

S. Brunschweiler, L. Hörner, T. Hofmann and K. Glas

Microbial fuel cells for brewery wastewater treatment – efficiency requirements and treatment performance

Development of scenario-based benchmarks involving conventional wastewater treatment plants

Water management and waste disposal are significant cost factors in the brewing industry, thus prompting breweries to install in-house wastewater treatment plants to reduce discharge costs. Conventional biological wastewater treatment consists of anaerobic processes or aerobic processes or a combination of anaerobic and aerobic processes to pre-treat the wastewater prior to direct or indirect discharge. Microbial fuel cells (MFCs), which can simultaneously degrade organic compounds in wastewater and generate electricity, have the potential to be used in combination with current wastewater treatment technologies. The energy efficiency and wastewater treatment performance required for MFCs to be effective in the treatment of brewery wastewater has not yet been quantified. To evaluate the application possibilities of MFCs in real-life situations, wastewater treatment plants in two breweries were examined for direct and indirect discharge. The plants were divided into sections and sub-sections to distinguish different treatment stages. Based on the data obtained from this examination, benchmarks for MFCs were determined for different application scenarios and feasible energy recoveries were calculated. From an energy perspective, the energy-intensive aerobic process (scenario 1A and 1B) is the most realistic to replace because of its negative energy balance, thus making MFCs an attractive option if self-sufficient treatment is provided. An overall energy efficiency of at least 18 % for direct discharge (scenario 2B) or 23 % for indirect discharge (scenario 2A) is required for MFCs to achieve an energy gain that is comparable to the energy gain in the anaerobic stage. Based on an energy perspective, a realistically achievable efficiency of 4.5 % (scenario 4B) is sufficient to replace the complete biological wastewater treatment in the case of direct discharge with several stacked MFCs. In terms of the required treatment performance, MFCs could achieve the chemical oxygen demand removal benchmarks for all the scenarios evaluated in this study, even if a longer hydraulic retention time (HRT) is currently required. Due to the compactness, stackability and direct power generation ability of MFCs, they could be very attractive for small breweries as a replacement for the aerobic stage or as a pre-treatment before aerobic treatment to reduce energy costs.

Descriptors: microbial fuel cell, brewery wastewater treatment, energy efficiency

1 Introduction

In the brewing industry, large quantities of water are consumed during the brewing process; the water is used not only as a product in the brewing process but also for cleaning processes [12]. The specific wastewater volume is in the range of 0.25–0.45 m³/hl

of beer produced [12]. Therefore, water management and waste disposal are significant cost factors in the brewing industry [31].

The wastewater in breweries is often biologically pre-treated with anaerobic treatment or aerobic treatment or a combination of both the treatments to comply with the limits for direct or indirect discharge of the wastewater and consequently save costs [33]. Coupling of different treatment processes as two- or three-stage processes can enhance economic and energy efficiency [31]. For example, a positive energy balance can be achieved with the combination of anaerobic (energy generation in the form of biogas) and aerobic (energy intensive) treatment of brewery wastewater [9].

<https://doi.org/10.23763/BrSc21-02brunschweiler>

Authors

Sarah Brunschweiler, Laura Hörner, Thomas Hofmann, Karl Glas, Chair of Food Chemistry and Molecular Sensory Science, Technical University of Munich, Freising, Germany; corresponding author: sarah.brunschweiler@tum.de

In addition, microbial fuel cells (MFCs), which have great potential for treating brewery wastewater, can be combined with conventional treatment processes [31]. In MFCs, organic compounds in

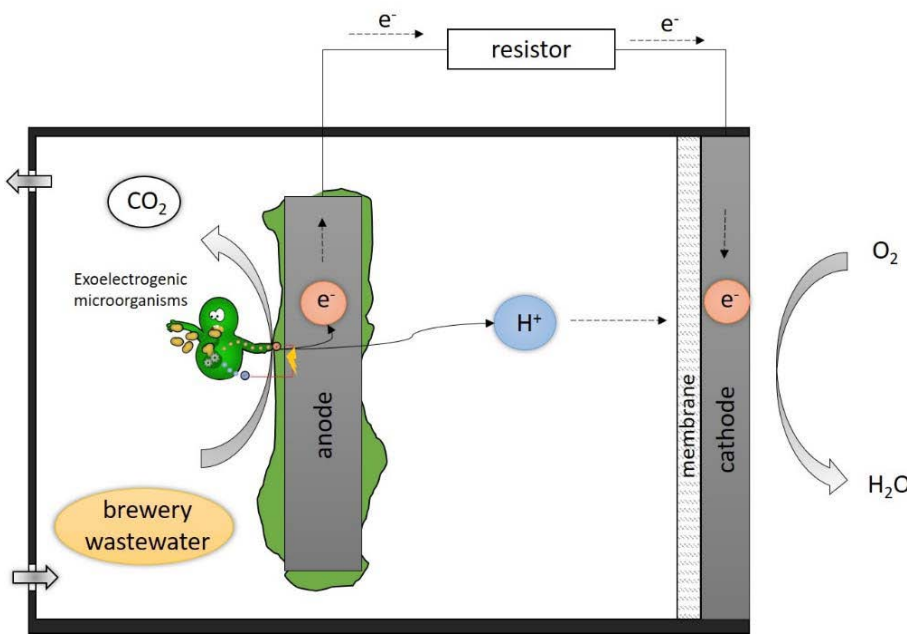


Fig. 1 Working principle of microbial fuel cells treating brewery wastewater (adapted from [3]).

wastewater can be degraded by exoelectrogenic microorganisms in the anode chamber with simultaneous generation of electrons, which are transferred together with the protons to the cathode, where the reduction of oxygen can take place (Fig. 1).

MFCs have several operational and functional advantages over currently used technologies for energy production from organic compounds. Some of these advantages are (1) the direct conversion of substrate energy into electricity, (2) operation performed at ambient temperature, (3) no gas treatment requirements and (4) no aeration requirements [31].

Presently, there are proposals to integrate MFCs into the conventional wastewater treatment systems of municipal wastewater treatment plants [15]. Moreover, possibilities have been identified for using MFCs in combination with conventional treatment systems [3, 24, 26]. However, presently there are no detailed energy- and wastewater-related benchmarks that can be used to quantify the requirements for industrial wastewater treatment with MFCs, especially the treatment of brewery wastewater.

Therefore, this paper aims to answer the following questions: what are the efficiency requirements for MFCs to compete with state-of-the-art technology for direct and indirect dischargers for brewery wastewater treatment? What treatment performance must be achieved by MFCs to be suitable for brewery wastewater treatment? Benchmarks for different scenarios were determined based on the detailed analysis of the wastewater treatment plants of two breweries: one with direct discharge and the other with indirect discharge. For this purpose, the processes of the wastewater treatment plants were divided into sections and sub-sections to allocate the energy consumption, energy gain and chemical oxygen demand (COD) degradation efficiency to individual treatment steps. All energy consumers are taken into account, and the possible electrical energy gain in the form of biogas is calculated. In this way, the potential energy recovery

that is achievable using MFCs at different COD degradation rates can be calculated. Thus, the various possible applications of MFCs in the treatment process of brewery wastewater can be evaluated.

2 Data basis and evaluation methods

The operating data of the wastewater treatment plant of two breweries were analysed to calculate specific key parameters. The investigation period for both the cases was one year with 365 days (2017), which allowed an overview of all product-specific and seasonal fluctuations to be taken into account. Both breweries documented the total energy demand for the entire wastewater treatment process, including consumption by auxiliary consumers (e.g. light and wastewater analytics), which was measured and recorded on a daily basis. Additionally, to allocate the total

energy requirement to individual energy consumers, the operating hours of the specific consumers (e.g. pumps and stirrers) were documented for four months in 2018 at both breweries.

Brewery 1 (B1) discharges the wastewater indirectly to a municipal wastewater treatment plant via a municipal sewer system. For breweries in Germany (Brewery 2, B2), the following specific limit values must be complied with for direct discharge, which are defined in the Waste Water Ordinance in Germany: 25 mg/L Biological oxygen demand (BOD_5); 110 mg/L COD; 10 mg/L NH_4-N , 2 mg/L P_{ges} ; 18 mg/L N_{ges} [27].

