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# Utilization of Thermophilic Aerobic Oxidation and Electrocoagulation to Improve Fertilizer Quality from Mixed Manure Influent

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**Abstract:** Thermophilic aeration and electrochemical reactions are well-established methods for wastewater treatment to reduce metallic content, organic and inorganic matter, turbidity, coloration, and nutrient levels. In this study, thermophilic aerobic oxidation (TAO) and electrocoagulation (EC) were implemented together to improve the quality of liquid fertilizer by reducing the nutrient load and toxicity of swine manure. The influent in this study was prepared by mixing anaerobic digestate and liquid swine manure at a 1:9 ratio and treating it for 3 days at 50–60 °C in a field-scale TAO system. The TAO effluent was then processed in an EC reactor for 180 min with a 30 V electric supply through two sets of iron and aluminum hybrid electrodes. The combined TAO and EC processes led to a germination index of 133% using the final efflux. The high retention of important nutrients such as total nitrogen and potassium, combined with the 100% reduction in heavy metals, over 60% reduction in trace minerals, and 89% reduction in pollutants in the final product, helped to achieve a higher germination index. Overall, the combination of TAO and EC was demonstrated to be an effective technique for enhancing the quality of liquid fertilizer derived from swine manure.

**Keywords:** swine manure; anaerobic digestate; liquid manure; treatment; maturity; germination index; heavy-metal removal; trace mineral; COD removal

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## 1. Introduction

The Korean livestock sector produced 51.94 million tons of manure in 2020, with pig manure accounting for over 40% of this. Over 74% of the manure produced by pig farms is converted into compost or liquid fertilizer [1]. Although liquid manure is the finest alternative to chemical and mineral fertilizers, the agronomic values and application rates of manure vary depending on the demand for plant nutrients, soil condition, physical and chemical features of the soil, and application frequency. However, without adequate treatment, the high concentrations of nutrients and organic compounds in liquid manure can have a negative effect on soil and water ecosystems [2–4]. Liquid manure also needs to be carefully managed to avoid odorous gas emissions and nutrient runoff into water sources [5]. As a consequence, the characteristics of liquid fertilizer are monitored to ensure that the quality is up to the required standards for application to farmland [6]. High levels of nutrients and heavy metals have harmful effects on the soil and vegetation [7–10].

Liquid swine manure (LSM) and anaerobic digestate (AD) are commonly used on farmland as organic fertilizers due to their high nutrient loads [5,11,12]. LSM contains all 13 essential nutrients [13], including 50–70% N, 90% K, and 35% P for plant consumption [14,15], while the high N, P, and K content in liquid or semiliquid AD increases its demand as a fertilizer [16,17]. However, the N content in AD primarily comes from $NH_4^+$-N due to the presence of nitrifying bacteria and the alkaline pH [18,19]. The concentration range for commercially manufactured LSM fertilizers should be within 2900 mg/L for N, 70 mg/L for P, and 660 mg/L for K, and the total NPK has to be 0.3% according to the Korean government standard [20,21]. It is also said that the maximum toxicity levels of Cu, Zn, and Ni are 50 mg/L, 130 mg/L, and 5 mg/L, respectively, and that the acceptable conductivity range for manure must be between 15 and 3 mS/cm [20,22]. Meanwhile, Korean fertilizer regulations prohibit the use of AD as a fertilizer if it contains more than 30% food waste. As a result, AD obtained only from food waste requires advanced treatment; alternatively, FWAD might be treated with another organic liquid waste [22,23].

In addition to these nutrients, LSM and AD are characterized by a high chemical oxygen demand (COD), biological oxygen demand (BOD), and heavy-metal content [24,25]. Although trace metals such as Zn, Cu, Mg, and Fe are valuable for plant growth, the over-application of LM and AD can contribute to soil acidification or secondary salinization and, thus, reduce the effectiveness of soil amendment [26,27]. The residual and additional N, P, and heavy metals can also leach into the soil and cause soil, surface water, and groundwater pollution [11,28]. Similarly, the high $NH_4^+$-N levels in AD can be toxic for plants and, thus, stunt their growth, while pathogens in improperly treated LSM and AD can also cause environmental problems for the soil [24,28–30]. Thus, AD requires effective treatment to meet soil amendment standards and plant nutritional needs [18,24]. Conventional manure treatment techniques often focus on treating one or a few of the components of manure and, thus, cannot completely fulfill liquid fertilizer standards on their own [31]. Moreover, several manure treatment processes generate $NH_4^+$ and odors, require significant treatment time to produce fertilizer of sufficient quality, and/or need to be stored for a long time before application [32]. To overcome these limitations, we designed in the present study a rapid two-step manure treatment method that combines thermophilic aeration oxidation (TAO) and electrocoagulation (EC). Aeration involves the oxidization of bioavailable compounds via continuous air injection; TAO offers a more rapid aeration-based manure treatment process by maintaining a high temperature under aerobic conditions without the use of an external heat source [33,34]. Generally, thermophilic aeration processes are maintained at around 62–67 °C [35], but TAO systems are maintained at around 55–65 °C during treatment [33,34]. The organic compounds in the manure are degraded via the aerobic respiration of thermophilic bacteria [36], and pathogens are eliminated by the thermophilic conditions [34]. However, heavy metals and inorganic matter still remain in the effluent from TAO systems.

