentrations in the fermentation up to 25 g COD L^{-1}.[46]

Mechanical pretreatment methods disintegrate and/or grind sludge particles, thus releasing cell compounds and increasing the specific surface area for biological conversion.[47] Sonication has been applied in multiple full-scale installations for sewage sludge pretreatment with improved biogas production between 30-58%.[48-50] Lysing centrifuges are another mechanical pretreatment option and their solubilizing effect can enhance biogas production by 15-26%.[51] According to the authors 'knowledge, no reports on the use of mechanical sludge pretreatment for acidogenic fermentation could be found. However, it is anticipated that pretreatment could improve VFA yields as they tackle the rate limiting hydrolysis process although it is hard to predict to what extent.

Other chemical or enzymatic pretreatments are currently under development for sludge digestion, although they have reached a higher level of technological maturity for other feedstocks/applications (*e.g.* agricultural residues, lignocellulosic wastes, among others).[42] As an example, alkaline pretreatment has been investigated at lab-scale and it proved to enhance organic matter solubilization, increasing biogas production up to 1.9 times compared to the baseline without pretreatment.[52]

An effective dewatering step is required to reduce the moisture content of the solids (remaining sludge) present in the VFA-rich fermentate. Technologies for digestate dewatering are well established at full scale and include a belt filter press, screw press and solid-bowl centrifuge, among others.[17] It is expected that similar technologies could be used for fermentate, although it is critical to ensure the highest dewatering possible to maximize the flow of VFA sent to the upgrading step.

2.2.2. Comparison and challenges.

As discussed, the yields and VFA concentrations of acidogenic fermentation without pretreatment are lower than those with sludge pretreatment (Figure 2). While one must be careful when extrapolating the outcomes of a single study, it is plausible that sludge pretreatment plays a critical role in overcoming the hydrolysis bottleneck and enhancing VFA production and yields. Future research should confirm this and further investigate how different sludge pretreatment strategies can be used to increase VFA yields, the benefits derived from their implementation and the implications in terms of capital and operational costs.

High VFA concentrations in the broth are required for cost-effective extraction and upgrading, but may also have some undesired effects.[18] VFA have an inhibitory effect on microbes[53] and may result in (partial) inhibition of acidogenic fermentation, especially when operating reactors at an acidic pH. Such inhibition may not only reduce VFA production rates, but also the extent to which the available substrate is converted. Pratt, et al. [54] reported a VFA thermodynamic inhibition threshold of 17 ± 1 g COD_{VFA} L^{-1} for the acidogenic fermentation of pretreated sludge at pH between 5.7-6.3. Higher VFA concentrations have been obtained in sugar-based fermentations, which authors attributed to the high protein content of biomass resulting in lower thermodynamic thresholds.[54] Interestingly, the same authors reported a maximum VFA concentration of 21.6 g COD_{VFA} L^{-1} in another study,[46] which may suggest that such a threshold is not only due to the substrate, but also subject to other variables such as pH, temperature, acclimation of the community, among others. The VFA profile does also impact toxicity, with longer carbon chains acids exerting stronger inhibition.[54,55] Therefore, controlling the product of the acidogenic fermentation may be key, not only when targeting specific products, but also to enhance conversion yields. To date, steering mixed-culture fermentations of complex waste streams to target VFA is yet to be achieved and remains a challenge for further research.

Finally, an important point is base addition requirements. VFA are weak acids with a pKa around 4.7-4.8[18] (depending on the carbon length). When acidogenic fermentations are conducted at pH above their pKa, upon production these will dissociate and generate protons that lead to a pH decrease. Such drop may be dampened if the sludge has a high buffer capacity. However, if acidogenic fermentation pH is to be kept at values above 5.5-6, the addition of alkali required will result in increased operational costs.

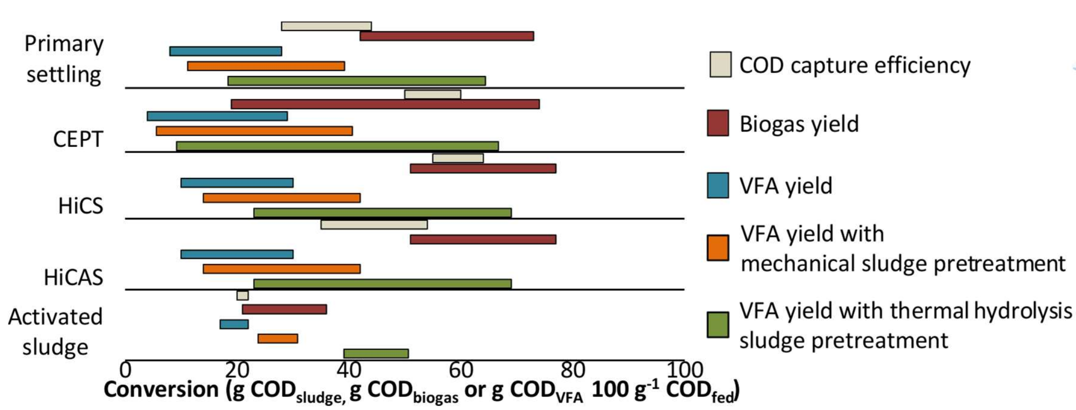


Figure 2 Overview of COD-capture efficiency, biogas yield and volatile fatty acid (VFA) yield for different sludge types and effect of thermal hydrolysis and mechanical sludge pretreatment on VFA yield.[17,19,23] Activated sludge as polishing with a sludge retention time of 15 days. CEPT: chemically enhanced primary treatment, HiCS: high-rate contact stabilization, HiCAS: high-rate conventional activated sludge. A detailed description of the underlying calculations and assumptions can be found in Supporting Information S2.

2.3. Upgrade VFA to commodities.

This subsection explores three potential VFA valorization routes, reviews the key features of their production processes from VFA and their state of development.