2.1 Classification of the wastewater treatment plants of the two breweries

The wastewater treatment plants were divided into three sections for balancing the energetic and treatment efficiencies of the different treatment steps. A detailed delimitation of plant components within the overall plant is possible, thus allowing for energy comparisons between various components.

The wastewater treatment plants were classified into the following sections:

- I wastewater treatment plant
- II gas route
- III exhaust air treatment

For clarity, only section I of the breweries is depicted schematically in figure 2. To compare the different treatment steps, section I was further divided into the following sub-sections:

- I.1 pre-treatment
- I.2 anaerobic treatment
- I.3 aerobic treatment

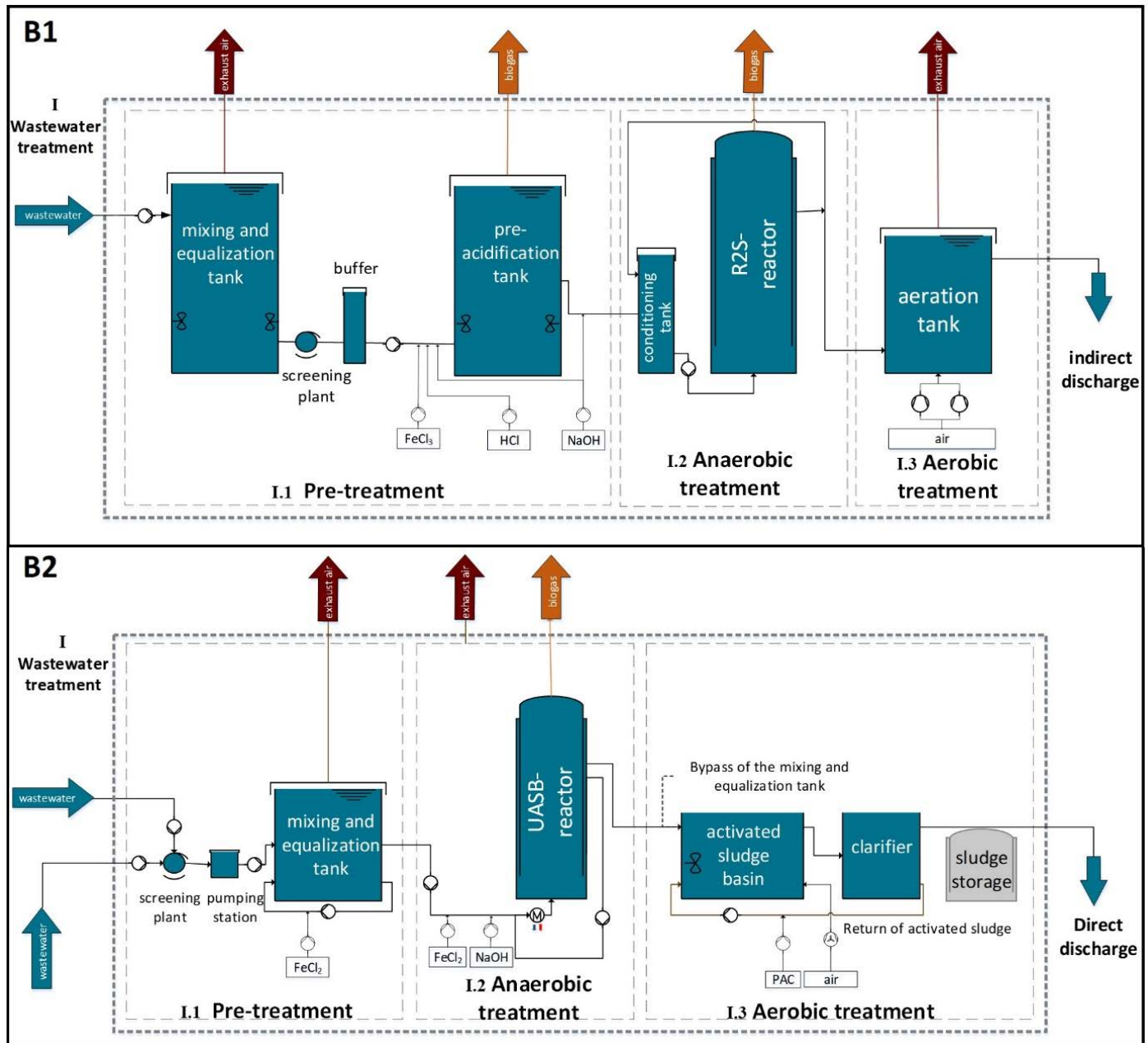


Fig. 2 Scheme of the wastewater treatment plants of B1 and B2

Comparing the wastewater treatment plants of B1 and B2 (Fig. 2), some differences in design and process engineering can be observed, which are described below:

- Pre-treatment: the position of the screening unit in B1 is located after the mixing and equalisation tank; this is in contrast to B2 in which the screening unit is located at the beginning of its treatment plant to remove larger particles.
- Pre-treatment: In B2, the treatment is called single-phase anaerobic treatment because there is no additional pre-acidification tank. According to *Rosenwinkel et al. (2015)*, a stable operation can be guaranteed by the separation of the pre-acidification tank from the anaerobic tank because targeted pre-acidification with adjustable hydraulic retention time (HRT) can be used [28]. The pre-acidification tank in B1 was assigned to the pre-treatment step because pre-acidification can take place in the mixing and equalisation tank in B2, which has a longer HRT than B1. In addition, the pre-acidification tank in B1 was connected to the gas system to feed the gas produced there (including H_2 and H_2S) into the gas system.
- Anaerobic treatment: The reactor type of the anaerobic stage in B1 is the R2S reactor (which is a further development of an expanded granular sludge bed (EGSB) reactor) and in B2, it is the upflow anaerobic sludge blanket (UASB) reactor. This might lead to different specific space loads in B1 and B2.
- Aerobic treatment: The most important differences between B1 and B2 can be found in the aerobic treatment sub-section (I.3). B1 only requires an aerobic tank for aeration to further reduce the wastewater compounds and minimise odour as the wastewater is indirectly discharged into the municipal wastewater treatment plant. In contrast, B2 requires a large activated sludge tank, clarifier and sludge storage tank to

treat the wastewater to reach the quality necessary for direct discharge.

2.2 Wastewater quantity and quality of the two breweries

The wastewater quantity of B1 is almost five times greater than the daily or annual wastewater quantity of B2 (Table 1), which indicates a higher production quantity of B1. The specific wastewater quantity typically ranges from 0.25–0.45 m³/hl produced beer [12]. The quantity of wastewater of both breweries is relatively low for two days a week because no production occurs on weekends, resulting in a significantly lower quantity of wastewater.

The brewery wastewater characteristics are listed in table 1, which is measured at the outlet of the mixing and equalisation tank in B1 and at the inlet of the anaerobic reactor in B2. The composition of the brewery wastewater fluctuates depending on factors such as work processes, equipment and cleaning chemicals [12]. Overall the composition of the wastewater in both the cases is in the typical range seen for brewery wastewater [1]. The C:N:P ratio of 800:5:1 is ideal for anaerobic treatment; thus, significantly less nitrogen and phosphorus are required in comparison to the quantity of carbon required [29]. Therefore, the brewery wastewater of B1, which had a C:N:P ratio of 800:16:11 (COD:TN_b:P_{tot}), and B2, which had a C:N:P ratio of 800:18:14 (COD:N_{tot}:P_{tot}), is generally suitable for anaerobic treatment.

2.3 Evaluation of the wastewater parameters

For the analysis of the extensive data from the two breweries, methods using descriptive statistics were applied. To obtain robust data, the position parameters including the median were calculated and used to evaluate the wastewater parameters of B1 and B2, which is useful for ordinal and metric-scaled data [22, 23]. Outliers were identified in the data, and data for the calculation of the medians were adjusted as the outliers are caused by maintenance-related conditions. However, the outliers must be taken into account when calculating totals (e.g. annual wastewater quantity) as these are absolute values.

