

## Article

# Ozonation Processes for Color Removal from Urban and Leather Tanning Wastewater

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**Abstract:** The need to ensure adequate levels of both human and environmental health protection calls for the identification of efficient wastewater treatment processes that target the removal of conventional pollutants as well as emerging contaminants, including synthetic dyes. This study explores the potential of ozone for use in the decolorization of both pretreated tannery wastewater and urban wastewater effluents. Different ozone contact times (15, 30, and 45 min) were applied to such wastewater samples at an uncontrolled (7.5–8.2) pH as well as at a pH adjusted to 10. The highest color removal efficiencies (REs) (>90%) were obtained with urban wastewater after a 45 min contact time and at pH 10. Under the same conditions, a COD RE from 31 to 51% was achieved. Even without pH adjustment, color and COD REs ranging from 81 to 92% and 39 to 41%, respectively, were obtained. A preliminary evaluation of the costs associated with the implementation of an ozonation stage within the wastewater treatment plant (WWTP) generating the urban wastewater used here was carried out. The energy cost of the ozone treatment would account for a 69% increase in the total energy cost of the WWTP, suggesting the need to identify proper strategies to enhance the cost-competitiveness of this technology.

**Keywords:** advanced oxidation processes; color removal; emerging contaminants; tannery wastewater; ozone



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## 1. Introduction

Significant population growth, urbanization, and the global water crisis have generated an increasing demand for freshwater worldwide. The proper treatment of wastewater plays a crucial role in supporting and maintaining the quality of aquatic ecosystem resources as well as human health. The main determinants of the quality of receiving freshwater bodies are chemical compounds and particles in water, such as nutrients, heavy metals, and micro-organisms, whose concentrations depend on several factors, such as the origin of the treated wastewater [1]. However, the presence of emerging contaminants (ECs), mainly organics, including endocrine disruptors, pesticides, pharmaceuticals, hormones, toxins, and industrial-related synthetic dyes [2,3], may compromise the water quality due to the complexity associated with their treatment [4,5].

Normally, wastewater treatment plants (WWTPs) are designed and operated to remove mainly ammonia, total suspended solids (TSS), and the chemical oxygen demand (COD) and to produce final high-quality effluents to be discharged in accordance with the legally established standards. However, conventional WWTP processes are poorly efficient for the removal of ECs [5], these being highly persistent and requiring particular operating or environmental conditions due to their physicochemical characteristics [5]. Although EC removal efficiencies (REs) in the ranges of 20–50% and 30–70% have been reported during primary and secondary treatments, respectively, in most cases, conventional WWTPs

do not allow acceptable EC abatement. Most of the ECs, in fact, are excreted via faeces and urine as a mixture of parent chemical and conjugates. During biological treatment, the conjugates can revert back to their parent compounds through enzymatic cleavage, resulting in an increased effluent EC concentrations [5]. EC removal can occur through physical, chemical, biological, or hybrid processes [4]. The main treatment technologies can be divided into phase-changing methods, biological treatment methods, and advanced oxidation processes [2,6–8]. Phase-changing technologies are defined as processes capable of moving contaminants from one phase to another. These include adsorption using activated carbon, biochar, clay minerals, other adsorbent materials (zeolites, meso- and microporous materials, resins, and metal oxides) or membrane technologies [6]. Biological processes target the biodegradation of ECs and depend on their structural complexity, bioavailability, functional groups, and operating conditions [5]. Conventional biological systems include activated sludge (nitrification and denitrification process, anaerobic/aerobic treatment) and biological filtration [4,6].

Advanced oxidation processes (AOPs) are technologies predominantly based on the production of hydroxyl radicals (oxidation potential, 2.8 V) [9]. AOPs include the use of UV, UV/H<sub>2</sub>O<sub>2</sub>, UV/ozone, ozone, ozone/H<sub>2</sub>O<sub>2</sub>, ozone/H<sub>2</sub>O<sub>2</sub>/UV, the Fenton process, and photo-Fenton and sonochemical processes [6]. In recent years, interest in AOPs has increased due to their capacity to degrade recalcitrant components without generating a secondary waste stream [9]. The use of AOPs is even more important in the treatment of industrial wastewater, as complex molecules derived from anthropogenic pollutants are rarely attacked by micro-organisms in biological processes [9].

