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## Anaerobic digestion-derived digestate valorization: green chemistry innovations for resource recovery and reutilization

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Anaerobic digestion (AD) plays a crucial role in sustainable waste management, converting biowaste into biogas while generating digestate as a nutrient-rich by-product. This review explores innovative digestate valorization strategies based on the principles of green chemistry, focusing on resource efficiency and waste minimization through reutilization routes involving environmentally benign processes. The study examines the physicochemical characteristics of digestate and highlights its applications in sustainable agriculture, bioprocessing for enzyme production, algal biorefineries and hydroponic systems. Advanced valorization pathways, including bio-based polymer synthesis, biochar production and recovery of high-value chemicals such as volatile fatty acids, lactic acid and humic substances for commercial viability are critically analyzed through technoeconomic feasibility and life cycle assessment insights. Inorganic nutrient recovery techniques, including ammonia stripping, struvite precipitation and membrane separation, were also explored for their potential to enhance resource utilization. Thus, by integrating digestate valorization within a circular bioeconomy framework and industrial symbiosis, this study underscores its role in reducing the environmental impact, improving the carbon footprint and contributing to net-zero emissions. Our discussion further highlights the challenges in digestate processing, regulatory considerations and future research directions to optimize sustainable valorization strategies by integrating green chemistry principles.

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### Green foundation

1. We explore sustainable strategies for digestate valorization, transforming waste into bio-based fertilizers, biofuels, bioplastics, and high-value chemicals. This aligns with green chemistry principles by reducing the reliance on fossil-based inputs and minimizing the environmental impact. Key advancements include catalytic upgrading, enzymatic bioprocessing, and nutrient recovery to enhance resource efficiency.
2. Digestate valorization addresses critical challenges in waste management, energy recovery, and climate change mitigation. By integrating circular bioeconomy strategies, it supports net-zero emissions, reduces landfilling, and promotes regenerative agriculture. The growing industrial and regulatory interest, such as the EU Fertilizer Regulation (CE 2019/1009), underscores its significance.
3. Future developments will focus on process optimization, biorefinery integration, and techno-economic feasibility. Advances in catalytic conversion, microbial engineering, and energy-efficient processing will drive innovation, accelerating the transition to a sustainable, low-carbon economy.

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# 1. Introduction

Anaerobic digestion (AD) is a key biological process that not only generates biogas but also yields digestate (microbially digested solid residue), a nutrient-rich by-product with vast potential for sustainable resource recovery. Thus, maximizing the utilization of digestate through innovative valorization strategies aligns with green chemistry principles, thereby reducing waste, enhancing energy efficiency and supporting the circular bioeconomy.<sup>1</sup> The advantages of adopting AD technology for waste management include waste volume reduction, deodorizing, decrease in pathogen load, minimal energy usage and high energy recovery. AD occurs in four stages, *viz.*, hydrolysis, acidogenesis, acetogenesis and methanogenesis, resulting in biogas production, which is influenced by pH, temperature, feedstock composition, nutrients, substrate particle size and the carbon/nitrogen (C/N) ratio.<sup>2</sup> The residual solid produced as a by-product of AD, along with biogas, is referred to as digestate. This nutrient-rich semi-solid material consists of partially decomposed organic matter (from source feedstock), microbial biomass, minerals and water.<sup>3</sup> It has been estimated that the digestate produced from rice straw AD operation is about 50–100 kg m<sup>-3</sup> of the generated biogas.<sup>4</sup> It is also predicted that a biogas facility from agricultural wastes with an energy production capacity of 500 kW can yield 10 000 tons of digestate annually.<sup>5</sup> Recently, the Hong Kong Environmental Protection Department (2020) reported that an AD plant (O PARK1) in Hong Kong capable of processing 200 tons of food waste per day generates about 20 tons of digestate. Moreover, in the European Union, 80 million tons of digestate is being generated from 117 AD plants that process a variety of organic materials, including food waste, farm waste, manure and crop residues.<sup>5</sup> In China, the sustainable treatment of approximately 30 000 tons of food waste per day is required. Around 74% of the planned projects for food waste treatment utilize AD, leading to the production of approximately 1500 tons of digestate per day (based on dry matter).<sup>6</sup> In this case, the challenges associated with the application of digestate arise from the presence of hazardous substances, pathogens and heavy metals, which vary depending on the treated feedstock.<sup>7</sup> According to the World Biogas Association (WBA), replacing one ton of chemical fertilizer with digestate can save one ton of oil, 108 tons of water and 5 to 9 tons of carbon dioxide (CO<sub>2</sub>) emissions.<sup>8</sup> Recently, Bergstrand *et al.*<sup>9</sup> revealed that the digestate (<100 mg L<sup>-1</sup> nitrite) can also be utilized as a nutrient solution in hydroponic systems.

Nevertheless, the direct application of unstable digestate to the land carries the risk of inducing soil acidification and releasing greenhouse gases uncontrollably,<sup>10</sup> also resulting in the potential introduction of toxic nano-sized metal derivatives into the food chain through food crops.<sup>11</sup> Alternatively, the landfill approach is limited in urban settings due to the emission possibilities of greenhouse gases, leachate and the rapid exhaustion of restricted landfill capacity.<sup>12</sup> Hence, the development of cost-effective and sustainable technology to manage digestate is imperative. In this regard, the process of convert-

ing digestate into high-value products holds significant importance in terms of enhancing the economic benefits of AD plants and augmenting their sustainable applications. Moreover, it creates enhanced possibilities for the recycling of biodegradable waste and the development of advanced biorefineries. In recent times, there has been significant interest in thermochemical processes such as pyrolysis, gasification and hydrothermal liquefaction/carbonization. These processes have garnered attention for their capability to convert digestate into various products, including biochar, bio-oil and syngas.<sup>13</sup> However, drying the feedstock is a key hurdle in thermochemical processes except in hydrothermal liquefaction. Recently, microalgae have been found to be promising in the simultaneous valorization of liquid digestate and resource recovery.<sup>3</sup> Besides their potential in biofuels such as biodiesel and bio-crude, they have garnered increasing interest as feed and food ingredients.<sup>14</sup> Furthermore, recent studies have stated that digestate can be utilized as a feedstock for the production of polyhydroxyalkanoates (PHA) and in bioelectrochemical systems (BES).<sup>15</sup>

With the rapid expansion of AD as a sustainable waste to energy technology, the management of digestate, its primary byproduct, has become a critical challenge that necessitates immediate intervention to make AD sustainable technology. Digestate valorization presents a promising avenue for closing the resource loop in AD systems, aligning with global sustainability goals and circular economy principles. This review systematically explores the potential of digestate-derived biomaterials, bio-chemicals and nutrient recovery strategies, integrating recent advancements in green chemistry to assess their environmental, economic and technological viability. By critically analyzing the state-of-the-art valorization technologies, including biochar production, PHA synthesis and advanced nutrient recovery methods, we provide a comprehensive overview of their scalability, commercialization prospects and regulatory challenges. The overarching goal is to bridge the gap between emerging innovations and large-scale industrial applications, ultimately contributing to a more resource-efficient and environmentally sustainable waste management option.

## 2. Anaerobic digestion products

The major products obtained through AD are biogas and digestate. Combined digestion or co-digestion has been developed as an alternative to the conventional methods for the production of biogas from agro-industrial waste, sewage, animal waste, farmyard manures, crop residues, dedicated bioenergy crops and wastewater treatment-derived microalgal biomass in various countries.<sup>16</sup> Previously, AD was associated mostly with a single-feed single-product process. Presently, in co-digestion, various substrates are digested simultaneously with complementary properties, and thus has been widely adopted given that the co-digestion of several substrates can result in a greater methane (CH<sub>4</sub>) yield than individual substrates. In addition, the decrease in noxious or repressive compounds,



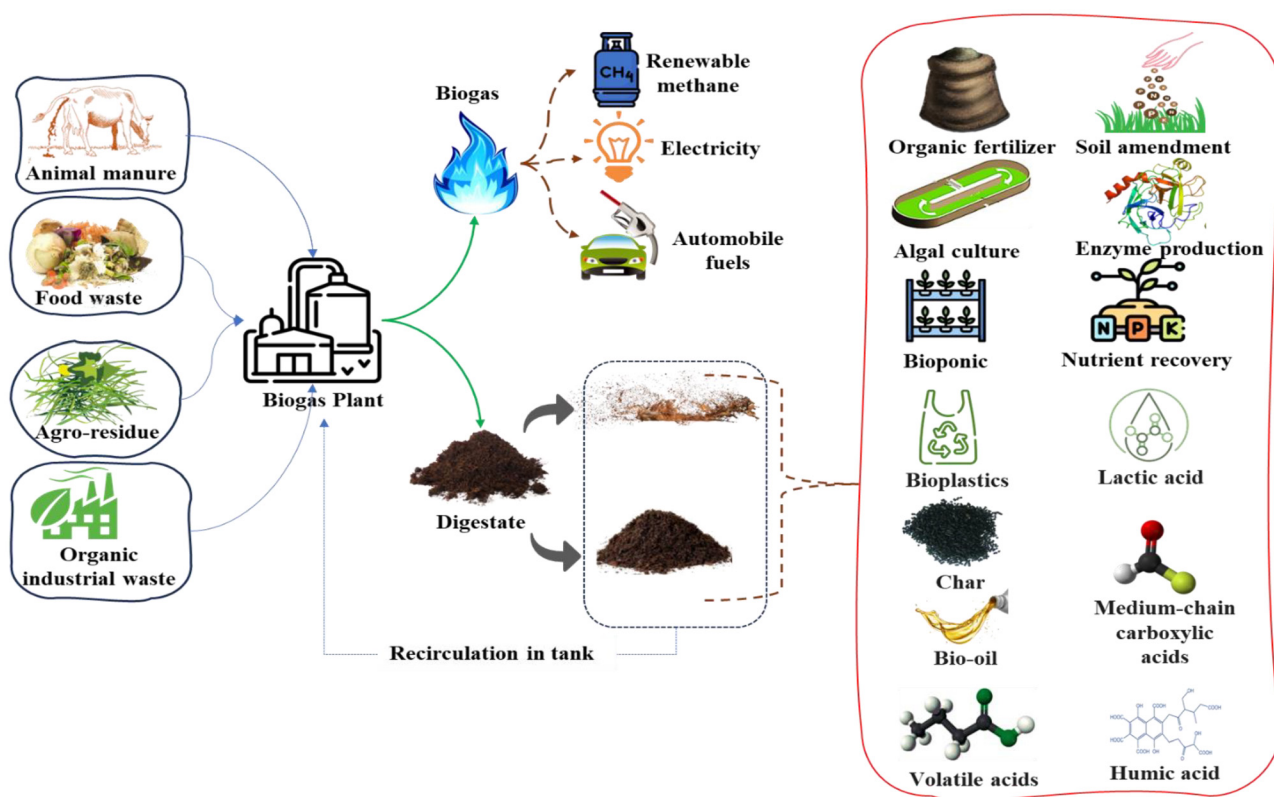


Fig. 1 Various valorized products derived from anaerobic digesters.

maintenance of balanced C/N ratio, and nutritional supplements to buffer the reactor can improve the biogas production efficiency.<sup>17</sup> The various valorized products derived from AD are illustrated in Fig. 1. Although the theme of this article is to highlight the importance of the byproducts produced from digestate, it is equally important to realize the significance of biogas and its associated products.

### 2.1. Biogas

Biological waste presents a diverse composition, marked by notable variations in moisture content and the presence of contaminants such as glass, stones, metals and sediment. For instance, animal waste from sources such as pigs, cattle, poultry, fish and other livestock is typically comprised of around 90% volatile solids and moisture within its solid fraction.<sup>18</sup> The conversion of organics into biogas unfolds through four key steps of hydrolysis, which disintegrates complex compounds into monomers, acidogenesis, transforming these monomers into short-chain fatty acids, acetogenesis, yielding hydrogen, carbon dioxide and acetic acid, and methanogenesis, subsequently converting these products into methane and carbon dioxide. The optimal conditions for methanogens are pivotal, given that each stage of AD exhibits varying reaction rates influenced by factors such as temperature, pH and substrate concentration. Innovations such as dry-digestion systems, two-stage processes, co-digestion, micronutrient boosters, appropriate reactor types and pre-treatment method-

ologies have been proposed to streamline and enhance AD processes.<sup>19,20</sup>

The composition of biogas significantly varies depending on its origin. The methane content in landfill gas ranges from 36% to 52%, while in wastewater treatment digesters and household waste digesters, it remains consistent at 65%. Conversely, industrial waste and animal manure digesters display a broader range of CH<sub>4</sub> content, fluctuating between 60% to 80% and 50% to 70%, respectively. The carbon dioxide content fluctuates across different sources. In landfill gas, it falls in the range of 30% to 41%, around 33.5% for wastewater treatment digesters and approximately 29% for household waste digesters. Industrial waste and animal manure digesters exhibit varying CO<sub>2</sub> levels, ranging from 20% to 40% and 30% to 50%, respectively. The hydrogen (H<sub>2</sub>) content in agricultural waste and industrial waste-derived biogas has been reported to be 2% and 5%, respectively, whereas landfill-derived biogas does not contain H<sub>2</sub>. The nitrogen (N<sub>2</sub>) content typically remains below 10% for landfill gas and below 5% for wastewater treatment digesters. Nitrogen is undetectable in biogas from household waste, industrial waste and animal manure digesters. The hydrogen sulfide (H<sub>2</sub>S) levels range from 0.001% to 0.1% in landfill gas, whereas wastewater treatment digesters yield biogas with H<sub>2</sub>S levels between 0.015% and 0.3%. In contrast, H<sub>2</sub>S is not detected in biogas from household waste digesters. In the case of industrial waste and animal manure digesters, the levels are below 0.3% and 0.5%, respectively.



The oxygen content varies across sources, typically falling below 3% in landfill gas, below 1% in wastewater treatment digesters and either not detected or below 1% in industrial waste and animal manure digesters. The water vapor content is in the range of 0.1% to 3.3% in landfill gas, approximately 2% in wastewater treatment digesters and 0.5% in household waste digesters. In contrast, the water vapor content is in the range of 1% to 4% in industrial waste and animal manure digesters. The ammonia content ( $\text{NH}_3$ ) in biogas remains minimal or undetected across various sources, with levels typically below 0.0005%.<sup>21–25</sup> These variations underscore the diverse nature of biogas compositions, emphasizing the importance of tailored processing techniques to maximize the utility of biogas as a renewable energy source. A summary of biogas composition from different sources is presented in Table 1 to facilitate visualization and comparison.

The refinement and enhancement of raw biogas to meet rigorous fuel quality standards are vital processes. The elimination of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  is essential to enhance the calorific value of biogas. Furthermore, biogas has the potential to be upgraded into renewable natural gas (RNG), *i.e.*,  $\text{CH}_4$ , which meets the same standards as conventional natural gas and can be utilized in natural gas vehicles without any issues. RNG refers to biogas that has undergone a purification process to meet specific purity standards, typically containing approximately 90%  $\text{CH}_4$ . RNG can be utilized as transport fuel in the form of compressed natural gas (CNG) or liquefied natural gas (LNG), similar to conventional natural gas.

The utilization of biogas in power production is not very well known, though it is gradually becoming a normal practice in developed countries.<sup>26</sup> A study conducted by GTZ authorities in Kenya on intermediate and large scale power plants (>50 kW) disclosed that the usual profit period is about six years under suitable conditions and about nine years under unsuitable conditions, based on an energy cost of  $\$0.15 \text{ kW}^{-1} \text{ h}^{-1}$ .<sup>27</sup> Further, research on the situations in other African and emerging countries exposed that grid-associated biogas energy production for small biogas plants is not economically viable. Thus, to encourage the adoption of small and medium biogas plants, it is essential for governments to offer incentives such as attractive feed-in tariff schemes and other technical and financial benefits. Research suggests that biogas plants may not be economically viable without grants, competitive pricing,

or feed-in schemes, offering approximately  $\$0.20 \text{ kW}^{-1} \text{ h}^{-1}$  for electricity generated by biogas power plants and supplied to the grid. In addition to financial incentives, providing mechanical support can further encourage the establishment and success of these biogas plants.<sup>27</sup> The growth of biogas power production in Germany and other developed countries has been facilitated by established feed-in tariffs. However, in developing nations, prominent biogas power facilities heavily rely on international donors and financial institutions for funding, indicating a lack of commercial and economic viability. Currently, the use of treated biogas as fuel for combustion engines, which convert it to mechanical energy, powering an electric generator to produce electricity, is a noteworthy progression. In addition, the use of biomethane to produce liquid biogas (LBG) as vehicular fuel can yield significant benefits. LBG surpasses biogas in terms of space efficiency by over 600 times and approximately three times compared to compressed biogas (CBG) at a pressure of 200 bar.<sup>27</sup>

## 2.2. Digestate

According to Ren *et al.*,<sup>28</sup> the production of digestate is a vital component of AD processes. This holds particular importance in biogas facilities that utilize agro-industrial waste and operate under mesophilic conditions through the wet fermentation process. The partial degraded or non-degraded solid residue is termed digestate, which needs to be regularly managed either as fertilizer or processed into other valuable products. The quality of the digestate mostly depends on the type of substrate, susceptibility of the substrate to decomposition, pretreatment and the type of fermentation employed (dry/wet). In biogas plant facilities, a significant volume of digestate is generated daily, typically constituting 70–90% of the feedstock weight.<sup>29</sup> This digestate production varies across regions and is influenced by the type of feedstock utilized. In the United Kingdom, AD plants processing food waste substantially contribute to digestate production, yielding approximately 36 400 metric tons annually. Similarly, in Greece, AD plants utilizing animal residues and vegetable oil contribute to digestate production, generating 100 metric tons and 800 metric tons annually, respectively. In Italy, AD plants processing agricultural residues significantly contribute to digestate production ranging from 20 000 to 22 000 metric tons per year. Additionally, in Malta, digestate production is augmented by wastewater treatment plant (WWTP) sludge, accounting for

**Table 1** Typical composition of biogas from different feedstocks<sup>21–25</sup>

Component	Landfill gas	Wastewater treatment digesters	Household waste digesters	Industrial waste digesters	Animal manure digesters
$\text{CH}_4$ (%)	36–52	65	65	60–80	50–70
$\text{CO}_2$ (%)	30–41	33.5	29	20–40	30–50
$\text{H}_2$ (%)	0	0	0	5	2
$\text{N}_2$ (%)	<10	<5	0	0	0
$\text{H}_2\text{S}$ (%)	0.001–0.1	0.015–0.3	0	<0.3	<0.5
$\text{O}_2$ (%)	<3	<1	<1	<1	<1
Water vapor (%)	0.1–3.3	~2	0.5	1–4	Not detected