2.4 Calculation of key parameters

The energy gain of the plants in brewery wastewater treatment is the result of the biogas produced, which was used for heating processes but not directly used as electrical energy for the wastewater treatment plant. Therefore, the daily electrical energy gain (P_{el} (kWh/d)) could be calculated from the product of the biogas quantity produced daily (V_{biogas} (m³/d)), concentration of methane in the biogas (c_{methane} (%)), electrical efficiency of a combined heat and power plant (η_{el} = 35 %) and heating value of methane (H_{methane} = 9.97 kWh/m³).

$$P_{el} = V_{biogas} \times c_{methane} \times \eta_{el} \times H_{methane} \quad (\text{Eq. 1})$$

Table 1 Wastewater composition of B1 (outlet mixing and equalisation tank) and B2 (inlet of the anaerobic reactor); (Q_{ww}: wastewater flow rate).

parameter	unit	B1			B2		
		Median	Min	Max	Median	Min	Max
Q _{ww}	m ³ /a	421757	–	–	88190	–	–
	m ³ /d	1424	0	2160	281	2	444
pH	–	7.6	5.8	12	6.8	5.8	7.7
COD	mg/L	3500	2000	5200	3750	1900	6300
BOD ₅	mg/L	–	–	–	2400	1200	4500
organic acids	mg/L	872	274	1577	–	–	–
TN _b	mg/L	78	53	83	–	–	–
N _{tot}	mg/L	–	–	–	84	39	166
NH ₄ -N	mg/L	447	–	–	–	–	–
NO ₃ -N	mg/L	2.5	1.9	14.7	–	–	–
P _{tot}	mg/L	51.6	44.8	70.8	64.3	18.9	113.6
PO ₄ -P	mg/L	44	35.2	57.2	–	–	–

For further evaluation of the wastewater treatment system and MFCs, the HRT (h) and COD removal efficiency (ΔCOD, g/L) are calculated.

$$HRT = \frac{V_R}{Q} \quad (\text{Eq. 2})$$

$$\Delta COD = \frac{COD_0 - COD_t}{COD_0} \times 100 \quad (\text{Eq. 3})$$

V_R Volume of the reactor or tank (m³)

Q Wastewater flow rate (m³/h)

COD₀ COD concentration (g/L) in the beginning

COD_t COD concentration (g/L) after time t

Additionally, by calculating the normalised energy recovery (NER) of the anaerobic system, the benchmark for MFCs can be determined. The power (P) generated indirectly by biogas (calculated with equation 1) or by MFCs is thereby normalised to the degraded COD concentration (NER_{kgCOD}) or to the treated wastewater volume (NER_{vol}) [11].

$$NER_{vol} = \frac{P * HRT}{V_{treat}} \quad (\text{Eq. 4})$$

$$NER_{kgCOD} = \frac{P * HRT}{V_{treat} \times \Delta COD} \quad (\text{Eq. 5})$$

P Electrical power output (kW)

V_{treat} Treated wastewater volume in HRT (m³)

In addition to the performance parameters, the overall efficiency (η_{MFC}) of MFCs can be described with two types of efficiencies: Coulombic efficiency (CE) and voltage efficiency (VE) [14, 32].

$$\eta_{MFC} = CE \times VE \quad (\text{Eq. 6})$$

VE is the ratio between the generated voltage (E_{MFC}) and theoretical maximum voltage (E_{emf}). The standard potential E_{emf} can be assumed to be 1.1 V, which is determined via the Nernst equation by assuming that the MFC is operated with acetate as the substrate and oxygen as the electron acceptor [20, 34].

$$VE = \frac{E_{MFC}}{E_{emf}} \quad (\text{Eq. 7})$$

Furthermore, the fraction of the degraded substrate effectively converted into electrons can be described with the CE [20].

$$CE = \frac{M \times \int_{t_0}^t I(t)dt}{F \times n \times V_{MFC} \times \Delta COD} \quad (\text{Eq. 8})$$

M molar mass of oxygen (32 g/mol)

I produced current (A) integrated over time t (s)

F Faraday's constant (96,485 C/mol)

n number of electrons exchanged per molecule of oxygen (4)

V_{MFC} liquid volume of the MFC (L)

ΔCOD degraded concentration of the COD (g/L)

3 Results and discussion

3.1 Energy analysis of the wastewater treatment plants

The differences in the energy balance between B1 and B2 become apparent when analysing the distribution of energy demand among the energy consumers and possible energy gain in the form of biogas. Therefore, for each biological treatment step, the corresponding NER_{vol} and NER_{kg} values can be calculated as benchmarks for MFCs.

Energy demand

A comparison of the median total energy demand of the wastewater treatment plants of the two breweries reveals that B1 consumes almost twice as much energy (1,041 kWh/d) as B2 (532 kWh/d), with energy demands of B1 ranging between 211–1,772 kWh/d and B2 ranging between 304–663 kWh/d. However, if the quantity of wastewater from the two breweries (Table 1) is considered, the quantity of wastewater from B2 is only 20 % of that from B1; therefore, the specific

energy demand in relation to the quantity of treated wastewater is significantly higher for B2. By calculating NER_{vol} , this difference between B1 and B2 that have values $0.72 \text{ kWh}_{el}/\text{m}^3$ and $1.89 \text{ kWh}_{el}/\text{m}^3$, respectively, can be quantified (Eq. 4).

One possible reason for this difference is the energy demand of both breweries in a week; the energy demand during weekends decreases much more in B1 than in B2. Nevertheless, the main explanation for this difference is probably the different requirements for discharge quality, resulting in the aerobic treatment in B2 being much more energy intensive than B1. By delimiting the entire wastewater treatment plants into sections and sub-sections (Fig. 2), the most important energy steps can be identified and attributed to specific energy consumers.

In both the cases, the major energy demand consumer is wastewater treatment (section I), which accounts for about 80 % and 90 % of the total energy demand in B1 and B2, respectively. Accordingly, the energy demand for the gas line (section II), which is 19 % in the case of B1 and 6 % in the case of B2, and exhaust air treatment (section III), which is 1 % in the case of B1 and 3 % in the case of B2, is relatively low (Fig. 3). To determine the energy demands of the individual treatment steps, section I was further divided into the following sub-sections: pre-treatment, anaerobic treatment