In particular, ozonation is one of the most promising processes to reduce the load of ECs (e.g., synthetic dyes, carboxylic acids, phenolics, amoxicillin, and other pharmaceuticals) in WWTPs [10]. Ozone can react with ECs either directly or indirectly after the formation of hydroxyl radicals [11]. This is usually promoted at high pH values through the addition of hydrogen peroxide, UV irradiation, or reactions with the organic compounds themselves [12,13]. Numerous studies have reported that the removal of synthetic dyes by ozonation can be highly efficient due to the high ozone oxidation ability [10,14–18]. In contrast, the main disadvantages of the process are the very limited ozone life, the by-products produced, and the high energy cost [16].

In this view, the main goal of this study was to investigate and compare the effect of ozonation on the decolorization of different real effluents from a WWTP and an Italian leather tanning WWTP. The influences of pH and contact time were evaluated with a view of a future full-scale application of ozonation. The biodegradability variation in ozonated samples was monitored as well. The experimental results allowed us to perform a preliminary economic assessment on the employment of an ozonation stage as a post-treatment of a biologically processed effluent for its decolorization.

## 2. Materials and Methods

### 2.1. Characteristics of Treated Wastewater

The wastewater samples used in this study were collected from the WWTP located in Mercato San Severino (Salerno, Campania Region, Italy) and from an Italian leather tanning WWTP. The Mercato San Severino WWTP is based on a conventional activated sludge system [19] and presently treats both civil and industrial wastewater. The incoming flow rate throughout the year varies in the range of 1200–2500 m<sup>3</sup>/h. The leather tanning WWTP is a centralized facility that treats wastewater from approximately 140 factories, which mainly produce leather for clothing and shoes. For the purposes of this study, two samples were collected from the secondary sedimentation tank effluent of the Mercato San Severino WWTP (E1 and E2), which is treated by a sand filter before disinfection and final discharge. An additional sample was withdrawn from the leather tanning WWTP finale effluent (E3) in the period from September to December 2022. A physicochemical characterization of these samples is shown in Table 1.

**Table 1.** Chemical–physical characteristics in terms of the pH, color (i.e., absorbance at 426, 558, and 660 nm), chemical oxygen demand (COD), and total suspended solids (TSS) of the effluent samples from Mercato San Severino (E1–E2) and from the leather tanning (E3) wastewater treatment plants.

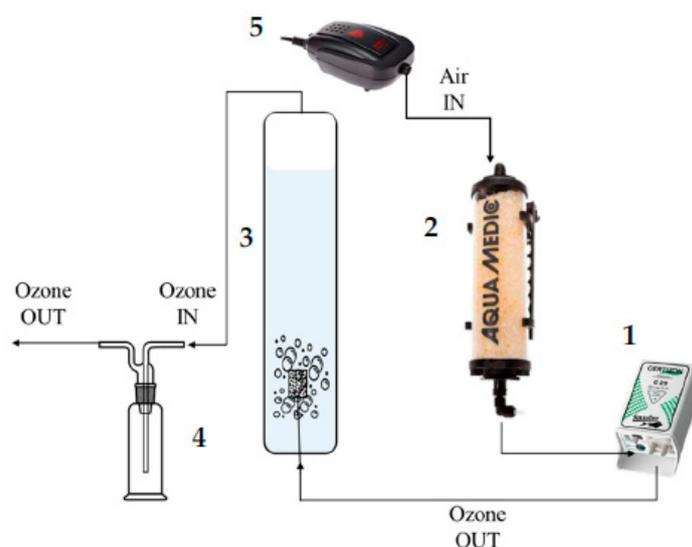
	E1	E2	E3
pH	7.5	7.8	8.2
Color ( $\lambda = 426$ nm)	$0.066 \pm 0.001$	$0.069 \pm 0.002$	$0.266 \pm 0.006$
Color ( $\lambda = 558$ nm)	$0.025 \pm 0.008$	$0.028 \pm 0.001$	$0.111 \pm 0.003$
Color ( $\lambda = 660$ nm)	$0.013 \pm 0.002$	$0.009 \pm 0.001$	$0.047 \pm 0.001$
COD ( $\text{mg}\cdot\text{L}^{-1}$ )	$119.0 \pm 2.0$	$148.0 \pm 3.5$	$457.0 \pm 5.2$
TSS ( $\text{mg}\cdot\text{L}^{-1}$ )	$39.0 \pm 1.0$	$66.0 \pm 0.0$	$225.0 \pm 0.0$
Cr ( $\text{mg}\cdot\text{L}^{-1}$ )	/	/	1.20
Cr III ( $\text{mg}\cdot\text{L}^{-1}$ )	/	/	0.81
Cr VI ( $\text{mg}\cdot\text{L}^{-1}$ )	/	/	0.38