2.3.1. Esters.

Esters are derived from a carboxylic acid and an alcohol. They are widely used as organic solvents in chemical processing, paints, coatings, adhesives, printing inks, and in the fragrance and personal care industry. Approximately 4 megatonnes of ethyl acetate were produced worldwide in 2015.[56] VFA esters can be produced through so-called "reactive extraction" by which the extraction of VFA from an aqueous broth into a solvent is coupled to their conversion into esters using an alcohol (*e.g.* methanol, ethanol, butanol) as a reactant.[57,58] This approach is advantageous because completely water-miscible VFA can be recovered from fermentate in their ester form by distillation, with a much lower energy input than that required to recover VFA from water broths (*i.e.* the boiling points of acetate and ethyl acetate are 118 and 77°C, respectively).[59,60] The ester produced has also a higher market value than its VFA precursor (*i.e.* ethyl acetate has a market value of €900-1200 tonne^{-1}, compared to the €450 tonne^{-1} for pure acetate).[56,59]

The production of VFA esters is a well-established process in the chemical industry and uses anhydrous VFA as reactants. However, the esterification of VFA in aqueous streams, such as those produced through acidogenic fermentation, is far from straightforward. Esterification is an equilibrium reaction that forms one mole of water per mole of ester produced. Exclusion of water, both in the feedstock and by-product formation, is crucial to obtain high ester yields. This is in stark contrast with the hydrophilic nature of VFA and their low concentrations in fermentation broths (seldom above 4% w/w in sludge fermentate, as previously discussed in 2.2), and could be seen as an inherent misfit to these streams. However, esterification is an attractive upgrading route for VFA, because: i) It is a straightforward and sustainable conversion approach for VFA, as it proceeds selectively and with high efficiency, without intermediate activation, under mild conditions and without toxic chemicals; ii) The ester market is attractive both in value as in size (section 3.2) and it offers multiple applications; iii) Esterification facilitates the isolation of the final product, due to the volatility of the produced esters, which can be selectively recovered through distillation.

To use the fermentation broths as esterification input, the first challenge is to isolate the VFA and acidify them to their undissociated form. Several techniques have been tested at lab-scale to concentrate/dewater VFA from fermentation broths. Pressure-driven nanofiltration, which relies on a combination of a sieving mechanism with electrostatic interactions between the membrane surface and the charged molecules, allows the concentration of ions (including VFA) in the retentate.[18] It has been successfully applied at lab-scale for the separation of VFA from complex waste streams, with concentration factors over 70-80%.[61-63] However, this approach does not deliver the necessary acidification, and therefore the addition of acid will be required in a reactive extraction downstream train.

Electromembrane processes, where ions are driven through ion-selective membranes and separated/concentrated under the influence of an electric field, have also long been explored as a means to extract/concentrate organic acids from fermentation broths.[64] Several configurations have been investigated for that purpose, including conventional electrodialysis,[65,66] bipolar membrane electrodialysis,[67,68] or membrane electrolysis.[14,69]

Specifically, electrodialysis (preceded by microfiltration) was applied to the recovery and concentration of VFA derived from acidogenic fermentation of waste activated sludge, and the VFA-rich stream was used for PHA production. About 92% of VFA was transferred to the concentrated stream *i.e.* 20 g_{VFA} L^{-1} (~32 g COD_{VFA} L^{-1}).[70] Membrane electrolysis has been coupled to an esterification step, a concept that was tested using synthetic mixtures of acetate and validated using thin-stillage fermentation broths.[69]

The extraction of VFA by adsorption/desorption using ion exchange materials has also been shown to be an effective technique to extract and concentrate VFA,[71] and has been coupled to esterification in sugar-based fermentations [72,73].

While all these concepts allow to extract VFA from fermentation broths and concentrate them, they usually require acid/base dosing and/or high energy inputs for pressure- or electricity-driven concentration/extraction, in addition of the capital costs of the equipment. For instance, Andersen [74] evaluated the cost-benefit of recovering mono- and di-carboxylic acids through membrane electrolysis and found that due to the low market price of acetate, a 5-year payback time would be needed to reach the breakeven-point. The use of membrane-based processes for VFA recovery from sludge fermentate may also result in additional operation/maintenance costs due to membrane fouling and/or clogging.

The second critical bottleneck after recovery from the fermentation broth and acidification is the isolation of the VFA. This is typically done by extraction, which is challenging due to the still low concentration of VFA after the recovery techniques described above. Furthermore, for the esterification to proceed, the extractant should provide an environment that is sufficiently hydrophobic for water exclusion, while still being able to extract the highly polar VFA.[57] Recently, ionic liquids have been proposed as a green alternative to current organic solvents,[3] with the additional benefit that their properties can be tailored to specific applications.[75] On the downside, ionic liquids are still in technological development, they are not yet available in large quantities for industrial use and their prices are much higher than those of organic solvents (5-20 times more expensive than conventional solvents), although recent work progresses towards competitive ionic liquids.[76] Future work on reactive extraction for the conversion of VFA from sludge fermentate to esters should: i) improve the efficiency, rates and cost of extraction/concentration technologies; ii) develop novel solvents to be used as extractant/reactant, with high extraction and esterification efficiencies and low production costs; iii) develop a scalable esterification pipeline from fermentations broths; and iv) demonstrate that such approach can be applied to produce esters from VFA-rich fermentate.