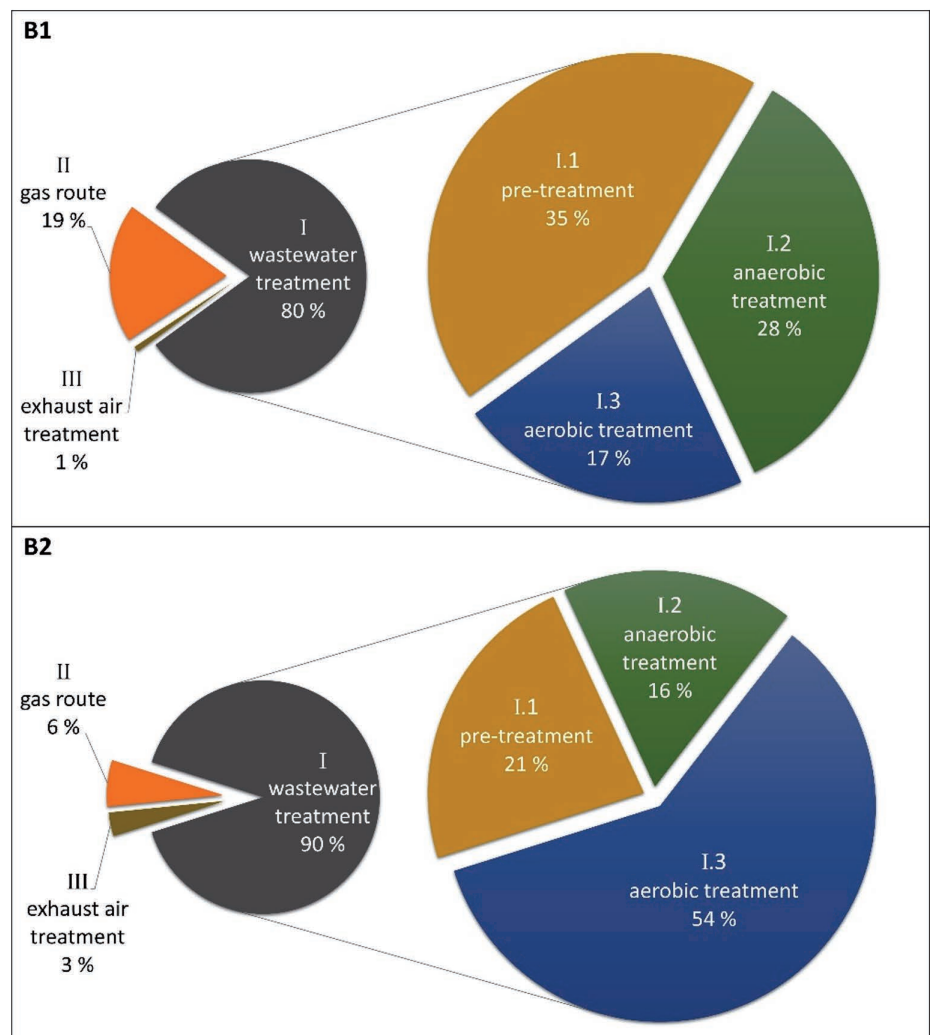


Fig. 3 Total energy demand of B1 and B2 divided into sections and subsections

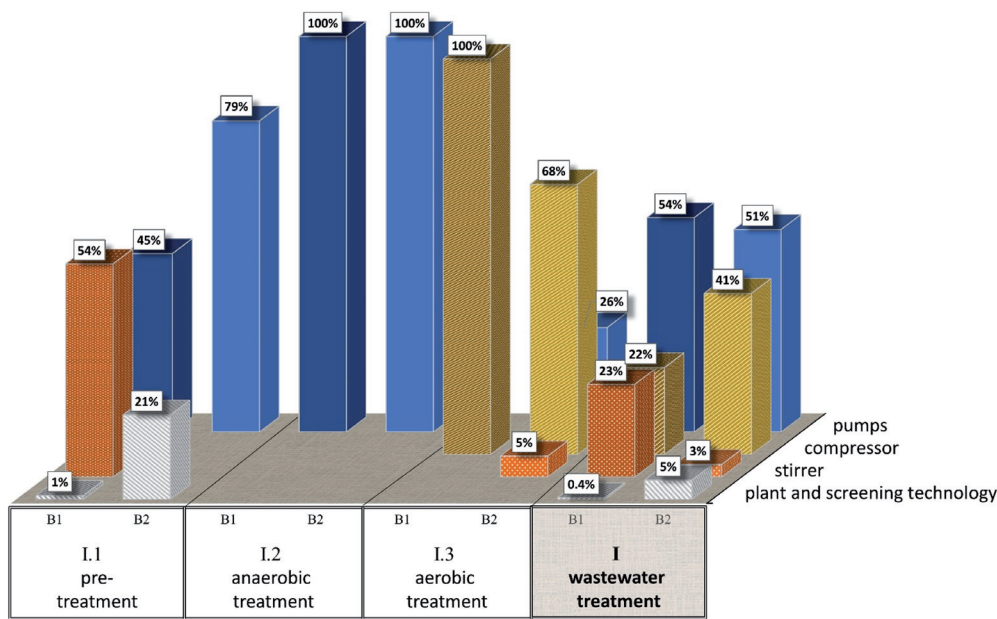


Fig. 4 Energy demand of B1 and B2 for different energy consumers in section I and subsections I.1, I.2 and I.3

and aerobic treatment. Considering the total energy demand, the main energy consumers in B1, which shows indirect discharge, are the pre-treatment and anaerobic treatment sub-sections. This is in contrast to B2, which shows direct discharge, where aerobic treatment accounts for over half of the energy requirement of the entire wastewater treatment plant. The high-energy demand for stand-alone aerobic wastewater treatment is already known [16, 18]; thus, the combination of anaerobic and aerobic treatments has reduced the total energy demand in both cases.

The energy demand is caused by several energy consumers, which were divided into categories such as pumps, stirrers, compressors and plant and screening technology, thus allowing the main energy consumers and their impact on the total energy demand to be identified in section I (Fig. 4). Pumps are the main energy consumers in both cases (B1: 54 %, B2: 51 %); compressors are a significant energy consumer in both cases (B1: 22 %, B2: 41 %) and are the second highest energy consumer in B2.

With regard to the pre-treatment step, the energy consumers differ significantly between B1 and B2 because B1 uses considerably more stirrers than B2. In B1, a stirrer is used in the mixing and equalisation tank and in the pre-treatment tank; in B2, a pump is used in the mixing and equalisation tank. The plant and screening technology account for the lowest proportion of the total energy consumption.

In conclusion, the main energy consumers in both breweries are pumps in the pre-treatment and anaerobic stages and the compressors require the most energy in the aerobic treatment stage.

Energy gain in the form of biogas

In both breweries, the energy gain is the result of the biogas produced in the anaerobic reactor. In B1, the energy gain includes the biogas produced in the pre-acidification tank. In both breweries,

the biogas produced is monitored in volume and composition. The total quantity of biogas produced, which is 1,319 m³/d for B1 and 258 m³/d for B2, correlates with the total quantity of wastewater produced, thus resulting in a similar specific quantity of biogas for B1 and B2, which is 0.92 m³_{biogas}/m³_{wastewater} and 0.93 m³_{biogas}/m³_{wastewater} respectively.

A decisive factor in energy production is the methane content of biogas, which in breweries is in the range of 70–85 % [9]. In the two breweries studied, the average methane concentration was 83 % in B1 and 75 % in B2, which is in the range. H₂S proportion has to be below 3 % because of its inhibitory effect toward methane formation [28], which was the case at both breweries.

A theoretical electrical energy gain of 3,820 kWh/d for B1 and 675 kWh/d for B2 can be calculated using equation 1. Consequently, the NER_{vol} values for B1 and B2 can be calculated as 2.683 kWh_{el}/m³ and 2.403 kWh_{el}/m³, respectively.

Energy Balance

Finally, the energy recovery from wastewater treatment in both breweries can be balanced based on the calculated energy demands

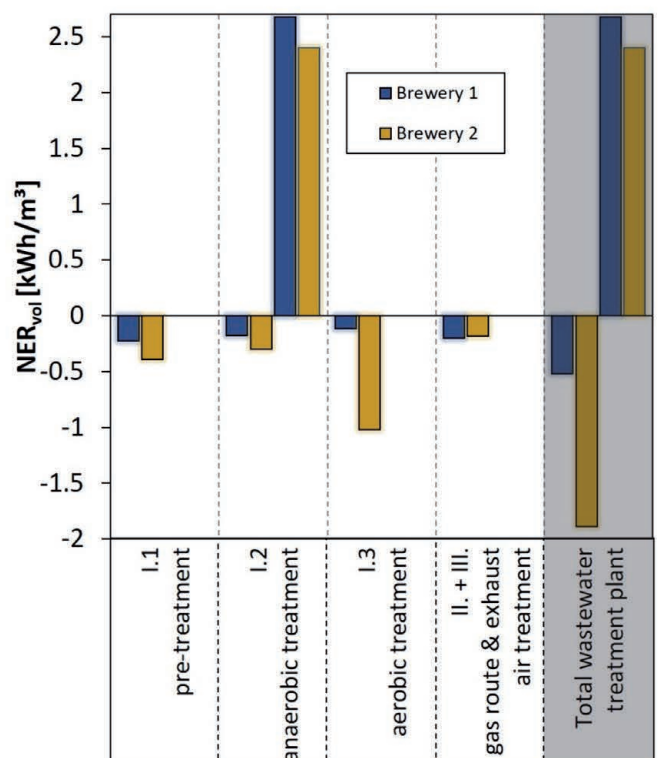


Fig. 5 Normalized energy recovery (NER_{vol}) of B1 and B2

Table 2 Specific key figures of B1 and B2 for each treatment step (n.a. not applicable)

Brewery (type of discharger)	Parameter	I.1 Pre-treatment		I.2 Anaerobic treatment	I.3 Aerobic treatment			Total treatment efficiency
		mixing and equalisation tank	pre-acidifica- tion tank	UASB-/ R2S- reactor	aeration tank	activated sludge tank	clarifier	
B1 (indirect)	V_R [m ³]	635	635	468	293	n.a.		–
	HRT [h]	11	11	8	5			34
	COD _{in} [mg/L]	3500	3500	3300	371			–
	Δ COD [mg/L]	–	200	2929	157			3286
	Δ COD [%]	–	6	89	42			94
B2 (direct)	V_R [m ³]	698	n.a.	222	n.a.	698	83	–
	HRT [h]	60		19		60	7	145
	COD _{in} [mg/L]	3750		3750		594		–
	Δ COD [mg/L]	–		3156		552		3708
	Δ COD [%]	–		84		93		99

and gains (Fig. 5). The energy recovery of the total wastewater treatment is 1.964 kWh/m³ for B1 and 0.511 kWh/m³ for B2. In theory, the treatment is therefore self-sufficient, and additional energy gains can be achieved by both breweries because of the calculated electrical energy gain from biogas, which is not directly used in the operation of these wastewater treatment plants.

