



Article Anodic Oxidation of Industrial Winery Wastewater Using Different Anodes

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Abstract: Winery wastewater represents the largest waste stream in the wine industry. This deals with the mineralization of the organic matter present in winery wastewater using anodic oxidation and two types of anodes—namely, a boron-doped diamond electrode (BDD) and two mixed metal oxides (MMO), one with the nominal composition $Ti/Ru_{0.3}Ti_{0.7}O_2$ and the other with $Ti/Ir_{0.45}Ta_{0.55}O_2$. To conduct the study, the variability of different quality parameters for winery wastewater from the Chilean industry was measured during eight months. A composite sample was treated using anodic oxidation without the addition of supporting electrolyte, and the experiments were conducted at the natural pH of the industrial wastewater. The results show that this effluent has a high content of organic matter (up to 3025 ± 19 mg/L of total organic carbon (TOC)), which depends on the time of the year and the level of wine production. With MMO electrodes, TOC decreased by 2.52% on average after 540 min, which may be attributed to the presence of intermediate species that could not be mineralized. However, when using a BDD electrode, 85% mineralization was achieved due to the higher generation of hydroxyl radicals. The electrolyzed sample contained oxamic, acetic, and propionic acid as well as different ions such as sulfate, chloride, nitrate, and phosphate. These ions can contribute to the formation of different species such as active species of chlorine, persulfate, and perphosphate, which can improve the oxidative power of the system.

Keywords: winery wastewater; anodic oxidation; BDD and MMO electrodes; hydroxyl radicals; ions

1. Introduction

Winery wastewater is mainly the result of a series of activities such as the cleaning of barrels and tanks, washing of transfer lines and floors, wine loss and extraction, and processes in filtration units and water drains from the wastewater management system [1–3]. Therefore, depending on factors that range from the size of the facility to production and cleaning methods, between one and four liters of residual water are generated per liter of wine produced [4,5].

In general, this industrial effluent has a high organic load that may lead to contamination if not treated correctly [6]. In addition, winery wastewater has a high concentration of suspended solids, low content of nutrients, and recalcitrant high molecular weight compounds such as polyphenols, fertilizers, and pesticides [7–10]. These compounds are not easily removed by the biological processes normally used to treat this type of wastewater, which makes it difficult to achieve a high removal of organic matter [11,12]. In order to efficiently eliminate these compounds, some authors have used advanced oxidation processes (AOPs) in which highly reactive oxygen species are generated in situ [7,13]. AOPs



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Copyright: © 2022 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/). based on electrochemical technology, known as electrochemical advanced oxidation processes (EAOPs), are a powerful tool for effectively removing organic matter from industrial wastewater [14].

EAOPs are environmentally friendly due to their low reagent requirements. Furthermore, they have high energy efficiency and low operating costs, provide rapid kinetics in the decomposition of different pollutants, and are safe under working conditions [15–18]. Among EAOPs, one of the most widely proposed and used has been anodic oxidation (AO) [14,19–23] due to its versatility, simplicity, and easy scalability [24]. According to Espinoza, et al. [25], this process can be implemented alone or as a pre- or post-treatment for other physicochemical and biological processes. In this way, it is possible to increase the electrode yield, reduce energy demand, and decrease water toxicity. In the AO process, the oxidation of organic contaminants can occur directly or indirectly depending on the nature of the anode [21,26]. In this sense, Comninellis and Chen [27] define two types of anode surfaces: (i) active and (ii) non-active. In both cases, the electrochemical discharge of water occurs on the surface of the anode (M), generating hydroxyl radicals ($^{\circ}$ OH, E $^{\circ}$ = 2.80 V/SHE) that remain physisorbed on the surface of the anode (reaction (1)). Nevertheless, active anodes have low overpotential for oxygen evolution and high adsorption enthalpies; therefore, the *OH formed can strongly interact with the anode surface, forming metal oxides (MO) or higher state superoxide by means of reaction (2). Subsequently, the redox couple (MO/M) acts as a mediator in the partial oxidation of organic pollutants (R), regenerating the metallic surface M by reaction (3). On the contrary, non-active anodes are characterized by high overpotentials for oxygen evolution and low adsorption enthalpies, which leads to •OH weakly adhering to the anode surface. In this case, [•]OH reacts with the organic compounds until their complete mineralization to carbon dioxide (CO_2), water (H_2O), and inorganic ions (reaction (4)).

$$M + H_2O \to M(^{\bullet}OH) + H^+ + e^-$$
(1)

$$M(^{\bullet}OH) \rightarrow MO + H^{+} + e^{-}$$
⁽²⁾

$$MO + R \rightarrow RO + M$$
 (3)

$$aM(^{\bullet}OH) + R \rightarrow aM + mCO_2 + nH_2O + xH^+ + ye^-$$
(4)

