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Influence of Electrode Material on the Electroflocculation Pre-Treatment Efficiency of Swine Wastewater †

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Abstract

Swine wastewater, composed of farm effluents, is frequently applied as fertilizer, but repeated use can lead to eutrophication and contamination. This study investigated the improvement of swine wastewater quality by means of the electroflocculation technique using various alternative electrodes (aluminum, stainless steel, carbon, copper, and zinc) under very short exposure durations (3, 6, and 9 min) and low voltage conditions (12 V), aiming to optimize the process. After the treatments, both treated and control samples were analyzed in the laboratory for pollutants including turbidity, organic matter, phosphorus and other minerals. The results showed that zinc and stainless steel electrodes were particularly effective in reducing turbidity (47–67%), organic matter (23%), phosphorus (36–62%), calcium (24–54%), magnesium (34–52%) and sodium (19–38%) respectively in the effluent after only 6 or 9 min of current exposure. However, these electrodes released some heavy metals into the solution, which should be further reduced through a complementary treatment. Overall, electroflocculation using alternative electrode materials with short treatment times appears to be a suitable pre-treatment strategy for swine wastewater, reducing pollutant loads while maintaining low energy consumption and preserving nutrients for subsequent use as fertilizer.

Keywords: wastewater management; eutrophication; pollutant removal; environmental impact; energy consumption

1. Introduction

Intensive swine farming is a significant branch of the agri-food industry. Its expansion, driven by the increasing demand for animal-derived protein, has intensified concerns about its environmental impacts as large volumes of wastewater accumulate in confined areas [1]. Swine wastewater, also known as slurry, is a dark and odorous effluent with a moisture content of at least 85%, high pH and elevated levels of organic matter, nitrogen, phosphorus, and heavy metals, all of which are potential pollutants [2–4]. The agricultural application of slurry as a nutrient source for soils and crops is a widespread practice; however, its repeated long-term use can lead to the accumulation of contaminants in the environment [5,6]. In regions with high concentrations of livestock farming, such as Casilla y León (Spain), soil and water contamination resulting from this practice has become a primary concern, prompting the development of specific regulations that designate "vulnerable areas" in which farmers must comply with mandatory action programmes [7].

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In addition, at the national level, other regulations limit the concentration of heavy metals in the fertilizers [8,9].

In recent years, various technologies such as aerobic and anaerobic processes, chemical oxidation, membrane separation, and electrolysis has been extensively studied to reduce the pollutant load of swine slurry [1]. Recent studies and reviews indicate that among these processes, electroflocculation is an efficient, sustainable, and cost-effective alternative for wastewater treatment, offering low energy consumption, safety, and ease of automation [10–13].

Electroflocculation (EF) is an efficient, eco-friendly electrochemical process for treating wastewater contaminated with heavy metals and organic pollutants [10,14]. By applying a low-intensity current to sacrificial anodes (typically aluminum or iron), metal ions are released to form insoluble (oxy)hydroxides. These act as coagulants, adsorbing contaminants into flocs that float via cathode-generated hydrogen gas. Upon completion of treatment, two distinct phases form: a creamy, foam-like flocculated layer of aggregated particles at the top, and a clearer liquid phase below representing the treated effluent (Figure 1) [15]. When the flocs precipitate the process is called electrocoagulation [16].

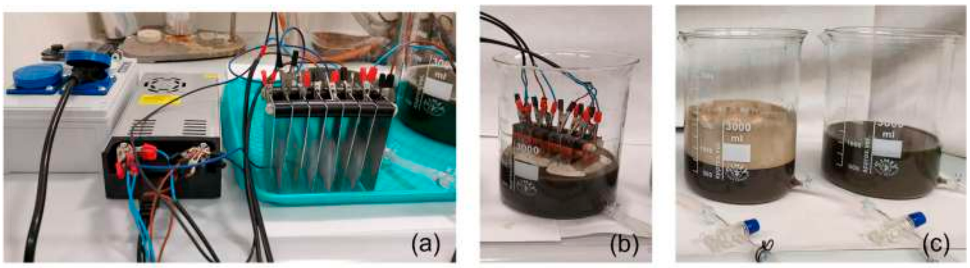

Figure 1. EF system setup (**a**) from left to right: DC power, potentiostat, stainless steel electrode and wires. (**b**) Ongoing electroflocculation using copper electrode, (**c**) aspect of the treated and untreated slurry after EF.

