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Effects of High Voltage Electrical Discharge Plasma on Olive Mill Wastewater Treatment

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Abstract: High voltage electrical discharge plasma technology (HVED) is considered as a promising technology for wastewater remediation due to its fast removal rate and environmental compatibility. Olive mill wastewater (OMWW) treatment presents crucial environmental issues because of its high organic load and intense toxicity and phytotoxicity. The effect of cold plasma at frequencies of 60 Hz and 120 Hz, with injected gas (air, oxygen and nitrogen) and with and without the addition of $\text{FeCl}_3 \times 6\text{H}_2\text{O}$, during 30 min, on degradation and removal of organic compounds, as well as polyphenols from OMWW, were investigated. The efficiency of cold plasma was monitored by pH, temperature, electroconductivity, redox potential, oxygen saturation and reduction of chemical oxygen demand (COD) and polyphenols. The best removal efficiency of 50.98% of organic compounds was achieved at 120 Hz with nitrogen and the addition of $\text{FeCl}_3 \times 6\text{H}_2\text{O}$, and a 60.32% reduction of polyphenols at a frequency of 60 Hz with the air and $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ added was obtained. Also, the plasma treatment resulted in a decrease in coloring intensity, with the most significant color change at 120 Hz with the addition of $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ with nitrogen and air.

Keywords: OMWW; cold plasma; polyphenols; COD



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1. Introduction

Olive mill wastewater (OMWW) represents the main liquid waste of the olive oil production process [1–4]. OMWW, a brown to blackish liquid, is a complex mixture of water, sugar, nitrogenous substances, organic acids, polyphenols, polyalcohols, pectins, mucilages, tanins, lipids and inorganic substances [2–4]. Due to complex composition and high organic load (4–18 g/100 g), low pH, high chemical oxygen demand (COD up to $170 \text{ gO}_2\text{L}^{-1}$) and extremely high phenolic content ($0.5\text{--}24 \text{ gL}^{-1}$), OMWW is highly ranked among the most polluting byproducts of the agro-industrial sector. Several studies show that phenolic compounds present a major disadvantage for the environment because of their resistance to biological degradation and responsibility for toxicity and phytotoxicity [3,5,6]. The qualitative and quantitative HPLC analysis of raw OMWW has shown that hydroxytyrosol and tyrosol are the most abundant phenolic compounds, but OMWW also contains 40 other phenolic compounds [1,5].

OMWW is still a challenge for efficient treatment, despite progress in research and development of treatment methods [7].

A promising method for OMWW degradation is plasma technology, mainly because of environmental compatibility and high removal efficiency. However, there is little information on the use of plasma in OMWW treatment [8,9]. Ibrahimoglu and Yilmazoglu [8] treated OMWW with the DC arc plasma method and reported that the rates of COD (chemical oxygen demand) and BOD (biological oxygen demand) of OMWW decreased by 94.42% and 95.37%, respectively, with a color removal rate of 99.2%. Kuşçu and Eke [9] reported that treatment of OMWW with pulsed high-voltage discharge plasma resulted in

72% COD and 74% phenol degradations with the addition of H_2O_2 , and 74% COD and 79% phenol degradation with the addition of ferrous ions.

Electrical discharge plasma technology leads to various physical and chemical effects, such as the primary formation of oxidizing species: radicals ($\text{H}\cdot$, $\text{O}\cdot$, $\text{OH}\cdot$) and molecules (H_2O_2 , O_3 , etc.), shockwaves, ultraviolet light and electrohydraulic cavitation [10]. A high voltage electrical discharge in liquid can either interact with gas molecules dissolved in the liquid (mostly nitrogen and oxygen) or water molecules. Therefore, plasma forms transient species ($\text{OH}\cdot$, $\cdot\text{NO}_2$, $\cdot\text{NO}$ radicals) and long-lived chemical products (O_3 , H_2O_2 , NO_3^- , NO_2^-). Hydroxyl radicals and ozone are able to hydroxylate phenol in water, causing its degradation on the phenoxyl radical. Conversely, radicals, such as $\cdot\text{NO}_2$, $\cdot\text{NO}$ (probably mediated by peroxyxynitrite), will form nitrated and nitrosylated products of phenol [11,12]. The addition of iron ions accelerates the decomposition process of the organic compounds and reduces the toxicity of OMWW by eliminating 60% of COD by the Fenton process [8]. Kallel et al. [13] investigated OMWW degradation with Fenton oxidation and reported that the coloration of OMWW disappeared and phenolic compounds decreased to 50% of the initial concentration after 3 h reaction time. The rate of COD removal was variable; it ranged from 78% at initial 4 g COD L^{-1} to 14% at initial 85 g COD L^{-1} . Genethliou et al. [5] investigated biodegradation of phenolic compounds of OMWW in a thermophilic anaerobic upflow packed bed reactor (UPBR) and assessed their toxicity in digester effluents. They reported a removal of 73.4% of the OMWW total phenolic in an anaerobic UPBR. Iervolino et al. [14] achieved the complete degradation and mineralization of different water pollutants from synthetic wastewater (methylene blue, phenol, caffeine, paracetamol and ceftriaxone) studied in a dielectric barrier discharge DBD non-thermal plasma reactor using pure oxygen and 20 kV applied voltage. Sugiarto and Sato [15] and Shen et al. [16] reported that plasma treatment with the addition of ferrous ions or hydrogen peroxide and bubbling the solution with various gases (oxygen, argon, nitrogen and ozone) improves the degradation rate of phenol. The efficiency of phenol removal in the hybrid electrical discharge reactor was further enhanced by the addition of ferrous sulfate or activated carbon to the liquid solution and varying electrode gap spacing [17].

Although there are some studies on OMWW plasma treatments [8,9], as well as the removal of phenol and phenolic compounds and organics by the plasma method [14–17], far too little attention has been paid to the effects of high voltage electrical discharge plasma (HVED) treatments on OMWW compounds, which is the goal of our paper.

The aim of this study is to explore the effect of HVED on OMWW treatment using selected process parameters: frequency, treatment time, injected gas (air, oxygen and nitrogen) and the presence of Fenton reagents.

