

Article

Combined Electrocoagulation and Physicochemical Treatment of Cork Boiling Wastewater

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Abstract: Cork boiling wastewater (CBW) is a highly polluted and difficult to treat effluent resultant from the cork manufacturing industry. This study aims to evaluate a new, reliable, efficient, and sustainable process to treat this effluent. This paper tested electrocoagulation as a pre- and post-treatment to improve the already existing physicochemical treatment in a cork production facility in Portugal. In the physicochemical procedures (PC), the addition of different volumes of coagulant (ferric chloride (III) 40% *w/w*), neutralizer (sodium hydroxide, 32% *w/w*), and flocculant (polyacrylamide, 0.2 g/L) were evaluated. Electrocoagulation (EC) was performed in a bench-scale reactor, using aluminum and stainless-steel electrodes. For EC, different initial pH, current density, and current tension values were tested. When electrocoagulation was used as a post-treatment, better performances were achieved. However, treatment costs were increased significantly. Coagulation/flocculation offers a viable and cheap treatment, achieving removal efficiencies of 88.2%, 81.0%, 76.9%, and 94.2% for total chemical oxygen demand (tCOD), total carbon (TC), total nitrogen (TN), and soluble chemical oxygen demand (sCOD), respectively. With a PC-EC combination, it is possible to achieve removal efficiencies of 92.4%, 88.0%, 91.4%, and 91.4% for tCOD, TC, TN, and sCOD, respectively. The increased TN removal efficiency can translate into great benefits for certain discharge conditions and should be taken into consideration for improving the sustainability of cork industry. On the other hand, when EC is used as a pre-treatment, there are no benefits either in terms of treatment performance or operating costs.

Keywords: cork boiling wastewater; cost assessment; electrocoagulation; physicochemical treatment



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1. Introduction

Cork is a natural renewable material extracted from *Quercus suber L.*, with considerable relevance in the Portuguese economy [1]. Its main application is the production of stoppers for the wine industry. One of the key steps in the manufacturing of cork stoppers is the boiling of cork planks [2]. In this process, the raw cork planks are boiled in water for one hour, to remove biological and chemical contamination. The boiling process also improves cork texture and mechanical properties but generates a recalcitrant effluent with significant organic loads, the Cork Boiling Wastewater (CBW) [3–5]. This wastewater is characterized by its dark color, acid pH, high toxicity, high organic load, and low biodegradability, and by high concentrations of total suspended solids (TSS), tannins, lignin, and phenolic compounds (i.e., concentrations exceed the values established by law). This effluent raises environmental concerns, once its characteristics are very similar to other agro-industrial

wastewaters known for their environmental impact, such as wine distillery, olive oil extraction, and wood debarking [6]. Studies regarding the treatment of CBW involve simple and combined technologies, such as: coagulation/flocculation [7–10], biological treatment technologies [3,5,11–13], combined bio and chemical degradation [1,14], advanced oxidation processes (AOP) [2,15–19], combined AOP and coagulation/flocculation [9], and combined AOP [20]. Ultra and nanofiltration have also been used for CBW treatment and for extraction of added-value components [21–23]. Most studies consider AOP in the treatment of CBW, with emphasis on Fenton. Nevertheless, two papers consider electrocoagulation. Fernandes et al. [18] tested EC with a boron-doped diamond anode, achieving removal efficiencies higher than 90% for COD, dissolved organic carbon, total phenols, and color. However, the material used as anode presents high costs [24]. Garcia-Costa et al. [20] tested a combination of EC (with iron electrodes) and Fenton, with electro-Fenton achieving, in both cases, a total organic carbon (TOC) removal of around 87% and a total phenolic compounds removal. According to the authors of this study, EC alone was not efficient in CBW treatment. However, an EC pre-treatment proved to reduce the costs related to Fenton oxidation by 40%, as it decreases the need for H₂O₂. The results of both studies indicate that EC can be applied in CBW treatment when certain electrodes are applied, or can be used as a pre-treatment technology with significant benefits.

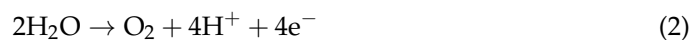
This study proposes an alternative for the treatment of CBW by employing a combination of electrocoagulation (EC) and traditional physicochemical (PC) treatment (coagulation/flocculation). Coagulation/flocculation is known worldwide for its ability to improve water/wastewater treatment efficiency and for being a cost-effective technique [25]. EC is efficient in the removal of various pollutants and has been intensively studied during the past decade, as described in the review paper of Moussa et al. [26] and Garcia-Segura et al. [27].

Usually, PC wastewater treatment involves coagulation, flocculation, and sedimentation. The coagulation/flocculation method has been used for more than a century and is particularly efficient in removing colloids [28]. According to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, colloidal suspensions are affected by attractive van der Waals forces and repulsive electrostatic forces. When the attraction forces prevail, the particles tend to coagulate/flocculate and suspensions might be destabilized. In contrast, when repulsive forces are dominant, particles remain dispersed. In wastewater, suspended particles are negatively charged, repelling each other and remaining in suspension [26,29–31]. The role of coagulants/flocculants in wastewater treatment processes is to reduce the repulsive forces between colloids, destabilizing them. This destabilization aims to force particles' agglomeration, making their separation a more straightforward process [26]. In summary, the coagulation process aims to destabilize the colloids in the water, enabling their flocculation and sedimentation. During flocculation, the micro clots formed in the coagulation process aggregate, resulting in larger flocs that can be easily removed by sedimentation [32].

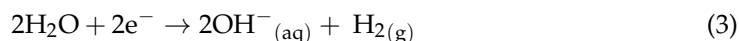
EC is a wastewater treatment technique that combines the advantages of coagulation, flocculation, and electrochemistry. Its actuation process is very similar to the one involving the traditional physicochemical methods. However, in this case, coagulant species are generated in situ, owing to electro dissolution of sacrificial anodes, usually made of iron or aluminum. This way, EC is considered a more environmental-friendly process, once it minimizes wastewater treatment footprint, sludge generation, and the need for chemical additives [33]. By employing an electrical current, it is possible to remove suspended solids, colloids, metals, and dissolved solids, as well as persistent pollutants, pesticides, and pathogens. In addition, this technique has a feasible adaptation to different pollutant loads and different flow rates [34–36]. In this process, two anodic reactions can occur. Equation (1) refers to the metal oxidation, by which the metallic cations are generated, where z is the number of electrons transferred during anode dissolution, per mole of metal [37].