Among the operational parameters electrode material is critical in EF, determining the chemical reactions and contaminants removed [17]. Aluminum and iron are most commonly used due to their low cost and effectiveness, while copper, titanium, zinc, and stainless steel have been employed in other industries, and carbon has been used primarily as electrode coatings [16,18–20]. Exposure time directly affects metal ion release, floc formation, and removal efficiency. Although longer times enhance recalcitrant compound removal, they increase energy consumption and sludge production, requiring optimization. Many treatments exceed 30 min, sometimes lasting hours, with high current intensities [11,20], making large-scale application costly for farmers. Investigating less-studied electrode materials could accelerate purification and reduce energy use, achieving fertilizer-safe contaminant levels more efficiently.

To address these limitations, the present work shifts the focus toward the evaluation of stainless steel, carbon, copper, and zinc as sacrificial electrodes, moving beyond the conventional reliance on aluminum and iron. Crucially, the experimental design prioritizes short treatment intervals, specifically below the 10 min threshold, to identify configurations that maximize pollutant removal while minimizing the operational footprint.

This study evaluates the performance of an EF system for the treatment of swine wastewater using different electrode materials. The main objectives are: (1) to compare the removal efficiency of contaminants using five different metallic electrodes (aluminum, stainless steel, carbon, copper, and zinc), and (2) to determine the effect of exposure time to electric current on the efficiency of the EF process.

2. Materials and Methods

2.1. Swine Wastewater

The slurry used in this study was collected from a storage pond at a swine farm located in Boadilla de Rioseco (Palencia, Spain). Before testing, the slurry was filtered through a 0.5 mm mesh to remove suspended solids and stored at 4 °C throughout the experimental period.

2.2. Electroflocculation System Setup

The electrodes were assembled from metal plates, aluminum (Al), stainless steel (Ss), carbon (C), copper (Cu), and zinc (Zn), and connected in an alternating anode–cathode configuration using insulated wires, with a 15 mm spacing between plates. Electrode dimensions are shown in Table 1. A 3000 mL Pyrex beaker (VILABO, Marinha Grande, Porturgal) of 200 mm height, 160 mm diameter was used as the electroflocculation reactor with 1 L of the filtered slurry. The system consisted of a regulated DC power supply with a circuit breaker, maintaining a constant current at 12 V (0.51 mA, Figure 1). The experiments were performed in a room at 19 °C. The electrical energy consumption per litre was 0.306, 0.612, and 0.918 Wh·L^{-1} for exposure times of 3, 6, and 9 min, respectively (Equation (1)). Three replicates per treatment were subjected to EF, while an untreated one was considered a control. After EF, the samples were settled for two hours to allow the flocculation stabilization [21]. A sample of each replicate of the clarified liquid was taken from the bottom outlet.

$$Energy\ consumption = \frac{Voltage\ (V) \times Current\ density\ (A) \times Time\ (h)}{Volumen\ (L)} \tag{1}$$

$$Efective\ area = width\ (cm) \times effluent\ height\ (cm) \times 2\ plate\ faces \tag{2}$$

$$Current\ density = \frac{Ampers\ (A)}{Effective\ area\ (cm^2)} \tag{3}$$

Table 1. Electrode dimensions and characteristics.

	Aluminum	Carbon	Copper	Stainless Steel	Zinc
Plate height (cm)	10.5	15.0	10.0	10.0	10
Plate width (cm)	4.5	0.7 (diameter)	3.8	5	5
Plate thickness (cm)	0.06	-	0.08	0.06	0.04
Effluent height (cm)	6	6	6	6	6
Electrode effective area (cm^2) [1]	54	13.2	45.6	60	60
Number of plates	8	4	8	8	8
Current density (A/cm^2) [2]	1.4	1.1	1.6	1.3	1.3

[1] Equation (2); [2] Equation (3).

2.3. Parameters Evaluated

Both untreated (control) and treated samples were submitted to the Itagra.ct laboratory for chemical characterization. The following analytical parameters were evaluated:

General properties: pH was measured using a potentiometer, and electrical conductivity (EC, mS·cm^{-1}) was determined with a conductivity metre. Ash content (% dry matter) and organic matter (% dry matter) were quantified by gravimetric analysis using a muffle furnace at 105 °C.