EC can be employed to effectively remove heavy metals and inorganic material from manure. Based on electrochemistry, EC systems employ coagulation and flotation to remove pollutants via oxidation–reduction reactions and the interchange of ions and electrons [37,38]. Iron (Fe) and aluminum (Al) electrodes are generally used for electrolysis in these systems [37,39]. Although heavy metals, trace minerals, and other contaminants are effectively removed using EC processes [37–42], the use of EC by itself can be economically unviable due to the excess electrical power required to remove large volumes of organic matter [43].

Because of the higher levels of nutrients and solids in AD compared with LSM, we mixed these in the present study and utilized a combination of TAO and EC to rapidly treat this influent. The main aim of this study was to investigate the treatment efficiency of the TAO–EC system in order to improve the quality of the resulting liquid fertilizer using a mixed AD influent.

## 2. Materials and Methods

### *2.1. Influent Collection*

The influent for the TAO system was prepared by mixing 100% FWAD derived from biogas production and aerated LSM at a 1:9 ratio. The influent was treated in the TAO system for 3 days. The thick FWAD slurry was stored in a semi-covered container and had high concentrations of all manure parameters including total solids (TS), while the LSM was treated in an aeration–circulation system and had lower concentrations (Table 1). The 1:9 mixing ratio was selected on the basis of the influent characteristics and the target optimal temperature (50–65 °C). The ability of a TAO system to maintain a steady temperature depends on the organic matter load and the external temperature. A high loading of organic matter in the influent in warm conditions quickly increases the internal temperature and leads to evaporation rather than fermentation. In a preliminary study, we found that, if the FWAD slurry made up more than 20% of the TAO influent, the system reached 70 °C too quickly, leading to technical issues. We found that 10% FWAD and 90% LSM generated the ideal conditions for the TAO system.

**Table 1.** Physiochemical parameters of the food waste anaerobic digestate (FWAD) and liquid swine manure (LSM).

| Items | Units | FWAD | LSM | Items | Units | AD | LSM |
|---|---|---|---|---|---|---|---|
| Conductivity | mS/cm | 36.17 ± 10.66 | 3.98 ± 0.25 | Cu | mg/kg | 2.14 ± 1.77 | 1.22 ± 0.20 |
| pH | | 8.85 ± 0.20 | 7.84 ± 0.13 | Ni | | 0.63 ± 0.02 | 0.17 ± 0.29 |
| TS | % | 2.83 ± 0.85 | 0.77 ± 0.31 | Zn | | 4.20 ± 0.72 | 6.87 ± 2.74 |
| N | mg/L | 5371.79 ± 1433.19 | 969.37 ± 168.07 | Mg | | 4.93 ± 3.20 | 119.64 ± 32.79 |
| $NH_4$-N | | 4247.35 ± 1183.20 | 270.21 ± 25.25 | Ca | | 398.30 ± 306.27 | 157.47 ± 25.85 |
| $NO_3$-N | | 260.23 ± 80.69 | 173.29 ± 47.39 | $SO_4$ | | 260.23 ± 137.68 | 140.96 ± 49.20 |
| P | | 199.36 ± 123.89 | 126.31 ± 50.53 | Fe | | 69.83 ± 41.49 | 24.40 ± 4.71 |
| K | | 1587.88 ± 297.11 | 787.85 ± 100.65 | COD | mg/L | 4012.00 ± 1426.38 | 1243.72 ± 452.13 |
| Cr | mg/kg | 1.51 ± 0.31 | 1.32 ± 0.17 | | | | |

### *2.2. Description of the TAO System*

The field-scale TAO system used in this study consisted of a main reactor and an ammonia ($NH_3$-N) collection tank (Figure 1). The rectangular main reactor tank was fabricated from stainless steel to prevent the accumulation of harmful substances and leaks or fissures due to the internal liquid pressure. An ejector-type aeration pump was attached to the bottom to mix the influent, and a pump was installed at the top to remove the foam. Although the overall operational volume capacity was 5 ton, this investigation was run using a capacity of 1 t to prevent overflows and excessive foam production. An inlet pipe used to inject air into the reactor and an outlet pipe for gas exhaust and $NH_3$-N collection were connected to the top of the reactor. A brief description of the TAO system is presented in Table 2.