As reported in Table 1, the effluent sample from the leather tanning WWTP (E3) was also characterized in terms of its chromium content, which was also monitored after ozonation to verify the potential oxidation of Cr(III) to the more toxic Cr(VI). The same parameter was not monitored in E1 and E2, since the results of previous ozonation tests highlighted that the Cr concentrations were always below the threshold limit values for discharge, and ozonation did not promote the oxidation of Cr(III) to Cr(VI) under the investigated conditions.

## 2.2. Experimental Set Up

As shown in Figure 1, the ozonation system consisted of a Certizone C25 ozone generator (Erwin Sander, Ueltze-Eltze, Germany), an air dryer to boost ozone production (Aqua Medic, Bissendorf, Germany), a glass contact column (750 mL), and a Drechsel trap for residual ozone measurements.

Air was transferred to the ozonizer at a flow rate of  $4.5 \text{ L min}^{-1}$  using an aquarium air pump. An ozone flow rate of  $12.5 \text{ mg}\cdot\text{h}^{-1}$  was injected into a contact column through a porous stone. The contact column was filled up to 0.5 L.



**Figure 1.** Scheme of the ozonation system: (1) ozone generator; (2) air dryer; (3) contact column; (4) Drechsel trap; (5) aquarium air pump.

After characterization in terms of the pH, color, TSS, and COD, the samples were subjected to ozonation experiments to investigate the impact of the ozone dose on the color removal as well as on the total COD (tCOD) and its fractions. Experiments with

ozone were carried out at both the natural pH of each effluent wastewater sample and with the initial pH adjusted to 10. pH adjustment was performed by dosing a 10.8 M NaOH solution. Contact times of 15, 30, and 45 min were used. All experiments were performed in triplicate at room temperature. Samples were collected at the end of the ozonation tests for the determination of tCOD, COD fractions, and color. Exhaust gases were extracted on the top and forced to pass through a Drechsel trap and filled in with about 200 mL KI at 2% for ozone residual measurements [20].

### 2.3. Analytical Methods

tCOD and TSS were analyzed according to the Standard Methods [20]. pH was measured with a Multi 9620 IDS laboratory pH meter (WTW™, Munich, Germany). Color was determined on 0.45 µm filtered samples at absorbances of 426, 558, and 660 nm, roughly corresponding to visible yellow, red, and blue [14] using a photoLab® 7600 UV-VIS spectrophotometer (WTW, Germany). Cr(III) and Cr(VI) concentrations were determined via colorimetric methods following the EN ISO 11083 and DIN 38405-D24 international standards.

The COD fractions were determined by means of respirometric tests, which were carried out using a BM-Advance Multipurpose respirometer (SURCIS SL, Barcelona, Spain). The control of aeration, pH, temperature, recycling pumping, and mechanical stirring was performed with BM-Advance software (SURCIS SL, Spain). Before starting the respirometric tests, an allylthiourea (ATU) solution was added to each wastewater sample to promote the inhibition of the nitrifying microbial population [21]. Initially, the heterotrophic biomass yield coefficient referring to the oxygen demand ( $Y_H$ ) was determined using a synthetic solution prepared by dosing 400 mg of sodium acetate in 1 L of distilled water. Afterwards, respirometric tests were carried out using both the real effluent samples (E1, E2 and E3) collected from the WWTPs and filtered samples to determine and calculate all COD fractions, i.e., the total biodegradable COD (bCOD), soluble biodegradable COD ( $S_S$ ), particulate biodegradable COD ( $X_S$ ), total inert COD (iCOD), soluble inert COD ( $S_I$ ), and particulate inert COD ( $X_I$ ). The following equations (Equations (1)–(5)) were used:

