

Article

The Combination of Anaerobic Digestion and Electro-Oxidation for Efficient COD Removal in Beverage Wastewater: Investigation of Electrolytic Cells

Huy N. Q. Phan ¹, Jyh Hoang Leu ^{2,*} and Vi N. D. Nguyen ³¹ Department of Materials Science and Engineering, Feng Chia University, Taichung 40744, Taiwan² Master's Program of Green Energy Science and Technology, Feng Chia University, Taichung 40744, Taiwan³ Department of Chemical Engineering, Feng Chia University, Taichung 40744, Taiwan

* Correspondence: hjleu@fcu.edu.tw

Abstract: The world's ever-growing population is driving an increased demand for clean water, which makes treating and reusing wastewater an essential practice. In recent years, biological and physicochemical methods have been preferred for wastewater treatment, with combined systems proving particularly effective. In this study, the combination of anaerobic digestion (AD) and electro-oxidation (EO) was investigated as a process for removing chemical oxygen demand (COD) from actual beverage wastewater. The effect of hydraulic retention time (HRT) on AD, electrolysis time, sodium chloride (NaCl) dosage, initial pH, and electro-properties on EO was investigated. At optimum conditions, namely an HRT of 2 days for AD, NaCl concentration of 3 g L⁻¹, 80 min of EO time, natural pH (7.45), and applied voltage of 20 V for EO, the removal efficiency for COD was an impressive 96.47%, with energy consumption and specific energy consumption calculating 177.33 kWh m⁻³ and 33.79 kWh kgCOD⁻¹, respectively. The amount of by-product gases (CH₄ and H₂) were also meagerly determined in this study. The results confirm that combining the AD and EO methods is an effective COD removal solution that can benefit the industry, while also offering a sustainable solution to combat water scarcity and meet the growing demand for clean water.



Citation: Phan, H.N.Q.; Leu, J.H.; Nguyen, V.N.D. The Combination of Anaerobic Digestion and Electro-Oxidation for Efficient COD Removal in Beverage Wastewater: Investigation of Electrolytic Cells. *Sustainability* **2023**, *15*, 5551. <https://doi.org/10.3390/su15065551>

Academic Editor: Ioannis Katsoyiannis

Received: 3 February 2023
Revised: 7 March 2023
Accepted: 10 March 2023
Published: 22 March 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Keywords: high-strength wastewater; combination system; electro-oxidation; real beverage wastewater; anaerobic digestion

1. Introduction

In recent years, the global population has been growing at an unprecedented rate, posing a significant challenge to sustainable development. According to United Nations projections, the population is predicted to reach 8 billion by 2025 [1], exacerbating the demand for clean water and affecting the sixth Sustainable Development Goal—Clean water and sanitation. As a result, there is a growing need to focus on the treatment, reuse, and recycling of wastewater to mitigate the water scarcity crisis. The beverage industry, in particular, generates a considerable amount of wastewater due to the high demand of fresh water as a primary ingredient and for cleaning processes such as flushing plants and washing bottles [2]. Consequently, this industry's practices have an enormous impact on water availability and quality. The wastewater released by the beverage industry typically has low concentrations of heavy metals and pesticides but high levels of organic compounds, as evidenced by high chemical oxygen demand (COD) values (~40,000 mg L⁻¹) [3]. Therefore, it is supposed to be high-strength wastewater (COD > 2000 mg L⁻¹) [4,5]. Discharging this hazardous and toxic fluid into natural water bodies may result in severe pollution of ground and surface water, presenting a risk to animal and human health [6]. Despite the existence of regulations to curb the discharge of pollutants, the sector's growth and global expansion pose significant challenges to achieving sustainable water management practices. Therefore, it is imperative to emphasize the importance of sustainable water management

practices within the beverage industry and explore potential solutions to the challenges posed by the increasing demand for clean water.

Recent studies have shown that high-strength wastewater can be treated to reduce its COD through the use of biological or physicochemical methods [7]. The up-flow anaerobic sludge blanket (UASB) system has been widely applied in the treatment of various types of wastewater, including high-strength beverage wastewater [8]. In the UASB process, HRT is a crucial parameter in the evaluation of degradation performance, particularly in relation to the removal of COD [9]. As reported by Nguyen et al. [10], the treatment of swine manure and pineapple wastewater through digestion led to a removal of 52.4%, 50%, 56.5%, 71.6%, and 75.2% COD for HRTs of 6 h, 12 h, 24 h, 48 h, and 96 h, respectively. Thus, it has been shown that an increase in HRT leads to an improvement in the percentage of COD removal. Sani et al. [11] also conducted a study on the effectiveness of anaerobic digestion for treating high-COD wastewater (78.29 g L^{-1}) and found that the highest COD removal efficiency was achieved at an HRT of 35 days. However, biological methods often require a large plant size or working area and can be complicated to control and operate [12]. Therefore, it may not be the preferred choice for the treatment of wastewater or the removal of COD in particular.

In addition, electro-oxidation (EO) is an advanced oxidation technology that can effectively eliminate organic pollutants and contaminants from wastewater through direct or indirect oxidation phenomena [13]. Direct EO, also known as anodic oxidation, occurs when electrons are transferred directly to the anode surface, resulting in the formation of reactive oxygen species with no additional agents required and limited unwanted side pollutants [14]. Durán et al. [15] conducted a study on the treatment of real washing machine wastewater using the direct oxidation method. They utilized lead dioxide and boron-doped diamond as working electrodes and achieved optimal COD removal with a 360 min electrolysis time. However, indirect electro-oxidation, where a mediator is electrochemically converted into an oxidizing agent in the electrolyte, has been found to be more effective. Active chlorine or hypochlorite are common indirect oxidants used in wastewater treatment [16]. Klidi et al. [17] confirmed indirect EO with chloride exists that has higher electro-efficiency. It reduced COD by 60% and 87% with no chloride and 2 g L^{-1} of chloride, respectively. Another study revealed that the addition of NaCl and NaOCl into textile printing wastewater with pairs of graphite electrodes also eliminated 86% of COD in 150 min of EO time [18]. Although the EO method rapidly reduces COD in the effluent, cost-effectiveness and chemical use remain concerns.

On the other hand, the efficiency of pollutant degradation has been also improved by combining biological and electrochemical processes for wastewater treatment. Barrios et al. [19] reported the integration of anodic oxidation treatment with a pair of boron-doped diamond electrodes and biological treatment removed 61.6% of COD from waste activated sludge effluent. Fontmorin et al. [20] implemented the research of enhancing peculiarity pollutant degradability and decreasing COD by designing a system with the integration of electrochemical and biological methods. Popat et al. [21] investigated Ti/Pt mesh and graphite felt as the electrodes in applying electrochemical advanced oxidation and biological processes for treating mixed industrial wastewater, and this removed 94% of COD in such wastewater under optimum conditions. According to prior studies, non-biodegradable or toxic effluent can be subjected to electrochemical pre-treatment followed by biological post-treatment, whereas biodegradable or non-toxic effluent can be treated in the reverse order. The result of these combined processes is a significant improvement in the removal efficiency of COD. However, there are no reports in the current literature that describe the application of the combined anaerobic digestion and electro-oxidation method for removing COD in real beverage wastewater.

The objective of this study was to evaluate the COD removal efficiency of a combined anaerobic digestion and electro-oxidation (AD/EO) system for the treatment of beverage wastewater. The AD process utilizing granular sludge was used as a pre-treatment, and the EO system was designed with a pair of platinum-coated titanium (Pt/Ti) electrodes

and a sodium chloride electrolyte. The study aimed to investigate the electrolytic cell and evaluate the impact of various parameters such as HRT, dosage amount, reaction time, pH, applied voltage, current efficiency, and energy consumption on COD removal efficiency. The percentage of methane and hydrogen in the AD reactor was analyzed by using GC, and the theoretical hydrogen production in the EO process was determined using Faraday's law equation.

2. Materials and Methods

2.1. Chemicals

Sodium chloride (NaCl), sodium hydroxide (NaOH), hydrochloric acid (HCl), and analytical chemicals for the COD test were purchased from Union Chemical Work, Taiwan. These chemicals were recorded as reagent grade with the highest purity and no further purification. Deionized water was used for dilution and mixing. Both granular sludge for fermentation and platinum-coated titanium electrodes for electrolysis were procured from a local market.

2.2. Characteristics of Beverage Wastewater

This study utilized wastewater samples obtained from a local beverage factory located in Taiwan. Upon examination, it was observed that under normal conditions, the wastewater had a strong odor and a brown-yellow coloration. To limit biodegradability, the samples were collected and stored at 4 °C for one month, after which they were prepared at ambient temperature for investigation and analysis. In the original wastewater, a high concentration of chemical oxygen demand was detected (30,000 mg L⁻¹), whereas the conductivity was found to be low (0.0094 mS cm⁻¹). The characteristics of the beverage wastewater before treatment are presented in Table 2.

