Treatment of recalcitrant wastewater and hydrogen production via microbial electrolysis cells

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Abstract: A large amount of real complex wastewaters are generated every year, which leads to a great environmental burden. Various treatment technologies were deployed to remove the contaminants in the wastewaters. However, these actual wastewaters have not been sufficiently treated due to their complex properties, high-concentration organics, incomplete utilization of hard-biodegradable substrates, the high energy input required, etc. Recently, microbial electrolysis cells (MECs), a great potential technology, has emerged for various wastewater treatment, because not only do they demonstrate satisfactory performance during wastewater treatment, but they also generate renewable H_2 as a clean energy carrier. Unlike previous reviews, this review introduced the characteristics of every complicated wastewater, and focused on analyzing and summarizing MEC development for wastewater treatment. The performances of MECs were systematically reviewed in terms of organics removal, H_2 production, Columbic efficiency, and energy efficiency. MEC performances for treating actual complex wastewaters and producing H_2 can be optimized through operation parameters, electrode materials, catalyst materials, etc. In addition, the challenges and opportunities including complexity of wastewaters, instability of H_2 production, robust microorganisms, effect of membrane on two-chamber MEC, and integration of MEC with other treatment processes were deeply discussed. Except for the technical feasibility, both environmental feasibility and economic feasibility also need to meet social requirements. This review can indeed provide a basis for high-efficiency treatment and practical commercial applications of recalcitrant wastewaters via MECs in the future.

Keywords: microbial electrolysis cells, complex wastewater, H_2 production, renewable energy, energy efficiency
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1 Introduction

A large amount of wastewater is discharged annually around the world, including municipal wastewater, landfill leachate, livestock wastewater, refinery wastewater, industrial wastewater, food-processing wastewater, etc.[1,2]. There is many biodegradable organics in these wastewaters, which are potential resources for chemicals and fuels production[3]. Conventional methods of wastewater treatment mainly include physical, chemical, and biological technologies (e.g. precipitation, membrane filtration, and fermentation treatment)[4]. However, these processes suffer from inevitable limitations, such as low wastewater treatment efficiencies, high-energy consumption, and enormous sludge output[5]. In recent years, microbial electrolysis cells (MEC) have been introduced for wastewater treatment. The principle of utilizing MECs for wastewater treatment and H_2 recovery is displayed in Figure 1. The organic matters are oxidized in MEC anode via exoelectrogens to release the protons and electrons, and H_2 is subsequently generated in MEC cathode with a little applied voltages (E_{ap}), compared with water electrolysis (theoretically calculated to be 0.11 V vs. 1.21 V). Moreover, the E_{ap} can be supplied by kinds of sustainable energy sources, such as solar panels, wind energy, and low-grade heat[6]. MEC was recognized as a green wastewater treatment technology because it can[7]: (i) utilize a wide source of substrates in the wastewaters; (ii) produce

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three times higher H_2 than that produced by traditional dark fermentation, which could meet the market of H_2 fuel with an annual growth rate of 6.3% and reduce the cost of wastewater treatment to some extent; (iii) reduce solid discharge and further reduce handling costs of the sludge; (iv) limit the release of harmful odors and mitigate climate change.

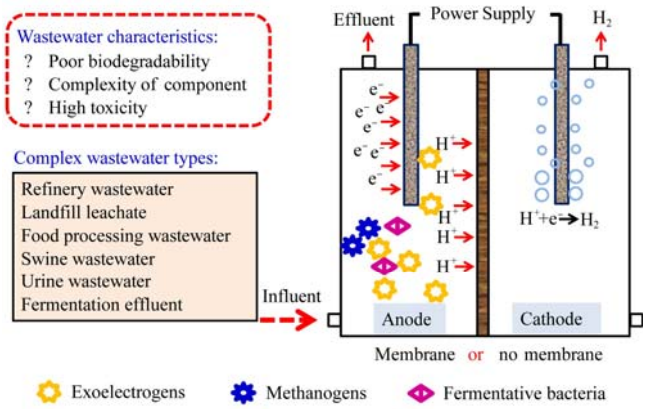

Figure 1 Overview and principle of the MECs for actual wastewater treatment and H_2 production

In the past decades, MEC research has made notable progress advancing system configurations and electrode materials, which has improved H_2 production efficiency greatly. MEC reactors have been enlarged from lab-scale to pilot-scale with a total volume increasing from 5 mL to 1000 L[8]. Two typical configurations have been reported, including single-chamber and dual-chamber with H-type[9], cube-type[10], rectangular-type[11], disc-type[12], and cylindrical-type[13,14]. In dual-chamber MECs, various kinds of membranes have been utilized as the separator, such as AEMs[15], CEMs[16], PEMs[17], CMMs[18], BPMs[18], and UMs[16]. The use of a dual-chamber MEC configuration could obtain purer H_2 in the cathode and also prevent H_2 from being consumed by methanogens in the anode, which are two major challenges faced by using single-chamber MECs. However, the use of membranes results in a pH gradient, and increases the total internal resistance. In contrast, single-chamber MECs are advantageous because of their simpler configuration and cheaper cost. However, the H_2 production capacity and the purity of H_2 are limited in single chamber MECs because of the presence of hydrogenotrophic methanogens, which produce CH_4 by combining H_2 and CO_2[19]. To restrain methanogen metabolism, some effective methods have been adopted, including periodically exposing the cathode chamber to air, lowering the pH[20], designing shorter retention times, pretreating the inoculum with heat, and adding inhibitors of methanogen growth (e.g. 2-bromoethanesulfonate)[21]. In addition, the electrode materials of MEC systems have been widely explored. The anode materials must have a good biocompatibility and the hydrogen evaluation catalytic performance is mostly emphasized by the cathode materials. The cathode materials tested in MECs mainly include carbon-based materials[22], graphite-based materials[23], stainless steel-based materials[24], titanium[25], titanium plate electrode[26], aluminum electrode[27], nickel foam[28], and gas diffusion electrode[29]. Some of electrodes have the characteristics of a low cost, good conductivity, lower over-potential, and stable performance[30], making these materials much more suitable for practical MEC application than platinum. So far, partial electrode materials such as stainless steel wire wool in a previous MEC study have been used in pilot-scale experiments[31], but their properties need to be further improved. Finally, for MEC performances, H_2 production rates have increased from 0.1 to 50 $m^3/m^3 \cdot d$, mainly through multiple optimizations of reactor configuration, electrode materials, catalyst materials, and experimental parameters[32]. In addition, some researches have been reported from other different perspectives, such as biocathode[33], recovery of nutrient[34], energy production[35,36], extracellular electron transfer[37]. However, many previous studies just focused on simple substrates such as defined compounds (sodium acetate, glucose, etc.) at the lab scale. Some previous review papers have reported the outstanding results of MECs[30,38], but few reviews have paid attention to the recalcitrant complex of actual wastewaters.