**Table 2** Characteristics of digestate from a variety sources

Digestate source	pH	Moisture content %/w/w (wb)	Ash content %/w/w (db)	Volatile content %/w/w (db)	Ref.
Agro industrial residue.	7.7	76.2	9.3	68.9	33
Biowaste	8.31	75.60	NA	63	34
Stockyard waste	8.23	96.98	39.53	NA	35
Organic household waste	NA	NA	35.8	85.1	36
Energy corps	NA	NA	28.7	78.4	36
Cow manure	NA	NA	15.7	79.8	36
Municipal solid waste	NA	82	NA	NA	37
Cow manure with maize	8.37	NA	NA	89.6	38
Agro waste with chicken manure	9.05	NA	12.7	72.1	39
Maize silage	8.5	NA	5.6	77.1	40
Water treatment wastes	7.9	74.1	NA	NA	41
Food and vegetable waste	8.42	88	NA	NA	42

wb – wet basis; db – dry basis; NA – not available.

approximately 7220 metric tons annually. These diverse sources and quantities of digestate highlight the broad spectrum of feedstocks and regional variations in biogas plant operations.<sup>30</sup> The notable characteristic of digestate is its high (60–99%) moisture content, together with a relatively lower proportion (3.1–5.4%) of solid materials.<sup>25–27</sup> Table 2 summarizes the characteristics of digestate from various waste biomass. According to Seppälä *et al.*,<sup>31</sup> the dry matter content of digestate derived solely from animal manure was determined to be 4.8%. However, when animal manure was mixed with low-feed maize, the dry matter content varied, with values of 5.0%, 4.5% and 4.0%. This suggests that the inclusion of low-feed maize affects the solid content of the digestate. Furthermore, in the case of a mixture comprised of animal manure and high-feed maize, the dry matter percentages were measured to be 4.7%, 4.7% and 4.9%, respectively.<sup>31</sup> These findings highlight the influence of different feedstock combinations on the dry matter content of the resulting digestate, providing insight into the composition and characteristics of the produced digestate. The key characteristic of the digestate is its reduced dry matter content and elevated moisture. The high moisture content required for wet fermentation from a technological perspective poses a difficulty in managing the resulting digestate. Once the moisture content surpasses 90%, the recovery process through composting becomes difficult. This is because the liquid or semi-solid form of the digestate is not suitable for the composting process. Hence, it is important to subject the digestate to a dehydration procedure before proceeding with composting or solid biofuel production. Dewatering is also a recommended approach for reducing the moisture content of digestate and is gaining recognition as a feasible strategy in the design and construction of biogas plants that utilize wet technology. Kovačić *et al.*<sup>32</sup> suggested that digestate dewatering can be accomplished using mechanical techniques such as filtration and centrifugation, as well as electrochemical and physicochemical methods such as electrocoagulation and chemical coagulation.

It is important to understand that despite the potential for generating a greater quantity of solid fractions as digestate

from AD plants, the costs associated with separation typically limit the procedure to the two specified fractions (solid and liquid). The equipment chosen for separation should be suitable in terms of type and capacity, considering the significant amount of digestate produced daily. The separation process offers a simple approach to broaden the scope and variety of management options for the digestate.<sup>43</sup> According to the findings of Beggio *et al.*,<sup>44</sup> it is imperative to consider the unique characteristics of each fraction produced during the management stage. Specifically, the solid fraction plays a vital role in the composting process. Therefore, it is necessary to separate the digestate into two distinct fractions prior to composting. The solid fraction, with a reduced water content typically ranging from 60–75%, is suitable for composting. This fraction possesses advantageous properties such as a substantial amount of organic matter, flow-friendly nature and increased porosity. These properties enhance the feasibility of the composting process, even when dealing with less favorable.

Understanding the environmental and economic implications of digestate management underscores the importance of maintaining its quality for effective utilization. Several intrinsic and extrinsic factors influence the digestate composition, directly affecting its suitability for agricultural applications. The following section explores these key factors, including feedstock selection, process parameters and quality management strategies essential for optimizing digestate valorization.

### 3. Factors influencing digestate quality

The prime application of anaerobic digestate involves its use as fertilizer for soil, which places a significant demand on its quality, encompassing physical, chemical and biological attributes. The properties of digestate suitable for direct application largely depend on the selection of an appropriate feedstock for AD.<sup>45</sup> Besides the feedstock, quality digestate meant for soil application purposes is governed by some essential



factors related to its characteristics such as desirable concentration of nutrients, pH, organic solid content and homogeneity. Additionally, it is important to verify the presence of plastics, microplastics, non-digestible material, metals, stones, *etc.*, together with sanitization, thereby ensuring that SD is devoid of any pathogens.<sup>46</sup>

The composition of digestate is influenced by several key factors, including the C/N ratio, pH, concentration of volatile fatty acids (VFA), feedstock retention time and process temperature, as illustrated in Fig. 2.

When the potential of digestate is fully utilized, it has been found that it could replace up to 7% of inorganic micronutrients supplied through synthetic fertilizers.<sup>47</sup> During the production of biogas, the digestate is removed and stored in large tanks, but due to incomplete digestion, it has been observed that the digestate releases some CH<sub>4</sub>, nitrous oxide (N<sub>2</sub>O), CO<sub>2</sub> and NH<sub>3</sub> directly into the atmosphere.<sup>48</sup> Thus, to prevent this emission, the digestate should be recycled appropriately. Digestate quality management and control measures are essential components of the complete closed AD cycle. This encompasses the entire process, starting from the production and supply of feedstock to the ultimate utilization of digestate as fertilizer. Effective quality management entails utilizing only high-quality feedstock, pre-processing specific types of

feedstock such as lignocellulosic materials before AD and maintaining a stable and robust process. Additionally, it involves monitoring the process parameters that influence the digestate quality to ensure the optimal results. Several feedstocks such as agro-waste from the food industry, animal waste and by-products from crop production, sewage sludge and municipal solid waste contribute a larger fraction of feedstock for AD.<sup>49,50</sup> However, pollutants such as heavy metals and xenobiotic recalcitrant are found in these waste, significantly affecting the macronutrient and micronutrient content of the digestate. In addition, the water source, reactor operation and the fertilizer application technique used after the reactor output are aspects that directly impact the quality of biogas digestate.

Sanitation is frequently performed for digestate to be utilized in a risk-free way. The digestate that is withdrawn from the reactor must be processed in a mixed flow reactor at 70 °C for 1 h in accordance with the European Union sanitation standard.<sup>45</sup> The sanitation procedure might pose the drawback of loss of N content in the form of NH<sub>3</sub> from the digestate. However, the addition of ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) after the sanitation process can make up for this loss, after which the digestate can be applied as fertilizer. When the mass balance of the biogas reactor is analyzed, substantial solid

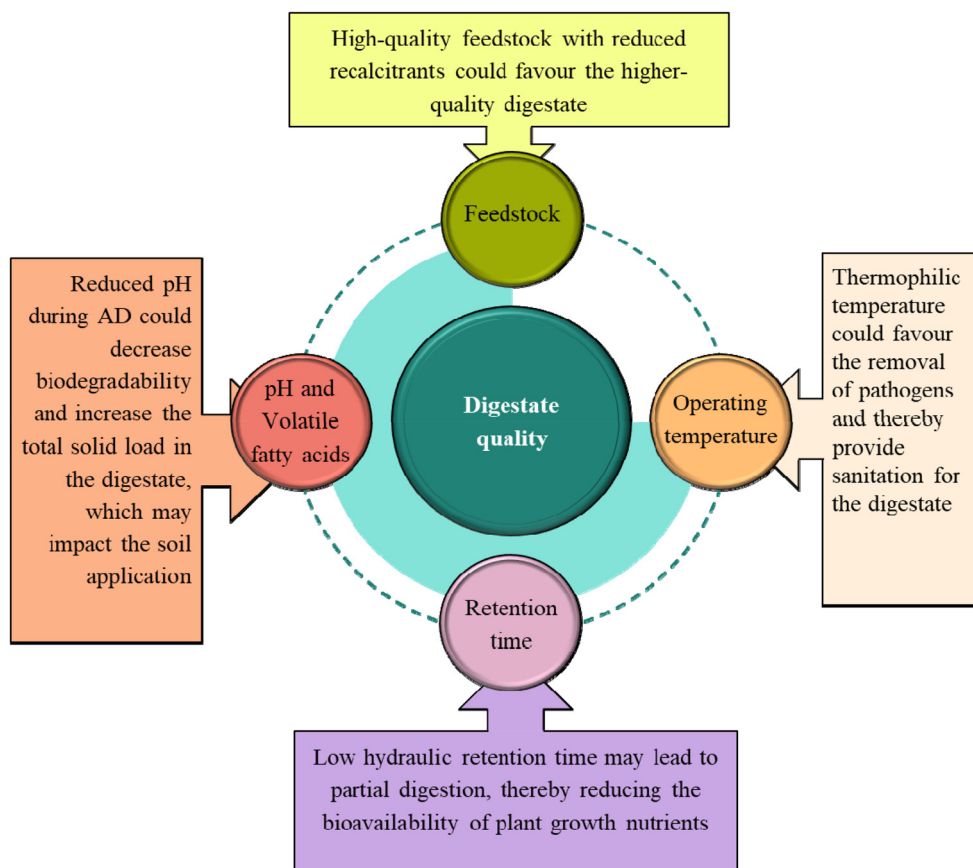


Fig. 2 Factors influencing the digestate quality.



removal is shown. Specifically, it was observed that the total solid content of the feed was reduced to 90–95% after the stabilization of AD or cessation of biogas production. Typically, a solid concentration of less than 6% in biogas digestate is obtained as digestate together with the liquid fraction termed leachate, which must be separated using a decanter and utilized separately as liquid manure.

The process temperature can vary in three distinct ranges in AD, *i.e.*, psychrophilic (less than 15 °C), mesophilic (range of 25–45 °C) and thermophilic (range of 45–70 °C).<sup>51</sup> The process temperature and hydraulic retention time (HRT) are inter-related to achieve the efficient digestion and reduction of the biological oxygen demand (BOD), for which mesophilic conditions are widely employed. Alternatively, in the case of pathogen inactivation, an increase in temperature (thermophilic digestion) and shorter HRT are recommended.<sup>52</sup> Thereby, the digestate that is taken out of the reactor is expected to be in a stable and sanitized state, which can mitigate the problem of digestate as a source of secondary pollutant with unrestricted emissions when applied to the soil.

Ensuring high-quality digestate is not only crucial for optimizing its agricultural benefits but also minimizing potential environmental and health risks. However, the safe and effective use of digestate requires adherence to strict regulatory guidelines. The following section explores the legislative frameworks governing the application of digestate, emphasizing their role in maintaining public health, environmental safety and market confidence.

#### 4. Regulatory frameworks for safe digestate utilization

The regulatory framework governing digestate usage plays a crucial role in ensuring environmental sustainability and public health safety. In line with green chemistry principles, these regulations aim to promote waste prevention, safer material design and sustainable resource utilization. Establishing clear policies for digestate quality standards can enhance its application as biofertilizer, while minimizing ecological risks. Given that the most prevalent end-use of digestate is biofertilizer application, which is interlinked with the food chain and public hygiene quality assurance, setting up a regulatory framework is deemed essential.<sup>45</sup> Although not a separate framework, the quality of digestate will be regulated by acts and legislation for environmental protection, water hygiene or waste management regulatory affairs formulated by different countries. However, only sporadic studies are available on the ecological impacts of digestate application and its risk assessment on public health and environmental aspects. This has led to the utilization of other standard operating procedures and methodologies for impact as well as life cycle assessment (LCA) for the application of digestate to the soil. Pardo *et al.*<sup>53</sup> reported an assessment strategy for source-segregated quality digestate in the form of composts in the United Kingdom using tools of LCA and ecological risk assessment to

establish a circular economy. There are certain factors that need to be considered, as described in Fig. 3, to improve our understanding of the ecology, community, nature of contaminants and the environment. Kapanen and M. Itävaara; Panuccio *et al.*; and Pivato *et al.*<sup>54–56</sup> demonstrated eco-toxicological analyses and test scheme soil amendments (compost), followed by adapting the same for digestate application, thereby justifying the fact that quality assurance is a paramount to gain confidence in the market to add economic value to digestate, which is otherwise disposed. Regulating these aspects ensures the compliance of digestate with quality standards, reduces the environmental/health risks and promotes safe agricultural and other applications.<sup>15</sup> A life cycle approach for digestate regulation can ensure minimal environmental burden and optimal resource recovery. Green chemistry-driven policies emphasize the valorization of organic waste streams, fostering a transition towards bio-based circular economy models. Encouraging sustainable digestate management through regulatory incentives, such as carbon credits for nutrient recovery and subsidies for eco-friendly processing technologies, can significantly enhance its safe and efficient utilization.

Industries that disseminate digestate as biofertilizer must consider several limiting factors that are set by legislation. These factors include the total amount of organic pollutants, BOD, chemical oxygen demand (COD), pathogens and heavy metals present in the products produced from waste. Based on the updated knowledge and experiences, new guidelines and amendments will be updated within the existing regulatory framework, which can restrict this process even more.<sup>45</sup> The main target in attaining the highest quality of digestate is to encourage its complete usage in agricultural farms, thereby ensuring sustainable and safe disposal practice. When feedstock is obtained from a high-quality agricultural segment, it is observed that the obtained digestate has a lower content of limiting factors. Most of the harmful materials, including weeds, intestinal parasites, bacteria and viruses, are effectively inactivated by the AD process. Biomass feedstock should not be acquired from farms where there are significant issues with animal health given that they will affect the feedstock quality and result in unsuitable digestate to be processed to produce fertilizer. In 1989, Denmark became the first nation in Europe to enact veterinary legislation on this aspect. Following this, other countries in Europe such as Germany, Austria, Sweden, Switzerland and the United Kingdom introduced similar standards and regulation.<sup>45</sup> Consequently, the transmission of disease between animals and humans can be prevented with strict pathogen control.

Although regulatory frameworks ensure the safe use of digestate, compliance often necessitates further treatment to meet environmental and agricultural standards. Thus, to enhance the quality of digestate and expand its application potential, various treatment technologies have been developed. The subsequent section explores these technologies, focusing on their role in improving properties of digestate and ensuring regulatory compliance.



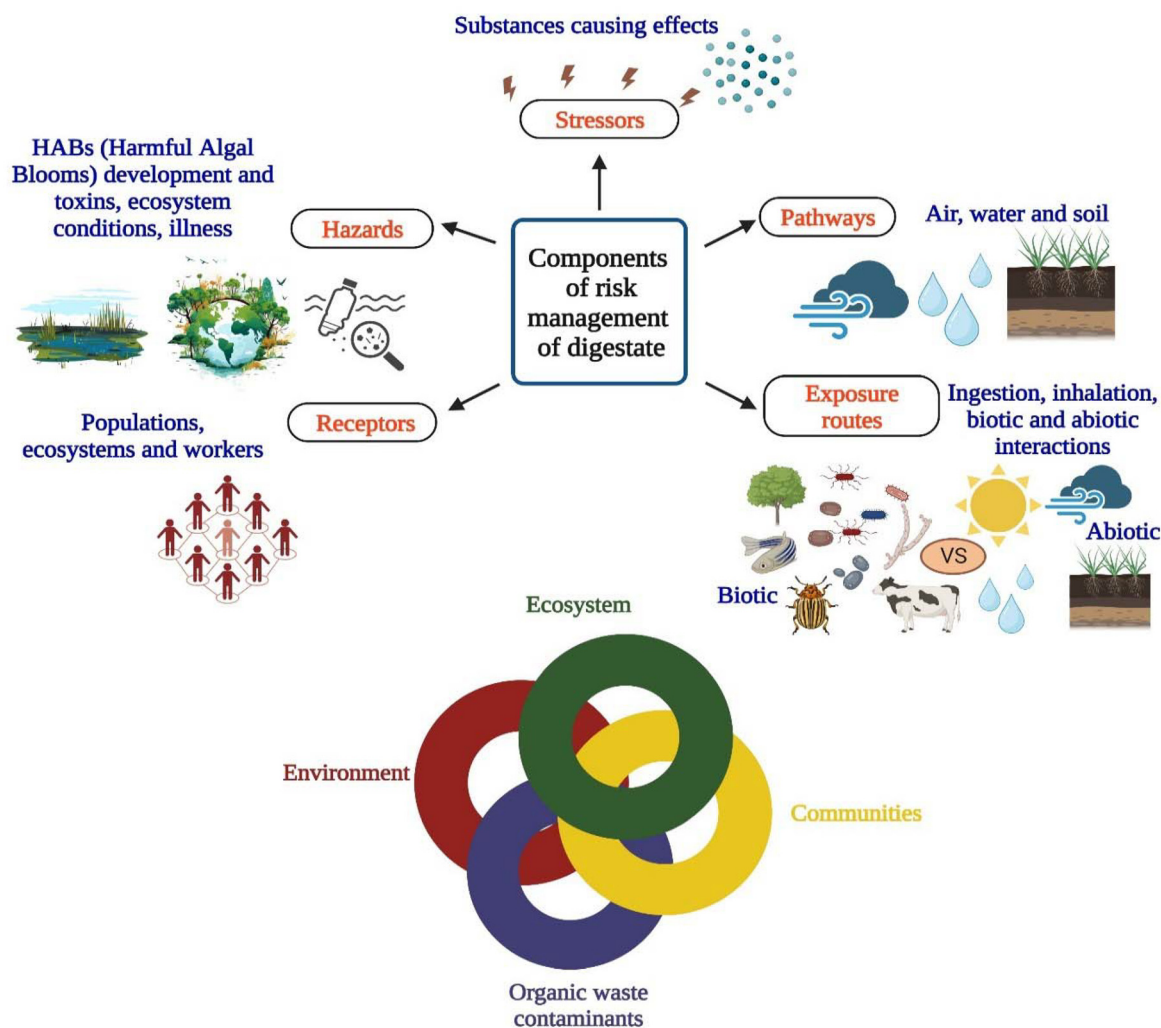


Fig. 3 Components of risk management of digestate and their implication on regulatory aspects to ensure product quality.