Among active anodes, mixed metal oxides (MMO) stand out. These anodes are based on mixed metal oxides of ruthenium (Ru), titanium (Ti), tantalum (Ta), antimony (Sb), or tin (Sn) in different proportions and supported on a Ti sheet [15,19]. They exhibit high stability, activity, excellent durability, and are easy to scale for industrial purposes [20,26,28]. In contrast, boron-doped diamond (BDD) thin-film electrodes are considered non-active anodes. These anodes have high corrosion stability and therefore can be used in strongly acidic environments. In addition, the weak interaction between [•]OH and its surface, together with its high overpotential for oxygen evolution, is favorable for the generation of greater amounts of M([•]OH) with the capacity to mineralize persistent organic compounds in water [17,29,30].

It is known that the AO process does not present restrictions in terms of pH [18] and that it is not easily influenced by temperature [31]. However, in many cases, the addition of a supporting electrolyte is required [32] to improve the conductivity of the solution and contribute to reducing the cost of energy. In this sense, several types of industrial wastewater contain sulfates, chlorides, phosphates, and oxygen, which contribute to the formation of oxidants such as persulfate ($S_2O_8^{2-}$), active chlorine species (Cl₂, HClO, ClO⁻), perphosphate ($P_2O_8^{4-}$), and hydrogen peroxide (H_2O_2), respectively [31]. This indicates that the use of agents present in the solution to be treated could be sufficient to improve conductivity and promote the generation of oxidizing species, simplifying the AO process by not having to add salts, which can also make the process more expensive.

There is a limited number of reports that have compared the efficiency of different electrocatalytic materials during the AO process in different electrolytic media [21,33–36].

Nevertheless, there are no studies in which the efficiency of different electrocatalytic materials is compared in the AO of real winery water and without the addition of supporting electrolytes. Therefore, the objective of this work is to study the electrochemical mineralization of a sample composed of real winery wastewater containing $1349 \pm 25.24 \text{ mg/L}$ of total organic carbon (TOC) under electrolysis at constant current density without the addition of a supporting electrolyte and using three anodic materials (BDD, MMO-Cl₂, and MMO-O₂). Moreover, the winery wastewater of a Chilean industry was monitored in order to find a representative sample to conduct the electrochemical experiments. Degradation of the organic compounds present in the wastewater was followed by spectrophotometric (decrease in maximum absorbance, turbidity) and chromatographic techniques (decay of specific pollutants present in the wastewater), while mineralization was measured through TOC decay. This study contributes with the application of AO for the treatment of real industrial wastewater, making the process simpler and more competitive, as it would not be necessary to adjust pH or add a supporting electrolyte.

2. Materials and Methods

2.1. Winery Wastewater

Winery wastewater was obtained between April and November 2018 from a Chilean wine industry located in Santiago de Chile. This period includes the vintage and the non-vintage stages; therefore, it allows studying the behavior of the industry and its wastewater under different real parameters (high and low polluting loads). The 22 samples were collected before the aerobic biological process in the industrial wastewater treatment plant and refrigerated at 4 °C for further characterization.

To carry out the electrochemical experiments, a composite sample made from the samples collected during October and November was employed. The results of the characterization of the composite sample (used in the electrochemical treatment) are shown in Table 1. In general, the sample shows a high content of organic matter, low concentrations of nitrogen and phosphorus compounds, low pH, and an unpleasant odor. In addition, it should be noted that although the initial turbidity of the sample was 321 ± 0.20 NTU, this parameter was reduced by approximately 96% after centrifuging the sample.

Parameters	Results			
Color	Light red			
Odor	Intense			
pН	4.28 ± 0.16			
Conductivity (mS)	2.60 ± 0.04 (T = 25.80 °C)			
Turbidity (NTU)	12.30 ± 1.50			
Total organic carbon (mg/L)	1349 ± 25.24			
Soluble chemical oxygen demand (mg/L)	4140 ± 28.28			
Biochemical oxygen demand (mg/L)	2678 ± 20.16			
Absorbance at 254 nm (U.A)	0.65 ± 0.01			
Nitrate (mg NO_3^-/L)	0.40 ± 0.05			
Phosphate (mg PO_4^{3-}/L)	24 ± 2.46			
Chloride (mg Cl^{-}/L)	364 ± 1.73			
Sulfate (mg SO_4^{2-}/L)	142 ± 2.92			
Acetic acid (mg/L)	2463 ± 69.64			
Propionic acid (mg/L)	356 ± 22.24			
Fecal Coliforms Lecture (NMP/100 mL)	$> 1.60 imes 10^4$			

Table 1. Parameters of composite sample.