The NER_{vol} estimate of B1 is significantly greater than that of B2 because of the following reasons:

- A slightly higher energy gain is possible because of the higher methane content of the biogas in B1.
- A slightly lower energy demand can be observed in the pre-treatment and anaerobic treatment sub-sections because of the higher volume of wastewater in B1.
- A significantly lower energy demand can be observed in the aerobic sub-section because of different discharge qualities of B1 and B2.

Consequently, the energy recovery of a wastewater treatment plant is most significantly influenced by the required discharge quality, but overall a positive energy balance can be achieved.

3.2 Treatment efficiency

To achieve the required wastewater quality, the focus of breweries is on treatment efficiency and in particular on COD reduction, and energy recovery is additionally done to reduce costs. Due to the organic components in brewery wastewater, this wastewater is characterised by high initial COD concentration [1, 9]. Therefore, a high COD removal rate must be achieved to meet the discharge conditions.

In general, the COD removal efficiency of wastewater treatment in breweries is about 70–80 % in the anaerobic stage, and up to 98 % of the COD can be removed in the subsequent aerobic stage [31].

The wastewater treatment plants of B1 and B2 achieve an overall median COD removal of 94% and 99 %, respectively (Table 2).

Most of the COD degradation takes place in the anaerobic reactor (B1: 89 % or a concentration of 2,929 mg/L; B2: 84 % or a concentration of 3,156 mg/L). The anaerobic reduction of the COD is almost identical in B1 and B2, and the small difference of 5 % may be because of the different reactor types or microbial composition. In the aerobic section of B1, a further COD reduction of only 42 % (157 mg/L) is required to meet the discharge limits. In contrast, aerobic treatment in B2 removes an additional 93 % (552 mg/L) of the COD content, as the limit for direct discharge is much lower.

In addition, the HRT in B1, which is 34 hours, is considerably shorter than in B2. The long HRT in B2, which is 145 hours, is the result of low discharge limits. Consequently, the NER_{kgCOD} can be calculated using equation 5 and the following values: 0.597 kWh/kg_{COD} for B1 and 0.137 kWh/kg_{COD} for B2.

Further nutrient removal must not be neglected because there are thresholds that have to be achieved or influence the COD treatment efficiency. In particular, nitrogen and phosphorous compounds are strictly regulated for direct discharge. In the wastewater treatment plant in B2, nitrogen and phosphorus were reduced to a median concentration of 1.3 mg/L (N_{tot}) and 6.0 mg/L (P_{tot}), respectively, at the end of treatment, and in B1, nitrogen and phosphorous compounds remained almost constant at 74 mg/L (TN_b) and 52 mg/L (P_{tot}), respectively, at the end of treatment. Consequently, intensive aerobic treatment was required to reduce nitrogen and phosphorus compounds.

For the evaluation of the MFC, a high COD treatment efficiency must be achieved in addition to the energy benchmark. Moreover, in the case of direct discharge, nitrogen and phosphorus concentrations must especially be taken into account.

3.3 Benchmark for the application of microbial fuel cells

In general, the same energy efficiency must be achieved with MFCs as calculated according to the state-of-the-art for brewery 1 and 2, resulting in a comparable energy recovery benchmark

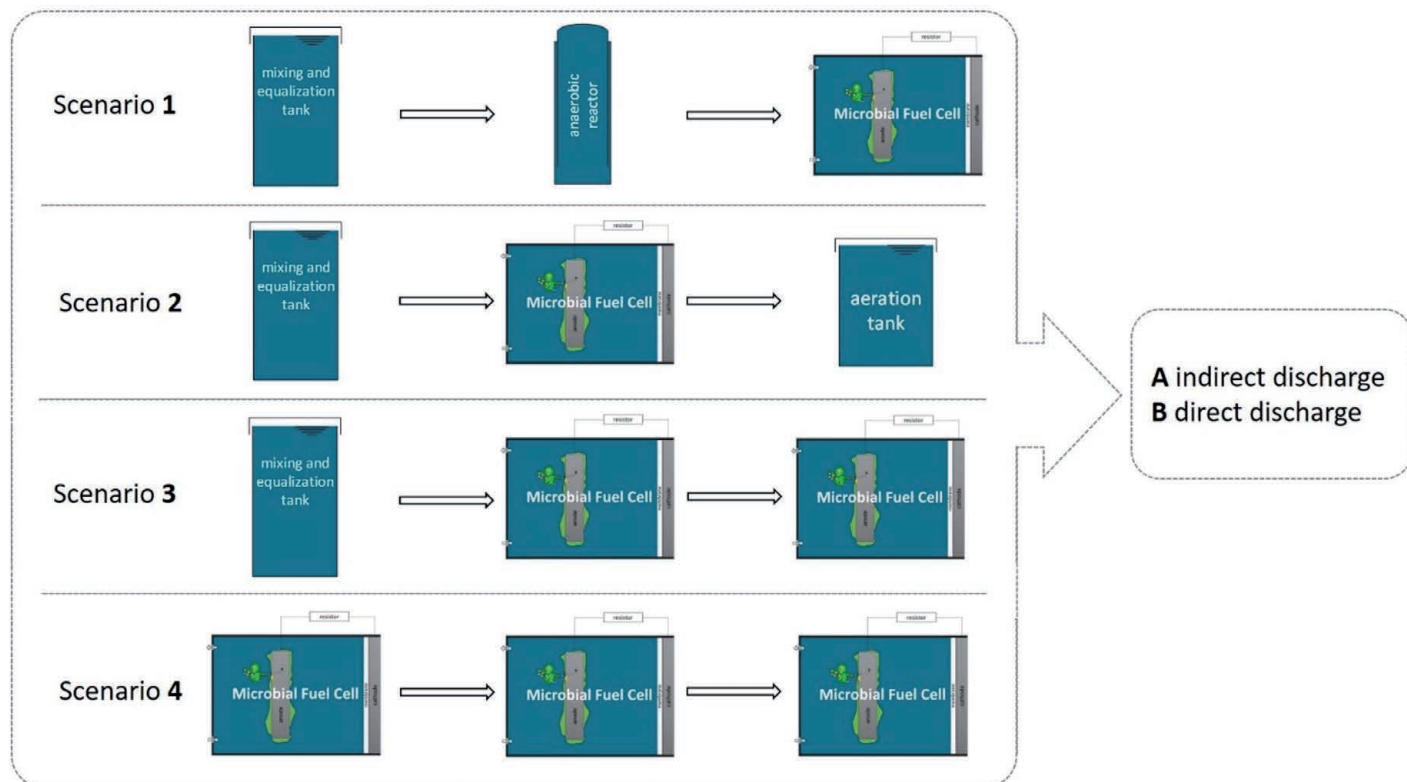


Fig. 6 Schematic representation of the different scenarios for the application of MFCs

for MFCs (1.964 kWh/m³ for indirect discharge; 0.511 kWh/m³ for direct discharge). A combination of conventional treatments (anaerobic and aerobic treatment) with MFC treatment might be beneficial and should not be considered as competing with each other [10, 24]. Several possibilities have already been suggested to replace conventional treatment steps with MFCs [3]. Specific key parameters for each treatment step, four different scenarios for brewery wastewater treatment can be evaluated (Fig. 6, Table 3). This allows the required energy efficiency and treatment performance of MFCs to be considered for the replacement of different treatment steps.

In scenario 1, MFCs replace energy-intensive aerobic treatment to reduce energy consumption. The substitution of anaerobic treatment in scenario 2 can be beneficial due to the direct gain in electrical energy instead of the indirect gain in the form of biogas. In scenario 3, the same pre-treatment is used, but the energy-intensive aerobic treatment and the necessary gas treatment in the anaerobic step can be avoided with stacked MFCs. Replacing the complete state-of-the-art treatment system with stacked MFCs in scenario 4 can bring further advantages in terms of the required energy efficiency.