The TAO system was operated for 3–5 days while maintaining a temperature of 50–65 °C without an external heat source due to the sustained aerobic fermentation via continuous stirring and air injection. To prevent $NH_3$-N emissions and to transfer the generated gas during operation, a pipeline was connected to a 3 ton PVC tank. The pH was adjusted to shift the $NH_3/NH_4$ equilibrium in order to trap $NH_3$ gas in an acidic solution [44]. For this, the $NH_3$ pipeline was submerged in a low-pH solution. We used $H_2SO_4$ to maintain a pH level lower than 5 to prevent complete $NH_3$ immersion and transformed it into ammonium sulfate [45,46]. This solution was then mixed with raw manure in the influent tank. A hot water supply tank was available to circulate warm water and maintain the thermophilic temperature during cold weather; however, during this study, this was not required.

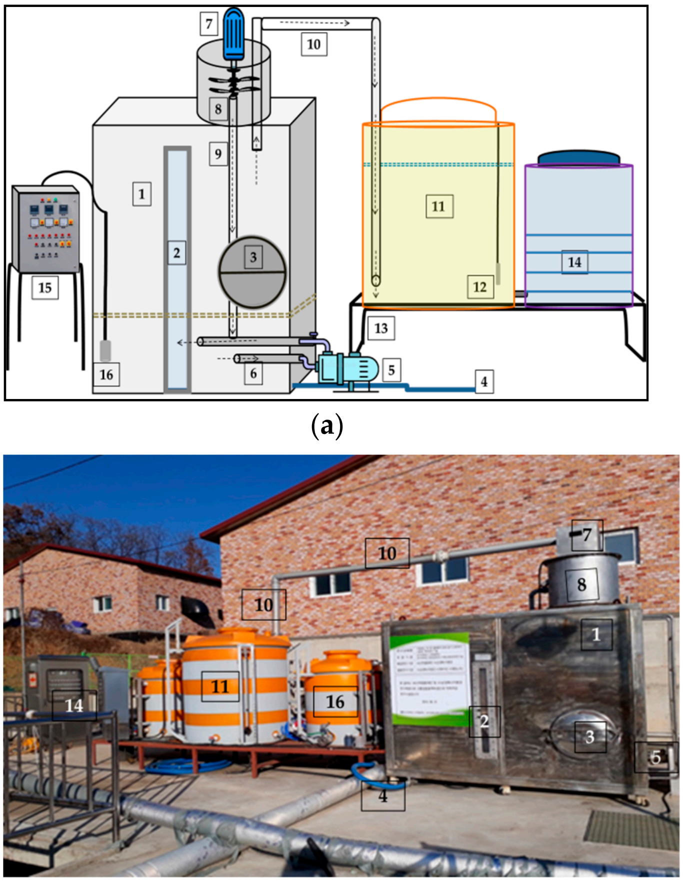


**Figure 1.** Field-scale TAO reactor (**a**) diagram and (**b**) the equipment. In the diagram, (1) main reactor tank, (2) looking glass, (3) hatch, (4) influent inlet pipeline, (5) ejector-type aeration pump, (6) manure circulation pipeline, (7) foam cutting motor, (8) foam cutting fan, (9) air circulation pipeline, (10) $NH_3$-N gas transfer pipeline, (11) $NH_3$-N trapping tank, (12) $NH_3$-N tank pH and temperature sensor, (13) tank supporting platform, (14) hot water supply tank, (15) control box, and (16) reactor pH and temperature sensor.

**Table 2.** Description of the TAO system.

| Unit | Category | Features | Description |
|---|---|---|---|
| 1 | Reactor tank | Material | Stainless steel |
| | | Total dimensions | 7.123 $m^3$ (L × W × H = 2.5 × 1.5 × 1.9) |
| | | Operational dimensions | 5 $m^3$ |
| | | Total volume capacity | 8–5 t |
| | | Operational volume capacity | 1–5 t |
| | | Operated volume | 1 t |
| | | Defoaming motor | 1 HP |
| | | Circulation tank | 3 HP |
| 2 | Ammonia collection tank | Material | CPVC |
| | | Size | 3 t |
| | | Operated volume | 2.8 t |
| | | Solution | Hydrogen sulfide solution (pH 2–5) |
| 3 | Sensors | pH | Submerged 1/3 of the height of the tank |
| | | Temperature | Reactor and ammonia collection tank |
| | Power supply and data logger | Installed beside unit 2 | Automatic data logger for temperature and pH |

*2.3. Description of the EC Process*

A diagram of the EC reactor is presented in Figure 2, and the EC equations are adopted from [46]. The reactor was a glass beaker with a height of 28 cm, a diameter of 20 cm, and a capacity of 5 L. The electrodes were a Fe cathode and an Al anode with a size of 28 × 3 × 1 cm and a depth of 22 cm. The power source (Toyotech TS3030A DC Power Supply) supplied a constant 30 V. A magnetic stirrer was used to ensure homogeneous circulation during the operating time of 180 min. The polarity of the cathode and anode changed every 30 min.