2. Materials and Methods

2.1. Experimental Setup

A pulse high-voltage generator (Spellman, UK) with a 1200 W output power was used to generate plasma. The generator was connected to the circuit with resistors ($9.5 \text{ M}\Omega$) and capacitor capacitance (0.75 nF) (Figure 1). Plasma frequencies of 60 Hz and 120 Hz were used, and the voltage was measured with a voltage probe (Tektronix P6015A) connected to the oscilloscope (Hantek DS05202BM, QingDao, China). A hybrid plasma reactor (glass reactor, total volume of 500 mL, working volume of 200 mL) was equipped with rubber caps and an adapted opening for the electrodes and gas injection (Figure 2). The carried gases N_2 (flow of 4 L min^{-1}), O_2 and air (flow = 6 L min^{-1}) were injected through a high-voltage electrode (stainless steel needle Microlance TM 3.81 cm) placed in the liquid phase at the bottom of the reactor. During the treatment, injected gases enabled sample mixing. In the gas phase, the ground electrode was placed in the upper portion of the reactor. This configuration allowed discharge on the top of the ground electrode in the air, discharging on the liquid surface and through the bubbles in the liquid.

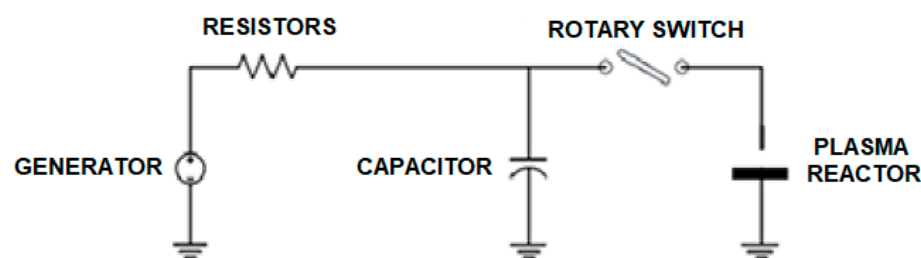


Figure 1. Schematic description of the circuit.

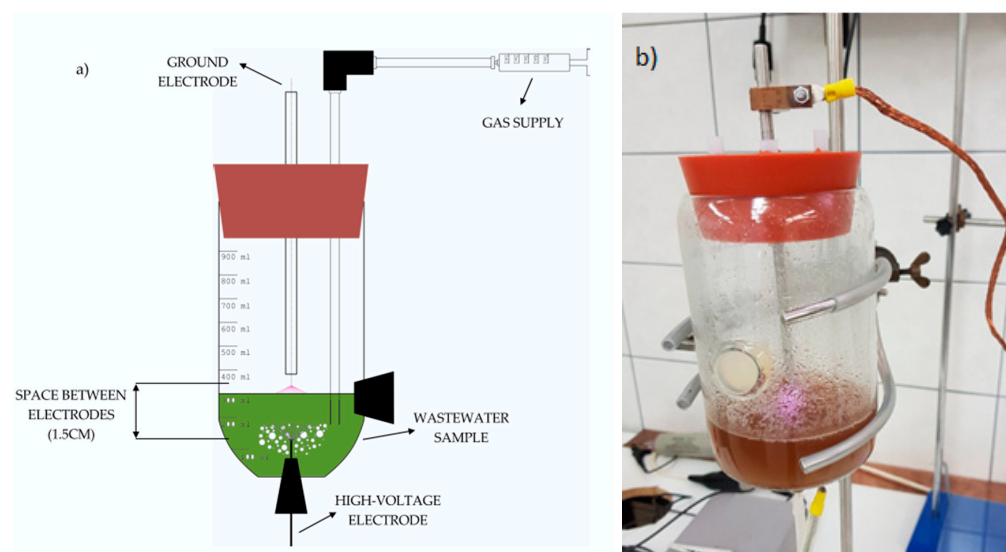


Figure 2. (a) Schematic of the hybrid plasma reactor (b) Photo of the hybrid plasma reactor.

The OMWW (200 mL) was treated at selected parameters (frequencies of 60 and 120 Hz) and gases (N_2 , O_2 , air) for 30 min in a hybrid plasma reactor, with and without $FeCl_3 \times 6H_2O$. Process optimization was performed through a series of experiments at different frequencies (60, 90, 120 and 150 Hz), process times (10, 20 and 30 min), with N_2 , air and O_2 gases.

For the purposes of the research, three batches of OMWW taken from a local producer in northern Dalmatia, Croatia were analyzed and stored at $-18^\circ C$ immediately after being delivered to the laboratory. Before the treatment, the samples were tempered to room temperature and filtered through an $11\mu m$ pore paper filter to remove agglomerated particles.

The OMWW was analyzed for physico-chemical parameters: pH, temperature, oxygen saturation, electric conductivity, color, polyphenol content and COD, before and after hybrid plasma treatment.

The samples were marked so that the letters A and B indicated the frequency (60 Hz or 120 Hz), the numbers 1, 2 and 3 indicated the applied gases (nitrogen, air and oxygen), and the letters “ad” indicated experiments with $FeCl_3 \times 6H_2O$.

2.2. Physico-Chemical Analysis

HANNA instruments (Woonsocket, RI, USA) were used for the determination of pH (HI11310), electrical conductivity (HI763100) and oxygen saturation (HI764080). The temperature was measured by a digital infrared thermometer (Infra Red Thermometer, PCE-777, PCE Instruments, Jupiter, Florida, USA).

The CIE-Lab color values were measured using a Specord 50 Plus spectrophotometer (Analytik Jena, Jena, Germany) with a 10 mm mesh mask. Light/dark (L^*), red/green (a^*) and yellow/blue (b^*) measurements were performed in SCI (specular component included) mode. The transmittance measurement was carried out in a plastic cuvette at wavelengths

of 380 to 780 nm, each 5 nm, with a D65 illuminator and a viewing angle of 10° versus distilled water as a blank probe. In the tested sample, color values were evaluated using CIE Lab software support.

For characterizing the color in the CIE-Lab system, chromatic coordinates L^* , a^* and b^* can be used, as well as their related parameters, such as chroma (C^*) and the ratio of absolute values of a^* and b^* . Higher L^* values reveal higher light transmittance through the sample. Moreover, the greater the absolute values of the a^* or b^* coordinates, the higher the levels of pheophytins (green hues) and carotenoids (yellow hues). When C^* values are greater, darker colorations of the samples are expected to be observed, while higher a^*/b^* ratio values are related to samples with more green tonalities [18,19].

The COD was measured by Standard Methods–COD_{Cr} [20].