The key parameters for the different scenarios summarized in table 3 has been calculated for each treatment step. The degraded COD concentration (Δ COD in %, mg/L) and HRT were calculated in table 2 for each treatment step for B1 and B2, respectively. Thus, these figures can be used for the direct and indirect

discharge scenarios in table 3. In terms of degradation rates, the final target COD concentration should be approximately less than 200 mg/L for indirect discharge and approximately less than 50 mg/L for direct discharge. The NER_{vol} of the individual treatment steps have already been shown in figure 5. Thus, for each scenario, the key parameter NER_{vol} can be calculated with them. By normalising the NER_{vol} with the degraded COD concentration for each step, the NER_{kgCOD} can be estimated.

In the first scenario, MFCs are planned to replace aerobic treatment. In this context, the energy demand for MFCs should not be higher than -0.114 kWh/m³ for indirect discharge (1A) and -1.020 kWh/m³ for direct discharge (1B). Thus, the benchmark set by B1 or B2 can also be achieved with MFCs, even if energy is consumed. However, positive energy balances of 0.034 kWh/m³ and 0.0092 kWh/m³ have been reached by MFCs in the treatment of brewery wastewater and municipal wastewater, respectively [8, 36].

Table 3 Key parameters for different scenarios (A: indirect discharge, B: direct discharge)

Scenario		NER_{vol} kWh/m ³	NER_{kgCOD} kWh/kg	Δ COD [%]	Δ COD [mg/L]	HRT [h]
1	A	-0.114	-0.726	42	157	5
	B	-1.020	-1.847	93	552	67
2	A	2.503	0.855	89	2929	8
	B	2.106	0.667	84	3156	19
3	A	2.390	0.774	88	3086	13
	B	1.086	0.293	99	3708	86
4*	A	1.964	0.598	94	3286	34
	B	0.511	0.138	99	3708	145

*NER incl. consumer in BII + BIII

Also, the feasibility of treating the effluent of an anaerobic digester with MFCs has been investigated in several studies [5, 7, 10, 13, 17, 30]. MFCs can further reduce the COD concentration of the anaerobic effluents so that they can be placed after the anaerobic stage [10]. However, when comparing MFCs treating brewery wastewater with and without an intermediate anaerobic digester, the direct treatment of brewery wastewater shows higher power densities due to the higher organic loading rates [5].

In addition to COD removal, the removal of other nutrients should not be neglected because the treated wastewater should meet all requirements for direct and indirect discharge. In general, MFCs can reduce nitrogen, total suspended solids (TSS) and sulphates [3]. In the combined system of anaerobic treatment and downstream MFC treatment, nitrogen components could be removed within MFCs [5, 17].

In summary, it is energetically possible to achieve the aerobic treatment limits and COD thresholds using MFCs. In this case, the challenge is to meet the requirements for other nutrients such as nitrogen, phosphorus, TSS and sulphate compounds.

In the second scenario, anaerobic treatment is replaced by MFCs. The benchmark NER_{vol} estimate of 2.503 kWh/m³ (indirect discharge) and 2.106 kWh/m³ (direct discharge) is currently difficult to achieve, and only a median energy recovery (energy gain) of 0.097 kWh/m³ (0.058 kWh/kg) could be achieved when treating industrial wastewater with MFCs [3]. However, with the combination of a MFC with an anaerobic fluidised bed membrane bioreactor on a laboratory scale, an energy-neutral treatment of domestic wastewater was possible [25].

The COD removal efficiency benchmark of greater than 3,000 mg/L (84–89 %) can be achieved with MFCs, but a longer HRT is currently required [3]. In the treatment of brewery wastewater with MFCs, for example, an average COD removal efficiency of 83 % in 48 h could be achieved on a laboratory scale [4] and a maximum removal efficiency of 87–95 % was achieved on a pilot scale with a minimum HRT of 48 h [8, 21, 37].

Consequently, although the COD removal performance is achievable, energetically the MFC should be considered as a pre-treatment stage for aerobic treatment, which can reduce high-energy costs. In addition, direct electricity generation is an advantage of MFCs [19, 26].

In scenarios 3 and 4, stacking systems of MFCs connected in series could enable the replacement of conventional biological treatment. Using power management systems with power tracking and storage units, the power output of the MFCs can be maximised [2]. However, an energy gain of 0.511–2.390 kWh/m³ (scenarios 3 & 4) would be as difficult to achieve as the benchmark in sce-

nario 2. With the above-mentioned energy management system, 0.015–0.060 kWh/m³ could be achieved with a 1,000-litre MFC stack system (64 x 16.25 L) for the treatment of municipal wastewater in long-term operation [2]. When treating brewery wastewater with a 2 x 10 L and 40 x 0.25 L MFC stack system, it was possible to attain the following values: 0.120 and 0.288 kWh/m³, respectively (calculated on the basis of the data in these paper) [21, 37].

With regard to COD removal, the same aspects discussed in scenario 1 are crucial; COD removal would be possible, but the removal of other nutrients would be a challenge. Furthermore, in scenario 4 without mixing and equalisation tank, the sometimes high fluctuations in brewery wastewater composition are not buffered. Consequently, the microbiology in the first MFC must be very robust against these fluctuations (e.g. pH), otherwise the microbiology would often have to be reactivated.

The 1,000-litre stack system treating municipal wastewater was already evaluated for over one year as a stand-alone treatment in which the COD concentration (80–95 %), ammonia (48 %) and phosphorous (up to 0.59 mg/L) could be reduced [2]. Therefore, in this case, the COD removal has achieved the legal requirements of a COD threshold of > 45–60 mg/L and a removal of > 80–85 % [2].

In conclusion, currently only self-sufficient treatment with MFCs can be considered realistic from an energy point of view. Consequently, the replacement of aerobic treatment or pre-treatment steps before aerobic treatment would be the most attractive measure to reduce energy costs. With regard to the treatment performance, the COD limits can be met in each scenario, and only the further removal of other nutrients to meet the required limits could be a challenge. As scaling-up the usage of MFCs is presently a huge challenge, MFC will be attractive for small breweries due to its compact design and

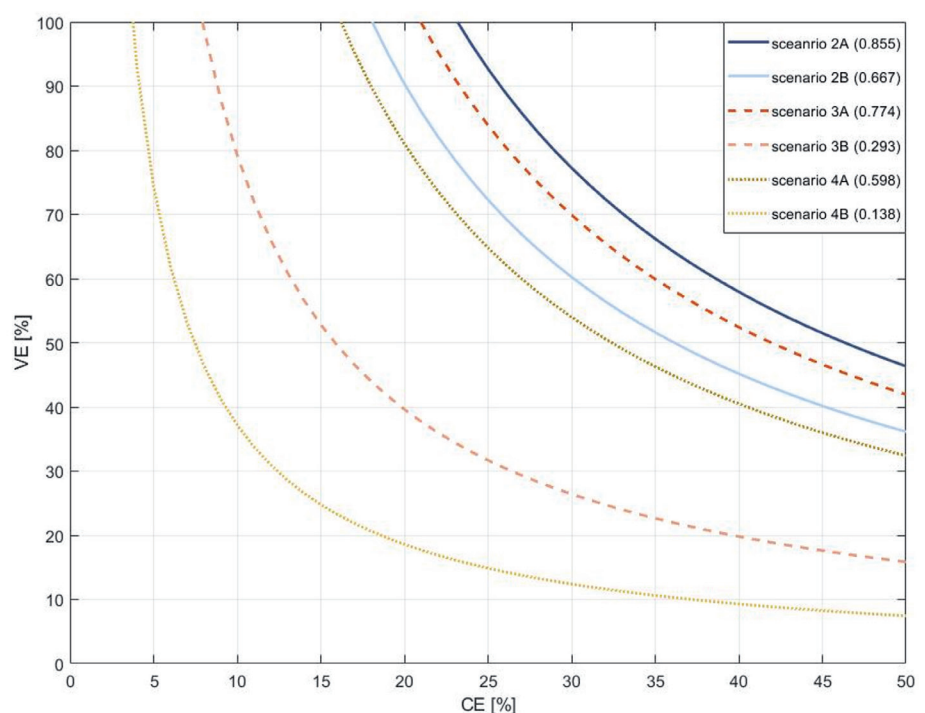


Fig. 7 NER_{kgCOD} thresholds (values in brackets) of different scenarios dependent on VE and CE

