Envisaging wastewater-to-energy practices for sustainable urban water pollution control: Current achievements and future prospects

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ABSTRACT

The organic carbon in municipal wastewater is an energetic substance and can be captured and reused for bioenergy production. A comprehensive evaluation of relevant technical advances and energy recovery potential is essential to provide guidance for sustainability improvement. Although several previous works have covered this topic, most of them have mainly focused on the technical evaluation of a single step, rather than the full treatment line. In this review the currently available processes and achievements related to the capture, recovery and reuse of organic carbon from municipal wastewater for bioenergy production are summarized. The techno-economic evaluation indicates that the biological capture process fails to achieve a good effluent quality when treating wastewater with a high soluble organic content. Chemical coagulants or membranes can be applied as effective methods to assist carbon capture. A fermentation-centered bioprocessing platform is beneficial for the conversion of captured carbon into versatile products. At present, bioenergy recovery is the most promising carbon recovery mode, and the global wastewater sector possesses a 51.06 billion kWh/year bioenergy production potential. Through hydrothermal or pyrolysis treatment, the organic residue arising from the bioprocessing platform can be circularly used. Based on the above analysis, a plant-wide wastewater-to-energy route including a carbon separation system, a bioprocessing platform, and a thermochemical conversion line is envisaged. Additionally, the challenges to achieving the proposed bioenergy production paradigm from municipal wastewater are examined. This review presents the gaps and future prospects in achieving sustainable municipal water pollution control.

1. Introduction

Wastewater treatment plants (WWTPs) act as terminal shield for urban cities to protect the water environment from contamination and achieve water resource circulation. Generally, the energy required for wastewater treatment accounts for approximately 2–4% of the total societal electricity consumption [1], which places a considerable pressure on city development. Recent concerns on sustainable development have inspired the public to reconsider previous pollution control patterns and recognize the importance of sustainable WWTPs operation. In 2016, the 17 United Nations sustainable development goals of the 2030 agenda [2] officially came into force. A series of actions in the fields of wastewater treatment and sanitation has already been implemented. The mission of WWTPs is not solely focused on pollutant removal, but also simultaneous energy and resource recovery [3].

The organic matter in municipal wastewater is an energy-containing substance that has been estimated to possess a minimal chemical oxygen demand (COD) of 13–14 kJ per gram [4]. Unfortunately, most of this energy is wasted in the current prevailing bioprocess through direct mineralization. Incorporation of carbon capture and conversion process in the overall treatment process is promising to offset the energy input and increase the overall sustainability. With the development and application of autotrophic nitrogen removal [5] and chemical dephosphorization [6] processes, bioenergy production from organic carbon in municipal wastewater has become possible.

To date, although numerous potential carbon recovery methods are available for municipal wastewater treatment, only a few WWTPs in Europe and the United States have successfully achieved energy-sufficient operation. The wastewater characteristic diversity makes the actual energy performance of the different methods uncertain. In developing countries such as China with a low organic strength [7], the
selection of suitable carbon capture and enrichment methods for municipal wastewater treatment remains ambiguous. In addition to bioenergy production, various intermediate byproducts are generated during the wastewater treatment process. Thus, properly disposing and reusing these byproducts is also essential to achieve overall sustainability. It has been reported that municipal wastewater-derived carbon could be recovered as value-added products such as bioplastics and alginites [8]. Nevertheless, such resource production routes are far from practical applications and full-scale facilities still do not exist. Due to the high cost of product enrichment and purification, the technical-economic superiority of resource production over energy recovery from municipal wastewater remains challenging. Herein, it is essential to comprehensively evaluate the technical feasibility and economic effectiveness of the whole process of carbon capture and conversion. Although several previous works have covered this issue, most of them mainly have focused on the technical evaluation of a single step, rather than the full treatment line [9, 10].

Based on the above considerations, this paper aims to provide a state-of-the-art evaluation of the full line of carbon capture, separation, and conversion from municipal wastewater. The technical-economic-environmental performance is comprehensively analyzed. Based on this analysis, the global energy production potential from municipal wastewater is envisaged. By further examining the possible circulating utilization routes for carbon residues, a plant-wide wastewater-to-energy conversion route is proposed, and the challenges are accordingly addressed. This work may provide valuable information for sustainable municipal wastewater treatment and wastewater-to-energy conversion management.

2. Carbon capture and separation from municipal wastewater

Carbon capture and separation constitute the fundamental step for further carbon conversion and processing. Through appropriate control, organics can be captured as biomass. By strengthening via chemical or physical means, the carbon capture efficiency can be further maximized. Nevertheless, the carbon capture and separation effectiveness notably depends on the size characteristics of the organic particles in municipal wastewater. Herein, a deep understanding of the chemical components and particle distribution is essential.

2.1. Size fraction of the organic carbon in municipal wastewater

Generally, the particles in wastewater can be classified as settleable (>100 μm), supracolloidal (1–100 μm), colloidal (0.08–1 μm), and soluble (<0.08 μm) constituents [11]. However, such a classification has been inconsistent between different studies. To date, a clear definition of the above particle categories with defined size ranges remains lacking. According to the Stokes equation (equation (1)) [12], particles of small sizes are hard to separate from the system through conventional gravitational clarifiers.

\[ V_s = \frac{g(\rho_s - \rho)d^2}{18\mu} \]  

where \( g \) (m/s\(^2\)) is the acceleration of gravity, \( \rho \) and \( \rho_s \) (kg/m\(^3\)) are the densities of the particles and fluids, respectively, \( d \) (m) is the particle diameter, and \( \mu \) (Pa-s) is the dynamic viscosity. In practice, the municipal wastewater characteristics are highly case-specific, and the fraction of settleable particles exhibits within various ranges [13,14]. The effective capture of unsettleable organics is meaningful for both efficient carbon recovery system construction and efficient quality management.

Carbohydrates, protein-like substances, oils, fats, lipids and fatty acids are the dominant organic matter components in municipal wastewater [15,16]. Detailed information on the chemical composition of particles of different sizes remains insufficient, and there are only a few works addressing this topic. For example, fibers have been identified as the main components of settleable particles [15,17], while the colloidal and soluble parts mainly consist of carbohydrates and protein-like substances [18]. From this perspective, the development of efficient and cost-effective processes aimed at carbohydrate and protein (colloidal and soluble) recovery is warranted.

2.2. Carbon separation assisted by chemicals

According to the Derjaguin-Landau-Verwey-Overbeek theory [19, 20], the repulsive force between the electrical double layers of colloidal particles is the leading cause of stable suspension. Commonly, the particles in wastewater are negatively charged [21], and trivalent metallic inorganic or cationic organic coagulants effectively neutralize electrons and condense the double electric layers of particles. Once the suspended particles have been destabilized, they can form large flocs via agglomeration and thereafter be separated through sedimentation. Based on the above theory, chemically enhanced primary treatment processes have been widely studied and applied in both scientific and engineering aspects in recent decades [21–23]. In addition to organic particle separation, phosphorus can also be simultaneously removed through chemical precipitation.