2.3. Extraction of Polyphenols

For determination of polyphenolic compounds, an extraction method was used according to De Marco et al. [21]. The OMWW samples were acidified with HCl to pH 2 and washed with hexane in order to remove the lipid fraction. Then, 10 mL of OMWW was mixed with 15 mL of hexane; intensively shaken for 30 s and centrifuged for 5 min at 3000 rpm. The phases were separated and the washing was repeated successively two times. The extraction of phenolic compounds was then carried out with ethyl acetate. Degreased OMWW samples were mixed with 10 mL of ethyl acetate; intensively shaken and centrifuged for 5 min at 3000 rpm.

The phases were separated and the extraction was repeated successively three times. The ethyl acetate was evaporated under vacuum at 40 °C. The dry residue was dissolved in 3 mL of methanol and filtered through a 0.2 µm pore polyvinylidene fluoride (PVDF) filter. The prepared extract was used for determination of phenolic compounds on the HPLC system

2.4. Determination of Polyphenols

The composition of the polyphenolic compounds was determined by high-performance liquid chromatography (HPLC) with a DAD detector (HPLC system using Agilent Technologies HPLC series 1200 with a DAD detector).

The separation of polyphenolic compounds extracted from the OMWW was carried out at 30 °C on a Phenomenex C18 non-polar column (Kinetex 150 mm × 4.6 mm, 2.6 µm, 100 Å). The amount of injected sample was 5 µL. A 0.1% formic acid solution in water (mobile phase A) and 0.1% formic acid solution in methanol (mobile phase B) were used as a mobile phase. The solvent flow was 0.9 mLmin^{−1}. The chromatograms of the polyphenolic compounds were recorded with a DAD at wavelengths of 280 and 330 nm, and during the whole duration of the analysis, the spectra were recorded in the ultraviolet area of 200 to 400 nm.

The phenolic compounds were identified by comparing their retention times and their UV spectras with those of commercially available standards. The phenolic compounds were quantified using calibration curves prepared from the corresponding standard solutions. All samples were determined in triplicate, and the tables show the mean values of polyphenolic compounds obtained.

3. Results and Discussion

3.1. Physico-Chemical Characteristics

The results for pH, EC and oxygen saturation in the untreated and treated OMWW are presented in Table 1. The difference in temperature at the beginning and end of the target experiment was recorded in all experiments as an increase in temperature, expressed in Table 1 as ΔT .

Table 1. Physico-chemical characteristics of OMWW before (C) and after 30 min of plasma treatment, at frequencies 60 Hz (A) and 120 Hz (B), with nitrogen (1), air (2) and oxygen (3), and with additive (_{ad}).

Treatment	t (min)	pH	EC (μScm^{-1})	O ₂ (%sat)	ΔT ($^{\circ}\text{C}$)
C	0	5.04 ± 0.01	874.50 ± 3.54	29.50 ± 0.42	/
A1	30	4.19 ± 0.01	1102.50 ± 2.12	10.25 ± 0.35	12.10 ± 0.28
A2	30	4.12 ± 0.01	940.00 ± 2.83	74.70 ± 0.57	20.55 ± 1.34
A3	30	4.61 ± 0.03	916.00 ± 1.42	280.40 ± 2.12	22.65 ± 0.35
B1	30	4.13 ± 0.03	1112.00 ± 5.66	10.60 ± 0.85	14.90 ± 0.28
B2	30	4.47 ± 0.04	944.00 ± 4.24	63.25 ± 0.64	26.95 ± 0.64
B3	30	4.59 ± 0.06	905.00 ± 4.24	239.85 ± 4.31	25.90 ± 0.85
C _{ad}	0	4.18 ± 0.01	949.50 ± 3.54	88.75 ± 0.50	/
A1 _{ad}	30	3.63 ± 0.02	1181.50 ± 0.71	21.95 ± 0.64	13.70 ± 0.28
A2 _{ad}	30	3.31 ± 0.04	1178.50 ± 0.71	50.00 ± 1.13	18.00 ± 0.14
A3 _{ad}	30	3.89 ± 0.09	1139.00 ± 2.83	227.40 ± 5.23	20.95 ± 0.64
B1 _{ad}	30	3.79 ± 0.01	1167.50 ± 2.12	14.60 ± 0.85	24.90 ± 0.57
B2 _{ad}	30	3.70 ± 0.01	1119.50 ± 0.71	39.20 ± 1.56	22.85 ± 1.06
B3 _{ad}	30	3.89 ± 0.01	1231.00 ± 5.66	234.05 ± 2.05	26.80 ± 0.21

The highest increase in temperature of 26.95 ± 0.64 $^{\circ}\text{C}$ was observed in B2 after air plasma treatments at a frequency of 120 Hz, while the minimum increase of 12.10 ± 0.28 $^{\circ}\text{C}$ was observed after nitrogen plasma treatment at a frequency of 60 Hz (experiment A1). In OMWW samples with the addition of $\text{FeCl}_3 \times 6\text{H}_2\text{O}$, the highest increase of 26.80 ± 0.21 $^{\circ}\text{C}$ was observed in B3_{ad} after oxygen plasma treatment at a frequency of 120 Hz, while the minimum increase of 13.70 ± 0.28 $^{\circ}\text{C}$ was observed in A1_{ad} after nitrogen plasma treatment at a frequency of 60 Hz (Table 1). The temperature rise in the reactor might be due to the relationship between the power and gas flow, i.e., the energy density, the mixture of gases, the retention time and the type of reactor, which was also noticed by Parvulescu et al. [22] and Hammer et al. [23], who investigated the influence of cold plasma chemistry and chemical kinetics in liquids. The higher temperature increase also has been observed in experiments after treatments at a higher frequency, because an increase in the discharge frequency leads to an increase of discharge power, due to a strong photoionization effect that causes energy transmission to the surrounding medium that consequently warms the treated liquid [24].

Electrical conductivity increased in all of the plasma treatment experiments, which correlates with the temperature increase (Table 1). The values that ranged from $900 \mu\text{Scm}^{-1}$ to $1200 \mu\text{Scm}^{-1}$ were reversely proportional to the temperature increase, more precisely the experiments A1, B1 and A1_{ad}, with the highest increase in electrical conductivity, had the lowest temperature rise during the treatment ($12\text{--}14 \Delta T$ $^{\circ}\text{C}$). The largest increase in electrical conductivity of $230 \mu\text{Scm}^{-1}$ was evident in the nitrogen plasma treatments irrespective of the applied plasma frequency. The solution conductivity had a large influence on the direct liquid phase electric discharge. An increase in conductivity resulted in higher discharge current, higher electron density, larger UV radiation power and shorter pulse duration (faster current dissipation between the gaps). Therefore, a shorter but brighter liquid phase discharge channel can be observed in a highly conductive solution [25].