Nutrients and contaminants: Total nitrogen (TN, % dry matter) was determined using the Kjeldahl method, and ammonia (NH_4^+, % dry matter) by distillation. Phosphorus, potassium, calcium, magnesium, sodium (% dry matter), copper, and zinc (mg·kg^{-1} dry matter) were analyzed following microwave digestion and inductively coupled plasma optical emission spectrometry (ICP-OES; SPECTRO Analytical Instruments, Kleve, Germany). Turbidity (NTU) was measured with a nephelometer, and chemical oxygen demand (COD, mg/L) was quantified through dichromate oxidation using redox titration.

2.4. Statistical Analyses

Electrode material and exposure time were evaluated as treatment factors. Due to the lack of normality and homogeneity of variances, the Kruskal–Wallis test was applied ($\alpha = 0.05$), followed by Bonferroni-adjusted post hoc comparisons when significant effects were observed.

3. Results and Discussion

This study evaluated the effects of various metallic electrodes and short exposure times on swine wastewater to lower pollutant load. Zinc and then stainless steel were the most effective electrode materials in removing pollutants from the treated wastewater starting from 6 min of current exposure. The mechanism of the pollutant removal can be explained as follows: while EF is taking place, a direct current applied to the zinc or stainless steel anode induces rapid oxidative dissolution, releasing Zn^{2+} or Fe^{2+} and Fe^{3+} ions that immediately hydrolyze to form insoluble $Zn(OH)_2$ and $Zn(OH)^-$ species or $Fe(OH)_2$ [20,22]. These electro-generated hidroxide species act as in situ coagulants, destabilizing suspended and dissolved pollutants into flocs while hydrogen gas bubbles generated at the cathode ($2e^- + 2H_2O \rightarrow H_2 + 2OH^-$) enhance flotation of flocs to the water surface, facilitating physical separation [15,20]. The stainless steel electrode was less effective than zinc. It might be due to its composition which also includes chromium and nickel which induces the formation of a pasivation film that prevents the rapid release of Fe^{3+} responsible for rust production [22].

3.1. Raw Swine Wastewater Characteristics

The physicochemical characteristics of the raw swine wastewater used in this study are summarized in Table 2 and reveal the complexity of the effluent typical of intensive swine farm operations. General properties such as the alkaline pH, humidity and ashes of the studied wastewater fall within the range of other raw materials [23–25]. Other studies reported electrical conductivity lower than 10 mS/cm [23,24,26], while our material showed higher values, probably due to the significant concentrations of salts within the effluent [24]. Initial turbidity was higher than the value of 3500 (NTU) reported by Bied et al. [26] which is likely attributable to their pre-treatment of excluding suspended solids from the measurement. The original COD of our study is consistent with the ranges reported by the review carried out by López-Pacheco et al. [24] of 1963–20,180 mg/L and it is slightly higher than the value of 11.2 g/L reported by Bied et al. [26]. In terms of total nitrogen, our sample slightly exceeded the upper limit of the range reported by López-Pacheco et al. [24] for swine wastewater (1434 mg/L) while it remained well below the values measured by Zhang et al. [25] of 6125 mg/L, who filtrated the material with a mesh half of the size employed in our study. Regarding ammonium, it was in accordance with the upper limit found by Chen et al. [27] of 2200 mg/L and, as in our study, it represented the majority of the total nitrogen. Copper and Zinc concentrations equivalent to approximately 4.556 and 7.54 mg/L respectively are consistent with the ranges reported by López-Pacheco et al. [24]. These values are also under the permitted limits of 1000 mg/kg of copper and 2500 mg/L of Zinc by the Spanish regulation [8]. Overall, the physicochemical profile of the raw wastewater is representative of the swine effluents reported in the literature, with observed deviations attributable to the specific characteristics of the farm system employed in this study.

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Table 2. Mean and standard deviation values of untreated slurry.

pH	Electrical Conductivity (mS/cm)	Humidity (%)	Ashes (%)	Organic Matter (%)
8.44 ± 0.24	13.20 ± 0.51	98.73 ± 0.09	46.7 ± 3.26	53.29 ± 3.26
Turbidity (NTU) 5467.58 ± 1153.49	COD (mg/L) 13,145.89 ± 2138.45	N_2 (mg/L) 1675.00 ± 75.38	NH_4^+ (mg/L) 1283.33 ± 57.74	
P (mg/L) 73.32 ± 24.98	K (mg/L) 1769.14 ± 34.68	Ca (mg/L) 251.86 ± 61.02	Mg (mg/L) 53.87 ± 18.20	Na (mg/L) 418.51 ± 16.25
Cu (mg/kg) 359.09 ± 56.34	Zn (mg/kg) 751.33 ± 160.23	Cr (mg/kg) 0.00	Ni (mg/kg) 0.00	