## 5. Sustainable utilization of digestate

The sustainable utilization of digestate is pivotal to advancing circular bioeconomy principles, while minimizing waste and its environmental impact. Through green chemistry-based valorization strategies, digestate can be repurposed into high-value bioproducts, contributing to climate mitigation and resource efficiency. This section explores the innovative approaches for digestate valorization, beginning with its role in the optimization of the anaerobic digestion process. This section explores the various valorization pathways for digestate, including its application in anaerobic digestion systems, agriculture, enzyme production, algal biorefineries and hydroponic systems, emphasizing their contributions to sustainability and circular resource management.

### 5.1. Recirculation in AD systems

Recirculating digestate within AD systems exemplifies the green chemistry principle of process optimization by enhan-

cing the biogas yield, reducing water and energy consumption and minimizing waste discharge. This closed-loop strategy fosters greater resource efficiency, while mitigating methane emissions and nitrogen loss. Besides reducing discharges, this recirculation method also minimizes the overall water consumption in biogas projects, resulting in cost savings and conservation of water resources. Additionally, the energy consumption is lowered through recirculation by harnessing retained heat in warm liquid digestate.<sup>57</sup> Liquid digestate is rich in biodegradable lignocelluloses, microbes and soluble nutrients. Liquid digestate recirculation (LDR) in anaerobic reactors not only decreases the liquid digestate discharge but also enhances the hydrolysis of organic matter, improving the buffer capacity and stability of the system. However, excessive LDR may increase the content of ammoniacal nitrogen ( $\text{NH}_4^+$ -N) and/or VFAs, potentially inhibiting bacteria and other microflora, and thereby reducing biogas production.<sup>58</sup>

In a study, thermophilic anaerobic sludge from a wastewater treatment plant was utilized for the production of bio-



hydrogen and CH<sub>4</sub>.<sup>59</sup> It was observed that the uncontrolled pH (averaging between 3.8–4.2) had a negative impact on the biogas (H<sub>2</sub> and CH<sub>4</sub>) yield. Digestate recirculation adversely affected the yield initially, with the optimal results observed at a recirculation ratio of 0.11. Lower recirculation ratios enhanced the performance of the two-stage AD process.<sup>59</sup> Chen *et al.*<sup>60</sup> investigated the AD of corn straw and cow dung, reporting that biogas production peaked at 60% recirculation (1.6 L d<sup>-1</sup>). VFA accumulation in the early stages was mitigated by increasing the recirculation ratio, promoting the growth of Vadin BC27 and methanobacterium strains. Recirculation proved beneficial for biomethane production and stability in corn stalk and straw/manure digesters. Wu *et al.* compared single-stage and two-stage AD with varying recirculation rates for CH<sub>4</sub> production from food waste.<sup>61</sup> Digestate recirculation positively impacted the CH<sub>4</sub> yield, organic loading rate system alkalinity and maintenance of the optimal pH for methanogens. However, meticulous control of two-stage AD systems with digestate recirculation is necessary to prevent ammonium accumulation.

Brémond *et al.*<sup>62</sup> focused on SD recirculation in continuously stirred tank reactors (CSTR) to enhance the energy efficiency. Direct SD recirculation without post-treatment increased the solid retention time by 11% to 38% and total solid content by 6% to 20%, demonstrating a simple and cost-effective means to improve the biogas plant efficiency.<sup>62</sup> Algapani *et al.*<sup>63</sup> explored biohydrogen and biomethane production from food waste and observed that a recirculation ratio of 0.3 resulted in optimized H<sub>2</sub> production. Digestate recirculation reduced the need for alkali addition by 54%, while maintaining overall energy production. Yuan *et al.*<sup>64</sup> reported biogas digestate recirculation to enhance the CH<sub>4</sub> content in anaerobic digesters. Their study demonstrated the cost-effectiveness of biogas recirculation, promoting CH<sub>4</sub> production through physiochemical and biological effects and improving the AD system efficiency. In the study by Ma *et al.*,<sup>65</sup> LDR in ethanol production from food waste improved the system stability. Notably, it increased the maximum organic load rates and enhanced the alkalinity of the methanogenic phase. Monitoring total VFAs/total alkalinity served as an early warning indicator of methanogenic phase instability. LDR enriched the microbial community diversity, contributing to increased stability and higher maximum organic load rates.<sup>65</sup>

## 5.2. Agricultural applications: organic fertilizers and soil amendments

Digestate-based fertilizers contribute to sustainable agriculture by reducing the dependence on synthetic fertilizers, which are energy intensive and contribute to greenhouse gas emissions. By closing the nutrient loop, digestate applications enhance soil health, promote microbial diversity and minimize nutrient leaching into water bodies, supporting the green chemistry goal of reducing environmental hazards.<sup>66</sup> Precisely, the digestate seems to contain a significant proportion of primary plant nutrients such as nitrogen (N), phosphorus (P) and potassium (K), which can improve soil fertility and support sustainable

agricultural practices without any chemical input.<sup>67,68</sup> The solid fraction of digestate, with its lower water content, yields granules with higher nutrient and organic matter concentrations compared to untreated digestate or the wet solid fraction. These granules can be pelletized alone or combined with other components, allowing their further processing and utilization. This process can result in both small pellets and larger briquettes, offering flexibility in the obtained end-products. Cathcart *et al.* performed an economic assessment of fuel pellet production from anaerobic digestate, considering the inclusion of mechanical separation to facilitate 'P' partitioning. A proposed solution was proposed by them, suggesting the utilization of the solid fraction of digestate for the dual purpose of fertilizer and fuel production.<sup>69</sup>

The direct use of digestate as fertilizer may be limited in P and K for plant growth. Nevertheless, nitrification of the digestate in the biofilm reactor prior to use as a fertilizer can resolve this issue.<sup>70</sup> It was experimentally proven that the content of nitrified digestate was 17% higher than in conventional mineral fertilizers for soil-less plant production.<sup>70</sup> However, this digestate may contain phytotoxins that are not desirable for plant growth. Therefore, Song *et al.*, proposed two solutions, *i.e.*, (i) dilution of the digestate (20–40% v/v) and (ii) applying wood-based biochar with the digestate (100 g biochar: 1 L digestate), which were validated with leafy vegetables.<sup>71</sup> For several years, researchers have studied the impact of using digestate on soil properties. According to the study conducted by Odlare and team in 2011, it was concluded that digestate has the potential to serve as a substitute for mineral fertilizers.<sup>72</sup> Nevertheless, it was observed that the impact of fertilization may exhibit a delay. The rationale behind this is that organic waste typically possesses a lower concentration of readily available N for plants compared to mineral fertilizers. According to their study, it was observed that digestate exhibited favorable impacts on various chemical properties of the soil. The study conducted by Slepiciene *et al.*<sup>73</sup> aimed to assess the viability of solid and liquid digestate as a means of organic matter and humic acid supplementation for soil amendment purposes. It was observed that the humification process had a favorable effect. Therefore, it is noteworthy that digestate has the potential to positively impact eroded soils and those with reduced productivity. The utilization of digestate as a fertilizer is currently a topic of extensive research worldwide.

## 5.3. Algal culture in liquid digestate

In recent decades, the cultivation of microalgae has garnered significant research interest as a promising avenue for the valorization of liquid digestate. The liquid anaerobic digestate, which is abundant in nitrogenous (N) compounds (139–3456 mg L<sup>-1</sup>) and P (7–381 mg L<sup>-1</sup>), stimulates the proliferation of microalga cells.<sup>74</sup> N-rich feedstocks such as manure, food waste, food processing waste, vegetable waste and industrial waste, can be readily converted to ammonium forms (free and/or ionic) that are preferred by microalgae compared with other forms of N.<sup>75,76</sup> This approach has gained immense



attention due to its ability to minimize the costs associated with scarce resources such as fertilizers and freshwater, while also promoting the sustainable production of biofuels. The combination of microalgae cultivation and anaerobic digestate management presents multiple benefits. Microalgae, being aquatic eukaryotic photosynthetic microorganisms, have the remarkable ability to produce biomass through photosynthesis. They can effectively utilize the nutrients found in digestate, while harnessing solar energy, enabling the production of valuable biochemicals and biofuels.<sup>77</sup>

They show promising potential in the integration of AD with microalgae cultivation, where digestate serves as a valuable culture medium. The digestate (30–50% v/v) from the AD of food waste was used as a nutrient source for the cultivation of *Dunaliella tertiolecta* and *Cyanobacterium aponinum*.<sup>74</sup> The algal biomass concentration for *D. tertiolecta* and *C. aponinum* was 3.52 g L<sup>-1</sup> and 1.36 g L<sup>-1</sup>, respectively, which eventually removed 80–98.99% of total N and 65% of total P. Furthermore, the biodiesel yields in the transesterification reaction were 68.7 mg g<sup>-1</sup> and 161 mg g<sup>-1</sup> for *C. aponinum* and *D. tertiolecta*, respectively. Similarly, *Chlorella vulgaris* grown in kitchen waste-based AD digestate (physically separated liquid from solid fractions) exhibited a biomass concentration of 0.86 g L<sup>-1</sup> in a pilot-scale photobioreactor (800 L).<sup>78</sup> Furthermore, microalgae have shown great potential in absorbing heavy metals from digestate.<sup>76</sup> In the study by Roberts *et al.*,<sup>79</sup> the successful integration of AD with a co-culture platform comprised *Chlorella sorokiniana* and *Methylococcus capsulatus* demonstrated effective digestate valorization and biogas upgrading. Similarly, AD of dairy wastewater coupled with microalgae cultivation could produce 4.25 g L<sup>-1</sup> biomass (*Chlorella* sp.) with a lipid content of 12.5% w/w.<sup>80</sup> However, utilizing anaerobic digestate as a growth medium for microalgae poses various challenges. These challenges include insufficient nutrient concentrations, elevated turbidity, the presence of competing biological contaminants, NH<sub>3</sub> toxicity, coarse suspended solid and metal toxicity. To overcome these challenges and maximize the effective utilization of anaerobic digestate in the cultivation of microalgae and cyanobacteria, Chong *et al.*<sup>75</sup> proposed various potential solutions (Fig. 4).

An example of successful microalgae cultivation using anaerobic digestate involves *Neochloris oleoabundans*, which showed the highest growth when cultivated in a 2.29% diluted supernatant (with a total N concentration of 100 mg N L<sup>-1</sup>), compared to filtered digestate and other dilutions. Noteworthy examples of robust microalgae genera that have shown resilience in wastewater or digestate environments include *Desmodesmus*, *Chlorella* and *Scenedesmus*. Among them, *Chlorella vulgaris* and *Scenedesmus obliquus* have demonstrated the ability to thrive under these conditions.<sup>81</sup> To realize the optimal growth, survival and dominance of the desired microalgae, it is advisable to carry out pre-treatment of the anaerobic digestate obtained during the AD process. This pretreatment focuses on altering the physicochemical properties of the digestate, such as reducing the turbidity, suspended solids, soluble COD, NH<sub>4</sub><sup>+</sup>-N, particulate matter, sulphides, patho-

gens, P and toxins. By implementing these modifications, the growth and survival of the desired microalgae can be ensured. Additionally, the combination of digestate nitrification with microalgae cultivation has been investigated in both batch and continuous experimental setups.<sup>15,75</sup>

The cultivated microalgae exhibit vast potential for various applications, such as biodiesel, bioethanol, biohydrogen, pharmaceuticals, biofertilizers, bioplastics, cosmetics and animal feed. Furthermore, the microalgae can be recycled back into the biogas plant to produce CH<sub>4</sub>. Other alternatives for their utilization include animal feed, fertilizers and biostimulants. Furthermore, microalgae have been extensively studied for their ability to upgrade biogas in various research conducted over the past decades.<sup>43</sup>

#### 5.4. Enzyme production

Enzymes represent valuable bioproducts that can be obtained through bioconversions using digestate. Digestate contains a significant amount of carbon, which is primarily preserved as solid structural components such as lignin and cellulose. This creates a fascinating value-added chain, wherein the remaining carbon in the solids of the digestate can be used by microorganisms that produce enzymes.<sup>5</sup> Recently, Bulgari *et al.*<sup>82</sup> developed a process to produce esterase enzyme biosynthesized by *Trichoderma asperellum* utilizing agricultural digestate. Furthermore, their study revealed that the digestate composition can significantly affect the enzyme activity. In another study, the solid fraction of digestate was fed to 21 different fungal strains to synthesize lignocellulolytic enzymes in submerged instead of solid-state fermentation.<sup>83</sup> Utilizing digestate as a substrate for enzyme production offers both technological feasibility and economic advantages over traditional substrates. Table 3 provides evidence of the successful production of significant enzymes using digestate. Notable examples include ligninolytic enzymes such as manganese peroxidase and laccase, as well as cellulases such as  $\beta$ -glucosidase and *endo*- $\beta$ -1,4-glucanase. These enzymes play an important role in various industrial processes, such as lignin degradation and cellulose hydrolysis, making them of great interest for a lignocellulosic biorefinery applications.<sup>5</sup>

#### 5.5. Hydroponic and bioponic systems for sustainable crop cultivation

Hydroponic and bioponic systems using digestate-based nutrient solutions reduce the dependence on chemical fertilizers, conserve water and enhance the crop yield. Thus, by integrating digestate into controlled-environment agriculture, these systems exemplify circular economy principles, ensuring efficient resource use, while minimizing agricultural runoff and pollution.<sup>15</sup> Bok choy (*Brassica rapa* var. *chinensis*) was grown using a hydroponic nutrient film technique system, with exclusive fertilization using biogas digestate. The substrate employed included plant material, crop residues and residues from the food industry. This study indicated that a slightly extended cultivation period of less than one week, specifically less than 20% longer, produced comparable results in terms of crop yield in the biogas digestate-based hydroponic



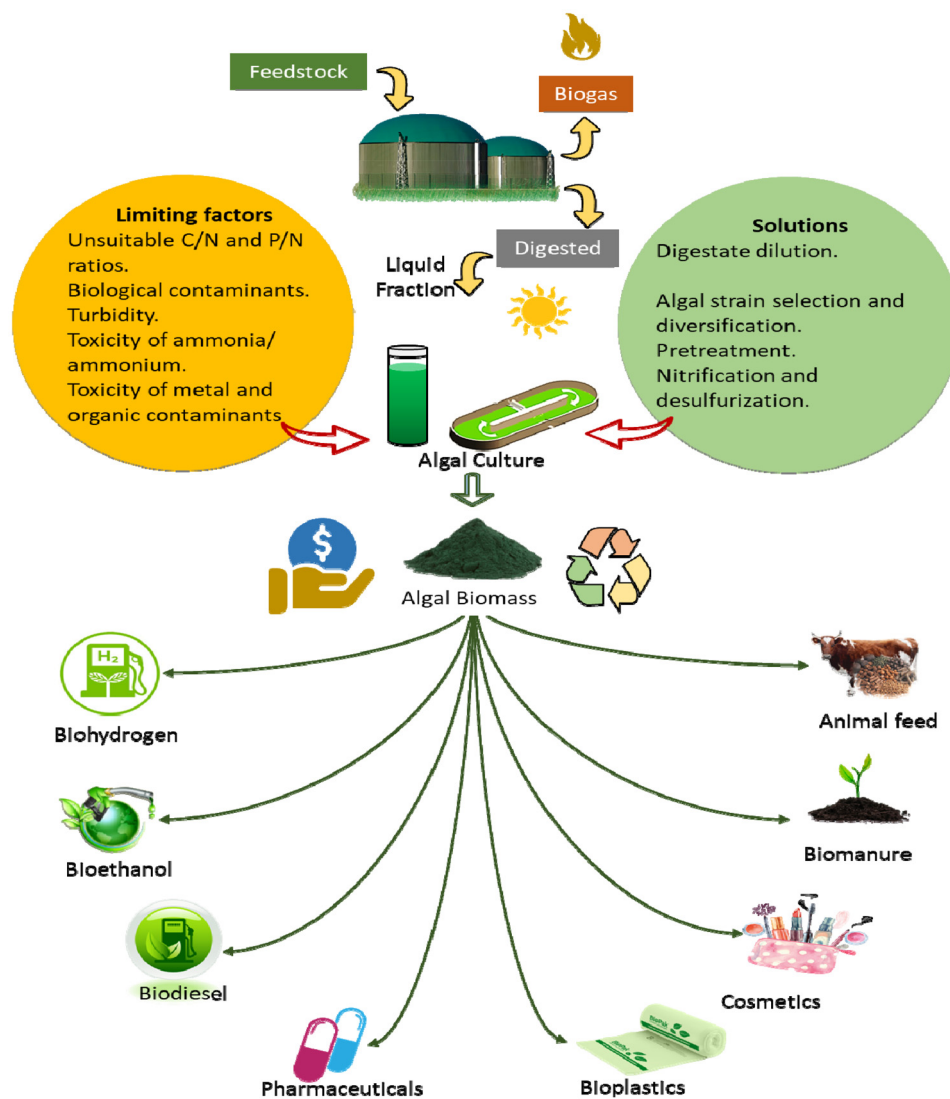


Fig. 4 Valorization of digestate liquid through algal culture.

nic system compared to conventional hydroponics relying on synthetic fertilizers.<sup>87</sup> In the hydroponic cultivation of baby leaf lettuce (*Lactuca sativa* L.), a comprehensive assessment was conducted, comparing nine different combinations of digestate and fertilization. The composition of the digestate included raw materials such as maize (*Zea mais* L.) silage, triticale (*X Triticosecale* Wittmack) silage, cow slurry and grape stalks (*Vitis vinifera* L.). The findings highlight the viability of digestate as a sustainable and alternative choice as both the growing medium and nutrient solution in hydroponic systems, ensuring the successful production of baby leaf lettuce.<sup>88</sup> Humic-like substances (HLS) obtained from sewage sludge and manure digestates were employed for biostimulation in the hydroponic cultivation of *Lactuca sativa* (lettuce). Various doses of HLS were compared to a commercial reference of leonardite HLS. The application of manure digestate extract with a higher dose of fulvic-like acids ( $4.6 \text{ mg L}^{-1}$  of dissolved organic carbon) demonstrated the most significant and favor-

able outcomes in terms of increased aerial biomass of lettuce plants. The observed average range of growth enhancement ranged from 7% to 30%, highlighting the effectiveness of the treatment compared to the control group.<sup>89</sup> Both solid and liquid digestates were utilized to test the hydroponic cultivation of basil (*Ocimum basilicum* L.) and peppermint (*Mentha × piperita* L.). The digestate was comprised of raw materials, namely maize (*Zea mais* L.) silage, triticale (*X Triticosecale* Wittmack) silage, cow slurry and grape stalks (*Vitis vinifera* L.). The presence of digestates had an impact on various growth parameters as well as the volatile components of the plants. SD shows potential as an alternative medium for plant growth, offering an alternative to traditional growing media. Alternatively, the liquid digestate can be utilized as a sustainable nutrient solution, providing a viable option for nutrient supplementation in hydroponic systems.<sup>90</sup>