Simultaneously, in the case of high anode potential, water suffers oxidation (Equation (2)), with hydronium and oxygen production [38].



At the cathode, water suffers reduction (Equation (3)). This reaction is independent of the metal used as cathode [39].



Both anodic and cathodic reactions produce species that can lead to water pH variation. At the anode, the formation of H_3O^+ (represented as H^+) occurs with simultaneous production of metal-oxy(hydr)oxides (Equation (4)), causing the pH to drop [40]. Subsequently, the H^+ produced at the anode diffuses and reacts with the OH^- formed at the cathode [41]. Even though metallic ions are only produced at the anode, the products of both anodic and cathodic reactions interact and react with each other, promoting the coagulation of pollutants, and their precipitation or flotation (Figure 1).

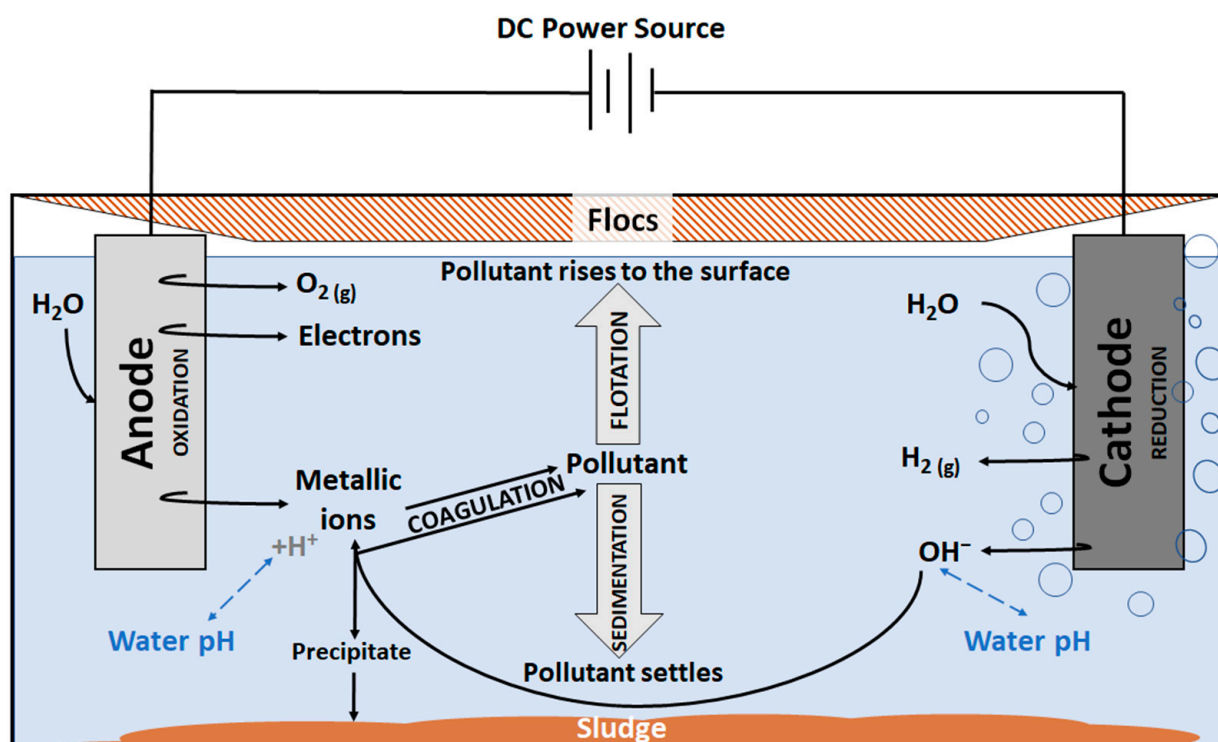
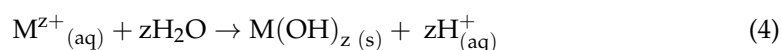


Figure 1. Schematic representation of reactions and phenomena occurring during the electrocoagulation process (adapted from Hakizimana et al. [38]).

To treat the wastewater by this method, it should possess a conductivity value that allows the ions transference between electrodes, with the cations moving to the cathode and the anions moving to the anode. When the effluent's conductivity is insufficient, it is common to add an electrolyte, usually NaCl [42].

The novelty of this work regarding CBW treatment relies on assessing the performance of PC, and PC with EC as pre- (EC-PC) and post- (PC-EC) treatment. The aim is to understand the influence and viability of adding electrocoagulation to the conventional PC treatment, forming a combined system for CBW treatment.

2. Materials and Methods

In this study, the treatment of real CBW was performed by combining two existing techniques, EC and PC. The order of the application of the two techniques was studied. For EC, a stainless-steel plate was used as the cathode and an aluminum one as the anode. For PC, the addition of different volumes of coagulant (ferric chloride (III) 40% *w/w*), neutralizer (sodium hydroxide, 32% *w/w*), and flocculant (polyacrylamide, 0.2 g/L) were tested, as well as the order in which the addition was performed. CBW was obtained from a cork industry located in the Alentejo region of Portugal. Table 1 presents the characterization of CBW used in this study, as well as the characterization of effluents used in other studies.

Table 1. Cork boiling wastewater characterization from this project and comparison with other studies.

Parameters	This Study	Vilar et al. [15]	Marques et al. [12]	Ponce-Robles et al. [2]	Mota-Panizio et al. [5]	Garcia-Costa et al. [19]
pH	5.2–6.8	7.5	5.8	6.4	4.4–4.8	4.4
Cond. ($\mu\text{S}/\text{cm}$)	1260–1299	2900	1500	1300	1130–1830	1443
tCOD (mgO_2/L)	5402–5979	4692	6500	5300	6960–7160	4609
sCOD (mgO_2/L)	4504–4998	-	6200	-	-	-
TC (mgC/L)	1439–1441	-	-	-	-	-
TN (mgN/L)	43.44–48.3	308.8	-	75.0	-	-

2.1. Experimental Apparatus and Procedures

Three sets of experiments PC, EC-PC, and PC-EC were performed in laboratory-scale reactors of 1 L. The reactional volume employed for PC and PC-EC experiments was 0.5 L. As for EC-PC, the reactional volume of 0.8 L was divided into two jars with 0.4 L each after the electrocoagulation step to perform two different PC procedures. The bench-scale EC unit used a power supply PL330 from Thurlby Thandar Instruments and a magnetic stirrer.