2.2. Experimental Procedure

Winery wastewater was treated through the AO process without the addition of salts as a supporting electrolyte at the original pH value and at room temperature. Electrolysis was performed in an undivided 0.10 L open cell by vigorously stirring in order to ensure mass transfer (Figure 1). Three different electrodes were used as anodes: (1) a boron-doped diamond (BDD) electrode supplied by Adamant Technologies, which had a 2.75-thick diamond layer doped with a concentration of 500 ppm of boron, (2) a mixed metal oxide (MMO-Cl₂ type: nominal composition Ti/Ru_{0.3}Ti_{0.7}O₂), and (3) a mixed metal oxide (MMO-O₂ type: nominal composition Ti/Ir_{0.45}Ta_{0.55}O₂) both from NMT Electrodes PTY LTD (Pinetown, South Africa). A stainless-steel plate (AISI 304) was used as the cathode for each electrolysis. The electrodes had a geometric area of 5 cm², with an inter-electrode gap of 1 cm. All the experiments were performed twice applying a current density of 30 mA/cm². To remove impurities from the surfaces of the cathode and anode, the electrodes were previously polarized in a 0.50 M of H₂SO₄ solution at 50 mA/cm² for 40 min.



Figure 1. Electrochemical system.

2.3. Apparatus and Analytical Procedures

The winery wastewater samples were centrifuged in order to reduce the solids in suspension. Electrolyses were performed using an MCP model M10-QD305 power supply, which provides the constant current to conduct electrolysis in galvanostatic mode and to deliver a potential difference between anode and cathode. During electrolysis, samples were always withdrawn from the same solution kept in the cell at regular time intervals and then refrigerated at 4 °C until analysis. The degradation of the organic compounds present in the wastewater was followed by spectrophotometric techniques, and mineralization was studied through TOC removal. This parameter was obtained using a Shimadzu model TOC-L analyzer.

Soluble chemical oxygen demand (sCOD) was measured using reactive HANNA COD tube tests HI 93754B-25 (range 0–1500 mg/L). The samples were chemically digested for 2 h at 150 ± 1 °C in a HANNA Instruments HI 839800 digestor and analyzed in a photometer HANNA Instruments HI 83214.

Total suspended solids (TSS), volatile suspended solids (VSS), and alkalinity were also measured according to the Standard Methods for the Examination of Water and Wastewater [37], as well as the 5-day biochemical oxygen demand (BOD₅), for which a dissolved oxygen meter analyzer Milwaukee, MW 600 model, was employed.

Absorbance decay at 254 nm was monitored in an Agilent model 8453 spectrophotometer. Water turbidity expressed as NTU (nephelometric units of turbidity) was measured using an HI 98703 Turbidimeter. A Lutron model pH-222 pH-meter was used to calculate pH. Conductivity was measured using a HANNA Instruments HI 98312 Multiparameter Meter. The presence of fecal coliforms was quantified through the NMP procedure and using the A-1 method [38].

Carboxylic acids were identified and quantified by ion exclusion chromatography. Aliquots were analyzed on a Shimadzu LC-20AD UFLC with a Shimadzu SPD-M20A diode array detector, which was equipped with a BIO-RAD Aminex HPX-87H 300 mm \times 7.8 mm

(i.d) ion exclusion column. The wavelength was set at 210 nm, and 4 mM H_2SO_4 was used as a mobile phase with a flow of 0.60 mL/min at 35 °C.

Inorganic ions (Cl⁻, PO₄³⁻, SO₄²⁻, NO₃⁻) were determined by ion chromatography using a 930 Compact IC Flex-Metrohm after filtering the samples through 0.22 μ m MLC disposable syringe filter. A Metrosep A Supp 5-250/4.0 column was used with 3.20 mM of sodium carbonate as eluent in a flow of 0.70 mL/min. The total ammonia nitrogen content, expressed as mg N-NH₄⁺/L, was quantified using a QuikChem 8500 Series 2 FIA system.

In order to compare the experimental data, *t*-test Two Sample Assuming Equal Variances were carried out using Excel 2110.

3. Results and Discussion

3.1. Characterization of Real Winery Wastewater in a Long Period

Figure 2 shows the results of the characterization obtained during the months of monitoring in terms of organic matter (sCOD, BOD₅, and TOC) and solids. sCOD, BOD₅, and TOC show the high content of organic matter that is typical for this type of wastewater [39]. The BOD₅/sCOD ratio for winery wastewater was in the order of 0.54 to 0.73. This result demonstrates the high biodegradability of these waters and agrees with other values reported in the literature [40,41].