In hydroponic systems, maintaining appropriate pH levels is pivotal for successful plant growth. The introduc-



**Table 3** Production of various enzymes using digestate products as precursors

Substrate	Process	Organism used	Enzyme produced	Activity	Ref.
Distillery spent wash digestate		<i>Proteus mirabilis</i> , <i>Bacillus</i> sp., <i>Raoultella planticola</i> and <i>Enterobacter sakazakii</i>	Manganese peroxidase	1.93 U mL <sup>-1</sup>	5
Corn silage digestate	SSF	<i>Pleurotus ostreatus</i>	Laccase Endoglucanase Cellobiohydrolase Xylanase	0.84 U mL <sup>-1</sup> 2300 U g <sup>-1</sup> protein 700 U g <sup>-1</sup> protein 3000 U g <sup>-1</sup> protein	84
Fruits and vegetables digestate	SSF	<i>Pleurotus sajor-caju</i> MES 03464	Manganese peroxidase	103.1 U g <sup>-1</sup> volatile solids	85
Digestate	SSF	<i>Trametes versicolor</i> strain MES 1191 Autochthonous microbes	Laccase Cellulases	284.9 U g <sup>-1</sup> volatile solids 0.5–1.5 FPU per gram dry matter	34
Solid agricultural waste digestate	Submerged fermentation (SMF)	<i>Irpex lacteus</i> DSM1183	Proteases Cellulase	~65 U per gram dry matter endoglucanase activity –236 IU g <sup>-1</sup> total solids	83
Distillery spent wash digestate + wheat straw		<i>Schizophyllum commune</i> CBS30132	Xylanase	494 IU g <sup>-1</sup> total solids	86
		<i>Pleurotus ostreatus</i> ATCC96997	Laccase	124 IU g <sup>-1</sup> total solids	
		<i>Aspergillus ellipticus</i>	Cellulase	β-Glucosidase activity-26.95 U g <sup>-1</sup> -substrate, <i>endo</i> -β-1,4-glucanase activity-130.92 U g <sup>-1</sup> -substrate	

SSF: solid-state fermentation, SMF: submerged fermentation.

tion of digestate and the uptake of nitrate–nitrogen by plants can increase the pH, while nitrification and the uptake of ammonium can lower it. Therefore, it is important to carefully monitor and adjust the pH to ensure optimal plant development. Additionally, when using digestate as a nutrient source for growing edible crops hydroponically, it is necessary to conduct a thorough evaluation of potential health risks posed by contaminants such as heavy metals, antibiotics and pathogens. Implementing pretreatment measures, such as reducing the solid content in digestate, can enhance the overall performance and safety of hydroponic systems.<sup>15</sup>

Effective treatment technologies not only improve the digestate quality but also align with the principles of green chemistry by enabling the sustainable transformation of waste into value-added products. By refining the digestate characteristics, these technologies support their utilization in diverse applications, reducing the environmental impact and enhancing circular resource recovery. The next section explores these emerging digestate-derived products and their role in advancing green and sustainable solutions.

## 6. Valorization of digestate into different products

Anaerobic digestate has potential economic benefit if value-added products besides CH<sub>4</sub> are harvested and inhibiting substances are eliminated.<sup>48</sup> It has been postulated that producing goods/byproducts from composites than traditional outputs is superior from an economic standpoint. In this

case, the valorization of AD digestate (either solid or liquid fraction) can produce a variety of value-added products/bio-materials or biochemicals following different technologies namely PHA biopolymer or PHA composite, production of different acids or liquid oils, including long-chain microbial exopolysaccharides and even direct recovery of ubiquitous fibers such as cellulose that have incredible qualities.<sup>91</sup> In addition, the production of sustainable and environmentally friendly products utilizing AD digestates is becoming increasingly important as companies strive to reduce their carbon footprint and meet the demands of consumers who are increasingly concerned about the impact of industry on the environment.

### 6.1. Bio-based polymer and bioplastic production

The PHA bioplastics obtained through the valorization of VFA from liquid digestate are most valuable by-products of AD due to their biodegradable characteristics and can serve as alternatives to traditional petroleum-based plastics in diverse sectors.<sup>92</sup> Presently, researchers have devised four scientific methods for manufacturing these environmentally conscious plastics from renewable substrates, as follows: (1) partly modifying naturally occurring polymers (such as starch, pullulan and cellulose); (2) manufacturing monomers through base substances using traditional chemical techniques, either *de novo* or using fermentation; (3) manufacturing polymers by culturing and adapting microbial communities separated from their natural habitats or generated *via* genetic modification (such as PHA); and (4) polymer manufacturing by partly biodegrading poly(butylene adipate-*co*-terephthalate), polyurethane and polybutylene succinate.<sup>93</sup> However for commercial pur-



poses, PHA bioplastics are currently manufactured utilizing a two-step fermentation culturing procedure by microbial species for achieving sustainability.<sup>94</sup> In the initial stage, renewable feedstocks derived anaerobic digestate are utilized to ferment a microorganism that generates PHA intracellularly. After the fermentation procedure is finished, bacterial cells are collected and the PHA polymers are taken out from these cells employing primarily a solvent-based procedure or water-based procedure. During this procedure, the non-PHA portion of the microbial cell wall is processed either with chemicals or enzymes before being eliminated from the PHA polymers.<sup>94</sup> More recently, renewable feedstock-derived anaerobic digestate has been utilized for the production of PHA for achieving sustainability.<sup>95,96</sup> The basic procedure for the production of PHA from anaerobic digestate is converting renewable feedstocks to VFAs, which are then utilized as substrates for producing PHA by microbes. For example, Raunhan *et al.* reported the production of PHA (0.043 g L<sup>-1</sup> h<sup>-1</sup> PHA) using food residue-derived anaerobic digestate (optimal level 23.98 ± 0.52 wt%), which primarily consisted of propionate and acetate, with the help of *T. mechernichensis* TL1.<sup>96</sup> Diaz Perez *et al.*<sup>95</sup> utilized a bubble column bioreactor equipped with internal gas recycling for the purpose of growing methanotrophic cultures and accumulating PHA in a single step from renewable substrate-derived AD digestate. In another study, Vicente *et al.*<sup>97</sup> reported the generation of about 117–199 g kg<sup>-1</sup> PHA using the organic fraction of municipal solid waste-derived AD digestate (liquid fraction) by utilizing CSTR. The substantial capital investment required for aerobic fermentation infrastructure, together with the costs associated with sustainable substances and polymeric recovery frameworks, are key considerations in this strategy. PHA bioplastics are integrated into resinous plastic granules, allowing conversion through standard polymeric transformation processes on widely accepted machinery. This broad compatibility enables a wide range of end-user applications, including films for cloth diapers, packaging and agriculture, thermoforming for beverage cups/pots, injection-molded products such as golf tees and electronics housings, non-woven materials for uses ranging from vehicle insulation to cleansers or cloth diapers, monofilament fibers, foaming for packaging and catering wear and coatings for paper packaging, owing to their adaptable properties.<sup>98</sup> The degradable nature of PHA bioplastics has attracted commercial interest as a solution to reduce landfill and environmental waste, particularly given the substantial use of petroleum-based polyethylene in packaging.

However, despite the promising potential of PHA bioplastics derived from digestate, challenges such as high production costs, biopolymer extraction complexities and market competitiveness remain barriers to their large-scale commercialization. Future advancements in microbial engineering, metabolic optimization and cost-effective recovery techniques will be crucial for improving the economic viability of digestate-derived bioplastics and accelerating their integration into sustainable plastic alternatives.

## 6.2. Sustainable carbon materials

Biochar, hydrochar and pyrochar are carbonaceous substances produced *via* different methods. Hydrochar is a byproduct of hydrothermal carbonization (HTC), while pyrochar is obtained by pyrolysis. HTC outperforms pyrolysis in char yield and energy efficiency. Unlike pyrochar, hydrochar has a lower carbon content, less robust aromatic framework and reduced biological durability.<sup>99</sup> The pyrolysis (Table 4) process produces biochar, which has a wide range of applications besides safeguarding the environment. Hung *et al.*<sup>100</sup> conducted a study in which biochar/pyrochar was derived from swine manure-based AD biogas digestate. The pyrolysis process took place within a temperature range of 300–900 °C, aiming at applications such as soil improvement and solid fuels. The findings of their research indicated an enhanced ash percentage (23.03 wt%), surface area (>100 m<sup>2</sup> g<sup>-1</sup>) and higher heating value, particularly under severe pyrolysis conditions (>700 °C) compared to lower temperatures. The optimal biochar production occurred at 800 °C.<sup>100</sup> In a separate investigation, Liu *et al.*<sup>101</sup> focused on producing biochar/pyrochar from SD originating from the AD of food waste. The temperature range for this process was 400–800 °C. The results showed an increase in surface area from 4.7396 m<sup>2</sup> g<sup>-1</sup> to 462.8257 m<sup>2</sup> g<sup>-1</sup>. Additionally, there was a decrease in the H/C ratio, O/C ratio and (O + N)/C ratio.<sup>101</sup> Cao *et al.*<sup>36</sup> employed the HTC process to generate hydrochar from cow manure and AD digestate of energy crops at a temperature of 210 °C. They observed a reduction in higher heating values depending on the residence time, with the optimal efficiency and improved char quality at a residence time of 30 min. However, there was an increase in the slagging and fouling indexes.<sup>102</sup> The study by Gao *et al.*<sup>103</sup> involved HTC of water hyacinth-derived AD digestate, indicating that the produced hydrochar exhibited a higher calorie content with a prolonged residence time. The carbon percentage in the hydrochar reached the maximum after an 8 h residence period.<sup>103</sup> By using digestate and biochar in land applications, it is possible to sequester carbon and enhance the net primary production.<sup>104</sup> Nevertheless, the feasible size depends on the bioenergy output growth and land availability.

Biochar, hydrochar, and pyrochar can be employed as a beneficial soil amendments, enhancing the fertility, water retention and nutrient uptake for improved plant growth.<sup>81,83</sup> Also, their application can contribute to soil health by increasing the water retention, reducing the acidity and improving nutrient absorption.<sup>109</sup> Additionally, these forms of materials have a significant advantage in carbon sequestration, storing carbon in soil for thousands of years, mitigating greenhouse gas emissions and reducing the reliance on harmful synthetic fertilizers and pesticides.<sup>110</sup> Furthermore, the production of biochar, hydrochar, and pyrochar from digestate offers notable advantages in industrial and environmental applications, demonstrating high efficiency in contaminant removal, cost-effectiveness and easy access to raw materials.<sup>111</sup> These char forms can be extensively used in water treatment for impurity



Table 4 Various pyrolysis processes and their products

Process	Operating conditions	Char yield (wt%)	Liquid yield (wt%)	Gas yield (wt%)	Energy efficiency	Carbon footprint	Cost metrics	Ref.
Slow pyrolysis	300–500 °C, low heating rate	40%–50%	30%–40%	10%–20%	Moderate energy efficiency; approximately 45%–55%	Low carbon footprint due to higher biochar yield	Biochar production cost ranges from £362–716 per ton	105
Intermediate pyrolysis	400–650 °C, moderate heating rate and residence time	Data not available	Data not available	Data not available	Balanced energy efficiency; approximately 60%–70%	Moderate carbon footprint	Moderate capital and operational costs; flexible feedstock handling	106
Fast pyrolysis	480–560 °C, high heating rate, short vapor residence time	<35%	45%–60%	18%–25%	Higher energy efficiency; approximately 65–75%	Higher carbon footprint due to lower biochar yield	Bio-oil production can be economically viable with manufacturing costs around \$3 per kg	107
Flash pyrolysis	>600 °C, very high heating rate, very short residence time (>200 °C s <sup>-1</sup> )	10%–25%	60%–75%	10%–30%	High energy efficiency; maximizes liquid yield	Higher carbon footprint due to minimal biochar production	High capital costs; advanced reactor technology required	106
Gasification	700–900 °C, controlled oxygen/steam	Minimal	Minimal	High	Cold gas efficiency up to 55% when co-gasifying digestate with almond shells	Electrical efficiency of 15.9% for digestate gasification; lower than lignocellulosic biomass gasification (~20%)	High capital costs; complex gas cleanup systems	108

removal and air filtration for eliminating volatile organic compounds and odors, as well as in gas separation, chemical processing, pharmaceuticals and the food industry. However, despite their benefits, their application is hindered by challenges including high energy requirements, uncertainties about long-term soil stability and potential contaminants in biomass feedstock. Overall, biochar, hydrochar, and pyrochar show promise for sustainable agriculture and climate change mitigation.<sup>112</sup> Nevertheless, although these char forms have the potential to be valuable resources in transitioning to a low-carbon economy, additional research is needed to fully understand their potential and establish best practices for their production and use. In recent years, numerous synergies have been identified through the combination of AD and pyrolysis, with biochar playing a central role in these processes (Fig. 5).<sup>113</sup> Despite the mature implementation of AD and pyrolysis at an industrial scale, there is currently no actual example of a dual symbiotic approach tested at the industrial level.

### 6.3. Sustainable bio-oil production from digestate

Bio-oil derived from digestate *via* pyrolysis and hydrothermal processing represents a promising renewable energy source. By integrating green chemistry principles, these processes minimize waste, reduce the reliance on fossil fuels and promote sustainable energy recovery. This section explores the various thermochemical techniques for bio-oil production and their efficiency and potential applications in energy and industrial sectors.

**6.3.1. Pyrolytic-oil or bio-oil.** Bio-oil or pyrolytic-oil is another valuable byproduct that can be produced by utilizing

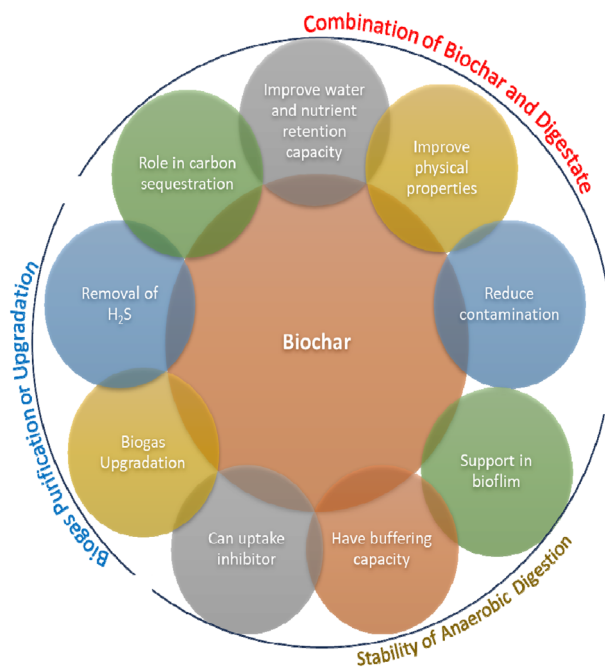


Fig. 5 Different dimensions of biochar application.

SD, specifically bio-solids produced through thermal or thermo-catalytic or hydrothermal processing. This process generally involves heating organic materials in an oxygen-free environment at high temperatures, which causes the oils and gases in the materials to be released, collected and processed into pyrolytic oil.<sup>114</sup> According to Huber *et al.*,<sup>115</sup> pyrolytic oil



is a light-brown substance made up of an extensive combination of numerous chemical molecules.<sup>116</sup> Pyrolytic oil is formed in the non-aqueous phase of the process.<sup>117</sup> Given that it is derived sustainably from diverse renewable materials, pyrolytic oil serves as a key renewable energy source, reducing landfill waste and lowering greenhouse gas emissions by replacing fossil fuels in specific applications. Furthermore, the high energy density of pyrolytic oil makes it valuable for power generation and transportation, including jet fuels.<sup>116</sup> It can also be used as a replacement for fossil fuels in diesel engines, gas turbines and boilers, among other applications. Another benefit of pyrolytic oil is that it can be refined and upgraded to produce a range of other products, such as biochar, which can be used as a soil amendment.<sup>118</sup> Yang *et al.*<sup>119</sup> conducted a study aimed at producing bio-oil from SD derived from AD of lignocellulosic biomass. The temperature range for this process was 300–900 °C, with the primary objective being the production of energy products. The results of this study revealed a decrease in bio-oil production, coupled with an increase in biochar production, shifting from 28.81% to 35.96%.<sup>119</sup> In a related investigation, Perez *et al.*<sup>26</sup> focused on the production of bio-oil from SD obtained through the AD of crop waste. Their study explored different combustion methods at varying temperature ranges. Slow combustion at temperatures between 355 °C and 530 °C resulted in bio-oil production ranging from 35% to 46% by weight. Fast pyrolysis, conducted at temperatures of 460–560 °C yielded bio-oil in the range of 36–40% by weight. Furthermore, microwave combustion at power levels between 500 and 700 W produced bio-oil in the range of 8–27% by weight from the digestate.<sup>95</sup> Pyrolytic oil shows potential for generating valuable chemicals such as phenols and furans suitable for various industrial applications. However, challenges, including the high energy requirements for mineral heating, extraction and refining, make its production currently more expensive than fossil fuels. Moreover, this process may result in environmental impacts, such as air pollution and greenhouse gas emissions. As new technologies emerge to address these challenges, the utilization of pyrolytic oil is expected to increase in the future.

Bio-oil derived from digestate valorization aligns with green chemistry principles by offering a renewable alternative to fossil-derived fuels. Its production reduces landfill waste, enhances carbon sequestration through biochar co-products and contributes to net-zero emission strategies. However, challenges such as high processing energy demand, product instability and refining costs must be addressed through process optimization and catalytic upgrading technologies.