3.2. Contaminant Removal

Turbidity significantly declined (χ^2 = 46.32, $p < 0.0001$), with the zinc electrode achieving 60.2–67.40% removal and the stainless steel electrode with a 43.2–47% removal rate at 6 and 9 min (Figure 2a). This reduction is consistent with rapid destabilization of suspended particles via electrochemically generated metal species and subsequent floc formation, which enhances solid–liquid separation. Our results were moderate compared with a study performed on wastewater from pig slaughterhouse which found a reduction in turbidity of almost 90% with stainless steel electrodes at 100 min of exposure and 30 V [12]. Also, a study performed with synthetic dairy wastewater from milk powder required significantly longer electrolysis periods (60–90 min) at higher voltage (20 V) to achieve complete turbidity removal [28]. Rapid reaction and low energy consumption make the EF process of our study a cost-effective pre-treatment. Despite incomplete turbidity removal, its efficient floc formation offers a practical alternative to conventional, longer-duration EF.

In our study, organic matter decreased significantly (χ^2 = 43.57, $p < 0.01$), with zinc electrodes achieving a 16.9–23.8% removal rate within 6 to 9 min (Figure 2b). In contrast, Rahman and Borhan [23] treated liquid swine manure effluent using conventional electrodes (Fe-Fe, Al-Al, and Fe-Al hybrids) at current densities of 5, 10, and 21 mA cm^{-2}. By employing fluctuating voltage over a considerably longer treatment period of 30 min, they achieved a higher total organic carbon (TOC) removal rate of 85% using Fe electrodes at the maximum current density (21 mA cm^{-2}). While conventional electrodes can achieve higher overall removal rate efficiencies, the zinc-based system developed in this study emphasizes faster treatment and improved operational efficiency.

Phosphorus, one of the main causes of eutrofication, markedly declined with zinc (50.75–62.09%) and stainless steel (29.42–36.37%) electrodes from 6 to 9 min (χ^2 = 43.32, $p < 0.01$; Figure 2c). The primary mechanism behind this reduction is attributed to the formation of metal precipitates with phosphates. Higher efficiencies have been reported with conventional electroes under longer treatment periods. For instance, Chen et al. [27] achieved 99.5% of total phosphorus removal, but using iron electrodes over 35 min and pH 6.3, while Rahman and Borhnan [23] achieved 100% of phospohorus removal using Aluminum electrodes with a current density of 21 mA/cm^2 in 20 min. Regarding alternative electrodes Zhang et Hu [25] achieved a phosphorus removal efficiency of 86.3% using a low carbon steel electrode at a current density of 263 A/m^2 and 100 min of current exposure. Dura and Breslin [22] investigated stainless steel anodes for phosphate removal from synthetic wastewater, finding phosphorus removal between 37 and 92% in over 60 min at 11.7 mA cm^{-2}. Reza et al. [19] evaluated multiple electrode combinations on onsite wastewater, demonstrating that Al-based systems and Mg/Mg combinations achieved >95% phosphate removal within 150 min. In our context, complete phosphorus removal is not necessarily desirable, as maintaining residual phosphorus is beneficial when the treated effluent is intended for agricultural reuse, where it can act as a nutrient, while still reducing concentrations sufficiently to mitigate the risk of eutrophication in receiving water bodies.

Calcium showed similar decreases with zinc (36.08–54.37%) from 6 min onwards and stainless steel (24.15–27.86%) at 6 and 9 min (χ^2 = 46.99, $p < 0.01$; Figure 2d). Finally, magnesium and sodium were also significantly reduced: zinc electrodes decreased magnesium by 26.15–52.7% and sodium by 27.06–38.49% (both at 6 and 9 min), while stainless steel achieved 34.06% magnesium and 19.23% sodium removal at 9 min (χ^2 = 40.4, $p < 0.01$ for Mg; χ^2 = 40.13, $p < 0.001$ for Na; Figure 2e–f). These elements in excess may lead to soil and water pollution problems. For instance, excessive magnesium can reduce soil infiltration rates and hydraulic conductivity, negatively affecting water movement and crop growth [29]. While sodium may lead to soil salinization and sodicity, which degrade soil structure and reduce permeability [30]. They may also cause nutrient imbalances due to competition with other nutrients, potentially disrupting nutrient availability for plants [31]. Despite their importance, these elements in swine wastewater treatment have been scarcely studied. Calcium and magnesium removal by electroflocculation has been studied in wastewater of other indutries, and sodium to our knowledge has not yet been studied. A study treating drainage water of a petrochemical company by electrocoagulation achieved a 94.71% calcium removal rate and 96.33% magnesium removal rate under the optimized conditions of pH 11, current density of 22 mA/cm^2, and reaction time of 46 min [32]. This removal rate was attributed to the formation of calcium carbonate and magnesium hydroxide precipitates [32]. Lei et al. [33], aiming to remove calcium and magnesium from domestic water, found a reduction of 53% of magnesium and 42% of calcium in the form of brucite and calcite, respectively using platinum and titanium electrodes for 24 h at high pH.