Iron- and aluminum-based metallic chemicals are the most popularly employed coagulants in practice. Although other metallic coagulants, such as titanium-based [24] and zirconium-based [25,26] coagulants, have been developed, their practical applications are absent. Organic particles are removed mainly through entrapment, charge neutralization, coagulation, and adsorption mechanisms [27]. The particle removal efficiency is affected by the coagulant properties, dosages and operation conditions [27]. In regard to polyvalent metals, a series of hydrolysis reactions occur in aqueous solutions [28,29]:

\[ \text{OH}^- + \text{MOH}^{n-1+} \rightarrow \text{M}^{n+} + \text{H}_2\text{O} \]

where \( M \) is the metal element and \( n \) is the oubtrance electron number. Metal hydroxides are soluble in acids or strong base solutions, and the organic separation efficiency is closely related to the species of hydrolysis products. For example, highly electropositive Al\(_2\)O\(_3\)\(\text{H}_2\text{O}\)\(_{12}\) has been identified as the active species for organic removal when aluminum salt is applied [30]. It has been found that pollutants are removed via charge neutralization under low dosage conditions, while sweep flocculation prevails when high coagulants dosages are adopted [31].
In addition to metal salts, polymers are more effective in improving the settling rates of settleable particles rather than increasing the suspended solids removal efficiency [32]. Thus, polymers are commonly used as flocculants to aid the coagulation process in many cases. By considering their environmental benignity and reduced toxicity, natural macromolecules such as chitosan and cellulose have been employed as raw materials to prepare coagulants [33,34]. Researchers have also adopted tannin-based agents as coagulants and proven their effectiveness in pilot-scale trials [35,36]. Moreover, organic monomer-grafted starch has been applied in simulated colloidal particle agglomeration [37]. A full-scale test has revealed that starch-based polymers are promising as a replacement of synthetic polymers in sludge dewatering [38]. However, the easy biodegradation and short shelf-life issues must be addressed in future studies of natural source-based coagulants [21].

Although chemical-based coagulation processes have been widely employed in municipal wastewater treatment, such processes have been criticized as yielding a low efficiency of soluble organic removal. The total organic removal efficiency via the coagulation process is approximately 50–60%, and this value decreases to 20–30% for soluble organics [39,40]. Soluble components are primarily removed through adsorption onto the hydrolyzed product of the coagulant (Fig. 1), and therefore, they are more difficult to remove than larger organics. In terms of municipal wastewater with a high level of soluble organics, subsequent polishing of the coagulation effluent may be required to meet local discharge limits.

### 2.3. Organic enrichment via biological redirection of the carbon metabolism

Organic removal by biological adsorption was initially proposed to expand the treatment capacity of wastewater facilities as early as the middle of the last century. Ulrich and Smith [42] first developed the biosorption process for the treatment of municipal wastewater at the Austin plant in Texas in 1951. In this process, raw municipal wastewater is quickly mixed with sludge within 15 min in a mixing tank, and the effluent is discharged after sedimentation in a clarifier. Part of the sludge is pumped to an aeration tank to reactivate its original adsorption capacity, and is then returned to the mixing tank for the next cycle. The excess sludge generated in both the clarifier and aeration tank is discharged to the settling tank, and the effluent is discharged after membrane filtration. Although membrane treatment is effective in separating organic particles, severe fouling may occur in the direct application of membranes in municipal wastewater treatment [52]. As a result, frequent maintenance and backwashing are required to maintain operation, which inevitably increases the overall cost. It was found that 1–8 μm biopolymers might be the main foulants causing the rapid decline in membrane flux [52]. To resolve this problem, coagulation pretreatment has been included in membrane separation processes to recover organics from municipal wastewater [52,53].

In addition to coagulation, biological processes are also combined with membranes to optimize the organic recovery. For example, Faust et al. [54] examined the feasibility of using a high-loading membrane bioreactor to enrich organics from municipal wastewater. The results indicated that nearly 90% of the influent colloidal organics could be recovered in the concentrate. Their subsequent work illustrated that when the reactor was operated under high dissolved oxygen concentrations, a higher carbon recovery and reduced membrane fouling could be achieved [55]. Thus, membranes separation could serve as a promising supplemental process to the carbon separation and recovery route.

### 2.4. Membrane separation process

Membrane modules are also embedded in carbon separation and recovery processes. Membrane separation is a physical process, and theoretically, a 100% carbon recovery efficiency could be achieved only if the membrane pores were smaller than the particle size. Generally, a good and stable water quality with particle-free effluent can be acquired after membrane filtration. Although membrane treatment is effective in separating organic particles, severe fouling may occur in the direct application of membranes in municipal wastewater treatment [52]. As a result, frequent maintenance and backwashing are required to maintain operation, which inevitably increases the overall cost. It was found that 1–8 μm biopolymers might be the main foulants causing the rapid decline in membrane flux [52]. To resolve this problem, coagulation pretreatment has been included in membrane separation processes to recover organics from municipal wastewater [52,53].

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### 2.5. Energy-economic-environment assessment of organic carbon separation and capture processes

To better understand the practical application performances of carbon capture processes, three different processes were compared, including the high-rate activated sludge (HRAS), chemical enhanced HRAS (CEHRAS), and chemical enhanced membrane bioreactor (CEMBR) processes. The performances of the three treatment processes in terms of energy consumption, economic costs, environmental benefits (i.e., effluent COD concentration), and carbon capture efficiency were examined. Fig. 2 shows the schematic diagrams of the above three carbon capture processes. The three systems were operated under a high organic loading with an HRT of 1 h. The generated sludge was discharged to maintain a stable biomass content. To maximally recover organic carbon, a short SRT of 0.7 h was adopted, which ensures the adsorption rather than degradation of organics. An assumed municipal wastewater flow at 20,000 m³/d scale with characteristics of 500 mg/L
COD, 50 mg/L Kjeldahl N, and 6.5 mg/L total P were adopted as the input data to conduct simulation. The treatment performance and carbon capture efficiency were acquired using the Biowin Process Simulator (V6.0, EnvironSim Assoc. Ltd., Canada). The electric requirements for the operation of the grit tank, primary clarifier, and second clarifier were estimated to be 0.011, 0.007, and 0.018 kWh/m³, respectively [56]. The aeration energy of the biological process was estimated by assuming an aeration efficiency of 2 kg O₂/kWh [57]. The oxygen requirement (kg O₂/d) was estimated with the BioWin aeration model. The economic costs for the daily operation were calculated based on the consumed electricity and chemical amount. The electricity price was assumed to be 0.215 $/kWh according to the Eurostat database [58]. In the treatment flows of b and c, an Fe-based coagulant at a dosage of 15 mg-ferric oxide/L was applied to enhance the carbon capture efficiency. The coagulant price was assumed to be 0.281 $/kg-FeCl₃ [59]. The working mode of the membrane module in the CEMBR process was set as filtration/relaxation (22/2 min), and citric acid (20,000 mg/L) and sodium hypochlorite (4100 mg/L) were dosed to control membrane fouling every three and six months, respectively [60]. The citric acid and sodium hypochlorite prices were $ 1.98/kg and $ 0.75/gallon, respectively [61]. To examine the impact of the organic carbon size on the treatment performances of the different carbon capture processes, three scenarios with different ratios of influent soluble COD (SCOD) to the total COD (TCOD), i.e., 0.25, 0.5, and 0.75, were defined.