2.3.2. Polyhydroxyalkanoates.

PHA are polyesters produced by microorganisms (mainly bacteria, but also some extremely halophilic archaea)[77], which can be converted to bio-based compostable plastics.[78] When exposed to feast-famine conditions and nutrient (nitrogen and/or phosphorus) limitation, microbes take up available organic substrates and convert them into PHA as intracellular storage polymers.[4,79-81] The microbial production of PHA from VFA has been explored using both pure strains and mixed-cultures.[82,83] The latter have the advantage that they can be fed using inexpensive VFA produced from domestic and agro-industrial waste and side streams, including wastewater. PHA accumulation from wastewater-derived VFA has been extensively investigated at bench-scale,[84-86] and successfully tested in a 500L pilot-scale for sewage, reaching a PHA content of 0.47 g PHA g^{-1} VSS, with COD yields for different WWTP ranging from 0.19-0.39 g COD_{PHA} g^{-1} COD.[4] These values are in line with those reported by Morgan-Sagastume and co-workers (0.25-0.38 g COD_{PHA} g^{-1} COD) in another pilot test.[40]

PHA are intracellular products that need to be recovered and purified. A common downstream processing stage consists of cell disruption (*i.e.* acidification), dewatering and drying steps. Ultimately, PHA is extracted at high temperature using organic solvents (*e.g.*

dichloromethane, butanol) and recovered as a bioplastic.[4,87] Multiple approaches have been investigated at lab-scale and are reviewed elsewhere.[80] The downstream processing of PHA-rich biomass to pure PHA has been conducted at 10L scale in batch mode, and the properties of the polymers obtained were tested. The process yielded mostly copolymer blends of poly-(3 hydroxybutyrate-co-3 hydroxyvalerate), their composition being dependent on the VFA spectrum of the waste stream used as a substrate, which was fairly constant for sludge fermentation and dominated by acetate, butyrate and propionate.

All these results are promising to the point that the PHARIO partners recently announced their intention to set up a first demonstration facility that will produce between 1-3 tonnes of PHA.[88] However, further work is required to make a commercial PHA route from sewage viable. First, PHA productivities from sludge-derived fermentate should be increased. They are at the present significantly lower than those obtained at lab-scale using synthetic substrates (0.90 g PHA g^{-1} VSS)[89] or at pilot-scale using carbohydrate-rich industrial wastewater (0.70 g PHA g^{-1} VSS)[90]. These deviations may be due to differences in substrate characteristics, operational conditions and composition of the PHA-accumulating microbial community. A larger PHA to active biomass fractions will make product recovery easier and more cost-effective.

Second, downstream processing is one of the key process bottlenecks, and their associated expenses can account for over 70% of the total production costs, as well as being responsible for about 60% of the environmental burden.[81] Assuming a productivity of 0.70 g PHA g^{-1} VSS, an estimated total polyhydroxybutyrate production cost (acidogenic fermentation included) from industrial wastewater is €1400-1950 $tonne^{-1}$ while the price of polyethylene terephthalate is €1300 $tonne^{-1}$.[81] More cost-effective process schemes are required to make PHA cost-competitive. Besides, PHA downstream processing is currently at a lower technology readiness level (Supporting Information S6) than the rest of the process steps (4-5 *vs*. 6-7), and hence additional efforts are needed to scale-up such a critical part of the PHA production route.

Finally, there is a plethora of conventional petrochemical plastics with a wide range of mechanical, thermal and chemical properties.[91] Sludge fermentate tends to have a rather stable composition dominated by acetate, butyrate and propionate to a lesser extent, which yields PHA with similar polymer composition. This is something desirable from the industrial production standpoint, but which may curtail the product applications due to the similar material properties of the various PHA produced. Several approaches may allow expanding the range of copolymers. It has been shown that the VFA profile of acidogenic fermented sludge may be shifted by co-fermenting sludge with other waste streams (*i.e.* propionate dominated, using food waste)[37] or operating at termophilic conditions (*i.e.* enrichment in valerate).[92,93] However, this remains one of the key challenges of the acidogenic fermentation step, as discussed in 2.2. Another alternative is blending PHA with other biopolymers, such as polylactic acid.[4] Finally, although PHA polymers have been tested in some test applications within the PHARIO project such as injection molding and films,[4] the development of commercial product applications is an important challenge yet to be addressed. However, this endeavor may be accelerated when larger amounts of PHA test samples are available to the (bio)plastics industry for product development, of course assuming adequate material properties of the polymers.

2.3.3. Microbial protein.

Microbial protein or single-cell protein (SCP) is the use of microbial biomass as a dietary protein source for feed or food.[94,95] Several SCP based feed (*e.g.* Feedkind™ by Calysta) and food (*e.g.* Quorn™) products are commercially available. SCP production on wastewater has been performed using axenic cultivation on lab- and pilot-scale (*e.g.* yeast, algae, or fungi).[96] However, this approach is cost prohibitive, because vast amounts of wastewater need to be sterilized (€8 m^{-3}; sterilization 0.4 tonne steam m^{-3} water [97] and €21 $tonne^{-1}$ steam[98]). The use of mixed-cultures, on the other hand, might offer a better alternative, provided quality control is in place (multi-barrier subsection 4.4).[96] In most laboratory and pilot-scale studies, SCP has been produced on industrial wastewater, with water treatment as the main goal.[94,99,100] However, production on extracted VFA could be advantageous because: it would simplify the composition of the feedstock for protein production, in contrast to the complex and fluctuating COD quantity of sewage; and the use of a membrane for the extraction of the VFA can act as a contamination barrier for pathogens. Two types of heterotrophic microorganisms are here proposed: purple non-sulfur bacteria (PNSB) and aerobic heterotrophic bacteria (AHB).

PNSB prefer an anaerobic photoorganoheterotrophic growth mode favoring VFA as carbon source.[101] Hence, they are a suitable partner to convert VFA, provided that cost-effective photobioreactors can be constructed. Limitations are infrared-light supplied per surface area and mixing speed (determines the contact between PNSB and light). Water has a 370 times higher absorbance coefficient for infrared-light compared to visible light.[102] Therefore, optimization of light supply is crucial for scale-up. Growth on VFA results in an COD-to-biomass carbon yield approaching one (0.8-0.9 g $COD_{biomass}$ g^{-1} $C_{VFA\ removed}$) as the bacteria also incorporate inorganic carbon to ensure redox homeostasis whenever consuming reduced VFA.[103] The production of PNSB from industrial wastewater has been studied up to pilot-scale using mixed-cultures and the biomass has proven to be an attractive aquatic and livestock feed.[99,104] Furthermore, also bioregenerative life support systems for manned space exploration envisage producing PNSB on fermentation filtrate, and using it to feed astronauts.[105]

The second type of considered microorganisms are AHB. In essence this corresponds to an activated sludge process, targeting a high production of sludge with a high protein quantity and quality.[96] In aquaculture, such an approach has been termed 'biofloc technology'.[106] For industrial wastewater, the company Nutrinsic (Glendale, USA, recently out of business) started up a full-scale installation[9] on brewery wastewater and Avecom (Wondelgem, Belgium) has implement one on potato processing wastewater.[107,108] The yield of AHB is 0.57 g $COD_{biomass}$ g^{-1} $COD_{VFA\ removed}$,[17] and thereby about half of PNSB. Compared to previous applications, we propose to grow AHB on extracted VFA and not directly on wastewater.