$$S_S = \frac{CO}{1 - Y_H} \quad (1)$$

$$X_S = bCOD - S_S \quad (2)$$

$$iCOD = tCOD - bCOD \quad (3)$$

$$S_I = \frac{iCOD * S_S}{bCOD} \quad (4)$$

$$X_I = iCOD - S_I \quad (5)$$

where

CO is the oxygen consumed during the test ( $\text{mg}\cdot\text{L}^{-1}$ ).

### 2.4. Removal Efficiencies

The removal efficiency (RE) of the analyzed parameters was calculated using Equation (6).

$$RE = \frac{(C_{i_{in}} - C_{i_{fin}})}{C_{i_{in}}} * 100 \quad (6)$$

where:

- $C_{i_{in}}$  is the initial concentration of parameter i;
- $C_{i_{fin}}$  is the final concentration of parameter i.

### 2.5. Economic Assessment of the Ozonation Stage

The total costs associated with the ozone treatment were obtained by the sum of the capital, operating, and maintenance costs. In this study, only capital and operating costs, in terms of electricity consumption, were considered. To assess the impact of both the capital and operating costs of the ozonation system on the overall investment and management of a WWTP with technology and capability similar to that of Mercato San Severino, the capital costs provided by the local plans of Campania Region [22] and literature data [23] for operating costs were taken as references. The WWTP capital costs depend on the type of treatment and the PE, as defined in Directive 91/271/EEC. The following equation [22] was considered for a conventional activated sludge system-based WWTP, defined only as a function of the number of PEs served, regardless of the specific process scheme:

$$y = 3669.3 * x^{-0.268} \quad (7)$$

where  $x$  is the PE, and  $y$  is the unit cost ( $\text{€} \cdot \text{PE}^{-1}$ ).

Regarding the energy consumption costs, Vaccari et al. [24] proposed a reference value as a benchmark equal to  $37 \text{ kWh} \cdot \text{PE}^{-1} \cdot \text{year}^{-1}$  for large plants ( $>100,000$  PE).

Both the capital and energy consumption costs estimated for a WWTP similar to that of Mercato San Severino were used to set a comparison with the corresponding costs estimated for the ozonation stage in accordance with the indications of different ozone technology suppliers.

### 2.6. Statistical Data Analysis

A one-way analysis of variance (ANOVA) was performed using the Data Analysis Tool of Excel 2016 (Microsoft Corporation, Redmond, WA, USA). The ANOVA was conducted to determine the statistical differences in the performance parameters in terms of color, tCOD, bCOD,  $S_5$ ,  $X_5$ , iCOD,  $S_I$ , and  $X_I$ . Significance was set at 95% ( $p < 0.05$ ).