2.3. Experimental Design

2.3.1. Stage 1: USAB Digester

Batch fermentation of effluents took place in a cylindrical glass UASB reactor with an internal radius of 3 cm, a height of 45 cm, and a volume of 1000 mL. A gas, liquid, and solid separator was attached to the top of the digester, and a 1 L Tedlar bag (Jensen Inert Products, Coral Springs, FL, USA) was used for collecting biogas. Initially, 300 g of granular sludge was inoculated into UASB, then organic matter was loaded in by a peristaltic pump (Longer Pump, Hebei, China). The microorganisms were stabilized in rich-COD conditions by incubating the initial mixture for 24 h at room temperature with a magnetic stir of 100 rpm until the appearance of gas bubbles. HRT investigation was adjusted for a gradual decrease from 3 days; each HRT would be run at least 3 times until it reached a stable state. The AD system was operated at room temperature and without pH control; the solids were fixed throughout the experimental period, which means a solid retention time of 20 days. During the digestion process, an attached funnel was utilized to prevent the generation of suspended solids. However, it is still necessary to completely eliminate any suspended solids that remain after the process. To achieve this, an aspirator was employed as a simple yet effective method. The treated effluent was subsequently transferred for further post-treatment. The equipment and illustration of this system is shown in Figure 1a.

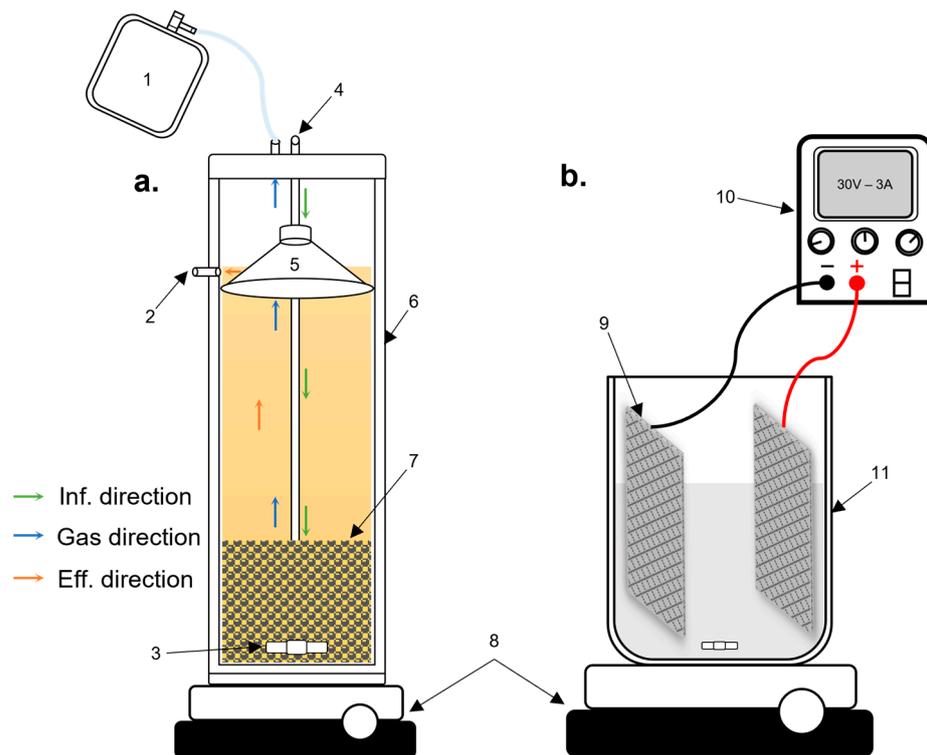


Figure 1. Experimental set-up. (a) AD system—1. Tedlar bag, 2. Effluent, 3. Stir bar, 4. Influent, 5. Funnel, 6. Cylinder reactor, 7. Granular sludge, 8. Magnetic stirrer. (b) EO system—9. Pt/Ti electrode, 10. DC supply, 11. Reactor.

2.3.2. Stage 2: Electrolytic Cell

The electro-oxidation of the digestion effluent proceeded in batch mode at room temperature. Platinum-coated titanium (Pt/Ti, 6 cm × 10 cm) mesh with a thickness of 0.5 mm was used for the electrodes for the electrolysis cells; each electrode was cleansed of contaminants attached on the surface by 1% hydrochloric acid. The anode and cathode were set up in parallel, and the inter-electrode gap remained at a constant distance of 4 cm; all details of the EO reactor are summarized in Table 1. For each experiment, 400 mL of fermentation-treated solution was transferred into a 500 mL beaker. A low concentration of NaCl was added to electrolytes as a proper additive to enhance electro-properties, and a magnetic stirrer (Barnstead Thermolyne, Osseo, MN, USA) was applied for mixing the solution to maintain homogeneity. Afterwards, to carry the system, a regulated DC power maximum 30 V–3 A (TES electrical, Taiwan) was installed to supply direct current. The equipment and illustration of this system are shown in Figure 1b.

This study examined several factors that impact COD removal in the electrochemical process, including electrolysis time (20, 40, 60, and 80 min), sodium chloride concentration (ranging from 0 to 7 g L⁻¹ or 0 to 0.7%), initial pH (5, 7.45, and 10), applied voltage (ranging from 5 to 30 V). All samples were collected from the EO reactor to analyze at a designated time during experiments.

2.4. Analytical Procedure

The conductivity and temperature were measured by using a benchtop meter with a stainless-steel probe (Suntex-SC2300, New Taipei, Taiwan), whereas the pH was recorded by a multi-meter (Jenco-6173, Taipei, Taiwan). Biogas from the anaerobic process was analyzed by gas chromatography (China Chromatography 8700T, Taipei, Taiwan) with a carrier gas (argon) thermal conductivity detector.

Table 1. Details of EO reactor.

Electrode Specification	
Material	Titanium—Grade: GR1
Platinum coating thickness	200 nm
Mesh hole size	3 mm × 2 mm
Mesh thickness	0.5 mm
No. of electrodes	2
Shape	Rectangular
Size	6 cm × 10 cm
Arrangement	Parallel
Exposed surface area	48 cm ²
Electrolytic cell	
Electrode gap	4 cm
Reactor	Beaker—500 mL
Volume	400 mL
Type	Batch
Stirring	Magnetic bar—100 rpm
DC supply	
Voltage	0–30 V
Current	0–3 A
Connector	Electrical wire with alligator clip

The chemical oxygen demand was determined using the open reflux method following the APHA standard 5220B. Each sample was diluted 500 times with reverse osmosis water and 2.5 mL of the diluted sample was mixed with 1.5 mL K₂Cr₂O₇ and 3.5 mL Ag₂SO₄. The mixture was heated to 150 °C for 2 h and titrated with ferrous ammonium sulfate (FAS) and ferroin indicator. The amount of titrated FAS was then converted to the COD value according to the standard method. Each sample was analyzed at least 3 times and the deviation was within 0.5–2% of the mean data, which was used for further calculations. The error bar of the residual COD was also included in the graph.

Based on initial and final concentrations, the removal efficiency of COD can be expressed as:

$$C_{RE} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where C_{RE} is COD removal efficiency, C_0 is the initial concentration (mg L⁻¹), and C_t is the final concentration according to treatment time (mg L⁻¹). All calculations and graphs were conducted using Microsoft Excel (Microsoft Corporation, Redmond, WA, USA) and Origin (OriginLab, Northampton, MA, USA).

3. Results and Discussion

3.1. The effect of HRT on Anaerobic Digestion

Figure 2 displays the results of the COD degradability assays of raw beverage wastewater through lab-scale anaerobic digestion. The COD removal efficiencies for HRT of 3 days, 2 days, and 1 day were in the ranges of 79.97–80.13%, 79.33–79.37%, and 13.33–33.33%, respectively. The results indicate that the microorganisms in this study could only achieve stable and significant COD elimination with an HRT of 2 days or more, whereas the COD removal rate was very low with an HRT of 1 day. This was consistent with the treatment of beverage wastewater by using an anaerobic reactor that removed 78, 60, and 42% of COD at HRT 12, 8, and 4 h, respectively [22]. The phenomenon that COD decreases as HRT increases is attributed to a sufficient exposure time between bacteria and influent [23]. The COD reduction in this study was also similar to the removal of 80% COD by anaerobic digestion of dairy and cheese whey wastewater using an HRT of 4.6 h at mesophilic temperature (35 °C) [24]. However, this HRT was shorter than the present study, as the anaerobic digester was well-controlled during operation. When the HRT was longer, the

pH of the mixture inside the UASB reactor tended to increase, ranging from 7.82 to 8 for an HRT of 3 days, 7.43 to 7.46 for an HRT of 2 days, and equaling 5.45 for an HRT of 1 day, indicating a shift from acidic to weak alkaline during digestion. The average COD removal efficiency between 2 and 3 days of HRT showed no significant difference (around 0.68%). This was probably because of the saturation in the biodegradation of organic pollutants. To optimize the COD removal rate and shorten treatment time, the effluent from an HRT of 2 days was used for further post-treatment by implementing the electro-oxidation process.