Sewage contains heavy metals, which can be accumulated by AHB and PNSB.[109] Vriens, et al. [96] reported that heavy metals levels in activated sludge can be 100 times higher compared to conventional animal feed, and may result in risk of toxicity in the feed-chain. However, in our approach, SCP will not be directly produced on sewage. Captured COD will be first channeled to a fermenter. After solid/liquid separation, VFA will be extracted and fed to a bioreactor to produce AHB or PNSB. Therefore, potential heavy metals should in principle already be accumulated in the sludge of the acidogenic fermenter (assuming sorption is similar to fermenting sludge) and diluted in the VFA-line. Nonetheless, heavy metal in SCP should be carefully examined. If accumulation of heavy metals in SCP still occurs, conventional removal methods can be used such as chemical extraction with inorganic acids (*e.g.* H_2SO_4 or HCl), organic acids (*e.g.* citric acid) or chelating agents (*e.g.* ethylenediaminetetraacetic acid).[110] Note that heavy metal extraction will solubilize the biomass and consequently deteriorates protein.[96] A comparative study will need to be performed to select the best extraction method based on metal removal and preserve of protein quantity and quality (*i.e.* amino acid profile).

After protein production, the biomass need to be recovered by stepwise concentrating the product which can entail gravitational settling (dry weight up to 3%)[17], membrane filtration (dry weight up to 13%)[111], centrifugation (dry weight up to 20%)[111] and drying. All these technologies are well established, yet harvesting is still expensive as the operational cost can amount to 20-30% of the total costs depending on the desired dry weight content.[112] AHB are potentially more interesting in terms of product recovery because they can be easily separated through settling.[17] More problematic is the solid/liquid separation of PNSB, due to their small size (0.4-2µm) and high electronegativity.[113,114] Research has already shown that sodium, pH and light intensity effect flocculation for *Rhodobacter sphaeroides*,[113] yet no similar studies were performed for mixed-cultures. If gravitational settling is eventually not possible, membrane filtration should be performed followed by centrifugation. However, filtration has high energy requirements (50-500 kWh tonne^{-1} dry weight) and will increase overall costs.[112]. After dewatering, the biomass still needs to be dried to a final dry weight of 80-90%. Several technologies are available such as spray drying,[115] drum drying[116] and convection drying[117]. Extensive research has been performed for algae, studying the relationship of drying technology, temperature and drying time on the final product quality.[115,116,118] Future research should also provide insight in the optimal technology and drying conditions for AHB and PNSB.

3. Estimating commodity production flows from sewage organics

The potential to valorize sewage into esters, PHA and SCP was estimated for the EU-28. A probabilistic approach was implemented to account for uncertainties including variable technological performance, changes in COD influent load and market value. Specifically, Monte Carlo simulations with 10,000 different combinations of input parameters were used. For each input parameter, probability distributions were defined from a literature review. For the assessment, only wastewater treatment works with a capacity of >50 kPE are included (details Supporting Information S1-S7).

3.1. Organics capture and conversion to VFA.

Figure 3 show the results of the Monte Carlo simulations for the captured COD and the specific VFA production as cumulative distribution functions. Comparison between distributions allows conclusions about technological performance under uncertainty, with distributions more to the right having higher specific yields and curves with a steeper slope implying a lower uncertainty of the results. For interpretation purposes an interval of 60% between the 0.2 and 0.8 probability was selected.

It can be seen that the HiCS system and CEPT have the highest COD-capture potential (Figure 3.A). At the interval between 0.2-0.8, or in 60% of the cases, a COD-capture of 66-86 COD PE^{-1} d^{-1} for HiCS and 71-89 COD PE^{-1} d^{-1} for CEPT can be achieved (Figure 3.A). At the median (intersection point of 50%) the values for HiCS and CEPT are 27-35% higher compared to primary settling or HiCAS. The effective COD-capture of HiCS results in the highest specific COD_{VFA} yield after acidogenic fermentation (between 10-19 and a median of 15 g COD_{VFA} PE^{-1} d^{-1}; Figure 3.B). Contrary to this, the expected specific VFA yields of CEPT for the interval between 0.2-0.8, ranges from the lowest value of all scenarios of 8 g COD PE^{-1} d^{-1} to a value of 19 g COD PE^{-1} d^{-1}, which is comparable to HiCS. This large range, and therefore uncertainty, reflects the differing inhibiting effect flocculants and coagulants may have on acidogenic fermentation of the captured sludge (subsection 2.1.2). The VFA production after acidogenic fermentation for HiCAS and primary settling is rather similar in terms of range and uncertainty. In the 60% interval the VFA production ranges between 8-14 g COD PE^{-1} d^{-1} for primary settling and 8-15 g COD PE^{-1} d^{-1} for HiCAS.

Pretreatment (Figure 3.C) will increase the specific VFA yields between 26-134% (at the median which is the intersection point of 50%). However, high-pressure thermal hydrolysis (Figure 3.C, dashed lines) will lead to an increase of the specific VFA yield between 1.5-1.6 times higher (measured at the median) compared to mechanical pretreatment (Figure 3.C, dotted lines). Specifically, for the HiCS process, followed by sludge pretreatment and acidogenic fermentation, the range at the defined 60% interval shifted from 10-19 g COD PE^{-1} d^{-1} without pretreatment, to 15-31 g COD PE^{-1} d^{-1} for mechanical pretreatment, to 23-44 g COD PE^{-1} d^{-1} for high-pressure thermal hydrolysis pretreatment (Figure 3.C, dotted lines). In conclusion, the HiCS system is the preferred capture technology as it results in a the highest specific VFA yields for all Monte Carlo simulation. The HiCS system is therefore taken forward for the following analysis of the potential for commodity production (Figure 3.D).