**6.3.2. Aqueous pyrolytic liquid (APL).** APL is another valuable byproduct that can be produced by utilizing liquid digestate, more specifically the as-called bio-solids through pyrolysis.<sup>120</sup> APL is formed in the aqueous phase of this process, which means that it is easily extracted from the water as well other byproducts produced during pyrolysis.<sup>121</sup> Generally, APL is a dark-brown liquid with an extremely higher COD value.<sup>116</sup> Hübner and Mumme<sup>38</sup> generated APLs using anaerobically

processed cow manure and maize-derived biosolids at temperatures of 330 °C, 430 °C and 530 °C, aiming for biogas production. Their study revealed that APL produced at 330 °C resulted in the highest CH<sub>4</sub> output at 199.1 ± 18.5 mL per gCOD, with a COD removal of 56.9 ± 5.3%. Conversely, APL produced at 430 °C showed slightly lower values, and at 530 °C, the production decreased to 129.3 ± 19.7 mL per gCOD, with 36.9 ± 5.6% COD elimination.<sup>38</sup> In a different study, Seyedi *et al.* produced catalytic and non-catalytic APLs from biosolids obtained from unprocessed activated sewage and anaerobically processed primary sludge at a temperature of 800 °C for toxicity assessment on CH<sub>4</sub> production.<sup>116</sup>

A key advantage of APL is its high water solubility, facilitating easy separation from other pyrolysis byproducts.<sup>121</sup> APL has diverse potential applications, serving as a fuel alternative for internal combustion engines and as a source of valuable compounds for the pharmaceutical and food industries. Considering that it is renewable, sustainable and has a low carbon footprint, APL stands as a promising alternative to fossil fuels.

**6.3.3. Aqueous hydrothermal carbonization liquids (AHL).** AHL can be produced by utilizing liquid digestate through HTC pathways.<sup>120,122</sup> Taufer *et al.*<sup>123</sup> generated AHL from cattle manure-derived AD digestate, employing HTC and supercritical water gasification techniques for the production of H<sub>2</sub>-rich gas. Their study revealed that an increased substrate level led to a higher gas production rate without affecting the carbon yield in the gas. Elevated supercritical water gasification temperatures contributed to greater quantities of H<sub>2</sub> in the gaseous phase and increased carbon production. Specifically, at 600 °C for 15 s residence time, the study achieved the highest gas production rate (9.33 mL min<sup>-1</sup>), the highest H<sub>2</sub> content (79%) and the highest carbon output (51%) in the gaseous phase.<sup>123</sup> In a separate investigation, Celletti *et al.* produced AHL from cow manure digestate for use as fertilizer and assessed its phytotoxicity by testing hydroponic maize (*Zea mays* L.) plants. Their findings indicated that an AHL solution dilution ratio of 1 : 30 (distilled water) hindered plant growth and exhibited toxicity, while dilution ratios of 1 : 60 and 1 : 90 were conducive to plant growth.<sup>124</sup>

The valorization of AHL poses significant challenges, mainly because it consists primarily of water together with varying quantities of inorganic and organic substances such as organic acids, sugars, aromatics, furans and phenols. Moreover, a considerable proportion of these organic substances, particularly aromatic compounds and furan-related products, have potential to be toxic to plants and tend to be concentrated in AHL due to their water-soluble nature.<sup>124,125</sup> Accordingly, the produced AHL were also utilized as a recirculation substrate in a closed-loop system for AD or HTC minimizing the AHL content.<sup>126,127</sup> Generally, AHL in the real field are utilized as a nutrient supply for microalgae growth, irrigation purposes for farm fields, generation of fertilizers, or the recuperation of compounds such as N and P.<sup>124–127</sup> Also, they can be used in wastewater treatment, given that their carbon content can help to absorb pollutants and improve water



quality. However, further research is needed to fully understand the performance and potential of AHL. Nevertheless, with the increasing demand for sustainable and renewable sources of energy and materials, AHL has the potential to play an important role in the future bioeconomy.

#### 6.4. Recovery of value-added biochemicals

**6.4.1. Short chain fatty acids (volatile acids).** Volatile acids, more specifically VFAs, are the most significant byproduct of the AD process, especially during different acidogenic bacterial fermentation pathways.<sup>128</sup> VFAs are organic acids that contain a relatively low number of carbon atoms. VFAs are dissolved in the liquid fraction of digestate (LFD).<sup>48</sup> Patel *et al.*<sup>129</sup> utilized a membrane bioreactor to produce various acids from anaerobic digestate derived from food waste. Their study focused on evaluating the production of value-added polyunsaturated fatty acids, primarily omega-3 fatty acids, using three distinct marine strains, namely *Aurantiochytrium* sp. T66, *Cryptocodinium cohnii* and *Schizochytrium limacinum* SR21. The results revealed that among them, *Aurantiochytrium* sp. T66 exhibited the greatest promise, yielding 13.56% docosapentaenoic acid and 43.19% docosahexaenoic acid in total lipids.<sup>129</sup> The VFAs from LFD can be extracted through membrane or non-membrane techniques. Non-membrane methods, including adsorption, stripping and solvent extraction, separate VFAs from LFD. Membrane techniques, such as nanofiltration (NF) and microfiltration (MF) under pressure, membrane contactor (MC) and pervaporation utilizing concentration variation or vapour pressure and electro dialysis (ED) using electricity, are applied for the extraction of VFA.<sup>48</sup> All membrane-based extraction processes are conducted under acidic pH conditions, except for ED, which operates at neutral pH.<sup>48</sup> VFAs are the preferred output of the AD process over CH<sub>4</sub>, serving as key components for aldehydes, alcohols, ketones, olefins and esters in the refining sector.<sup>130</sup> Inhibiting the methanogenesis stage in the AD process allows the production of VFAs. In fact, hindering CH<sub>4</sub> generation, achieved through reduced retention time (including pH adjustment and addition of methanogenic inhibitors), enhances the production of VFAs.<sup>131</sup> VFAs serve as carbon sources for bio-nitrogen extraction from effluent and as precursors for the bioproduction of medium-chain carboxylic acids (MCCAs).<sup>132,133</sup> In wastewater treatment, volatile acids, measured as COD, are indicators of organic matter degradation.<sup>134</sup> However, excessive concentrations of volatile acids can negatively impact wastewater treatment processes by causing a decrease in pH, inhibiting microorganism growth, reducing treatment efficiency and potentially leading to issues such as foam formation and odors.

**6.4.2. Lactic acid (LA).** LA is a significant by-product of the anaerobic breakdown of carbohydrates (*i.e.*, acidogenic stage of AD process) and advantageous in regard to price, environmental sustainability and operating simplification.<sup>48</sup> LA is highly hydrophilic in nature. Generally, it is produced in heterogeneous culture during AD of low-value organic waste (*i.e.*, renewable in nature). Bühlmann *et al.*<sup>135</sup> enhanced LA production from food waste-derived anaerobic digestate by

supplementing sucrose. Their study revealed that both digestate and NH<sub>4</sub>Cl similarly increased the LA production rates ( $0.04 \pm 0.02$  and  $0.03 \pm 0.02$  h<sup>-1</sup>, respectively), resulting in an increase in the final LA concentration from 25–30 g L<sup>-1</sup> to 59–68 g L<sup>-1</sup>. The digestate was found to be a valuable nutrient source.<sup>135</sup> In another study, Acedos *et al.* achieved LA production of up to 41.5 gO<sub>2</sub> L<sup>-1</sup> from the organic fraction of municipal solid waste digestate.<sup>136</sup> Separating LA from LFD is important given that it contains impurities.<sup>48</sup> Although calcium (Ca) precipitation is the widely preferred method for the recovery of LA, the LA extraction from LFD typically necessitates the integration of several methods, including solvent extraction (including reactive extraction, two-step extraction and salting-out), membrane filtration, adsorption and ED, given that other anions can precipitate alongside ionized Ca.<sup>48,137</sup> LA has widespread application in the cosmetics, chemical and pharmaceutical sectors and a considerable market share in the production of biodegradable polymers.<sup>138,139</sup> According to Hetényi *et al.*,<sup>140</sup> pure cultures employing materials obtained from food crops generate over 90% of the LA used in industrial manufacturing worldwide.

**6.4.3 Medium-chain carboxylic acids (MCCAs).** MCCAs, in comparison to other AD products such as CH<sub>4</sub> and VFAs, have been recognized as the most advantageous AD end-products and possess a higher energy density. MCCAs are the end byproducts of biological carboxylic acid chain elongation, employing ethanol and LA as electron-donors, and generally contain 6–10 carbon atoms.<sup>48</sup> Butyric acid and caproic acid are successively generated from acetic acid according to the reversed  $\beta$ -oxidation cycles.<sup>141,142</sup> MCCA-producers may reside together and react syntrophically with fermentative bacteria.<sup>143</sup> Renewable AD substrates with a higher VFA concentration are typically preferred for the production of MCCAs. This preference stems from the production of MCCAs being reliant on various factors including the presence of electron donors, methanogenic inhibitors and lower pH conditions.<sup>48</sup>

Arhin *et al.*<sup>144</sup> produced MCCAs from anaerobic digestate derived from food waste. Their study highlighted that mesophilic fermentation at pH 6 is optimal for generating mixed VFAs (719  $\pm$  94 mg COD per g VS) and increasing the food to microorganisms (F/M) ratio (g VS/g VS) to 6, creating favorable conditions for producing mixed VFAs at 22  $\pm$  2 g COD per L and caproic acid at 2 g COD per L. They observed a significant reduction in LA yield under thermophilic conditions and higher F/M ratios exceeding 3 g VS/g VS. The valorization of food waste through this method has the potential to generate 442–468€ per t VS per year by converting LA and butyric acid produced through acidic fermentation into caproic acid.<sup>144</sup> Generally, MCCAs were extracted/recovered from digestate employing an *in situ* biphasic solvent extraction technique.<sup>48,145</sup> In addition, membrane-based techniques such as MC and membrane electrolysis are also widely applied for the recovery of MCCAs from AD digestate.<sup>48,146</sup> MCCAs have wide application in diverse fields such as plasticizers, multi-functional feed additives, antimicrobials, personal care products, and substrates for the production of biofuels.<sup>147</sup>



**6.4.5 Humic acid (HA).** HA, an important byproduct of AD, has intricate structural framework and redox activities. HA, an important part of humic substances, has been proven to be an essential ingredient and typically makes up 10–20% of the overall solids in the AD process.<sup>148</sup> However, the presence of HA generally prevents the AD activity of biomass because of its attachment to the active region of essential enzymes (such as hydrolytic enzymes), ultimately blocking these enzymes from accessing the substrates.<sup>149</sup> Wang *et al.*<sup>150</sup> revealed the potential of a newly developed struvite-humic acid composite extracted from anaerobic digestate. Their findings suggest that the struvite-humic acid composite possesses elevated levels of oxygen-containing and aromatic functional groups (47.05% and 34.13%, respectively), together with a greater specific surface area ( $19.3 \text{ m}^2 \text{ g}^{-1}$ ).<sup>150</sup> Recently, it has been shown that HA can be utilized as an AD process terminal electron-acceptor precursor in microbial respiration, transport electrons to drive  $\text{CH}_4$  oxidation anaerobically and speed up the uptake of organic materials during AD.<sup>151,152</sup> The complex structure of HA also hinders its efficacy as a fertilizer and remediating agent. Alternatively, in wastewater treatment, humic acid can be used as an adsorbent to remove pollutants from water.<sup>153</sup> It can bind to heavy metals, organic compounds and other pollutants, helping to purify the water.

## 7. Nutrient recovery

Organic and inorganic nutrients coexist in digestate, with organic nutrients bound to carbon and requiring mineralization for plant availability. Organic nutrients are primarily found in the solid phase of organic waste. In contrast, inorganic nutrients are water-soluble and predominantly present in the liquid phase or bound to soluble minerals. These readily accessible inorganic nutrients can be effectively recovered. During AD, a portion of organic P and N is converted into their inorganic forms, representing approximately 24% of the initial  $\text{NH}_3$  and 16% of the original phosphate, respectively. This conversion process enhances the availability of inorganic P and N in digestate, making them more accessible and beneficial for plant growth.<sup>154</sup> The solid and liquid fractions of digestate derived from the AD process contain significant quantities of N and P. The solid fraction has a moisture content below 15%, while the liquid fraction contains more than 15% moisture. The initial step in digestate processing involves the mechanical separation of the material into a liquid fraction and a solid fraction to facilitate dewatering. The solid fraction is mainly comprised of resistant organic matter, as well as Ca, magnesium (Mg) and occasionally P. However, nutrient recovery from the solid fraction is restricted due to the prevalence of organically bound nutrients. Alternatively, the liquid fraction contains soluble N, P, K, organic compounds and mineral salts. Thus, the liquid fraction offers promising opportunities for extracting soluble nutrients using various extraction techniques.<sup>155</sup> The

different approaches for the recovery of inorganics are depicted in Fig. 6.

### 7.1. Ammonia stripping

The ammonia stripping process removes the total ammonia nitrogen from sludge by shifting the  $\text{NH}_4^+/\text{NH}_3$  equilibrium towards free ammonia nitrogen. Subsequently, it is eliminated from the system using a gas stream.  $\text{NH}_3$  stripping is conventionally performed in heated packed column reactors on the liquid fraction obtained from sludge dewatering. Air blown from the bottom of the column carries the  $\text{NH}_3$  over the contact material. The stripped  $\text{NH}_3$  is absorbed into sulfuric ( $\text{H}_2\text{SO}_4$ ) or nitric acid ( $\text{HNO}_3$ ) solution, producing  $(\text{NH}_4)_2\text{SO}_4$  or nitrate, respectively, which are valuable chemicals for fertilizers and other products. This process is vital for preventing environmental pollution and ensuring that the treated liquid is free from excessive  $\text{NH}_3$ .<sup>156</sup>

$\text{NH}_3$  stripping technology efficiently captures  $\text{NH}_3$  from exhaust gases using acid, allowing the production of valuable ammonium salt fertilizers such as  $(\text{NH}_4)_2\text{SO}_4$  and ammonium nitrate. Packed towers are commonly used for ammonia stripping due to their large surface area for efficient mass transfer, although fouling can be an issue. Various alternative configurations have been documented, including bubble diffusers, spray towers, aspirators and surface aerators. Additionally, innovative gas/liquid contactors, such as semi-batch jet loop vessels, have been suggested as alternative options.<sup>157</sup> Nitrogen recovery costs range from 2 to 7€ per kilogram of nitrogen removed. Operational expenses mainly include acid requirements (1.5 L of  $\text{H}_2\text{SO}_4$  per kg of  $\text{NH}_3$ ) and energy consumption ( $0.057 \text{ W h m}^{-3}$  of air). The successful marketing of  $(\text{NH}_4)_2\text{SO}_4$  can generate potential revenues of 90 to 120€ per ton of fresh digestate, making the process economically viable.<sup>158</sup>

In the ammonia stripping process of biogas slurry, a commonly used method is using an  $\text{H}_2\text{SO}_4$  solution to absorb the tail gas, resulting in the formation of an  $(\text{NH}_4)_2\text{SO}_4$  solution. This bio-based fertilizer is rich in N and sulfur and is both reusable and commercially available. However, although the majority of studies primarily examine bio-based ammonium sulfate liquid fertilizer (BAS-L), it should be noted that the concentration of bio-based ammonium sulfate solid fertilizer (BAS-S) obtained through crystallization is higher.<sup>157</sup>

### 7.2. Struvite recovery

Nutrient recovery from digestate is a crucial step in enhancing the sustainability of biogas production. Various methods are available to recover valuable nutrients, including P, which can be precipitated and crystallized into useful compounds. Two widely recognized processes for P recovery include conversion to calcium phosphate and struvite recovery. P recovery from digestate can be achieved through the conversion of P into calcium phosphate. By introducing calcium hydroxide in the liquid fraction at 70 °C, the pH increases to 10, leading to the rapid precipitation of P as  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  or  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  within 5 min. Several com-



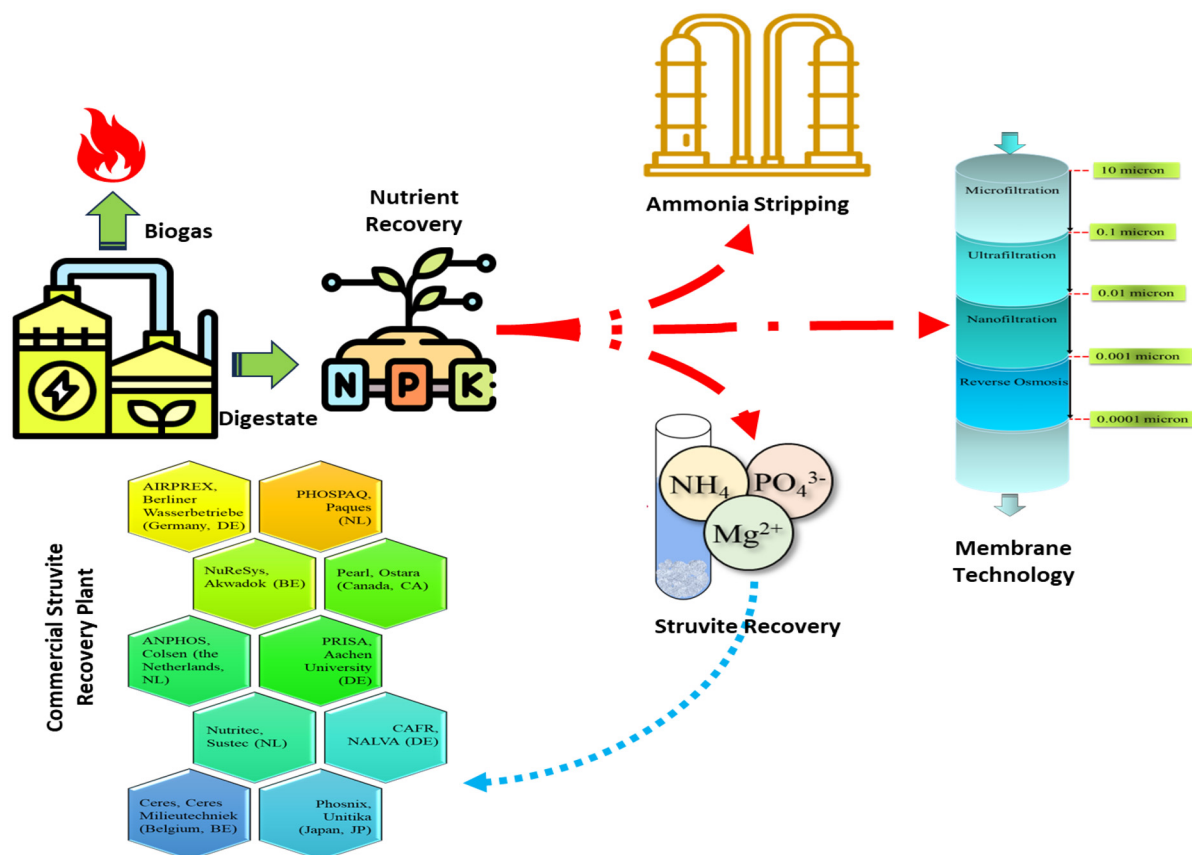


Fig. 6 Technologies for the recovery of inorganics from anaerobic digestate.

