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Phosphorus Removal Rate and Efficiency in an Electrochemical Sequencing Reactor for the Treatment of Wastewater with Low Organic Carbon Content

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Abstract: Energy is essential for the operation of wastewater treatment systems. Simultaneously, it can be a factor facilitating the electrochemical purification processes. Previous studies have shown that under specific conditions, there is no technological justification for using bio-electrochemical reactors designed for the simultaneous removal of both phosphorus and nitrogen compounds. This is because similar dephosphatation process effects can be achieved in an electrochemical reactor. Additionally, in a bio-electrochemical reactor, a portion of the organic substrate introduced for biological treatment is lost due to the electrocoagulation process. The aim of the research was to determine the influence of low direct current densities (0.4–2.0 A/m²) on the rate and efficiency of phosphorus and other compound removal in a sequencing electrochemical reactor treating real wastewater from a greenhouse with low organic compound content. In the conducted studies, an increase in electric current density resulted in an increase in the removal rates of phosphorus from 26.45 to 34.79 mg/L·h, nitrogen from 2.07 to 6.58 mg/L·h, and organic compounds from 0.44 to 1.50 mg/L·h. This corresponded to maximum removal efficiencies of 88.6 ± 2.5% for phosphorus, 7.4 ± 2.5% for nitrogen, and 51.1 ± 8.3% for organic compounds. As a result of electrocoagulation, sludge rich in phosphorus was obtained, ranging from 347 ± 38 mg/L (18.1% P) to 665 ± 36 mg/L (11.7% P). The obtained results can be utilized in the future for the development of two-stage systems for wastewater treatment with a low content of organic compounds, aiming at the removal of phosphorus and nitrogen.

Keywords: electrocoagulation; phosphorus recovery; iron electrode; electrocoagulation kinetics; soilless cultivation; quality of electrocoagulation sludge



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1. Introduction

Soilless cultivation of tomatoes is often conducted in open systems, where the excess nutrient-rich medium (wastewater) is discharged into the environment in an uncontrolled manner. The concentrations of nutrients in wastewater, such as nitrate reaching up to 614 mg N/L and total phosphorus up to 370 mg P/L, pose a serious threat to both aquatic and groundwater environments [1–3]. On the other hand, this represents a case of wasting biogenic substances that could potentially be reused for fertilizing specific types of crops [4–6].

There are methods that allow for the recirculation of wastewater generated in soilless plant cultivation and their reuse. These methods primarily rely on the analysis of electrical conductivity and disinfection. However, these technologies do not solve the ultimate problem of managing drainage water by discharging it into the environment, as well as the challenge of properly balancing nutrient solutions or the accumulation of chloride and

sodium ions [7,8]. Therefore, their practical application is mainly limited to soilless seedling cultivation, where changes in the concentration of individual nutrient components undergo minimal variations due to low transpiration and nutrient uptake by the plants. It should be emphasized that even with the application of recirculation, a portion of the wastewater must still be directed outside the system. Hence, there is a need to explore methods for their proper disposal [9].

The unique composition of wastewater led researchers to hypothesize that effective purification could be achieved by combining physicochemical processes such as electrocoagulation with biological processes. Bio-electrochemical reactors were considered a potential solution [10,11]. A previously tested solution for greenhouse wastewater was the flow-through aerobic rotating electrobiological disc contactor (REBDC), where the flow of electric current was expected to create favorable conditions for the simultaneous removal of phosphorus through electrocoagulation, nitrate through hydrogenotrophic denitrification, and electrochemical reduction [12]. To enhance nitrate removal efficiency, an external source of organic carbon was introduced into the REBDC, assuming that this would increase the participation of heterotrophic denitrification and biomass growth in nitrate removal [12]. The cited studies demonstrated that in the case of the aerobic bio-electrochemical reactor like REBDC, the introduction of an external carbon source created conditions not only for heterotrophic and hydrogenotrophic denitrification but also for nitrogen consumption in biofilm growth. This led to higher nitrogen removal effectiveness in REBDC compared to the rotating electrochemical disk contactor (RECDC). Despite this technological intervention, the nitrogen concentrations in the effluent from REBDC did not meet the required standards for wastewater discharged into the environment. Simultaneously, for phosphorus, its concentration in wastewater treated with electric current densities of 2.50, 5.00, and 10.00 A/m² and retention times of 8, 12, and 24 h was below 1.0 mg P/L [12]. It is worth noting that similarly low phosphorus concentrations were observed in the effluent from RECDC for an electric current density of 10.00 A/m², where phosphorus removal was solely a result of the electrocoagulation process [12]. These studies revealed that under specific conditions, there is no technological justification for using bio-electrochemical reactors designed for the simultaneous removal of both phosphorus and nitrogen compounds, as similar dephosphatation effects can be achieved in an electrochemical reactor. The external source of organic carbon did not significantly contribute to the efficiency of phosphorus removal [12].

This hypothesis was confirmed by research results using sequential anaerobic reactors: a bio-electrochemical and an electrochemical reactor of the SBBR type (sequencing batch biofilm reactor) [13]. Higher efficiencies of nitrogen and phosphorus removal were achieved in reactors subjected to high current densities (4.4 A/m², 8.8 A/m², and 13.3 A/m²) compared to aerobic RECDC and REBDC reactors. At the highest current density, the phosphorus concentration in the effluent from the electrochemical reactor was lower than in the bio-electrochemical reactor. The studies also demonstrated that in the bio-electrochemical reactor, a portion of the introduced organic substrate was not utilized by heterotrophic denitrifying bacteria but was removed through the electrochemical process of electrocoagulation [13,14].