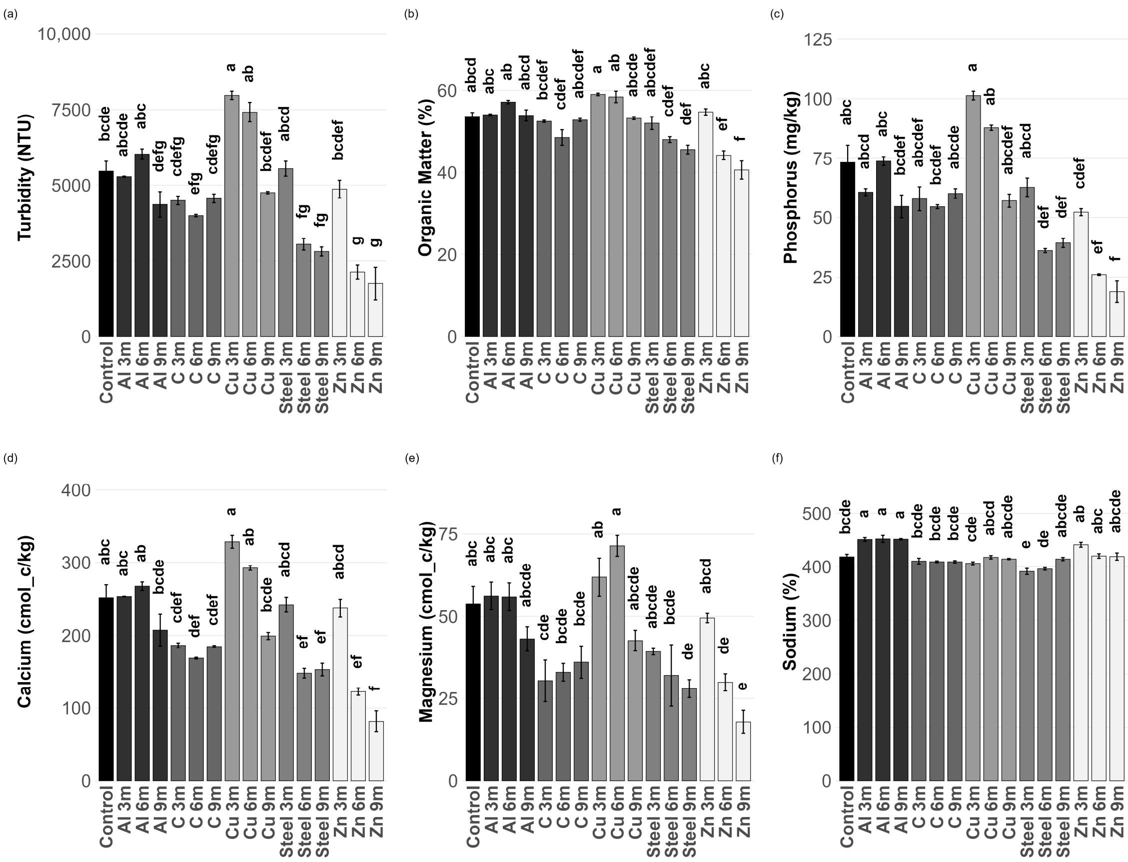

Figure 2. Effect of treatment on turbidity (**a**), organic matter (**b**), phosphorus (**c**), calcium (**d**), magnesium (**e**), sodium (**f**). The lowercase letter on top of the bars are the groups from the Bonferroni-adjusted post-hoc comparisons.