After treatment, the wastewater was subjected to a settling period of 1h. This short settling time aimed to reduce treatment duration, as electrocoagulation already takes up to one hour. After this period, the removal efficiencies for tCOD, sCOD, TC, and TN were evaluated. An assessment of all the experiments is present in Table 2 (PC), Table 3 (EC-PC), and Table 4 (PC-EC). PC experiments followed the procedure adopted in the cork production plant from where the effluent was collected. The chemicals' addition considered the optimum pH for ferric chloride and a final neutral pH. For EC-PC experiments, the procedure was optimized in terms of conductivity and initial pH.

Table 2. Description of the tested PC processes. Employed volumes of neutralizer (sodium hydroxide, 32% *w/w*) (N), coagulant (Ferric Chloride (III), 40% *w/w*) (C), and flocculant (polyacrylamide, 0.2g/L) (F), and pH values observed in the final of each stage.

	Initial pH	Stage 1	Stage 1 pH	Stage 2	Stage 2 pH	Stage 3	Final pH
I	5.43	1.60 mL/L C	2.58	2.00 mL/L N	7.74	1.00 mL/L F	7.74
II	5.63	1.40 mL/L N	11.32	3.80 mL/L C	3.02	2.00 mL/L N + 2.00 mL/L F	7.12
III	6.49	1.60 mL/L C	2.76	1.40 mL/L N	7.67	4.00 mL/L F	7.41
IV	6.27	2.00 mL/L C	4.54	1.00 mL/L N	6.98	-	-
V	6.44	4.20 mL/L C	2.38	3.30 mL/L N	7.18	-	-

Table 3. Description of the tested EC-PC processes. Employed volumes of neutralizer (sodium hydroxide, 32% *w/w*) (N) and coagulant (Ferric Chloride (III), 40% *w/w*) (C), and pH values for each stage.

	Initial pH Value	Pre-treatment	pH		pH	Applied PC	Final pH
<u>1.1</u>	5.53	-	-	Electrocoagulation	9.68	0.25 mL/L C	7.20
<u>1.2</u>						2.50 mL/L C + 2.40 mL/L N	7.04
<u>2.1</u>	5.52	0.95 g/L S	5.61		9.22	0.25 mL/L C	7.14
<u>2.2</u>						2.75 mL/L C + 1.75 mL/L N	7.02
<u>3.1</u>	5.17	0.10 mL/L N + 0.90 g/L S	6.13		9.41	2.00 mL/L C	7.01
<u>3.2</u>						3.00 mL/L C + 1.80 mL/L N	7.02
<u>4.1</u>	5.94	0.01 mL/L N + 0.90 g/L S	6.42		9.39	0.75 mL/L C	6.89
<u>4.2</u>						2.00 mL/L C + 1.75 mL/L N	7.01
<u>5.1</u>	5.94	0.30 mL/L N + 1.00 g/L S	6.92		9.25	0.75 mL/L C	6.95
<u>5.2</u>						3.50 mL/L C + 2.50 mL/L N	7.18
<u>6.1</u>	5.37	0.50 mL/L N + 0.75 g/L S	7.54		9.31	0.50 mL/L C	6.97
<u>6.2</u>						3.00 mL/L C + 2.00 mL/L N	6.92

Table 4. Description of the tested PC-EC processes. Employed volumes of neutralizer (sodium hydroxide, 32% *w/w*) (N), coagulant (Ferric Chloride (III), 40% *w/w*) (C), and flocculant (polyacrylamide, 0.2 g/L) (F) and pH values for each stage.

	Initial pH	Stage 1	pH	Stage 2	pH		Final pH
A	6.14	1.45 mL/L C	3.06	1.40 mL/L N	6.48	Electrocoagulation	8.90
B	6.36	2.00 mL/L N	11.50	1.90 mL/L C	7.05		9.71
C	6.15	1.40 mL/L C	2.90	1.40 mL/L N	6.49		8.35
D	6.83	1.80 mL/L N	11.50	1.80 mL/L C	6.92		9.30

To ensure that the conductivity was roughly the same for the electrocoagulation step in the PC-EC and EC-PC tests, a 5% (*w/w*) solution of sodium chloride (S) was added to the EC-PC (Table 3) prior to electrocoagulation, to raise conductivity to 3.0 mS/cm, corresponding to a salinity value of 1.6 g/kg. Electrocoagulation was performed for 60 min, under an electrical tension of 15V. During this stage, electrodes were separated by a 2 cm gap. Since initial pH influences EC, the initial pH was adjusted from 5.5 to 7.5. Experiments 1.1 and 1.2 were performed with the raw effluent, without adding salt or another chemical.

For PC-EC experiments (Table 4), the electrocoagulation stage was performed for 60 min, with electrodes separated 2 cm. Experiments A and B were performed under an electric tension of 15 V and experiments C and D under 20 V.

For EC-PC and PC-EC experiments, both current intensity (*I*) and electric tension (*V*) provided by the power supply were measured every 5 min. This allowed the determination of power consumption (*P*) for each 5 min of EC operation, using Equation (5).

$$P = V \times I \quad (5)$$

where *V*, in volts, and *I*, in amperes, are the corresponding readings for each 5 min period. With the power consumption determination, it is possible to estimate the energy related costs (*E*), in euros, using Equation (6).

$$E = \text{electricity cost} \times \sum_{i=0}^{11} \frac{P_{5i} + P_{5(i+1)}}{24,000} \quad (6)$$

Using Equation (7), it is possible to estimate the costs related to anode dissolution (DP), in euros,

$$DP = \frac{m_{exp} \times Al_{price}}{\rho_{Al}} \quad (7)$$

where m_{exp} is the experimental dissolved aluminum mass (kg), Al_{price} is the plate price per volume unit (€/m³) and ρ_{Al} is the plate volumetric mass (kg/m³).

Operational costs (C) for EC-PC and PC-EC can be estimated using Equation (8). For PC experiments, the costs are estimated considering only the reagents' costs (RC).

$$C = E + DP + RC \quad (8)$$

2.2. Analytical Methods

Total Suspended Solids (TSS) were determined according to the Method 2540D of the Standard Methods for the Examination of Water and Wastewater [43]. Total Carbon (TC) present in the water was measured by nondispersive infrared detector (NDIR) after oxidative combustion, using Shimadzu TOC-VCPH/CPN Total Organic Carbon Analyzer and TOC-Control V software. Total Nitrogen (TN) was measured by chemiluminescence, using a Shimadzu Total N Measuring Unit TNM-1. pH and conductivity were measured using a WTW Multi 9269 IDS analyser, equipped with the pH-Electrode Sentix 980 and the TetraCon925 conductivity probe. Total and soluble chemical oxygen demand (COD) was determined by the Closed Reflux, Colorimetric Method 5220D of the Standard Methods for the Examination of Water and Wastewater [43].