In this study, we specifically review the development of MECs for complex wastewater treatment and hydrogen production. MEC performances achieved for different types of complex wastewater treatment including TCOD removal rate, H_2 production rate, Coulombic efficiency (C_E), and energy efficiency were systematically summarized. The challenges and future perspectives from the points of view of integration of MECs with other wastewater treatment processes, the natural complexity of actual wastewaters, the instability of H_2 production, and the robustness of mixed culture were discussed in depth with regard to the improvement of wastewater treatment efficiency and H_2 production efficiency.

2 Recent advances on actual complex wastewater treatment via MECs

In this section, we firstly comprehensively summarized the individual characteristics of various actual complex wastewaters in order of biodegradability difficulty from different fields, such as the petrochemical industry, human activity, food processing, animal activity, and fermentation industry. Different real wastewaters mainly included post-hydrothermal liquefaction wastewater (PHWW), pyrolysis wastewater, de-oiled refinery wastewater, landfill leachate, animal manure wastewater, urine-rich wastewater, brewery wastewater, winery wastewater, dairy wastewater, potato wastewater, molasses wastewater, and fermentation effluent. Subsequently, current performances of MECs for different wastewater treatment were reviewed, which demonstrated significant differences with regard to the wastewater removal efficiency (TCOD or SCOD removal), H_2 production rate, H_2 content in the gases, H_2 yield, energy efficiency, C_E, and current density.

2.1 Refinery wastewater

Refinery wastewater mainly includes PHWW, hydrothermal treatment wastewater, pyrolysis wastewater, and de-oiled refinery wastewater. All of the preceding wastewaters originate from different types of refinery processes depending on the primary refinery reaction mechanisms and wastewater produced following physicochemical separation processes like oil-water separation methods[39]. Refinery wastewaters mainly consisted of organic acids, furans, and phenolic compounds, which were related to the types of wastewaters they originated from. The individual performances after these wastewaters were treated via MECs are showed in Table 1.

2.1.1 Post-hydrothermal liquefaction wastewater

Hydrothermal liquefaction (HTL) is a promising and attractive thermo-chemical conversion technology, which can directly transform wet biomass to valuable biocrude oil at high temperatures (200°C-370°C) and pressures (20-23 MPa)[44], which can be further refined into transportation fuels. However, PHWW is created as one of the main by-products during this process[45].

Table 1 Design properties and performances of the MECs fed with refinery wastewaters.

Actual wastewater types	MEC system	Operation mode	Anode material	Cathode material	MEC Volume /mL	Separator	Catalyst in cathode	BOD_5/ COD	TCOD removal	H_2 production Rate /L $H_2 \cdot L^{-1} \cdot d^{-1}$	C_E /%	η_{E+S} /%	Ref.
PHWW	Dual	Continuous	Carbon nanotubes	Carbon fiber felt	290	PEM	-	0.16	80.2%	0.0039	7.0	106.5 (η_E)	[40]
APBP	Dual	Continuous	Carbon felt	Carbon cloth	29.3	MEA	Pt	-	-	4.3	54	48	[41]
APBP	Dual	Batch	Carbon felt	Carbon cloth	29.3	MEA	Pt	-	48%	2.5	79	60	[41]
APBP (sawdust)	Dual	Batch	Carbon felt	Carbon	16	Nafion 115	Pt	-	60%	5.8	98	-	[42]
Switchgrass biorefinery stream	Dual	Continuous	Carbon felt	Carbon rod	32	Nafion 115	Pt	-	74.2%	2.92	62	-	[43]
Refinery wastewater	Single	Batch	Graphite plates	SS mesh	5	NO	NO	-	79%	-	-	-	[23]

Note: "TCOD" stands for total chemical oxygen demand; "C_E" stands for columbic efficiency; "η_{E+S}" stands for energy efficiency based on electricity and substrates; "MEA" stands for membrane electrode assembly; "PEM" stands for proton exchange membrane; "PHWW" stands for post-hydrothermal liquefaction wastewater; "η_E" stands for energy efficiency based on electricity; "SS" stands for stainless steel; "APBP" stands for aqueous phase from biomass pyrolysis.