3.3. Treatment Limitations: Insufficient Nutrient Removal and Electrode Metal Release

Concerning nitrogen, ammonium, and COD, although significant differences were observed among treatments ($p < 0.05$ in all cases), the post hoc comparison revealed no significant differences between the control and treatments (Figure 3), most likely because optimal removal of these nutrients requires considerably longer treatment durations (30–90 min) [34] than the exposure times employed in this study, as shown by Rahman and Borhan [23], who achieved 85% total organic carbon removal with 30 min of electrolysis.

The rest of the electrodes, including aluminum, did not show any effect on contaminant removal under the tested time and voltage. Regarding the lack of effect of aluminum electrodes, this might be due to their pH sensitivity. Under basic pH, aluminum stops forming solid hydroxide clumps that trap contaminants, and instead dissolves back into the water as soluble aluminate species [$Al(OH)_4^-$] [11,35]. This condition likely occurred during the first few minutes of treatment given the initial pH of the slurry (mean 8.4 ± 0.24). In contrast, zinc and stainless steel electrodes, which form effective hydroxides in alkaline pH ranges (>7.5), proved to be more suitable for the treatment of swine effluents under these operational conditions [22].

Heavy metal concentrations starkly increased during treatment: copper levels increased by more than 200% ($\chi^2 = 44.4$, $p < 0.01$) when using the copper electrode and zinc by more than 2000% ($\chi^2 = 45.80$, $p < 0.01$) when using the zinc electrode (Figure 4). Chromium and nickel, part of the stainless steel composition, were also detected in the treated effluent when the stainless steel electrode was used while they were absent in the untreated slurry (Table 2). Comparing the amount of metal released with the actual regulation, the use of zinc electrodes results in zinc mean concentrations of 21,546.31, 21,225.68 and 22,006.87 mg/kg at 3, 6 and 9 min of current exposure respectively. This amount exceed regulatory limits (2500 mg/kg from the earliest treatment time); therefore, post-treatment is mandatory before agricultural reuse. Conversely, stainless steel electrodes presented a more favourable compliance profile with a mean concentration of 11.23, 109.21 and 403.57 mg/kg of nickel, at 3, 6 and 9 min of current exposure respectively. And a mean concentration of 32.83, 253.19 and 572.84 mg/kg of chromium at 3, 6 and 9 min of current exposure respectively. The regulatory limit for nickel is 300 mg/kg and for chromium 1000 mg/kg; it means, that under the treatment of 6 min these heavy metals remain below regulatory thresholds [8,9]. This suggests that 6 min of treatment is a good compromise to reduce turbidity, phosphorus, calcium and trends in magnesium and sodium, maintaining safety without the need of post-treatment.

In terms of nitrogen, Spanish regulations establish a maximum application limit of 170 N kg/ha for sustainable soil nutrition in vulnerable areas [7]. In the untreated effluent the mean nitrogen concentration was 1675.00 mg/L (Table 2) and assuming a typical slurry application depth of 10 mm, the nitrogen load per hectare would be approximately 16.00 kg N/ha, keeping below the regulatory threshold [7]. This demonstrates that compliance with nitrogen limits can be readily achieved by regulating slurry application rates and, if necessary, diluting the effluent with water, as outlined in the Code of Good Agricultural Practices, thereby enabling safe agronomic reuse of electrocoagulation-treated swine wastewater [8].

It is important to highlight that the objective of the electroflocculation treatment is not to achieve complete wastewater purification; the goal is to achieve a balanced reduction between adequate plant nutrition and lowering contamintant concentration to minimize pollution risk.

It should be noted that electrode reusability and cycling stability were not evaluated in this study. In practical applications, repeated use of the electrodes may alter their surface properties, affect dissolution rates, and consequently reduce treatment efficiency over time. This aspect remains a key factor for assessing the long-term operational viability and cost-effectiveness of the electroflocculation system, and will be addressed in future work.