After plasma treatment, the pH value of all samples was decreased (Table 1). The highest drop in pH value of 0.92 pH units was noticed in experiment A2, while the lowest pH reduction of 0.43 pH units was measured in experiment A3, in the oxygen plasma treatment at a frequency of 60 Hz (Table 1). When oxygen was present in the electrical discharge process, reactive atoms or radicals such as N, O, H and OH were formed and recombined either among themselves or with initial molecules (N_2 , O_2 , H_2O , etc.), inducing new products such NO_2 , HNO_2 and HNO_3 . These nitrate and nitric products, when dissolved in water, can induce a steep lowering of the solution's pH and an increase in conductivity, and can participate in various reactions [10]. In the experiments with $\text{FeCl}_3 \times 6\text{H}_2\text{O}$, the highest pH decrease (0.87 pH units) was noticed in experiment A2_{ad} with

air plasma treatment, while the smallest decrease in the pH value (0.29 pH units) was noticed at the 60 Hz and 120 Hz frequencies in the oxygen plasma treatment, in experiments A3_{ad} and B3_{ad} (Table 1).

Temperature and pH were not controlled in the experiments, only monitored. The result of chemical reactions and the response of targeted processes was an increase in temperature up to a max of 26.95 °C (120 Hz, O₂, FeCl₃·6H₂O), while the pH decreased for all selected process conditions. Furthermore, with increasing temperature, the pH of OMWW decreases less. Plasma discharge causes a temperature increase as well as a variation in pH due to the development of various radical species.

Some papers have shown how better phenol degradation occurs at a higher pH, but in our case, we found acceptable degradation even at a lower pH. The control of pH is possible by adding chemicals, but also depends on an expectable degradation rate. Thus, Jiang et al. [10], Sayed [12], and Lukeš [26] stated that at pH ≥ 10, the best values of phenol degradation in water are achieved, while Sugiarto et al. [27] state that lower pH values have a positive effect on the decomposition of dyes in water by applying plasma discharges. Sayed [12] stated that the degradation of phenol at 35 °C at pH 10 was higher than the degradation of phenol at 10 °C, whereas in contrast, Chen et al. [28] pointed out that lower process temperatures favor phenol degradation.

After the oxygen plasma treatment, in all the OMWW samples, the oxygen saturation expectedly increased (Table 1), and it was the highest of all measured samples (>280% sat). Slightly lower saturation values were observed in samples after the air plasma treatment (63–75% sat), while oxygen saturation in samples of nitrogen plasma treatment was the lowest (10% sat), irrespective of the plasma frequency applied.

After plasma treatment, coloring intensity of samples decreased (Figure 3).

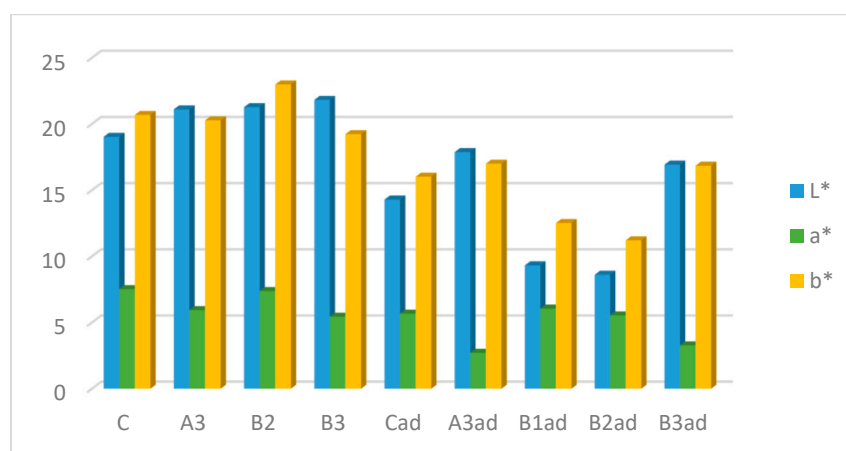


Figure 3. L*, a* and b* values in experiments before (C) and after 30 min of plasma treatment, at frequencies of 60 Hz (A) and 120 Hz (B), with nitrogen (1), air (2) and oxygen (3), and with additive (ad).

The most significant color change occurred in experiments B1_{ad} and B2_{ad}, for which the pH values were between 3.70–3.79 (Table 1, Figure 3). Our results are in agreement with Tufaner [2], who pointed out that color removal is not present at high pH values, but removal starts and increases while the pH decreases from approximately 5.0 to 3. As the pH falls below 3, the removal efficiencies decrease significantly. In acidic pH (values lower than 2.5), Fe²⁺ ions are deactivated and (Fe(II)(H₂O))²⁺ is formed. Since this iron complex reacts slowly with H₂O₂ and the production rate of OH· slows down, the removal efficiency decreases. The high concentration of H⁺ ions leads to the scavenging effect of hydroxyl radicals, which reduces the removal efficiency [2]. Hydroxyl radicals and ultraviolet radiation dominate the treatment of wastewater with cold plasma. The decoloration rate at the pH value of 3.5 was found to be approximately three times higher than that at the pH value of 10.3. A small effect of the initial pH during the decoloration process by spark and

spark-streamer discharge mode means that the physical effects, such as a shockwave and ultraviolet radiation, may play an important role in the oxidation process [27].

3.2. COD Removal

Results of the COD removal in cold plasma treatment are shown in Table 2. The initial COD expressed as mean value was 4202 mgL^{-1} .

Table 2. COD removal efficiency after plasma treatment at frequencies 60 Hz (A) and 120 Hz (B), with nitrogen (1), air (2) and oxygen (3), and with additive (_{ad}).