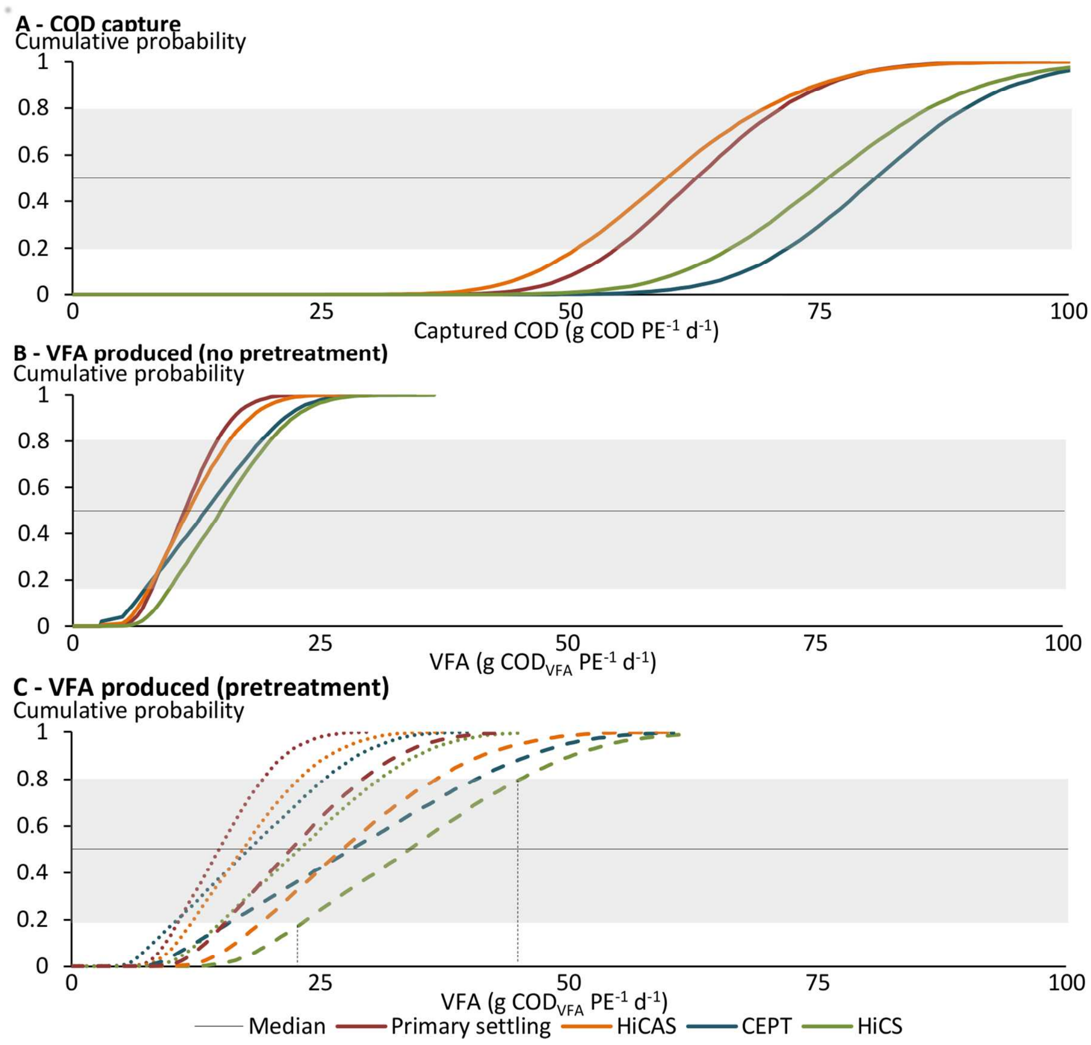


Figure 3 Monte Carlo probability functions for: (A) COD-capture from sewage; (B) COD-capture coupled to volatile fatty acid (VFA) production by acidogenic fermentation; (C) COD-capture coupled to VFA production by acidogenic fermentation with mechanical

pretreatment (dotted lines) and high-pressure thermal hydrolysis (dashed lines). Grey zone represents the interval between the 0.2-0.8 probability. CEPT: chemically enhanced primary treatment, HiCS: high-rate contact stabilization, HiCAS: high-rate conventional activated sludge.

3.2. Upgrade VFA to commodities.

In order to estimate potential PHA, protein and ester market volumes and market values, the results for the HiCS combined with high-pressure thermal hydrolysis system presented in section 3.1 were combined with expected VFA to commodity conversion rates (Supporting Information S6, Figure 4.A) and current market price of products to be substituted (Supporting Information S6, Figure 4.B). The data presented in Figure 5.B combine total market volume and market prices, the information should be interpreted as an indicator for the revenue the different products can generate.

Ethyl acetate derived from EU-28 sewage can, on average, substitute 43% (1.5 megatonnes yr^{-1}) of the global production, while the replacement for butyl acetate is 198% (2 megatonnes yr^{-1}) on average. Global compostable bioplastic production could be replaced if sewage would be used as a feedstock, as it is expected to be equal or higher than current global production (average 120% or 1.2 megatonnes yr^{-1}). Finally, PNSB and AHB production could substitute respectively 55% (1.7 megatonnes yr^{-1}) and 31% (0.9 megatonnes yr-1) of the current global fishmeal production.

Production volumes alone, can be misleading, as small quantities of high value products can result in a higher revenue. Comparison of the total market values shows that there is little differences in the potential market size between butyl acetate, PHA and PNSB protein (Figure 4.B). While the average value is highest for butyl acetate, followed by PNSB and PHA, their expected values at the 0.2-0.8 interval overlap and it is hence possible that each product obtains a similar total market potential. Simply based on the production quantity and potential market price no priority for a specific product can be defined. It can only be conclude that ethyl acetate, ethyl butyrate, PHA and PNSB will potentially result in largest revenue; yet an overall decision should also take legislation, technology readiness, investment cost and operational cost into consideration as will be discussed in section 5.

