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Energy Production in Microbial Fuel Cells (MFCs) during the Biological Treatment of Wastewater from Soilless Plant Cultivation

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Abstract: The management of drainage water (DW), which is produced during the soilless cultivation of plants, requires a high energy input. At the same time, DW is characterized by a high electrolytic conductivity, a high redox potential, and is also stable and putrefaction-free. In the present study, the natural properties of drainage water and a biotreatment method employing an external organic substrate in the form of citric acid (C/N 1.0, 1.5, 2.0) were utilized for energy recovery by a microbial fuel cell (MFC). The cathode chamber served as a retention tank for DW with a carbon felt electrode fixed inside. In turn, a biological reactor with biomass attached to the filling in the form of carbon felt served as the anode chamber. The filling also played the role of an electrode. The chambers were combined by an ion exchange membrane, forming an H letter-shaped system. They were then connected in an external electrical circuit with a resistance of 1k Ω. The use of a flow-through system eliminated steps involving aeration and mixing of the chambers' contents. Citric acid was found to be an efficient organic substrate. The voltage of the electric current increased from 44.34 ± 60.92 mV to 566.06 ± 2.47 mV for the organic substrate dose expressed by the C/N ratio ranging from 1.0 to 2.0. At the same time, the denitrification efficiency ranged from 51.47 ± 9.84 to $95.60 \pm 1.99\%$ and that of dephosphatation from 88.97 ± 2.41 to $90.48 \pm 1.99\%$ at C/N from 1.0 to 2.0. The conducted studies confirmed the possibility of recovering energy during the biological purification of drainage water in a biofilm reactor. The adopted solution only required the connection of electrodes and tanks with an ion-selective membrane. Further research should aim to biologically treat DW followed by identification of the feasibility of energy recovery by means of MFC.

Keywords: microbial fuel cell; soilless cultivation wastewater; wastewater treatment; energy recovery; drainage water; citric acid



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1. Introduction

Recently, environmental engineering has been extensively focused on bioelectrochemical systems for, both, the production of electrical energy (like microbial fuel cells—MFCs), as well as for wastewater treatment via biological and electrochemical processes [1]. MFCs enable the conversion of chemical energy carried by the organic matter in wastewater into electrical energy [2]. They function on the principles of oxidation and reduction processes and can be configured with two chambers (anode and cathode chamber), separated by an ion-exchange membrane or a sufficient distance. In the anode chamber, microorganisms can undergo anaerobic oxidation of substrates within their metabolic pathways, releasing electrons and protons simultaneously. Through specific mediators, self-generated substances like cytochrome, pili, and filaments, or direct transfer mechanisms, these electrons can reach the anode and are then transferred to the cathode via current collectors and the external circuit. In the cathode chamber, oxygen is commonly employed as the final

electron acceptor, combining with the protons generated at the anode to produce water and complete the electrical circuit. With a continuous or intermittent supply of substrate, MFCs can operate at a steady state, consistently generating electrical output. [3,4]. A two-chamber MFC can operate in a variety of configurations, the most common among which is the two-chamber MFC built in the “H” letter shape. The H-shaped systems are employed for basic investigations, e.g., analyses of energy production efficiency using new materials or communities of microorganisms responsible for organic matter degradation [5]. Another option is a single-chamber MFC, which is built of only one chamber containing both oxic and anoxic compartments. The system is devoid of an ion-selective membrane, which reduces the exploitation costs of this technology. The membrane-free systems are characterized by simplicity of design and are more economically viable than the conventional two-chamber MFC systems [6]. However, in order to obtain a potential difference on the electrodes, they need to be made of different materials featuring different electrocatalytic properties. The material of which the anode is made should be an electrocatalyst for fuel oxidation, and the cathode material should promote the oxidant’s reduction [7]. The potential difference between electrodes can also be generated by the osmosis process. This phenomenon is utilized in Osmotic Microbial Fuel Cells [8].

The MFC efficiently converts over 90% of bioenergy [9], prompting extensive investigations into MFC-based systems to enhance their technical and economic capabilities [10]. Despite the benefits of using wastewater for energy production, MFCs typically produce low voltages. The practical working voltage of MFCs usually ranges from 0.2 V to 0.7 V, compared to the theoretical maximum of 1.14 V in an open circuit. To boost the overall voltage, MFCs can be combined in series or parallel, resulting in a nearly additive increase in the total generated voltage [1,11,12].

The mechanism and efficiency of wastewater treatment with this technology is largely determined by: MFC design [13], wastewater pH, temperature [14], the configuration of electrodes [15], mediators [16], membranes [17], and biofilm formation [18]. Key issues include the availability of organic substrates to microorganisms [19] and the type of wastewater to be treated [20]. Various development initiatives have been undertaken to optimize MFC technology for the simultaneous treatment of wastewater from diverse sources to generate electrical energy. However, achieving widespread commercial implementation and realizing the full spectrum of MFC applications remain challenges. Additionally, there is a lack of information on the utilization of MFC for treating drainage water (DW) from soilless plant cultivation under cover.