Treatment	t (min)	COD _{removal} (%)
C	0	-
A1	30	38.71
A2	30	9.73
A3	30	1.32
B1	30	8.07
B2	30	13.16
B3	30	44.08
C _{ad}	0	-
A1 _{ad}	30	39.80
A2 _{ad}	30	34.33
A3 _{ad}	30	37.25
B1 _{ad}	30	50.98
B2 _{ad}	30	15.69
B3 _{ad}	30	49.02

COD removal was observed in all experiments and in all combinations of treatment, but with substantial differences (Table 2). The COD removal ranged from 1.32% (60 Hz, O₂, experiment A3) to 50.98% (120 Hz, N₂, FeCl₃×6H₂O, experiment B1_{ad}). With the N₂ gas, the highest COD removal was achieved in experiments at 60 Hz (38.71%, experiment A1), 60 Hz + FeCl₃×6H₂O (39.80%, experiment A1_{ad}) and 120 Hz + FeCl₃×6H₂O (50.98%, experiment B1_{ad}); while the O₂ gas was the most effective at 120 Hz (44.08%, experiment B3). Results in this study suggest N₂ gas as the favorable one, contrary to other studies. Oxygen as a feeding gas was recognized as the first-rank treatment performance, then air and argon, and the least for nitrogen [16,28–32]. In accordance with the assumption that oxygen is involved in the oxidation pathway of phenol is that, in the presence of phenol, a lower increase in the concentration of dissolved oxygen in the solution was found than in the solution without phenol [16]. Ibrahimoglu and Yilmazoglu [8] reported a 99.3% reduction of COD, and color reduced by 99.2% in OMWW treated with DC arc plasma. Pulsed high-voltage discharge plasma resulted in 72% COD and 74% phenol degradations with the addition of H₂O₂, and 74% COD and 79% phenol degradation with the addition of ferrous ions from OMWW [9].

An increase in frequency improved the COD removal with O₂ both with and without FeCl₃×6H₂O, with opposite effect using N₂ and air. In experiments without FeCl₃×6H₂O, the increase of the frequency had an adverse effect on N₂ and a favorable effect on air and O₂. In experiments with FeCl₃×6H₂O, the increase of the frequency showed a favorable effect on N₂ and O₂, and an adverse effect on air (Table 2). The addition of FeCl₃×6H₂O improved the COD removal efficiency at both frequencies with all investigated gases, with the strongest impact to N₂ at 120 Hz (COD removal increased from 8.07% to 50.98%), and the lowest impact to N₂ at 60 Hz (COD removal increased from 38.71% to 39.80%) (Table 2). The Fenton reaction, a homogeneous catalytic oxidation process involving the reaction of hydrogen peroxide with ferrous ions (H₂O₂/Fe²⁺), generates highly reactive oxidizing free radicals. Hydrogen peroxide reactivity is enhanced by dissolved iron salts responsible for the decomposition of hydrogen peroxide into a hydroxyl radical [4,33]. Electrical plasma technology for the degradation of organics primarily depends on the chemical active species, and this process is enhanced by other physical effects [10]. For the

improvement of plasma-oxidation efficiency, the addition of ferrous salt can catalytically transform formed H_2O_2 into hydroxyl radicals via Fenton reactions [34]. The addition of Fenton reagents in the plasma system causes Fenton reactions and intensifies the efficiency of the plasma chemical removal of organics from water [10]. The Fenton method has proven to be the fastest in decomposing organic compounds and very successful in reducing the COD values, coloration and concentration of polyphenols in OMWW. The main advantage of the Fenton method is that all the components involved in the reactions are safe to handle and environmentally benign [4,33].

The increment in frequency did not substantially affect the pH value; it remained in a narrow range. The addition of $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ mildly lowered the pH value at both frequencies for all investigated gases. The lowest pH decrease was recorded with O_2 , at both frequencies, and both with and without $\text{FeCl}_3 \times 6\text{H}_2\text{O}$. No obvious relationship between pH and COD removal was observed (Tables 1 and 2). Nitrogen-containing gases in the plasma system finally formed NO_2 , HNO_2 and HNO_3 , which, when dissolved in water, can induce a steep pH decrease in the solution and an increase in conductivity, and can participate in various reactions [10].

As expected, the oxygen saturation increased in the following order: $\text{N}_2 < \text{air} < \text{O}_2$ at both frequencies, both with and without $\text{FeCl}_3 \times 6\text{H}_2\text{O}$. The COD removal was inversely proportional to the oxygen saturation in all experiments, except in the experiment with O_2 at 120 Hz (at 239.85% oxygen saturation, the highest COD removal of 44.08% was recorded in experiment B3). The N_2 gas with oxygen saturation in a range of 10.25–21.95% was favorable for COD removal at 60 Hz (38.71%, experiment A1), 60 Hz + $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ (39.80%, experiment A1_{ad}) and 120 Hz + $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ (50.98%, experiment B1_{ad}) (Tables 1 and 2).

The temperature difference increased with the increment of frequency, for all investigated gases, both with and without the $\text{FeCl}_3 \times 6\text{H}_2\text{O}$. The lowest increase in temperature was recorded at 60 Hz and N_2 , with the highest COD removal without $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ (38.71%, 12.10 °C, experiment A1) and with $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ (39.80%, 13.70 °C, experiment A1_{ad}). However, no obvious relationship between temperature difference and experiments at 120 Hz were observed (Tables 1 and 2).

3.3. Polyphenol Composition

The results of the cold plasma treatment with and without the addition of $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ (Table 3) showed a trend of reducing the concentration of total polyphenols in OMWW.

The highest reduction of polyphenol compounds was achieved by applying the air plasma treatment at a frequency of 60 Hz (Table 3). The value of degradation under the mentioned conditions in experiments with $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ was 60.32% (A2_{ad}), while in experiments without the addition of $\text{FeCl}_3 \times 6\text{H}_2\text{O}$, it was 51.65% (A2). The lowest removal of polyphenolic compounds in the OMWW without the addition of $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ (16.65%) was observed in experiment B1 (Table 3).

In the treatments with nitrogen and air, an increase in the concentration of certain polyphenolic compounds (phenolic alcohols (hydroxytyrosol, tyrosol), phenolic acid (vanillic acid) and the most common, secoiridoidoleuropein) was noticed. The explanation for this is that the main degradation products of oleuropein are tyrosol and hydroxytyrosol, as well as modification of the polyphenolic compounds [1,5,21,35,36].

