

Article

Effect of Bio-Electrochemical Treatment of Hydroponic Effluent on the Nutrient Content

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Abstract: This study examined the effect of bio-electrochemical treatment processes on nitrogen and phosphorus removal, but it also evaluated the impact of the treatment processes on the concentration of other nutrients present in hydroponic effluent. A bio-electrochemical reactor (BER) was used in the experiment to treat effluent from the hydroponic cultivation of tomatoes. It was stated that the nitrogen removal efficiency decreased with increasing current density. The study showed that an electric current density of 0.63 A/m² ensured the lowest effluent nitrate concentration. The nitrogen removal efficiency ranged from 41.6%-R1 (density of 0.63 A/m²) to 8.9%-R4 (density of 5 A/m²). Electric current density higher than 1.25 A/m² resulted in lower total nitrogen removal efficiency. The total phosphorus removal efficiency increased with increasing electric current density. The phosphorus removal efficiency was the lowest—95.1%—in the R1 reactor, whereas it was the highest in R4—99.1%. The concentration of the other elements in the effluent was determined. The content of molybdenum, boron, sulphates, and potassium did not meet the acceptable norms for discharging hydroponic effluent into the environment. The study showed that bio-electrochemical processes taking place in BER caused secondary contamination of hydroponic wastewater with molybdenum ions.

Keywords: hydroponic effluent; macro- and micro elements; bio-electrochemical wastewater treatment; current density



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1. Introduction

Climate change, an increase in population, and environmental pollution present the world with two challenges in the near future: providing a sufficient amount of adequate-quality food and sustainable use of natural resources [1]. An opportunity for facing these challenges is created by soilless (hydroponic) cultivation, which allows for reducing soil contamination (by pesticides), gives a high-quality yield and reduces the amount of water consumed [2,3]. The cultivation is conducted on a special substrate (for tomatoes, it is mainly mineral wool), which is permeated by an aqueous solution of fertilizers. The medium contains macronutrients (nitrogen, phosphorus, potassium, calcium, magnesium and sulphur); trace elements (iron, manganese, boron, copper, zinc and molybdenum) and microelements: sodium, chlorine and aluminium [4]. The crops are mainly fertilized in open systems [5]. According to Dyśko et al. [6], 70% of the medium supplied is used by plants, with the remaining 30% being used as overflow and discharged, untreated, into the environment. According to the regulations in Poland, horticultural effluent should be treated, and the nitrogen and phosphorus levels, before being discharged to the environment, should not exceed 30 mg N/L and 3 mg P/L [5,7,8]. Therefore, effluent treatment and nutrient recovery are still research objects worldwide. The effluent treatment methods currently under development can be divided into: methods based on denitrification, systems using constructed wetlands (CWs), systems based on microalgae cultivation, and the use of activated carbon methods [9].

Nitrogen removal can be performed with the use of heterotrophic or autotrophic denitrification or by electrochemical nitrogen reduction. Autotrophic denitrification uses inorganic carbon (and gaseous hydrogen) as an electron donor. Cathode water electrolysis is a source of hydrogen in the bio-electrochemical reactor [5,10,11]. The use of an electric current also allows for cathode nitrate reduction [12,13].

Monomeric and polymeric forms of aluminium or iron hydroxides are formed when a current flows through the electrodes. This is followed by agglomeration of the hydroxides with destabilised contaminations and the formation of flocs [14,15]. Applying electric current and suitable pH helps to retrieve phosphorus by electrochemical means without adding chemical substances [16]. Due to lower sludge formation and lower energy demand, an iron electrode is a better solution than an aluminum one [17]. Shahedi et al. [18] noted that a combination of electrocoagulation with biological treatment methods helps to remove many contaminants from effluents.

The authors' earlier research showed that the application of a current with an aluminium electrode and an external carbon source helps to purify hydroponic effluent effectively [5,11,19,20]. Other studies have focused on nitrogen and phosphorus removal from hydroponic effluent. Kwon et al. [21] point out that not enough emphasis is placed on the removal of secondary elements (classified as macro- and micro elements) from effluent. The findings of Bryszewski et al. [11] suggest that sludge formed as a result of bio-electrochemical treatment of wastewater from hydroponic tomato cultivation could be applied as a fertilizer.