PHWW, considered to be an emerging pollutant, has a high concentration of organics and contains hundreds of different types of chemical compounds. The characteristics of these components are entirely dependent on the characteristics of the HTL feedstock and its operational conditions. In general, a considerable organics (20%-50%) can be transformed into the PHWW[46]. In addition, about 60%-70% of the nitrogen from the feedstock is distributed into the PHWW[47]. Many toxic organic compounds are commonly detected in the PHWW produced from biomass feedstock. Specifically, phenols, toluene, benzene, aziridine, 2-methylarizidine, cyclopentenones, and organic acids are all present in the PHWW to some extent[48]. Thus, inappropriate disposal of the PHWW could impact the environment and threaten public health[45]. Now, studies on HTL have often focused on the biocrude oil production yield, its characteristics, and process nutrients recovery like nitrogen migration and transformation[49], etc.[50], while scant attention is attracted on PHWW utilization and treatment. In recent years, some researchers have treated PHWW using single anaerobic digestion technology[51-53], pretreatment by organic solvents before anaerobic digestion, and microalgae cultivation[44]. Although it could produce biogas like methane, partial organic matters in the PHWW were not degraded or had a deleterious effect on fermentative microbes and microalgae, which limited its further development.

Some researchers have demonstrated that the MEC technology itself can remove furaldehyde and 5-HMF without adopting extraction treatment[54,55]. Our previous MEC study has achieved the high-efficiency degradation and H_2 production of PHWW[40]. However, H_2 production rate and efficiency need to be improved in the future by optimizing MEC configurations and operational conditions, and adding cathode catalysts that are cost effective and lead to a high performance. In addition, compared with the above HTL technology, hydrothermal treatment is an important pretreatment method at lower reaction temperatures of 170°C-195°C, which could make biomass highly hydrolysable with cellulytic enzymes for bioethanol production[56]. For example, the cotton stalks can be used for producing bioethanol[57], but before putting it to practical use, a hydrothermal pretreatment process was needed to release the cellulose in the wheat straw. After hydrothermal pretreatment, most of the cellulose (96%) was transferred to the solid fiber fraction. However, during hydrothermal pretreatment, half of the hemicellulose stayed in the hydrolysate (wastewater), and it needed to be treated further[58]. When the hydrothermal treatment wastewater produced from wheat straw was treated via dual-chamber MECs, a TCOD removal efficiency of 61% and an average H_2 production rate of 0.61 L/L·d were obtained at 0.7 V in spite of a lower C_E[59].

2.1.2 Pyrolysis wastewater

Pyrolysis is one of the primary thermochemical technologies to produce renewable fuel from biomass. Generally, biomass for producing bio-oil is rich in water (~20%)[41], and this water would be converted into a pyrolysis by-product. The separation of the main products and by-products results in wastewater generation, which mainly consisted of acetic acid, 5-hydroxymethyl furfural (5-HMF), vanillic acid, 3-ethylphenol, 2-methoxyphenol, furfural[41], etc.

Fortunately, the wastewater could be successfully treated via MECs. For example, when MECs was fed with aqueous phase of switchgrass pyrolysis, both COD removal efficiency feasible and the H_2 production capacity were considerable. The batch operation achieved a higher C_E (79% vs. 54%) but lower H_2 production rate (2.5 L/L·d vs. 4.3 L/L·d) than those produced in continuous mode[41]. Almost all furan aldehydes (furfural), organic acids (acetic acid, propionic acid), sugar derivatives (levoglucosan), and phenolic molecules in the wastewater were degraded through the MECs. Additionally, when the anode liquid was recycled in a continuous MEC, TCOD removal efficiency and H_2 production rate were enhanced to a certain extent compared with one-pass operation[43]. The reason for this may be due to the acceleration of mass transfer, more complete degradation of pyrolysis wastewater, and the mitigation of kinetic limitations in the anode of the MEC under the circulation mode of the anolyte.

2.1.3 De-oiled refinery wastewater

The organic strength and biodegradability of refinery wastewater varies based on the primary oil separation processes. However, the COD values of most refinery wastewaters range from 400 to 1000 mg/L. In addition, this kind of wastewater with a suitable pH (7.2-8.9) and high conductivity (1.3-6.4 mS/cm) is beneficial for bioelectrochemical treatment, and higher current densities and lower MEC internal resistances would be obtained[23].

In particular, a previous study has explored the performance of MECs fed with different de-oiled refinery wastewaters from three different refinery facilities, which were from the final combination of all processing wastewaters. It was found that the single-chamber MECs in batch mode showed good performances with regard to TCOD removal (79%) and current density (2.1 A/m^2) at an E_{ap} of 0.7 V[23]. Then, five model compounds to represent this type of wastewater were chosen to deeply explore its treatment efficiency and degradation mechanism or pathways via the MECs, which included furans and phenolic compounds[54]. When a

mixture of these model compounds were used as the energy or substrate for the MEC bioanode for H_2 production in batch mode, the exoelectrogenesis pathway was inhibited and 91% of the current was reduced with an increase of mixture initial concentration from 0.8 to 8.0 g/L[60]. This inhibition was mainly due to furanic and phenolic compounds rather than their biotransformation products (catechol and phenol). Compared with batch mode, continuous operation mode may be a good way to decrease the effect of the inhibitors on exoelectrogens of the MEC bioanode. Moreover, a previous study has confirmed that the H_2 production rate (0.22 L/L·d) could be enhanced in MECs fed with the mixture in continuous mode at an E_{ap} of 1.0 V[61]. In addition, a recent study thoroughly illustrated the biotransformation fate of phenolic compounds and individual contribution extent to exoelectrogens in the MEC bioanode. Based on the individual fermentation extent of these compounds, syringic acid showed the higher fermentative transformation and electrochemical activity compared to other phenolic compounds[62].