The separation of electrochemical and biological processes and their implementation in sequentially connected SBBR-type reactors (electrochemical and biological) could potentially impact electricity consumption and the amount of organic carbon required to support denitrification. It is also expected to result in lower concentrations of biogenic and organic compounds in treated wastewater. Validating these assumptions requires further research, which should consider the possibility of applying lower current densities than those commonly used [15–17]. This would provide additional support for this technological solution. It would also allow for the powering of such reactors with electrical energy from sources such as photovoltaic cells [18] or microbial fuel cells [19] without the need for converting direct current (DC) to alternating current (AC). This could facilitate the diversification of energy sources and reduce dependence on electricity from the grid.

The aim of this research was to determine the influence of electric current density on the kinetics (1) and efficiency (2) of phosphorus removal through electrochemical processes in a sequential reactor treating real wastewater from soilless tomato cultivation. Additionally, the scope of the study included the quantitative (3) and qualitative (4) analysis of the generated sludge. The impact of the applied electric current density on the nitrogen concentration (5) and organic compounds (6) in treated wastewater was also assessed. The obtained results may be utilized in the future to design two-stage systems for wastewater treatment with low organic compound content, targeting the removal of phosphorus and nitrogen.

2. Materials and Methods

2.1. Experimental Setup and Research Organization

The research was conducted on a sequential electrochemical reactor model. The reactor's construction and the research scheme are presented in Figure 1. To carry out the process, an anode made of iron with an electrochemical surface area of 0.023 m^2 was utilized, while the cathode consisted of discs with a total electrochemical surface area of 0.113 m^2 . The difference in the size of electrode surfaces resulted from the technological solution applied in the reactor, which, in addition to electrochemical processes, can be used for biological treatment. In such a configuration, a biofilm can develop on the cathode. The discs were made of stainless steel and mounted on a vertically rotating shaft with a speed of 14 rpm. The electrodes were connected to a DC power supply (Rohde & Schwarz HMP 4040, Munich, Germany). The reactor's effective volume was 2 L. The hydraulic retention time (HRT) of the wastewater was set at 24 h based on previous studies. At the end of each cycle, the entire reactor volume was replaced, introducing a new batch of wastewater (2 L). The kinetics of pollutant removal were determined from samples collected at 0, 3, 6, 12, and 24 h. The following electric current densities (J) were applied: 0.4, 1.2, and 2.0 A/m^2 , corresponding to current intensities of 0.045, 0.136, and 0.226 A , respectively. These values were selected based on the literature data and previous studies [12,20–22].

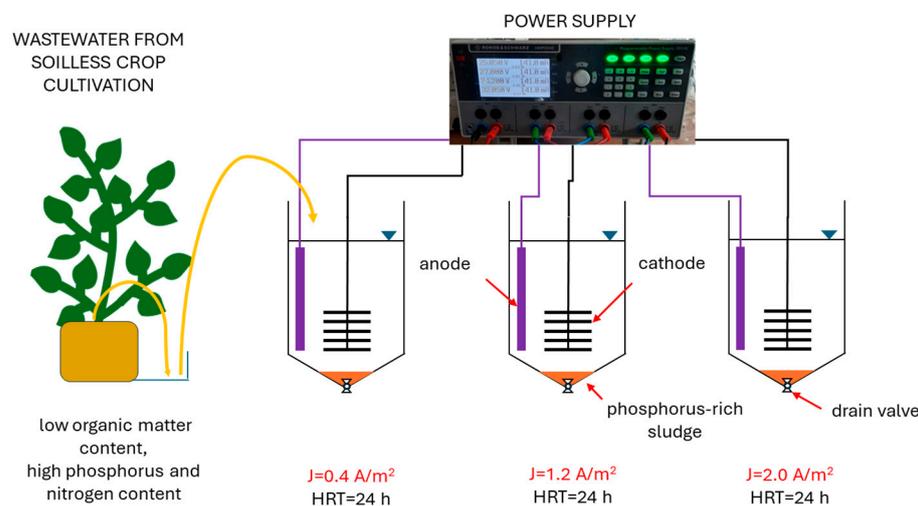


Figure 1. Research scheme.

The obtained results from kinetic studies allowed for the determination of reaction orders, the rate of organic compound utilization, and the removal of nitrogen and phosphorus compounds. Reaction rate constants and statistical analysis of the results were performed using the STATISTICA 13.3 PL computer program. A significance level of $\alpha = 0.05$ was adopted.

2.2. Wastewater

The study utilized wastewater (drainage water) from a greenhouse where tomatoes were cultivated using mineral wool as a substrate. The greenhouse, located in northern Poland,

covers an area of approximately 20 hectares. Wastewater for the study was collected in July and August 2023 and exhibited the following physicochemical indicators: pH—6.21; electrolytic conductivity— 6.213 ± 0.202 mS/cm; total organic carbon (TOC)— 15.6 ± 3.1 mg C/L; total nitrogen (TN)— 536.9 ± 10.7 mg N/L; nitrate— 535.71 ± 7.40 mg N/L; nitrite— 0.07 ± 0.05 mg N/L; ammonium nitrogen— 0.02 ± 0.01 mg N/L; and total phosphorus (TP)— 103.8 ± 5.3 mg P/L. The wastewater was stored in a tank with a volume of 1 m^3 made of synthetic material. Based on the measurement of wastewater parameters during retention, it can be concluded that they do not exhibit changes in composition and can be retained in this way for at least 6 months.