Previous research on the treatment of hydroponic wastewater focused on the removal of phosphorus and nitrogen, due to their high concentrations. It was proved that the efficiency of nitrogen and phosphorus removal in BERs with aluminum electrodes depended on the electric current density [3,5,9,20,21]. Analyses of macro- and micro element concentrations in sludge, formed during hydroponic wastewater treatment, were performed sporadically [11]. However, the concentrations of macro- and micro elements in treated wastewater, and the role of electric current density in the elements' removal, were not investigated. The results of such research would show the scale of the loss of natural resources resulting from discharging hydroponic cultivation wastewater into the environment.

Therefore, the aim of this study was to determine: (1) the impact of the current density on the nitrogen and phosphorus removal in BER with an iron electrode, (2) the impact of bio-electrochemical treatment on the content of the other macro- and micro elements in treated effluent from hydroponic tomato cultivation. The results enabled determination of the efficiency of the contaminants' removal.

2. Materials and Methods

The effluent from hydroponic tomato cultivation in an open system, on a mineral wool substrate, was used. It was collected in summer and subsequently used in the tests during a 3-month period. This allowed for maintenance of its constant physical and chemical parameters. The properties of the effluent were: pH 5.35 ± 0.42 ; electrolytic conductivity (EC) 7.572 ± 0.479 mS/cm; temperature 19.5 ± 1.0 °C; total organic carbon (TOC) 15.8 ± 1.2 mg C/L; total nitrogen (TN) 592.3 ± 9.7 mg N/L; ammonium nitrogen 0.67 ± 0.19 mg N/L; nitrites 0.18 ± 0.07 mg N/L; nitrates 591.3 ± 10.1 mg N/L and total phosphorus (TP) 145.9 ± 4.4 mg P/L.

A bio-electrochemical reactor was used in the experiment. The active reactor volume was 2 L. Five stainless steel disks were used as the cathode, and they also acted as the reactor packing (chemical composition C ≤ 0.030 ; Si ≤ 0.75 ; Mn ≤ 2.25 ; P ≤ 0.025 ; S ≤ 0.01 ; N ≤ 0.1 ; Cr 17.00–19.00; Ni 13.00–15.00; Mo ≤ 2.25 ; Cu ≤ 0.5). An anode made of carbon steel was mounted inside the reactor (chemical composition: C ≤ 0.12 ; Mn ≤ 0.60 ; P ≤ 0.045 ; S ≤ 0.045).

Each reactor was connected to a direct current (DC) with the following density (J): 0.63 A/m^2 (R1), 1.25 A/m^2 (R2), 2.5 A/m^2 (R3), 5 A/m^2 (R4) (Figure 1). The current density

was selected based on earlier research by Rodziewicz et al. [19]. The power was supplied with a Rohde & Schwarz HMP 4040 (Munich, Germany).

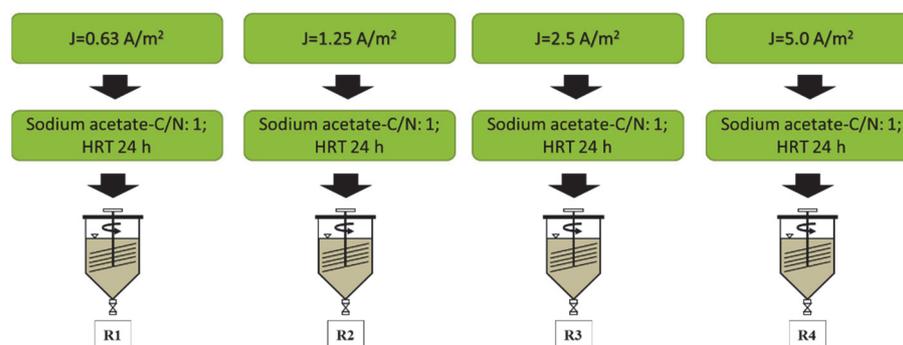


Figure 1. Experimental design.

Sodium acetate, at a carbon to nitrogen (C:N) ratio of 1.0 (TOC 592 ± 4.2 mg C/L), was added to facilitate the biofilm development in the BER. The reactor operation supervision began after the reactor start-up period of 4 weeks. Subsequently, the experiment was conducted for two months. Hydraulic retention time (HRT) in the reactor was 24 h, and the reactor operated at 20–22 °C. Reactors worked in anaerobic conditions.

Physicochemical analyses of raw and treated wastewater were carried out on filtered samples.

The analyses used a TOC-L CPH/CPN total organic carbon analyser (Shimadzu, Japan) and included: the content of total organic carbon (TOC) (the oxidizing incineration—infra-red) and the content of total nitrogen (the incinerating-chemiluminescence method).