Figure 2. Characterization of winery wastewater during eight months of monitoring, (**a**) content of organic matter (\blacksquare) sCOD, (•) BOD₅, (**a**) TOC, polynomial fit; (**b**) concentration of solids (\blacksquare) TSS, (\circledast) VSS, (X) VSS/TSS ratio. Specification: the values of the parameters correspond to the average value of the parameter according to the samples collected in each month.

Figure 2a shows that the highest sCOD, BOD₅, and TOC concentrations were obtained between April and June (Months 1–3), with values as high as $7863 \pm 50 \text{ mg/L}$ in the case of sCOD, $5720 \pm 11 \text{ mg/L}$ for BOD₅, and $2405 \pm 19 \text{ mg/L}$ in the case of TOC. Subsequently, the values of sCOD, BOD₅, and TOC decreased by approximately 4361 mg/L, 2649 mg/L, and 1574 mg/L, on average, respectively. This indicates that during and immediately after vintage, wastewater contains the highest concentration of organic matter. However, it should be noted that sometimes, a slight increase in organic load may occur sporadically (as in the sample collected in August (Month 5)). According to [42], this is related to the pressing and refiltration of newly fermented wine.

Regarding the presence of solids in wastewater, the situation was different (Figure 2b). Solids concentration did not show a special high value around vintage. Indeed, the average values of TSS and VSS were 827 mg/L and 602 mg/L, respectively, between April and June (Months 1–3), while between July and November (Months 4–8), the average values of TSS and VSS were 1319 mg/L and 744 mg/L. The highest solid concentration was observed in

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September (1998 \pm 0.05 mg/L, month 6), during the non-vintage period, with a VSS/TSS ratio equal to 0.59.

According to these analyses, winery wastewater presents variable concentrations of sCOD between 3560 ± 94 and 7863 ± 50 mg/L, as well as TOC (957 ± 20 and 2405 ± 19 mg/L), and a high content of easily biodegradable organic matter (BDO₅ between 1760 ± 2 and 5720 ± 11 mg/L). In addition, regarding the concentration of solids, it is noteworthy that the samples were collected after three physical filtration units that reduced most of the suspended solids.

These results demonstrate the seasonality of this type of wastewater, which is directly related to the period of work (vintage or non-vintage period) and the type of wine produced (red, white, sparkling, special wines, etc.) [39]. In this sense, wastewater generated during vintage has a higher flow rate and organic content than the water produced during the rest of the year [4,43]. Regarding the type of wine, Montalvo, et al. [44] found that wastewater from the production of red wine usually contains ethanol, carbohydrates, organic acids, and polyphenols, while wastewater from tropical fruits wine has a high sugar content and sulfur compounds. Likewise, Braz, et al. [45] studied the characterization of winery wastewater from two Portuguese wineries and found that wastewaters from the production of red wine different and suspended solids than wastewaters from the production of white wine. As it may be seen, this variability causes significant fluctuations in the quantity and quality of this effluent. Therefore, several authors currently propose EAPOs to treat winery wastewater [8,14,40].

Table 2 shows the behavior of other wastewater parameters measured over time. The samples presented color differences, which is related to the type of wine produced and mostly due to the natural colors of grapes [12]. In this sense, the spectrum exhibited a band at 254 nm, which might correspond to different organic compounds that absorb in this wavelength region. Candia-Onfray, et al. [14] observed a characteristic band at 280 nm, which they associated mainly with the presence of polyphenols but also with other organic compounds such as acetic acid, butyl ester, ethylbenzene, cyclohexanol, ethanol, and isopropyl stearate, among others.

Parameters	April	May	Jun	July	August	September	October	November
Color	Light red	Orange	Yellow	Orange	Brown	Brown	Brown	Brown
Odor	Intense	Intense	Intense	Intense	Intense	Intense	Intense	Intense
pН	6.30	9.30	6.95	9.23	9.38	8.10	8.42	11.34
Total alkalinity (mg CaCO ₃ /L)	493	1534	817	2257	1091	998	468	2309
Partial alkalinity (mg CaCO ₃ /L)	240	934	501	1619	715	583	319	1887
Turbidity (NTU)	234	463	500	286	555	821	317	782
Absorbance at 254 nm (U.A)	1.20	2	0.79	1.39	0.76	0.60	1.31	0.87
Conductivity (mS)	1.98	4.16	2.95	4	3.21	3.54	3.24	2.38
Total ammonia nitrogen (mg N-NH4 ⁺ /L)	1.02	3.94	1.09	1.20	0.63	2.41	3.07	1.57
Nitrate (mg NO_3^-/L)	4.20	3.01	2.08	6	1.47	3.93	4.33	2
Phosphate (mg PO ₄ ³⁻ /L)	15.60	20.54	14.73	27.73	27.20	27.60	27.08	26.42
Chloride (mg Cl ⁻ /L)	350	919	388	832	1020	968	927	861
Fecal Coliforms Lecture NMP/100 mL	$\geq 1.60 \times 10^3$	$>6 \times 10^4$	$>9 \times 10^3$	$7 imes 10^4$	$2.90 imes 10^4$	$1.05 imes 10^5$	$4 imes 10^4$	$1.60 imes 10^5$

Table 2. Parameters monitored in winery wastewater over time.