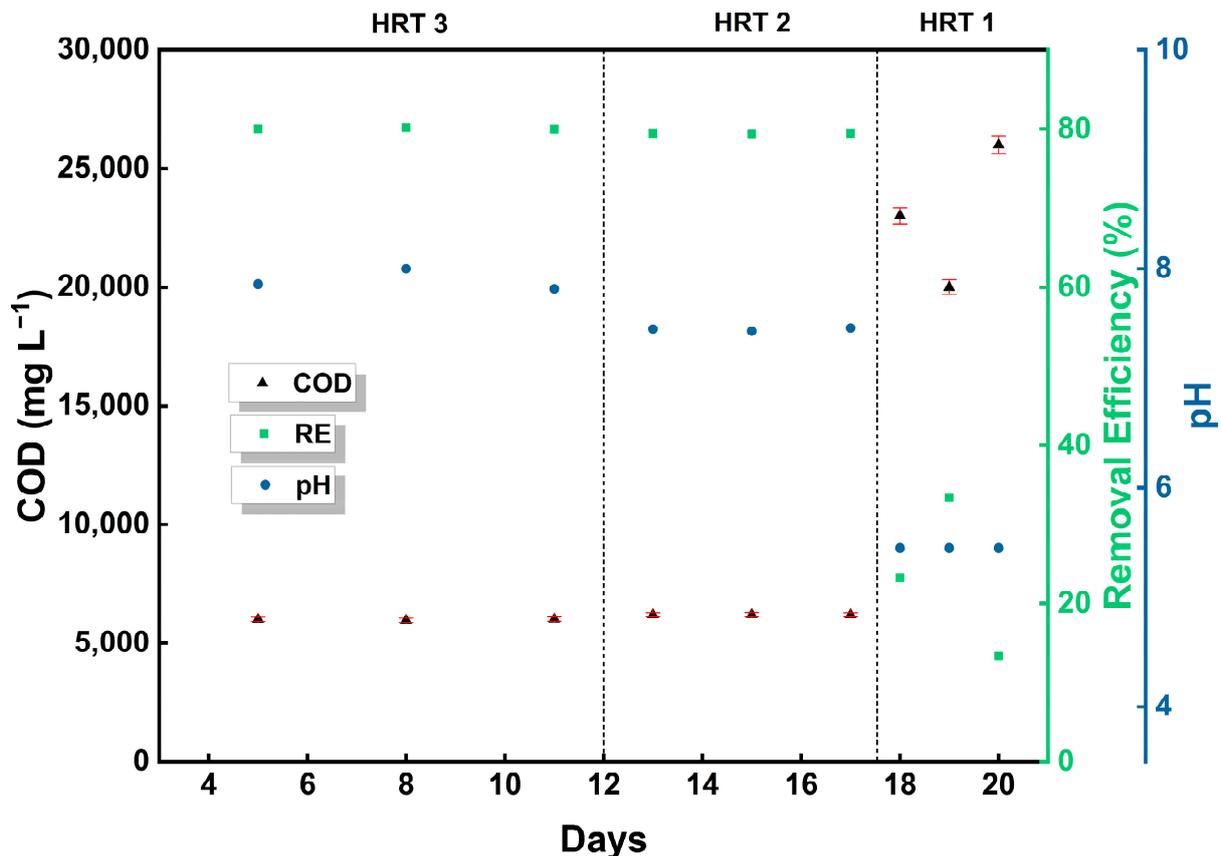


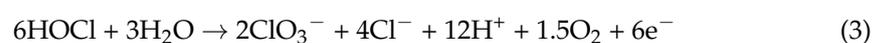
Figure 2. Effect of HRT on COD removal and pH change with the first day for incubation (HRT 3 runs from the 2nd day to the 11th day, HRT 2 runs from the 11th to the 17th day, and HRT 1 runs from the 17th to the 20th day).

3.2. Electro-Oxidation as a Post-Treatment

3.2.1. Mechanisms

Although anaerobic fermentation was an effective method for reducing COD by treatment of biocompatible organic pollutants in beverage wastewater, there were still a large amount of refractory organic matter. Hence, electro-oxidation was considered for the post-treatment of beverage wastewater. According to Deng and Englehardt [13], electrochemical oxidation of contaminants in wastewater appeared in two different ways that are summarized in Figure 3. Nevertheless, the utilization of platinum-coated titanium (Pt/Ti) in this study was not the prerequisite for direct electro-oxidation, which was obligatory electrolysis by an oxide anode (M_xO_y) [25]. A series of indirect oxidation reactions in the presence of chloride during electrolysis are shown in Equations (2)–(8).

Anodic reactions:



Bulk reactions:



Cathodic reactions:



Formed hypochlorous acid (HOCl) and hypochlorite ions (OCl^-) in bulk reactions (Equations (5) and (6)) are strong oxidants that are used for oxidizing soluble organic compounds [26,27]. Thus, this oxidation agent was a primary factor in removing the COD in the study. Moreover, electroflotation was known to support treating wastewater by electrochemical methods with inert electrodes. Pure hydrogen and oxygen gas bubbles from Equations (4) and (7) generated during the electrolysis of water can carry suspended particles to float to the top of the electrochemical system [1]. However, the particles observed in this study were negligible. Therefore, the floatation phenomena appeared insignificant.

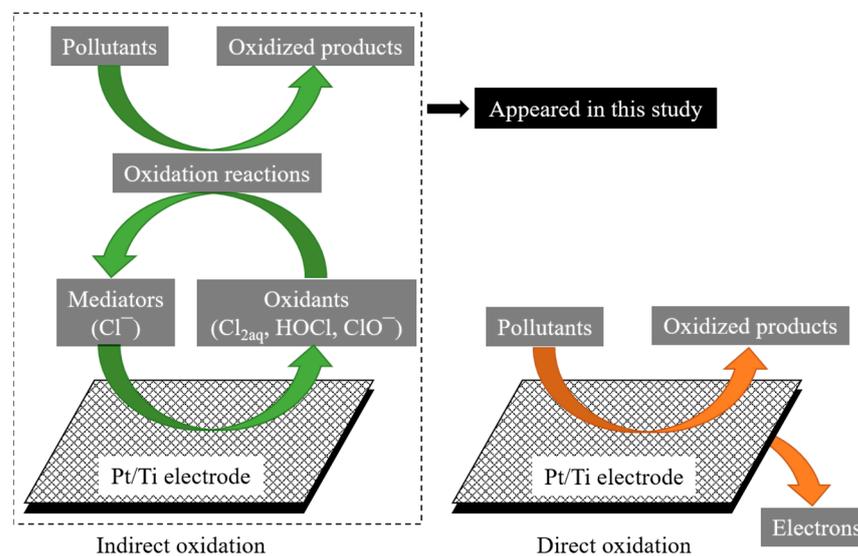


Figure 3. Mechanisms of electro-oxidation.

3.2.2. The Effect of Electrolysis Time

Firstly, the treatment time of the electrochemical system was considered from 0 to 100 min to determine the proper period and to avoid wastage of energy. In addition, unnecessarily extending the treatment time also harms to the longevity of the electrodes. All data from this investigation are summarized in Figure 4. In general, the results showed that COD was removed by increasing the treatment time for all sets. The concentration of COD reduced from an initial value of 6190 mg L^{-1} to 3741, 2300, 1203, 1058, 900, and 1059 mg L^{-1} for 5, 10, 15, 20, 25, and 30 V at the final time of electrolysis, respectively. Obviously, the COD removal efficiency improved during the electrochemical progress, 39.56, 62.84, 80.56, 82.91, 85.46, and 82.89% for 5–30 V, respectively. The results show that the longer the electrolysis time, the more excess organic pollutants were oxidized. It means that the COD removal efficiency increased with the electrolysis time. The results in Figure 4b indicate that the concentration of chemical oxygen demand (COD) decreased as the treatment time increased. The COD removal efficiency improved during the electrochemical process, with the highest removal efficiency of 82.88% reached after 80 min of treatment at a voltage of 20–30 V. However, the removal efficiency slightly decreased from 80 to 100 min of treatment. Figure 4c shows the decrease in the concentration of chemical oxygen demand over time. The rate of decrease in COD per minute was highest in the first 40 min and decreased gradually until the 80th minute. From 0 to 40 min, the decrease in COD per minute

was 16.05, 62.21, 78.35, 84.00, 89.75, and 97.25 $\text{mg L}^{-1} \text{m}^{-1}$ for voltages of 5 V to 30 V, respectively. This shows that the oxidation of organic matter was strong during the first 40 min due to the formation of chlorine species from brine electrolysis. However, the rate of decrease slowed down between 40 and 80 min and became insignificant from 80 to 100 min. There are a few previous studies with similar results that indicated a longer electrolysis time leads to an increase in the COD removal efficiency. Sandoval et al. [28] reported the COD removal efficiencies were increased from 60% in 150 min to 72% in 300 min by using stainless steel as the cathode and Ti/RuO₂-TiO₂ as the anode with NaCl as a supporting electrolyte. Meanwhile, Tran et al. [29] also revealed the relationship between electrolysis time and COD removal efficiency; according to their study, COD was removed at 20, 43, and 60% within 20, 50, and 60 min, respectively. Based on the electrolysis mechanisms, the phenomena of eliminated COD increasing by reaction time can be described due to the chlorine species being abundantly formed and reacting with contaminants in the first 80 min. The electrochemical in the 20 min left in this investigation was redundant, causing a waste of electricity. Hence, the period of electrolysis time within 80 min was chosen for the next considerations in this work.