In a soilless system, plants grow without soil contact, instead, their roots are embedded in a specialized substrate like mineral wool or coconut fiber and nourished with a liquid nutrient solution. This system allows for consistent high yields and product quality throughout the entire year. This plant production system generates an overflow, resulting from providing the root system of plants with excess (water and nutrients). Otherwise, there would be an increase in substrate salinity and impairment of nutrient absorption. In the case of tomato cultivation, this results in 4.5 to 12.6 L of overflow generated per each square meter of crops [21,22]. This overflow is characterized by different element ratios compared with fresh medium, high levels of nutrients and salt, as well as low levels of organic compounds. Its total nitrogen (TN) levels usually range from 150 to 600 mgN/L, total phosphorus (TP) from 30 to 400 mgP/L, organic compound levels are <80 mgCOD/L, and its electrolytic conductivity varies from 3.5 to 7.0 mS/cm [22–24]. The treatment of drainage water is challenging with conventional biological methods relying on activated sludge, mainly due to the composition [25]. Therefore, alternative treatment approaches are explored, such as biotreatment with an external organic substrate [26,27], using microalgae [28], wetlands [29] and the application of hydrogenotrophic denitrification assisted by direct electric current [30] or alternating electric current [31]. However, adopting alternative treatment methods frequently leads to an increase in overall treatment costs, including those associated with energy consumption. Previous studies have shown that the removal of nitrogen and phosphorus using electrobiological reactors, with a direct electric current

flow and an organic substrate in the form of sodium acetate, allowed for effective DW treatment. Electric current consumption using the Rotating Electrobiological Disk Contactor ranged from 118 to 2170 kWh/kgN (removed nitrogen) and from 104 to 9456 kWh/kgP (removed phosphorus) depending on the electrical current density (from 0.62 to 10.0 A/m²) and the wastewater hydraulic retention time (from 4 to 24 h). In the case of another solution, namely Sequencing Batch Biofilm Reactor, the energy consumption ranged from 49 to 144.5 kWh/kgN (removed nitrogen) and from 82 to 787 kWh/kgP (removed phosphorus) depending on the electric current density used (0.62–5.0 A/m²) at HRT 1d [32]. At the same time, DW is effectively pre-treated upon the precipitation of mainly phosphorus with calcium and magnesium ions already at pH > 7.5 [33]. Although this is a desired effect, it poses many operational hurdles caused by installation clogging [34]. This calls for the need to use, among others, an organic substrate that would aid biotreatment processes and ensure long-term operation of the system, including the ion-exchange membranes in MFC.

The energy demand depends on many factors, such as the treatment method used, system design, and the type of wastewater to be treated. This is confirmed by literature data on the treatment of other types of wastewater [35]. The need to treat wastewater while meeting specific pollution reduction demands requires constructing energy-intensive and surface-intensive facilities [36]. The use of MFC would allow reducing the energy consumption and operation costs of wastewater treatment plants and further diversifying renewable energy sources [37]. At the same time, MFC can be combined with other technologies deployed for DW treatment, such as electrocoagulation [38] or hydrophyte treatment [39]. In parallel, the phosphorus recovery from drainage water can reduce production costs by 9–719 €/d·ha. Additionally, the savings associated with the reuse of purified drainage water amount to ~16,139–33,352 €/year·ha [34].

Taking into account the composition of drainage water from the soilless tomato cultivation and the factors affecting MFC operation, a study was conducted to establish (1) the influence of the dose of organic substrate in the form of citric acid expressed by the C/N ratio of 1.0, 1.5, and 2.0 on the efficiency of DW treatment, (2) electrical energy production, and (3) the feasibility of constructing a two-chamber MFC. In the proposed solution, a biological reactor with the filling in the form of disks with biofilm served as the anode chamber for DW treatment, and a retention tank for non-treated DW—as the cathode chamber. The use of the flow-through system resulted in no need for additional aeration of the cathode chamber, due to the naturally high redox potential and oxygen concentration of raw DW. At the same time, due to its ability to dissolve calcium and magnesium deposits, citric acid was expected to aid the biological processes and ensure longevity of the ion exchange membrane.

2. Materials and Methods

2.1. Microbial Fuel Cell (MFC)

An MFC was constructed in order to investigate the possibility of energy recovery during the biotreatment of DW from the soilless tomato cultivation. The MFC consisted of two chambers separated by an ion-exchange membrane (9.08 cm²). The R1 chamber was a retention tank for DW with a submerged cathode in the form of 1 disk 12 cm in diameter. The R2 chamber, on the other hand, was a biological reactor for DW treatment with biomass attached to the filling in the form of 4 disks each measuring 12 cm in diameter, which at the same time served as an anode (Figure 1). The chambers with a capacity of 2.0 L each were made of Plexiglass and separated by membrane (in the “H” letter shape) of Nafion™117 ((C₇HF₁₃O₅S.C₂F₄)_x; Sigma-Aldrich, St. Louis, MO, USA). Carbon felt (CGT Carbon GmbH, Asbach, Germany) was used to construct the electrodes. The cathode surface area was 113 cm², and the anode surface area was 452 cm². The anode disks were connected to each other by a copper wire. The external circuit was made of copper wire and a 1 kΩ resistor. The electric current produced as result of connecting the electrodes was measured with the UT71E electric current meter (UNI-Trend Technology, Dongguan City, China). The MFC operated at ambient temperature of 20–22 °C. The biotreatment processes were

aided by an organic substrate (citric acid) fed to the R2 in a concentration expressed as the C/N ratio of 1.0 (series 1), 1.5 (series 2) and 2.0 (series 3). Based on previous studies, citric acid provided effective support for denitrification and dephosphatation processes, small growth of excessive biomass, and also reduced deposition of contaminants on reactor walls and other elements of the system thanks to its ability to remove calcium and magnesium deposits. The flow rate of the citric acid solution was kept stable and reached $100.0 \text{ cm}^3/\text{d}$. The chambers operated in a flow-through system. The flow of DW between R1 and R2 and from R2 to the external tank for the treated DW took place by gravity. The hydraulic retention time (HRT) was 2 d. Samples for analyses were taken from raw DW, from DW in R1, and from the effluent from R2. Prior to the start of the exact analyses, the system was adapted for 3 months. This aimed to establish a stable biofilm on the filling. The inoculum originated from the Municipal Wastewater Treatment Plant in Olsztyn. Each series of studies, differing in the C/N ratio, lasted 5 weeks. The first week involved adapting to the applied C/N ratio. Samples were collected over the next 4 weeks, 3 times per week ($n = 12$). Such frequency allowed for the complete turnover of the reactor's volume. At the end of each series, the reactor walls and pipes were cleaned, and the ion-exchange membrane was replaced with a new one.