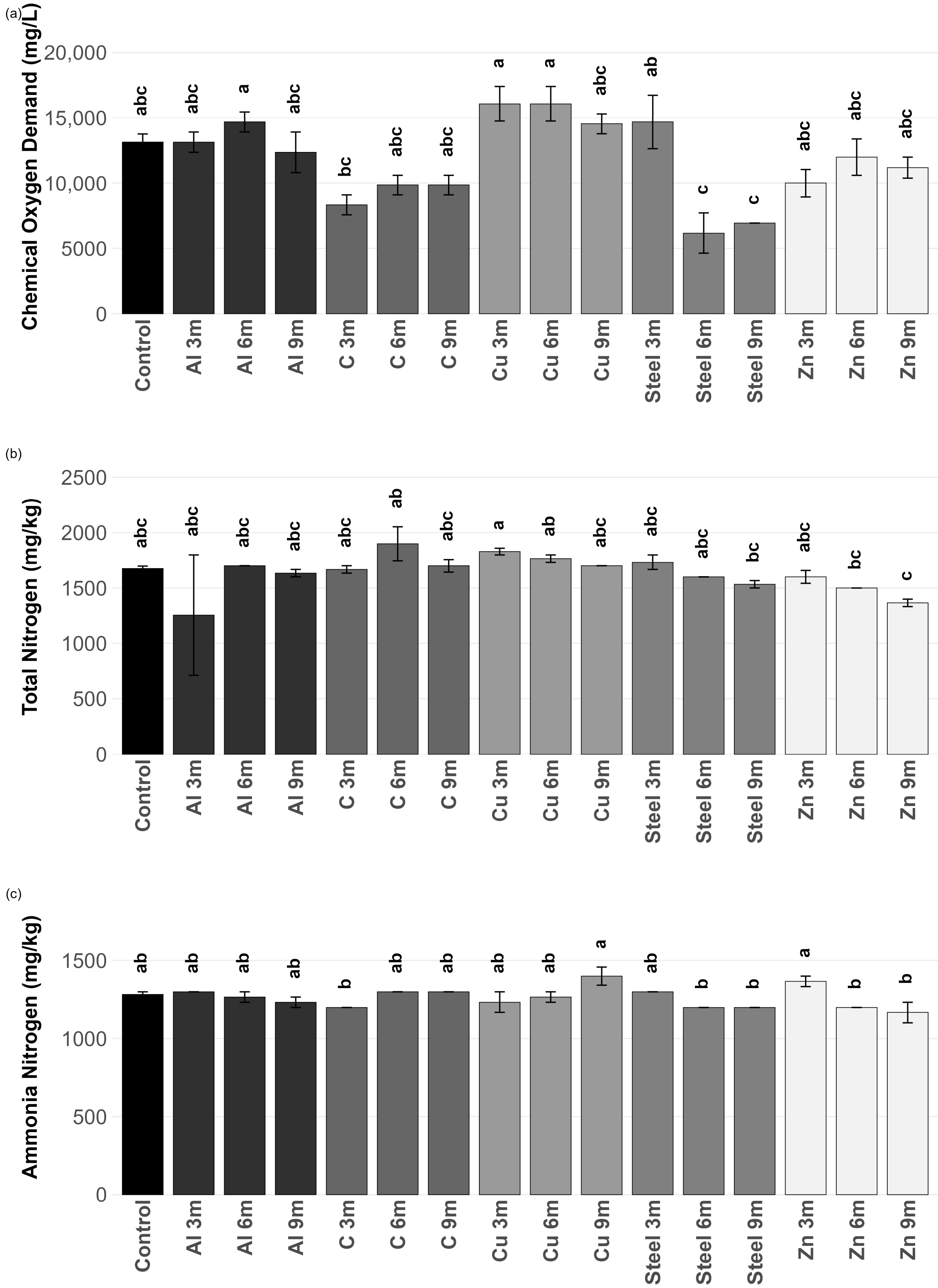

Figure 3. Effect of treatment on COD (**a**), total nitrogen (**b**), ammonia (**c**). The lowercase letter on top of the bars are the groups from the Bonferroni-adjusted post-hoc comparisons.