2.3. Physicochemical Analysis of Wastewater

The following parameters of wastewater were measured: pH value, electrolytic conductivity, and temperature using an HQ4300 multimeter (HACH Company, Loveland, CO, USA); total nitrogen (TN) and total organic carbon (TOC) using a TOC-L CPH/CPN device (Shimadzu Corporation, Kyoto, Japan; oxidative combustion-chemiluminescence method—TN; oxidizing incineration—infrared analysis—TOC); total phosphorus (TP; HACH Lange LCK 348–350 method), ammonia nitrogen (N-NH₄; HACH Lange LCK303–305), nitrite (N-NO₂; HACH Lange LCK341–342), and iron (Fe; HACH Lange LCK 321 and LCK 521) using a DR5000 HACH Lange Spectrophotometer (Malente, Germany).

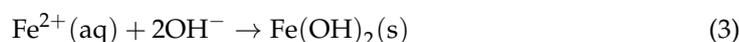
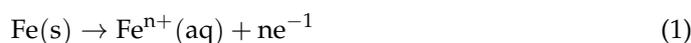
2.4. Quantity and Quality of Sludge

The quantity of generated sludge in the form of total suspended solids (TSS) and volatile suspended solids (VSS) was determined according to APHA 2012 [20]. For qualitative analysis of the sludge, the content of nitrogen (N), phosphorus (P), carbon (C), and iron (Fe) was determined. For this purpose, the sludge was dried at 105 °C. The determination of elements (Fe, P) involved mineralizing 0.2 g of dried sludge in a Teflon container (easy prep) with the addition of 7.5 mL of 69–70% nitric acid and 2.5 mL of 36% hydrochloric acid. Microwave-assisted mineralization was carried out using a MARS CEM 5 device (CEM Corporation, Matthews, NC, USA) at a temperature of 210 °C for 15 min. After the completion of sample dissolution, the samples were quantitatively transferred to a Falcon-type container and diluted to a volume of 20 mL using 2% nitric acid [21,22]. The content of elements (Fe, P) in the prepared sample was determined using inductively coupled plasma optical emission spectrometry (ICP-OES; Avio 220 ICP-OES; Perkin Elmer, Waltham, MA, USA). The amount of N and C in the dried sludge was determined using a Flash 2000 elemental analyzer (Thermo Fisher Scientific, Waltham, MA, USA).

3. Results and Discussion

The conducted research aimed to determine the impact of electrical current density on the kinetics and efficiency of treating wastewater generated in a greenhouse during soilless tomato cultivation. These wastewaters are characterized by low organic compound content, high phosphorus and nitrogen compound content, and electrolytic conductivity. The electrocoagulation (EC) process employed integrates the benefits of coagulation, flotation, and electrochemistry into a single system [17]. Throughout the electrocoagulation process, both reduction and oxidation processes take place at both the anode and cathode, influencing the characteristics of pollutants in the treated wastewater, as well as the interactions among them and with the dissolved metal [23]. Due to the flow of electric current, the anode undergoes dissolution (Equations (1)–(3)), and water electrolysis occurs at the cathode, leading to the release of hydroxyl ions and hydrogen (Equation (4)) [24].

Anode reactions:



Cathode reaction:



The research demonstrated an increase in the rate of pollutant removal with the rise in applied electrical current density. Simultaneously, the applied solution ensured high efficiency.

3.1. pH, Electrolytic Conductivity, Iron Content

The pH of treated wastewater significantly impacts both physicochemical and biological processes. Depending on the pH, the electrode dissolves and forms metal ions. The formation of Fe ions is more complex than Al ions when using aluminum anodes. The ferric ion predominates in highly acidic solutions, while the ferrous ion is more common at $\text{pH} < 6.5$. Most studies indicate that Fe^{2+} is initially formed by iron electrolysis and then oxidized to Fe^{3+} by dissolved oxygen under suitable conditions (e.g., $\text{pH} 5\text{--}9$). Subsequently, it hydrolyzes to form insoluble $\text{Fe}(\text{OH})_3(\text{s})$ and $\text{FeOOH}(\text{s})$ [23,25]. Fe^{2+} is highly soluble but a weak coagulant, with a lower pollutant adsorption capacity compared to Fe^{3+} . Simultaneously, in the electrocoagulation reactor, an uneven pH distribution occurs during the flow of electric current. The solution around the anode becomes slightly acidic due to the formation of H^+ , while the solution around the cathode becomes slightly alkaline due to the production of OH^- and the release of H_2 . This may affect the efficiency of electrocoagulation in removing pollutants [26]. In most studies using electrocoagulation, pH increases due to the production of OH^- ions. However, in the conducted research, no such relationship was observed (Figure 2A). With an initial pH of 6.1, as the electric current intensity increased, the pH decreased. For the highest current density (2.0 A/m^2), the pH of the treated wastewater was 2.8, possibly due to high sulfate concentrations. Greenhouse wastewater contains 58 to 1425 mg SO_4^{2-} [27]. Nariyan et al. [28], treating sulfur-rich mine waters with a concentration of 13,000 $\text{mg SO}_4^{2-}/\text{L}$ using electrocoagulation at a density of 25 mA/cm^2 , achieved removal efficiencies of 83.75% and 84.38% for sulfates in monopolar and bipolar electrode configurations, including aluminum and stainless steel electrodes. In their study, the initial pH was 11.3, and after the purification process, it decreased to pH 6.8 and 6.6 for monopolar and bipolar electrode configurations, respectively. In Lei et al.'s research [29], the pH of municipal wastewater decreased during purification when treating wastewater with a pH below 6. Purifying wastewater with a pH of 5 resulted in a pH drop to 3.2 after 24 h using a platinum anode and titanium cathode. Under these conditions, phosphorus was removed in the form of struvite with an efficiency of 50% at a current density of 8.3 A/m^2 . The pH decrease in the cited studies was attributed to the consumption of OH^- ions by Mg^{2+} and NH_4^+ , leading to the accumulation of H^+ ions and a subsequent drop in pH.