2.2 Landfill leachate

Landfill leachate has a high pollution potential in soil, groundwater, and poses a large threat to human health[5]. Further, landfill leachate's composition is undefined and affected by many factors like the waste type, seasonal variations, landfill age, and soil conditions. The ratio of BOD_5 to COD for young landfill leachate was previously reported as being >0.30, intermediate landfill leachate was 0.10-0.30, and mature landfill leachate was <0.10[15]. In addition to biodegradable organics, landfill leachate also has inorganics, VFAs and metal ions[63]. Most of the previous studies about bio-electrochemical treatment of landfill leachate focused on the microbial fuel cells (MFCs)[64]. Only three studies treated the landfill leachate via MECs (Table 2), and a proper pretreatment of landfill leachate before MEC was necessary and helpful.

Landfill leachate after fermentation pre-treatment had better MEC performances than raw landfill leachate (Current density: 23 A/m^3 vs. 2.5 A/m^3; C_E: 68% vs. 56%; biochemical oxygen demand based on 5 days (BOD_5) removal efficiency: 83% vs. 5.6%)[65]. Overall, the pre-fermentation of landfill leachate had two advantages for further MEC treatment: 1) The MEC could obtain simpler organic matter from the fermentation effluent of landfill leachate like succinate, acetate, etc. which were oxidized more directly and easily by the anode-respiring bacteria of MECs; 2) Pre-fermentation of landfill leachate may also remove compounds that are partially toxic to the anode respiring bacteria, like phenolic compounds.

Table 2 Design properties and performances of the MECs fed with landfill leachate, animal manure wastewater, and urine wastewater

Actual wastewater types	MEC system	Operation mode	Anode material	Cathode material	MEC Volume /mL	Separator	Catalyst in cathode	BOD_5/ COD	TCOD removal	H_2 production rate /L $H_2 \cdot L^{-1} \cdot d^{-1}$	C_E /%	η_{E+S} /%	Ref.
Fenton-treated landfill leachate	Dual	Continuous	Graphite rod	Graphite rod	640	AEM	NO	0.31	52% (BOD_5)	-	29	-	[15]
Raw landfill leachate	Dual	Continuous	Graphite rod	Graphite rod	640	AEM	NO	0.31	3% (BOD_5)	-	1.8	-	[15]
Simulated landfill leachate	Dual	Batch	Carbon felt	Stainless steel plate	1000	CEM	NO	-	62-65%	0.04	12-41	-	[67]
Landfill leachate via pre-treatment	Dual	Batch	Graphite fibers; SS rod	Graphite rods	320	AEM	-	0.32	83% (BOD_5)	-	68	-	[65]
Piggery wastewater	Dual	Batch	Graphite felt; Carbon rod	Titanium plate electrode	720	Nafion 424 Membrane	Pt	-	48%	0.061	-	124	[26]
Swine wastewater	Single	Batch	Graphite fiber brush	Carbon cloth	28	NO	Pt	-	72%	1	43	190 (η_E)	[68]
Dairy manure wastewater	Single	Batch	Graphite fiber brush	Carbon cloth	28	NO	Pt	-	-	-	-	-	[69]
Urine	Dual	Batch	Graphite felt	Titanium	1300	CEM	Pt	-	46%	48.6	97	-	[25]

Note: "TCOD" stands for total chemical oxygen demand; "BOD_5" stands for biochemical oxygen demand based on 5 days; "C_E" stands for columbic efficiency; "η_{E+S}" stands for energy efficiency based on electricity and substrates; "η_E" stands for energy efficiency based on electricity; "CEM" is cation exchange membrane; "AEM" is anion exchange membrane; "SS" stands for stainless steel.

Besides fermentation pretreatment, Fenton pretreatment is also an advanced oxidation processes commonly employed for pretreating landfill leachate. Fenton pretreatment of landfill leachate led to a much better MEC performance than that of the raw landfill leachate, leading to an improvement of the BOD_5 removal efficiency from 3% to 52%, and C_E from 1.8% to 29%[15]. However, the current density of the MECs fed with the landfill leachate after different pretreatments were still far below the target current density (~140 A/m^3)[15,66].

2.3 Animal manure wastewater and urine-rich wastewater

Due to the increasing demand for meat-rich food, large numbers of pigs are being bred in swine farms, and at the same time a considerable amount of swine wastewater is produced every year[68]. If swine wastewater was directly discharged into the environment, surface water and well would be polluted[70]. Besides, the noxious odors due to the ammonia may be released into the air. Therefore, some feasible treatment methods need to be explored in order to avoid environmental pollution from swine wastewater. In such wastewater, the ratio of BOD_5 to COD has been reported to be ~0.60[71]. This kind of wastewater has a total solid content of 1%-3% and a TCOD of 12000-17000 mg/L[71], which consisted of organic matters with high concentrations, phosphorus, salts (e.g. nitrates), microbes, and pharmaceutically active compounds[72].

Kiely et al. firstly tried to treat dairy manure wastewater via MECs, but this experiment failed to produce gases and a current, which probably due to the low content of *Geobacter* species on MECs anode biofilm[69]. However, different from dairy manure wastewater, swine wastewater could be treated effectively (highest TCOD removal: 75%) and produced the highest H_2 production rate (1.0 L/L·d) via MECs (Table 2). Further, the highest H_2 production efficiency (based on the electrical energy) was 91% in a batch MEC fed with full-strength swine wastewater[68].

Similar to swine wastewater, urine wastewater is also rich in

nitrogen in the form of urea[25,73]. In batch mode, the urine after five times dilution could be used to produce H_2 via a dual-chamber MECs, and high H_2 production (48.6 L/L·d) and TCOD removal (171.0 g COD/m^2/d) were obtained successfully[25]. In addition, the urine can be used as the source of ammonia recovery.