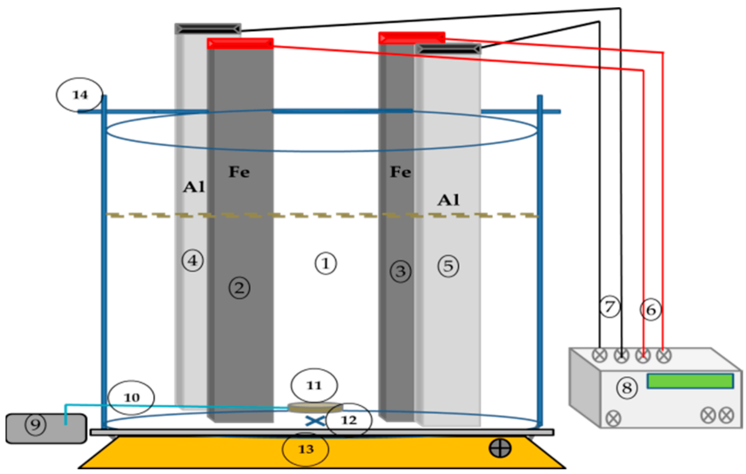


**Figure 2.** Diagram of the lab-scale EC reactor: (1) glass beaker (reactor), (2) cathode-1, (3) cathode-2, (4) anode-1, (5) anode-2, (6) positive wire, (7) negative wire, (8) dc power supply, (9) air pump, (10) air tube, (11) air stone, (12) magnetic bar, (13) magnetic stirrer, and (14) supporting stands.

Reaction for Iron (Fe)

$$\text{Cathode: } 2H_2O\ (l) + 2e^- \rightarrow H_2\ (g) + 2OH^- \quad (1)$$

$$\text{Anode: } Fe\ (s) \rightarrow Fe_2{}^+\ (aq) + 2e^- \downarrow \quad (2)$$

$$\text{Overall: } Fe\ (s) + 2H_2O\ (l) \rightarrow Fe(OH)_2\ (s) + H_2\ (g) \quad (3)$$

Reaction for Aluminum (Al)

$$\text{Cathode: } 3H_2O\ (L) + 1.5H_2\ (g) \rightarrow 1.5H_2\ (g) + 3OH^-\ (aq) \quad (4)$$

$$\text{Anode: } Al\ (s) \rightarrow Al^{3+}\ (aq) + 3e^- \quad (5)$$

$$\text{Overall: } Al^{3+} + 3OH^- \rightarrow Al(OH)_3Al\ (s) + 3H_2O\ (l) \rightarrow Al\ (s)\downarrow + 1.5H_2\ (g) \quad (6)$$

We used two sets of Fe and Al electrodes. The gap between two opposite electrodes was 1 cm to match the thickness of the electrodes. The distance between the two sets was 9 cm, and they were placed 4 cm from the reactor wall. At a high voltage, the EC process often raises the temperature and creates a thick flock layer on the surface, which prevents air accumulation in the reactor. To avoid this, air was injected into the solution using an aquarium air pump and aeration stones. The injected air also prevents clogging between the electrodes.

*2.4. Sample Analysis*

The physicochemical composition of the manure was examined using the liquid fertilizer quality certification (LFQC) method. The influent for the TAO system and the effluent from the EC process were sampled and analyzed three times. The physicochemical parameters (i.e., electrical conductivity, pH, TS total nitrogen (TN), $NH_4$-N, nitrate-nitrogen ($NO_3$-N), total phosphate (TP), potassium (K), and metals) of the samples were analyzed and categorized as physical parameters, nutrients, heavy metals, and trace minerals. The conductivity and pH were measured using a YSI meter (Multilab IDS 4010-2, Xylem Inc., Washington, DC, USA). The TS, TN, $NH_4^+$-N, $NO_3$-N, TP, and K were measured using APHA standard analysis methods [47]. The TN and $NO_3$-N were measured on the basis of Cd reduction in a flow-injection auto analyzer, and the $NH_4$-N concentration was measured using spectrophotometry. TP was measured using the molybdenum blue method. The levels of the heavy metals chromium (Cr), copper (Cu), nickel (Ni), and zinc (Zn) were measured using Spectroblue IPS.OES (FMX36, Germany) according to US EPA method 200.8 [48] as per the manufacturer's protocol. The concentrations of the trace minerals magnesium (Mg), calcium (Ca), sulfate ion ($SO_4$), and Fe were determined following US EPA method 200.7 [48]. COD was employed as a pollution indicator and measured using the $KMnO_4$ titration method.