As indicated in Table 1, although the economic cost of the HRAS process was the lowest under the three scenarios, the energy consumption, effluent COD concentration, and captured carbon content were all inferior to those of the CEHRAS and CEMBR processes. When the

### Table 1

<table>
<thead>
<tr>
<th>Treatment flow</th>
<th>Energy Consumption (kWh/d)</th>
<th>Economic cost ($/d)</th>
<th>Effluent COD (mg/L)</th>
<th>Captured carbon (kg-COD/d)</th>
<th>Reclamation cost ($/kg-COD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario 1, SCOD/TCOD = 0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HRAS</td>
<td>1841</td>
<td>396</td>
<td>62</td>
<td>7454</td>
<td>0.053</td>
</tr>
<tr>
<td>CEHRAS</td>
<td>1719</td>
<td>618</td>
<td>46</td>
<td>7869</td>
<td>0.079</td>
</tr>
<tr>
<td>CEMBR</td>
<td>1362</td>
<td>663</td>
<td>35</td>
<td>8074</td>
<td>0.082</td>
</tr>
<tr>
<td>Scenario 2, SCOD/TCOD = 0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HRAS</td>
<td>1960</td>
<td>421</td>
<td>80</td>
<td>7107</td>
<td>0.059</td>
</tr>
<tr>
<td>CEHRAS</td>
<td>1881</td>
<td>653</td>
<td>60</td>
<td>7534</td>
<td>0.086</td>
</tr>
<tr>
<td>CEMBR</td>
<td>1544</td>
<td>703</td>
<td>34</td>
<td>7990</td>
<td>0.088</td>
</tr>
<tr>
<td>Scenario 3, SCOD/TCOD = 0.75</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HRAS</td>
<td>2054</td>
<td>442</td>
<td>100</td>
<td>6752</td>
<td>0.065</td>
</tr>
<tr>
<td>CEHRAS</td>
<td>1997</td>
<td>678</td>
<td>72</td>
<td>7175</td>
<td>0.095</td>
</tr>
<tr>
<td>CEMBR</td>
<td>1739</td>
<td>745</td>
<td>34</td>
<td>7962</td>
<td>0.094</td>
</tr>
</tbody>
</table>
fraction of the SCOD component in the influent increased to 0.75 (Scenario 3), the effluent COD of the HRAS process reached 100 mg/L. In comparison, supplying ferric salt to the primary clarifier was found to be beneficial regarding carbon reclamation and effluent quality improvement. The introduction of a membrane module in the biological tank to replace the second clarifier further improved the carbon capture efficiency. Although a stable and low-organic content effluent could be produced by the CEMBR process, its overall carbon reclamation cost was the highest ($0.082/kg-COD) under Scenario 1. Only when the SCOD/TCOD increased to 0.75, did the CEMBR process ($0.094/kg-COD) then outperform the CEHRAS process ($0.095/kg-COD).

3. Bioprocessing platform for the production of biofuels

Biofuels such as biogas or bioelectricity are exploitable energy sources that can be directly retrieved from organic residues. Compared to other types of biomass, i.e., agricultural waste, the components of municipal wastewater derived organics are more complex. Microorganism-oriented conversion is a feasible process to convert mixed organics into biofuels. The most efficient and cost-effective organic carbon processing process for value-added substance production is anaerobic fermentation. However, controlling the fermentation stage and obtaining profitable output remain unclear.

3.1. Fermentation-centered bioprocessing platform

Carbohydrate-rich substrates can be effectively composed into volatile fatty acids (VFAs) in the fermentation process, along with the generation of hydrogen [62]. Although great efforts have been devoted to achieving a high product yield, low hydrogen production remains the primary challenge limiting its application. Theoretically, 1 mol of glucose could produce 4 mol of H$_2$. Nevertheless, the practical H$_2$ yield rarely exceeds 2 mol per mol of glucose when processing mixed cultures and real waste streams [63]. Dark fermentation of concentrated municipal organics for VFA production, instead of merely focusing on hydrogen production, is recommended as an alternative platform for versatile products bioprocessing. VFAs are the most widely available carbon sources that can be consumed by different microorganisms to synthesize valuable products. By combining this approach with other featured bioprocesses, the production of fuels and value-added chemicals can be developed (Fig. 3).

3.1.1. Biofuel production

Anaerobic digestion has been proposed and used for over a century at the worldwide scale to produce biogas. Under strictly anaerobic conditions, the captured municipal organics can be converted into volatile acids, hydrogen, and CO$_2$ by specific microorganisms, finally resulting in methane synthesis. Both methane and hydrogen, which have high calorific values, are viewed as clean energy sources. In practice, methane production can be accomplished in one stage via mixed cultures or in two stages by more specialized microbes. However, the two-stage configuration, through separation of the hydrolysis/acidogenesis and methanogenesis steps, is more flexible in controlling carbon conversion and recovering versatile products [64,65]. By individually cultivating specific bacteria in different reactors, the stability of the overall process could be enhanced [66]. Another merit of the two-stage configuration is the improved methane and hydrogen yields, as reported in the literature. Siddiqui et al. [67] found that compared to the single-stage process, the total methane yield greatly increased from 0.48 to 0.67 m$^3$/kg solids treated when food waste and sewage sludge were co-digested in the two-stage process. Similarly, Yang et al. [68] obtained an increased methane yield and energy efficiency by using two-stage fermentation. In addition to higher energy recovery efficiency, the two-stage process is more flexible in alleviating the adverse effect of irrelevant biogas production processes. For example, sulfate commonly occurs in municipal wastewater, and the H$_2$S produced under anaerobic conditions reduces the biogas purity. However, this issue can be greatly mitigated via the removal of sulfate at the acidogenesis stage in two-stage anaerobic digestion [69].

Although two-stage fermentation has been widely applied worldwide to recover biofuels from organics, it still suffers from several limitations. It has been documented that methanogenic communities are sensitive to VFAs [70]. As a consequence, the organic load at the second methanogenic stage should be stringently controlled, which might limit the possible advantages of the two-stage process. Furthermore, undergraded intermediate metabolites more easily accumulate at the second stage, which is thought to be partially responsible for the decreased efficiency of the system [71]. Finally, the spatial separation of the methanogenesis and hydrolysis/acidogenesis stages also inhibits syntrophic association and interspecies hydrogen transfer between the relevant microorganism communities [72]. The above restrictions still require extensive future research.

3.1.2. Coupled fermentation-bioelectrochemical process for electricity production

Benefiting from the extracellular electron transfer capacity of certain specific microbes, bioelectricity can be extracted from organics. In a typical bioelectricity generation system, i.e., microbial fuel cell (MFC), organics are oxidized by bacteria at the anode. Simultaneously, the electrons are generated and transferred to the cathode to catalyze the oxygen reduction reaction. Zhang et al. [73] investigated the feasibility of the direct application of an MFC in municipal wastewater treatment to recover bioelectricity. Although the COD removal efficiency could reach 65–70% by using an MFC with a platinum-based cathode, the average bioelectricity recovery rate was 0.0092 kWh/m$^3$ wastewater. Further carbon balance analysis indicated that only 13.2% of the organic carbon was recovered as electricity. Subsequent work conducted by the same group demonstrated that the MFC may not be suitable to directly treat primary sludge for energy recovery [74]. One of the reasons for the inefficiency of MFCs is the complicated and unstable compound composition of practical organic residues, which inhibits the activity of electron-active bacteria. However, if anaerobic fermentation is applied to convert enriched organics in municipal wastewater into VFAs, the produced VFAs can be readily consumed as a carbon source in MFCs to generate electricity. Previous studies have already validated the feasibility of using acetate [75], propionate [76], butyrate [77], and mixed VFAs [78] as feedstock for electricity generation.