2.4 Food processing wastewater

In modern society, food production is very important and leads to a variety of different products, including milk, sugars, starches, etc. However, different kinds of wastewaters appeared during different food production processes. In the US, approximately 1.4 billion liters of food processing wastewater can be produced annually[74]. Fortunately, most of them are non-toxic because its constituents are mainly simple sugars, starch, cellulose, hemicelluloses, lipids, proteins, organic acids, etc. The specific constituents of the wastewater depend on the raw materials, terminal products, and processing technologies. This type of wastewater has the characteristic of having a high BOD, so it can be readily biodegradable. Based on the above description, these organics-rich food processing wastewaters theoretically may be used as the substrates of MECs for H_2 production (Table 3). Furthermore, different food processing wastewaters from food processing plants offer different individual H_2 production values, which are demonstrated as follows.

Table 3 Design properties and performances of the MECs fed with food processing wastewater

Actual wastewater types	MEC system	Operation mode	Anode material	Cathode material	MEC Volume /mL	Separator	Catalyst in cathode	BOD_5/ COD	TCOD removal	H_2 production Rate /L H_2·L^{-1}·d^{-1}	C_E /%	η_{E+S} /%	Ref.
Potato wastewater	Single	Batch	Graphite fiber brush	Carbon cloth	28	NO	Pt	-	79%	0.74	80	-	[69]
Food processing wastewater	Single	Batch	Graphite fiber brushes	Carbon cloth	336	NO	SS; MoS_2; Pt	0.25-0.62	49%; 56%; 67%	0.103; 0.146; 0.312	29; 26; 35	-	[75]
Winery wastewater	Single	Continuous/ Batch	Graphite fiber brush	SS mesh/ Carbon cloth	1000000/28	NO	-/ Pt	-	62%/47%	0.07/0.17	-/50	-/ 78 (η_E)	[76]
Brewery wastewater	Single	Batch	Carbon brush	Nickel foam	25	NO	Pt	-	87-94%	2.12	66	170 (η_E)	[28]
Cheese whey from a cheese facility	Single	Continuous	Carbon felt	Gas diffusion electrode	100	NO	Ni	0.4-0.8	>80%	~0.8	-	-	[77]
Molasses wastewater	Single	Batch	Graphite-fiber brush	Carbon cloth	25	NO	Pt	-	-	1.82-2.27	93-95	220-269 (η_E)	[78]

Note: "TCOD" is total chemical oxygen demand; "SCOD" stands for soluble chemical oxygen demand; "C_E" stands for columbic efficiency; "η_{E+S}" stands for energy efficiency based on electricity and substrates; "η_E" stands for energy efficiency based on electricity; "SS" stands for stainless steel.

2.4.1 Brewery wastewater and winery wastewater

Brewery wastewater mainly consists of sugars, proteins, organic acids, amino acids, alcohols, and vitamins. The ratio of BOD_5 to TCOD is 0.57-0.73 (the BOD_5 of 1285-1540 mg/L; the TCOD of 2106-2250 mg/L). Further, this type of wastewater has the following characteristics: its pH and conductivity are 6.7 and 1.8 mS/cm, respectively[79].

When brewery wastewater was previously used as the substrate of MECs for H_2 production while using the cathode catalyst of NiFe layered double hydroxide, a high-efficiency H_2 production rate (2.01-2.12 L/L·d) could be achieved[28]. In addition, it was also designed to produce methane in continuous, tubular up-flow membrane-free MECs with the cathode of Ni catalysis at an E_{ap} of 0.8 V. In this setup, better performances were obtained with a TCOD removal efficiency of 85%[79].

Winery wastewater has similar properties to that of brewery wastewater. When it was chosen as the feed of MECs, H_2 production rate and η_E were 0.17 L/L·d and 78% (based on electrical energy) were obtained at an E_{ap} of 0.9 V[80]. Here, compared with MFC treatment of winery wastewater, although the TCOD removal efficiency in the MECs was a little lower than it was in the MFCs (47% vs. 65%), C_E was obviously higher than it in MFCs (50% vs. 18%)[80]. For scale-up from laboratory tests, a pilot-scale single-chamber MEC of 1000 L fed with real winery wastewater under continuous mode showed a comparable SCOD removal (62%), but the H_2 production rate and the H_2 content in the product gases were only 0.07 L/L·d and 14%, respectively[76]. Therefore, the performances of pilot-scale MEC reactors need to be improved further via optimizing the critical factors like the experimental temperature, initial pH, E_{ap}, etc.

2.4.2 Dairy wastewater

Milk residuals, milk fats and whey particles are all present in dairy wastewater. Further, it was reported that dairy wastewater has a pH of 6.2 and a high TCOD concentration (5-50 g/L)[81]. Before investigating real milk wastewater from the dairy industry, firstly synthetic dairy wastewater by commercial powder milk was chosen as the substrate of single-chamber MEC for H_2 production without adding any methanogenesis inhibitors. After more than three-months of long-term operation, stable H_2 production, C_E, and TCOD removal were obtained at 0.8 V[82]. As for the treatment of real dairy wastewater, up to now, although only photo-biological treatment processes have been conducted for this type of feedstock[81], it could be predicted that if it was used as the substrate for MECs, ideal performances could be achieved.