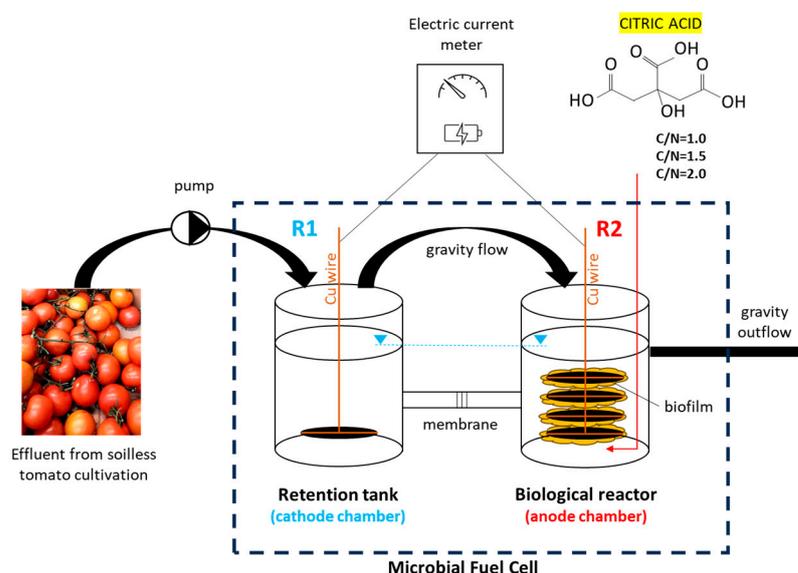


Figure 1. Research scheme.

2.2. Drainage Water (DW)

The study was carried out with drainage water from real soilless tomato cultivation at full technical scale, on a substrate of mineral wool. The cultivation space covered 20 hectares. The greenhouse was equipped with an automated system controlling temperature, humidity, solar radiation, and fertilizer dosing. The water source was the company's groundwater intake. The drainage waters studied had elevated concentrations of nitrates, total phosphorus, calcium, and magnesium, along with low levels of organic compounds (Table 1).

Table 1. Physicochemical parameters of drainage waters applied in the study.

Parameter		Series 1	Series 2	Series 3
pH	–	6.14–6.19	6.15–6.31	6.14–6.34
Electrolytic conductivity	mS/cm	6.79 ± 0.03	6.98 ± 0.06	6.95 ± 0.12
Total organic carbon		3.17 ± 0.52	12.68 ± 0.20	11.02 ± 1.12
Total nitrogen	mg/L	563.46 ± 36.11	608.20 ± 13.40	590.60 ± 9.10
N-NO ₃		562.00 ± 27.00	607.54 ± 12.50	498.54 ± 5.54
N-NO ₂		0.334 ± 0.216	0.267 ± 0.027	0.354 ± 0.052

Table 1. Cont.

Parameter		Series 1	Series 2	Series 3
N-NH ₄		0.025 ± 0.002	0.108 ± 0.003	0.017 ± 0.016
Total phosphorus		79.87 ± 0.17	77.80 ± 1.20	81.90 ± 1.40
Ca	mg/L	618.33 ± 26.39	675.50 ± 27.50	325.00 ± 50.00
Mg		213.67 ± 17.46	251.00 ± 31.00	224.00 ± 17.00

2.3. Physicochemical Analyses

The following parameters were measured: pH value, electrolytic conductivity, temperature (HQ4300 multimeter, HACH Company, Loveland, CO, USA); total nitrogen (TN) and total organic carbon (TOC) (TOC-L CPH/CPN device, Shimadzu Corporation, Kyoto, Japan; oxidative combustion-chemiluminescence method—TN; oxidizing incineration—infra-red analysis—TOC); total phosphorus (TP; HACH Lange LCK 348–350 method), nitrate (N-NO₃; HACH Lange LCK339-340), (ammonia nitrogen (N-NH₄; HACH Lange LCK303-305), and nitrite (N-NO₂ HACH Lange LCK341-342) using a DR5000 HACH Lange Spectrophotometer (Malente, Germany).

2.4. Computation Methods

The power of the electric current was determined using Equation (1).

$$P = U \times I \quad (1)$$

where:

P—electric current power [W],

U—electric current voltage [V],

I—electric current intensity [A].

The pollutant removal efficiency was calculated for COD, TN, and TP based on Equations (2) and (3).

- Pollutant load:

$$L = C \times Q \quad (2)$$

where:

L—pollutant load [mg/d],

C—concentration of pollutants [mg/L],

Q—daily wastewater flow [L/d].

- Pollutant removal efficiency:

$$\eta = \left(\frac{L_{in.} - L_{eff.}}{L_{in.}} \right) \times 100\% \quad (3)$$

where:

η —effectiveness of pollutant removal [%],

$L_{in.}$ —pollutant load in the inflowing wastewater [mg/d],

$L_{eff.}$ —pollutant load in the effluent [mg/d].

3. Results and Discussion

In the conducted study, a laboratory model of MFC was constructed based on a retention tank (R1) for DW connected by an ion-selective membrane with a reactor (R2) for bioremoval of pollutants from DW. The electrodes were linked through an external electrical circuit featuring a resistance of 1 k Ω . The system was designed to determine the feasibility of energy recovery during biotreatment of DW with the least possible interference in the basic system. Both the retention tank and biological reactors are standard equipment

for wastewater treatment systems. The use of the flow-through system enabled exploiting natural physicochemical properties of DW, i.e., high positive redox potential and dissolved oxygen concentration $>7 \text{ mgO}_2/\text{L}$. As a result, there was no need to aerate the cathode chamber, i.e., the retention tank (R1) that was continuously fed with a new portion of DW. A proven reactor with biomass attached to the filling (biofilm) served as the bioreactor. In turn, carbon felt was used as a biomass carrier (previously the filling was made of stainless-steel disks) [40,41].