Apart from bioelectricity, the fermentation-microbial electrochemistry coupled process is also promising for the synthesis of valuable chemicals. By applying a voltage bias to an MFC, hydrogen gas can be generated in the cathode. Through reactor configuration optimizing and coupling with other systems, the overall hydrogen gas producing
efficiency can be greatly improved [79]. With a similar strategy, other chemical products, such as struvite [80] and H$_2$O$_2$ [81], can also be produced.

Although microbial electrochemistry systems are promising for energy and resource recovery, practical applications are still lacking. The low anode current density is one of the main obstacles that inhibit the efficiency of the whole system. Moreover, system performance maintenance and stabilization when scaling up the reactor require more stringent research efforts.

### 3.1.3. Other bioprocess-coupled routes for value-added chemical production

In addition to biofuels and bioelectricity, other value-added chemicals can be produced with microbes. Among the wide applications of VFAs, polyhydroxylalkanoate (PHA) production is attractive. PHAs are intracellular storage polymers and are accumulated in large quantities when microorganisms are exposed to nutrient limitations and feast-famine conditions. PHAs are biodegradable materials that can be used to produce plastics as a substitute for petroleum-derived materials. Poly (3-hydroxybutyrate) and poly (3-hydroxy-butyrato-co-3-hydroxyvalerate) are the most common forms of PHAs. Currently, there are more than 90 genera of both gram-positive and gram-negative bacteria capable of PHA accumulation [82]. According to the synthesis mechanism, VFAs appear to be the preferred carbon sources for PHA accumulation by bacteria, as they are direct metabolic precursors of PHAs [83]. As a result, acidogenic fermentation coupled with PHA production and accumulation is commonly implemented as the main production route [84]. PHAs are produced by many companies worldwide, and approximately 80% of PHAs are biosynthesized [85]. The sales price of PHAs is estimated to range from 1.5 to 5.0 €/kg, which is not competitive with petroleum-derived plastics at present (~1.0 €/kg) [86]. However, with the increasing appeals and policies opposing petroleum-based consumer packaging, increased demand for PHAs might occur.

Although PHAs have been successfully produced in the industry, only several pilot-scale facilities have been established recently for wastewater treatment processes. Table 2 summarizes the latest achievements in PHA production with sludge fermentation liquor or synthetic organic wastewater as the feed stocks. Although PHAs can constitute 90% of the cell dry weight in some cases, this value is commonly maintained at 27–59%. The full-scale application of this process for carbon recovery from municipal wastewater remains a challenge.

First, the improvement of the PHA accumulation levels in microorganisms is warranted. In contrast to laboratory operations, the composition and content of VFAs under practical conditions varies. To steadily increase PHA production, the addition of other organic residues, such as VFAs, polyhydroxyalkanoates (PHA), and polyhydroxybutyrate (PHAs) is estimated to range from 1.5 to 5.0 €/kg. PHA production is attractive. PHAs are intracellular storage polymers and are accumulated in large quantities when microorganisms are exposed to nutrient limitations and feast-famine conditions. PHAs are biodegradable materials that can be used to produce plastics as a substitute for petroleum-derived materials. Poly (3-hydroxybutyrate) and poly (3-hydroxybutyric co-3-hydroxyvalerate) are the most common forms of PHAs. Currently, there are more than 90 genera of both gram-positive and gram-negative bacteria capable of PHA accumulation [82]. According to the synthesis mechanism, VFAs appear to be the preferred carbon sources for PHA accumulation by bacteria, as they are direct metabolic precursors of PHAs [83]. As a result, acidogenic fermentation coupled with PHA production and accumulation is commonly implemented as the main production route [84]. PHAs are produced by many companies worldwide, and approximately 80% of PHAs are biosynthesized [85]. The sales price of PHAs is estimated to range from 1.5 to 5.0 €/kg, which is not competitive with petroleum-derived plastics at present (~1.0 €/kg) [86]. However, with the increasing appeals and policies opposing petroleum-based consumer packaging, increased demand for PHAs might occur.

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In addition, the development of efficient and cost-effective extraction and purification methods from mixed consortia is another critical issue. Currently, solvent extraction routes via lyophilization, cell disruption, PHA extraction, and PHA separation are well studied (Table 3). A high recovery efficiency and purity of PHA in the final product could be achieved. However, such a solvent-intensive extraction procedure not only increases the overall costs, but is also not environmentally friendly. Thus, further studies to develop less energy- and solvent-intensive methods are highly desired.

In addition to bioplastics, other biopolymers such as biopesticides [112], biofloculants [113], and biosurfactants [114] can be produced through microbial cultivation by uptake of fermented VFAs. However, all of these chemical polymers have been criticized for their variable components, low purity, and high costs for extraction and separation. Recently, alginate-like exopolysaccharides have been extracted and recovered from aerobic granular sludge at a yield of 160 ± 4 mg/g volatile suspended particles [115]. In the near future, a full-scale alginate recovery facility will be constructed in the Netherlands [116].

### 3.2. Feasibility of energy or resource processing technologies

MFC and anaerobic digestion are two possible energy generation processes from organic streams. However, compared to the already widely applied anaerobic digestion process, technology readiness level of MFCs is very low. First, the full-scale application of the MFC-based process is closely related to its economic cost. It is estimated that the cathode catalyst and ion exchange membrane are the major expensive elements, which account for 45–65% of the total material cost for a liter-scale MFC [117,118]. Utilizing a non-platinum cathode catalyst effectively reduces the overall cost. As reported by Liang et al. [119], granular activated carbon could be adopted as a catalyst in 1000-L staked MFC modules, and the economic cost of the material was approximately $36,000. Although the treatment performance and overall cost are comparable to those of other biological systems, the energy output of MFCs is inferior to that of combined heat and power plants. The actual output voltage is commonly lower than 1 V, and the energy performance of this process has remained stagnant over the years [120]. Although an electricity harvesting facility can be integrated to increase the output voltage [121], it remains difficult to satisfy either the high power motor operation or power grid interconnection requirements. It would be more feasible to apply the electricity produced by MFCs to drive low-power

<table>
<thead>
<tr>
<th>Feed stock</th>
<th>PHA content g/g-VSS</th>
<th>PHA yield g/g-COD</th>
<th>Feed mode</th>
<th>pH</th>
<th>T °C</th>
<th>Capacity L/d</th>
<th>Consortium</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>glucose</td>
<td>0.54</td>
<td>n.a.</td>
<td>batch</td>
<td>7</td>
<td>29</td>
<td>n.a.</td>
<td>acclimated sludge</td>
<td>[87]</td>
</tr>
<tr>
<td>sludge fermented liquor</td>
<td>0.28</td>
<td>n.a.</td>
<td>continuous</td>
<td>8</td>
<td>20</td>
<td>15</td>
<td>activated sludge</td>
<td>[88]</td>
</tr>
<tr>
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<td>0.17</td>
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<td>8</td>
<td>20</td>
<td>750</td>
<td>activated sludge</td>
<td>[88]</td>
</tr>
<tr>
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<td>[90]</td>
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<td>batch</td>
<td>6</td>
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<td>7.5</td>
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<td>[91]</td>
</tr>
<tr>
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<td>batch</td>
<td>7</td>
<td>30</td>
<td>3</td>
<td>activated sludge</td>
<td>[92]</td>
</tr>
<tr>
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<td>0.21</td>
<td>batch</td>
<td>un.</td>
<td>un.</td>
<td>140</td>
<td>activated sludge</td>
<td>[93]</td>
</tr>
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<td>artificial biogas</td>
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<td>n.a.</td>
<td>batch</td>
<td>un.</td>
<td>25</td>
<td>n.a.</td>
<td>pure culture</td>
<td>[94]</td>
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<tr>
<td>carboxylic acids</td>
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<td>0.25</td>
<td>batch</td>
<td>7</td>
<td>20</td>
<td>n.a.</td>
<td>pure culture</td>
<td>[95]</td>
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<tr>
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<td>0.53</td>
<td>n.a.</td>
<td>batch</td>
<td>8.9</td>
<td>n.a.</td>
<td>n.a.</td>
<td>activated sludge</td>
<td>[96]</td>
</tr>
<tr>
<td>sludge fermented liquor</td>
<td>0.2–0.9</td>
<td>0.1–0.2</td>
<td>batch</td>
<td>un.</td>
<td>23</td>
<td>0.3</td>
<td>acclimated sludge</td>
<td>[97]</td>
</tr>
<tr>
<td>n.a. not available; u.n. uncontrolled</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
apparatus operation or valuable chemical synthesis systems [122]. From this point of view, the energy performance of anaerobic digestion (AD) technology is advantageous.