2.4.3 Potato wastewater

Potato wastewater was reported to have a SCOD of 0.69 g/L[69]. When synthetic potato wastewater simulated with starch (analytical grade reactant) was used as the substrates of a MEC, the TCOD removal was up to 70%. However, H_2 was not detected, even if the retention time of H_2 was shortened by continuous nitrogen sparging[82]. Interestingly, when 4-times diluted potato wastewater without the addition of a buffer was used as the substrate for single-chamber cubic MECs, better performances were obtained with a TCOD removal of 79% and a C_E of 80%[69].

2.4.4 Molasses wastewater

Molasses wastewater is a by-product during sugar beet process, which has a high-concentration organics (65000-130000 mg/L) and mineral salts[83]. Furthermore, this nutrient-rich wastewater contains mainly sugar, protein, and vitamins (70% of solid substance)[78]. This type of wastewater can be used for producing

ethanol and amino acids[83], but actually its quantity is too large to be treated. Therefore, its potential application should be explored further. When this molasses wastewater was treated via MECs with the inclusion of a Pt catalyst in the cathode, the C_E was 93% at an E_{ap} of 0.6 V at 25°C[78]. In addition, the H_2 content in the gases could be enhanced from 34.6% to 48.2% through lowering the temperature from 25°C to 9°C, due to the fact that methane production at lower temperatures was successfully inhibited[78].

Table 4 Design properties and performances of the MECs fed with fermentation effluent

Actual wastewater types	MEC system	Operation mode	Anode material	Cathode material	MEC Volume /mL	Separator	Catalyst in cathode	BOD_5/ COD	TCOD removal	H_2 production rate /L $H_2 \cdot L^{-1} \cdot d^{-1}$	C_E /%	η_{E+S} /%	Ref.
Lignocellulose effluent	Single	Continuous	Graphite fiber brush	Carbon cloth	28	NO	Pt/C	-	65%	1	110	61	[89]
Fermentation effluent	Single	Continuous	Carbon fiber brush	Carbon cloth	72	NO	Pt	-	64%	0.48	58	23	[90]
Fermentation effluent	Single	Batch	Graphite brush	Carbon cloth	26	NO	Pt	-	~38.5%	1.41	87	70	[91]
Brewery wastewater fermentation effluent	Single	Batch	Carbon brush	Nickel foam	25	NO	NiFe LDH	-	87-94%	2.11	82	190 (η_E)	[28]
Effluent from an ABR	Single	Batch	Carbon cloth	SS mesh	85	NO	Ni	-	99%	1.31	-	139 (η_E)	[92]
Effluent from WWTP	Dual	Batch	Graphite plates	SS plates	60000	PEM	NO	-	67%	-	11	-	[17]

Note: "TCOD" stands for total chemical oxygen demand; "C_E" stands for columbic efficiency; "η_{E+S}" stands for energy efficiency based on electricity and substrates; "η_E" stands for energy efficiency based on electricity; "PEM" stands for proton exchange membrane; "LDH" stands for layered double hydroxide; "SS" stands for stainless steel; "ABR" stands for anaerobic baffled reactor; "WWTP" is wastewater treatment plant.

2.5 Fermentation effluent

There are a few methods to produce H_2 from lignocellulosic biomass, such as bio-photolysis, photo-fermentation, and dark-fermentation (DF)[84]. Among these routes, DF showed the highest H_2 yield in practice[85]. However, compared with theoretical values, the H_2 yield was still very low because the fermentation end-products like acetic, formic, succinic, lactic acids, etc. cannot be transformed to H_2 via fermentative microorganisms further[86]. Thus, these residual matters remained in the fermentation effluent. The original real fermentation effluent from the cornstalk contained total VFAs (8021.2 mg/L), COD value (11986.4 mg COD/L), HAc (4121.5 mg/L), HBu (3208.1 mg/L), HPr (88.8 mg/L), Ethanol (602.8 mg/L), etc.[87].

However, these organic matters in the fermentation effluent have proven to be ideal substrates for MECs (Table 4). Here, it was confirmed that the acetate and the butyrate were demonstrated to be easily degraded by exoelectrogens in MECs, and the propionate was recalcitrant to degradation[29]. The accumulation of acetic acid during the fermentation stage can improve the H_2 production rate and TCOD removal efficiency for the MECs. Note that the component of fermentation pretreatment wastewater could have important effects on MEC performances. The MEC treatment for fermentation pretreatment wastewater (gradient utilization of the substrates) had several benefits: it improved the effluent quality and enhanced H_2 production. In theory, the integration of fermentation and MEC can increase the H_2 yield to 12 mol H_2/mol glucose[88].

In practice, when dark fermentation effluent was used as the substrates of MECs, a H_2 production and C_E were obtained (1 L/L·d and 110%) at an E_{ap} of 0.5 V[89]. In fact, overall H_2 production via MECs fed with cellulose fermentation effluent increased by 41% in comparison to dark fermentation alone[90]. When diluted fermentation liquid was used as the substrates, the SCOD removal was higher than that of the original fermentation liquid (60% vs. 50%) in the MEC[93]. In addition, fermentation effluent pH has an important effect on MEC performances. One study confirmed that MECs fed with raw ethanol-type fermentation effluent (initial pH 4.5-4.6) had a lower H_2 production rate (0.04 L/L·d) compared to that fed with the buffered ethanol-type of fermentation effluent (1.41 L/L·d) at an E_{ap} of 0.6 V[91]. If the fermentation stage was optimized in an anaerobic baffled reactor before the MEC process, a higher H_2 production rate (1.31 L/L·d) and a higher TCOD removal efficiency (99.0%) could be obtained in a single-chamber MEC due to the acetic acid-rich fermentation effluent[92]. Thus, dark fermentation can be considered as a pretreatment path for biomass into H_2 via MECs.