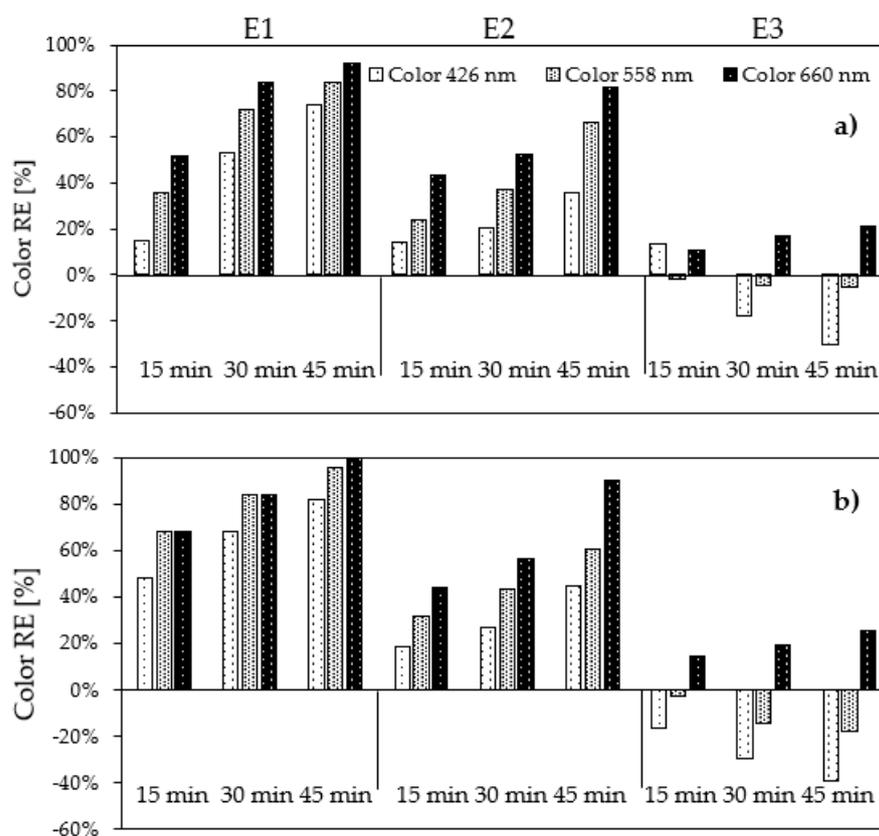
## 3. Results and Discussion

The following section reports the results of the ozonation process obtained in terms of the color and tCOD and COD fractions. The results obtained in terms of the residual ozone concentrations are not shown, as these were extremely low.

### 3.1. Effect of Ozonation on Color Removal from Urban and Leather Tanning Wastewater

Figure 2 shows the color RE depending on the ozonation time. For both E1 and E2, it can be observed that the color RE increased with the ozonation time at all wavelengths and pH values used. After 45 min of ozonation, REs ranging from 74 to 92% were achieved for E1. REs further increased in the range of 82–100% when the initial pH was adjusted to 10, indicating that alkaline solutions are more suitable for ozonation, likely due to the generation of highly reactive products, such as hydroxyl radicals [24]. Indeed, ozone is a strong oxidizing agent, which reacts directly or indirectly—via hydroxyl radicals—with organic substances, depending on the pH. At higher pH values, indirect oxidation prevails, and the nonselective action of the hydroxyl radicals enhances the ozonation yield [25]. Thus, various contact times and pH conditions were evaluated to assess the optimal operating parameters to obtain a nearly complete color removal at the three reference wavelengths of 426, 558, and 660 nm, roughly corresponding to visible yellow, red, and blue, respectively.

A similar color removal trend at different pH values was also observed for E2 samples, although lower color REs (45–90%) were obtained. The highest REs of 81 and 90% at a natural pH and a pH of 10, respectively, were observed when the color was detected at a wavelength of 660 nm (Figure 2). As E1 and E2 showed similar values of absorbance at the selected wavelengths, the different REs can likely be attributed to the higher presence of other organic compounds in E2, which competed with the dyeing substances for the oxidizing agents provided during ozonation.



**Figure 2.** Color removal efficiency (RE) for effluent samples collected from the Mercato San Severino treatment plant (E1 and E2) and from the leather tanning wastewater treatment plant (E3) at natural pH values of 7.5–8.2 (a) and with the pH controlled at 10 (b).

The absorbance at the three wavelengths of the nonozonated E3 samples was constantly higher than nonozonated E1 and E2 (Table 1), due to their different origins [26]. E3 samples were also characterized by higher COD and TSS contents, being typical of tannery wastewater already subjected to physical and biological pretreatments [27]. Additionally, for E3, 45 min of ozonation resulted in the highest color REs, but values only reached 21% (at an uncontrolled pH) and 26% (at pH 10) at a wavelength of 660 nm, suggesting that this is the prevailing wavelength for all analyzed samples, corresponding to a perceived blue-green hue [28]. At the wavelengths of 426 and 558 nm, the color removal in E3 did not vary linearly with an increasing ozonation time, as plotted in Figure 2.