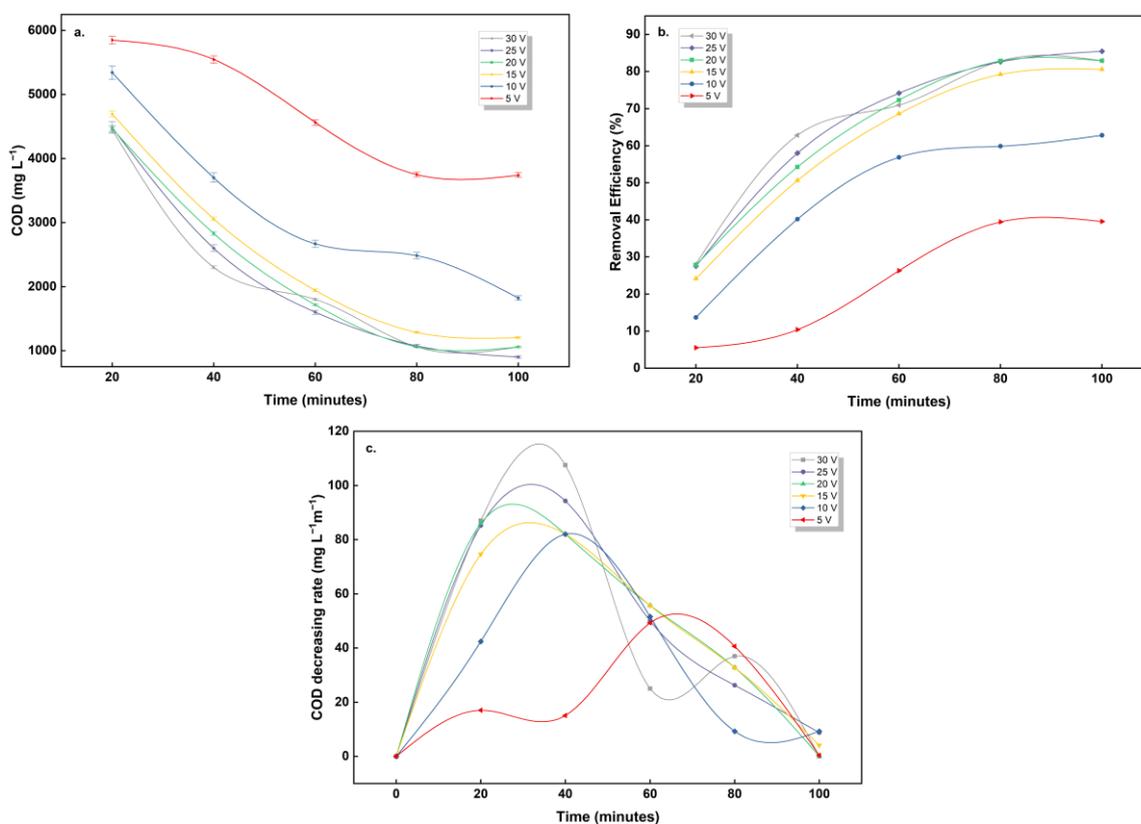


Figure 4. Effect of electrolysis time (0–100 min) on COD removal. (a) Residual COD. (b) Removal efficiency of COD. (c) COD reducing rate.

3.2.3. The Effect of NaCl Dosage

The additive is an important factor to improve the electro-efficiency. Therefore, the electrolytic cell was operated under different percentages of NaCl to investigate the effect on COD removal efficiency. All results of the investigation of NaCl amounts (0, 1, 3, 5, and 7 g L^{-1}) for 5–30 V in 80 min are shown in Figure 5a,b. The COD removal efficiencies observed without the addition of NaCl were found to be in the range of 0.16 to 0.32%. This can be attributed to the low conductivity of the raw effluent, resulting in weak electroflotation through water electrolysis. Additionally, the absence of oxidation agents, caused by the deactivation of indirect EO in the absence of chloride ion, also contributed to the low efficiencies. The variations in COD removal efficiencies for NaCl of 1, 3, 5,

and 7 g L^{-1} were recorded from 6.30–39.56%, 26.50–62.84%, 33.40–80.56%, 46.70–82.91%, 43.79–85.46%, and 42.43–82.90% for 5–30 V, respectively. Comprehensively, the COD concentration tended to decrease with the rise in NaCl dosage. Based on the anodic reaction (Equations (2)–(4)), chloride ions (Cl^-), as a mediated agent, can be easily converted into different products such as chlorine gases (Cl_2), hypochlorous acid (HOCl), hypochlorite (OCl^-), and/or chlorate ions (ClO_3^-) through the electrochemical process. These active chlorine species are the main factors to rapidly oxidize organic pollutants; in this way, the COD concentration can be diminished significantly. This effect occurred strongly with NaCl concentrations of 3 g L^{-1} but was unchanged at 5 and 7 g L^{-1} . Yao et al. [30] also reported a similar result, the COD removal improved when increasing chloride concentrations, from 77.4% (0 mg L^{-1}) to 88.6% (250 mg L^{-1}) with Ti/ PbO_2 as anode and Ti as cathode at initial COD concentration of 337 mg L^{-1} . Another study reported the utilization of 50 mM NaCl as an additive to increase the degradability of organic compounds in the treatment of winery wastewater through electrochemical oxidation. During the experiment, the COD was reduced by 75.8% after 400 min of electrolysis using a BDD anode and a stainless-steel cathode in the electrolytic cell [31].

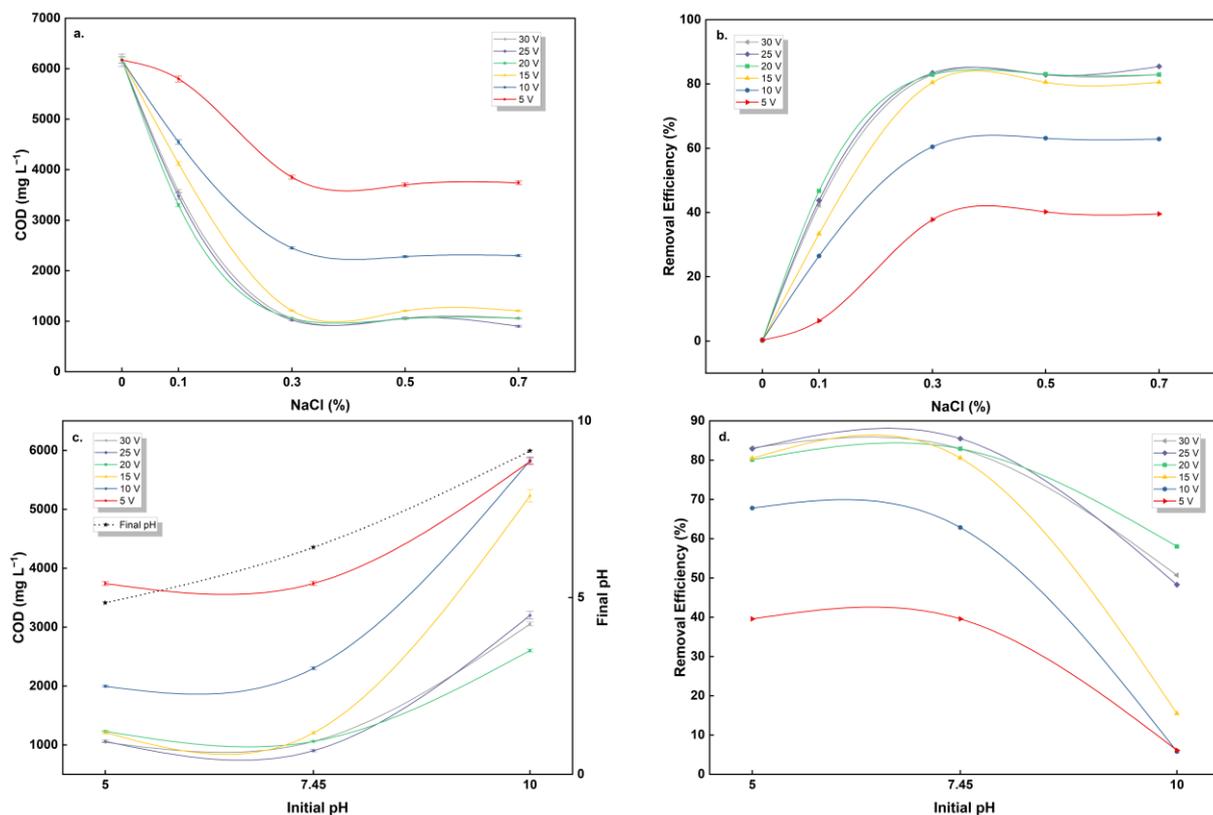


Figure 5. Effect of % of NaCl and initial pH on COD. (a,c) Residual COD. (b,d) RE of COD.