Bioplastic synthesis is one of the most promising routes to extract organic carbon from municipal wastewater and upgrade it into a chemical commodity. As discussed above, the achievable PHA content within microbial consortia and the subsequent extraction and purification processes are the two important factors determining the overall cost. At present, according to several pilot-scale trials [89,123], a PHA content ranging from 0.5 to 0.6 g/g-dry cell weight seems to be the attainable accumulating value by using sludge-fermented VFA as the organic feed. The 140-L PHA synthesis pilot-scale trial conducted by Valentino et al. [93] indicated that a minimal sales price threshold of 0.9 €/kg-PHA could ensure that the entire PHA production line was profitable. However, the PHA extraction cost was not considered in their work. A techno-economic analysis conducted by Fernandez-Dacosta et al. [124] revealed that an overall cost of 1.4 €/kg poly-hydroxybutyrate (PHB) was required for the synthesis and extraction of PHA from organic wastes. Another 500-L pilot-scale test indicated that an operational cost of 2.1 €/kg-PHA was required for the entire production line [125]. If the capital investment was considered, a total economic cost of ca. 3.4 €/kg-PHA was needed.

### 3.3. Potential of bioenergy recovery from municipal wastewater at the global scale

To evaluate the global bioenergy production potential, the CEHRAS process coupled with anaerobic fermentation for biogas production is chosen as the representative carbon capture and recovery line. According to the regional diversity of wastewater properties, global municipal wastewater treatment facilities are divided into 12 different regions, i.e., North America, South America, North Africa, South Africa, East Asia, Southeast Asia, the Middle East, North Europe, South Europe, East Europe, West Europe and Australia. The organic concentration (represented by the biochemical oxygen demand, BOD) of a specific area is estimated by dividing the BOD discharge per capita by municipal wastewater discharge per capita. The BOD discharge per capita is calculated as:

$$\text{BOD discharge per capita} = \sum \frac{(a-b)}{b}$$

where $a$ is the BOD discharge per capita and $b$ is the population of a specific region. The BOD discharge per capita is strongly correlated to the local income, which was set to between 30 and 100 g/d-capita [126]. According to the World Bank classification [127], these regions could be approximately divided into low-, lower-to-middle-, upper-to-middle-, and high-income economies. Accordingly, the BOD discharge per capita in these different economies was set to 50, 60, 70, and 80 g BOD/d-capita, respectively. The municipal wastewater discharge per capita was calculated by dividing the total municipal wastewater production by the total population. The wastewater production and the total population of each country were acquired from the Food and Agriculture Organization of the United Nations AQUASTAT database [128] and the United Nations Population Division [129], respectively. The wastewater treatment rate was acquired from the UN database [130]. The wastewater temperature estimation and energy consumption algorithm can be found in previous work [131].

Under the above assumptions, Africa is estimated to have the highest organic carbon concentration (Table 4), as the per capita wastewater discharge amount in this area is lower than that in the other regions. In the envisaged paradigm, a maximal bioenergy production is allowed from municipal wastewater globally based on the potential net energy gain in each region (Fig. 4a). Specifically, the highest net energy production (0.321 kWh/m²-wastewater) could be expected in North Africa, which is due to its high organic content. North Europe exhibits the lowest (0.122 kWh/m²) energy recovery. Based on the municipal wastewater production amount and treatment rate, such a carbon capture and recovery paradigm may turn the global wastewater sector into a net energy producer at a bioenergy production level of 51.06 billion kWh/year (Fig. 4b).

### 3.4. Strategies to enhance the carbon conversion efficiency

Although the global municipal wastewater is a potential bioenergy production resource, there is still room for technical optimization and management. Several engineering measures can be adopted to achieve a higher reaction rate and improved bioenergy yield. To date, pretreatment and bioreinforcement processes are effective in improving the system efficiency.

#### 3.4.1. Enhanced pretreatment

It has been widely validated that the hydrolysis of particulate and colloidal substances is the rate-limiting step in the anaerobic fermentation process. Incomplete hydrolysis will not only lead to carbon metabolism inefficiency but also decrease the final product yield. Compared to organic macromolecules, sludge is much more complex and difficult to hydrolyze and degrade. Both the EPS and cell envelope of microbes provide a protective shielding preventing cell lysis [132]. Even at a very long retention time of 20–30 d, only a 30–50% volatile solid destruction efficiency was achieved [132]. Even at a very long retention time of 20–30 d, only a 30–50% volatile solid destruction efficiency was achieved [132]. Even at a very long retention time of 20–30 d, only a 30–50% volatile solid destruction efficiency was achieved [132]. Even at a very long retention time of 20–30 d, only a 30–50% volatile solid destruction efficiency was achieved [132]. Even at a very long retention time of 20–30 d, only a 30–50% volatile solid destruction efficiency was achieved [132]. Even at a very long retention time of 20–30 d, only a 30–50% volatile solid destruction efficiency was achieved [132]. Even at a very long retention time of 20–30 d, only a 30–50% volatile solid destruction efficiency was achieved [132]. Even at a very long retention time of 20–30 d, only a 30–50% volatile solid destruction efficiency was achieved [132]. Even at a very long retention time of 20–30 d, only a 30–50% volatile solid destruction efficiency was achieved [132]. Even at a very long retention time of 20–30 d, only a 30–50% volatile solid destruction efficiency was achieved [132]. Even at a very long retention time of 20–30 d, only a 30–50% volatile solid destruction efficiency was achieved [132]. Even at a very long retention time of 20–30 d, only a 30–50% volatile solid destruction efficiency was achieved [132]. Even at a very long retention time of 20–30 d, only a 30–50% volatile solid destruction efficiency was achieved [132].

Mechanical destruction, thermal hydrolysis, and chemical and biological pretreatments processes have been widely studied, and some of these methods have already been commercialized, as previously reviewed [134]. Recently, it was reported that anaerobic sludge pretreatment with free nitrous acid greatly improved the hydrolysis rate and methane potential [135]. Although different pretreatment processes for hydrolysis rate acceleration have been extensively reported, comprehensive evaluations of these processes are scarce. To increase the
sustainability of the entire process, additional considerations, i.e., the energy input, chemical consumption, etc., other than the fermented product yield need to be addressed.