### 2.5. Liquid Fertilizer Germination Index (LFGI)

The maturity of the samples was determined using the liquid fertilizer germination index (LFGI) [49]. The LFGI is a customized germination index based on the response of seeds to the phytotoxicity of liquid manure. The key difference between LFGI and conventional germination index (GI) tests is the dilution ratio for the liquid fertilizer samples. First, the dilution ratio was determined according to the compost fertilizer GI formula as a function of the moisture content of the sample, which was then multiplied by 1.5325. Aliquots of 25 mL were applied to 150 radish seeds in each of five Petri dishes. The seeds were incubated for 5 days in a dark incubator at a temperature of 25 °C and a humidity of 85%. The seed GI was determined by multiplying the seed germination by the root elongation (RE) (GI% = (GR × RE)/100). Halder [49] provides more details for this process.

### 2.6. EC Process Efficiency in Combination with the TAO System

The concentration reduction (CR) efficiency of the EC process in conjunction with the TAO system was calculated using Equation (7).

$$\mathrm{CR}\ (\%) = \frac{C_0 - C_1}{C_0} \times 100. \tag{7}$$

Three TAO samples were tested three times each with the EC process. All of the samples were analyzed in terms of their physiochemical properties and the GI. The mean and standard deviation were calculated for the collected data using SPSS (Statistical Package for the Social Sciences).

## 3. Results and Discussion

### 3.1. Removal Efficiency of the TAO System

In this study, N, P, and K were categorized as nutrients, while the heavy metals were classified as hazardous because not all plants require them as nutrients, and their intake is not as high as N, P, or K. Thus, heavy metals from liquid manure can accumulate in the soil and enter water sources, leading to pollution. Table 1 summarizes the differences in the chemical characteristics of the two waste streams. The AD had a higher nutrient concentration than did the LSM, particularly for $NH_4$-N, conductivity, TS, and COD. Because the composition of manure differs between individual farms, the LSM influent in the present study had a higher nutrient load than that reported for public liquid manure recycling centers by Jeon [6] and Halder [49]. Because the AD was mixed with the LSM at a 1:9 ratio, the TAO influent had lower nutrient and heavy-metal concentrations than the raw AD influent. However, the maturity of the influent was below the standard, while the COD was higher (1738.5 mg/L on average; Table 3).

**Table 3.** Characteristics of the influent and TAO effluent.

| Items | Unit | Influents ± SD | TAO ± SD | CR% | Items | Unit | Influents ± SD | TAO ± SD | CR% |
|---|---|---|---|---|---|---|---|---|---|
| Conductivity | mS/cm | 9.2 ± 0.7 | 8.6 ± 0.6 | 7 | Cr | | 1.1 ± 0.3 | 1.4 ± 0.3 | −33 |
| pH | % | 8.7 ± 0.2 | 8.6 ± 1.7 | 1 | Cu | | 1.2 ± 0.2 | 0.74 ± 0.2 | 37 |
| TS | | 0.6 ± 0.1 | 0.6 ± 0.4 | 0 | Ni | | 0.5 ± 0.1 | 0.6 ± 0.2 | −18 |
| N | | 1481.8 ± 16.5 | 1510.8 ± 172.2 | −2 | Zn | mg/kg | 5.7 ± 4.3 | 1.0 ± 1.09 | 82 |
| $NH_4$-N | mg/kg | 751.4 ± 119.1 | 608.1 ± 180.8 | 19 | Mg | | 100.2 ± 45.1 | 42.1 ± 57.8 | 58 |
| $NO_3$-N | | 162.4 ± 33.7 | 298.2 ± 226.6 | −84 | Ca | | 164.9 ± 26.4 | 127.8 ± 23.4 | 22 |
| P | | 140.9 ± 64.2 | 57.3 ± 56.4 | 59 | $SO_4$ | | 134.6 ± 83.3 | 149.2 ± 30.3 | −11 |
| K | | 916.1 ± 49.8 | 958.3 ± 18.4 | −5 | Fe | | 29.5 ± 1.2 | 21.9 ± 1.5 | 26 |
| | | | | | $COD_{Mn}$ | mg/L | 1738.5 ± 411.8 | 1163.5 ± 183.9 | 33 |

The TAO effluent reduced the concentration of $NH_4$-N and TP by about 19% and 59%, respectively, while it increased $NO_3$-N by 84% (Table 3). The TAO system also reduced the COD by 33% and Zn by 82%. Previous studies on TAO systems reported similar changes [50–52]. The aeration and circulation of the TAO system decreased the $NH_4$-N levels and increased the $NO_3$-N levels via the nitrification process involving oxidative reactions [53], which also led to a slight increase in TN. Aerobic breakdown also reduced the TP by 59% because the TAO effluent remained alkaline, leading to the precipitation of P under thermophilic conditions (Table 3) [53,54]. Furthermore, according to Juteau [55], a similar reduction in COD took place during thermophilic aeration at 60 °C as a result of the hydraulic residence time, temperature, oxygen transfer, stabilization of the mixing characteristics, and the degradation of organic matter [56]. According to Zhang [57], the reduction of Cu, Zn, and Mg occurred before thermophilic aeration reached its thermophilic stage due to steering and air injection.