Physicochemical analyses made on a UV-VIS 5000 DR spectrophotometer included: the content of total phosphorus (TP, with the colorimetric method, HACH Lange LCK 348–350); the content of nitrates (with the colorimetric method, HACH Lange LCK 339 and LCK 340); the content of ammonia, nitrogen and nitrites (with the colorimetric method HACH Lange LCK 303 and LCK 342); the content of aluminium, (with the colorimetric method, HACH Lange LCK 301); the content of iron (with the colorimetric method, HACH Lange LCK 301); the content of molybdenum (with the colorimetric method, HACH Lange LCK 330); the content of copper (with the colorimetric method, HACH Lange LCK 329); the content of chloride (with the colorimetric method, HACH Lange LCK 311); the content of sulphate (with the colorimetric method, HACH Lange LCK 153); the content of manganese (with the colorimetric method, HACH Lange LCW 032); the content of boron (with the colorimetric method, HACH Lange LCK 307); the content of zinc (with the colorimetric method, HACH Lange LCK 360); the content of potassium (with the colorimetric method, HACH Lange LCK 328); the content of calcium and magnesium (with the colorimetric method, HACH Lange LCK 327).

Electrolytic conductivity, pH, and temperature were measured with a CX-461 meter (Elmetron, Zabrze, Poland).

3. Results and Discussion

3.1. Nitrogen and Phosphorus Removal

The total nitrogen concentration in hydroponic effluent was 580.3 ± 21.6 mg N/L. The concentrations of various nitrogen forms in treated wastewater are shown in Figure 2. The total nitrogen concentration in reactors R1 and R2 was found to be similar— 338.7 ± 30.2 mg N/L and 338.9 ± 37.3 mg N/L, respectively. Subsequently, the TN concentration grew, with increasing current density, to 488.0 ± 38.3 mg N/L (R3) and 528.0 ± 37.9 mg N/L (R4). The nitrate's concentration grew with increasing current density. The lowest value was found in R1 (206.6 ± 15.5 mg N/L) and the highest in R4 (542.8 ± 41.0 mg N/L). The ammonium concentration was also the lowest in R1— 0.5 ± 0.5 mg N/L, and the highest in R4— 7.5 ± 5.1 mg N/L. The nitrite's concentration at

the start of the treatment process was 0.2 ± 0.1 mg N/L. The NO_2^- concentration in reactor R1 effluent increased to 131.5 ± 14.2 mg N/L. Lower nitrite concentrations were found in reactors R3 and R4— 1.1 ± 0.9 mg N/L and 1.0 ± 0.3 mg N/L, respectively. Despite a similar TN effluent concentration in the R1 and R2 reactors, the nitrite’s concentration was lower in the R2 reactor. This implies that use of a higher electric current density lowers the nitrite concentration. Tong et al. [22] used a synthetic effluent containing high levels of organic compounds and applied a current of 0–1600 mA/m². They also found that nitrite concentration could be reduced at an appropriate current density (400 mA/m²). Similar findings were observed by Liu et al. [23] during treatment of synthetic groundwater at a current density exceeding 200 mA/m².

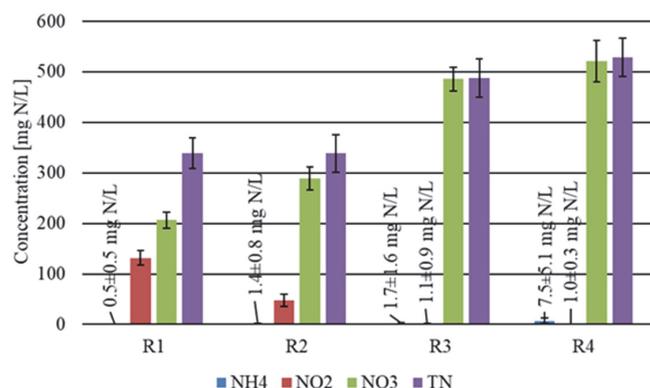


Figure 2. Concentration of various nitrogen forms in BER effluent.