3. Results and Discussion

3.1. Treatment Efficiency and Associated Costs

As mentioned before, the removal efficiencies of tCOD, sCOD, TC, and TN were accessed for every tested treatment procedure, as well as the total associated costs per cubic meter of wastewater to be treated. The results are presented in Figure 2. Human labor and equipment maintenance were not included in the operational costs, but it is possible to infer that the costs related to human labor should be lower in the case of EC, when compared to PC.

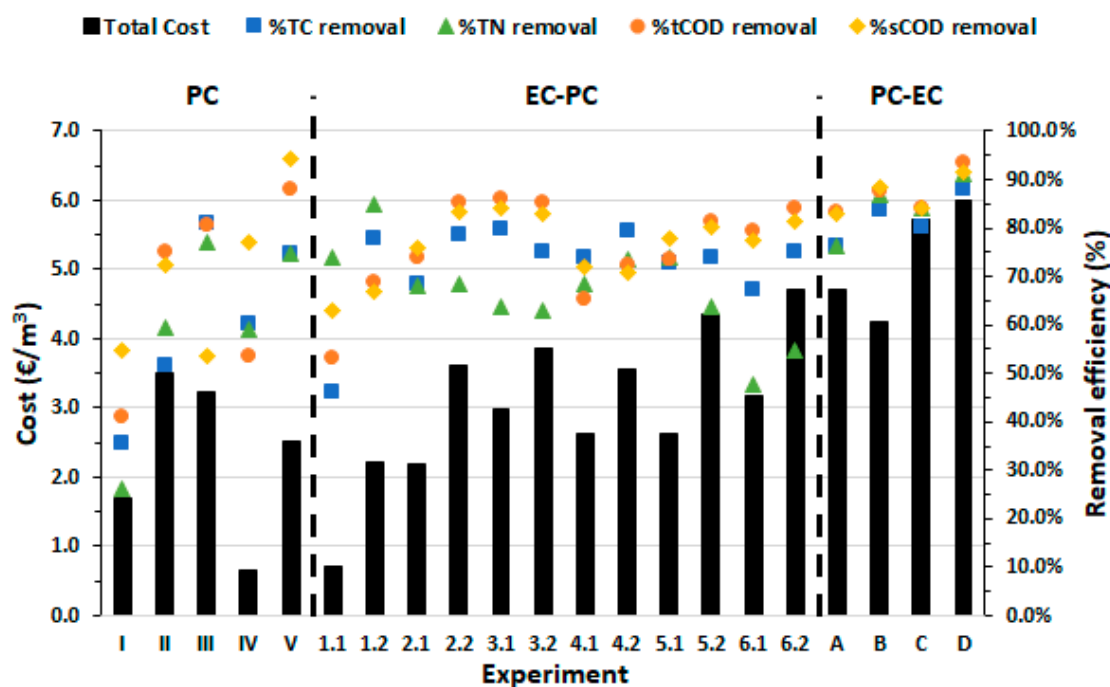


Figure 2. TC, TN, tCOD, and sCOD removal efficiencies and treatment cost per volume of CBW.

Regarding PC experiments (Table 2), these results indicate that procedure V presents the best removal for both COD forms, TC and TN. However, for the two last parameters, procedure III displays very similar values. The two procedures are very similar in terms of interstage pH values, although different reagent volumes had been applied to achieve similar conditions. This way, it is possible to infer that the addition of a higher volume of coagulant and neutralizer, without the addition of flocculant, is beneficial for COD removal, particularly in its soluble form. On the other hand, TC and TN removal slightly benefit from the addition of flocculant.

Procedures I and III were performed using the same coagulant volume in stage 1 and similar interstage pH values. Comparing the results from these two experiments, it is possible to verify that adding higher volumes of flocculant enhances treatment performance. This benefit is particularly relevant on TC and TN removal, as it leads to the best results of the tested PC procedures. On the other hand, procedure V was performed without the addition of flocculant and with higher volumes of coagulant and neutralizer, achieving the highest removal performance of all the experiments. The former indicates that increasing the volume of added coagulant and neutralizer eliminates the necessity for a flocculant to be added, to achieve the same results as in experiment III. Other studies have also concluded that higher coagulant dosages enhance treatment performance until agglomeration saturation [44–46].

Procedure IV presents the lower cost and intermediate removal efficiency for all the considered pollutants, as procedure II presents the highest cost, without benefits in treatment performance.

For the EC-PC experiments (Table 3), one can observe in Figure 2 that procedure 3.1 presents the best removal efficiency for all considered pollutants, except for TN, for which the best removal is observed for procedure 1.2. In fact, TN removal seems to decrease with the addition of the electrolyte and with increasing pH values. This is notorious when comparing 1.1 and 1.2 (73.9 and 84.8%) with 6.1 and 6.2. (47.9 and 54.9%). These results indicate that most of the considered pollutants can be removed with electrocoagulation followed by a one-step PC treatment, which decreases pH until values are around 6, using a coagulant. However, the removal of TN can benefit from electrocoagulation performed with lower current density, followed by a PC treatment involving the decrease of the pH and its sequential increase, until pH is around 7. PC experiments have also found that the best TN removal is obtained for this sequence of pH changes (procedures III and V). This way, it is possible to infer that TN removal during EC must be negligible, compared to PC.

Procedure 1.1 has the lowest cost, but at the same time presents the worst treatment efficiency for all pollutants, except TN. Procedure 6.2 presents the highest cost without benefits in the removal of TN. For other pollutants, the treatment efficiency is similar to the one verified for 3.1, which has the best performance, without the increased costs. From Figure 2, it is also possible to verify a general increase in treatment costs when an EC treatment precedes PC.

Experiments 1.1 and 1.2 were performed with raw effluent. The main difference between procedures 1.1–1.2 and 2.1–2.2 is the absence of addition of the electrolyte, which leads to a decrease of wastewater conductivity and, consequently, to a decrease in the current density for the same voltage. This way, performing EC without the addition of an electrolyte leads to a decrease in the removal efficiency of tCOD, sCOD, and TC; however, it improves TN removal. The negative influence of decreasing current density in tCOD, TOC, and DOC removal from CBW has already been reported by other studies [18,20].