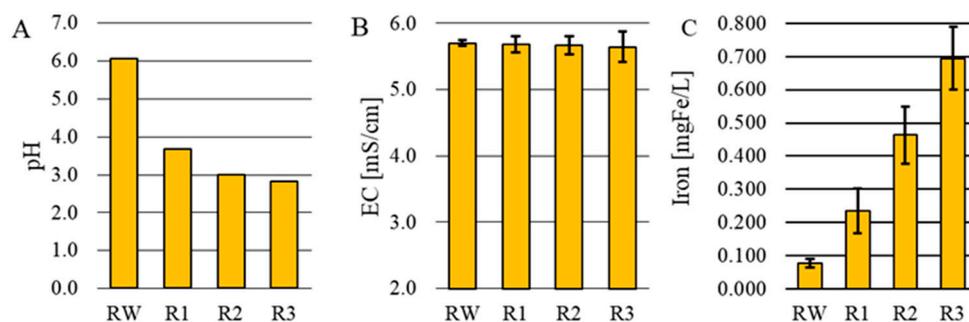


Figure 2. pH (A), electrolytic conductivity (B), and iron concentration (C) in raw wastewater (RW) and treated wastewater (R1–R3).

The electrolytic conductivity of greenhouse wastewater depends on the quality and quantity of ions in the aqueous solution, varying widely based on weather conditions and plant growth phases [3]. Electrolytic conductivity ensures the free flow of electric current in treated wastewater and reduces electricity consumption [30]. The type of cations and anions influences the electrocoagulation kinetics, affecting the ability of coagulants to form flocs. The electrolytic conductivity of the applied wastewater was $5.704 \pm 0.049 \text{ mS/cm}$

(Figure 2B). Different electric current densities did not significantly affect the electrolytic conductivity of treated wastewater despite achieving higher pollutant removal efficiencies, as described in subsequent chapters. This may be because the removed ions did not play a major role in creating electrolytic conductivity, and/or their removal was compensated by an increase in iron ion concentration in the treated wastewater compared to raw wastewater.

Iron is a commonly used electrode material due to its reliability and availability [16]. Iron electrodes are less efficient than aluminum ones but are significantly cheaper, which is crucial for wastewater treatment. Additionally, greenhouse wastewater naturally contains iron ions essential for plant development, and their presence, unlike aluminum ions, does not negatively impact plants [31]. The overall iron concentration in raw wastewater was 0.077 ± 0.012 mg Fe/L.

With an increase in electric current density, there was an increase in iron ion concentration in treated wastewater, reaching 0.695 ± 0.095 mg Fe/L at $J = 2.0$ A/m² (Figure 3). This value is sometimes observed in raw wastewater as well [13]. This is also the permissible value for wastewater discharged into the environment (maximum allowable concentration of 10.0 mgFe/L) [32]. Excessive electric current density can cause secondary pollution of wastewater with ions from the electrode and shorten its lifespan [33]. Behbahani et al. [34], treating synthetic wastewater with an initial concentration of 400 mg P/L and pH 3 using electrocoagulation, removed 84.7% (iron electrode) and 94.15% (aluminum electrode) of orthophosphates. However, there was an increase in iron and aluminum concentrations in the solution to 2 mg Fe/L and 14.5 mg Al/L, respectively. In the cited study, despite a shorter electrocoagulation time (40 min), higher concentrations of iron and aluminum were noted than in the presented research (Figure 3). This is due to the much higher current density used in the cited study, which was 250 A/m². It also suggests the use of lower electric current densities when planning the subsequent use of treated wastewater, for example, in plant irrigation.

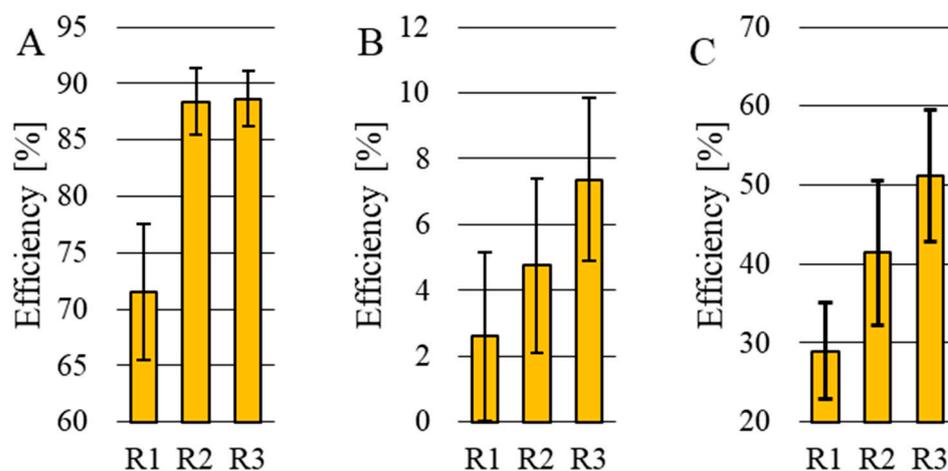


Figure 3. Efficiency of total phosphorus removal (A), total nitrogen removal (B), and total organic carbon removal (C).