3.4.2. Promoting the microbial activity

In addition to enhancing pretreatment, improving the microbial activity for a more efficient bioprocessing platform for organic carbon conversion is required. Recently, several strategies, including the supply of external electron-rich substances, strengthening the interspecies electron transfer, and installation of membranes, were found to be effective in this aspect.

The first approach to achieve the above goal is the external supply of electron-rich substances. During the bioprocessing of organic products, energy conversion and utilization based on electron flow are fundamental processes for microbial activities. Under specific conditions, external electron sources may be assimilated by bacteria and involved in metabolite synthesis. For instance, studies have widely reported that zero-valent iron can significantly improve the activities of acidogenic and methanogenic bacteria [136,137]. The main advantages of supplying zero-valent iron in anaerobic fermentation systems include reducing the oxidation-reduction potential, enhancing hydrogen evolution, releasing ferrous Fe after corrosion, and stimulating anaerobic microbe activities [138]. The dosing of nanozero-valent iron in the fermentation process needs to be carefully controlled, as an overdosage will cause system deterioration. Yang et al. [139] found that a nanozero-valent iron concentration above 1 mM induced cell integrity disruption and methanogenesis inhibition by more than 20%. In comparison, Suanon et al. [140] indicated that a 0.5% nanozero-valent iron dosage was beneficial for methane production, but an overdosage of 1% proved harmful. Granular sludge was found to be more tolerant to nanozero-valent iron than suspended sludge, as evidenced by the improvement in bacterial activities even at a 30 mM dosage [141]. To gain a better understanding of the promotion of biological fermentation by iron, extensive studies focusing on the influences of the metal particle size, surface passivation layer, and sludge origins on the system performance are required in the future. Moreover, external electron suppliers with a low cost and easy access other than iron remain to be developed.

The second strategy to improve the carbon conversion efficiency is to strengthen the interspecies electron transfer. A previous study revealed that the Geobacter and Metanosaeta species were capable of exchanging electrons via direct interspecies electron transfer [142]. Via such an approach, this process could be promoted to reduce the carbon loss and achieve high organic carbon recovery efficiency. Interspecies electron transfer could be enhanced via conductive materials. It was found that different species could be effectively wired for electron exchange through conductive materials such as granular activated carbon [143], carbon cloth [144], and biochar [145]. Through the addition of granular activated carbon, the methane yield was improved by 17% in the sludge anaerobic digestion process [146].

In addition to the above biological means, reactor configurations with a high efficiency should be developed and optimized. Benefiting from material-industry developments and cost reduction, low-pressure-driven membrane separation processes have been widely applied in the wastewater treatment industry. Due to the excellent retention performance, the HRT and SRT of a bioreactor can be completely separated. Microorganisms with long doubling times and particles that are difficult to degrade can be effectively retained, and their interactions can be intensified. Therefore, the membrane separation process can be coupled with the organic carbon bioprocessing route to greatly improve the overall efficiency. Anaerobic fermentation coupled with membranes has been proposed to directly treat municipal wastewater to recover organic carbon and achieve carbon-neutral operation conditions [147,148]. Although membrane fouling issues result in membrane flux decline and operation cost increase, several newly developed fouling control methods might be able to effectively mitigate these issues. For example, fluidizing granular activated carbon was found to be effective in maintaining a stable flux, although this approach might cause minor physical damage to the membrane material [149]. Moreover, the in situ utilization of generated electricity via an MFC was found to greatly mitigate
membrane fouling [150]. In addition to physical and chemical measures, a more economically feasible biofouling control method based on microbial quorum quenching has also been developed and validated [151].

### 3.4.3. Elucidating the microbial network and metabolic mechanisms by meta-omics tools

A deep understanding on the microbial metabolism and interactive networks is fundamental for accurately regulating chemical product synthesis by biological platforms. Although full-scale projects have already been constructed for certain processes (i.e., sludge anaerobic digestion), the microbiome remains only partially elucidated. In recent years, the rapid development of meta-omics, including metagenetics, transcriptomics, proteomics, and metabolomics, has shed light on the above “black box” system. For example, Ju et al. [152] revealed the biological drivers of microbial community assembly during the anaerobic digestion of primary sludge through bioinformatics analysis. Rotaru et al. [142] demonstrated the interspecies electron transfer mechanism during anaerobic digestion via RNA sequencing. Park et al. [153] further proved that the supply of granular activated carbon enhanced the direct interspecies electron transfer process. Recently, Zhu et al. [154] deciphered the metabolic functions of anaerobic populations via metagenetics and found that the electron transport and energy conservation strategies chosen by microbes were the key factors in the selection of syntrophic partners. Similar to metatranscriptomics, metaproteomic analysis is also an effective tool in the discovery of specific microbial functions, such as the recent identification of Coprothermobacter proteolyticus strains acting as scavengers and/or predators performing proteolysis and fermentation [155].

The technical advances in bio-omics have provided us with the possibility of investigating the metabolic potentials of microorganisms and determining the conditions under which certain biological functions are optimally performed. In addition, diagnostic tools can be developed based on the information retrieved from meta-omics studies to determine whether genes along key enzymatic pathways are expressed or whether a key population is present/absent [156].

### 4. Circulating utilization of biosolid residues

Generally, byproducts or residues are inevitable for any treatment line. Anaerobic fermentation-based processes are effective in converting enriched organic carbon into versatile products. However, for the biosolid residues generated from anaerobic bioprocesses, their appropriate disposal is essential considering their potential environmental impacts. Benefiting from the development of material synthesis methods, such organic residues can be employed as precursors for functionalized material preparation. Through further application of the synthetic material for wastewater remediation, a waste treatment by waste paradigm can be expected.

#### 4.1. Thermochemical conversion of biosolids into functionalized materials

Biosolids are outstanding and low-cost precursors to prepare functionalized materials. The inorganic elements in a mixture could act as a heteroatom doping source and improve the material activity. Therefore, catalytic materials aimed at a more efficient energy conversion, utilization, and municipal pollutant control can possibly be fabricated.

Thermochemical synthesis in the absence of oxygen is one of the most widely applied processes for the preparation of functionalized materials. In addition, the autogenerated pressure formed during the liquid hydrothermal conversion process at low to moderate temperatures efficiently transforms biomass into carbon-based materials. To reduce the carbon loss during the hydrothermal reaction process, zeolites have been implemented as catalysts to increase the product yield [157]. However, the produced hydrochar commonly contains a high level of oxygen functional groups with a low aromatization degree [158], which favors chemical activation to further improve the crystallinity and porosity. As a result, post-treatment of hydrothermally carbonized products by annealing under an inert atmosphere is often performed [159].

For carbon-based materials, a well-developed porous structure is beneficial for surface area improvement and their subsequent application performance. However, due to the various components of the enriched organic carbon from municipal wastewater, it is difficult to directly synthesize ordered porous materials. Templates supposedly promote the formation of ordered pores and increase the material surface area. SiO₂, which can be removed via KOH or HF washing, has commonly been used as a hard template to produce porous materials [160]. Similarly, zeolites, NaCl, Al₂O₃, etc., have also been applied as template materials to increase the surface area [161–163]. The initial structure and composition of the carbon precursor greatly influence the size, shape, and surface structure of the carbonated product. Pyrolysis has been proven to be an efficient route for the preparation of functionalized materials. However, a universal synthesis method that can precisely control the morphology and structure of a product and is effective with complex precursors is still lacking. Recently, Yu’s group proposed a transition-metal-salt-assisted pyrolysis strategy to synthesize functional carbon materials, which was found to be widely effective for different organics [164]. Such a synthesis strategy might also be effective in the conversion of municipal wastewater-derived carbon precursors, as iron or aluminum is commonly applied at the pretreatment stage.