Except NaCl, other chemicals such as KCl, Na_2SO_4 , NaNO_3 , Na_2CO_3 , and NaClO_4 are also generally known as supporting electrolytes [16]. However, NaCl still takes advantage of its superiority for indirect EO, not only is it more effective for oxidizing a variety of refractory organic pollutants but it has high solubility and is a low-cost material. In many cases of wastewater treatment, NaCl has been selected as a priority electrolyte more than the others. Zhu et al. [32] conducted an experiment to investigate the effectiveness of four different electrolytes on COD degradation. They found that the highest COD degradation efficiency was achieved with NaCl as a supporting electrolyte, 82% of COD was removed from simulated dye wastewater after 3 h of treatment. Similarly, Titchou et al. [33] mentioned that efficient COD removal was due to the presence of NaCl, whereas Na_2SO_4 was better at elimination of total carbon and phenol. As such, NaCl can be

appropriate in this study. To be unaffected for further treatments because of excess chlorine and also gain the optimal COD removal rate, an NaCl concentration of 3 g L^{-1} was adopted for the next considerations of this study.

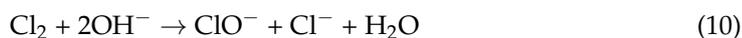
3.2.4. The Effect of Initial pH

The initial pH of the effluent in the electrochemical system in the presence of chloride plays a crucial role in the formation of oxidant species. Thus, varying the initial pH conditions can significantly affect the removal of COD. Figure 5c,d shows the effect of initial pH (pH 5, 7.45, and 10) on the COD reduction of applied voltages 5–30 V with constant conditions—80 min of electrolysis and 3 g L^{-1} of chloride concentration. At pH 5, the COD removal efficiency changed in a range 39.57–83.1% for 5–30 V. A similar result appeared for natural pH 7.45 of the effluent, COD was removed at 39.56–83.00% for 5–30 V. In the final condition, pH 10, the COD removal efficiency was relatively low, which changed in a range of 6.10–50.68% for 5–30 V. The findings of the investigation suggest a correlation between the initial pH of the effluent and the reduction of COD. Specifically, a decrease in the initial pH was observed to result in an increased percentage of COD reduction. In general, low pH is supposed to be a considerable factor in enhancing the oxidation of organics by electro-generated active chlorine [34]. Furthermore, the relative amount of these chlorine species can be specified following Equations (9) and (10) [35,36].

Acidic and neutral medium (pH 3–8):



Alkaline medium (pH > 8):



As the above equations suggest, HOCl is the dominant oxidation agent in the pH range from 3 to 8, whereas ClO^- mainly appears at pH > 8 [37]. Based on this theory, it is concluded that the removal of organic pollutants in terms of COD was more effective at a low to moderate pH with the formation of HOCl in our study. Likewise, Lu et al. [38] revealed that high COD removal efficiency appeared at acidic and neutral conditions, whereas alkaline conditions were more effective for ammonia nitrogen removal. This can be explained, as a low pH medium may increase oxygen overpotential and inhibit the oxygen evolution reaction leading to enhanced electrochemical possibilities [39]. Another study presented the relationship of a low pH value and COD for real textile wastewater treatment by electrochemical oxidation. The optimum operational conditions for COD removal were applied as 3 g L^{-1} NaCl, electrolysis time of 3 h, pH 2, and using a boron-doped diamond anode [40]. Meanwhile, Periyasamy and Muthuchamy [41] reported the most effective pH condition to remove 82% COD for the electrochemical oxidation of paracetamol-containing wastewater was at low pH 4. In this study, it was observed that pH 5 exhibited better performance compared with natural pH 7.45, although the difference was insignificant. As a result, a natural initial pH was considered to be the optimal choice due to its cost-effectiveness.

3.2.5. Technical Investigation—Electro-Properties

Figure 6a shows the change in current and temperature in different applied voltages under the constant conditions of 80 min of electrolysis time, 3 g L^{-1} NaCl, and natural initial pH. The lowest temperature ($50 \text{ }^\circ\text{C}$) was gained at a current density of 43.2 A m^{-2} , whereas the temperature reached $84 \text{ }^\circ\text{C}$ at a current density of 156.25 A m^{-2} . For the electrochemical system, the temperature rises when accumulating more power. Sun et al. [42] also revealed that under no temperature control conditions for an electrochemical reactor, the temperature tends to be higher with longer treatment times. The temperature of the study reached $50 \text{ }^\circ\text{C}$ after 3 h of treatment. This result is significantly lower than the present study. This discrepancy can be attributed to the utilization of a higher voltage in the present study,

which aimed to reduce the treatment time. As a result, the application of additional energy to the electrolytic cell led to an increase in both current and temperature. These factors have the potential to impact the durability and safety of the system.

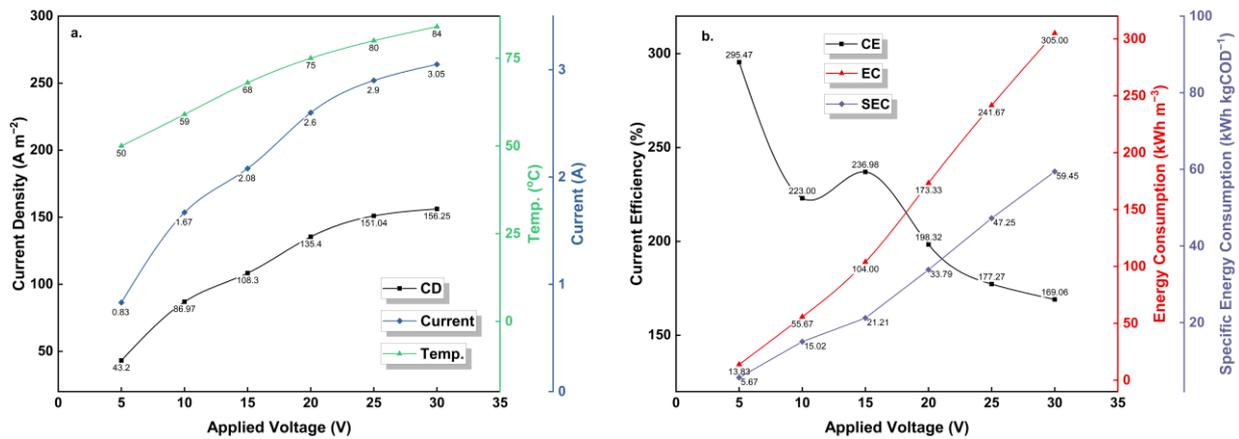


Figure 6. The changing of electrical parameters under optimal conditions (80 min of electrolysis time, 3 g L⁻¹ of NaCl concentration, and natural pH of 7.45). (a) CD, current, and temperature of 5–30 V. (b) Current efficiency, energy consumption, and specific energy consumption.

The current efficiency (CE) for COD removal was determined by Equation (11) [43]:

$$CE = \frac{FV(C_i - C_f)}{8It} \times 100\% \quad (11)$$

where F is Faraday constant of 96,487 C mol⁻¹, I is the current of electrochemical system (A), V is treated sample volume (L), and C_i and C_f represent the initial and final COD (mg L⁻¹), respectively, during the electrolysis time of t (s).

Meanwhile, the change in energy consumption (EC) per cubic meter of COD was calculated according to Equation (12) [44]:

$$EC = \frac{UIt}{1000V} \quad (12)$$

where U and I represent the electric potential of the electrolytic cell (V) and constant current (A), respectively, that is supplied for the electrochemical system. V is the volume of treated wastewater (m³) and t is the retention time (h) for EC in kWh m⁻³.

In addition, the specific energy consumption of COD (kWh kgCOD⁻¹) also can be expressed as [45]:

$$SEC = \frac{UIt}{1000V\Delta COD} \quad (13)$$

As seen in Figure 6b, an applied voltage of 5 V performs the most efficient current with CE = 295.47%, EC = 13.83 kWh m⁻³, and SEC = 5.67 kWh kg COD⁻¹. However, this voltage presented quite poor COD removal efficiency with the optimal conditions of electrolysis. Also, the voltages in the range of 10–15 V exhibited a similar result, high current efficiency but low COD removal. Meanwhile, the performance of current slightly shifted from 198.32–169.06% for 20 to 30 V of applied voltages, respectively. A current density of 135.4 A m⁻² seems to be the best choice for the objective of this study. It not only removed COD at 82.88% but was also cost-effective in operation and much more energy saving for high treatment efficiency. Energy consumption reached 173.33 kWh m⁻³, whereas specific energy consumption was 33.79 kWh kgCOD⁻¹ for this electrochemical condition. To evaluate the economic and electricity efficiency, some previous studies have been mentioned to compare with this study. Nurhayati et al. [46] have shown that a CE of 74% and a SEC of 145 kWh kgCOD⁻¹ for an EO system could remove 80% of COD.

Another study has revealed that removing of 55% COD consumes just 1 kWh m⁻³ and has a CE of 400% [47]. According to the electricity price in the local market [48], the maximum energy cost for beverage wastewater treatment of the whole system (anaerobic digester considered insignificant) was 16.23 USD m⁻³ or 3.16 USD kgCOD⁻¹.