3 Challenges and Future Perspectives

MEC technology has been demonstrated to be more preferable than that of bioelectricity generation (the MFC) for treating actual complex wastewaters[94]. However, this wastewater treatment technology is still in the infancy stages of development. As an emerging and versatile technology, MECs integrate microbial interaction processes and electrochemical processes, so the limiting factors of the system are complex and hard to identify[94]. The important challenges and future perspectives are addressed towards the practical application of MEC technology.

3.1 Complexity of actual wastewater

The treatment of actual wastewater via MECs is restricted by the water quality features such as a lower conductivity, unsuited alkalinity to catalysts, the toxicity of some compounds to anodic microorganisms, and the variation of the organic loading rate[88]. The characteristics of real complex wastewaters have great effects on the performances of MECs[75]. In particular, lower conductivity and unsuitable alkalinity to catalysts can lead to considerable Ohmic losses and high pH gradients, respectively. MECs undergo an electrochemical process and a microbial catalytic process, so the microorganism on the anode requires ambient conditions to maintain bioactivity. Generally speaking, when real wastewaters were fed to MECs, electrochemical performances were reduced (e.g. C_E) compared with simple, easily biodegradable, or definite substrates. The reason for this may be due to the presence of competitive consumption of the substrates by the methanogenesis pathway and not being able to completely degrade the complex organic matters in the real wastewater via electrochemically active microorganisms in the anode[95]. Thus, one major challenge is improving the C_E and H_2 production rate in future practical applications. Now, many studies focused on actual wastewater treatment via MECs are still only conducted at the bench scale[96]. Now, there are few full-scale treatment plants

for recalcitrant wastewaters, some challenges still need to be overcome even if in small-scale or lab-scale studies like the complexity of actual wastewaters, inhibition of recalcitrant organics in the wastewaters for electro-active bacteria, instability of H_2 production, cultivation and modification of robust microorganisms, etc. However, MEC treatment of complex wastewaters had great potential in practical application due to its many advantages as described previously.

To better solve this problem, several approaches could be attempted, such as comprehensively investigating the complexity of different real wastewaters via the advanced equipment, optimizing MEC system configurations, acclimating the higher electro-active bacteria, studying the mechanisms and kinetics of electron transfer in depth, choosing cathode catalysts of high-efficiency to decrease the over-potential of electrochemical reactions, and exploring electrode materials of high performances[97]. In addition, it is worthwhile to explore in depth the degradation pathways of substances like heterocyclic compounds from actual wastewaters, which mainly depend on the electron acceptors and electron donors[98]. Besides the aforementioned approaches, it is also essential to investigate the degradation of the final products, because sometimes the final products were more toxic to the anode bacteria than the parent compounds themselves.

3.2 Instability of H_2 production

H_2 production performance is a comprehensive result of different E_{ap}, pH, temperature, hydraulic retention times (HRTs), substrate types, electrode materials, substrate concentration, anode inoculum, cathode catalyst, the start-up mode, the running mode, etc. In single-chamber MECs, the instability of H_2 production is probably due to the competitive consumption of the substrates by methanogens in the MEC anode. To restrain methanogen metabolism, some methods could be adopted like exposing the cathode chamber to air periodically, lowering the pH[20], designing shorter retention times, heat pretreatment of the inoculum, and adding inhibitors to methanogens growth (e.g. 2-bromoethanesulfonate)[21]. However, methanogen growth cannot be entirely inhibited. In dual-chamber MECs, except for CH_4 diffusion though membranes, another key reason for this may be mass transfer resistance, including proton transfer resistance though the membrane and electron transfer resistance though exoelectrogenic bacteria. In addition, the instability of the operation process leads to unstable H_2 production. Thus, the enhancement of H_2 purity is still a great challenge for future MEC practical applications, which needs to be further explored though breakthrough optimization in reactor configurations, operation parameters, and the electrode materials.

3.3 Robust microorganisms

It is known that electron transfer activity of exoelectrogenic bacteria is very important for H_2 production in the MEC. Many previous cases used the mixed bacteria as the initial inoculum of the MEC from the previous MFC/MEC reactor, fresh municipal/domestic wastewater, or activated sludge. The cultivation or enrichment of exoelectrogenic bacteria from the mixture bacteria needs a long time ranging from one month to several months. In MEC, microbial community was consisted of fermentative bacteria (like *Paludibacter*, *Enterococcaceae*, *Petrimonas*), exoelectrogenic bacteria exoelectrogens (like *Geobacter*, *Geoalkalibacter*), and a little other bacteria (like *Acetobacterium*)[99], when the substrates were supplied, firstly fermentative bacteria degraded various organics (like sugar, carbohydrates, protein) into organic acids (like acetate, butyrate, and propionate), then exoelectrogenic bacteria produced electricity by these organic acids[100]. However, there were substrate and electron competition between fermentative bacteria and exoelectrogens. If pure bacteria like *S. oneidensis MR-1* was used for the inoculum, the total H_2 output and H_2 purity would be improved greatly, because pure bacteria would prevent the consumption of H_2 and methane formation from other bacteria like fermentative bacteria, methanogens. Further, pure bacteria are expensive and make the cost higher than that when using the mixed bacteria in the actual application. In addition, considering the inhibition of substances in actual high-strength wastewaters, the improvement of the microbial consortia tolerance against these substances may be necessary and important. Thus, the identification of new microbes or genetic modification of microbes is a promising aspect for actual wastewater treatment via METs[101].