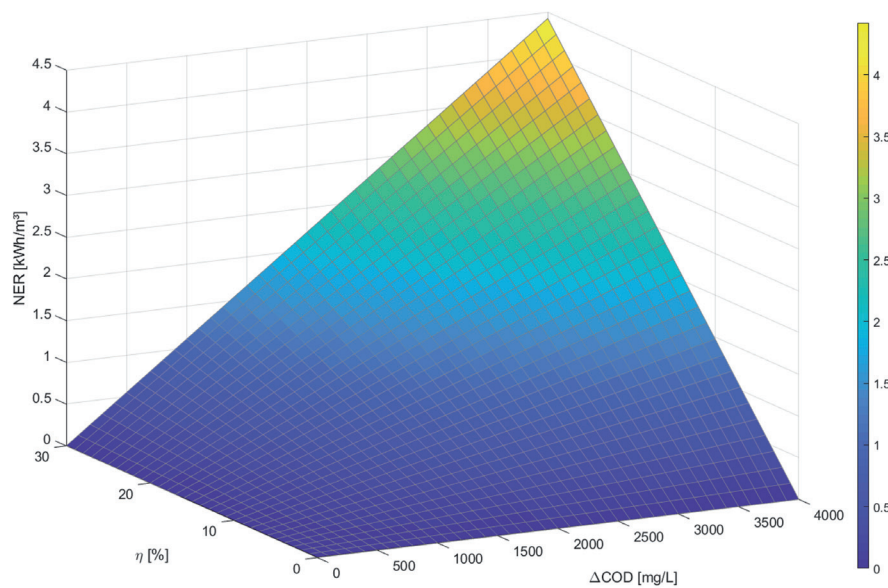


Fig. 8 Correlation of NER_{vol} with the overall efficiency η and degraded COD concentration ΔCOD

ability to directly generate electricity so that no combined heat and power plant (CHP) is needed.

3.4 Modelling of energy recovery using MFCs

After the benchmarks for different scenarios were determined, the required efficiency of MFCs could be calculated. The required efficiencies can be determined independent of the HRT; thus, the kinetics of the COD removal efficiency determination are not relevant in this case.

NER_{kgCOD} can be formulated as a function of VE and CE using a combination of equations 5, 7 and 8 and the calculation of electrical power represented by the product of voltage and current. In this way, figure 7 shows possible NER_{kgCOD} estimates independent of the treated wastewater volume and COD removal efficiency. The NER_{kgCOD} estimates of scenarios 1A and 1B are not taken into account here as they are negative and can therefore already be achieved with a neutral energy balance of MFCs.

Considering the CE and VE of a MFC to be independent of its COD removal performance, the benchmarks of scenarios 1A and 1B are the easiest to achieve. In addition, it is most realistic to reach the benchmark of scenarios 4B and 3B with 0.138 kWh/kg and 0.293 kWh/kg, respectively. The maximum measured open-circuit voltage is only about 0.8 V, which is because of potential losses at all types of internal resistances [6]. Currently, an average voltage of 0.3–0.6 V is reported with glucose or acetic acid as the substrate, starting from a theoretical value of 1.1 V [20, 35]. Due to different inocula and wastewater composting, the CE in industrial wastewater treatment varies greatly, having a range of 1–65 % and a median value of 15 % [3]. For example, assuming a VE of 30 % and CE of 15 %, scenario 4B seems realistic and scenario 3B is a possible target that can be reached. Nevertheless, the energy consumption of MFCs has to be taken into account in the energy balances.

To achieve the other benchmarks, MFC technology needs to be improved, and strategies to optimise power output are already being reported [6].

As a consequence, only considering the electrical energy efficiency of MFCs, the replacement of aerobic treatment (scenarios 1A and 1B) and the MFC as a stand-alone option for direct discharge (scenario 3B and 4B) are both currently possible.

For the complete evaluation of MFC technology, COD removal efficiency must also be taken into account especially in wastewater treatment, where it is very important. In this way, the possible NER_{vol} estimates can be depicted in relation to the overall efficiency of an MFC and the COD removal efficiency (Fig. 8) independently of the treated wastewater volume. From the product of the assumed VE (30 %) and CE (15 %), an overall efficiency, η_{MFC} , of 4.5 % can be calculated

using equation 6. With the removal of 157 mg/L and 552 mg/L (benchmark scenarios 1A and 1B), NER_{vol} estimates of 0.026 kWh/m³ and 0.092 kWh/m³ can be achieved with MFCs, respectively.

Considering the higher COD removal in scenarios 3B and 4B with 3,708 mg/L, a significantly higher NER_{vol} with 0.615 kWh/m³ can be achieved, making the benchmark of scenario 4B with 0.511 kWh/m³ achievable. Again, the energy demand of the MFC treatment is not taken into account. The efficiency of MFCs must be at least 23 % and 18 % if the benchmarks of scenarios 2A and 2B, respectively, are to be achieved.

In summary, it can be concluded that with regard to COD removal efficiency, the NER_{vol} estimates of scenarios 1A, 1B and 4B can be realistically achieved if the same COD concentration can be removed as in conventional wastewater treatment.

4 Conclusion

Through the analysis of the two brewery wastewater treatment plants, energy efficiency and treatment performance benchmarks could be determined for four different scenarios (depicted in Fig. 6) and a distinction could be made between direct and indirect discharge. Considering energy, the replacement of aerobic treatment (scenarios 1A and 1B) is the most favourable option because there is a negative energy balance in the cases. In the case of self-sufficient wastewater treatment with MFCs, the challenge lies in complying with the limits for direct or indirect discharge. Replacing the complete wastewater treatment plant in the case of direct discharge with MFCs with or without pre-treatment (scenario 3B and 4B) is the most realistically achievable option in terms of energy. Taking into account the COD degradation efficiency, MFCs with an overall efficiency of 4.5 % can reach the benchmarks of scenario 4B. The benchmarks of the anaerobic treatment replacement scenarios with MFCs (scenarios 2A and 2B) can only be achieved with an energy

efficiency of at least 23 % and 18 %, respectively.

In summary, the efficiency of COD treatment with MFCs could be achieved in all proposed scenarios, but the energy efficiency of the MFCs needs to be increased. If self-sufficient treatment is adequate for brewery requirements, the compact MFC system with direct power generation can become attractive for small breweries.

Acknowledgements

The authors would like to thank the breweries for their support and for providing all the necessary data. This work was supported by the ZIM and IGF funding programmes of the German Federal Ministry for Economic Affairs and Energy, grant numbers: ZF4025017SA7 and 20789 N/1.