mercially available processes are suitable for calcium phosphate recovery, with estimated capital costs ranging from 2300 to 2900€ per kg of P per day. The operational costs are influenced by the demand for  $\text{Ca}(\text{OH})_2$ .<sup>158</sup>

The process of nutrient recovery through P precipitation and crystallization is widely recognized and established technology. It involves the introduction of Mg (in the form of  $\text{MgO}$  or  $\text{MgCl}_2$ ) and caustic soda ( $\text{NaOH}$ ) in a solution containing soluble orthophosphate ( $\text{PO}_4\text{-P}$ ) and ammonium. This results in an increase in pH in the range of 8.3 to 10, leading to the precipitation of struvite, specifically  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . Struvite is a valuable source of nutrients, particularly P and finds application in various contexts.<sup>155</sup> The process of struvite formation occurs in two phases, crystal initiation and development. Numerous factors, such as pH, supersaturation, temperature, existence of other ions (specifically  $\text{Ca}^{2+}$ ), agitation energy, reaction time and ratio of  $\text{Mg}^{2+}$  to  $\text{PO}_4^{3-}$ , influence these stages.<sup>158</sup>

K-struvite ( $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ ) can also be obtained from digestates if the concentration of potassium ions surpasses that of ammonium ions. This condition is based on the solubility constants of both struvite and K-struvite.<sup>155</sup> Fig. 6 illustrates the established commercial struvite production plants. In the Netherlands, there are four significant-scale facilities that produce K-struvite from calf manure digestate.<sup>158</sup> The LFD is

treated through ion exchange and adsorption using solid sorbents such as zeolites, resins and clays to extract nutrients (up to 100% P and 83% N). These processes have low energy requirements and minimal personnel costs, despite the higher chemical costs for zeolite compared to other methods.<sup>155,158</sup>

### 7.3. Membrane technology

Membrane-based separation has emerged as a viable option for nutrient recovery. This approach involves the application of membrane filtration to the liquid fraction of the digestate, where pressure is utilized to force the liquid through a membrane. Pressure-driven membrane filtration, which includes MF, ultrafiltration (UF), NF and/or reversed osmosis (RO), is well-established technology in wastewater treatment. MF and UF membranes effectively remove suspended solids and macromolecules, respectively, from the feed stream. However, dissolved compounds such as ammonium nitrogen ( $\text{NH}_4^+\text{-N}$ ) pass through the membranes and remain in the permeate. For further purification of the permeate, researchers have employed NF and RO technologies. NF has demonstrated the ability to partially remove  $\text{NH}_4^+\text{-N}$ , with reported efficiencies ranging from 5% to 23%, while achieving the excellent P removal of 97–98%.<sup>159</sup> RO, in contrast, acts as a barrier for all dissolved solids due to its highly selective semi-permeable membrane operating at pressures of 10–100 atm.<sup>160</sup> This



technology delivers a permeate virtually free of all pollutants, with recovery rates of dissolved solids reaching 99–100%.<sup>161</sup> However, RO has a higher energy demand compared to other methods, with estimated values of around 4–6 kW h m<sup>-3</sup>.<sup>162</sup> In the study by Gerardo *et al.*,<sup>159</sup> membrane filtration coupled with acid treatment and dialysis techniques were employed. The results demonstrated the recovery of 271.11 mg L<sup>-1</sup> N-NH<sub>3</sub> and 25.60 mg L<sup>-1</sup> P-PO<sub>4</sub><sup>3-</sup> from the filtered ADS supernatant, which originally had concentrations of 686.2 mg L<sup>-1</sup> N-NH<sub>3</sub> and 41.51 mg L<sup>-1</sup> P-PO<sub>4</sub><sup>3-</sup>.<sup>163</sup> Nir *et al.*<sup>164</sup> suggested a two-stage NF/RO system for the simultaneous removal and recovery of P from wastewater treatment plant secondary effluents. This system could also be applied to the liquid fraction of anaerobically digested sewage sludge.

However, a major challenge associated with membrane filtration is the issue of membrane clogging and fouling, which leads to significant chemical and energy requirements. Thus, to address the limitations of conventional membrane filtration, non-pressure membrane technologies are being developed. These technologies include ED, BES, *trans*-membrane-chemosorption and bipolar membrane electro dialysis. These advancements aim to overcome the drawbacks associated with traditional membrane filtration methods.<sup>155,156,158</sup> Shi *et al.* found that ED removed more ammonium than RO, with concentrations reaching up to 16–21 g L<sup>-1</sup>. However, it also led to higher ammonium concentrations in the treated water.<sup>165</sup> BES offers a promising alternative for nutrient recovery. Microbial fuel cells, for example, can achieve complete ammonia recovery from wastewater digestate. However, although this approach boasts low energy requirements, full-scale implementation remains a challenge.<sup>166</sup> *trans*-Membrane-chemosorption presents another option. As demonstrated with pig manure digestate, this method involves capturing ammonia by diffusion through hollow fiber membranes into an H<sub>2</sub>SO<sub>4</sub> solution.<sup>167</sup> Bipolar membrane electro dialysis is a more advanced technique that utilizes a special “bipolar membrane” to split water into H<sub>2</sub> and hydroxide ions. This allows the selective separation and concentration of various nutrients.<sup>158</sup>

The discussed technologies offer various pathways for digestate utilization, each with distinct benefits and limitations. Thus, to provide a more comprehensive perspective, the following section systematically consolidates these technologies into physical, biological, chemical and thermochemical approaches, highlighting their effectiveness and challenges.

## 8. Systematic discussion on existing technologies for digestate valorization

Various approaches, including physical, biological, chemical and thermochemical valorization, have been developed to optimize digestate utilization, each with specific advantages and drawbacks.<sup>15</sup> However, their scalability, technological maturity and commercial viability vary significantly, influencing the feasibility of their large-scale implementation. A comparative

evaluation of digestate valorization technologies based on scalability, technological readiness level (TRL) and commercial viability is presented in Table 5. This synthesis highlights the maturity and implementation potential of each pathway and identifies key bottlenecks restricting its widespread industrial adoption. Although some methods have reached commercialization, others remain in the experimental or pilot phase, requiring further optimization and investment for widespread adoption.

Physical treatment methods, including solid–liquid separation (centrifugation, screw pressing and membrane filtration), are widely applied to reduce the moisture content of digestate, lowering transport costs and enabling more efficient downstream processing. Mechanical separation is mature technology and frequently employed in large-scale anaerobic digestion plants to improve nutrient recovery efficiency by concentrating phosphorus in solid fractions and nitrogen in liquid fractions, thereby facilitating targeted fertilizer production.<sup>168</sup> However, challenges such as incomplete separation, high maintenance costs and potential loss of fine particulate nutrients hinder its widespread adoption.<sup>45</sup> Advanced membrane technologies, such as ultrafiltration and reverse osmosis, have demonstrated potential for the treatment of liquid digestate, but membrane fouling, their high energy demand and the disposal of concentrated retentates remain critical concerns.<sup>169</sup> Although membrane filtration is an advanced and promising approach, its scalability remains limited by its high operational costs and technological complexities, restricting its full-scale commercial adoption.

Biological processes, including composting, vermicomposting and microalgae cultivation, are promising for digestate stabilization and nutrient recycling. Composting enhances the degradation of organic matter and pathogen reduction, making the final product suitable for soil application. However, the prolonged composting durations and ammonia volatilization can result in nutrient losses, reducing the efficiency of the fertilizer and making its large-scale implementation less attractive. Also, although composting is a well-established and widely used process, its scalability is constrained by space requirements and long processing times. Vermicomposting improves the nutrient bioavailability but requires careful moisture and aeration control to maintain the optimal worm activity, which limits its large-scale adoption despite its environmental benefits.<sup>66</sup>

The integration of microalgae cultivation with digestate treatment presents a novel approach for carbon capture and bioresource production. Microalgae efficiently absorb nutrients from the liquid digestate, converting them into biomass for biofuels, bioplastics and animal feed. However, high ammonia concentrations and variable digestate composition can inhibit algal growth, necessitating pre-treatment or dilution strategies.<sup>170</sup> Recent advancements in photo-bioreactor design and genetic engineering have improved the resilience of microalgae to digestate stressors, increasing their potential for commercialization.<sup>171</sup> Nevertheless, microalgae-based systems remain in the early commercial stage, given that



**Table 5** Comparative evaluation of digestate valorization pathways based on their scalability, technological readiness level and commercial viability

Valorization pathway	Scalability potential	TRL (1–9)	Commercial viability	Key barriers & challenges	Ref.
PHA production	Low	4–5	Emerging	Low conversion efficiency; high production costs; need for optimized microbial strains and processes	15
Biochar production <i>via</i> pyrolysis	Medium–high (centralized systems)	7–8	Growing	High CAPEX; biochar quality variability; regulatory standards	179 and 180
Hydrothermal carbonization (HTC)	Moderate (pilot-scale)	5–7	Limited	Hydrochar quality; organic micropollutants; market development	180 and 181
Gasification	Moderate (large-scale plants)	7–8	Emerging	Tar formation; catalyst deactivation; high operational cost	182
Enzyme production from digestate	Low to moderate (lab/pilot scale)	5–6	Emerging	Limited large-scale demonstrations; dependence on fungal/microbial strain efficiency; substrate variability affects enzyme yield	82
Microalgae cultivation	Moderate (integrated systems)	5–7	Emerging	Algal biomass harvesting; high energy demand; ammonia inhibition	183
Struvite precipitation	Moderate (wastewater & AD plants)	7–8	Established	Chemical cost; market acceptance; process control	184
Ammonia stripping & absorption	Moderate (industrial plants)	7–8	Emerging	High energy input; process complexity	185
Nutrient recovery	Medium	7–8	Established	Chemical costs; process optimization; market development for recovered nutrients	186
Liquid biofertilizer production	High	8–9	Established	Pathogen control; nutrient consistency; regulatory compliance	187
Composting	High (widely adopted)	9	High	Land requirement; long processing time; odor management	15 and 188
Membrane filtration	Moderate (centralized facilities)	7–8	Emerging	Membrane fouling; high energy cost; retentate disposal	78 and 169
Vacuum evaporation	Medium	6–7	Limited	High energy consumption; equipment costs; management of condensate	186

CAPEX = capital expenditure, TRL = technology readiness level.

cost-effective biomass harvesting and scalability challenges persist.

Chemical processes focus on nutrient recovery and material conversion, transforming digestate into value-added products. Struvite precipitation, an established phosphorus recovery method, enables the production of slow-release fertilizers but requires precise pH control and costly magnesium salts, limiting large-scale adoption.<sup>172</sup> However, despite its technological maturity, struvite precipitation remains economically constrained in decentralized anaerobic digestion facilities due to chemical costs and the requirement for strict operational conditions. Similarly, ammonia stripping and absorption allow nitrogen recovery for fertilizer production but involve high energy input and operational complexities.<sup>173</sup>

Emerging chemical approaches include HTC, which converts digestate into hydrochar, a stable carbon-rich material with applications in soil conditioning and bioenergy storage. Unlike conventional drying methods, HTC operates in wet conditions, reducing the energy requirements. However, organic micropollutants in the digestate can limit the safety and soil application potential of hydrochar. Thus, further optimization is needed to enhance the process efficiency and pollutant removal, given that HTC is still in the pilot-stage development phase and requires extensive research to ensure its economic feasibility.<sup>174–176</sup>

Thermochemical valorization techniques, such as pyrolysis, gasification and supercritical water gasification (SCWG), provide high-energy recovery potential but face significant scalability and economic barriers. Pyrolysis, which converts digestate into biochar, bio-oil and syngas, has been widely researched for its ability to enhance soil fertility and sequester carbon. However, precise temperature control and pre-treatment are required to minimize contaminants, which increases the processing costs and limits commercial deployment.<sup>177</sup> Although the biochar market is growing, the high initial investments and feedstock variability affect the product consistency, posing challenges to full-scale commercialization. Gasification, which produces hydrogen-rich syngas, offers a promising renewable energy source but suffers from tar formation and catalyst deactivation due to digestate impurities, requiring further technological advancements to improve its efficiency. However, although gasification has been successfully implemented in some industrial applications, it remains capital-intensive, reducing its viability for smaller-scale operations. SCWG efficiently converts wet digestate into hydrogen and methane-rich gas without the need for pre-drying, significantly improving the process efficiency. Furthermore, reactor corrosion, high-pressure requirements and scalability issues remain barriers to its commercialization, necessitating further research into cata-



lyst development and reactor material innovation to enhance SCWG feasibility.<sup>178</sup>

Despite the technological advancements in digestate valorization, its widespread adoption remains limited due to the high capital costs, regulatory barriers and the variability of the digestate composition. Although mechanical separation and composting have achieved commercial viability, membrane filtration, microalgae cultivation and advanced chemical processes require further innovation to improve their cost-effectiveness and scalability. Thermochemical methods, particularly pyrolysis and gasification, show promise for energy recovery but necessitate significant infrastructure investments and technological refinements to enhance their efficiency and economic returns.

Having explored various digestate valorization techniques, it is crucial to assess their integration within sustainable industrial systems. The next section delves into industrial symbiosis, demonstrating how the strategic incorporation of digestate into industrial networks can enhance the resource efficiency, minimize the environmental footprint and advance net-zero emission objectives, which are the core principles of green chemistry.

## 9. Digestate valorization, industrial symbiosis and net zero emission

Industrial symbiosis represents a groundbreaking approach for resource management, harnessing the potential of by-products, waste and energy across industries to enhance sustainability and efficiency. By optimizing resource use, minimizing waste and fostering environmental improvements through strategic routes, this method redefines industrial processing.<sup>189</sup>

The valorization of anaerobic digestate through industrial symbiosis is a transformative approach that converts waste into valuable resources, enhancing sustainability across industries (Fig. 7(a)). For example, digestate from one facility can be used as a resource in another, creating a symbiotic relationship that minimizes waste and optimizes resource utilization. This approach is envisaged to repurpose the digestate into products such as fertilizers and easy assimilable substrates for biogas plants and the bio-manufacturing of bioplastics and biochar.<sup>190</sup> Integrating digestate into various industrial processes offers significant environmental benefits, including decreased waste disposal, lower methane emissions, minimized leachate production and reduced nutrient (nitrates and phosphates) leaching, which can help combat eutrophication and lower greenhouse gas emissions. In agriculture, digestate enriches soils as an organic fertilizer, closing the nutrient loop and replacing synthetic alternatives.

Attaining net-zero emissions in digestate valorization is the key goal in the transition towards a sustainable bioenergy system. Nutrient recovery from digestate, particularly N, P and K, is a critical step toward reducing emissions. By using digestate as a fertilizer, industries can reduce the need for energy-intensive synthetic fertilizers, whose production and appli-

cation are associated with substantial carbon dioxide and nitrous oxide emissions. The utilization of digestate helps sequester carbon in the soil, promoting healthier soil ecosystems and decreasing the overall carbon footprint of agricultural activities. Another valuable pathway is the conversion of digestate into biochar through pyrolysis or hydrothermal carbonization. Biochar acts as a stable form of carbon that can be sequestered in soil for long periods, effectively storing carbon and mitigating climate change. It improves the properties of soil, such as fertility and water retention, while serving as a carbon sink that offsets emissions from other sectors, directly contributing to net-zero goals. Achieving net-zero emissions is a critical goal in the fight against climate change. The valorization of digestate is increasingly being recognized as an essential component of this effort, given that it provides opportunities to reduce greenhouse gas emissions from both the waste management and agricultural sectors. By recovering nutrients from digestate, the reliance on synthetic fertilizers, the production of which is energy intensive and releases significant emissions during their application, is reduced. Additionally, the conversion of digestate into bioenergy and bio-based products further offsets fossil fuel use and mitigates emissions.<sup>15</sup> As technological innovations continue to emerge, the role of digestate in creating sustainable, circular economies will grow, providing a vital tool in the global effort to combat climate change.<sup>191</sup> Fig. 7(b) presents a schematic diagram of a few strategies to attain net zero emissions in digestate valorization.