In experiments without the addition of $\text{FeCl}_3 \times 6\text{H}_2\text{O}$, the reduction of polyphenols ranged from 25% to 35%, and was lower than reductions in wastewater with the addition of $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ (Table 3). Reduction results in experiments with $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ ranged between a 30% and 60% reduction, with the highest value of 60.32% polyphenol removal obtained in experiment A2_{ad}. The lowest polyphenol reduction in experiments with the addition of $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ was observed for cold plasma treatment at a 120 Hz frequency with the use of nitrogen in experiment B1_{ad} (Table 3). In an investigation by Kallel et al. [13], OMWW degradation with Fenton oxidation resulted in a 50% removal of phenolic compounds.

Table 3. Polyphenol composition and concentration ($\mu\text{g mL}^{-1}$) before (C) and after plasma treatment at 60 Hz (A) and 120 Hz (B), with nitrogen (1), air (2) and oxygen (3), and with additive (ad).

Polyphenols ($\mu\text{g mL}^{-1}$) Treatment	Hydroxytyrosol	Tyrosol	Oleuropein Derivatives	Vanillic acid	Secoisolaricires- inoldiglocoside	Oleuropein	Pinoresinol	Total Unidentified Compounds	Total
C	2.76 \pm 0.09	8.66 \pm 0.28	10.06 \pm 0.24	1.06 \pm 0.08	2.61 \pm 0.34	0.30 \pm 0.51	0.48 \pm 0.56	18.87 \pm 4.85	44.80 \pm 6.96
A1	5.36 \pm 1.20	8.65 \pm 0.71	7.64 \pm 0.62	0.83 \pm 0.20	0.00	0.00	0.00	6.21 \pm 2.38	28.69 \pm 5.10
A2	1.91 \pm 0.20	6.98 \pm 0.53	7.09 \pm 0.27	0.85 \pm 0.21	0.00	0.00	0.62 \pm 0.60	4.22 \pm 1.03	21.66 \pm 2.85
A3	0.00	8.09 \pm 0.44	9.53 \pm 0.33	1.00 \pm 0.07	0.83 \pm 0.28	0.00	0.00	10.50 \pm 0.70	29.95 \pm 1.83
B1	8.16 \pm 0.44	10.80 \pm 0.11	10.29 \pm 0.28	1.26 \pm 0.34	0.00	0.00	0.00	6.83 \pm 0.84	37.34 \pm 2.01
B2	4.62 \pm 0.62	10.51 \pm 1.30	9.76 \pm 0.67	0.87 \pm 0.12	0.00	0.00	0.00	6.59 \pm 0.58	32.35 \pm 3.27
B3	0.00	8.78 \pm 0.84	9.36 \pm 0.79	1.04 \pm 0.06	0.88 \pm 0.36	0.35 \pm 0.61	0.00	10.01 \pm 1.81	30.43 \pm 4.47
Cad	2.76 \pm 0.09	8.66 \pm 0.28	10.06 \pm 0.24	1.06 \pm 0.08	2.61 \pm 0.34	0.30 \pm 0.51	0.48 \pm 0.56	18.87 \pm 4.85	44.80 \pm 6.96
A1ad	2.33 \pm 0.09	6.80 \pm 0.31	7.34 \pm 0.32	0.81 \pm 0.03	0.00	0.00	0.00	5.23 \pm 0.61	22.51 \pm 1.36
A2ad	0.00	7.45 \pm 0.46	7.79 \pm 0.17	0.29 \pm 0.26	0.00	0.00	0.00	2.24 \pm 0.19	17.78 \pm 1.08
A3ad	0.00	10.84 \pm 0.50	9.43 \pm 0.29	0.95 \pm 0.02	1.43 \pm 0.78	0.00	0.00	7.77 \pm 0.70	30.42 \pm 2.28
B1ad	3.95 \pm 0.35	11.08 \pm 0.25	9.43 \pm 0.46	0.90 \pm 0.02	0.00	0.51 \pm 0.44	0.00	6.18 \pm 0.22	32.05 \pm 1.75
B2ad	1.55 \pm 0.08	11.56 \pm 0.41	9.50 \pm 0.10	0.77 \pm 0.08	0.00	0.00	0.00	5.99 \pm 0.91	29.39 \pm 1.57
B3ad	0.00	8.59 \pm 0.29	8.46 \pm 0.22	0.90 \pm 0.04	0.32 \pm 0.28	0.00	0.00	5.80 \pm 0.24	24.06 \pm 1.07

Fenton's reaction has a significant effect on the phenol removal, because of the rapid increase in the reaction rate upon the addition of ferrous salt. Since $\cdot\text{OH}$ is the most powerful oxidizing species among the produced reactive species, a higher phenol removal is expected when Fe^{2+} and Fe^{3+} ions exist [28]. In a pulsed discharge system, an O_2 -containing gas application would induce the production of O_3 and other O-based active species, which have the most important role in the removal of organic compounds from the aqueous solution, which is difficult due to nitrogen disturbance, because the radicals are not produced directly by a series of reactions. The obtained results are in accordance with the data of Jiang et al. [10], in which the authors noticed that oxygen application would achieve better elimination of organic compounds at 60 Hz treatment than would nitrogen application. Iervolino et al. [14] studied the performance of a DBD plasma reactor for phenol removal from an aqueous solution of phenol, showing that a 78% phenol degradation was achieved after only 5 min of non-thermal plasma treatment of the aqueous solution using pure oxygen and 20 kV of applied voltage, while the complete degradation and mineralization was reached after 20 min. In plasma treatment the addition of ferrous ions or hydrogen peroxide and bubbling the solution with various gases (oxygen, argon, nitrogen and ozone) improved the degradation rate of phenol [15,16].

In samples with a larger pH, a lowering of the highest phenol degradation was observed (Tables 1 and 3). The lowering of the pH occurs due to the partial oxidation of the phenolic compounds into low molecular weight carboxylic acids, which predominantly occurs within the first stage of the Fenton process, and which can lead to the acidification of the solution and lowering of the pH value [4].

The treatment temperature range also affects polyphenol reduction. In the experiments with higher polyphenol reduction values, a lower temperature increase was observed during plasma treatment (Tables 1 and 3). According to Jiang et al. [10], a temperature increase causes a decrease in the degradation rate. The liquid temperature increase causes a larger rate constant, and hydroxyl radicals can be rapidly interrupted by surrounding substances, which are in a higher concentration than the pollutant. As a result, the radical can no longer react with the pollutant, and the degradation rate is reduced.

During the plasma oxidation processes with ozone generation, ozonation efficiency may be also temperature-dependent, due to Henry constants of ozone that vary at different temperatures. As a result, treatment temperature can lead to enhanced absorption of ozone into water favorable for organic abatement [10].