3.2. Removal of Phosphorus Compounds, Nitrogen and Organic Compounds

The concentration and efficiency of phosphorus removal are directly associated with the concentration of iron ions available in the solution and the pH of the treated wastewater. The concentration of total phosphorus in the greenhouse wastewater subjected to purification was 88.0 ± 4.9 mg P/L. The average efficiency of total phosphorus removal is presented in Figure 3A.

The efficiency of phosphorus removal in electrochemical reactors through electrocoagulation increased with the applied current density, ranging from $71.5 \pm 6.0\%$ in R1 (pH = 3.7) to $88.6 \pm 2.5\%$ in R3 (pH = 2.8). The concentration of TP in the treated effluents in R2 and R3 was similar, measuring 10.2 ± 2.6 mg P/L and 10.0 ± 2.2 mg P/L, respectively

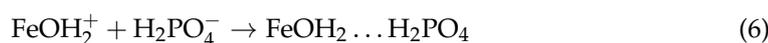
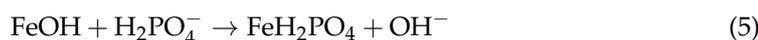
(no statistically significant differences, $\alpha = 0.05$). In reactor R1, where the lowest current density was applied, the phosphorus concentration was significantly higher, reaching 25.1 ± 2.3 mg P/L. Analyzing the obtained results, the increase in electrical current density from 0.4 A/m² to 1.2 A/m², along with a simultaneous rise in the concentration of iron ions and a decrease in the pH of the treated wastewater, had a significant impact on the purification efficiency. However, the subsequent increase in electrical current density from 1.2 A/m² to 2.0 A/m² did not have a substantial effect. Simultaneously, the concentrations of phosphorus in the treated wastewater exceeded the permissible value. For the wastewater to be discharged into the environment, the phosphorus concentration should be below 3.0 mgP/L [32]. Electrocoagulation does not cause microbiological contamination of the wastewater. Therefore, these effluents can be used in re-fertigation or directed to further purification processes.

A fivefold increase in electric current density resulted in only a 32% increase in the dephosphatation rate. This corresponded to a phosphorus removal rate of 26.45 mg P/L·h at $J = 0.4$ A/m² and 34.79 mg P/L·h at an electric current density of $J = 2.0$ A/m² (Table 1). The obtained results allow for a precise estimation of the required time for phosphorus removal from greenhouse effluents, given the knowledge of phosphorus concentration in raw effluents. Meanwhile, the use of significantly higher electric current densities seems unjustified.

Table 1. Kinetic parameters of total phosphorus, total nitrogen, and organic compounds removal (k—rate constant—[1/h], r—removal rate—[mg/L·h], R²—coefficient of determination).

	Total Phosphorus			Total Nitrogen			Organic Compounds		
	k	r	R ²	k	r	R ²	k	r	R ²
R1	0.421	26.45	0.996	0.137	2.07	0.998	0.130	0.44	0.988
R2	0.396	30.65	0.982	0.109	2.78	0.980	0.125	0.61	0.983
R3	0.448	34.79	0.992	0.190	6.58	0.969	0.262	1.50	0.999

Under the conditions of electric current flow, phosphorus was mainly removed through the electrocoagulation process. The precipitation of phosphorus ions with other ions, including calcium and magnesium ions, was limited due to the low pH of the treated effluents. In the pH range of 2.2–7.2, most orthophosphates exist in the form of an anion H_2PO_4^- [35,36]. These ions, along with calcium and magnesium ions, form water-soluble compounds [4]. Due to the pH, direct precipitation of PO_4^{3-} with Fe^{2+} and Fe^{3+} ions was also limited. As a result of the electric current flow, monomeric and polymeric iron complexes with OH^- ions were most likely formed [37]. Generally, the pH of the point of zero charge (pHpzc) for iron oxides is 5.4–8.6 [38]. Therefore, when the solution $\text{pH} < \text{pHpzc}$, the surface of iron oxides occupies a positive charge due to the protonation of surface hydroxyl. Thus, it can adsorb P anions by electrostatic adherence and further immobilize them by ligand exchange (Equation (5)) [39,40]. Iron oxides could also capture P via electrostatic attraction (Equation (6)) [41]. Phosphate can be adsorbed on the surface of iron oxides through surface complexation, including monodentate mononuclear, bidentate mononuclear, and bidentate binuclear [42].



The efficiency of removal increased with the current density from 0.4 A/m² to 1.2 A/m². However, a subsequent increase in current density from 1.2 A/m² to 2.0 A/m² did not result in a significant improvement in phosphorus removal efficiency. The amount of coagulant increases with the rise in current density, but likely, the quantity of coagulant generated from the increase in current density from 1.2 A/m² to 2.0 A/m² did not cause a significant enhancement in phosphorus removal efficiency, potentially due to the retention time of the effluent in the reactor. The obtained results confirm that the removal of phos-

phate ions was not caused by direct precipitation with iron ions, whose quantity increased with the rise in electrical current density, but rather due to various types of interactions. Most likely, the dominant process, influenced by the low pH resulting in the protonation of iron-based materials, was the sorption of phosphorus through electrostatic adsorption [36]. This underscores the need to test the electrocoagulation process using actual wastewater under different conditions to determine its real efficiency and optimize the process. Similar dependencies were reported by Shalaby et al. [43]. The cited authors argue that an increase in density beyond the optimal level does not lead to an increase in the efficiency of pollutant removal since the quantity of generated coagulant is no longer a limiting factor. Kłodowska et al. [20], in experiments with a hydraulic retention time of 24 h in a sequencing batch biofilm reactor with an aluminum electrode, removed between 71.01% and 86.99% of total phosphorus, increasing the density from 0.053 mA/m² to 0.210 mA/m². In these studies, an increase in current density from 0.105 mA/m² to 0.210 mA/m² resulted in a slight efficiency increase of only 4.19%. The cited research involved treating municipal wastewater with a low carbon-to-nitrogen ratio and a total phosphorus concentration of 5.16 mg P/L.