The nitrogen-removal efficiency decreased with increasing current density—from 41.6% (R1) to 8.9% (R4) (Figure 3). This is probably a consequence of the fact that mainly heterotrophic denitrification processes dominated in R1 and R2 (because of low J), hence the high nitrate concentration in effluent from these reactors. However, in the R3 and R4 reactors, nitrogen was probably removed by cathode reduction and autotrophic denitrification processes. In an earlier study, authors treated synthetic hydroponic wastewater in a rotating electrobiological contactor (RBC), with an aluminium anode and sodium acetate as an external carbon source (C/N-0.5), and they found that TN removal efficiency increased, with increasing current density, from 23.4% ($J = 0.63$ A/m²) to 68.6% ($J = 10$ A/m²). The present study showed that the use of a current with a density exceeding 1.25 A/m² resulted in lower efficiency of total nitrogen removal. This may be due to different wastewater characteristics and different anode material. According to Tong et al. [10], current with a density of 1.6 A/m² has an inhibitory effect on denitrification. Liu et al. [24] removed 85.2% of nitrates in a bio-electrochemical reactor at an initial concentration of 50 mg N/L.

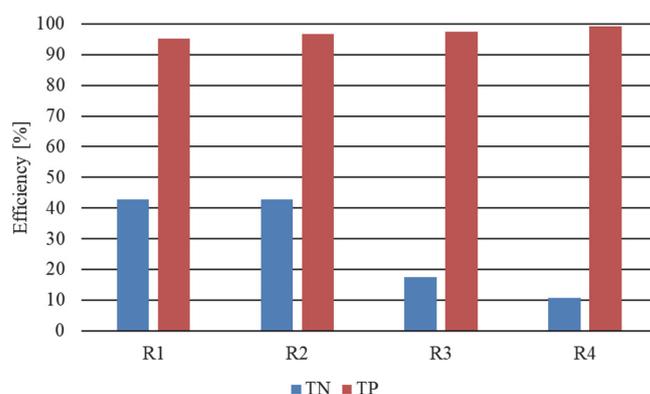


Figure 3. Efficiency of total nitrogen and total phosphorus removal from hydroponic effluent in a BER.

Phosphorus was removed owing to the formation of iron cations: Fe^{2+} and Fe^{3+} on the anode, which destabilises colloid particles in the aqueous solution and forms monomeric and polymeric hydroxy complexes. Hydroxy iron complexes show adsorptive properties and form large aggregates with phosphorus. Additionally, it should be taken into account that hydroponic effluent contains high concentrations of calcium and magnesium, which can form phosphates with phosphorus in the effluent, at a pH above 7.2 [14,25].

The total phosphorus concentration decreased with increasing electric current density amperage. The lowest phosphorus concentration was in R4— 1.28 ± 0.97 mg P/L ($J = 5$ A/m²), and the highest in R1— 7.11 ± 1.8 mg P/L ($J = 0.63$ A/m²). The total phosphorus removal efficiency grew with increasing electric current density (Figure 3). It was the lowest—95.1%—in the R1 reactor and the highest in R4—99.1%.

Phosphorus removal in this study was effected by electrocoagulation and phosphorus precipitation with calcium and magnesium ions. TP removal in R1 and R2 was probably effected mainly by means of precipitation of phosphorus with calcium and magnesium ions, because the pH value was above 8. According to the findings of Mielcarek et al. [5], the precipitation of calcium and magnesium phosphate is mainly responsible for PO_4^{3-} removal in a bioreactor at a pH of above 7.5.

The pH in R3 and R4 was 6.09 ± 0.99 and 5.58 ± 0.86 , respectively. According to Józwiak et al. [26], phosphorus removal by precipitation with Ca^{2+} and Mg^{2+} is also possible, but with lower efficiency, at a pH of over 6.2. It can be assumed, based on the mentioned studies [5,26], that phosphorus removal in these reactors was dominated by electrocoagulation. These assumptions are confirmed by an increase in Ca^{2+} and Mg^{2+} concentrations in the effluent, in accordance with growing electric current density (Figure 4).

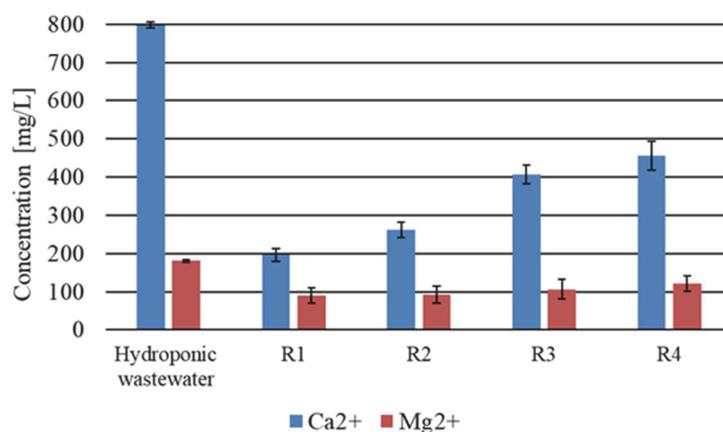


Figure 4. Ca^{2+} and Mg^{2+} concentration in hydroponic effluent and in treated wastewater.