3.4. Future Investigation Direction

This research combines different scientific disciplines such as engineering, environmental protection and economy, as well as aspects of sustainable development, with aims to limit the environmental impact and improve the efficiency of wastewater treatment. Such an interdisciplinary approach provides limits and possibilities of environmental engineering technologies. Sustainable management for OMWW is one of the crucial environmental challenges.

The application of HVED technology is one of the possible and promising solutions to this problem, although there are still gaps in knowledge in the field. Further investigation is needed to explore the optimization of HVED as a sustainable technology, both in the lab and in full-scale treatment of OMWW, as an innovative solution with integrated pre- and post-treatments.

Croatian law [37] does not prescribe standards for OMWW effluent. It is necessary that discharges into the public sewage system meet the following values: $\text{pH} = 6.5\text{--}9.5$ and $\text{COD} \leq 700 \text{ mgL}^{-1}$.

For the proposed treatment method, the removal of suspended solids is required as pretreatment, and pH correction and additional COD removal as post treatment. The achieved results of OMWW treatment with a 50% removal of COD represent the basis for further research with the aim of achieving the legally prescribed limits.

At the end of each experiment, total nitrogen was determined, and was found to be $N \leq 20 \text{ mgL}^{-1}$ for all investigated selected conditions.

Scale-up factors of the current plasma system include variations of electrode configurations, as well as reactor design (applying gas and liquid plasma discharge), using different electro factors (frequency and voltage) and plasma discharge in different gasses.

4. Conclusions

The cold plasma treatment combined with Fenton's reagents resulted in the most efficient degradation and reduction of organic and polyphenol compounds in OMWW. By selecting the appropriate operating conditions, it is possible to achieve a good result in degradation of polyphenol compounds, with respect to the available literature about the use of non-thermal plasma technology in wastewater treatment. The highest reduction of polyphenolic compounds of 60.32% was achieved at 60 Hz with air and $\text{FeCl}_3 \times 6\text{H}_2\text{O}$, while the highest COD removal of 50.98% and 49.02% was achieved with the addition of $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ at 120 Hz, with nitrogen and oxygen, respectively. The most significant reduction of color intensity was achieved at 120 Hz with the addition of $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ with nitrogen and air.

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References

1. Rahmanian, N.; Jafari, S.M.; Galanakis, C.M. Recovery and Removal of Phenolic Compounds from Olive Mill Wastewater. *J. Am. Oil Chem. Soc.* **2014**, *91*, 1–18. [\[CrossRef\]](#)
2. Tufaner, F. Evaluation of COD and color removals of effluents from UASB reactor treating olive oil mill wastewater by Fenton process. *Sep. Sci. Technol.* **2019**, *55*, 3455–3466. [\[CrossRef\]](#)
3. Zghari, B.; Doumenq, P.; Romane, A.; Boukir, A. GC-MS, FTIR and ^1H , ^{13}C NMR Structural Analysis and Identification of Phenolic Compounds in Olive Mill Wastewater Extracted from Oued Oussefrou Effluent (Beni Mellal-Morocco). *J. Mater. Environ. Sci.* **2017**, *8*, 4496–4509. [\[CrossRef\]](#)
4. Esteves, B.M.; Rodrigues, C.S.D.; Madeira, L.M. Synthetic olive mill wastewater treatment by Fenton's process in batch and continuous reactors operation. *Environ. Sci. Pollut. Res.* **2017**, *25*, 34826–34838. [\[CrossRef\]](#)
5. Genethliou, G.; Kornaros, M.; Dailianis, S. Biodegradation of olive mill wastewater phenolic compounds in a thermophilic anaerobic up flow packed bed reactor and assessment of their toxicity in digester effluents. *J. Environ. Manag.* **2020**, *255*. [\[CrossRef\]](#)
6. Landeka Dragičević, T.; Zanoški Hren, M.; Gmajnić, M.; Pelko, S.; Kungulovski, D.; Kungulovski, I.; Čvek, D.; Frece, J.; Markov, K.; Delaš, F. Biodegradation of olive mill wastewater by *Trichosporon cutaneum* and *Geotrichum candidum*. *Arch. Ind. Hyg. Toxicol.* **2010**, *61*, 399–405. [\[CrossRef\]](#)
7. Kilic, M.; Kaya, G.; Kestioglu, K. An inventory study for treatment of olive mill wastewater by chemical, biological and advanced treatment methods. *Uludağ Univ. J. Fac. Eng.* **2009**, *14*, 183–198. [\[CrossRef\]](#)
8. Ibrahimoglu, B.; Yilmazoglu, M.Z. Disposal of olive mill wastewater with DC arc plasma method. *J. Environ. Manag.* **2018**, *217*, 727–734. [\[CrossRef\]](#)