### 9.1. Life cycle assessments (LCAs)

Conducting LCA and TEA ensures that emissions are tracked throughout the entire digestate management process, from digestion to application, allowing continuous optimization. LCA is a vital tool used to evaluate the environmental impact of products or processes from cradle to grave, encompassing the extraction of raw materials, production, use and disposal. When applied to digestate valorization, LCA plays a key role in understanding and optimizing environmental outcomes. It enables the identification of sustainable strategies for transforming digestate, a by-product of anaerobic digestion, into valuable resources such as biofertilizers, energy, and bio-based materials. Digestate, a by-product of anaerobic digestion of organic waste, contains valuable nutrients such as nitrogen, phosphorus and potassium, which can be utilized as biofertilizers. However, the direct application of digestate has associated risks, such as heavy metal accumulation, GHG emissions and potential contamination by pathogens. This has led to the need for the further processing and valorization of digestate into more stable and eco-friendly products. LCA provides a framework for quantifying the environmental impacts of these digestate treatment options. It assesses different treatment scenarios, comparing them against conventional practices and identifying the most sustainable solution. Angouria-Tsorochidou *et al.*<sup>192</sup> examined the valorization of digestate valorization in 3 scenarios, where Scenario 1 (S1) involves the direct application of raw digestate to the soil. Scenario 2 (S2) includes centrifugation to separate digestate into solid and



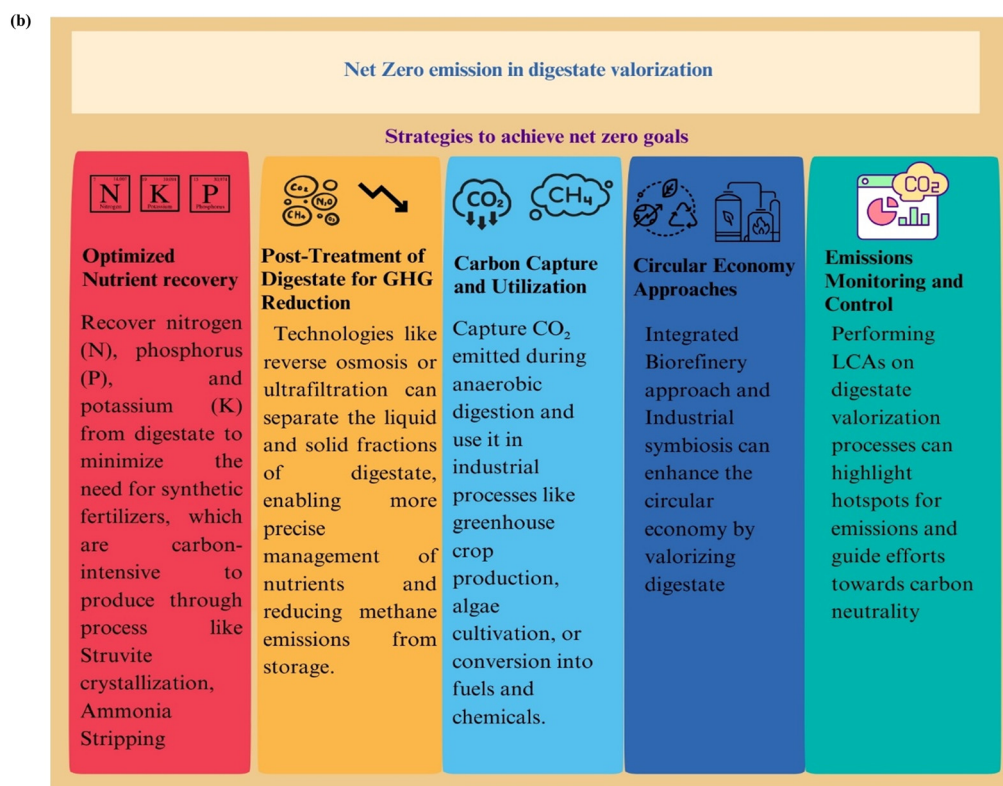
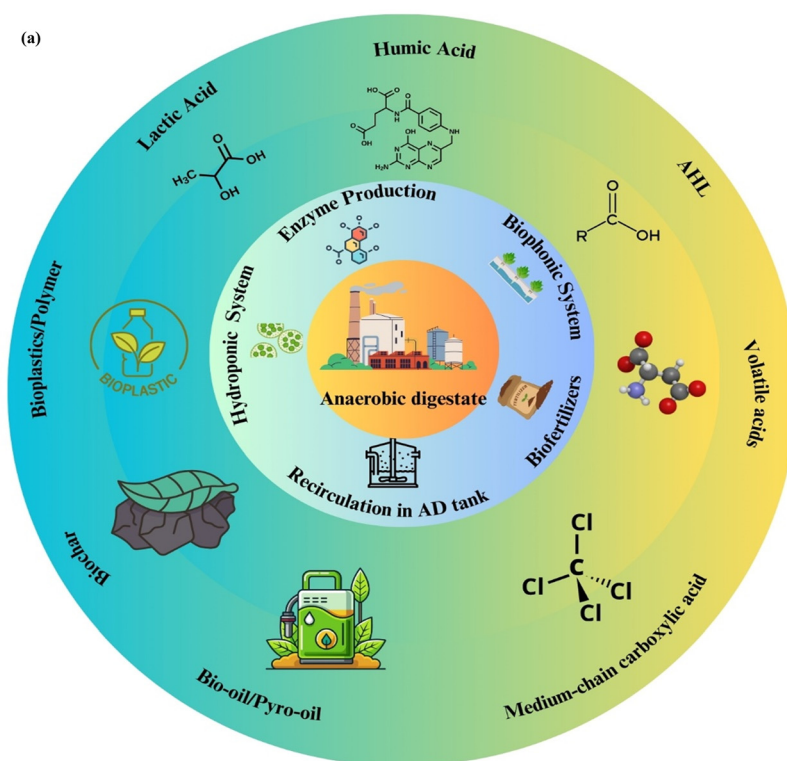


Fig. 7 Schematic representation of (a) industrial symbiosis achieved and (b) strategies to attain net-zero emissions in digestate valorization.



liquid forms, both applied to soil. Scenario 3 (S3) models a more advanced process of centrifugation, drying of the solid digestate and membrane filtration (ultrafiltration and reverse osmosis) of the liquid. The life cycle assessment results reveal that S1 has the lowest global warming potential (0.36 kg CO<sub>2</sub> equivalents per kg of digestate) but the highest acidification potential (0.18 kg SO<sub>2</sub> equivalents). S2 performs better overall in terms of freshwater eutrophication and resource scarcity. S3, though more resource-intensive due to energy use (fossil resource depletion of 0.002 kg oil equivalents), reduces marine eutrophication to  $1.09 \times 10^{-3}$  kg N equivalents and acidification to 0.09 kg SO<sub>2</sub> equivalents. By comparing various forms of biofertilizers produced from valorizing anaerobic digestate such as biofertilizer pellets, bio-compost, liquid biofertilizer (LBF) and powder biofertilizer, the study by Alengebawy, *et al.*<sup>193</sup> assessed environmental impacts using the LCA methodology, focusing on global warming potential, marine aquatic ecotoxicity and other impact categories. The LBF scenario exhibited the highest environmental benefits, particularly in marine aquatic ecotoxicity (−141 304.03 kg 1,4-dichlorobenzene eq. per tonne), with notable reductions in five impact categories. Conversely, the bio-compost scenario contributed the most to global warming, emitting 25.68 kg CO<sub>2</sub>-eq. per tonne digestate. The LCA results provide valuable insights into selecting sustainable digestate treatment options, with the LBF scenario emerging as the most environmentally friendly solution, offering significant reductions in greenhouse gas emissions, ecotoxicity and resource depletion compared to the other treatment options.

## 9.2. Techno-economic analysis (TEA)

TEA plays a critical role in assessing the viability of digestate valorization, which involves transforming the by-product of anaerobic digestion (digestate) into valuable products. By evaluating both the technical feasibility and economic performance of various valorization strategies, TEA helps identify the most cost-effective pathways and guides decision-making for large-scale implementation. Grandas Tavera *et al.*<sup>194</sup> reported details on digestate valorization focused on maximizing the economic viability of biogas (BG) projects. The key finding was that vacuum evaporation (VE) technology was the most profitable pathway, concentrating 27% of nitrogen, 18% of phosphorus and 33% of potassium from the feedstock. VE reduced the water content, making the product easier to transport and more commercially viable. Their study demonstrated that the treated digestate has the potential for higher revenues compared to raw or separated digestate.

Patria *et al.*<sup>195</sup> examined the techno-economic feasibility of a rhamnolipid production process that utilizes digestate from AD of food waste. Three scenarios were created and contrasted, including production with one large fermenter (Scenario I); two small fermenters operating alternately (Scenario II); and production with two small fermenters operating concurrently (Scenario III). All the scenarios were determined to be economically viable, but Scenario III proved to be the most lucrative given that it enabled the most optimum fermenter operation

and employed several small-scale equipment to reduce the equipment downtime, boost the production capacity and improve the overall productivity. Finally, a sensitivity analysis was carried out to show how changes in variables such as the cost of the feedstock (digestate), the selling price of rhamnolipids, the recyclability of the extractant and the process capacity affected the process economics. Valorizing digestate through industrial symbiosis not only enhances the resource efficiency but also plays a pivotal role in achieving net-zero emissions and advancing the circular economy. By fully harnessing the potential of digestate, industries can reduce waste, lower greenhouse gas emissions and contribute to global climate goals.

Although several valorization pathways exhibit promising techno-economic feasibility, their environmental performance, nutrient recovery efficiency and adoption barriers vary significantly. Table 6 summarizes the comparative techno-economic and environmental performance of key digestate valorization strategies, highlighting their strengths, limitations and practical bottlenecks.

Thus, the choice of appropriate digestate valorization technology depends not only on economic viability but also site-specific factors such as resource availability, regulatory constraints and environmental sustainability goals. This aligns with the broader objectives of industrial symbiosis and circular bioeconomy, discussed in the following section.

## 10. Digestate valorization and contribution to the circular economy

An AD-based economy requires an integrated biorefinery approach to address the hurdle of digestate management and recovery of value-added products. Adopting integrated and multifunctional processes for the valorization of digestate towards the production of commercial products can promote the transition of conventional processes to a circular bioeconomy.<sup>203</sup> Transitioning to a circular bioeconomy is expected to result in increased competitiveness, economic growth and employment opportunities through advances in social, organizational and technological aspects. However, it is important to consider both economic viability and environmental sustainability, exemplified by a reduced carbon footprint, when developing these bioprocesses. Historically, digestate has been predominantly employed for the purpose of augmenting soil nutrient levels and serving as a feedstock for composting.<sup>204</sup> Over the course of ten years, researchers have explored various methods for harvesting energy and value-added products from digestate. Several potential applications have been identified for digestate, such as utilizing it as a substrate for the cultivation of microalgae and fungi, nutrient recovery, biofuel production, generation of PHA and other related purposes. Fig. 8 provides an illustration of the potential integration strategies for liquid and SD, aligning with the principles of the circular economy concept.



Table 6 Comparative techno-economic and environmental performance of digestate valorization pathways

Valorization pathway	Energy input requirement	Product yield	Main product(s)	Environmental benefit	Techno-economic barriers	Industrial adoption barriers	Ref.
PHA production	Low-to-moderate energy intensity, (aerobic shake-flask culture at 37 °C, 200 rpm)	PHA content 23.98% ± 0.52% PHA yield: 0.52 ± 0.02 g L <sup>-1</sup>	Polyhydroxyalkanoate, poly(3-hydroxybutyrate-co-3-hydroxyvalerate)	Food waste valorization, biodegradability, and carbon neutrality	Low PHA yields from digestate (only 0.52 g L <sup>-1</sup> ), need for controlled conditions, cost of downstream processing and purification	Inconsistent feedstock composition. Competing microbes. Market maturity	96
Biochar production <i>via</i> pyrolysis	Energy intensive (2 h under oxygen-limited conditions at 300 °C)	At 300 °C: 76.92%	Biochar, biogas, and improved volatile fatty acid degradation	Digestate recycling, reduction of VFAs and ammonia toxicity, and reduced reliance on synthetic fertilizers	High pyrolysis temperatures, scaling challenges, and process optimization	Lack of standardized systems. Logistical complexity. Economic feasibility	196
Hydrothermal carbonization (HTC)	Less energy-intensive (moderate temperatures (200–240 °C) for 1 h)	Hydrochar yield: up to 78.3% (w/w), carbon retention in hydrochar: ~75%, gas yield: ~4.4% to 5.1% (mainly CO <sub>2</sub> )	Hydrochar, gas: primarily CO <sub>2</sub> , small amounts of CH <sub>4</sub> , CO, H <sub>2</sub>	Carbon sequestration, nutrient recycling, offset GHG emissions, and avoids incineration or landfilling	Energy costs, complexity of treating or utilizing HTC, and optimisation of process parameters	Uncertainty in long-term stability, heavy metals or toxins in HTC, and regulatory issues	175
Gasification	High energy intensive (steam gasification at 1000 °C)	Syngas, especially hydrogen-rich, H <sub>2</sub> yield: up to 62.7%, CO yield: up to 40.4%, lower heating value: 12.0–12.4 MJ m <sup>-3</sup>	Hydrogen (H <sub>2</sub> ): 62.7%	Utilization of digestate waste, low emissions, and circular economy	Steam production, high capital cost, and need for syngas purification	Scalability, technology readiness and feedstock variability	182
Enzyme production from digestate	Low energy input (no biomass pretreatment)	Cellulase (FPase): ~1.2 FPU g <sup>-1</sup> , xylanase: ~81 U g <sup>-1</sup> , protease: ~50 U g <sup>-1</sup>	Cellulase, xylanase and protease	Waste valorization, no chemical pretreatment, and potential reduction in synthetic enzyme use	Low enzyme yields, inhibitory pH (alkaline ~8–9), high buffering capacity, high variability, and presence of proteases	Inconsistent enzyme activity, need for specialized or adapted inocula, enzyme recovery challenges, and low fiber content (<10%)	34
Microalgae cultivation	Low energy intensive (paddlewheels consumed 60 423 kW h per year in cultivation ponds)	Algal biomass productivity: 9.5 ± 6.4 g TSS m <sup>-2</sup> d <sup>-1</sup>	Algal-bacterial biomass (rich in proteins, carbohydrates, and lipids)	85.1% TAN (ammoniacal nitrogen) removal efficiency, 36.2% orthophosphate removal efficiency, CO <sub>2</sub> biofixation: 1.88 kg CO <sub>2</sub> per kg dry biomass	High operational costs, high CAPEX, phosphorus removal efficiency is low, and biomass has low market value	Large land area needed, variable productivity depending on weather, effluent may still need polishing, and limited scalability without guaranteed biomass valorization route	171
Struvite precipitation	Low energy intensive	Ammonium sulphate (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> : 0.69 kg N per m <sup>3</sup> of anaerobic digestion supernatant, struvite (NH <sub>4</sub> MgPO <sub>4</sub> ·6H <sub>2</sub> O): 0.25 kg P per m <sup>3</sup>	Ammonium sulphate (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , struvite (NH <sub>4</sub> MgPO <sub>4</sub> ·6H <sub>2</sub> O)	Lowest net environmental impact in: global warming potential, human non-carcinogenic toxicity, and freshwater ecotoxicity	High chemical costs, moderate capital expenditure, membrane maintenance and replacement	Limited full-scale experience, operational complexity, and integration with existing WWTP infrastructure	197
Ammonia stripping & absorption	Moderately energy-intensive (stripping unit operates at 50 °C, continuous air supply at 40 L min <sup>-1</sup> )	Ammonia stripping efficiency: up to 94%, ammonia absorption efficiency: around 70%–90%	Ammonium nitrate (NH <sub>4</sub> NO <sub>3</sub> ), nitrate fertilizer	Reduces ammonia toxicity, avoids use of strong acids, and improves sustainability	Energy cost, complexity of integration, and potential need for additional treatment	Scale-up challenges, need for robust process control, corrosion and material compatibility	198
Nutrient recovery using drying system	High energy demand (~1.1 MW h per ton of water evaporated)	15%–20% of total nitrogen as ammonium sulfate, 100% phosphorus remains in the solid dried product	Dried digestate (solid, rich in N and P), ammonium sulfate	Reduction in volume and weight, stabilization of organic matter, retention of nutrients, minimized nutrient leaching and runoff, and supports circular economy goals	High operational and capital costs, high energy consumption, labor-intensive, and maintenance issues	Regulatory hurdles, lack of standardized quality control and certification for bio-fertilizers, market competitiveness, and limited incentives	199





Table 6 (Contd.)

Valorization pathway	Energy input requirement	Product yield	Main product(s)	Environmental benefit	Techno-economic barriers	Industrial adoption barriers	Ref.
Liquid biofertilizer production	High energy intensive (~75 °C during NH <sub>3</sub> stripping)	Liquid biofertilizer: 73.38 kg per tonne of digestate, nutrient content in final product: nitrogen (N): 4.02 kg Phosphorus (P <sub>2</sub> O <sub>5</sub> ): 3.21 kg Potassium (K <sub>2</sub> O): 1.61 kg	Ammonium sulfate ((NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> )	Highest net environmental benefit: reduction in marine aquatic ecotoxicity potential: -141 304.03 kg 1,4-DB-eq., human toxicity potential: -71.89 kg 1,4-DB-eq., global warming potential is positive (224.63 kg CO <sub>2</sub> -eq.)	High heat and electricity consumption, chemical usage, technology complexity, and requires filter press and specialized storage	High capital investment, logistics of liquid fertilizer transport and field application, standardization of product quality	193
Composting	Low to moderate energy (mechanical separation and electricity consumption)	2.824 kilo tonnes per year of compost	Compost and liquid fertilizer	93.4 kilo tonnes of CO <sub>2</sub> equivalent GHG emissions mitigated annually, offsetting the use of chemical fertilizers	Increased capital cost, higher production costs, and need for integrated systems	Lack of profitability without composting, policy and subsidy dependence	200
Membrane filtration + ultrafiltration	Low Energy Intensive (10×–13.5× higher flux)	Retentate yield: COD: 51.2 g, total nitrogen: 13.2 g, total phosphorus: 1.3 g Permeate yield: 50% of feed volume COD: ~91 mg L <sup>-1</sup> Total nitrogen: ~358 mg L <sup>-1</sup> Total phosphorus: ~23 mg L <sup>-1</sup>	Permeate for microalgae cultivation Retentate for organic fertilizer	Prevents water eutrophication and nitrogen pollution, enables circular use, and decreases energy demand	Membrane fouling, energy cost, and cost of ceramic membranes	Limited field-scale data and infrastructure upgrade needed	169
Vacuum evaporation	Low to moderate energy (~40–45 °C) and low vacuum pressure ( $\Delta p < 15\text{--}20$ mbar)	Ammonia removal efficiency 85% to 98% Final product concentration (as TAN in the acid scrubber): up to 600 mg L <sup>-1</sup> From 5 t h <sup>-1</sup> digestate gasification: methane – 170.5 kg h <sup>-1</sup> H <sub>2</sub> – 49.8 kg h <sup>-1</sup>	Ammonium sulfate ((NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> )	Nutrient recovery, circular economy contribution, and reduced chemical demand	Membrane fouling and scaling, process optimization, and ammonia selectivity	Lack of full-scale demonstrations, scrubbing solution handling, membrane durability and cost	201
Combined methane and H <sub>2</sub> production through gasification	Low-to-moderate (better than individual methane and H <sub>2</sub> production through the same process)	CO <sub>2</sub> – 986.5 kg h <sup>-1</sup>	Combined methane and hydrogen from digestate	Valorization of digestate containing 62% (w/w) of water and 38% (w/w) of solid (of which 79% (w/w) organics)	High cost intensive as the digestate processing using gasification technology rather natural AD	Effective integration of power to methane system with digestate valorization provides better heat integration possibilities that H <sub>2</sub> and CO <sub>2</sub>	202

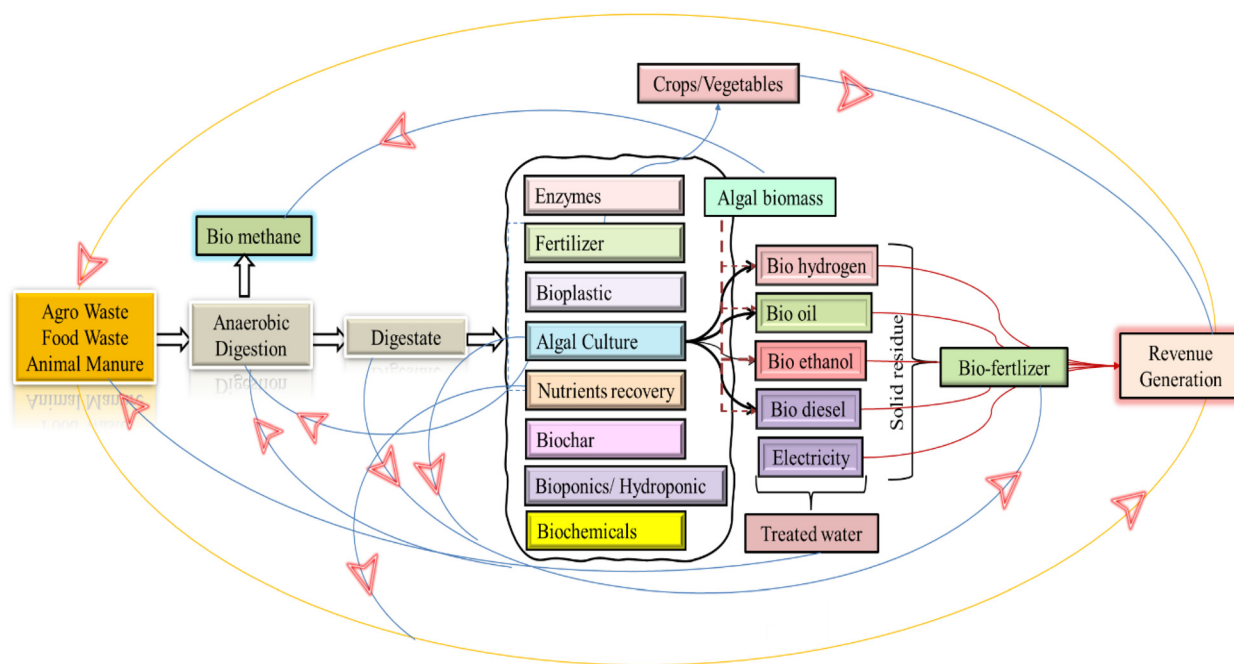


Fig. 8 Circular approach for the valorization of anaerobic digestate.