DW is characterized by a low C/N ratio; hence, a solution of citric acid was used as an external organic carbon source in order to aid the biofilm development. Citric acid has previously proven itself as an effective carbon source in denitrification and dephosphatation. It also ensured a small growth of excess biomass, which reduced costs of its management [40,41].

3.1. pH, EC, Dissolved Oxygen, Redox Potential

The DW used in the study had $\text{pH} < 7.0$ (Table 1). The effluent's pH was influenced by a combination of factors, including a reduction in pH due to citric acid, partial utilization of the organic substrate by microorganisms, and an elevation in DW alkalinity attributed to denitrification. This increase in alkalinity is assumed to be about 3.0 gCaCO_3 per gram of nitrate removed, which causes an increase in wastewater pH. The pH value affects the metabolism of energy-producing microorganisms [42]. In the case of DW, it also plays a key role in the removal of TP by precipitation. The pH values measured in the treated wastewater were 7.20–7.44, 7.19–7.7 and 6.54–7.75 at the C/N ratios of 1.0, 1.5 and 2.0, respectively. These were higher values compared to the raw DW (Table 1). Despite increasing citric acid dose, there were no significant differences in pH values, which was most likely due to the higher efficiency of denitrification and a greater increase in alkalinity of the treated wastewater.

Electrolytic conductivity is one of the main parameters determining the concentration of compounds in DW. It is employed to assess the extent of nutrient medium dilution with water, ensuring plants receive sufficient water and nutrients. Moreover, elevated electrolytic conductivity facilitates electric current flow in the solution, ensuring the effectiveness of processes such as electrocoagulation or hydrogenotrophic denitrification. The EC values measured in the treated wastewater were 5.37 ± 0.47 , 5.41 ± 0.48 and $5.15 \pm 0.51 \text{ mS/cm}$ at the C/N ratios of 1.0, 1.5 and 2.0, respectively. The conducted research indicates that, despite the addition of an organic substrate, the electrolytic conductivity of the treated DW was lower in all experimental series compared to the initial electrolytic conductivity. (Table 1).

The concentration of dissolved oxygen and the redox potential were also monitored in MFC chambers throughout the experimental period. The high oxygen concentration in the retention tank (R1; cathode chamber) is indicative of the biological stability of DW and the feasibility of its long-term retention [22]. It also enables using the MFC without the need to aerate the cathode chamber. The oxygen concentration in R1 was 7.34 ± 0.49 , 7.22 ± 0.09 and $6.87 \pm 0.11 \text{ mgO}_2/\text{L}$ at C/N 1.0, 1.5 and 2.0, respectively. A slight decrease in dissolved oxygen concentration is likely due to oxygen consumption in the reaction with H^+ ions from the anode chamber and water production upon this reaction. Oxygen consumption by microorganisms for organic substrate oxidation in the anode chamber (R2; biological reactor) caused the oxygen concentration to drop below $0.5 \text{ mgO}_2/\text{L}$.

The high concentration of dissolved oxygen and oxidized pollutants (nitrates, orthophosphates, sulphates) in the cathode chamber (R1) resulted in a strongly positive redox potential of 263.90 ± 14.11 , 234.03 ± 28.10 and $192.37 \pm 15.62 \text{ mV}$ in series 1–3, respectively. The organic compounds delivered to the anode chamber (R2) caused the microorganisms to consume oxygen. Once oxygen was depleted, they reduced pollutants (including nitrates) in the denitrification process, reducing the redox potential to 110.70 ± 62.16 , 72.45 ± 34.4 and $-122.46 \pm 79.24 \text{ mV}$ at C/N 1.0, 1.5 and 2.0, respectively. A clearly negative redox potential achieved in series 3 corresponded to the highest efficiency of nitrate removal. It

also allowed concluding that the negative redox potential of MFC is achieved during DW treatment in the anode chamber only after depletion of the oxidized forms of nitrogen. The contrast in redox potentials between MFC chambers plays a crucial role in determining the electric current power, as elaborated in the subsequent section of the article.

3.2. Electrical Energy Production

The main goal of constructing a microbiological fuel cell based on a retention tank for untreated drainage water from soilless tomato cultivation (R1; cathode chamber) and a biological reactor (R2; anode chamber) was to determine the possibility of producing electrical energy to reduce the demand for grid electricity in the DW treatment system. The electrical energy generated in the form of a direct electric current could also be harnessed in DW electrocoagulation or in the bioelectrochemical treatment stage. The usefulness of both direct and alternating current in DW treatment has been confirmed in previous studies [32].

With the increase in the dose of organic substrate, the DC voltage generated in MFC increased as well, i.e., from 44.34 ± 2.47 mV (1 series) to 566.06 ± 60.82 mV (3 series). This corresponded to an electric power ranging from 0.0020 ± 0.0002 mW (1 series) to 0.3241 ± 0.0623 mW (3 series; Figure 2). The increase in current voltage between series 1 and series 2 was more than 2-fold (208%). The greatest, over 3-fold increase (314%) in DC voltage was noted between series 2 and series 3, which corresponded to a 9-fold and a 16-fold increase in MFC electric power. Such a pronounced increase in the electric current voltage was probably due to the depletion of oxidized forms of chemical compounds in the anode chamber, including primarily nitrates, with the continued presence of citric acid. This led to several consequences, including an increasing disparity in the redox potential of DW between R1 and R2.