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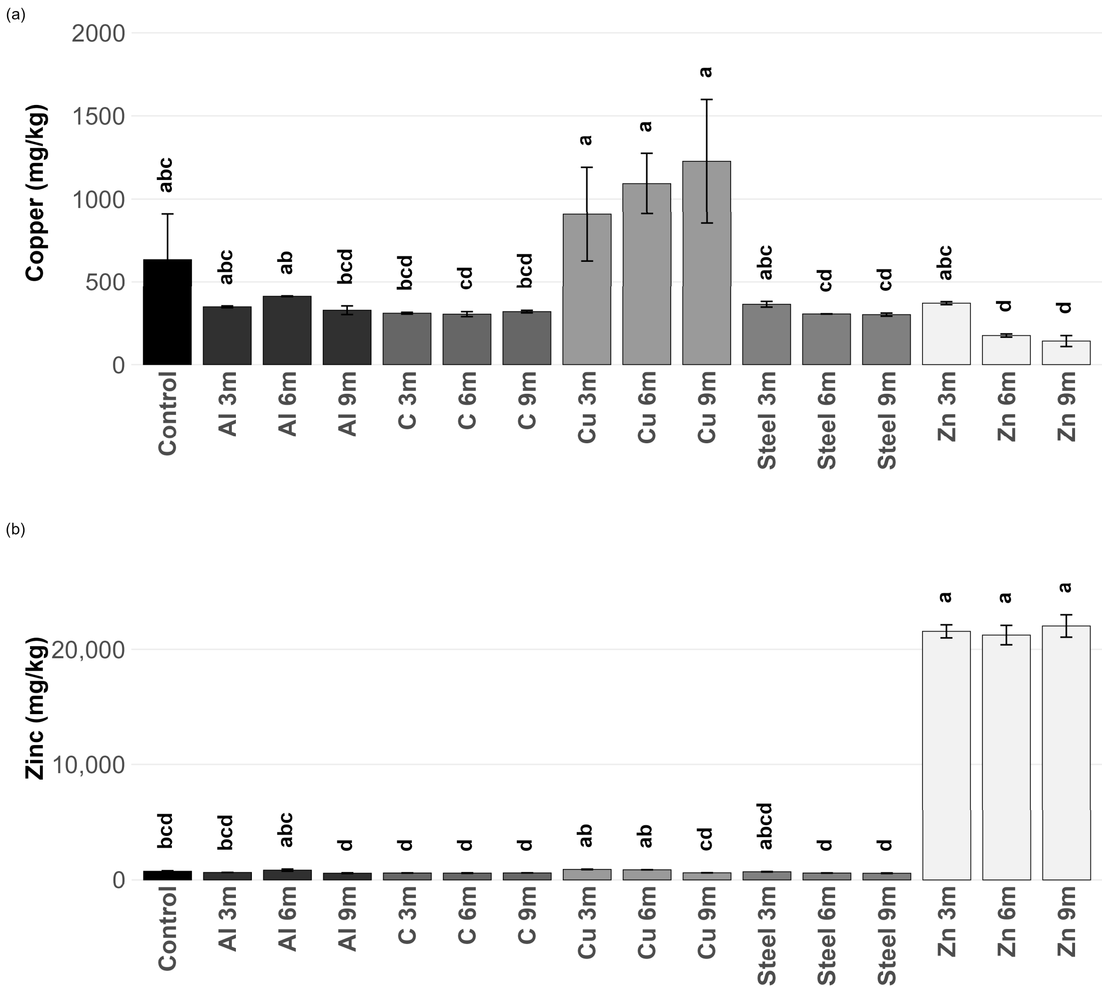

Figure 4. Levels of copper and zinc in the effluent when using copper and zinc electrodes after treatment. Copper (**a**), Zinc (**b**). The lowercase letter on top of the bars are the groups from the Bonferroni-adjusted post-hoc comparisons.

4. Conclusions and Future Perspectives

This study shows that EF can act as an effective, low-energy pre-treatment for swine wastewater when using alternative electrode materials for short periods. Zinc and stainless steel electrodes performed best, reducing turbidity, organic matter, phosphorus, and minerals like calcium, magnesium, and sodium in just 6–9 min. The mean energy consumption of 0.612 Wh/L may offer cost advantages. However, nitrogen, ammonium, and COD were not significantly reduced, suggesting longer treatment times are needed for these contaminants. Critically, the main challenge is that whilst zinc and stainless steel electrodes were highly effective, they released heavy metals into the solution. However, for stainless steel, 6 min of treatment keeps chromium and nickel below regulatory limits, allowing agricultural reuse without additional treatment. Future research should refine stainless steel parameters or investigate hybrid and pulsed-current configurations to mitigate leaching while trying to decrease nitrogen and COD. Integrating the process with low-cost absorbents can further sequester residual heavy metals from electrodes. Future work will systematically evaluate electrode reusability and cycling stability, an aspect not assessed in this study but critical for determining the practical scalability of the proposed electroflocculation system. A successful pilot-scale trial in this field should prioritize the management of sludge, alongside the evaluation of long-term soil health, while maintaining the current energy-efficient performance.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/eesp2026042005/s1, Table S1: Mean and standard deviation of physico-chemical Pollutant Removal per treatment; Table S2: Mean and standard deviation of nutrient and oxygen demand per treatment; Table S3. Mean and standard deviation of mineral elements per treatment; Table S4. Mean and standard deviation of heavy metals per treatment.

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