#### 4.2. Potential applications of biosolid-based chars

Porous carbon adsorbents are one of the potential applications of biosolid-derived char. Generally, the surface area and pore diversity of an absorbent are closely related to its adsorption capacity. The Brunauer-Emmett-Teller (BET) surface area of sludge annealing products typically ranges from 100 to 150 m²/g [165,166]. The pyrolysis temperature and retention time greatly affect the creation of pores. A high carbonation temperature favors the recombination of carbon into aromatic structures, in which case the BET surface area increases with increasing annealing temperature [167]. More importantly, a short retention time is required when a high temperature is applied. For example, the porous structure will collapse and shrink when the temperature exceeds 900 °C [168]. Acid pickling of the pyrolysis product promoted porosity development [169].

Steam and CO₂ have been widely used to increase the material surface area because these reagents do react with carbon [170]. Inorganic ingredients might impose adverse influences on pore construction if the activation conditions are not suitably controlled. Chemical activation based on KOH or ZnCl₂ reagents can greatly improve the overall porosity, and a BET surface area of 1882 m²/g can be achieved [171]. An as-prepared carbon adsorbent originating from municipal wastewater effectively treated water contaminated with heavy metals, dye, and other refractory organics (Table 5).

Carbon-enriched biosolids can also be used to fabricate catalysts to initiate advanced oxidation reactions. By using an Fe²⁺-premixed excess sludge as a precursor, a photocatalyst for H₂O₂ activation to degrade rhodamine-B was successfully fabricated [183]. With a similar strategy, an Fe–C complex could be obtained to catalyze a heterogeneous Fenton reaction, whose performance was superior to that of a commercial activated carbon-supported Fe catalyst [184]. In addition to providing an external supply source of Fe, FeCl₃-coagulated sludge can also be reused as a precursor to prepare electrocatalysts. Previous work indicated that the Fe containing sludge originating from municipal wastewater pretreatment revealed a high electrochemical selectivity toward a 2 e⁻ oxygen reduction reaction after annealing under an NH₃ atmosphere [185]. The average H₂O₂ yield of the catalyst reached 432 mg/h/g in an acid electrolyte, and the catalyst could be applied as a cathode catalyst in an electro-Fenton system for phenol degradation.
Additionally, biological sludge is an outstanding precursor to prepare materials to catalyze advanced oxidation reactions. By adopting a facile one-pot pyrolysis strategy, sewage sludge could be converted into an efficient persulfate activator for bisphenol-A degradation [186]. A trace amount of metal salts in sludge was found to enable catalyst activity tuning, which might inspire researchers to develop a more universal catalyst preparation route with the assistance of metals. Recently, Zhang’s group used hydrothermally carbonized sewage sludge as a visible light-driven catalyst to degrade pollutants with the assistance of oxalate [187]. The above results clearly open up wide possibilities for the utilization of municipal wastewater-derived carbon as a catalyst to initiate advanced oxidation reactions for wastewater remediation.

Municipal sludge-derived materials can also be applied in energy conversion and storage. For example, Ye et al. [188] synthesized sludge-based carbon that was rich in mesoporous structures and graphitic N and showed a good 4 e⁻/oxygen reduction activity in a 0.1 M KOH solution. Similarly, Yuan and Dai [189] prepared porous carbon by using biological sludge and revealed its bifunctional properties. Benefitting from its low cost and favorable oxygen reduction activity, sludge-based carbon could be used as a cathode catalyst in MFCs. It was found that the power density of an MFC containing sludge-based carbon reached 969 mW/m², which is comparable to that of Pt [190]. By employing a different tuning strategy in the material preparation process, sludge-based carbon is capable of electron storage in supercapacitors [191,192]. Herein, through appropriate tuning, wastewater-derived organic residues could be reused for pollution control and energy conversion purposes.

5. Future perspectives and challenges

Organic carbons are principally removed from municipal wastewater in the form of CO₂ in conventional bioprocess-based WWTPs. To reduce the need for excess sludge disposal, a long SRT and extended aeration are commonly employed to reduce the sludge yield. With the development of autotrophic nitrogen removal technology [5] and the widespread application of chemical phosphate removal processes [5], the independent treatment of C, N, and P is becoming a possibility. As a result, in contrast to the conventional oxidation process, a carbon-to-energy line based on the available processes is proposed in this work (Fig. 5). This route compiles organic carbon capture, bioproccessing, and thermochemical conversion stages. By using CEHRAS- or CEMBR-based carbon capture processes and their combinations, the organics in municipal wastewater can be separated as chemically enriched sediments or sludge. The carbon-enriched product is suitable for bioenergy production and resource recovery via an anaerobic fermentation-based bioprocessing platform. The carbon enriched biosolid residues are appropriate for fabrication of functionalized materials to achieve efficient wastewater remediation. With such a process, a more sustainable municipal wastewater treatment process than that of current energy- and chemical-intensive activated sludge-based WWTPs can be expected.

Although the specific technological means to achieve the above proposed concept have already been established, the actual practice still faces challenges, and the following issues need to be addressed.

5.1 More efficient carbon capture and separation to ensure a qualified effluent

Although organic carbon separation and enrichment processes have been well established and studied, their applications are restricted due to the poor removal performance of the soluble COD. The effluent quality might not be comparable to that of conventional activated sludge processes when treating wastewater containing high contents of soluble organics. Moreover, the total COD concentration is commonly adopted as a strictly controlled effluent parameter in developing countries. Thus, the development of an enhanced soluble organic carbon recovery process is still required. The combination of enhanced pretreatment and biological enrichment processes might be employed as an effective strategy to improve the overall carbon recovery efficiency. For practical design and operation purposes, a deep understanding of the microbial ecology and precise mathematical model development of biological adsorption processes are imperative. Moreover, the adsorption materials can be supplemented to enhance the carbon removal performance. For example, β-cyclodextrin polymer was identified as an outstanding