Specification: the values of the parameters correspond to the average value of the parameter according to the samples collected in each month.

Winery wastewater also presented a strong smell attributed to the production process and the presence of fecal coliforms ($\geq 1.60 \times 10^3$ NMP/100 mL). These microorganisms may originate from dirty grapes and water used for floor cleaning.

The concentrations of $CaCO_3$ varied between 468 and 2309 mg/L, displaying the highest values in May, July, and November. The values obtained for pH are within the

established range for this type of effluent [39], with the lowest values during vintage. Conversely, the highest values are reported during the non-vintage period, which is related to cleanings carried out with sodium hydroxide (NaOH). These results are in accordance with those obtained by Milani, et al. [46] in Italian wineries.

Turbidity showed values between 234 and 821 NTU. This parameter is associated with the presence of suspended and dissolved particles [14]. In this sense, the turbidity values obtained are consistent with the concentration of suspended solids, where the higher concentration of TSS (1998 \pm 0.05 mg/L) is related to higher turbidity (821 NTU).

The conductivity values were associated with the presence of NH_4^+ , NO_3^- , SO_4^{2-} , PO_4^{3-} , Cl^- , and other elements in wastewater. Table 2 shows that all the samples contain high concentrations of chloride, but it is evident that this type of water presents a deficit of nutrients (especially nitrate), which is consistent with other studies [47].

3.2. Anodic Oxidation of Winery Wastewater

Several electrolyses were performed to treat 0.10 L of winery wastewater containing 1349 \pm 25.24 mg/L of TOC using an open cell with constant agitation. In order to study the effect of the anode material on the degradation of the organic pollutants present in the wastewater, three electrodes were used in different experiments, namely MMO-Cl₂, MMO-O₂, and BDD. All the tests were carried out at room temperature, with an initial pH of 4.28 \pm 0.16, without the addition of electrolyte support and applying a current density of 30 mA/cm². Each electrolysis took 540 min (min.).

Figure 3 shows that when MMO electrodes were used as anodes, only a degradation of organic matter of 1.70% and 3.34% was achieved for MMO-Cl₂ and MMO-O₂, respectively. Similar results were obtained by Ribeiro, et al. [35]. The researchers used the MMO-Cl₂ and MMO-O₂ electrodes as anodes to study the electrochemical degradation of 50 mg/L of the Ponceau 2R dye with NaClO₄ as a supporting electrolyte at different values of current density and at room temperature. The results obtained showed that organic matter fails to be removed when applying 25 mA/cm². Furthermore, it is only possible to reduce TOC up to 7% and 11% in the case of the MMO-O₂ and MMO-Cl₂ anodes, respectively, when 200 mA/cm² is applied. This poor decrease in TOC was attributed to the formation of intermediates and the catalytic effect on the oxygen evolution reaction, which leads to the lower efficiency of these electrodes.



Figure 3. Mineralization by TOC decay of winery wastewater during electrolysis without the addition of electrolyte support at 25 °C and pH 4.28 applying 30 mA/cm². (\blacksquare) MMO-Cl₂, (\triangle) MMO-O₂, (\bullet) BDD. Samples tested: 11.

Conversely, when working with the BDD electrode, 85% of the organic matter is removed without the addition of a supporting electrolyte. This may be because, since BDD is a non-active anode, the weak interaction of BDD - $^{\circ}$ OH, together with its high overpotential for oxygen evolution, generates higher amounts of reactive physisorbed BDD($^{\circ}$ OH) radicals that mineralize more effectively the contaminants present in the water [22,34]. Another key factor in this result may also be the formation of active chlorine species (Cl₂, HClO, ClO⁻) that can oxidize organic contaminants [15,24]. These species can be generated from the direct oxidation of the chloride ion on the anode surface to soluble chlorine (Cl_{2aq}) (reaction (5)) [14,24,32]. According to Brillas and Martínez-Huitle [15], if the local concentration of dissolved chlorine exceeds its solubility, supersaturation propels the generation of bubbles of chlorine gas. The electrogenerated Cl₂ can react with the chloride ion to form the trichloride ion (reaction (6)) or can be hydrolyzed to allow for the formation of hypochlorous acid (HClO) (reaction (7)), being in equilibrium with the hypochlorite ion (ClO⁻) in the bulk solution (reaction (8)).