5 References

- Arantes, M.; Alves, H.; Sequinel, R. and Silva, E.: Treatment of brewery wastewater and its use for biological production of methane and hydrogen, *International Journal of Hydrogen Energy*, **42** (2017), no. 42, pp. 26243-26256.
- Blatter, M.; Delabays, L.; Furrer, C.; Huguenin, G.; Cachelin, C. P. and Fischer, F.: Stretched 1000-L microbial fuel cell, *Journal of Power Sources*, **483** (2021), pp. 229130.
- Brunschweiler, S.; Hofmann, T. and Glas, K.: Industrial wastewater treatment with simultaneous energy recovery using microbial fuel cells – a review, *BrewingScience*, **73** (2020), no. 9/10, pp. 111-125.
- Brunschweiler, S.; Ojong, E. T.; Weisser, J.; Schwaferts, C.; Elsner, M.; Ivleva, N. P.; Haseneder, R.; Hofmann, T. and Glas, K.: The effect of clogging on the long-term stability of different carbon fiber brushes in microbial fuel cells for brewery wastewater treatment, *Bioresource Technology Reports* 11 (2020), pp. 100420.
- Çetinkaya, A. Y.; Köroğlu, E. O.; Demir, N. M.; Baysoy, D. Y.; Özkaya, B. and Çakmakçı, M.: Electricity production by a microbial fuel cell fueled by brewery wastewater and the factors in its membrane deterioration, *Chinese Journal of Catalysis*, **36** (2015), no. 7, pp. 1068-1076.
- Chen, S.; Patil, S. A.; Brown, R. K. and Schröder, U.: Strategies for optimizing the power output of microbial fuel cells: Transitioning from fundamental studies to practical implementation, *Applied Energy*, **233-234** (2019), pp. 15-28.
- Dhar, B. R.; Gao, Y.; Yeo, H. and Lee, H.-S.: Separation of competitive microorganisms using anaerobic membrane bioreactors as pretreatment to microbial electrochemical cells, *Bioresource Technology*, **148** (2013), pp. 208-214.
- Dong, Y.; Qu, Y.; He, W.; Du, Y.; Liu, J.; Han, X. and Feng, Y.: A 90-liter stackable baffled microbial fuel cell for brewery wastewater treatment based on energy self-sufficient mode, *Bioresource Technology*, **195** (2015), pp. 66-72.
- Driessen, W. and Vereijken, T.: Recent developments in biological treatment of brewery effluent, *The Institute and Guild of Brewing Convention*, Livingstone, Zambia, March, 2003.
- Durruty, I.; Bonanni, P. S.; González, J. F. and Busalmen, J. P.: Evaluation of potato-processing wastewater treatment in a microbial fuel cell, *Bioresource Technology*, **105** (2012), pp. 81-87.
- Ge, Z.; Li, J.; Xiao, L.; Tong, Y. and He, Z.: Recovery of Electrical Energy in Microbial Fuel Cells, *Environmental Science & Technology Letters*, **1** (2013), no. 2, pp. 137-141.
- Glas, K.: Waste Water, *Handbook of Brewing*, (Ed.) EBlinger, H. M., 2009, pp. 621-641.
- Gregoire, K.; Tatinclaux, M.; Biffinger, J.; Tender, L. and Lansing, S.: Hybrid Anaerobic Digester-Microbial Fuel Cell for Waste Water Treatment, *ECS Meeting Abstracts*, 2013,
- Hamelers, B.; Sleutels, T.; Jeremiassé, A.; Post, J. W.; Strik, D. and Rozendal, R.: Technological factors affecting BES performance and bottlenecks towards scale up, *Bioelectrochemical systems : from extracellular electron transfer to biotechnological application*, IWA Publishing, 2010, pp. 205-224.
- Hiegemann, H.; Herzer, D.; Nettmann, E.; Lübken, M.; Schulte, P.; Schmelz, K.-G.; Gredigk-Hoffmann, S. and Wichern, M.: An integrated 45 L pilot microbial fuel cell system at a full-scale wastewater treatment plant, *Bioresource Technology*, **218** (2016), pp. 115-122.
- Kelly, P. T. and He, Z.: Understanding the application niche of microbial fuel cells in a cheese wastewater treatment process, *Bioresource Technology*, **157** (2014), pp. 154-160.
- Kim, T.; An, J.; Jang, J. K. and Chang, I. S.: Determination of optimum electrical connection mode for multi-electrode-embedded microbial fuel cells coupled with anaerobic digester for enhancement of swine wastewater treatment efficiency and energy recovery, *Bioresource Technology*, **297** (2020), pp. 122464.
- Kushwaha, J. P.; Srivastava, V. C. and Mall, I. D.: An overview of various technologies for the treatment of dairy wastewaters, *Crit. Rev. Food Sci. Nutr.*, **51** (2011), no. 5, pp. 442-52.
- Logan, B.: *Microbial fuel cells*, Wiley-Interscience, 2008.
- Logan, B. E.; Hamelers, B.; Rozendal, R.; Schröder, U.; Keller, J.; Freguia, S.; Aelterman, P.; Verstraete, W. and Rabaey, K.: *Microbial Fuel Cells: Methodology and Technology*, *Environmental Science & Technology*, **40** (2006), no. 17, pp. 5181-5192.
- Lu, M.; Chen, S.; Babanova, S.; Phadke, S.; Salvacion, M.; Mirhosseini, A.; Chan, S.; Carpenter, K.; Cortese, R. and Bretschger, O.: Long-term performance of a 20-L continuous flow microbial fuel cell for treatment of brewery wastewater, *Journal of Power Sources*, **356** (2017), pp. 274-287.
- Matthäus, H. and Matthäus, W.-G.: *Statistik und Excel: Elementarer Umgang mit Daten*, Springer, 2016.
- Mittag, H.-J.: *Statistik: eine Einführung mit interaktiven Elementen*, Springer-Verlag, 2017.
- Pham, T. H.; Rabaey, K.; Aelterman, P.; Clauwaert, P.; Schampelaire, L. D.; Boon, N. and Verstraete, W.: *Microbial Fuel Cells in Relation to Conventional Anaerobic Digestion Technology*, *Engineering in Life Sciences*, **6** (2006), no. 3, pp. 285-292.
- Ren, L.; Ahn, Y. and Logan, B. E.: A Two-Stage Microbial Fuel Cell and Anaerobic Fluidized Bed Membrane Bioreactor (MFC-AFMBR) System for Effective Domestic Wastewater Treatment, *Environmental Science & Technology*, **48** (2014), no. 7, pp. 4199-4206.
- Rosenbaum, M.; Agler, M. T.; Fornero, J. J.; Venkataraman, A. and Angenent, L. T.: Integrating BES in the wastewater and sludge treatment line, *Bioelectrochemical systems: from extracellular electron transfer to biotechnological application*, IWA Publishing, 2010, pp. 393-421.
- Rosenwinkel, K.-H.; Austermann-Haun, U.; Köster, S. and Beier, M.: *Taschenbuch der Industrieabwasserreinigung*, Vulkan Verlag GmbH, 2019.
- Rosenwinkel, K. H.: *Anaerobtechnik: Abwasser-, Schlamm- und Reststoffbehandlung, Biogasgewinnung*, Springer-Verlag GmbH, 2015.
- Sahm, H.; Antranikian, G.; Stahmann, K.-P. and Takors, R.: *Industrielle Mikrobiologie*, 2013.
- Sharma, Y. and Li, B.: Optimizing energy harvest in wastewater treat-

- ment by combining anaerobic hydrogen producing biofermentor (HPB) and microbial fuel cell (MFC), *International Journal of Hydrogen Energy*, **35** (2010), pp. 3789-3797.
31. Simate, G. S.; Cluett, J.; Lyuke, S. E.; Musapatika, E. T.; Ndlovu, S.; Walubita, L. F. and Alvarez, A. E.: The treatment of brewery wastewater for reuse: State of the art, *Desalination*, **273** (2011), no. 2-3, pp. 235-247.
32. Sleutels, T.; Molenaar, S.; Heijne, A. and Buisman, C.: Low Substrate Loading Limits Methanogenesis and Leads to High Coulombic Efficiency in Bioelectrochemical Systems, *Microorganisms*, **4** (2016), no. 1, pp. 7.
33. Stiefel, R.: *Energierückgewinnung aus Industrieabwässern, Abwasserrecycling: Technologien und Prozesswassermanagement: Das Konzept Prozesswasserautarkie*, Springer Fachmedien Wiesbaden. Wiesbaden, 2017, pp. 137-163.
34. Varanasi, J. L. and Das, D.: Bioremediation and Power Generation from Organic Wastes Using Microbial Fuel Cell, *Microbial Fuel Cell: A Bioelectrochemical System that Converts Waste to Watts*, (Ed.) Das, D., Springer International Publishing. Cham, 2018, pp. 285-306.
35. Varanasi, J. L. and Das, D.: Characteristics of Microbes Involved in Microbial Fuel Cell, *Microbial Fuel Cell: A Bioelectrochemical System that Converts Waste to Watts*, (Ed.) Das, D., Springer International Publishing. Cham, 2018, pp. 43-62.
36. Zhang, F.; Ge, Z.; Grimaud, J.; Hurst, J. and He, Z.: Long-Term Performance of Liter-Scale Microbial Fuel Cells Treating Primary Effluent Installed in a Municipal Wastewater Treatment Facility, *Environmental Science & Technology*, **47** (2013), no. 9, pp. 4941-4948.
37. Zhuang, L.; Yuan, Y.; Wang, Y. and Zhou, S.: Long-term evaluation of a 10-liter serpentine-type microbial fuel cell stack treating brewery wastewater, *Bioresource Technology*, **123** (2012), pp. 406-412.

Received 8 January 2021, accepted 10 February 2021