3.2. Use of Organic Compounds

The addition of the external carbon source was dispensed gradually, in order to ensure sufficient amounts of carbon for biofilm development, because hydroponic effluent has a low C/N ratio. An external carbon source added in incorrect quantities can become a secondary contaminant [27]. The organic load, supplied to the reactor with the effluent, was 1184.4 ± 9.6 mg C/d. The value of organic load removed decreased with growing electric current density (Figure 5). The TOC removal efficiency ranged from 67.7% (R4) to 95.9% (R1). Organic compounds in this study were used as a carbon source by the microorganisms, effecting heterotrophic denitrification. Moreover, part of the organic compounds in electrochemical systems can be removed by adsorption of dissolved organic compounds on the surface of hydroxy flocules, and by direct oxidation of organic matter on the anode surface [28–30].

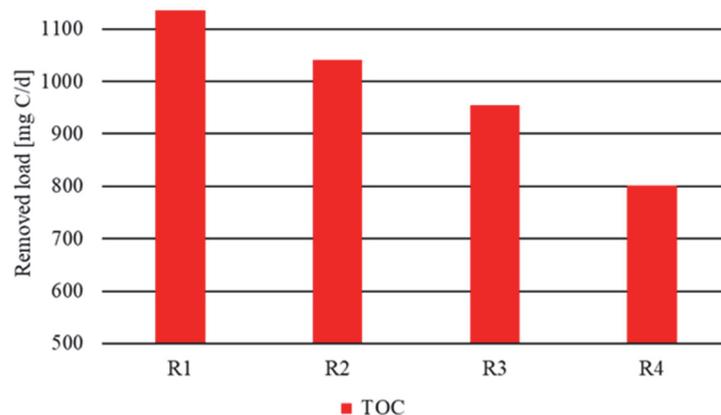


Figure 5. Organic compound load removed in the BER.

Tong et al. [10] and Rodziewicz et al. [19] showed that the growth of organic compound concentration with increasing current density in the bioreactor is a consequence of the decreasing activity of heterotrophic bacteria. Kwon et al. [21] treated effluent from hydroponic cultivation in an SBR reactor with methanol as an external carbon source, and showed that phosphorus, nitrogen and COD removal efficiency of 99.8%, 89.5% and 100%, respectively, can be achieved with a carbon dose of 2.86 g O₂ COD/g NO₃[−].

3.3. pH and Electrolytic Conductivity

The pH and EC in the hydroponic effluent were 5.35 ± 0.42 and 7.57 ± 0.48 mS/cm, respectively. The pH in wastewater after treatment decreased with increasing J , from 8.57 ± 0.72 (R1) to 5.58 ± 0.80 (R4). This results from the production of larger amounts of H⁺ ions at higher electric current densities and a decrease in the heterotrophic denitrification process share, in which nitrate reduction results in the use of acid equivalent (H⁺) [11]. The solution pH does not change in bio-electrochemical systems with electrocoagulation. This is attributed to “ion buffering”, and neutralisation of H⁺ produced on the anode by OH[−] ions generated on the cathode [31]. However, as OH[−] ions are consumed for precipitation reactions, the accumulation of H⁺ results in a pH decrease, which particularly manifests at high current densities and with the use of the solution buffer capacity [16,32]. The pH decrease in the R3 and R4 reactors in this study is attributed to the exhaustion of the effluent buffer capacity.

The lowest EC was found in the R2 reactor— 6.03 ± 0.63 mS/cm. The highest levels were found in the R3 and R4 reactors— 6.70 ± 0.79 mS/cm and 6.64 ± 0.79 mS/cm, respectively. A greater conductivity decrease at lower current densities results from larger amounts of removed NO₃[−] and precipitation of calcium, magnesium and phosphorus ions as deposits. Similar findings were observed by Mielcarek et al. [5] when they treated hydroponic effluent with alternating current ($J = 8.8$ A/m²) and sodium acetate at C/N-1. Kwon et al. [21] treated hydroponic effluent in an SBR with methanol and found EC to decrease, as a result of denitrification, from 4 mS/cm to 2.3 mS/cm.