Table 5

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Synthetic procedure</th>
<th>Surface area m²/g</th>
<th>Pollutants</th>
<th>pH</th>
<th>Adsorption capacity mg/g</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sewage sludge</td>
<td>Immersed in ZnSO₄·7H₂O solution, dry, and pyrolysis at 500 °C for 2 h</td>
<td>550</td>
<td>PO₄²⁻</td>
<td>5.0</td>
<td>123</td>
<td>[172]</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>Polymer conditioned, dry, and pyrolysis at 300 °C for 1 h</td>
<td>116</td>
<td>Methylenblue</td>
<td>5.0</td>
<td>123</td>
<td>[175]</td>
</tr>
<tr>
<td>Primary sludge</td>
<td>Alkaline modification and dry at 105 °C</td>
<td>4-10</td>
<td>PO₄²⁻</td>
<td>2.0</td>
<td>22</td>
<td>[176]</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>Pyrolysis at 550 °C for 1 h, then blending with dicyandiamide and pyrolysis at 800 °C for 2 h</td>
<td>2327</td>
<td>Cr²⁺</td>
<td>5.0</td>
<td>112</td>
<td>[177]</td>
</tr>
<tr>
<td>Sewage sludge</td>
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<td>792</td>
<td>Phenol</td>
<td>5.0</td>
<td>117</td>
<td>[178]</td>
</tr>
<tr>
<td>Metal hydroxides sludge</td>
<td>Pyrolysis at 400 °C for 2 h</td>
<td>14</td>
<td>Congo Red</td>
<td>6.0</td>
<td>40</td>
<td>[179]</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>Pyrolysis at 400 °C for 2 h</td>
<td>14</td>
<td>Congo Red</td>
<td>6.0</td>
<td>40</td>
<td>[179]</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>Fenton reagent pretreated initially, then pyrolysis at 600 °C for 2 h</td>
<td>321</td>
<td>2-Naphthol</td>
<td>5.0</td>
<td>112</td>
<td>[176]</td>
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<td>Sewage sludge mixed with reed straw</td>
<td>Immersed in 0.8 M KOH solution, dry, and pyrolysis at 600 °C for 2 h</td>
<td>471</td>
<td>1-diazo-2-naphthol-4-sulfonic acid</td>
<td>5.0</td>
<td>117</td>
<td>[179]</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>Pyrolysis at 700 °C for 2 h</td>
<td>202</td>
<td>Methylen blue</td>
<td>7.12</td>
<td>12</td>
<td>[180]</td>
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<tr>
<td>Anaerobic sludge</td>
<td>Immersed in 1 M ZnCl₂ solution, dry, and then pyrolysis at 800 °C for 2 h</td>
<td>77</td>
<td>Acid Orange II</td>
<td>−7.0</td>
<td>98</td>
<td>[181]</td>
</tr>
<tr>
<td>Anaerobic sludge</td>
<td>Mixed with 10% fish wastes and pyrolysis at 950 °C for 1 h</td>
<td>77</td>
<td>Carbamazepine</td>
<td>37</td>
<td>37</td>
<td>[182]</td>
</tr>
</tbody>
</table>
absorbent with a low cost for organic micropollutant removal [193] and may be implemented to the biosorption of organics. In addition to carbon separation enhancement, effluent polishing steps can be coupled with the carbon capture process. In this respect, algae cultivation under suitable conditions might be a promising effluent polishing process. Carbon and nutrients can be simultaneously removed and the produced algae are favorable ingredients for diesel production [194,195].

The separation and collection of organic carbon materials with similar components is necessary for a more efficient catalytic material fabrication. For instance, a previous study revealed that the activity of catalysts prepared using proteins as a precursor is superior to that of catalysts prepared using humic-like substances or carbohydrates [186]. Thus, by using specific organics as precursors, more precise functionalized material fabrication could be performed. The easier destabilization of proteins than carbohydrates under disturbed external conditions (i.e., temperature, ionic strength, pH, etc.) might enable engineers to separate these components.

5.2. Concerns related to micropollutant enrichment

Micropollutants, including pesticides, hormones, pharmaceuticals and personal care products, have been widely detected at equivalent concentrations varying by more than an order of magnitude across global WWTPs [196]. Although the fate and transformation of various micropollutants have been intensively investigated in conventional biological processes, their distribution and pathway in carbon separation and enrichment processes are rarely studied. Compared to both the biosorption and degradation in conventional carbon elimination systems, a higher accumulation level of these micropollutants in carbon-enriched sediments might be achieved. Therefore, the removal efficiency and effluent concentration level of micropollutants in carbon separation require further extensive studies. Moreover, the influence of adsorbed trace contaminants on the bioprocessing of enriched organics remains unclear. More importantly, the potential risk of the application of micropollutant-containing materials also requires careful evaluation. In summary, the concerns of the environmental toxicity and fate of emerging micropollutants in the whole carbon separation, bioprocessing, and application process should be strictly addressed in the future.

5.3. Separation, purification, and upgrading of the biorefined products

The separation and purification of biorefined products (e.g., either biofuels or value-added chemicals) from mixtures is a substantial challenge. During the anaerobic biogas production process, other undesirable substances, such as H₂S, NH₃, or CO₂, are often produced. However, the presence of such undesirable gases in biogas mixtures could greatly restrict the feasible application of the biogas. Both H₂S and NH₃ can be converted into corrosive, toxic and environmentally hazardous substances (i.e., SO₂ and NOₓ, respectively) during combustion. CO₂ is an inert gas and decreases the energetic content of the biogas. As stated above, H₂S might be efficiently removed at the first acid fermentation stage in a two-stage methanogenesis process. Moreover, sludge derived absorbents can be applied to upgrade the biogas purity [167,197]. In comparison to biofuel purification and upgrading processes, the extraction and recovery of biologically produced value-added chemicals is more complicated and challenging. Not only is the extraction procedure costly, but the acquired product purity is also not comparable to that of products acquired from the chemical industry. Accordingly, both the extraction procedure and the exploitation of the feasible application market are in urgent need of optimization.

5.4. Applications of membrane separation processes

Membrane separation processes have been proven to be efficient in increasing the efficiency of carbon separation, enrichment, and bioprocessing. However, the membrane fouling issue emerges as one of the greatest challenges to their practical applications. The in-depth elucidation of the membrane fouling mechanism remains necessary. Only a few previous studies have revealed the membrane fouling mechanism when directly applying it to municipal wastewater treatment. An analysis of the influences of the chemical composition, physical size, and content on membrane fouling is required in future studies. In addition, the importance of specific microbial cells in initial biocake development on the membrane surface should be studied. Recently, molecular spectroscopy methods have been identified as useful in-situ characterization tools to explain membrane fouling [198], and can be applied in membrane-coupled carbon separation and transformation processes.

5.5. Comprehensive evaluation of the carbon-to-energy line

Although bioenergy can be accessed via carbon capture and recovery, the economic efficiency and the overall integrated sustainability of the carbon-energy line remain unclear. Compared to the financial benefit of recovering carbon as a product, the total cost of this process needs to be considered. Furthermore, the on-site emission of CO₂ could be greatly reduced via carbon recovery. However, off-site emissions of greenhouse gases due to the consumption of energy for extraction and purification are inevitable. Thus, the net environmental footprint for the acquisition of carbon-based products from municipal wastewater is ambiguous. Life cycle assessment is a useful tool to quantify and evaluate the above effects. Future studies evaluating the costs and benefits of carbon-to-energy lines based on different carbon separation and recovery routes are required.

6. Conclusions

The capture and recovery of organic carbon from municipal wastewater is of great importance in energy reduction, resource recycling and sustainable development of urban cities. The understandings of the size fraction and chemical component characteristics remain insufficient. The HRAS process is the preferred carbon capture method to treat wastewater with a low content of organics. Chemical coagulants or membranes can be applied to assist carbon capture from wastewater with a high content of soluble components. At present, bioenergy production via anaerobic fermentation is the preferred carbon recovery method. At the global scale, a total bioenergy production potential of 51.06 billion kWh/year is expected. Moreover, the biosolid residues stemming from the bioprocessing stage can be converted into functionalized materials for a more efficient energy conversion, utilization and pollutant control. Hence, by integrating available processes, a plant-wide efficient wastewater-to-energy route including a carbon separation system, a bioprocessing platform, and a thermochemical conversion line could be developed. Future works on improving the system efficiency and economic effectiveness are required.

Declaration of competing interest

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

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References

[33] Eustat database. Electricity prices components for non-household consumers - annual data.
B.-C. Huang et al.


[127] Bank W. World Bank country and lending groups.


[129] World Bank country and lending groups.