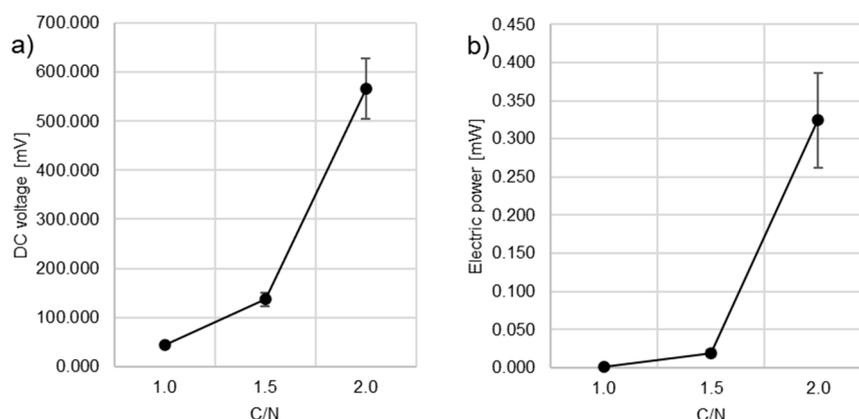


Figure 2. The voltage (a) and power (b) of the electric current generated in an MFC.

The analysis of the ratio of the electric current power generated to the organic carbon consumed and to the nitrogen load removed enabled concluding that increasing the substrate dose (and thus the C/N ratio) at the inlet to the anode chamber resulted in an increase in the current power generated per 1 mg of the consumed substrate or removed nitrogen. This increase was approximately 5-fold and 13-fold between series 1 and series 2 and between series 2 and series 3, respectively. These results indicate that the voltage and, thus, the power of the electric current obtained in the applied treatment system did not depend directly on the substrate dose supplied, but rather on the redox conditions induced in the reactor by the increased substrate load. They also allow concluding that the power of the electric current obtained per 1 mg of organic carbon consumed depended on the operating parameters of the MFC, namely: the greater was the difference in redox potentials between the anode chamber and the cathode chamber, the higher the current power generated per 1 mg of organic carbon was. This is all the more important that the electric current voltage obtained in MFC will remain at a relatively low level until denitrification or reduction of other oxidized forms of pollutants are completed. However,

these findings require further research, as the results obtained by various researchers differ significantly. Nosek and Cydzik-Kwiatkowska [43] studied electricity production in two H-type double-chamber reactors differing in the anode surface. The source of organic carbon consisted of volatile fatty acids from the anaerobic digestion of primary sludge. The cited authors observed that when fresh substrate was added, the cell voltage rose sharply to 50–70 mV and 80–90 mV when the anode surfaces were 600 cm² and 1200 cm², respectively. The voltage was then reduced to approximately 20–30 mV. The voltage generated in the cited study was significantly lower compared to the experiment described in this work, which additionally did not demonstrate so distinct changes in the generated voltages. This could be due to the effective adaptation of the system, as well as the removal of pollutants from the ion-selective membrane and other elements of the system, thanks to the use of citric acid known for its chelating properties and ability for deposit dissolution [44]. The decline in MFC efficiency is primarily attributed to fouling of the membrane. The utilization of an organic substrate to mitigate this phenomenon is justified both technically and economically [45]. At the same time, Kelly and He [46] have pinpointed the need to establish the main objective of the MFC system, i.e., choosing whether the system will focus on energy recovery from wastewater or rather on the removal of pollutants, as these two aims usually exclude one another.

3.3. Efficiency of Citric Acid Consumption

The type of the available organic substrate has a key impact on MFC performance because it serves as a nutrient medium for bacteria and, consequently, exerts selective pressure, leading to the development of an optimal biofilm [47]. The substrate is an electron donor; hence, careful control of its feeding can be used for biofilm development optimization and, thereby, for electrical energy production [48].

Citric acid is a solid, non-toxic, naturally occurring stable substance that is industrially produced, playing important roles in metabolism [49]. Thus, it can positively affect electron production by microorganisms attached to the anode in MFC [50]. Its positive effect on aiding heterotrophic denitrification and dephosphatation has been proven in both activated sludge [51] and biofilm [41,52] technology. Additional benefits of citric acid use include minimal excess biomass production and the formation of a thin biofilm, facilitating microbial activity throughout the entire biofilm depth and preventing the formation of inactive zones [40]. Close physical contact between bacterial cells and the anode is essential for the direct transfer of electrons [53,54].

Drainage water has a low content of organic compounds [22]. DW used in the present study was no exception in this case (Table 1). Three doses of citric acid used to aid the bio-removal of pollutants and provide an organic substrate for the microorganisms present on the anode were tested in MFC. They were selected based on the C/N ratio criterion, which was 1.0, 1.5 and 2.0. This aimed to determine how the dose of the organic substrate would affect both the efficiency of DW treatment in the flow-through system as well as the electric current power generated.

The daily load of organic carbon into the anode chamber (R2) in the first experimental series was 301.59 kgC/m³·d. After the treatment process, the mean TOC concentration in the effluent reached 228.73 ± 30.43 mgC/L, which corresponded to the mean TOC load discharged daily from the system, i.e., 175.79 ± 16.74 kgC/m³·d. The efficiency of organic compounds consumption reached 58.3 ± 5.5% (Figure 3). Feeding a greater load of organic compounds in the experimental series 2 and 3 caused no significant changes in their consumption efficiency, which was 65.8 ± 4.0% and 61.0 ± 5.6% in series 2 and 3, respectively. At the same time, the load of organic compounds that was consumed by the MFC microorganisms in series 2 and 3 was much higher than in series 1 and reached 300.32 ± 19.23 kgC/m³·d (series 2) and 369.08 ± 14.13 kgC/m³·d (series 3; Figure 3). Analyzing the above data, it may be concluded that the organic compounds were not fully consumed, and their consumption further decreased along with the increasing citric acid dose. The TOC concentration of DW treated in series 2 and 3 was 283.69 ± 33.00 mgC/L

and 429.87 ± 62.06 mgC/L, respectively. The increase in C/N in the subsequent series contributed to the increased efficiency of denitrification, probably due to the increase in the reaction rate and in the electrical power generated in MFC. Due to the high content of organic compounds, purified drainage waters require further treatment before being discharged into the environment. The incomplete utilization of citric acid may result from the relatively short retention time of wastewater in the reactor (2 days). This indicates the need for further research to optimize the use of substrates in the processes of purifying drainage waters and generating electrical energy.