3.4 Effect of membrane on two-chamber MEC

In two-chamber MEC, the function of membrane was mainly in order to improve hydrogen purity, alleviate hydrogen consumption by anodic microbes, and finally increase energy recovery of substrates[102]. Up to now, various membranes were used in MECs. However, the substantial internal resistance from membranes during proton transfer cannot be ignored. And their selectivity for protons were very limited, it has still no membranes only allowed protons to pass through. In addition, membrane fouling was a serious problem for long-term stable operation of MEC, which had great effect on matter transfer and desired product generation (like hydrogen). Thus membranes need to be modified and cleaned, but the cost was high[103]. In the future, for decreasing the membrane fouling, some other low-cost methods could be tried such as reactor structure optimization, proper choice of important parameters, new membrane development, etc.

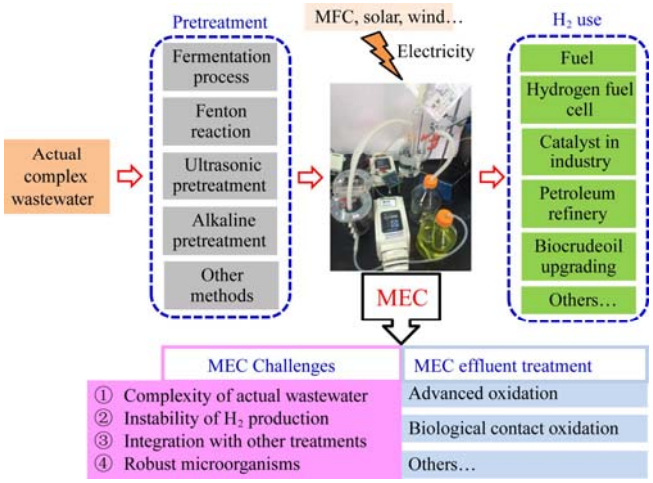

Figure 2 Integration of MEC with other treatment processes

3.5 Integration of MEC with other treatment processes

The combination of MECs and other technologies has been suggested to enhance the treatment of wastewaters (Figure 2). For instance, a fermentation- MEC integrated process has been previously proposed, since the fermentation process is beneficial for high-strength wastewater with complex organic compounds, while the fermentation effluent containing VFAs was regarded as the ideal substrate of MECs for further H_2 recovery. Furthermore, some typical physicochemical technologies such as ultrasonic pretreatment, alkaline pretreatment, and Fenton reactions, could be adapted as pretreatment methods before MECs for toxic compound removal to relieve the inhibition of anode respiring bacteria. In addition, the MFC-MEC integrated system was invented to reduce

the cost of power supply for MECs by timely use of the renewable electricity generated from MFCs. Recently, the usage of MFC-MEC studies have been more focused on the treatment and selective metal recovery from heavy metal contaminated wastewater, taking advantage of the difference of the redox potentials at the cathodes.

Moreover, the combination of MECs with other treatment processes has also been suggested for timely use of the MEC products (like H_2O_2, H_2) as the reagents of the following process, which could cut down the storage cost and transportation cost of MEC products. For example, The MEC-Fenton integrated process has been proposed to address this need, by timely use of the H_2O_2 production from MECs to react with Fenton's reagent to form hydroxyradical for refractory pollutant removal. Another example is the MEC-HTL integrated process, which has been recently proposed, in which HTL is used for bio-crude oil production from wet organic waste, while the H_2 recovered during the treatment of PHWW via MECs, could be used for onsite bio-crude oil upgrading. Overall, the combination of several treatment processes has great potential for thorough treatment of actual recalcitrant wastewaters.

4 Conclusions

This review introduced the characteristics of various complicated wastewater, and focused on analyzing and summarizing MEC development for wastewater treatment. The performances of MECs mainly depend on the ingredients of individual wastewaters, especially the content of recalcitrant compounds in the wastewaters. Up to now, it has been proven that MEC technology efficiently treats PHWW, pyrolysis wastewater, de-oiled refinery wastewater, landfill leachate, animal manure wastewater, brewery wastewater, winery wastewater, dairy wastewater, potato wastewater, molasses wastewater, etc. MEC performances for treating actual complex wastewaters and producing H_2 can be optimized through operation parameters, electrode materials, catalyst materials, etc. However, some niches and challenges such as the complexity of actual wastewaters, inhibition of recalcitrant organics in the wastewaters for electro-active bacteria, instability of H_2 production, cultivation and modification of robust microorganisms, etc., have to be overcome one by one. Except for the technical feasibility, both environmental feasibility and economic feasibility also need to meet social requirements, which could be met by controlling the investment cost and increasing the H_2 production rate. Until all difficulties are solved one by one, practical commercial applications cannot be realized successfully in the future.

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Nomenclature

MEC	Microbial Electrolysis Cell
MFC	Microbial Fuel Cell
AD	Anaerobic Digestion
COD	Chemical Oxygen Demand
TCOD	Total Chemical Oxygen Demand
TOC	Total Organic Carbon
VFAs	Volatile Fatty Acids
TS	Total Solid
VS	Volatile Solid
C_E	Coulombic Efficiency
η_E	Energy Efficiency (Electricity)
PHWW	Post-hydrothermal Liquefaction Wastewater
AEM	Anion Exchange Membrane
CEM	Cation Exchange Membrane
PEM	Proton Exchange Membrane
BPM	Bipolar Membrane
CMM	Charged Mosaic Membrane
UM HTL	Ultrafiltration Membrane Hydrothermal Liquefaction
SCOD	Solluted Chemical Oxygen Demand
BOD	Biochemical Oxygen Demand
5-HMF	5-Hydroxymethyl Furfural
HRTs	Hydraulic Retention Times
E_{ap}	Applied Voltage
PBS	Phosphate Buffer Saline

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