The ozonation effects on aqueous reactive dyes have been widely investigated in previous studies, contributing to the elucidation of ozone mechanisms for color removal. By studying the ozone decolorization of reactive blue 171 dye, Patil and Shukla [15] found that the extent of color removal decreased as the concentration of dye increased, likely due to the higher amount of dye molecules compared to the soluble oxidizing species as well as due to the competition of dye degradation intermediates with virgin dye molecules for the available oxidants. This evidence could explain the lower color RE obtained in this study on E3 with respect to those observed on both E1 and E2 samples. The greater complexity of real tannery wastewater compared to synthetic solutions used elsewhere as well as the simultaneous presence of different dyes further accounts for the limited color RE in E3.

It is worth highlighting that ozone is very active with double bonds. For this reason, He et al. [29] investigated the overall effect of color fading ozonation on the color yield of cotton dyes by Reactive Blue FL-RN (RB-RN), Reactive Red FL-2BL (RB-2BL), and Reactive Yellow FL-2RN (RY-2RN) and observed different reaction kinetics between ozone and dyeing substances. This evidence reflects the greater simplicity of the ozone interaction with RB-RN (or RY-2RN) with respect to that with RB-2BL, characterized by fewer N=N

bonds than in the former. In this study, the compositions of the effluent samples are unknown, and this makes difficult to unveil the possible mechanisms underlying color RE by ozonation. Nonetheless, as increasing ozonation times resulted in increased absorbance at 426 and 558 nm as well as decreased absorbance at 660 nm for the E3 samples (Figure 2a), it is possible that the dye providing the blue color had a greater affinity with ozone than the other dyes. The reduction in color visible at a wavelength of 660 nm may have, in turn, brought the other visible colors up, thus determining the observed increases in absorbance at 426 and 558 nm. At pH 10, a similar trend in the color RE from E3 was observed (Figure 2b), although an indirect oxidation mechanism via nonselective hydroxyl radicals was expected to be prevailing, suggesting a higher availability for oxidation of the substance providing the blue color over the other dyes.

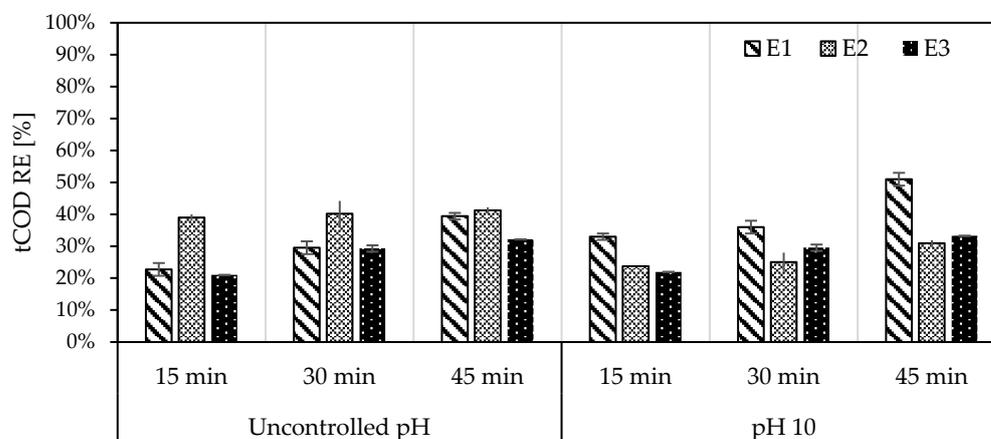
The moderate color removal obtained for the E3 samples was compared with the results of previous studies. Preethi et al. [30] observed that a continuous supply of ozone for a batch of real tannery effluent resulted in an increase in the color RE of up to 90% as the contact time increased to 60 min. Consistently, as reported by Saranya et al. [31], a rapid color RE of around 20% was observed during 20 min of ozonation. Then, gradually increasing removal of up to around 60 and 52% was obtained by dosing at an ozone concentration of  $2 \text{ g}\cdot\text{L}^{-1}$  at pH values of 7.6 and 9.0, respectively, after 120 min. At ozone concentrations of 4 and  $6 \text{ g}\cdot\text{L}^{-1}$ , the color REs observed were similar and were equal to 70 and 75% at pH values of 7.6 and 9.0, respectively, after 90 min [31]. However, higher ozone doses than those applied in the present study were used in the mentioned works, suggesting that the efficient decolorization of real tannery wastewaters requires intensive ozonation, even when wastewaters have been pretreated in conventional WWTPs. Hence, the use of ozone as the very tail-end option for decolorization may turn out to be more effective and cost-competitive due to the possible reduction of the ozone dose.