3.3. Summary of the Combination Process

All of the wastewater characteristics before and after treatment are presented in Table 2. In summary, the treatment process removed 96.47% COD from initial COD concentrations of 30,000 to 1059.73 mg L⁻¹. The raw wastewater had a low conductivity of 0.0094 mS cm⁻¹; the addition of an enhancing agent such as NaCl to improve the electro-properties of the electrolytes is appropriate. Moreover, the color of the effluent was also reduced completely, which is shown in Figure 7. The color reduction reached 100% in the range of the visible wavelength from 400–600 nm. Meanwhile, Table 3 presents a comparison of COD removal efficiencies achieved by various wastewater treatment methods. The results of this study indicate relatively high effectiveness when compared with other methods. This may be attributed to the successful combination of anaerobic digestion and optimal application of the electro-oxidation system. However, it is important to note that the comparison may be limited by differences in operational conditions, wastewater characteristics, and analytical methods used. Further investigations are needed to fully assess the potential of this integrated approach in wastewater treatment. Additionally, future studies may consider the economic feasibility of the method and its scalability for large-scale applications.

Table 2. Characteristics of wastewater before and after treatment.

Parameter	Before Treatment	AD Treatment	EO Treatment
COD (mg L ⁻¹)	30,000	6190	1059.73
Removal efficiency (%)	-	79.37	96.47
Color	Brown-yellow	Light brown-yellow	Colorless
Conductivity (mS cm ⁻¹)	0.0094	0.0094	10.31
Temperature (°C)	25	-	-

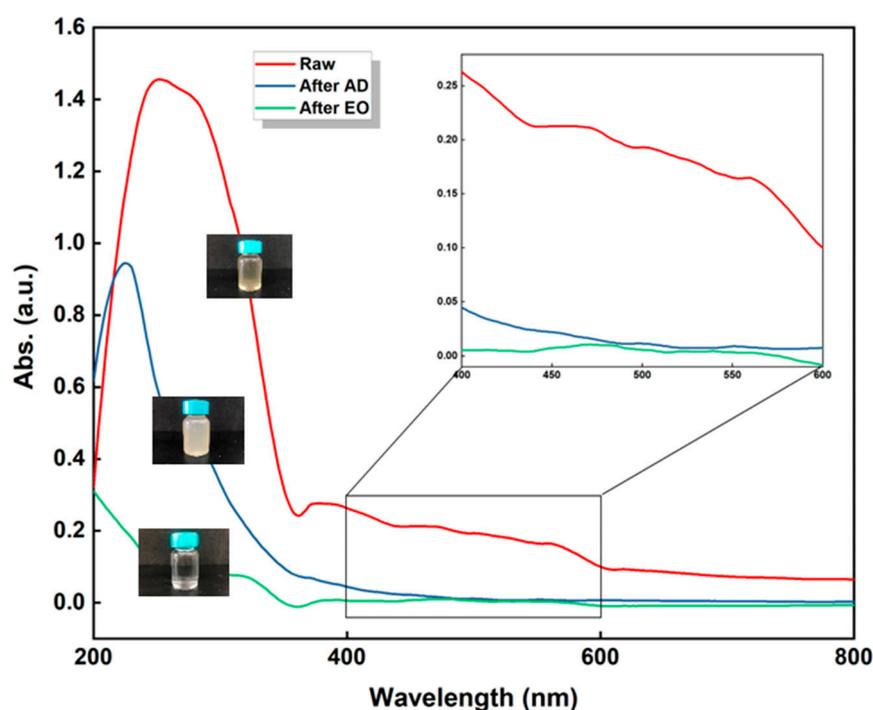


Figure 7. UV-Vis spectrum for color reduction during each stage of treatment.

Table 3. Comparison of COD removal efficiency for different systems for wastewater treatment.

Treatment Method	Type of Wastewater	Initial COD	COD Removal Efficiency	Reference
Pre-treatment: AD Post-treatment: EO	Beverage wastewater	30,000 mg L ⁻¹	96.47%	This work
Pre-treatment: EC ¹ Post-treatment: EO	Soft drink wastewater	4300 mg L ⁻¹	85%	[49]
Pre-treatment: EC Post-treatment: EO	Dairy wastewater	4010 mg L ⁻¹	60%	[50]
Pre-treatment: UASB reactor Post-treatment: RO ²	Landfill leachate	4200 mg L ⁻¹	95.4%	[51]
Pre-treatment: EC Post-treatment: NF ³ , RO	Textile effluent	370 mg L ⁻¹	93%	[52]
Pre-treatment: Fungal Post-treatment: EO	Green table olive processing wastewater	11,750 mg L ⁻¹	96%	[53]
Pre-treatment: Electro-Fenton Post-treatment: AF ⁴ , ultrafiltration	Olive mill wastewater	95,000 mg L ⁻¹	88.4%	[54]
Pre-treatment: EO Post-treatment: UASB	Textile dye	847.5 mg L ⁻¹	70%	[55]
Pre-treatment: Electrochemical Post-treatment	Textile effluent	1201 mg L ⁻¹	72%	[56]
Pre-treatment: GAC ⁵ Post-treatment: Electrochemical cell	Blackwater	1732 mg L ⁻¹	69%	[57]

¹. EC: Electrocoagulation; ². RO: Reverse osmosis; ³. NF: Nanofiltration; ⁴. AF: Anaerobic Filter; ⁵. GAC: Granular activated carbon.

On the other hand, some fuel gases as by-products were generated during the operation of the system. This was also evaluated in this study; all results are recorded in Table 4. These gases might be supposed to be an advantage of this system compared with the others. Sathe et al. [50] also built a combination system based on microbial fuel cells to reduce COD but there was no presence of such by-products as in the current study. Methane and hydrogen from the digestion system were analyzed by GC, methane occupied 8.2%, whereas hydrogen was 10.8%. Typically, the methane percentage is higher than hydrogen in a biohythane mixture from an anaerobic system [58]. The percentage of this mixture can be affected by some parameters such as pH, solid retention time, and nutrients [59,60]. Therefore, the non-controlling of these parameters led to the concentration of hydrogen that is higher than methane in this study.

Table 4. By-product gases from the system.

Biogas from AD	
H ₂ (%)	10.8
CH ₄ (%)	8.2
CO ₂ (%)	1.9
Theoretical Gas from EO	
H ₂ (g)	0.012826

In addition, hydrogen is continuously released throughout the EO process (Equation (7)). This hydrogen gas was known as one of the purest hydrogen resources. The amount of hydrogen electrogenerated (m (g)) was determined by Faraday's law, given by Equation (14) [61]:

$$m_{\text{Hydrogen}} = \frac{M}{n} \times \frac{It \times CE}{F} \quad (14)$$

where M is molar mass of hydrogen (g mol⁻¹), n is electrons exchange, F represents the Faraday constant, whereas I , t , and CE indicate electrical parameters of current (A),

electrolysis time (s), and current efficiency (%), respectively. The number of by-products was trivial since all conditions were set for maximizing the removal of COD. However, the products might be advantageous for other works, and further investigation in another study to optimize these products is necessary.

4. Conclusions

In the present study, the main objective was to evaluate the effectiveness of a sequential combined AD/EO system for the removal of COD from high-strength beverage wastewater. The experiment was carried out in batch-mode lab-scale under a non-control temperature. Anaerobic digestion was a pre-treatment for raw rich-COD effluent, and COD was removed from 30,000 to 6190 mg L⁻¹ (efficiency of 79.37%) at the optimum condition of an HRT of 2 days. Meanwhile, the EO as a post-treatment attracted more focus in this study. Some important parameters such as electrolysis time, NaCl dosage, initial pH, and electro-properties were investigated for the EO reactor. COD was removed from 6190 to 1059.73 mg L⁻¹ (efficiency of 82.87%) at the optimum conditions of 3 g L⁻¹ NaCl and a natural pH. The EO system was operated under 20 V, current density of 135.4 A m⁻², 80 min of electrolysis time, and the use of Pt/Ti electrodes. As consequence, this system can reduce 96.47% of COD and 100% of color. The energy consumption and specific energy consumption were relatively low at 177.33 kWh m⁻³ and 33.79 kWh kgCOD⁻¹, respectively. Furthermore, fuel gases such as methane and hydrogen can collect during operating this system. However, some potential limitations exist in this study, such as the inability to control the conditions inside the UASB reactor, the absence of analysis on biogas production, and the lack of exploration of different electrolytes and electrodes. As a result, it is essential to address these factors in future work.

Author Contributions: Investigation, H.N.Q.P. and V.N.D.N.; Conceptualization, H.N.Q.P. and J.H.L.; Methodology, H.N.Q.P.; Supervision, J.H.L.; Validation, J.H.L.; Writing—original draft, H.N.Q.P.; Writing—review and editing, J.H.L. and V.N.D.N. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financed by the Ministry of Science and Technology, Taiwan (MOST 110-2926-I-035-001-MY4).