The results obtained from the electrical current-based studies suggest that the most favorable current density for efficient phosphorus removal is 1.2 A/m². Beyond this value, a significant increase in the efficiency of total phosphorus removal from wastewater was not observed. Simultaneously, the achieved effectiveness using a DC was higher than when using AC. In the research conducted by Bryszewski et al. [13] with a hydraulic retention time of 24 h and a current density of 4.4 A/m², but with AC, the phosphorus removal efficiency was 17.2%. Meanwhile, in the study by Rodziejewicz et al. [12], the use of a DC in the RECDC and a DC along with an external source of organic carbon in the REBDC for synthetic wastewater with parameters similar to those from greenhouse effluents provided slightly higher efficiency and lower phosphorus concentration in the treated effluents.

Similarly to phosphorus, the conducted studies demonstrated that the rate and efficiency of nitrogen removal increased with the applied electric current density. However, the obtained values for nitrogen were several times lower compared to those achieved for phosphorus. The concentration of TN in the treated effluents was 467.0 ± 12.3 mg N/L, 456.6 ± 12.8 mg N/L, and 444.1 ± 11.9 mg N/L in R1–R3, respectively. This corresponded to nitrogen removal efficiencies ranging from 2.6 ± 2.6% to 7.4 ± 2.5%. The nitrogen removal rate in electrochemical reactors increased with the rise in current density, ranging from 2.78 mg N/L·h (R1) to 6.58 mg N/L·h (R3).

During electrocoagulation, electrochemical reduction occurs at the cathode, and electrochemical oxidation takes place at the anode (direct oxidation) or the generation of oxidants such as free radicals, ozone, or chloric acid, which then oxidize compounds present in wastewater (indirect oxidation). In the case of greenhouse wastewater, reduction processes play a significant role. Reducing nitrates to gaseous nitrogen can be challenging because it is one of the possible products (N₂, NO₂⁻, NH₃, NH₂OH, N₂O, NO). A crucial indicator that most influences the final product of electrochemical nitrate reduction is the pH. At neutral and alkaline pH, by-products of this process are nitrites, ammonia, hydroxylamine, and hydrazine. In acidic conditions, undesired products of the reduction process are nitrites and ammonia [44]. If chloride ions are present in the treated wastewater, they undergo anodic oxidation, forming hypochlorous acid. Ammonium ions and nitrites react with hypochlorous acid to form nitrates and molecular nitrogen [45]. These reactions affect the overall efficiency of total nitrogen removal.

In the conducted studies, the predominant form of nitrogen was nitrates, both in raw and treated wastewater. After a 24-h retention time, the percentage of nitrates was 99.78, 99.76, and 99.70%, and the percentage of nitrites was 0.10, 0.09, and 0.09%, while the remainder consisted of ammonium and organic nitrogen, respectively, in R1–R3. This corresponded to nitrite concentrations in the treated effluents of 0.48 ± 0.13, 0.40 ± 0.14, and 0.40 ± 0.12 mg N/L, respectively, in R1–R3.

By analyzing the obtained results and literature data, it can be concluded that higher electrical current density leads to a faster reduction of nitrates on the electrode surface and, consequently, higher efficiency. However, the applied low electrical current densities did not result in a significant decrease in the nitrogen concentration in the treated wastewater.

The composition of treated wastewater, including the presence of other pollutants and the process operation, can significantly influence the final efficiency. Benekos et al. [46], in the current density range of 20–40 mA/cm², removed 100% of nitrates from real nitrate-contaminated groundwater (initial nitrate concentration of 25 mg N/L). However, with the increase in current density, ammonium nitrogen accumulation occurred, ranging from 4.5 mg N/L to 6.5 mg N/L. Ghanim and Ajjam [47], electrochemically treating synthetic wastewater with a nitrate concentration of 150 mg N/L, achieved efficiency ranging from 40% (2 mA/cm²) to 88% (10 mA/cm²). Ghazouani et al. [48], treating synthetic wastewater with an electric current density from 1 mA/cm² to 40 mA/cm², observed an initial nitrate concentration of 350 mg N/L and a phosphate concentration of 50 mg P/L. The efficiency of nitrogen and phosphorus removal in the investigated range of current density was 37–99% and 51–99%, respectively. Despite the high efficiency of nitrate removal, the main product of the process was ammonium ions, constituting approximately 90% at the highest current density. In the case of greenhouse wastewater treatment, previous studies have shown that the addition of an external organic carbon source improves denitrification efficiency. However, this solution is ineffective due to the loss of organic substrate during electrocoagulation and the formation of sludge containing phosphorus and a high proportion of organic compounds [12,13]. This complicates their storage and subsequent utilization. There is also no justification for nutrient solution recirculation [9].