$$2\mathrm{Cl}^- \to \mathrm{Cl}_{2(\mathrm{aq})} + 2\mathrm{e}^- \tag{5}$$

$$\operatorname{Cl}_{2(\operatorname{aq})} + \operatorname{Cl}^{-} \rightleftharpoons \operatorname{Cl}_{3}^{-}$$
 (6)

$$Cl_{2(aq)} + H_2O \rightleftharpoons HClO + H^+ + Cl^-$$
(7)

$$HClO \rightleftharpoons ClO^{-} + H^{+} \tag{8}$$

Figure 4a shows the variation of maximum absorbance over time, which was measured at 254 nm. The absorbance decay of the solution is dependent on the anode material used. In addition, absorbance decay reaches 60% and 65% with the MMO-Cl₂ and MMO- O_2 electrodes, respectively. This indicates a decrease in compounds that absorb at that wavelength, for example, polyphenols. In the case of BDD, an increase in maximum absorbance is observed during the first 180 min. This increase could have been caused by the formation of reaction intermediates. However, at the end of the process, an 85% decrease in absorbance is observed. This is a result of the higher generation of •OH when using a BDD electrode, which attacks the contaminants in the solution, causing a more pronounced decay than MMO electrodes. A similar trend to that obtained in this work when the BDD electrode is used was reported by Collivignarelli, et al. [48] in a study on the discoloration of a real effluent from the pharmaceutical industry.



Figure 4. (a) Evolution of normalized absorbance at 254 nm and (b) turbidity decay of winery wastewater during electrolysis without the addition of electrolyte support at 25 °C and pH 4.28 applying 30 mA/cm². (\blacksquare) MMO-Cl₂, (\triangle) MMO-O₂, (\bullet) BDD. Samples tested: 11.

Figure 4b shows a decrease in turbidity in all three cases. However, statistically significant differences were found in experiments using BDD as an anode compared to experiments employing MMO (value; p < 0.05). In this sense, values are better for BDD, in whose case turbidity is reduced to 5.03 NTU. This result agrees with that reported by Candia-Onfray, et al. [14], who only achieved complete elimination of turbidity when using a current density of 60 mA/cm². This indicates that increasing the density current promotes the hydrolysis of solids, which is possibly due to an increase in the amount of •OH generated. At this point, it is important to mention that when working with a higher density current, higher energy expenditure can occur; therefore, in this study, it was decided to work with 30 mA/cm² to maintain a balance between both factors.

Figure 5a shows the behavior of pH over time for each electrolysis. An increase in pH is expected in all cases due to the possible decrease in the concentration of protons in the medium as a result of the reduction of these on the stainless-steel cathode to produce H₂. In this context, when MMO anodes were used, a small increase in pH was observed, being 4.45 ± 0.16 and 4.36 ± 0.13 the final pH when working with MMO-Cl₂ and MMO-O₂, respectively. No statistically significant differences were found between experiments with MMO as anode (value-*p* > 0.05). However, in the case of BDD, pH increased to 8.15 ± 0.10 . In this case, statistically significant differences were found in the experiments with BDD as an anode compared to the experiments with MMO (value-*p* < 0.05). This may be related to the electrocatalytic effect on the evolution of chloride and the active chlorine species present in wastewater, i.e., BDD forms more •OH than the MMO electrodes, as it has a higher overpotential for oxygen evolution. These radicals react with the chlorides present in the medium and form chlorine oxides and active chlorine species, which increase pH. This result promotes a further expansion of wastewater treatment technologies because it would not be necessary to add any chemical compound to adjust pH.



Figure 5. (a) Evolution of pH and (b) conductivity of winery wastewater during electrolysis without the addition of electrolyte support at 25 °C and pH 4.28 applying 30 mA/cm². (\blacksquare) MMO-Cl₂, (\triangle) MMO-O₂, (\bullet) BDD. Samples tested: 11.

The variation in conductivity over time is shown in Figure 5b. In general, there was no significant changes in this parameter in any of the three cases. The lowest conductivity occurred when the BDD electrode was used; however, after two hours, conductivity increases until 2.86 \pm 0.02 mS. In the case of the MMO electrodes, statistically significant differences were found (value-*p* > 0.05). Conductivity varied between 2.60 \pm 0.04 and 2.57 \pm 0.01 mS (MMO-Cl₂) and 2.60 \pm 0.04 and 2.66 \pm 0.02 (MMO-O₂). These variations in conductivity are associated with the variation of the ions in the medium (as discussed in Section 3.3).