Experiments 4.1 and 5.1 were performed with different pH values before EC, but achieved the same price per cubic meter of wastewater treated. An increase in pH value proved to be beneficial for tCOD and sCOD removal. As for TN and TC removal, the differences are as significative.

Regarding PC-EC experiments (Table 4), the results of Figure 2 demonstrate that procedure D presents the best performance in terms of pollutant removal and, simultaneously, the highest associated costs. For this set of experiments, procedure B achieves a lower cost,

without a considerable decrease in performance. In general, PC-EC produced better results, however with a significant increment in treatment costs. From this set, it is possible to conclude that using higher volumes of reagents, the conductivity is increased, thus improving treatment efficiency when the same electric tension is applied. Experiments A and C were performed under the same conductivity conditions but with different applied electric tensions. By comparing these experiments, it is possible to conclude that independently of the performed PC treatment, under the same conductivity conditions, TN removal is enhanced by an increase in electric tension; as for other pollutants, the performance does not suffer considerable changes.

From Figure 2, it is possible to verify that experiment V has a slightly better performance on sCOD removal than experiment D. The lower sCOD removal of the combined methods can be explained by the differences of coagulant dosage in the PC stage. Chloride ions have a strong oxidant power. In experiment V, a higher concentration of ferric chloride was added to CBW, enhancing the removal of soluble COD.

Garcia-Costa et al. [20] performed an EC + Fenton and electro Fenton treatment using iron electrodes for in-situ Fe liberation at 80 °C. Both processes achieved COD removal above 90%, being the main difference in the time of reaction, which for Electro Fenton was four times faster. Their preliminary economic study, considering the operational costs, places electro Fenton at the cost of 9.78 EUR/m³ and EC + Fenton at 16.30 EUR/m³. Attaining that the predicted operational costs, including chemicals, energy, plates, and sludge management, for all experiments were lower and achieved similar removal efficiencies, all the three presented processes in this paper offer better cost-efficiency in treating CBW. The integration of Fenton-coagulation/flocculation was studied for the decontamination of CBW. The authors only included the costs of the applied chemicals. For COD removal of 73%, Garcia-Costa and co-authors attribute a cost of 11.5 EUR/m³ of CBW, which is also higher than the one obtained in this study [20]. According to Beltrn et al. [47], a great part of the costs associated with Fenton processes are due to the chemicals used in wastewater treatment; while, for EC, electricity consumption presents the majority of the costs.

Fernandes et al. [18] studied the depuration of CBW by anodic oxidation using a boron-doped diamond anode, but they do not include the associated costs. COD reductions were greater than 74%. However, the experiments to achieve high COD removals required treatments longer than 1 h, representing a significant drawback, especially when compared with PC treatment and the proposed 1 h of EC.

3.2. Electrode Wear

The anode oxidation results in its dissolution, leading to a significant mass loss, that can be theoretically estimated by Faraday's Law (Equation (9)):

$$m_{theo} = \frac{I \times t \times M}{Z \times F} \quad (9)$$

where, I is current intensity, t is the electrolysis time, M is the atomic weight of the anode material, Z is its number of valence electrons (Z), and F represents the Faraday's constant [38]. However, Equation (9) is only valid when all the electrons participate in the anodic dissolution. When parallel reactions occur, current efficiency (φ) is applied to account for the difference between the theoretical and experimental plate's dissolution (Equation (10)) [48,49]. Current efficiency is usually lower than 1 [50]. However, when the electrode is attacked both chemical and electrochemically, φ can be higher than 1 [51].

$$\varphi = \frac{m_{exp}}{m_{theo}} \quad (10)$$

Figure 3 represents the relation between theoretical and experimental aluminum plate mass loss. According to this figure, φ is approximately 1.20. Once that current efficiency is higher than 1, it is possible to conclude that aluminum electrodes suffered a chemical attack. Part of the chemical corrosion can be attributed to the NaCl concentration. As described

by Wan et al. [52] and Kang et al. [53], NaCl solution is considered a neutral corrosive media, with the penetration of the corrosive media increasing with time of immersion, as it forms a rusting product on the surface of the metal substrate. Chloride links to the active site of the metal surface, promoting the intrusion of chloride ions into the mobile sites of aluminum alloy [54]. Cl^- ions are readily adsorbed to the surface of a film, resulting in the destruction of the passivation layer formed on the aluminum plate, leading to a greater rate of aluminum dissolution and resulting in increased pitting [55].

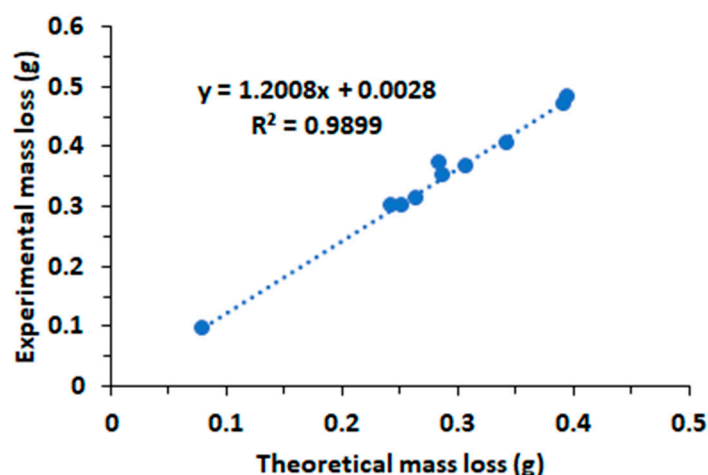


Figure 3. Correlation between theoretical and experimental aluminum mass loss (g).

Additionally, NaOH, used as a neutralizer, can react directly with aluminum oxide, damaging the aluminum surface and hampering particle distribution throughout the surfaces [56]. These aspects are linked to reducing electrode wear time, especially at higher concentrations and reaction times. Consequently, the amount of dissolved aluminum during EC exceeds the one predicted by Faraday's Law. These results are in accordance with previous studies [57].