Wastewater from soilless tomato cultivation is characterized by a low content of organic compounds. This is due to the infiltration of root exudates into the wastewater, as well as the presence of plant fragments [3]. In the case of electrochemical processes applied to such wastewater, the removal of organic compounds is considered an added value and is not the primary objective. The low content of organic compounds also prevents the use of conventional biological methods for removing biogenic compounds based, for example, on activated sludge [49]. When electrical current is applied, the mechanism for removing organic compounds is complex and involves processes such as complexation, charge neutralization or destabilization, coagulation, flocculation, oxidation, entrapment, and adsorption [50]. The initial content of organic compounds in raw wastewater was 11.3 ± 2.1 mg C/L. The efficiency of organic compound removal increased with the electrical current density, ranging from $28.9 \pm 6.1\%$ (R1) to $51.1 \pm 8.3\%$ (R3) (Figure 3C). This corresponded to an organic carbon concentration ranging from 8.0 ± 0.7 mg C/L (R1) to 5.5 ± 0.9 mg C/L (R3). The higher efficiency of pollutant removal also correlated with a higher removal rate observed during the study (Table 1). Statistical analysis indicated a significant impact of electrical current density on the concentration of organic compounds in the treated wastewater. The absence of external organic carbon supplementation prevented secondary pollution of the treated wastewater, a situation that can occur, especially in anaerobic systems characterized by lower efficiency in utilizing organic compounds. This is due to the lack of electron acceptors such as oxygen or oxidized forms of compounds, e.g., nitrates, after complete denitrification [13,51].

3.3. Quantity and Quality of Sludge

The application of DC and the dissolution of the anode result in the formation of sludge. This sludge not only contains dissolved metal from the anode but also the pollutants removed from the wastewater.

In the conducted studies, the amount of generated sludge expressed as TSS increased with the applied electric current density, ranging from 347 ± 38 to 665 ± 36 mg/L in R1–R3 (Figure 4A). A fivefold increase in electric current density resulted in approximately a twofold increase in the amount of generated sludge. This results in the formation of sludge ranging from 0.347 kgTSS/m³ to 0.665 kgTSS/m³ for 1 m³ of greenhouse wastewater,

depending on the process parameters. Assuming that an average of 45 m³ to 120 m³ of wastewater is discharged daily from 1 hectare of soilless tomato cultivation [52], the amount of generated sludge would be between 16–42 kgTSS/d·ha and 30–80 kgTSS/d·ha. The formed sludge was mainly characterized by the content of the mineral fraction, which ranged from 96.7% (R1) to 97.8% (R3; Figure 4B). Simultaneously, the amount of milligrams of TSS per milligram of removed phosphorus ranged from 5.5 to 8.5 (Figure 4C). The decrease in the phosphorus content in the discharged sediment corresponded to an increase in the iron content with the applied current density (Table 2). Additionally, the obtained sludge had a phosphorus content at a similar level to sludge obtained by precipitation with the use of alkalizing agents in the treatment of greenhouse wastewater [4]. Electrocoagulation led to a decrease in pH rather than an increase, which is crucial for the further utilization of treated wastewater. The applied electric current density of 1.2 A/m² proved to be the most efficient in terms of dephosphatation, as well as the quality and quantity of obtained sludge. Using both electrocoagulation and biologically enhanced treatment with an external carbon source in REBDC results in a sediment amount that is an order of magnitude higher. In the studies by Rodziewicz et al. [53], the amount of sediment ranged from 3944 mg/L to 4783 mg/L for HRT = 24 h and 4 h, and J = 1.25 A/m². Additionally, in the cited studies, for electric current densities ranging from 0.63 A/m² to 10 A/m², the sediment amount ranged from 3873 mg/L (HRT = 24 h; J = 0.63 A/m²) to 5215 mg/L (HRT = 4 h; J = 10 A/m²). This sludge also had a much higher content of organic compounds (77–88%) and a lower phosphorus content (0.68–0.84%) [53]. In the studies by Bryszewski et al. [13], using alternating current and an external organic carbon source, they recorded the amount of generated sludge ranging from 416.0 ± 267.3 mg/L (HRT = 24 h; J = 4.4 A/m²) to 1079.4 ± 251.3 mg/L (HRT = 24 h; J = 13.3 A/m²). The share of organic compounds was 28.6% and 22.4%, and phosphorus was 1.3–2.1%. The amount and quality of sludge resulting from electrocoagulation can vary widely and depend primarily on the quality of the treated wastewater, the type of electrode used, and the applied electric current density and electrocoagulation time [54,55]. Akyol [56], using electric current density in the range of 5–10 A/m², noted the amount of sludge resulting from electrocoagulation in the range of 4570–5330 mg/L. The studies concerned the treatment of wastewater from paint manufacturing, and aluminum electrodes were used. In the studies by Mansoorian et al. [57], where the electric current density ranged from 2 mA/cm² to 10 mA/cm², the amount of generated sludge ranged from 81 mg/L to 84 mg/L. The research focused on treating wastewater from battery production, and iron electrodes were used.