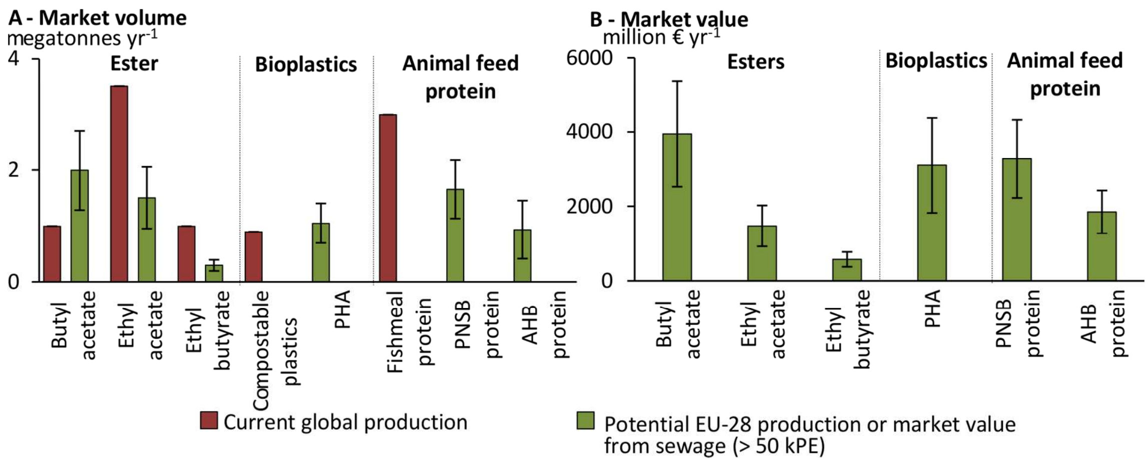


Figure 4 Overview of (A) the current global esters,[56] bio-based compostable plastics production[78] and fishmeal protein,[119] along with their potential production from sewage treatment plants with a capacity higher than 50 kPE and (B) the potential turnover for all commodities. Bars show overall average and error represent the 0.2-0.8 probability interval.

4. Sewage-to-commodities: Challenges, opportunities and prospects

The goal of this study was to evaluate the technologies available to upgrade sewage-COD. While the potential to recycle COD into marketable products is high (section 3.2), a number of challenges and bottlenecks need to be addressed to allow the implementation of technologies, namely:

i) maximizing COD recovery and VFA conversion efficiency

ii) developing nitrogen removal processes that perform adequately when COD-capture is maximized

iii) demonstrate the economic viability of processes, as well as their environmental benefits

iv) ensure product quality and safety

4.1. Maximizing COD recovery and VFA conversion efficiency.

Technological advances are required at each of the three steps, namely COD-capture needs to be improved, VFA production potential must be enhanced and nutrient limitation to PHA production needs to be realized.

COD-capture technologies should aim at efficiencies higher than 70% (maximal of CEPT currently in use). Existing technologies can recover most of the particulate and colloidal COD, leaving dissolved COD recovery as the greatest challenge. Based on current efficiencies (Figure 2), biological processes show the best prospects, but they face problems with sludge washout. Therefore, more attention should be paid to improve bioflocculation and their floc formation and surface adsorption of particulate and colloidal COD, while preventing sludge washout. In particular the interaction between different controlling parameters such as shear, dissolved oxygen, contact time and stabilization time must be investigated.

For the VFA production step, an important technological hurdle is the gap between VFA and biogas yields (ca. 0.30 g COD_{VFA} g^{-1} COD_{fed} *vs.* 0.80 g COD_{biogas} g^{-1} COD_{fed}; Figure 2). While this gap may not be closed because COD lost as hydrogen in acidogenic fermentation is converted into methane by hydrogenotrophic methanogens, VFA yields can be increased through sludge pretreatment. Further research is required to increase its efficiency potential in a cost-effective manner. It is important to bear in mind that this approach may bring in solution additional nitrogen and/or phosphorus, preventing the much needed nutrient limitation as a trigger for PHA accumulation in the upgrading step. This needs to be further evaluated and a tradeoff between maximal PHA production or VFA yield may be essential. Other potential bottlenecks such as VFA product toxicity,[120] or thermodynamic bottlenecks due to product and hydrogen accumulation may also negatively affect the performance of the acidogenic fermentation step and should not be ruled out.[8]

The upgrading of VFA remains a critical challenges of the proposed approach, due the nature of the stream and the concentrations of the VFA in solution. On the upside, a key benefit of the routes proposed here is that they can make use of VFA mixtures and convert them into products (*i.e.* all VFA will be used for SCP or PHA production, while VFA esters can be selectively recovered based on their boiling point). The specific technological challenges for each of the valorization routes have been outlined in Section 2.3 and will not be further discussed.

4.2. Developing mainstream shortcut nitrogen removal.

For large plants, nitrogen removal would often be required. In conventional sewage treatment, nitrogen is removed through denitrification with a minimum biodegradable COD demand of around 4 g COD g^{-1} N removed.[121] If, as suggested above, dissolved COD-capture is further improved, this may limit the capacity of the sewage treatment works to conventionally remove nitrogen. Several shortcut nitrogen removal technologies such as nitritation/denitritation (nitrite shunt) or partial nitritation/anammox (deammonification) enable nitrogen removal with less or no COD. Both approaches share the need to suppress nitratation, *i.e.* the oxidation of nitrite to nitrate by nitrite oxidizing bacteria, for which a number of successful strategies have been proposed.[122]