3.4. Impact of Treatment in a BER on the Concentration of Other Macro- and Micro Elements

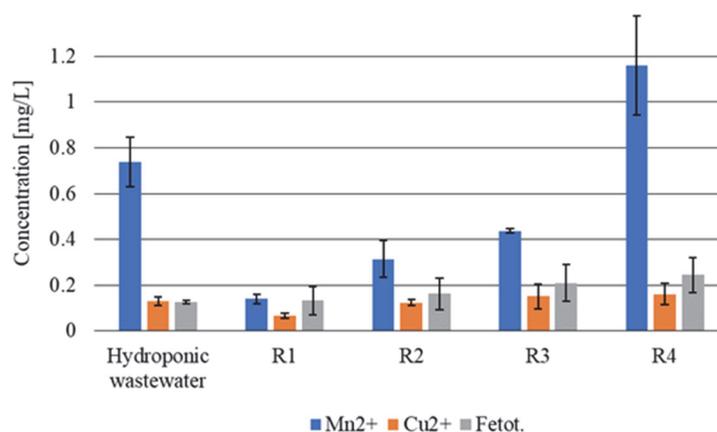
Previous studies that involved hydroponic effluent treatment have focused on nitrogen and phosphorus removal. However, not enough emphasis has been placed on the other macro- and micro elements [9]. The acceptable content of organic compounds, nitrogen and phosphorus in horticultural effluent (including hydroponic wastewater) is defined in the relevant legal regulations. Apart from the basic physicochemical parameters (TOC, TN, TP), hydroponic effluents should meet acceptable levels with respect to the other elements contained in them [5,7,8]. The macronutrients- and micro elements' concentration in the hydroponic wastewater, and their acceptable levels, according to Polish legislation are presented in Table 1.

Table 1. The macronutrients- and micro elements' concentration in the hydroponic wastewater, and their acceptable levels, according to Polish legislation [7,8].

Chemical Element	Mean Value with Standard Deviation	Maximum Permissible Values of Pollutants for Biodegradable Industrial Wastewater Generated during the Production and Processing of Fruit and Vegetables Discharged into Water or Ground	Permissible Values of Pollution Indicators in Industrial Wastewater Introduced into Sewage System
Mo ⁶⁺	2.87 ± 0.17 mg Mo ⁶⁺ /L	1	1
Mn ²⁺	0.738 ± 0.109 mg Mn ²⁺ /L	-	-
B ²⁺	1.75 ± 0.06 mg B ²⁺ /L	1	10
Cu ²⁺	0.130 ± 0.019 mg Cu ²⁺ /L	0.5	1
Zn ²⁺	1.65 ± 0.26 mg Zn ²⁺ /L	2	5
K ⁺	1276.9 ± 96.7 mg K ⁺ /L	80	-
SO ₄ ²⁻	1425.0 ± 102.6 mg SO ₄ ²⁻ /L	500	500
Cl ⁻	91.8 ± 6.1 mg Cl ⁻ /L	1000	1000
Al ³⁺	<0.02 mg Al ³⁺ /L	3	3
Fe _{tot.}	0.127 ± 0.006 mg Fe _{tot.} /L	10	10
Ca ²⁺	797.0 ± 3.6 mg Ca ²⁺ /L	-	-
Mg ²⁺	181.1 ± 3.4 mg Mg ²⁺ /L	-	-

Apart from the high nitrogen and phosphorus content, the concentrations of molybdenum, boron, sulphates and potassium prevent untreated hydroponic effluent from being discharged into the environment. According to the regulations on horticultural effluent discharge into the environment, the molybdenum and sulphate concentrations in effluent from hydroponic tomato cultivation also exceed the norms. Therefore, current and future studies should include extended physicochemical analysis.

The copper and iron concentrations in the effluent, after treatment in BERs, grew with increasing electric current density (Figure 6). The mean total iron concentration in the effluent ranged from 0.133 ± 0.062 mg Fe_{tot.}/L (R1) to 0.244 ± 0.076 mg Fe_{tot.}/L (R4). It was higher in the R2-R4 reactors' effluent than in wastewater entering the reactors. The Cu²⁺ concentration was 0.066 ± 0.011 mg Cu²⁺/L at the lowest current density, and it was the highest in R4— 0.162 ± 0.048 mg Cu²⁺/L. The copper concentration in R3 and R4 was higher than in the untreated effluent. The manganese concentration ranged from 0.141 ± 0.021 mg Mn²⁺/L (R1) to 1.160 ± 0.217 mg Mn²⁺/L (R4). The Mn²⁺ concentration in R4 was higher than in the hydroponic.