### *3.2. Removal Efficiency of the EC Process*

#### 3.2.1. Physical Properties

The conductivity, pH, and TSs are critical parameters for electrochemical treatment, including EC systems, because they regulate the electrolysis rate [6,58]. The conductivity of the influent affects the current flow during the electrolysis process and the resistance of the electrolyte due to the formation of ionic compounds. In the study conducted by Mondor [59], the mean current density increased from 193 A/m$^2$ to 203 A/m$^2$, while the conductivity decreased from 69.2% to 57.1%. A higher current density is directly related to the removal efficiency for pollutants, increasing cathode metal ion diffusion and removing more pollutants by producing more hydroxyl ions ($OH^-$) [60,61]. In our study, the total reduction efficiency of the combination of TAO and EC led to a 34% decrease in conductivity, which may have increased the pollutant removal effect (Table 4). The pH changed with the formation of Fe–Al hydroxides and polymeric species during the electrolysis process [62,63]. The EC process increases the pH via the release of $OH^-$ from the Fe cathode [64,65], while $OH^-$ ions also coagulate and reduce the TS by trapping destabilized organic and inorganic species via electrolysis [66]. However, the TS removal rate was relatively low due to the low initial concentration in the influent (Table 4).

**Table 4.** Physiochemical properties during the EC process.

| Category | Items | Unit | EC | * CREC% | $^\wedge CR_{TAO–EC}$% |
|---|---|---|---|---|---|
| Physical properties | Conductivity | mS/cm | 6.04 ± 0.6 | 30 | 34 |
| | pH | | 10.6 ± 0.4 | −23 # | −22 |
| | TS | (%) | 0.5 ± 0.2 | 23 | 23 |

**Table 4.** *Cont.*

| Category | Items | Unit | EC | * CREC% | ^CR$_{TAO–EC}$% |
|---|---|---|---|---|---|
| Nutrient contents | TN | mg/kg | 1108.4 ± 149.2 | 27 | 25 |
| | $NH_4$-N | | 498.2 ± 118.4 | 18 | 34 |
| | $NO_3$-N | | 193 ± 121.3 | 35 | −19 |
| | TP | | 13.7 ± 3.1 | 76 | 90 |
| | K | | 829.4 ± 24.7 | 13 | 9 |
| Heavy metals | Cr | mg/kg | 1.01 ± 0.1 | 28 | 4 |
| | Cu | | ND | ≈100 | ≈100 |
| | Ni | | ND | ≈100 | ≈100 |
| | Zn | | ND | ≈100 | ≈100 |
| Trace minerals | Mg | mg/kg | ND | ≈100 | ≈100 |
| | Ca | | 36.3 ± 18.8 | 72 | 78 |
| | $SO_4$ | | 41.0 ± 14 | 73 | 70 |
| | Fe | | 10.1 ± 2 | 54 | 66 |
| Pollutant | $COD_{Mn}$ | mg/L | 185.4 ± 37.1 | 84 | 89 |

* $CR_{EC}$ = reduction efficiency by EC; ^$CR_{TAO-EC}$ = combined removal efficiency; # = increment; ND+ = not detected; ≈ = approximately equal to 100.

3.2.2. Nutrient Levels

Electrochemical reactions during the EC process were responsible for the reduction of N species via the attachment to dislocated $OH^-$ and the chemical reaction between $NH_4$-N and $NO_3$-N. The $OH^-$ transforms $NH_4$-N and $NO_3$-N into $NH_3$-N, $NO_2$, and $H_2O$ via $NH_3$-N stripping and denitrification, respectively [67–69]. The combined reaction of $NH_4$-N with $NO_3$-N releases $N_2$, $O_2$, and $H_2O$ as byproducts [67,68]. In addition, the $H_2O$ in the electrolyzed liquid can promote the $NO_3$-N removal reaction by converting it to $N_2$ and $OH^-$ via a pulse technique [68]. The decrease in the $NH_4$-N concentration also occurs due to the transformation of $NH_4$-N to $NH_3$-N with an increase in the pH (pH 10) [70–74]. The emitted $NH_3$-N was captured in the $NH_3$-N collection tank and remixed with the raw manure in the influent tank.