Nitritation/denitritation allows to remove nitrogen with 40% less COD than nitrification/denitrification (2.4 g biodegradable COD g^{-1} N removed).[121] First full-scale references are available in warm weather conditions (*i.e.* wastewater temperature above 20°C)[123], and next steps should focus to implement nitritation/denitratation in colder climates. Partial nitritation/anammox is a fully autotrophic process, and as such eliminates the COD requirement for N removal. The additional challenge for this process is to retain sufficient activity of anammox bacteria in the system, particularly at lower temperatures (<15°C). Also here a set of solutions has been elaborated.[122] First full-scale examples are promising,[124,125] and further development and implementation should target a year-round stable process performance. Current research and development efforts on mainstream shortcut nitrogen removal have gained critical mass, and their activities in piloting and upscaling the processes will likely spur its implementation over the coming 5 years. It should be noted that perfect COD-capture is not feasible, and that the activated sludge process will always receive a certain dose of biodegradable COD (*e.g.* 1-2 g COD/g N). Given this, a hybrid combination between nitritation/denitritation and partial nitritation/anammox will provide the best solution, making use of the available organics to remove nitrite (and some nitrate), as such avoiding energy use for aerobic COD removal.

4.3. Demonstration of economic viability and environmental benefit.

While technological improvements are needed to increase process efficiency, the biggest obstacle towards implementation of the three-step approach is not technical; the proposed valorization routes need to be economically viable. Taking PHA as an example, the processes to make their production technically feasible are available, but there is still a discrepancy between the wastewater-based PHA cost (*e.g.* polyhydroxybutyrate €1400-1950 $tonne^{-1}$) and the market price of petrochemical plastics (*e.g.* polyethylene terephthalate €1300 $tonne^{-1}$).[81] Despite a positive public attitude towards renewable resources and "green" products, market price need to be on a par with their counterparts.[81]

Considering that sewage has no cost as a substrate, production costs will be governed by the construction and operational costs of the different units. Meerburg [20] performed a comparative economic analysis of the different capture technologies based on capital and operational expenditure. Capital expenditure was lowest for primary settling (€0.24 PE^{-1} d^{-1}) and roughly 2.5 and 1.7 times higher for HiCAS and HiCS, respectively. Regarding operation, the cost of implementing CEPT was around €10 PE^{-1} d^{-1}, 2.1-2.3 times higher than primary settling, HiCAS and HiCS due to higher costs for sludge disposal and coagulant addition. As such, primary settling is most appealing in terms of total cost, yet the amount of sludge that can be captured is much lower and this analysis ignores the cost of sludge capture, the VFA yields from each sludge, etc.

Similarly a thorough economic analysis is needed to select an target product. Based on the market value (Figure 4.B, section 3.2) one could think that it is economically more interesting to produce butyl acetate over ethyl acetate (million €3950 kg^{-1} *vs.* million €1450 kg^{-1} measured at median). However, the production requires the addition of an equimolar amount of their respective alcohol. A tonne of butanol is 3-4 times more expensive than that of ethanol, which implies that the potential net revenue that can be obtained from either of the esters may be similar.[126]

From a policy point of view, a review of the bio-economy strategies shows that, although a majority of these strategies promote the production of higher value commodities, the actual policies in most countries incentivize the production of bioenergy and biofuels, the lowest level products of the value pyramid.[127] One specific example is the EU's "Renewable Energy Directive" which encourages the production of renewable energy such as methane through subsidies,[128] which has a value of 20% of PHA per unit of weight, and only 6% per unit COD.[7] New legislation is needed to support the development of sewage valorization routes to products other than biogas.

The environmental benefits of the production of PHA, SCP and esters from sewage should also be evaluated. Evidence suggest that the environmental impact of PHA derived from sewage is 70% lower than that of currently available PHA.[4] For PNSB and AHB production as protein source, there is no specific information on their environmental impact, evidence for other SCP, such as algae, show promising results. For production of *Nannochloropsis sp.* in a photobioreactors at industrial scale (2.5ha) results show that micro-algae systems have a 68% lower environmental impact for abiotic resource consumption than fishmeal production.[129] To the knowledge of the author no information on the environmental impact of alternative ways of ester production is available yet.

4.4. Ensuring product quality and safety.

To realize sales of recovered products, their quality must at least be comparable to that of their current alternatives. Among the three different routes proposed here, sludge-derived esters will likely have similar properties as their petrochemical analogues, since they are selectively recovered by distillation. For PHA there is evidence that plastics, containing PHA derived from sewage, result in similar or even improved material properties including impact strength, rheology during molding and transparency.[4] For SCP, protein content is high (50-83% on dry weight basis *cf.* 69% fishmeal) [130] and the protein quality (*i.e.* amino acid profile) compares well with fishmeal and soybean meal.[96,131,132] The fact that PHA and esters originate from sewage will not affect their utilization, as biological contamination is likely to be reduced during membrane filtration processes and further processing. More importantly, the use of these products can focus on applications that do not pose health risks (*e.g.* no contact with food or drinks). For SCP it is however important that potential risks are minimized and managed to ensure the safety of the final products. Currently, European legislation does not permit the use of protein produced on a fecal substrate.[133] However, in the drinking water industry, wastewater is reused for drinking water purposes (*e.g.* Torreele water plant on the Belgian North Sea coast) by applying a multi-barrier approach to ensure a successive reduction of the contamination risk.[134,135] [133] In adopting this approach, the precautionary principle is followed, which states that in the light of scientific uncertainty about the harmful effects of certain substances, additional measures are to be taken to ensure the high level of health protection adopted.[136] In the multi-barrier approach proposed for SCP, the first barrier is the inactivation. Evidence suggests that anaerobic digestions does lead to a die-off of pathogens (*e.g. Listeria monocytogenes, Salmonella enterica, Escherichia coli,* and *Campylobacter jejuni*).[137] Similar, results can be expected for thermophilic acidogenic fermentation as the high temperature, low pH and high VFA conditions in the fermentation stage may also exert a toxic effect on microbes. While the toxicity of VFA for microorganisms is well described in literature,[53] the effectivity of VFA-rich fermentation broths for that purpose is yet to be proven. A second barrier is provided by the membrane-based concentration/extraction step. Ultrafiltration membranes prevent the passage of microbes, while a nanofiltration step can remove particles as small as 0.002 to 0.005 μm in diameter including enteroviruses and rotaviruses, pesticides and other contaminants.[138] A third barrier consists of implementing selective culturing conditions. For PNSB this is for instance the use of infrared-light under anaerobic conditions, which results in a community dominated by PNSB (*e.g.* dominance of 75-90% in anaerobic membrane bioreactor treating sewage).[139] However, there are to the authors' knowledge no similar parameters to produce AHB selectively available today. Finally, the fourth barrier is pasteurization or drying of the