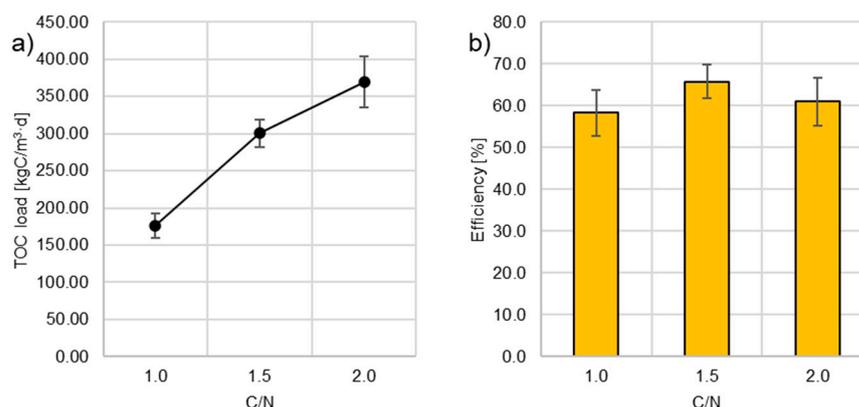


Figure 3. Load (a) and efficiency (b) of organic carbon consumption.

3.4. Nitrogen Removal Efficiency

The overflow from the soilless tomato cultivation had a high concentration of nitrates and, at the same time, practically no organic compounds that could be used by microorganisms (Table 1). The discharge of untreated DW directly into the natural environment causes eutrophication of water bodies, as well as the penetration of nitrates and nitrites into groundwater, which can continue to migrate and be absorbed, for example, with water from wells, which poses a threat to human and animal health. This also precludes or significantly hinders the use of the contaminated waters for the preparation of a new nutrient medium [55]. Previous studies have shown citric acid to be an efficient source of organic carbon expected to aid heterotrophic denitrification [41], which entails nitrate reduction under anoxic conditions mediated by anaerobic bacteria which use nitrates as an electron acceptor. Denitrification produces molecular nitrogen, nitrogen oxides and nitrites (in the case of incomplete denitrification). The denitrification process, which occurred in the MFC anode chamber covered by the biofilm, included both autotrophic denitrification and heterotrophic denitrification. In MFC, the autotrophic denitrification plays an essential role in reducing the demand for organic carbon necessary to reduce nitrates by using an anode as an electron donor [41].

The initial TN concentration in DW was 563.5 ± 36.1 , 608.2 ± 13.4 and 590.6 ± 9.1 mg N/L in series 1–3, respectively. The efficiency of TN removal increased along with the increasing C/N ratio, with the highest efficiency of $95.6 \pm 2.0\%$ obtained at C/N 2.0 and the lowest one, reaching $51.5 \pm 9.8\%$, at C/N 1.0 (Figure 4). The concentration of TN in the effluent reached 248.6 ± 50.4 , 109.6 ± 41.8 and 25.7 ± 8.4 mgN/L in series 1–3, respectively. An appropriate C/N ratio is crucial for achieving efficient denitrification [41]. Many projects have attempted to modify MFC and search for new configurations that would enable more effective treatment of different types of wastewater. For instance, Park et al. [56,57] used a flat-panel air-cathode for domestic sewage treatment, which after eight months of operation was able to remove 85% of the COD and 94% of TN. In turn, Zhang Y. et al. [58] proposed harnessing algae in a microbial fuel cell, because during growth resulting from photosynthesis, algae exhibit the ability to assimilate organic components. More than 87% of nitrogen was removed in the cited study, of which 75% through the algae biomass synthesis [46,58].

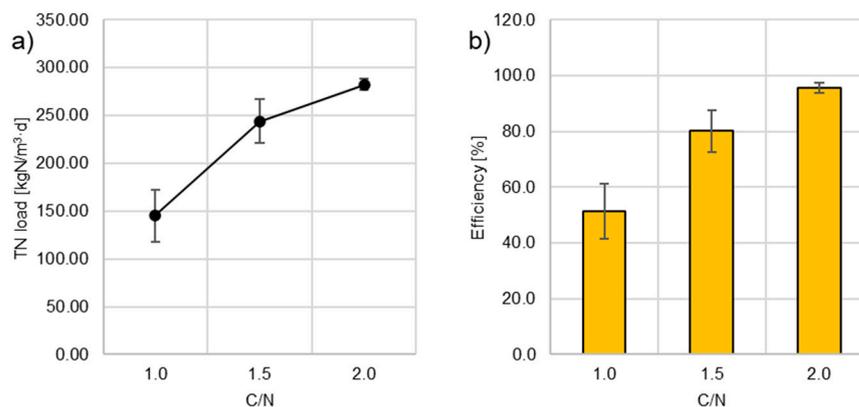


Figure 4. Removed nitrogen load (a) and denitrification efficiency (b).