Overall, the chemical activity associated with physical properties impacted the reduction of $NH_4$-N and $NO_3$-N in the final effluent liquid. The combination of TAO and EC led to a reduction of 34% in $NH_4$-N (Tables 3 and 4), while the increase in $NO_3$-N in the TAO system was the result of converting $NH_4$-N to $NO_3$-N via aeration. TP was reduced by 59% within the TAO system and by 76% during the EC process, leading to a total reduction of 90% (Tables 3 and 4). During the EC process, soluble P primarily precipitated in the form of $H_3PO_4$ due to $OH^-$ ions liberated from the cathode (Equation (8)) and the covalent bonds with metallic ions of the electrodes [75,76]. For example, Al reacted with soluble P and settled at the bottom as micro-colloidal particles of $AlPO_4$ (s) (Equation (9)) [77,78].

$$H_3PO_4\ (aq) + 3\ OH^-\ (aq) \rightarrow 3H_2O\ (l) + PO_4^{3-}\ (aq) \quad (8)$$

$$Al\ (s) + H_2O\ (aq) \rightarrow Al^{3+}\ (aq) + 3e^- + PO_4^{3-}\ (aq) \rightarrow AlPO_4\ (s) \quad (9)$$

The reduction in TN and K was relatively lower compared with TP (Table 4). In general, the TN in swine manure is present in the soluble form of $NH_4$-N (50−70%) [79], with a small amount of $NO_3$-N/$NO_2$-N [80]. Almost 90% of $NH_4$-N can be emitted in alkaline conditions [81]. The smaller increase in TN in the TAO effluent was associated with the lower decrease in $NH_4$-N and the increase of $NO_3$-N compared to the influent. In the final product after EC treatment, the concentration of TN was lower because of the removal of both $NH_4$-N and $NO_3$-N. It can be assumed that the reduction in TN and K would positively affect seed germination (see Section 3.2 for further discussion).

3.2.3. Heavy-Metal Levels

Cr, Cu, Ni, and Zn are known to be highly toxic, mutagenic, and carcinogenic pollutants [82]. Although their concentrations were lower than other compounds in the influent (Table 4), they were at levels sufficient to disrupt manure maturity and cause soil pollution [30,83]. In the final effluent from the TAO–EC system, Cu, Ni, and Zn decreased by almost 100% (Table 4), with the removal rates similar to those reported by other studies [84,85]. However, Cr was only reduced by 4%. This is because the optimal pH for Cr removal is 3 [86–89], but the pH of the effluent eluted from the EC process was 8 (Table 4), thus lowering the Cr removal rate. However, the measured Cr concentrations were nontoxic [90] according to LFQC standards [91]. The metal removal performance of electrochemical processes has been reported by several previous studies [60,92–95]. Oxidation and absorption are the most common reactions in the EC process. The $OH^-$ from the cathodes leads to the formation of $Cu(OH)_2$, $Zn(OH)_2$, $Ni(OH)_2$, and $Cr(OH)_6$ [67,83,92]. Under the alkaline conditions of the manure, $Al(OH)_3$ was precipitated by adsorbing the metal ions [46].

3.2.4. Trace Minerals

Trace minerals often lead to salt stress for plants due to the formation of soluble salts and can inhibit nutrient transport from the roots to shoots [95–98]. The physicochemical reactions with the TAO–EC system reduced the trace minerals by over 50% (Tables 3 and 4). Similar to the removal of heavy metals, the $OH^-$ ions in the EC process trapped trace minerals in hydroxides such as $Mg(OH_2)$, $Ca(OH_2)$, $SO_4(OH_2)$, and $Fe(OH_2)$, reducing the concentration of these minerals in the final effluent [48,53,92,93].

3.2.5. COD Reduction

COD was used as an indicator of pollution levels for biodegradable organics, nonbiodegradables, and inorganic oxidizable compounds [73]. The TAO–EC system reduced the COD by 89% (Figure 3) via oxidizing reactions with the injection of air (TAO) and $OH^-$ ions (EC). The organic compounds were converted into $CO_2$ and $H_2O$ [67,87].