4. Conclusions

The results presented in this study allow us to conclude that the use of electrocoagulation after the physicochemical treatment leads to very high removal efficiencies. Thus, this treatment solution proves to be relevant, insofar as it contributes to increasing the sustainability of the cork sector by reducing the impact of its wastewater treatment. For the tested physicochemical procedures (PC), it was accessed that higher added volumes of neutralizer and flocculant improve the removal of tCOD, sCOD, TC, and TN. Still, it is possible to achieve higher COD removals, by adding more coagulant and neutralizer. Coagulation/flocculation offers a viable and cheap treatment, achieving removal efficiencies of 88.2%, 81.0%, 76.9%, and 94.2% for tCOD, TC, TN, and sCOD, respectively.

The combination of the two treatment methods increases costs. A PC pre-treatment of CBW increases treatment performance and significantly increases its costs. With a PC-EC combination, it is possible to achieve removal efficiencies of 92.4%, 88.0%, 91.4%, and 91.4% for tCOD, TC, TN, and sCOD, respectively. On the other hand, when electrocoagulation is used as a pre-treatment for PC, there are no benefits for either treatment performance or costs. Overall, the achieved efficiencies might not be significant to justify the increased costs of EC, unless increased TN removal is necessary. However, biological treatments should be compared to EC, to understand which could be a better fit with PC; especially considering that adding NaCl to the treatment might be significant when assessing chlorides discharge. Additionally, increasing energy consumption might actually increase the carbon footprint of the factory.

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References

1. Dias-Machado, M.; Madeira, L.M.; Nogales, B.; Nunes, O.C.; Manaia, C.M. Treatment of Cork Boiling Wastewater Using Chemical Oxidation and Biodegradation. *Chemosphere* **2006**, *64*, 455–461. [\[CrossRef\]](#)
2. Ponce-Robles, L.; Miralles-Cuevas, S.; Oller, I.; Agüera, A.; Trinidad-Lozano, M.J.; Yuste, F.J.; Malato, S. Cork Boiling Wastewater Treatment and Reuse through Combination of Advanced Oxidation Technologies. *Environ. Sci. Pollut. Res.* **2017**, *24*, 6317–6328. [\[CrossRef\]](#)
3. Gomes, A.; Stefanakis, A.; Albuquerque, A.; Sim, R. Cork Boiling Wastewater Treatment in Pilot Constructed Wetlands. In *Constructed Wetlands for Industrial Wastewater Treatment*; Stefanakis, A., Ed.; Wiley: Hoboken, NJ, USA, 2018; pp. 285–305. [\[CrossRef\]](#)
4. Ponce-Robles, L.; Oller, I.; Agüera, A.; Trinidad-Lozano, M.J.; Yuste, F.J.; Malato, S.; Perez-Estrada, L.A. Application of a Multivariate Analysis Method for Non-Target Screening Detection of Persistent Transformation Products during the Cork Boiling Wastewater Treatment. *Sci. Total Environ.* **2018**, *633*, 508–517. [\[CrossRef\]](#)
5. Mota-Panizio, R.; Hermoso-Orzáez, M.J.; Carmo-Calado, L.; Lourinho, G.; De Brito, P.S.D. Biochemical Methane Potential of Cork Boiling Wastewater at Different Inoculum to Substrate Ratios. *Appl. Sci.* **2021**, *11*, 3064. [\[CrossRef\]](#)
6. Mendonça, E.; Picado, A.; Silva, L.; Anselmo, A.M. Ecotoxicological Evaluation of Cork-Boiling Wastewaters. *Ecotoxicol. Environ. Saf.* **2007**, *66*, 384–390. [\[CrossRef\]](#)
7. Domínguez, J.R.; González, T.; García, H.M.; Sánchez-Lavado, F.; Beltrán de Heredia, J. Aluminium Sulfate as Coagulant for Highly Polluted Cork Processing Wastewaters: Removal of Organic Matter. *J. Hazard. Mater.* **2007**, *148*, 15–21. [\[CrossRef\]](#)
8. González, T.; Domínguez, J.R.; Beltrán-Heredia, J.; García, H.M.; Sanchez-Lavado, F. Aluminium Sulfate as Coagulant for Highly Polluted Cork Processing Wastewater: Evaluation of Settability Parameters and Design of a Clarifier-Thickener Unit. *J. Hazard. Mater.* **2007**, *148*, 6–14. [\[CrossRef\]](#)
9. De Torres-Socias, E.; Fernández-Calderero, I.; Oller, I.; Trinidad-Lozano, M.J.; Yuste, F.J.; Malato, S. Cork Boiling Wastewater Treatment at Pilot Plant Scale: Comparison of Solar Photo-Fenton and Ozone (O_3 , O_3/H_2O_2). Toxicity and Biodegradability Assessment. *Chem. Eng. J.* **2013**, *234*, 232–239. [\[CrossRef\]](#)
10. Peres, J.A.; Beltrán de Heredia, J.; Domínguez, J.R. Integrated Fenton's Reagent—Coagulation/Flocculation Process for the Treatment of Cork Processing Wastewaters. *J. Hazard. Mater.* **2004**, *107*, 115–121. [\[CrossRef\]](#)
11. Mendonça, E.; Pereira, P.; Martins, A.; Anselmo, A.M. Fungal Biodegradation and Detoxification of Cork Boiling Wastewaters. *Eng. Life Sci.* **2004**, *4*, 144–149. [\[CrossRef\]](#)
12. Marques, I.P.; Gil, L.; La Cara, F. Energetic and Biochemical Valorization of Cork Boiling Wastewater by Anaerobic Digestion. *Biotechnol. Biofuels* **2014**, *7*, 1–11. [\[CrossRef\]](#)
13. Ponce-Robles, L.; Polo-López, M.I.; Oller, I.; Garrido-Cardenas, J.A.; Malato, S. Practical Approach to the Evaluation of Industrial Wastewater Treatment by the Application of Advanced Microbiological Techniques. *Ecotoxicol. Environ. Saf.* **2018**, *166*, 123–131. [\[CrossRef\]](#)
14. Ponce-Robles, L.; Oller, I.; Polo-López, M.I.; Rivas-Ibáñez, G.; Malato, S. Microbiological Evaluation of Combined Advanced Chemical-Biological Oxidation Technologies for the Treatment of Cork Boiling Wastewater. *Sci. Total Environ.* **2019**, *687*, 567–576. [\[CrossRef\]](#)
15. Vilar, V.J.P.; Maldonado, M.I.; Oller, I.; Malato, S.; Boaventura, R.A.R. Solar Treatment of Cork Boiling and Bleaching Wastewaters in a Pilot Plant. *Water Res.* **2009**, *43*, 4050–4062. [\[CrossRef\]](#)
16. Pintor, A.M.A.; Vilar, V.J.P.; Boaventura, R.A.R. Decontamination of Cork Wastewaters by Solar-Photo-Fenton Process Using Cork Bleaching Wastewater as H_2O_2 Source. *Sol. Energy* **2011**, *85*, 579–587. [\[CrossRef\]](#)
17. Papoutsakis, S.; Pulgarin, C.; Oller, I.; Sánchez-Moreno, R.; Malato, S. Enhancement of the Fenton and Photo-Fenton Processes by Components Found in Wastewater from the Industrial Processing of Natural Products: The Possibilities of Cork Boiling Wastewater Reuse. *Chem. Eng. J.* **2016**, *304*, 890–896. [\[CrossRef\]](#)