In this era of limited resource access, transitioning from a linear to circular economy by utilizing digested sludge as a source of nutrients and energy is significant for alleviating the growing demand for natural resources.<sup>205</sup> The utilization of cutting-edge technologies in waste management presents diverse opportunities to recover and convert resources from waste streams, thereby generating revenue through the production of nutrients, fertilizers, bioproducts and energy. The implementation of a circular economy has the potential to facilitate achieving sustainable development objectives at both the national and international levels.<sup>206</sup> Eventually, the AD-based biorefinery platform can play numerous roles in the closed-loop circular economy, offering information and laying the groundwork for future commercial-scale applications. A circular economic approach for the valorization of digestate not only diverts organic waste from disposal but also contributes to sustainable material cycles, reinforcing industrial symbiosis strategies and promoting a green chemistry-driven bioeconomy.

A well-structured circular economy approach not only enhances resource efficiency but also strengthens sustainability by reducing environmental burdens. The next section builds on this discussion, examining how the valorization of digestate contributes to broader sustainability frameworks and supports global environmental goals.

## 11. Digestate valorization and sustainability

The valorization of anaerobic digestate plays a key role in advancing multiple Sustainable Development Goals (SDGs)

outlined in the United Nations 2030 Agenda for Sustainable Development. By promoting sustainable practices and resource efficiency, waste valorization aligns with the principles of reduce, reuse and recycle. It offers a viable pathway towards achieving the SDGs by 2030 and addressing the challenges posed by climate change.<sup>206,207</sup> Fig. 9 depicts the valorization approaches that help to achieve different SDGs. The application of digestate as organic fertilizer is a prime example of waste valorization aligning with the SDGs. By supporting sustainable food production systems and resilient agricultural practices, it contributes to increased productivity and production, thereby advancing the goals of the 2030 Agenda for Sustainable Development (Target 2.3). Thus, the valorization of digestate contributes to Goal 2 of the SDGs. Additionally, recovering valuable water from digestate for agricultural, industrial and domestic purposes can address the growing issue of water scarcity. By promoting wastewater treatment, recycling and reuse technologies, this approach is in line with SDG 6, particularly Target 6.7. Additionally, it contributes to SDG 7, which aims to ensure universal access to affordable, reliable, sustainable and modern energy. Waste valorization plays a vital role in achieving this goal by enabling the generation of green energy from waste, reducing greenhouse gas emissions and fostering sustainable development. Industries adopting this approach not only convert waste into a valuable resource but also contribute to establishing a circular economy and reducing their dependence on fossil fuels.<sup>208</sup> The direct and indirect application of digestate in energy generation supports the objective of SDG 7. The waste sector presents significant employment opportunities in both formal and informal settings.<sup>209</sup> The valorization of digestate across different scales



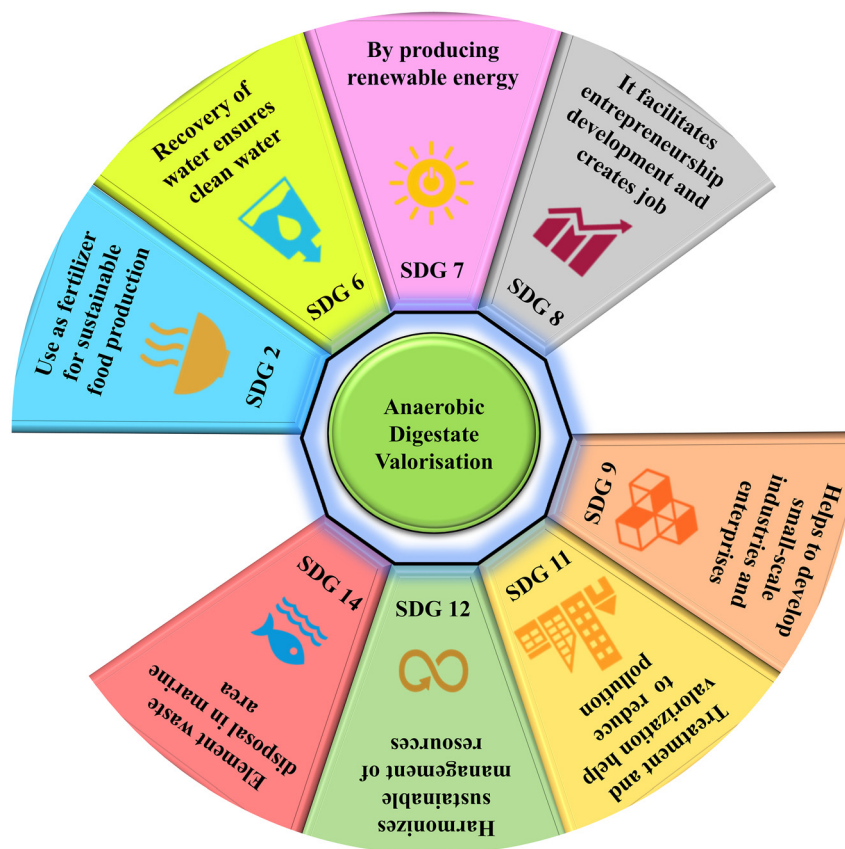


Fig. 9 Link between different SDGs and the valorization of anaerobic digestate.

can foster development-oriented policies that facilitate productive activities, job creation, entrepreneurship, creativity and innovation. It also encourages the formalization and expansion of micro, small and medium-sized enterprises, thereby contributing to Target 8.3. Waste valorization further enhances global resource efficiency in consumption and production, supporting economic growth decoupled from resource consumption (Target 8.4) and striving to provide decent work opportunities for all individuals (Target 8.5).

The valorization of anaerobic digestate towards biochemical, biomaterial and bioenergy products enhance access for small-scale industries and enterprises, integrating them into value chains and markets (Target 9.3). Additionally, it promotes the enhancement of infrastructure in industries through upgrades and retrofits, with the aim of improving sustainability, resource efficiency and the adoption of clean and environmentally friendly technologies and processes. This action aligns with Target 9.4, with all countries taking action based on their capabilities. The increase in valorization efforts promotes scientific research, upgrades technological capabilities in various industries, encourages innovation and substantially boosts public and private research spending (Target 9.5). Within SDG 11, Target 11.6 specifically addresses the reduction of environmental impacts in cities, particularly through effective waste management. Hence, the treatment and valorization of waste from AD systems contrib-

utes to the goals of SDG 11. The valorization approach makes it easier to achieve sustainable management and efficient utilization of natural resources (Target 12.2). By implementing environmentally sound waste management practices, we can reduce the release of waste into the air, water and soil, thereby minimizing its negative impacts (Target 12.4). Furthermore, by focusing on waste prevention, reduction, recycling and reuse, we can substantially decrease waste generation (Target 12.5). Adopting a circular approach for valorization eliminates the need for disposal steps, which in turn helps prevent and significantly reduce marine pollution resulting from land-based activities, including marine debris and nutrient pollution (Target 14.1). Through these various avenues, anaerobic digestate valorization plays a significant role in meeting the SDGs and fostering a sustainable future. Integrating digestate valorization within sustainable frameworks strengthens resource recovery, mitigates environmental pollution and advances green chemistry solutions for a resilient, low-carbon future.

However, although digestate valorization presents numerous sustainability benefits, its large-scale implementation faces several technical, economic and regulatory challenges. Thus, addressing these barriers is crucial for advancing its role in a circular bioeconomy. The following section explores key challenges and outlines future prospects for enhancing the feasibility and impact of digestate utilization.



## 12. Challenges and future prospective

### 12.1. Challenges in digestate valorization

Based on the current situation, it has been estimated that a biogas plant with a capacity of 1 MW electricity has the potential to generate a daily income of €1414. The value of the digestate generated by the plant can amount to an incremental sum of €334.40 on a daily basis if the digestate is managed properly.<sup>210</sup> However, there are many challenges associated with the valorization and utilization of digestate. The variability of the digestate composition depends on the characteristics of the organic substrate employed as feedstock in AD. Eventually, the variability in process requirements can pose challenges in identifying appropriate valorization methods. This issue can be solved to some extent by classifying and separating different waste used as feedstocks for AD processes.

The presence of organic micropollutants, heavy metals and pathogens has been identified as a significant concern.<sup>211</sup> The implementation of hydrophobic membranes and deep eutectic solvents for the treatment of digestate exhibits potential; however, it necessitates meticulous assessment and refinement tailored to the particular contaminants and circumstances of the digestate under consideration.<sup>212</sup> In many cases, these technologies may need to be integrated with supplementary treatment methods to achieve the desired level of contaminant removal, adding to the complexity and cost of the process. The bulky nature of digestate presents logistical challenges, particularly concerning transportation, which can substantially increase management costs. Identifying nearby customers and end-users can help mitigate these costs, making digestate utilization more economically viable. Additionally, integrating AD with downstream strategies and novel biorefinery approaches is essential for unlocking the full potential of digestate valorization. This integration not only enhances the overall process but also aligns with circular economy principles by maximizing resource recovery and minimizing waste.

One of the primary challenges is the high moisture content of digestate, which makes its handling, storage and transportation inefficient and costly.<sup>213</sup> The high water content, often exceeding 70%, necessitates dewatering or drying processes that demand substantial energy input, adding to the overall operational costs. Another major issue is the nutrient imbalance and heterogeneity in digestate composition. The variability depends on the feedstock type and digestion conditions, leading to inconsistent nutrient ratios that complicate its direct application as fertilizer.<sup>47</sup> Over-application can lead to nutrient leaching and environmental pollution, while under-application may reduce its agronomic value. Moreover, the presence of contaminants, including heavy metals, persistent organic pollutants and pathogens, raises concerns regarding its safe use in agriculture.<sup>214</sup> Thus, advanced treatment methods, such as thermal hydrolysis, biochar conversion and membrane filtration, are being explored to improve the safety and usability of digestate.<sup>192</sup>

Despite its potential, integrating digestate valorization into industrial processes faces the issues of regulatory hurdles, variability in digestate composition and technological scalability. Thus, addressing these issues is crucial to improving the reliability and market acceptance of digestate-derived products. Future efforts should prioritize standardizing digestate treatment processes, enhancing the product quality and fostering collaboration across industries to fully exploit the benefits of digestate valorization.

Regulatory challenges also play a significant role in limiting digestate valorization. Stringent environmental regulations in different regions impose restrictions on digestate application rates, storage duration and heavy metal content, making compliance difficult for AD operators.<sup>215</sup> Additionally, public perception and market acceptance are crucial barriers. Concerns regarding odor, hygiene and potential soil contamination can lead to resistance from farmers and policymakers, thereby limiting widespread adoption.

Economic viability remains a critical concern, given that the current cost of digestate valorization is often not competitive with conventional alternatives. Adopting a cascaded biorefinery approach, which uses co-products from each stage for biomass upgrading, can help improve the economic, energy and environmental performance of digestate management. This approach will facilitate a shift towards a circular bioeconomy, promoting sustainable waste management and reducing the environmental footprint of AD systems.

### 12.2. Future perspective

To overcome the above-mentioned challenges, technological advancements in digestate treatment, such as pyrolysis, nutrient recovery and biochar production, can play a crucial role in enhancing its value.<sup>213</sup> Additionally, policy interventions promoting circular economy models and incentivizing digestate use in agriculture can improve its marketability. Developing standardized guidelines for digestate application and quality control will also facilitate wider acceptance. Future research should focus on optimizing digestate processing technologies and exploring innovative applications, such as biopolymer synthesis and bioenergy generation, to maximize its potential.

Interdisciplinary collaboration is essential for advancing digestate valorization, as technical and scientific efforts within interdisciplinary frameworks can provide detailed insights into proposed strategies. For example, cultivating microalgae in liquid digestate offers a promising pathway for further valorization, given that microalgae can serve as feedstocks for various high-value products, including biofuels and bioplastics. However, achieving the complete valorization of organic waste and effluents, including nutrient and by-product recovery and the recycling of treated water, remains a significant challenge.

Looking ahead, the valorization of digestate should explore new pathways for energy production through biological and thermochemical processes, guided by evolving regulatory frameworks and circular economy principles. This approach can offer sustainable alternatives to traditional fertilizer use,



particularly in urban areas that require innovative cultivation methods. The integration of digestate valorization into a sustainable biorefinery concept is expected to become a prominent field of research, driven by the increasing number of AD plants and the need for effective and sustainable waste management solutions.

## 12. Conclusion

This review highlighted the potential of anaerobic digestate valorization as a key driver of sustainability, emphasizing its organic and inorganic content and energy potential. Beyond its conventional use as a soil amendment, digestate presents a unique opportunity for resource recovery through various biotechnological and thermochemical valorization pathways. These pathways include its transformation into bio-based fertilizers, biofuels, biochemicals, enzymes, microalgal biomass and hydroponic/bioponic systems, contributing to a circular and resource-efficient bioeconomy.

The integration of green chemistry principles into digestate valorization ensures waste minimization, promotes renewable feedstock utilization and reduces the environmental impact. The application of biorefineries, enzymatic conversions and nutrient recovery technologies exemplifies a waste-to-value approach, reducing the reliance on fossil-derived materials and synthetic fertilizers. Moreover, emerging regulatory frameworks, such as the EU Fertilizer Regulation (CE 2019/1009), are paving the way for the large-scale commercialization of digestate-derived products, strengthening market confidence and fostering sustainable agriculture.

Despite its vast potential, technical and economic challenges remain, including digestate variability, process optimization and regulatory compliance. Addressing these challenges requires innovative valorization strategies, advancements in waste-to-resource conversion technologies and enhanced industrial symbiosis to create a closed-loop system. Future research should focus on standardizing digestate treatment processes, improving techno-economic feasibility and integrating LCA to optimize environmental benefits.

As explored throughout this review, digestate valorization is a pivotal strategy for achieving a sustainable circular bioeconomy, seamlessly integrating green chemistry principles to maximize resource efficiency, while minimizing the environmental impact. Although significant progress has been made in developing innovative conversion technologies, their large-scale adoption remains hindered by economic, technological and policy-related challenges. Future research must prioritize optimizing these processes through advancements in catalytic bioconversion, process intensification and regulatory alignment to ensure industrial scalability. By integrating green chemistry principles with circular economy strategies, digestate valorization can transition from a niche concept to a mainstream sustainable solution, paving the way for future research and industrial applications.

## Abbreviations

AD	Anaerobic digestion
AHL	Aqueous hydrothermal carbonization liquids
APL	Aqueous pyrolytic liquid
BES	Bioelectrochemical systems
BOD	Biological oxygen demand
COD	Chemical oxygen demand
CBG	Compressed biogas
CNG	Compressed natural gas
ED	Electrodialysis
HA	Humic acid
HRT	Hydraulic retention time
HTC	Hydrothermal carbonization
HLS	Humic-like substances
LA	Lactic acid
LCA	Life cycle assessment
LNG	Liquefied natural gas
LBG	Liquid biogas
LBF	Liquid biofertilizer
LDR	Liquid digestate recirculation
LFD	Liquid fraction of digestate
MCCAs	Medium-chain carboxylic acids
MC	Membrane contactor
MF	Microfiltration
NF	Nanofiltration
PHA	Polyhydroxyalkanoates
RNG	Renewable natural gas
RO	Reversed osmosis
SD	Solid digestate
TRL	Technological readiness level
CSTR	Stirred tank reactors
SDGs	Sustainable development goals
SCWG	Supercritical water gasification
UF	Ultrafiltration
VFA	Volatile fatty acids
WBA	World biogas association

## Author contributions

Debajyoti Kundu: Conceptualization, methodology, and writing – original draft; Samuel Jacob, Anjani Devi Chintagunta, N. S. Sampath Kumar, Palas Samanta, Chandan Mahata, Sukhendu Dey, R. G. Shibirathna, Arun Barathi, and Gaurav Goel: Writing – original draft; Sunil Kumar and Zhiwu Wang: Writing – review & editing.

## Data availability

All relevant data supporting this review are provided within the manuscript. This review does not include primary research results, software, or code, and no new data were generated or analyzed as part of this work.



## Conflicts of interest

There are no conflicts to declare.

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