3.3. Evolution of Carboxylic Acids and Ions during Electrolysis

Figure 6 shows the changes in the concentration of carboxylic acids during electrolysis. Ion exclusion chromatography reveals the presence of oxamic ($r_t = 8.53 \text{ min}$), acetic ($r_t = 14.31 \text{ min}$), and propionic acid ($r_t = 17.65 \text{ min}$) in the electrolyzed samples. Oxamic acid is often one of the main intermediates of the degradation of N-aromatics by EAOPs [19,49]. Furthermore, it is one of the ultimate carboxylic acids, since it is directly oxidized to CO₂ [21,50,51]. Figure 6 shows that the oxamic acid concentration did not exceed 4.59 mg/L, being rapidly degraded when using MMO electrodes (Figure 6a,b). In this case, there are no statistically significant differences between the experiments where these electrodes are used as anodes (value-p > 0.05). However, statistically significant differences were found in the experiments with BDD as an anode compared to the experiments with MMO (value-p < 0.05).



Figure 6. Evolution of carboxylic acid during electrolysis without the addition of electrolyte support at 25 °C and pH 4.28 applying 30 mA/cm². (a) MMO-Cl₂, (b) MMO-O₂, and (c) BDD. The inset panels present the expansion of oxamic acid during each electrolysis: (\bigcirc) Oxamic, (\square) Acetic, (\blacklozenge) Propionic acids. Samples tested: 11.

Acetic acid is characteristic of winery wastewater [12,40]. Figure 6c shows that acetic acid is removed after 480 min only when using BDD as an anode. Conversely, with the MMO-Cl₂ and MMO-O₂ electrodes, the concentration of acetic acid increased by 27% and 3%, respectively (Figure 6a,b). Regarding the concentration of propionic acid, a variation was found between 239 ± 11.24 and 448 ± 8.36 mg/L. When using the BDD and MMO-O₂ electrodes, a mineralization percentage of 14% and 33% is obtained, respectively (Figure 6b,c). However, when using MMO-Cl₂, the concentration of propionic acid increased by 16% (Figure 6a). It should be noted that propionic acid is also part of the composition of winery wastewater [52]; however, this can be generated as an intermediate product of the action of •OH.

Both in the measurement of acetic and propionic acid, statistically significant differences were found in all experiments. The low mineralization of organic matter when working with MMO electrodes may be related to the presence of these acids that could not be mineralized.

Another important factor to consider in the mineralization process is the change in the concentration of inorganic ions. Figure 7 shows the variation of the concentration of the six ions detected by ion chromatography: chloride (Cl⁻), chlorate (ClO₃⁻), hypochlorite (ClO⁻), nitrate (NO₃⁻), phosphate (PO₄³⁻), and sulfate (SO₄²⁻).



Figure 7. Monitoring of ion concentration during each electrolysis without the addition of electrolyte support at 25 °C and pH 4.28 applying 30 mA/cm². (a) Chloride, (b) Chlorate, (c) Hypochlorite, (d) Nitrate, (e) Phosphate, (f) Sulfate. (\blacksquare) MMO-Cl₂, (\triangle) MMO-O₂, (\bullet) BDD. Samples tested: 11.

The concentration of the Cl⁻ ion decreased over time (Figure 7a), specifically from $364 \pm 1.73 \text{ mg/L}$ to 295 ± 0.51 , 194 ± 0.85 , and $283 \pm 0.68 \text{ mg/L}$ when using MMO-Cl₂, BDD, and MMO-O₂, respectively. This decrease is due to the continuous oxidation of the Cl⁻ ion on the anode, which produces active chlorine species [53].

Figure 7b shows that after 540 min, there is an increase of approximately 9.40 times in ClO_3^- ion concentration when the BDD electrode is used. In the case of the MMO electrodes, the generation of ClO_3^- ion was low, which is revealed by the low decrease in Cl^- .

The ClO_3^- ion can be formed by the chemical reaction between the ClO^- ion and the hypochlorous acid (HClO) (reaction (9)) or by direct oxidation of the ClO^- ion on the electrode without the action of the hydroxyl radicals (•OH) (reaction (10)).

$$ClO^{-} + 2HClO \rightarrow ClO_{3}^{-} + 2Cl^{-} + 2H^{+}$$
(9)

$$6ClO^{-} + 3H_2O \rightarrow 2ClO_3^{-} + 4Cl^{-} + 6H^{+} + 3/2O_2 + 6e^{-}$$
(10)

It is noteworthy that in this work, chlorite (ClO_2^-) was not observed in any case. According to Espinoza, et al. [19], this may be because ClO_2^- is an intermediate in the formation of ClO_3^- (reaction (11)) and therefore can be consumed quickly.

$$ClO_2^- + {}^{\bullet}OH \rightarrow ClO_3^- + H^+ + e^-$$
(11)