18. Fernandes, A.; Santos, D.; Pacheco, M.J.; Ciriaco, L.; Simões, R.; Gomes, A.C.; Lopes, A. Electrochemical Treatment of Cork Boiling Wastewater with a Boron-Doped Diamond Anode. *Environ. Technol.* **2015**, *36*, 26–35. [\[CrossRef\]](#)
19. Garcia-Costa, A.L.; Carbajo, J.; Quintanilla, A.; Yuste-Córdoba, F.J.; Casas, J.A. Treatment of Cork Boiling Wastewater by Thermal Wet Oxidation Processes. *Sep. Purif. Technol.* **2022**, *280*, 119806. [\[CrossRef\]](#)
20. Garcia-Costa, A.L.; Carbajo, J.; Masip, R.; Quintanilla, A.; Yuste-Córdoba, F.J.; Casas, J.A. Enhanced Cork-Boiling Wastewater Treatment by Electro-Assisted Processes. *Sep. Purif. Technol.* **2020**, *241*, 116748. [\[CrossRef\]](#)
21. Teixeira, A.R.S.; Santos, J.L.C.; Crespo, J.G. Sustainable Membrane-Based Process for Valorisation of Cork Boiling Wastewaters. *Sep. Purif. Technol.* **2009**, *66*, 35–44. [\[CrossRef\]](#)
22. Oliveira, J.; Nunes, M.; Santos, P.; Cantinho, P.; Minhalma, M. Cork Processing Wastewater Treatment/Valorisation by Nanofiltration. *Desalin. Water Treat.* **2009**, *11*, 224–228. [\[CrossRef\]](#)
23. Bernardo, M.; Santos, A.; Cantinho, P.; Minhalma, M. Cork Industry Wastewater Partition by Ultra/Nanofiltration: A Biodegradation and Valorisation Study. *Water Res.* **2011**, *45*, 904–912. [\[CrossRef\]](#)
24. Muddemann, T.; Neuber, R.; Haupt, D.; Graßl, T.; Issa, M.; Bienen, F.; Enstrup, M.; Möller, J.; Matthée, T.; Sievers, M.; et al. Improving the Treatment Efficiency and Lowering the Operating Costs of Electrochemical Advanced Oxidation Processes. *Processes* **2021**, *9*, 1482. [\[CrossRef\]](#)
25. Cui, H.; Huang, X.; Yu, Z.; Chen, P.; Cao, X. Application Progress of Enhanced Coagulation in Water Treatment. *RSC Adv.* **2020**, *10*, 20231–20244. [\[CrossRef\]](#)
26. Moussa, D.T.; El-Naas, M.H.; Nasser, M.; Al-Marri, M.J. A Comprehensive Review of Electrocoagulation for Water Treatment: Potentials and Challenges. *J. Environ. Manag.* **2017**, *186*, 24–41. [\[CrossRef\]](#)
27. Garcia-Segura, S.; Nienhauser, A.B.; Fajardo, A.S.; Bansal, R.; Conrad, C.L.; Fortner, J.D.; Marcos-Hernández, M.; Rogers, T.; Villagran, D.; Wong, M.S.; et al. Disparities between Experimental and Environmental Conditions: Research Steps toward Making Electrochemical Water Treatment a Reality. *Curr. Opin. Electrochem.* **2020**, *22*, 9–16. [\[CrossRef\]](#)
28. Panhwar, A.A.; Kandhro, A.; Qaisar, S.; Gorar, M.; Sargani, E.; Khan, H. Chemical Coagulation: An Effective Treatment Technique for Industrial Wastewater. *Turk. J. Agric. Eng. Res.* **2021**, *2*, 508–516. [\[CrossRef\]](#)
29. Ghernaout, D.; Elboughdiri, N.; Ghareba, S.; Salih, A. Coagulation Process for Removing Algae and Algal Organic Matter—An Overview. *Open Access Libr. J.* **2020**, *7*, 1–21. [\[CrossRef\]](#)
30. Shehzad, F.; Hussein, I.A.; Kamal, M.S.; Ahmad, W.; Sultan, A.S.; Nasser, M.S. Polymeric Surfactants and Emerging Alternatives Used in the Demulsification of Produced Water: A Review. *Polym. Rev.* **2018**, *58*, 63–101. [\[CrossRef\]](#)
31. Tadros, T.F. Prevention of Formation of Dilatant Sediments in Suspension Concentrates. *Colloids Surf.* **1986**, *18*, 427–438. [\[CrossRef\]](#)
32. Bratby, J. *Coagulation and Flocculation in Water and Wastewater Treatment*, 3rd ed.; IWA Publishing: London, UK, 2016; ISBN 1780407491.
33. Shahedi, A.; Darban, A.K.; Taghipour, F.; Jamshidi-Zanjani, A. A Review on Industrial Wastewater Treatment via Electrocoagulation Processes. *Curr. Opin. Electrochem.* **2020**, *22*, 154–169. [\[CrossRef\]](#)
34. Crini, G.; Lichtfouse, E. Advantages and Disadvantages of Techniques Used for Wastewater Treatment. *Environ. Chem. Lett.* **2019**, *17*, 145–155. [\[CrossRef\]](#)
35. Islam, S.M.D.U. Electrocoagulation (EC) Technology for Wastewater Treatment and Pollutants Removal. *Sustain. Water Resour. Manag.* **2019**, *5*, 359–380. [\[CrossRef\]](#)
36. Martínez-Huitle, C.A.; Rodrigo, M.A.; Scialdone, O. (Eds.) *Electrochemical Water and Wastewater Treatment*, 1st ed.; Elsevier: Amsterdam, The Netherlands, 2018; ISBN 9780128131602.
37. Ingelsson, M.; Yasri, N.; Roberts, E.P.L. Electrode Passivation, Faradaic Efficiency, and Performance Enhancement Strategies in Electrocoagulation—A Review. *Water Res.* **2020**, *187*, 116433. [\[CrossRef\]](#)
38. Hakizimana, J.N.; Gourich, B.; Chafi, M.; Stiriba, Y.; Vial, C.; Drogui, P.; Naja, J. Electrocoagulation Process in Water Treatment: A Review of Electrocoagulation Modeling Approaches. *Desalination* **2017**, *404*, 1–21. [\[CrossRef\]](#)
39. Barrera-Díaz, C.E.; Frontana-Urbe, B.A.; Roa-Morales, G.; Bilyeu, B.W. Reduction of Pollutants and Disinfection of Industrial Wastewater by an Integrated System of Copper Electrocoagulation and Electrochemically Generated Hydrogen Peroxide. *J. Environ. Sci. Health Part A Toxic/Hazard. Subst. Environ. Eng.* **2015**, *50*, 406–413. [\[CrossRef\]](#) [\[PubMed\]](#)
40. Lakshmanan, D.; Clifford, D.A.; Samanta, G. Ferrous and Ferric Ion Generation during Iron Electrocoagulation. *Environ. Sci. Technol.* **2009**, *43*, 3853–3859. [\[CrossRef\]](#)
41. Yasri, N.; Hu, J.; Kibria, M.G.; Roberts, E.P.L. Electrocoagulation Separation Processes. In *Multidisciplinary Advances in Efficient Separation Processes*; American Chemical Society: Washington, DC, USA, 2020; pp. 167–203. [\[CrossRef\]](#)
42. Sahu, O.; Mazumdar, B.; Chaudhari, P.K. Treatment of Wastewater by Electrocoagulation: A Review. *Environ. Sci. Pollut. Res.* **2014**, *21*, 2397–2413. [\[CrossRef\]](#)
43. Baird, R.; Eaton, A.; Rice, E. (Eds.) *Standard Methods for the Examination of Water and Wastewater*, 23rd ed.; American Public Health Association: Washington, DC, USA; American Water Works Association: Denver, CO, USA; Water Environment Federation: Alexandria, VA, USA, 2017; ISBN 9781625762405.
44. Precious Sibiya, N.; Rathilal, S.; Kweinor Tetteh, E. Coagulation Treatment of Wastewater: Kinetics and Natural Coagulant Evaluation. *Molecules* **2021**, *26*, 698. [\[CrossRef\]](#)
45. Tetteh, E.K.; Rathilal, S. Application of Magnetized Nanomaterial for Textile Effluent Remediation Using Response Surface Methodology. *Mater. Today Proc.* **2021**, *38*, 700–711. [\[CrossRef\]](#)