The ratio of organic carbon consumption to the TN removed was further analyzed. In the case of experimental series 1 and 2, the TOC/TN ratio was similar and reached 1.28 ± 0.23 and 1.23 ± 0.10 mgC/mgN. In series 3, it increased to 1.31 ± 0.12 mgC/mgN. From the presented data, we can conclude that organic carbon was most efficiently utilized in the MFC during the denitrification of nitrate-rich wastewater. The analysis of TOC concentration in the effluent (229 ± 30 mgC/L in series 1 at the lowest tested C/N), demonstrated that a significant amount of unused organic substrate remained in each experimental series, which indicates that the HRT of DW in the R2 was too short. In addition, the higher concentration of TOC resulted in a higher rate of denitrification, which is consistent with the assumption that in reactors of this type denitrification follows the reaction described with first-order equation, i.e., the higher the concentration of substrates (in this case: organic carbon and nitrates), the faster the reaction [40]. Extending the HRT of DW in the reactor or reducing the pollutant load on reactor's filling surface could result in a more efficient citric acid consumption in the heterotrophic denitrification.

Raw DW had a low concentration of ammonia nitrogen, reaching 0.025 ± 0.002 mgN/L in series 1, 0.108 ± 0.003 mgN/L in series 2 and 0.017 ± 0.016 mgN/L in series 3. A similar observation was made for the effluent, where its concentration reached 0.025 ± 0.010 , 0.241 ± 0.127 and 0.253 ± 0.230 mgN/L in series 1–3, respectively. A high concentration of ammonia nitrogen may inhibit the activity of anode-related bacteria [46]. Based on the results obtained, it can be concluded that ammonia nitrogen was not a significant factor in the conducted experiment.

Nitrite concentration in the effluent was low compared to the TN concentration and, depending on the C/N ratio, reached: 2.794 ± 0.851 mgN/L, 1.895 ± 0.359 mgN/L and 0.211 ± 0.201 mgN/L in series 1–3, respectively. An increased concentration of nitrites in the effluent, compared to that determined in untreated DW (Table 1), was probably due to the use of citric acid. Previous studies have demonstrated a periodic increase in nitrite concentration as an intermediate product of heterotrophic denitrification aided by this carbon source [40]. Nitrite accumulation may also result from insufficient adaptation of the reactor. Microorganisms of the second phase of denitrification, reducing nitrites to molecular nitrogen, are characterized by slower growth, which requires their longer adaptation time. However, the values obtained in the present study correspond respectively to 1.12%, 1.73% and 0.82% of the total nitrogen in the effluent, which indicates stable operation of R2. The accumulation of nitrites may upset the balance of denitrifying microorganisms, whereas their excess may competitively inhibit nitrate reduction, leading to suppressed denitrification. However, in MFC, both nitrites and nitrates can be used interchangeably by exogenous bacteria as electron acceptors to reduce nitrogen from wastewater while producing bioelectricity [59].

3.5. Phosphorus, Calcium and Magnesium

Phosphorus is one of the biogenic elements, the excess of which in the natural environment affects water eutrophication, leading to the imbalance of aquatic ecosystems. It can be removed from wastewater via biological methods, via incorporation into the cell biomass or via physicochemical processes, including precipitation and sorption. According to various sources, the phosphorus content in dry matter of activated sludge or ash from activated sludge varies from a few to several percent. Phosphorus removal from wastewater via the biological method is based on the use of specific activated sludge bacteria, which are able to accumulate phosphorus in their biomass in amounts exceeding their metabolic demand (>2% P in sludge dry matter) [52]. Phosphorus can also be removed from wastewater via a chemical pathway including processes such as precipitation, coagulation, flocculation, particulate separation and sorption.

The removal efficiency of TP was similar in all experimental series and reached $89.0 \pm 2.4\%$, $89.7 \pm 1.9\%$ and $90.5 \pm 2.0\%$ in series 1–3, respectively. This corresponded to the total phosphorus concentration in the effluent reaching 8.78 ± 2.48 , 7.25 ± 1.35 , 6.83 ± 1.72 mgP/L, respectively. The removed TP load ranged from 34.91 ± 0.74 kgP/m³·d (C/N 1.5) to 37.06 ± 0.82 kgP/m³·d (C/N 2.0). Incrementing the external carbon source dose did not markedly enhance the overall phosphorus removal efficiency (Figure 5). The consistently high efficiency of phosphorus removal, irrespective of the citric acid dose, is likely attributed to precipitation with calcium and magnesium ions. At pH levels below 7.2, phosphates predominantly exist in the H₂PO₄ form, forming easily soluble compounds in conjunction with calcium and magnesium ions. In turn, at pH 7.2–12.3, most phosphates occur as HPO₄²⁻, form stable compounds with calcium and magnesium ions and are further precipitated [60,61]. The concentration of calcium ions in untreated DW ranged from 300.00 ± 50.00 mgCa/L to 675.50 ± 27.50 mgCa/L (Table 1). The reduction of nitrates in the anode chamber (R2) resulted in the increased alkalinity and pH value of the treated wastewater. The calcium ion concentration in the treated DW reached 323.72 ± 88.34 , 446.80 ± 64.41 and 222.79 ± 25.62 mgCa/L in experimental series 1–3, respectively. This corresponded to the $47.65 \pm 14.29\%$, $33.95 \pm 9.52\%$ and $31.45 \pm 7.88\%$ removal efficiency of calcium ions, respectively. The lower efficiency of calcium and magnesium removal in series 3 was, probably, due to the highest applied dose of citric acid, which exhibits chelating properties and dissolves calcium and magnesium compounds [44]. However, the highest substrate dose did not result in any substantial decrease in dephosphatation efficiency. In addition to the formation of compounds with calcium and magnesium, phosphates can also undergo sorption on the previously produced sludge. The concentration of magnesium ions in DW was similar in all experimental series (Table 1). The efficiency of magnesium removal reached $28.48 \pm 12.57\%$, $28.56 \pm 8.25\%$, $18.30 \pm 7.87\%$ in the series 1–3, respectively, which corresponded to the magnesium concentration in the treated DW at 165.74 ± 39.03 mgMg/L, 179.31 ± 20.71 mgMg/L, 183.00 ± 17.63 mgMg/L, respectively.