For E3 samples, the oxidative effect of ozonation was also monitored in terms of the chromium concentration. Under all experimental conditions, ozonated samples did not show any significant variation in terms of the Cr(III) and Cr(VI) concentrations. Average values of  $0.81 \pm 0.04 \text{ mg L}^{-1}$  of Cr(III) and  $0.38 \pm 0.03 \text{ mg L}^{-1}$  of Cr(VI) were observed, consistent with those reported in the scientific literature to be achieved from tannery wastewater treatment [32]. The possible oxidation of Cr(III) to Cr(VI) represents one of the main limitations of ozonation, limiting the widespread application of ozone-based processes for leather tanning wastewater. Nonetheless, it is worth highlighting that the presence of Cr in tannery effluents has promoted the adoption, within the leather industry, of novel tanning procedures that leverage metal-free solutions containing vegetable tannins to replace the Cr-based ones. In this regard, the presence of Cr may not necessarily be an obstacle to the ozonation of tannery wastewater, as confirmed by the results obtained in this study.

### 3.2. Variation of COD and Its Fractions Due to the Ozonation Process

The ozonation effects were also monitored in terms of the decrement in the organic matter concentration. Figure 3 shows the COD RE at different pH values and contact times. COD REs of 23, 39, and 21% were obtained within the first 15 min at uncontrolled pH values for the E1, E2, and E3 samples, respectively. Increasing the contact time resulted in a significant reduction in the COD in the E1 and E3 samples ( $p < 0.05$ ) but not for E2 ( $p > 0.05$ ). Alkaline conditions led to higher COD REs (Figure 3), which reached 51, 31, and 33% at a contact time of 45 min and pH 10 for the E1, E2, and E3 samples, respectively. Preethi et al. [30] found that the COD removal gradually increased with the contact time up to a maximum of 70% after 90 min of ozonation. By comparing different AOPs for the treatment of tannery wastewater, Sivagami et al. [27] reported COD REs with ozonation ranging from 10 to 50%, depending on the contact time as well as on the initial COD concentrations. The results obtained in this study are consistent with the literature and confirm the suitability of this method for the effective degradation of COD for both urban and tannery wastewater [33,34]. Overall, at different contact times and pH values, the

residual COD concentrations were within the Italian standard (D. Lgs. 152/2006, Annex V, Part III) for wastewater discharge into surface water bodies (for E1 and E2) and into sewers for E3.