46. Sun, Y.; Zhou, S.; Chiang, P.-C.; Shah, K.J. Evaluation and Optimization of Enhanced Coagulation Process: Water and Energy Nexus. *Water-Energy Nexus* **2019**, *2*, 25–36. [\[CrossRef\]](#)
47. Beltrán de Heredia, J.; Domínguez, J.R.; López, R. Treatment of Cork Process Wastewater by a Successive Chemical–Physical Method. *J. Agric. Food Chem.* **2004**, *52*, 4501–4507. [\[CrossRef\]](#)
48. Brillas, E.; Martínez-Huitle, C.A. Decontamination of Wastewaters Containing Synthetic Organic Dyes by Electrochemical Methods. An Updated Review. *Appl. Catal. B Environ.* **2015**, *166–167*, 603–643. [\[CrossRef\]](#)
49. Den, W.; Wang, C.-J. Removal of Silica from Brackish Water by Electrocoagulation Pretreatment to Prevent Fouling of Reverse Osmosis Membranes. *Sep. Purif. Technol.* **2008**, *59*, 318–325. [\[CrossRef\]](#)
50. Bagga, A.; Chellam, S.; Clifford, D.A. Evaluation of Iron Chemical Coagulation and Electrocoagulation Pretreatment for Surface Water Microfiltration. *J. Membr. Sci.* **2008**, *309*, 82–93. [\[CrossRef\]](#)
51. Gu, Z.; Liao, Z.; Schulz, M.; Davis, J.R.; Baygents, J.C.; Farrell, J. Estimating Dosing Rates and Energy Consumption for Electrocoagulation Using Iron and Aluminum Electrodes. *Ind. Eng. Chem. Res.* **2009**, *48*, 3112–3117. [\[CrossRef\]](#)
52. Wan, S.; Chen, H.; Ma, X.; Chen, L.; Lei, K.; Liao, B.; Dong, Z.; Guo, X. Anticorrosive Reinforcement of Waterborne Epoxy Coating on Q235 Steel Using NZ/BNNS Nanocomposites. *Prog. Org. Coat.* **2021**, *159*, 106410. [\[CrossRef\]](#)
53. Kang, L.; Shi, L.; Zeng, Q.; Liao, B.; Wang, B.; Guo, X. Melamine Resin-Coated Lignocellulose Fibers with Robust Superhydrophobicity for Highly Effective Oil/Water Separation. *Sep. Purif. Technol.* **2021**, *279*, 119737. [\[CrossRef\]](#)
54. Padash, R.; Sajadi, G.S.; Jafari, A.H.; Jamalizadeh, E.; Rad, A.S. Corrosion Control of Aluminum in the Solutions of NaCl, HCl and NaOH Using 2,6-Dimethylpyridine Inhibitor: Experimental and DFT Insights. *Mater. Chem. Phys.* **2020**, *244*, 122681. [\[CrossRef\]](#)
55. Soltis, J. Passivity Breakdown, Pit Initiation and Propagation of Pits in Metallic Materials—Review. *Corros. Sci.* **2015**, *90*, 5–22. [\[CrossRef\]](#)
56. Hossain, N.; Chowdhury, M.A.; Iqbal, A.K.M.P.; Ahmed, A.K.M.F.; Islam, M.S. Corrosion Behavior of Aluminum Alloy in NaOH and Syzygium Samarangense Solution for Environmental Sustainability. *Curr. Res. Green Sustain. Chem.* **2022**, *5*, 100254. [\[CrossRef\]](#)
57. Mouedhen, G.; Feki, M.; Wery, M.D.P.; Ayedi, H.F. Behavior of Aluminum Electrodes in Electrocoagulation Process. *J. Hazard. Mater.* **2008**, *150*, 124–135. [\[CrossRef\]](#) [\[PubMed\]](#)