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: We gratefully acknowledge the devoted support for analytical instruments and laboratory from the Department of Materials Science and Engineering and Green Energy Development Center, Feng Chia University, Taichung, Taiwan.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Mohtashami, R.; Shang, J.Q. Electroflotation for Treatment of Industrial Wastewaters: A Focused Review. *Environ. Process.* **2019**, *6*, 325–353. [[CrossRef](#)]
2. Gumbo, B.; Mlilo, S.; Broome, J.; Lumbroso, D. Industrial water demand management and cleaner production potential: A case of three industries in Bulawayo, Zimbabwe. *Phys. Chem. Earth Parts A/B/C* **2003**, *28*, 797–804. [[CrossRef](#)]
3. E.C. European Integrated Pollution Prevention and Control Bureau (EIPPCB). *Reference Document on Best Available Techniques (BAT) in the Food, Drink and Milk Industries*; EIPPCB: Seville, Spain, 2017.
4. Li, Y.; Yu, T.; Kang, D.; Shan, X.; Zheng, P.; Hu, Z.; Ding, A.; Wang, R.; Zhang, M. Sources of anammox granular sludge and their sustainability in treating low-strength wastewater. *Chemosphere* **2019**, *226*, 229–237. [[CrossRef](#)] [[PubMed](#)]
5. Hidalgo, D.; Martín-Marroquín, J.M. 1—Adding Sustainability to the Beverage Industry Through Nature-Based Wastewater Treatment. In *Processing and Sustainability of Beverages*; Grumezescu, A.M., Holban, A.M., Eds.; Woodhead Publishing: Sawston, UK, 2019; pp. 1–36. [[CrossRef](#)]
6. Foo, K.Y.; Hameed, B.H. An overview of landfill leachate treatment via activated carbon adsorption process. *J. Hazard. Mater.* **2009**, *171*, 54–60. [[CrossRef](#)]

7. Ghosh Ray, S.; Ghangrekar, M.M. Comprehensive review on treatment of high-strength distillery wastewater in advanced physico-chemical and biological degradation pathways. *Int. J. Environ. Sci. Technol.* **2019**, *16*, 527–546. [[CrossRef](#)]
8. Li, W.c.; Chen, H.; Jin, Y.; Zhang, H.; Niu, Q.; Qi, W.; Zhang, Y.; Li, Y.-Y.; Gao, Y. Treatment of 3,4,5-trimethoxybenzaldehyde and Di-bromo-aldehyde manufacturing wastewater by the coupled Fenton pretreatment and UASB reactor with emphasis on optimization and chemicals analysis. *Sep. Purif. Technol.* **2015**, *142*, 40–47. [[CrossRef](#)]
9. Han, Y.; Yang, L.; Chen, X.; Cai, Y.; Zhang, X.; Qian, M.; Chen, X.; Zhao, H.; Sheng, M.; Cao, G.; et al. Removal of veterinary antibiotics from swine wastewater using anaerobic and aerobic biodegradation. *Sci. Total Environ.* **2020**, *709*, 136094. [[CrossRef](#)]
10. Nguyen, T.-T.; Ta, D.-T.; Lin, C.-Y.; Chu, C.-Y.; Ta, T.-M.-N. Biohythane production from swine manure and pineapple waste in a single-stage two-chamber digester using gel-entrapped anaerobic microorganisms. *Int. J. Hydrogen Energy* **2022**, *47*, 25245–25255. [[CrossRef](#)]
11. Sani, K.; Kongjan, P.; Pakhathirathien, C.; Cheirsilp, B.; O-Thong, S.; Raketh, M.; Kana, R.; Jariyaboon, R. Effectiveness of using two-stage anaerobic digestion to recover bio-energy from high strength palm oil mill effluents with simultaneous treatment. *J. Water Process Eng.* **2021**, *39*, 101661. [[CrossRef](#)]
12. Crini, G.; Lichtfouse, E. Advantages and disadvantages of techniques used for wastewater treatment. *Environ. Chem. Lett.* **2019**, *17*, 145–155. [[CrossRef](#)]
13. Deng, Y.; Englehardt, J.D. Electrochemical oxidation for landfill leachate treatment. *Waste Manag.* **2007**, *27*, 380–388. [[CrossRef](#)] [[PubMed](#)]
14. Särkkä, H.; Bhatnagar, A.; Sillanpää, M. Recent developments of electro-oxidation in water treatment—A review. *J. Electroanal. Chem.* **2015**, *754*, 46–56. [[CrossRef](#)]
15. Durán, F.E.; de Araújo, D.M.; do Nascimento Brito, C.; Santos, E.V.; Ganiyu, S.O.; Martínez-Huitle, C.A. Electrochemical technology for the treatment of real washing machine effluent at pre-pilot plant scale by using active and non-active anodes. *J. Electroanal. Chem.* **2018**, *818*, 216–222. [[CrossRef](#)]
16. Moreira, F.C.; Boaventura, R.A.R.; Brillas, E.; Vilar, V.J.P. Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters. *Appl. Catal. B Environ.* **2017**, *202*, 217–261. [[CrossRef](#)]
17. Klidi, N.; Clematis, D.; Delucchi, M.; Gadri, A.; Ammar, S.; Panizza, M. Applicability of electrochemical methods to paper mill wastewater for reuse. Anodic oxidation with BDD and TiRuSnO₂ anodes. *J. Electroanal. Chem.* **2018**, *815*, 16–23. [[CrossRef](#)]
18. Cifcioglu-Gozuacik, B.; Ergenekon, S.M.; Ozbey-Unal, B.; Balcik, C.; Karagunduz, A.; Dizge, N.; Keskinler, B. Efficient removal of ammoniacal nitrogen from textile printing wastewater by electro-oxidation considering the effects of NaCl and NaOCl addition. *Water Sci. Technol.* **2021**, *84*, 752–762. [[CrossRef](#)] [[PubMed](#)]
19. Barrios, J.A.; Cano, A.; Rivera, F.F.; Cisneros, M.E.; Durán, U. Efficiency of integrated electrooxidation and anaerobic digestion of waste activated sludge. *Biotechnol. Biofuels* **2021**, *14*, 81. [[CrossRef](#)]
20. Fontmorin, J.-M.; Hugué, S.; Fourcade, F.; Geneste, F.; Floner, D.; Amrane, A. Electrochemical oxidation of 2,4-Dichlorophenoxyacetic acid: Analysis of by-products and improvement of the biodegradability. *Chem. Eng. J.* **2012**, *195–196*, 208–217. [[CrossRef](#)]
21. Popat, A.; Nidheesh, P.V.; Anantha Singh, T.S.; Suresh Kumar, M. Mixed industrial wastewater treatment by combined electrochemical advanced oxidation and biological processes. *Chemosphere* **2019**, *237*, 124419. [[CrossRef](#)]
22. Lay, C.-H.; Vo, T.-P.; Lin, P.-Y.; Abdul, P.M.; Liu, C.-M.; Lin, C.-Y. Anaerobic hydrogen and methane production from low-strength beverage wastewater. *Int. J. Hydrogen Energy* **2019**, *44*, 14351–14361. [[CrossRef](#)]
23. Ni, J.; Ji, J.; Li, Y.-Y.; Kubota, K. Microbial characteristics in anaerobic membrane bioreactor treating domestic sewage: Effects of HRT and process performance. *J. Environ. Sci.* **2022**, *111*, 392–399. [[CrossRef](#)]
24. Charalambous, P.; Shin, J.; Shin, S.G.; Vyrides, I. Anaerobic digestion of industrial dairy wastewater and cheese whey: Performance of internal circulation bioreactor and laboratory batch test at pH 5–6. *Renew. Energy* **2020**, *147*, 1–10. [[CrossRef](#)]
25. Comminellis, C. Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for waste water treatment. *Electrochim. Acta* **1994**, *39*, 1857–1862. [[CrossRef](#)]
26. Bonfatti, F.; Ferro, S.; Lavezzo, F.; Malacarne, M.; Lodi, G.; De Battisti, A. Electrochemical Incineration of Glucose as a Model Organic Substrate. II. Role of Active Chlorine Mediation. *J. Electrochem. Soc.* **2000**, *147*, 592. [[CrossRef](#)]
27. Martínez-Huitle, C.; Ferro, S.; Reyna, S.; Cerro-López, M.; De Battisti, A.; Quiroz, M.A. Electrochemical oxidation of oxalic acid in the presence of halides at boron doped diamond electrode. *J. Braz. Chem. Soc.* **2008**, *19*, 150–156. [[CrossRef](#)]
28. Sandoval, M.A.; Espinoza, L.C.; Coreño, O.; García, V.; Fuentes, R.; Thiam, A.; Salazar, R. A comparative study of anodic oxidation and electrocoagulation for treating cattle slaughterhouse wastewater. *J. Environ. Chem. Eng.* **2022**, *10*, 108306. [[CrossRef](#)]
29. Tran, T.-K.; Leu, H.-J.; Chiu, K.-F.; Lin, C.-Y. Electrochemical Treatment of Heavy Metal-containing Wastewater with the Removal of COD and Heavy Metal Ions. *J. Chin. Chem. Soc.* **2017**, *64*, 493–502. [[CrossRef](#)]
30. Yao, J.; Mei, Y.; Jiang, J.; Xia, G.; Chen, J. Process Optimization of Electrochemical Treatment of COD and Total Nitrogen Containing Wastewater. *Int. J. Environ. Res. Public Health* **2022**, *19*, 850. [[CrossRef](#)]
31. Candia-Onfray, C.; Espinoza, N.; Sabino da Silva, E.B.; Toledo-Neira, C.; Espinoza, L.C.; Santander, R.; García, V.; Salazar, R. Treatment of winery wastewater by anodic oxidation using BDD electrode. *Chemosphere* **2018**, *206*, 709–717. [[CrossRef](#)] [[PubMed](#)]