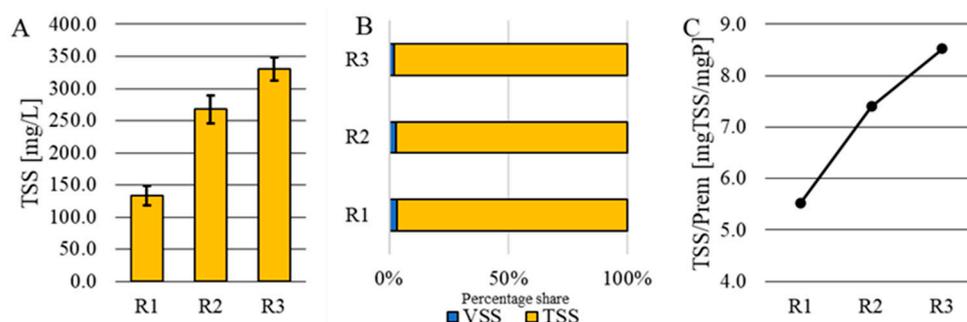


Figure 4. Amount of sediment discharged from the reactor (A), the proportion of volatile suspended solids (VSS) in total suspended solids (TSS) (B), and the amount of mgTSS per mg of removed phosphorus (C).

Table 2. Percentage content of selected elements in the sediment.

W	N	Average Elemental Content [%]			Fe
		P	C		
R1	4.18	18.1	0.65	8.08	
R2	2.28	13.5	0.43	8.67	
R3	2.68	11.7	0.55	13.1	

Sludge containing over 30% organic compounds is not stabilized and should be directly managed or subjected to stabilization processes [58]. In the conducted studies, the sludge had a much lower organic compound content, making it easy to store and utilize in the future. The choice of a method for managing sediments after electrocoagulation depends on the type of pollutants, sediment composition, as well as local regulations and norms. Sediments from EC can be utilized as fertilizer [59,60], pigment [61], construction material (mainly in the form of blocks) [62], adsorbent [60], or catalyst [63]. Analyzing the composition of sediments generated during the electrocoagulation of wastewater from soilless tomato cultivation, it can be inferred that these sediments are rich in phosphorus and iron. Therefore, their management should focus on the reuse of these elements.

The presence of iron and iron oxides may facilitate the reuse of sediments as sorbents for phosphorus ions or as catalysts in reactions such as pyrolysis [63] or the Fenton reaction [64]. This could extend the so-called “product life cycle”, but at the same time, it might make phosphorus in the sediments unsuitable for agricultural use. Due to the significant role of phosphorus in human activities, this element should play a decisive role in sediment management, where agricultural utilization currently appears to be the best solution.

Simultaneously, greenhouse wastewater subjected to electrocoagulation has no contact with domestic wastewater or other biological factors, making it safe in terms of hygiene and not posing a threat to cultivation.

4. Conclusions

The research presented in the paper complements existing studies on the impact of various treatment methods on the quality of wastewater from soilless tomato cultivation. The obtained results indicate that electrocoagulation allows for the purification of wastewater, which can subsequently be used to prepare fresh nutrient solutions or subjected to processes such as biological treatment. Electrocoagulation is a method that does not cause microbiological contamination, a crucial aspect of reusing purified wastewater in cultivation. Bacteria and fungi present in biological treatment systems could potentially induce diseases in cultivated plants. Simultaneously, the sediment generated during electrocoagulation is characterized by a low content of organic compounds and a high phosphorus content, making these sediments suitable as a substitute for mineral fertilizers. Greenhouse wastewater, due to its lack of contact with domestic wastewater, is safe in terms of hygiene and can be utilized in various branches of agriculture. The resulting sediments do not require a stabilization process; they only need to be dewatered.

In addition, it was found that:

1. A threefold increase in electrical current density (from 0.4 to 1.2 A/m²) resulted in a 16% increase in dephosphatation rate, while a fivefold increase in electrical current density (from 0.4 to 2.0 A/m²) resulted in a 32% increase.
2. The rate of TP removal ranged from 26.45 to 34.79 mg/L·h, TN from 2.07 to 6.58 mg/L·h, and organic compounds from 0.44 to 1.50 mg/L·h, respectively, for electrical current densities of 0.4 and 2.0 A/m².
3. Increasing the electrical current density above 1.2 A/m² did not significantly increase the efficiency of TP removal. The observed effectiveness was 71.5 ± 6.0%, 88.0 ± 4.9%, and 88.6 ± 2.5%, respectively, for electrical current densities of 0.4, 1.2 and 2.0 A/m².
4. Due to the low pH of the treated wastewater, phosphorus was likely removed through electrostatic adsorption on the surface of iron oxides via surface complexation.

5. The use of DC and iron electrodes also allowed for the removal of a maximum of $7.4 \pm 2.5\%$ TN and $51.1 \pm 8.3\%$ organic compounds for an electrical current density of 2.0 A/m^2 .
6. The amount of sludge resulting from electrocoagulation using an iron electrode and HRT = 24 h increased with the increase in electrical current density, ranging from $347 \pm 38 \text{ mg/L}$ ($J = 0.4 \text{ A/m}^2$) to $665 \pm 36 \text{ mg/L}$ ($J = 2.0 \text{ A/m}^2$). This sludge was characterized by a high percentage of the mineral fraction, ranging from 96.7% to 97.8%.
7. With the increase in applied electrical current density and the increase in the amount of generated sludge, the percentage of phosphorus in the sludge decreased, ranging from 18.1% ($J = 0.4 \text{ A/m}^2$) to 11.7% ($J = 2.0 \text{ A/m}^2$).
8. Electrocoagulation led to a decrease in the pH of the treated wastewater from 6.1 to 2.8 ($J = 2.0 \text{ A/m}^2$), while no significant change in electrolytic conductivity was observed.
9. Dissolving the iron electrode led to an increase in the iron concentration in the treated wastewater from $0.077 \pm 0.012 \text{ mg Fe/L}$ to $0.695 \pm 0.095 \text{ mg Fe/L}$ ($J = 2.0 \text{ A/m}^2$).

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