**Figure 6.** Concentration of Mn²⁺, Cu²⁺ and Fe_{tot.} in BER effluent.

The aluminium concentration in R1 was outside the detectability range (<0.2 mg Al³⁺/L), as was the effluent entering the reactor. The Al³⁺ concentration grew with increasing current density, from 0.067 ± 0.003 mg Al³⁺/L to 0.351 ± 0.048 mg Al³⁺/L, in R1

and R4, respectively (Figure 4). This is probably because low-carbon steel, which was the material for the anode used in the experiment, can contain up to 0.3% aluminium [33].

The molybdenum concentration in treated wastewater from R1 and R2 was 74.9 ± 14.0 mg Mo⁶⁺/L and 116.7 ± 6.9 mg Mo⁶⁺/L, respectively. It was much higher than in the hydroponic wastewater. In R3, the molybdenum content was lower, and was 9.7 ± 3.6 mg Mo⁶⁺/L. The molybdenum concentration in R4 was similar to that in the untreated hydroponic wastewater— 2.8 ± 0.5 mg Mo⁶⁺/L.

A stainless steel cathode and a low-carbon steel anode were used in the reactor. It can be assumed, based on the steel's chemical composition, that part of the Mn²⁺, Cu²⁺, Fe_{tot} and Mo⁶⁺ ions were supplied to the effluent of the BERs as a result of electrode corrosion. Aluminium electrodes can undergo cathodic dissolution by hydroxyl ions formed during water hydrolysis [34,35]. Electrode corrosion can also be caused by the action of salts, alkalis and acids [36]. A lower molybdenum concentration in BER's effluent at higher current densities is probably a consequence of the molybdenum consumption from the electrodes at the start-up, or coagulant removal on floccules, the amount of which is larger at higher current densities. The literature provides information on the possibility of removal of 99.9% of molybdenum from potable water (reduction from 9.95 mg/L to 0.006 mg/L) [37]. The findings of Zhang et al. [38] show that effective molybdenum removal from the solution takes place in an acidic environment at a suitable Fe/Mo ion ratio.

The highest concentrations of Mg²⁺ and Ca²⁺ in the BER effluent were 132.9 ± 41.4 mg Mg²⁺/L in R1 and 455.4 ± 37.6 mg Ca²⁺/L in R4. The lowest calcium ion concentration was found in R1, and the lowest concentration of magnesium ions was found in R4 (196.2 ± 16.5 mg Ca²⁺/L and 93.8 ± 27 mg Mg²⁺/L, respectively). These ions are removed mainly by precipitation of calcium and magnesium phosphates in an alkaline environment [11,26,39,40]. Calcium and magnesium in hydroponic effluent can form sludges with SO₄²⁻; they create an insulation layer on the electrodes, which can be dissolved by adding Cl⁻ [41]. Earlier studies by Bryszewski et al. [11] and Mielcarek et al. [5] showed also that magnesium and calcium concentrations decreased following the application of bio-electrochemical and biological processes in an alkaline environment.

No considerable concentration changes for boron ions were observed following the treatment in the BER. The lowest boron content was in R2 effluent (1.46 ± 0.09 mg B²⁺/L), and the highest was in R4 (1.61 ± 0.23 mg B²⁺/L). Similar levels were found in R1 and R3: 1.55 ± 0.03 mg B²⁺/L and 1.53 ± 0.02 mg B²⁺/L, respectively.

The zinc content decreased during treatment with increasing current density, and it was similar in R1 and R2, as well as in R3 and R4. The Zn²⁺ content in R1 and R2 was 0.078 ± 0.090 mg Zn²⁺/L and 0.079 ± 0.068 mg Zn²⁺/L, respectively. With these figures, the efficiency of removal was 95%. The Zn²⁺ content in R3 and R4 were 0.313 ± 0.295 mg Zn²⁺/L and 0.314 ± 0.208 mg Zn²⁺/L, respectively. The mean removal efficiency in both reactors was approximately 81%.