9. Kuşçu, Ö.S.; Eke, E. Treatment of olive oil mill wastewater by apulsed high-voltage discharge process; process optimization and combination with Fe^{+2} and H_2O_2 . *J. Chem. Technol. Biotechnol.* **2015**, *90*, 1040–1050. [\[CrossRef\]](#)
10. Jiang, B.; Zheng, J.; Qui, S.; Wu, M.; Zhang, Q.; Yan, Z.; Xue, Q. Review on electrical discharge plasma technology for wastewater remediation. *Chem. Eng. J.* **2014**, *236*, 348–368. [\[CrossRef\]](#)
11. Banaschik, R.; Lukes, P.; Jablonowski, H.; Hammer, M.U.; Weltmann, K.-D.; Kolb, J.F. Potential of pulsed corona discharges generated in water for the degradation of persistent pharmaceutical residues. *Water Res.* **2015**, *84*, 127–135. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Sayed, M. Efficient removal of phenol from aqueous solution by the pulsed high-voltage discharge process in the presence of H_2O_2 . *Chem. Int.* **2015**, *1*, 81–86. [\[CrossRef\]](#)
13. Kallel, M.; Belaid, C.; Boussahel, R.; Ksibi, M.; Montiel, A.; Elleuch, B. Olive mill wastewater degradation by Fenton oxidation with zero-valent iron and hydrogen peroxide. *J. Hazard Mater.* **2009**, *163*, 550–554. [\[CrossRef\]](#)
14. Iervolino, G.; Vaiano, V.; Palma, V. Enhanced removal of water pollutants by dielectric barrier discharge nonthermal plasma reactor. *Sep. Purif. Technol.* **2019**, *215*, 155–162. [\[CrossRef\]](#)
15. Sugiarto, A.T.; Sato, M. Pulsed plasma processing of organic compounds in aqueous solution. *Thin Solid Films* **2001**, *386*, 295–299. [\[CrossRef\]](#)
16. Shen, Y.; Lei, L.; Zhang, X.; Zhou, M.; Zhang, Y. Effect of various gases and chemical catalysts on phenol degradation pathways by pulsed electrical discharges. *J. Hazard Mater.* **2008**, *150*, 713–722. [\[CrossRef\]](#)
17. Grymonpré, D.R.; Finney, W.C.; Clark, R.J.; Locke, B.R. Hybrid gas-liquid electrical discharge reactors for organic compound degradation. *Ind. Eng. Chem. Res.* **2004**, *43*, 1975–1989. [\[CrossRef\]](#)
18. Kiritsakis, K.; Melliou, E.; Magiatis, P.; Gerasopoulos, D. Enhancement of bioactive phenols and quality values of olive oil by recycling olive mill waste water. *J. Am. Oil Chem. Soc.* **2017**, *94*, 1077–1085. [\[CrossRef\]](#)
19. Sharma, G.; Rodríguez-Pardo, C.E. The dark side of CIELAB. In *Color Imaging XVII: Displaying, Processing, Hardcopy, and Applications*; International Society for Optics and Photonics: Bellingham, WA, USA, 2012; p. 82920D. [\[CrossRef\]](#)
20. APHA. *Standard Methods for the Examination of Water and Wastewater*, 21st ed.; American Public Health Association/American Water Works Association/Water Environment Federation: Washington, DC, USA, 2005.
21. De Marco, E.; Savarese, M.; Paduano, A.; Sacchi, R. Characterization and fractionation of phenolic compounds extracted from olive oil mill wastewaters. *Food Chem.* **2007**, *104*, 858–867. [\[CrossRef\]](#)
22. Parvulescu, V.I.; Magureanu, M.; Lukes, P. *Plasma Chemistry and Catalysis in Gases and Liquids*; Wiley-VCH Verlag & C.o. KGaA: Weinheim, Germany, 2012.
23. Hammer, T.; Kappes, T.; Baldauf, M. Plasma catalytic hybrid processes: Gas discharge initiation and plasma activation of catalytic processes. *Catal. Today* **2004**, *89*, 5–14. [\[CrossRef\]](#)
24. Briels, T.M.P.; Van Veldhuizen, E.M.; Ebert, U. Positive streamers in air and nitrogen of varying density: Experiments on similarity laws. *J. Phys. D Appl. Phys.* **2008**, *41*. [\[CrossRef\]](#)
25. Shih, K.Y.; Locke, B.R. Chemical and physical characteristics of pulsed electrical discharge within gas bubbles in aqueous solutions. *Plasma Chem. Plasma Process.* **2010**, *30*, 1–20. [\[CrossRef\]](#)
26. Lukeš, P. Water Treatment by Pulsed Streamer Corona Discharge. Ph.D. Thesis, Institute of Chemical Technology, Prague, Czech Republic, 2001.
27. Sugiarto, A.T.; Ito, S.; Ohshima, T.; Sato, M.; Skalný, J.D. Oxidative decoloration of dyes by pulsed discharge plasma in water. *J. Electrostat.* **2003**, *58*, 135–145. [\[CrossRef\]](#)
28. Chen, Y.-S.; Zhang, X.-S.; Dai, Y.-C.; Yuan, W.-K. Pulsed high-voltage discharge plasma for degradation of phenol in aqueous solution. *Sep. Purif. Technol.* **2004**, *34*, 5–12. [\[CrossRef\]](#)
29. Krause, H.; Schweiger, B.; Schuhmacher, J.; Scholl, S.; Steinfeld, U. Degradation of the endocrine disrupting chemicals (EDCs) carbamazepine, clofibric acid and iopromide by corona discharge over water. *Chemosphere* **2009**, *75*, 163–168. [\[CrossRef\]](#)
30. Zhang, Y.; Zhou, M.; Hao, X.; Lei, L. Degradation mechanisms of 4-chlorophenol in a novel gas-liquid hybrid discharge reactor by pulsed high voltage system with oxygen or nitrogen bubbling. *Chemosphere* **2007**, *67*, 702–711. [\[CrossRef\]](#)
31. Njatawidjaja, E.; Tri Sugiarto, A.; Ohshima, T.; Sato, M. Decoloration of electrostatically atomized organic dye by the pulsed streamer corona discharge. *J. Electrostat.* **2005**, *63*, 353–359. [\[CrossRef\]](#)
32. Sun, B.; Sato, M.; Sid Clements, J. Optical study of active species produced by a pulsed streamer corona discharge in water. *J. Electrostat.* **1997**, *39*, 189–202. [\[CrossRef\]](#)
33. Bampalioutas, K.; Vlysidis, A.; Lyberatos, G.; Vlyssides, A. Detoxification and methane production kinetics from three-phase olive mill wastewater using Fenton's reagent followed by anaerobic digestion. *J. Chem. Technol. Biotechnol.* **2019**, *94*, 265–275. [\[CrossRef\]](#)
34. Venny; Gan, S.; Ng, H.K. Current status and prospects of Fenton oxidation for the decontamination of persistent organic pollutants (POPs) in soils. *Chem. Eng. J.* **2012**, *213*, 295–317. [\[CrossRef\]](#)
35. Suárez, M.; Macià, A.; Romero, M.P.; Motilva, M.J. Improved liquid chromatography tandem mass spectrometry method for the determination of phenolic compounds in virgin olive oil. *J. Chromatogr. A* **2008**, *1214*, 90–99. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Mulinacci, N.; Romani, A.; Galardi, C.; Pinelli, P.; Giaccherini, C.; Vincleri, F.F. Polyphenolic content in olive oil waste waters and related olive samples. *J. Agric. Food Chem.* **2001**, *49*, 3509–3514. [\[CrossRef\]](#) [\[PubMed\]](#)
37. Ordinance on limit values for wastewater emissions. *Nar. Novine* **2020**, *26*. Available online: https://narodne-novine.nn.hr/clanci/sluzbeni/2020_03_26_622.html (accessed on 1 February 2021).