32. Zhu, C.; Jiang, C.; Chen, S.; Mei, R.; Wang, X.; Cao, J.; Ma, L.; Zhou, B.; Wei, Q.; Ouyang, G.; et al. Ultrasound enhanced electrochemical oxidation of Alizarin Red S on boron doped diamond(BDD) anode: Effect of degradation process parameters. *Chemosphere* **2018**, *209*, 685–695. [[CrossRef](#)]
33. Titchou, F.E.; Zazou, H.; Afanga, H.; Gaayda, J.E.; Ait Akbour, R.; Nidheesh, P.V.; Hamdani, M. An overview on the elimination of organic contaminants from aqueous systems using electrochemical advanced oxidation processes. *J. Water Process Eng.* **2021**, *41*, 102040. [[CrossRef](#)]
34. Trasatti, S. Progress in the understanding of the mechanism of chlorine evolution at oxide electrodes. *Electrochim. Acta* **1987**, *32*, 369–382. [[CrossRef](#)]
35. Li, L.; Liu, Y. Ammonia removal in electrochemical oxidation: Mechanism and pseudo-kinetics. *J. Hazard. Mater.* **2009**, *161*, 1010–1016. [[CrossRef](#)]
36. Ghimire, U.; Jang, M.; Jung, S.P.; Park, D.; Park, S.J.; Yu, H.; Oh, S.-E. Electrochemical Removal of Ammonium Nitrogen and COD of Domestic Wastewater using Platinum Coated Titanium as an Anode Electrode. *Energies* **2019**, *12*, 883. [[CrossRef](#)]
37. Martínez-Huitle, C.A.; Rodrigo, M.A.; Sirés, I.; Scialdone, O. Single and Coupled Electrochemical Processes and Reactors for the Abatement of Organic Water Pollutants: A Critical Review. *Chem. Rev.* **2015**, *115*, 13362–13407. [[CrossRef](#)]
38. Lu, J.; Zhuo, Q.; Ren, X.; Qiu, Y.; Li, Y.; Chen, Z.; Huang, K. Treatment of wastewater from adhesive-producing industries by electrocoagulation and electrochemical oxidation. *Process Saf. Environ. Prot.* **2022**, *157*, 527–536. [[CrossRef](#)]
39. Fornaciari, J.C.; Weng, L.-C.; Alia, S.M.; Zhan, C.; Pham, T.A.; Bell, A.T.; Ogitsu, T.; Danilovic, N.; Weber, A.Z. Mechanistic understanding of pH effects on the oxygen evolution reaction. *Electrochim. Acta* **2022**, *405*, 139810. [[CrossRef](#)]
40. Zou, J.; Peng, X.; Li, M.; Xiong, Y.; Wang, B.; Dong, F.; Wang, B. Electrochemical oxidation of COD from real textile wastewaters: Kinetic study and energy consumption. *Chemosphere* **2017**, *171*, 332–338. [[CrossRef](#)] [[PubMed](#)]
41. Periyasamy, S.; Muthuchamy, M. Electrochemical oxidation of paracetamol in water by graphite anode: Effect of pH, electrolyte concentration and current density. *J. Environ. Chem. Eng.* **2018**, *6*, 7358–7367. [[CrossRef](#)]
42. Sun, D.; Hong, X.; Cui, Z.; Du, Y.; Hui, K.S.; Zhu, E.; Wu, K.; Hui, K.N. Treatment of landfill leachate using magnetically attracted zero-valent iron powder electrode in an electric field. *J. Hazard. Mater.* **2020**, *388*, 121768. [[CrossRef](#)]
43. Comninellis, C.; Pulgarin, C. Anodic oxidation of phenol for waste water treatment. *J. Appl. Electrochem.* **1991**, *21*, 703–708. [[CrossRef](#)]
44. Kumar, A.; Nidheesh, P.V.; Suresh Kumar, M. Composite wastewater treatment by aerated electrocoagulation and modified peroxi-coagulation processes. *Chemosphere* **2018**, *205*, 587–593. [[CrossRef](#)] [[PubMed](#)]
45. Güven, G.; Perendeci, A.; Özdemir, K.; Tanyolaç, A. Specific energy consumption in electrochemical treatment of food industry wastewaters. *J. Chem. Technol. Biotechnol.* **2012**, *87*, 513–522. [[CrossRef](#)]
46. Nurhayati, E.; Juang, Y.; Huang, C. The kinetics, current efficiency, and power consumption of electrochemical dye decolorization by BD-NCD film electrode. *AIP Conf. Proc.* **2017**, *1855*, 050005. [[CrossRef](#)]
47. Nidheesh, P.V.; Kumar, A.; Syam Babu, D.; Scaria, J.; Suresh Kumar, M. Treatment of mixed industrial wastewater by electrocoagulation and indirect electrochemical oxidation. *Chemosphere* **2020**, *251*, 126437. [[CrossRef](#)]
48. Chen, Y.-T. The Factors Affecting Electricity Consumption and the Consumption Characteristics in the Residential Sector—A Case Example of Taiwan. *Sustainability* **2017**, *9*, 1484. [[CrossRef](#)]
49. Linares Hernández, I.; Barrera Díaz, C.; Valdés Cerecero, M.; Almazán Sánchez, P.T.; Castañeda Juárez, M.; Lugo Lugo, V. Soft drink wastewater treatment by electrocoagulation–electrooxidation processes. *Environ. Technol.* **2017**, *38*, 433–442. [[CrossRef](#)]
50. Chakchouk, I.; Elloumi, N.; Belaid, C.; Mseddi, S.; Chaari, I.; Kallel, M. A combined electrocoagulation–electrooxidation treatment for dairy wastewater. *Braz. J. Chem. Eng.* **2017**, *34*, 109–117. [[CrossRef](#)]
51. Bohdziewicz, J.; Kwarciak, A. The application of hybrid system UASB reactor-RO in landfill leachate treatment. *Desalination* **2008**, *222*, 128–134. [[CrossRef](#)]
52. Güneş, E.; Gönder, Z.B. Evaluation of the hybrid system combining electrocoagulation, nanofiltration and reverse osmosis for biologically treated textile effluent: Treatment efficiency and membrane fouling. *J. Environ. Manag.* **2021**, *294*, 113042. [[CrossRef](#)]
53. Kyriacou, A.; Lasaridi, K.E.; Kotsou, M.; Balis, C.; Pilidis, G. Combined bioremediation and advanced oxidation of green table olive processing wastewater. *Process Biochem.* **2005**, *40*, 1401–1408. [[CrossRef](#)]
54. Khoufi, S.; Aloui, F.; Sayadi, S. Pilot scale hybrid process for olive mill wastewater treatment and reuse. *Chem. Eng. Process. Process Intensif.* **2009**, *48*, 643–650. [[CrossRef](#)]
55. Carvalho, C.; Fernandes, A.; Lopes, A.; Pinheiro, H.; Gonçalves, I. Electrochemical degradation applied to the metabolites of Acid Orange 7 anaerobic biotreatment. *Chemosphere* **2007**, *67*, 1316–1324. [[CrossRef](#)] [[PubMed](#)]
56. Vilaseca, M.; Gutiérrez, M.-C.; López-Grimau, V.; López-Mesas, M.; Crespi, M. Biological Treatment of a Textile Effluent After Electrochemical Oxidation of Reactive Dyes. *Water Environ. Res.* **2010**, *82*, 176–182. [[CrossRef](#)] [[PubMed](#)]
57. Rogers, T.W.; Rogers, T.S.; Stoner, M.H.; Sellgren, K.L.; Lynch, B.J.; Forbis-Stokes, A.A.; Stoner, B.R.; Hawkins, B.T. A granular activated carbon/electrochemical hybrid system for onsite treatment and reuse of blackwater. *Water Res.* **2018**, *144*, 553–560. [[CrossRef](#)]
58. Abdur Rawoof, S.A.; Kumar, P.S.; Vo, D.-V.N.; Devaraj, T.; Subramanian, S. Biohythane as a high potential fuel from anaerobic digestion of organic waste: A review. *Renew. Sustain. Energy Rev.* **2021**, *152*, 111700. [[CrossRef](#)]

59. Lee, I.-S.; Parameswaran, P.; Rittmann, B.E. Effects of solids retention time on methanogenesis in anaerobic digestion of thickened mixed sludge. *Bioresour. Technol.* **2011**, *102*, 10266–10272. [[CrossRef](#)]
60. Ta, D.-T.; Lin, C.-Y.; Ta, T.-M.-N.; Chu, C.-Y. Effect of pH shock on single-stage biohythane production using gel-entrapped anaerobic microorganisms. *Int. J. Hydrogen Energy* **2022**, *47*, 3679–3689. [[CrossRef](#)]
61. He, T.; Kar, M.; McDaniel, N.D.; Randolph, B.B. Electrochemical Hydrogen Production. In *Springer Handbook of Electrochemical Energy*; Breitkopf, C., Swider-Lyons, K., Eds.; Springer: Berlin/Heidelberg, Germany, 2017; pp. 897–940. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.