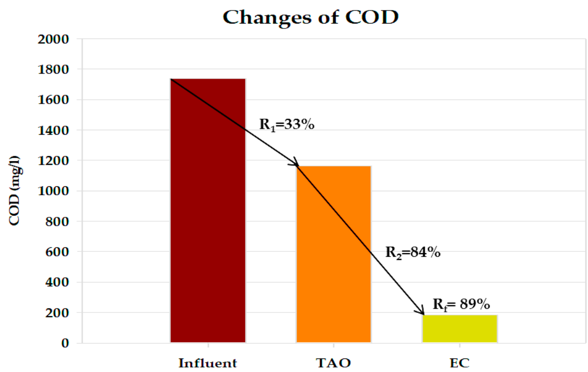


**Figure 3.** COD levels in the proposed TAO–EC system.

*3.3. Germination Index Assay*

The estimation of field application rates for LSM and TAO influents demonstrates their field applicability (supplemental Tables S1 and S2). In addition, the TAO influent and effluent conductivity levels were substantially reduced to avoid greater germination. On the other hand, their seed germination rates were way lower than the phytotoxicity quality criteria for liquid fertilizers. The maturity of the effluent, as measured by the degradation of phytotoxic organic materials, was analyzed using GI testing. A GI of over 70% represents nonphytotoxic conditions [62,66,99]. The GI was 80% in the TAO efflux at 80%, rising to 135% after the EC process (Table 5 and Figure 4). The GIs for the FWAD and LSM were similar to those reported by Halder [49,91], where manure samples with higher EC, $NH_4$-N, and TP concentrations had the lowest GI as the FWAD and LSM, respectively.

**Table 5.** Seed GI for the manure samples before and after TAO and EC treatment.

| Samples | | LFGI (%) |
|---|---|---|
| FWAD | Max<br>Min<br>Mean ± SD | ND |
| LSM | Max<br>Min<br>Mean ± SD | 63<br>47<br>54 ± 7 |
| Influent | Max<br>Min<br>Mean ± SD | 64<br>60<br>62 ± 2 |
| TAO | Max<br>Min<br>Mean ± SD | 90<br>70<br>81 ± 8 |
| EC | Max<br>Min<br>Mean ± SD | 141<br>121<br>133 ± 7 |

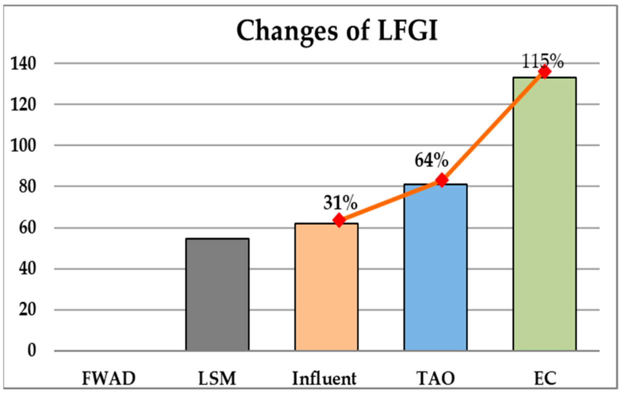


**Figure 4.** Maturity of the effluent as measured using the LFGI.

Improvement in the maturity of the effluent was due to changes in the nutrient, heavy-metal, and trace-mineral levels. Toxic chemical compounds should make up less than 5% of liquid fertilizer to ensure plant growth [98,99]. In this study, the 100% removal of heavy metals and the more than 60% removal of trace minerals increased the fertilizer quality for germination (Tables 4 and 5). In contrast, TN, TP, and K are essential nutrients for plant growth, with TN and K positively associated with protein synthesis metabolism, photosynthetic translocation [100–103], and germination signaling [104,105]. TP also plays an important role in cell division, reproduction, and growth metabolism [100–103]. However, high TP levels can lead to the inhibition of seedling growth [106,107]. In the final TAO−EC effluent, the removal of 90% of the TP (Tables 3 and 4) possibly led to greater germination. In addition, the TN and K, which had a lower removal rate compared with TP, facilitated seed germination. As the GI rises, the conductivity of all three phases of treatment decreases, and the likely cause is a decrease in salinity or NaCl, while other salt-creating substances may also contribute to the decrease in conductivity.

## 4. Conclusions

Mixing FWAD (10%) with LSM (90%) produced an influent suitable for use in the TAO system due to their contrasting physicochemical composition in their untreated states. The GI for FWAD and LSM was lower than 70%. The combined processes of TAO and EC reduced the metal concentrations, COD, and the balance of the nutrient content. The near-100% removal of Cu, Ni, Zn, and Mg led to suitable conditions for seed germination, and the ~60% removal of Ca, $SO_4$, and Fe led to low salt damage, thus promoting nutrient uptake by the seeds. The COD was reduced by 89% in the final effluent, which also improved germination by preventing eutrophication. The only slight reduction in TN and K combined with the high removal of P had a positive effect on germination. Overall, the proposed TAO–EC system successfully improved the quality of the fertilizer derived from LSM. Using this two-step process, liquid manure can be transformed into nutrient-rich irrigation water that may reduce the pressure on freshwater sources. The end product of this treatment may be more suitable for agriculture in harsh environments. Low-concentrated nutrients, on the other hand, might be employed in other types of agricultural practices such as hydroponics. However, further studies are needed to devise strategies to reduce the energy required by the EC process and to improve the handling and storage of the resulting sludge, as well as how to use these two treatment processes to produce liquid manure fertilizer for conventional agriculture practice.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/agronomy12061417/s1, Table S1: Application rate for TS and plant-available nutrients; Table S2: Application rate for heavy metals and minerals.

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