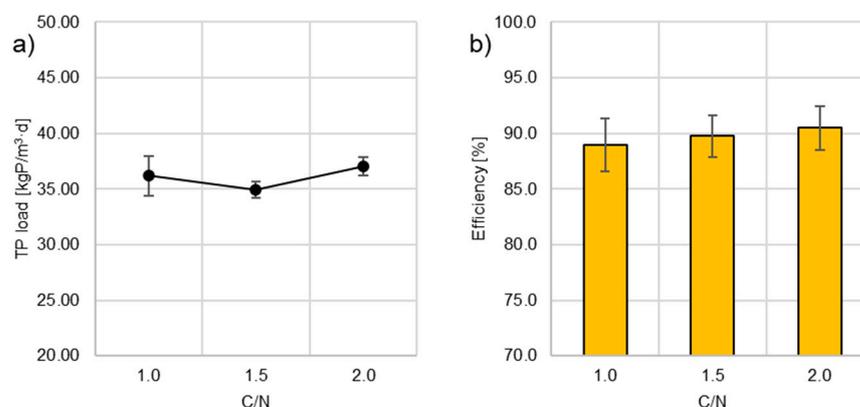


Figure 5. Removed phosphorus load (a) and dephosphatation efficiency (b).

For drainage water, past research indicates a significant impact of pH changes on phosphorus precipitation, particularly with calcium and magnesium ions. However, an alkalizing agent such as $\text{Ca}(\text{OH})_2$, KOH , or NH_4OH needed to be added to DW to elevate its pH to above 7 [34]. In the present study, the used of the alkalizing agent was replaced by a natural alkalinity increase due to nitrate reduction. In our previous work [62], we presented the effectiveness of removing nitrates and orthophosphates using chitosan in the form of hydrogel beads. The efficiency of nitrate removal ranged from 53.2% to 76.7%, while for phosphate removal, it varied between 79.4% and 92.8%. Another solution may be the use of electrocoagulation, which allows for the effective removal of phosphorus compounds via adsorption and precipitation. Electrocoagulation typically involves the use of anodes that undergo electrolytic dissolution. This process allows the introduction of appropriate ions into the treated wastewater or water, which continue to serve as coagulants. However, there are no results so far regarding the use of this method for DW treatment [63].

4. Conclusions

Drainage water from soilless tomato cultivation under greenhouse conditions, characterized by high nitrogen and phosphorus concentrations and low organic compounds, poses challenges for treatment technologies. The conducted research aimed to assess the denitrification and dephosphatation potential enhanced by an external carbon source, specifically citric acid, in a biofilm reactor. Three citric acid doses expressed as the C/N ratio were applied: 1.0, 1.5, and 2.0. Simultaneously, due to the high electrolytic conductivity and redox potential of untreated drainage waters, the possibility of electricity production through a microbial fuel cell was tested. For this purpose, a biological reactor was coupled with an ion-selective membrane to a retention tank for untreated drainage waters. The findings from the conducted research allowed for the formulation of the following conclusions:

- Citric acid is an efficient organic substrate for both aiding biological treatment and for generating electrical energy in a microbial fuel cell.
- With the increase in the C/N ratio from 1.0 to 2.0, the voltage of the electric current increased from 44.34 ± 60.92 mV to 566.06 ± 2.47 mV, corresponding to the electric current power increase from 0.0020 ± 0.0002 mW to 0.3241 ± 0.0623 mW.
- The electric current's power per 1 mg of consumed organic carbon is contingent on the operating parameters of the Microbial Fuel Cell (MFC). A greater disparity in redox potentials between the anode and cathode chambers results in higher current power generated per 1 mg of organic carbon.
- The best performance of MFC is achieved after depletion of the oxidized forms of pollutants, when the redox potential decreases in the anode chamber in the presence of an organic substrate.
- Citric acid consumption efficiency was $58.3 \pm 5.5\%$, $65.8 \pm 4.0\%$, and $61.0 \pm 5.6\%$ at C/N ratios of 1.0, 1.5, and 2.0, respectively. Simultaneously, the substrate facilitated the formation of a stable biofilm on the filling, which served as both the anode in the MFC. The chelating properties of citric acid, along with its sludge-dissolving ability, contributed to a decrease in ion-exchange membrane contamination.
- The denitrification efficiency increased with higher citric acid doses, reaching $51.47 \pm 7.57\%$, $80.18 \pm 9.84\%$, and $95.60 \pm 1.99\%$ at C/N ratios of 1.0, 1.5, and 2.0, respectively. Simultaneously, there was no rise in ammonia nitrogen concentration in the effluent, and nitrites accounted for 1.12%, 1.73%, and 0.82% of the total nitrogen, respectively.
- Regardless of the organic substrate dose applied, the efficiency of dephosphatation was high and reached 88.97 ± 2.41 ; 89.75 ± 1.90 and $90.48 \pm 1.99\%$ at C/N 1.0, 1.5 and 2.0, respectively. This was due to the removal of phosphates by precipitation with calcium and magnesium ions upon the increased alkalinity of the treated DW caused by nitrate reduction.

- The MFC constructed based on a retention tank for untreated DW and a biological reactor for DW treatment fed with an external carbon source seems to represent a promising source of sustainable, renewable energy, allowing for its further diversification.
- Future research should focus on assessing the influence of substrate type and technological parameters, including hydraulic retention time and pollutant load, on the effectiveness of treating DW and generating energy in MFCs.

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