Concerning the ClO⁻ ion, in Figure 7c, when working with the BDD electrode, ClO⁻ concentration reached its maximum value at 60 min (769 \pm 23.70 mg/L), which later decreased to 36 \pm 0.13 mg/L at 480 min. In the case of MMO electrodes, the maximum concentration of the ClO⁻ ion was obtained at 30 min, being 247 \pm 0.24 mg/L and 318 \pm 25.14 mg/L for MMO-Cl₂ and MMO-O₂, respectively. This ion completely disappeared at 240 min when working with the MMO electrodes; however, when the BDD electrode was used, ClO⁻ disappeared at the end of electrolysis (540 min). This result indicates that when a BDD electrode is used, because more °OH is formed than in MMO electrodes, °OH can react with the chlorides present in the water, producing a greater quantity of active chlorine species such as ClO⁻, as shown in reaction (12). Reaction (8) shows another way of obtaining ClO⁻ ion.

$$Cl^{-} + {}^{\bullet}OH \rightarrow ClO^{-} + H^{+} + e^{-}$$
(12)

It should be noted that since the final concentration of the chlorine species is lower than the initial concentration of Cl⁻, there could be a risk that halogenated organic compounds have been formed [54], which could explain the low mineralization of organic matter when MMO electrodes are used.

Regarding NO₃⁻ ions (Figure 7d), they totally disappeared after 30 min when working with the MMO electrodes, whereas an increase of 23 times was observed with the BDD electrode compared to the initial value at 540 min, which is associated with the decomposition of organic compounds that present atoms of nitrogen [40]. Nevertheless, this value (9.28 mg/L) is within the values accepted by Chilean regulations. No other nitrogenated ions such as ammonium (NH₄⁺) or nitrite (NO₂⁻) were detected.

In Figure 7e, the PO_4^{3-} ions decreased in all three cases. When working with the MMO electrodes, decreases of 17% and 29% were obtained for MMO-Cl₂ and MMO-O₂, respectively. In the case of the BDD electrode, the PO_4^{3-} ion disappears after 480 min. According to [54], this decrease can be attributed to scaling in the electrolysis cell.

The concentration of SO_4^{2-} ions increased by 8% and 6% when working with MMO-Cl₂ and MMO-O₂, respectively (Figure 7f). In the case of BDD, the sulfate ion concentration increased by 20% at the end of electrolysis (540 min) compared to the initial value. This increase can be attributed to the degradation of organic compounds containing sulfur atoms [24,40,54]. It is noteworthy that depending on the salts dissolved in the wastewater, other oxidants can be produced that, despite having a lower oxidation power than $^{\circ}$ OH, can also improve the oxidation power of the system. Among these oxidants that are formed in the solution when current is applied are $P_2O_8^{4-}$ and $S_2O_8^{2-}$. The formation of these oxidants occurs when $^{\circ}$ OH reacts with the phosphate and sulfate salt dissolved on the anode surface [18], with the subsequent formation of radical species (reactions 13 and 14) that are then combined as shown in reactions 15 and 16.

$$PO_4^{3-} + {}^{\bullet}OH \to (PO_4^{2-})^{\bullet} + e^-$$
 (13)

$$\mathrm{SO_4}^{2-} + {}^{\bullet}\mathrm{OH} \to (\mathrm{SO_4}^{-})^{\bullet} + \mathrm{e}^{-}$$
 (14)

$$(PO_4^{2-})^{\bullet} + (PO_4^{2-})^{\bullet} \to P_2O_8^{4-}$$
 (15)

$$(SO_{4-})^{\bullet} + (SO_{4-})^{\bullet} \to S_2 O_8^{2-}$$
 (16)

These results demonstrate the importance of inorganic ions in the formation of different species that can improve the oxidative power of the system.

4. Conclusions

The monitoring of different parameters in the winery wastewater of a Chilean industry confirmed the presence of a high content of easily biodegradable organic matter and great seasonality. This work demonstrated that the effectiveness of the anodic oxidation process is directly related to the type of anodic material used. In this sense, only with the use of a BDD anode, 85% of the organic matter present in the winery wastewater was removed without the need of modifying the initial characteristics of the sample or adding a support electrolyte. In addition, using the BDD anode, the highest percentage of decrease in absorbance and turbidity was achieved, which were 85% and 59%, respectively. These results demonstrate the greater oxidative power exhibited by the BDD anode by forming more hydroxyl radicals than the MMO electrodes. The presence of carboxylic acids such as acetic and propionic acid was found, which could not be removed when working with the MMO electrodes. The monitoring of ions during electrolysis demonstrated the importance of inorganic ions already in the water to the formation of different species that can improve the oxidative power of the system. These results may contribute to the future implementation of the technology at an industrial level.

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