Potassium concentrations in treated hydroponic wastewater were 1077 ± 86.5 mg K⁺/L and 1078.3 ± 18.9 mg K⁺/L in R1 and R3, respectively. R2 and R4 effluent concentrations were higher— 1140.0 ± 32.0 mg K⁺/L and 1142.5 ± 74.0 mg K⁺/L, respectively. The highest results for potassium removal efficiency were achieved in R1 and R3—15.6% and 15.5%, respectively. The efficiency showed the lowest results in R2 and R4—10.7% and 10.5%, respectively. Kwon et al. [21] treated hydroponic effluent in an SBR at a methanol dose of 3.27 g O₂ COD/g N-NO₃⁻ and removed from 10.4% to 30.9% of the potassium ions.

The lowest sulphate concentration was found in R3 effluent (982.5 ± 135.2 mg SO₄²⁻/L). The SO₄²⁻ removal efficiency in this reactor was 31.1%. The highest removal efficiency was observed in R2 (1317.3 ± 89.6 mg SO₄²⁻/L). In R1 and R4 a similar SO₄²⁻ ion concentration was observed— 1082.5 ± 60.156 mg SO₄²⁻/L and 1063.3 ± 98.0 mg SO₄²⁻/L, respectively. With an excess of organic carbon, the full denitrification process is followed by sulphate reduction to hydrogen sulphide, which is toxic to bacteria [42]. Kwon et al. [21] removed up to 81.5% of sulphates in their study.

The Cl^- concentration in treated wastewater increased with increasing current density. The values were within the range from $80.7 \pm 0.3 \text{ mg Cl}^-/\text{L}$ (R1) to $88.0 \pm 5.7 \text{ mg Cl}^-/\text{L}$ (R4). Among the drawbacks of electrocoagulation, there is electrode passivation (formation of oxide layers on electrodes), which limits the electrochemical process efficiency. Chloride ions help to crush the layer of oxides being formed, by penetrating the oxide layer where acid is formed [43]. Yang et al. [44] also claim that the use of Cl^- ions helps to counteract electrode passivation. They also report that the use of alternating current helps to reduce oxide formation on electrodes.

An increase in the Fe_{tot} and Cu^{2+} concentrations, as a result of secondary contamination during the treatment process, does not cause the effluent to exceed the maximum permissible levels in accordance with legal acts [7,8]. The zinc and chloride concentrations also meet the maximum permissible levels laid down in these regulations. However, the effluent after bio-electrochemical treatment does not meet the regulations for the maximum permissible potassium or sulphate concentrations. Due to the fact that the boron ion concentration is exceeded, it is not possible to discharge treated wastewater into the environment. Nevertheless, its concentration, both in hydroponic effluent and treated in BER wastewater, enables it to be discharged to the sewage collection system, where the maximum element concentration is $10 \text{ mg B}^{2+}/\text{L}$ [7].

Particular emphasis should be placed on high secondary contamination of hydroponic wastewater with molybdenum ions, as a result of treatment. Neither the hydroponic effluent nor wastewater treated in BERs meets the norm.

Polish legislation does not provide information on the highest permissible concentrations of Ca^{2+} , Mg^{2+} or Mn^{2+} ions in effluent discharged into the environment or in the sewage collection system.

4. Conclusions

This study shows that the application of a BER is an effective method of phosphorus removal from hydroponic effluent.

Investigation showed that—depending on the pH value—dephosphatation can be effected by electrocoagulation (in an acidic environment) or phosphorus precipitation with calcium and magnesium ions (in an alkaline environment). The total phosphorus removal efficiency increased with increasing electric current density. The lowest value was 95.1%, whereas the highest was 99.1%.

Denitrification of hydroponic effluent is possible only with an external carbon source. Moreover, the use of an electric current of a suitable density helps to reduce the nitrite concentration, thereby increasing the rate and efficiency of denitrification. It was noted that the nitrogen removal efficiency decreased with increasing current density.

The current flow in BER also had an impact on the macro- and micro elements' concentration. The physicochemical analysis of hydroponic effluent showed that it cannot be discharged into the environment, not only because of high nitrogen or phosphorus content, but also because the permissible concentrations of molybdenum, boron, potassium and sulphates were exceeded. Because of the disks' steel chemical composition, part of the Mn^{2+} , Cu^{2+} , Fe_{tot} and Mo^{6+} ions were supplied to the effluent of the BERs, as a result of electrode corrosion. During bio-electrochemical treatment of hydroponic effluent, significant secondary contamination of hydroponic wastewater, with molybdenum ions, occurred.

Future research should include the physicochemical analysis of the other micro elements and macronutrients in the effluent, after treatment, for a better understanding of the processes involved.

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