SCP to produce a final bio-product.[140] Future research must provide evidence that these multiple barriers ensure compliance to feed and safety regulations. Eventually, these evidence must lead to further amendments of current legislation such as the EC Directive 82/471/EEC concerning products used in animal nutrition.[141] Indeed, current trends in policy making certain types of SCP are already legalized as a protein source in animal feed and there are prospects that new types of SCP and insect protein will be legalized as a feed ingredient in the short and medium term.[136]

5. Conclusions and Outlook

This critical review demonstrates that sewage is an abundant resource that can be exploited in a bio-economy, as a result of technological progress in capturing COD as sludge, the production of VFA from it and their conversion into commodities. The estimation of the production potential from sewage show that respectively in 60% of the simulations 28-273% (0.2-2.0 megatonnes), 70-140% (0.7-1.4 megatonnes) or 21-72% (0.6-2.2 megatonnes) of the current global acetate-derived ester, compostable plastic and fishmeal production could be substituted.

When considering the potential market value that could be generated from sewage, production of butyl acetate could be the most lucrative valorization route, followed by bioplastic and protein production. However, other factors such as maturity of the technology and safety need to be taken into consideration. Currently, production of bioplastic from sewage is the most mature technology (technology readiness level; TRL 6-7), and products derived from PHA should be marketable under the existing legislation framework. Further developments are needed to bring esters and SCP to the par in the short- to mid-term. The ester valorization route would require further research to increase the TRL. On the contrary, SCP production is at a similar TRL as bioplastics (Supporting Information S6), but commercialization as feed/food is hindered by legislation and scientific evidence for its safety.

The review further indicates a set of key scientific and societal challenges that remain for a successful implementation of the proposed three-step approach. These are summarized below.

Step 1 – Capture COD as sludge

- Maximize COD recovery into a highly anaerobically biodegradable sludge by enhancing the capture of colloidal and dissolved COD fractions. Additionally, for biological COD-capture technologies, sludge settlability needs to be improved to prevent washout.

Step 2 – Ferment sludge to VFA

- The VFA yields need to be improved by, developing cost-effective sludge pretreatment methods that enhance sludge hydrolysis and COD solubilization. Steering acidogenic fermentation to target VFA profiles is an additional remaining challenge.

Step 3 - Upgrade VFA to commodities

- Downstream processing is one of the key bottlenecks of the three routes proposed here (*i.e.* extraction and recovery of PHA; extraction and concentration of VFA and their isolation in a water-free phase for esterification; recovery of SCP).

Shortcut nitrogen removal in the water line

- The proposed three-step approach with enhanced COD-capture requires the implementation of nitrogen removal technologies in the water line with reduced or no COD requirements, such as the nitritation/denitritation (nitrite shunt) or partial nitritation/anammox (deammonification).

Economy and environment

- With the exception of PHA, there is little information on the economic and environmental benefits of the proposed valorization routes. Further research should address these knowledge gaps to provide evidence for their economic potential and environmental footprint.
- The commodities derived from the three-step approach are only raw materials, yet to be converted into marketable products. The necessary product development requires, in addition to good economic prospects, a critical production volume to attract companies that may be interested in further processes esters, PHA and SCP.

<u>Regulation and legislation</u>

- SCP produced from fecal-contaminated waste materials cannot be marketed under the current legislation framework. Further work should provide scientific evidence of the health and safety of the final product and the appropriate function of the multi-barrier approach to support changes in policy.

6. Associated content

Supporting Information. Methodology, literature-based assumptions and explanation of probability distributions used in Monte Carlo simulations to calculate captured COD as sludge, VFA production and the flow of upgraded commodities: esters, polyhydroxyalkanoates and microbial protein.

7. Notes

The authors declare no competing financial interest.

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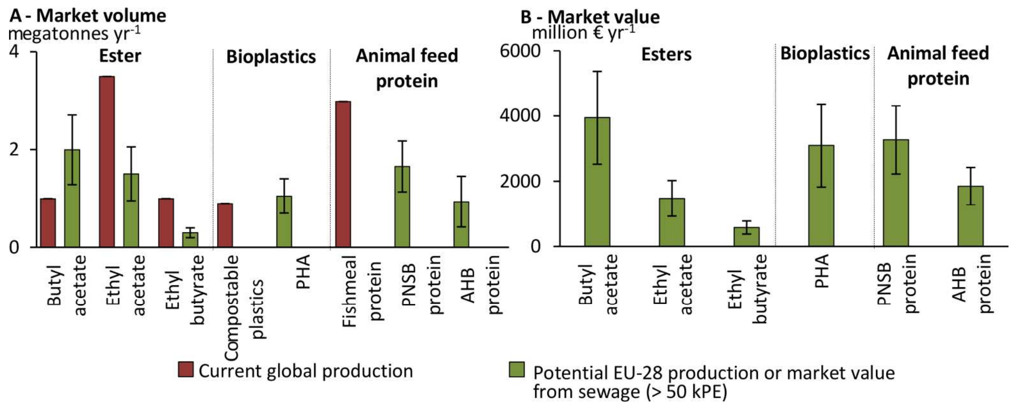

Figure 4 Overview of (A) the current global esters,56 bio-based compostable plastics production78 and fishmeal protein,119 along with their potential production from sewage treatment plants with a capacity higher than 50 kPE and (B) the potential turnover for all commodities. Bars show overall average and error represent the 0.2-0.8 probability interval.

172x67mm (300 x 300 DPI)