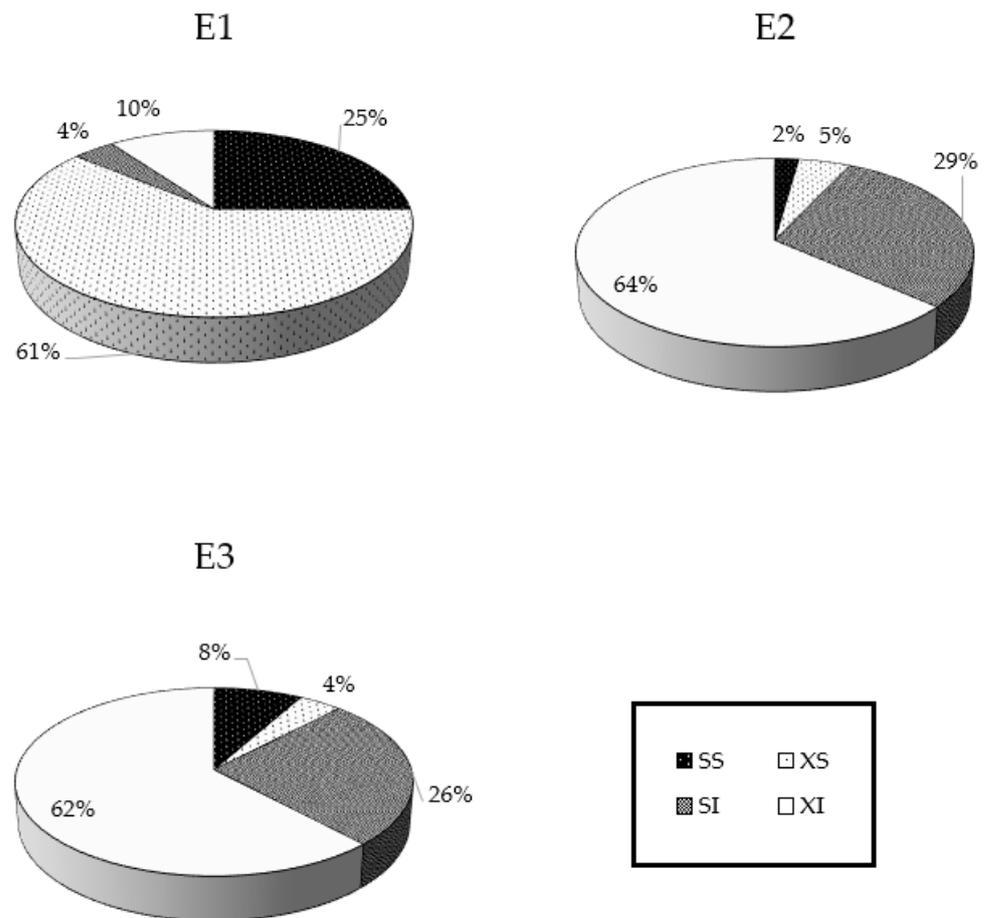
**Figure 3.** Total COD (tCOD) removal efficiency (RE) for effluent samples collected from the Mercato San Severino (E1 and E2) and the leather tanning (E3) wastewater treatment plants at uncontrolled pH values (7.5–8.2) and at pH 10.

Furthermore, COD fractionation was used to evaluate the changes in the wastewater composition and biodegradability after ozonation through the quantification of the  $S_S$ ,  $X_S$ ,  $S_I$ , and  $X_I$  aliquots. An increase in the biodegradable fraction of organic matter could be particularly interesting for E3 samples, which are destined for further biological treatment.

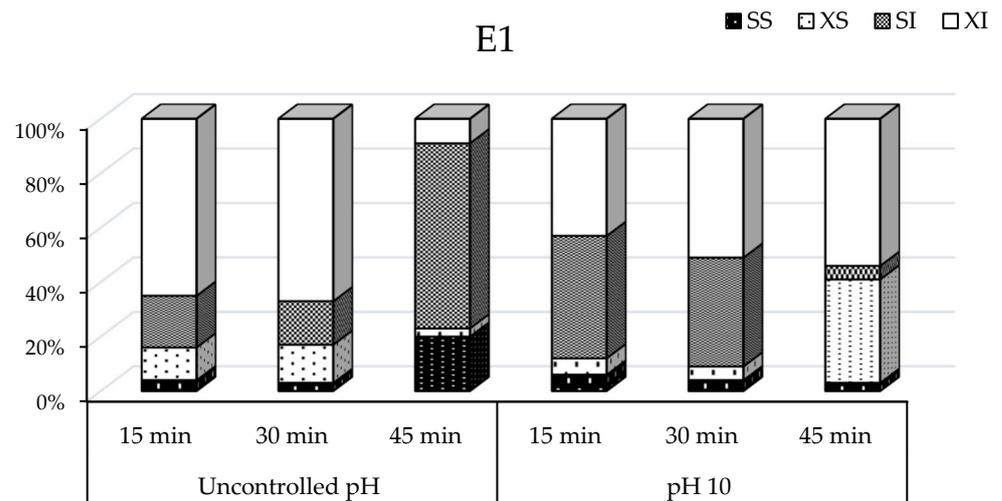
The analysis of COD fractions on the non-ozonized effluent E1 sample demonstrated that the particulate biodegradable fraction ( $X_S$ ) was predominant (61%), followed by the soluble biodegradable COD (25%) (Figure 4). The content of iCOD in E1 reached only 14%. Conversely, the main COD fraction in E2 was  $X_I$ , which was found to be 64% of the tCOD. For E2, COD and TSS were also found to be higher than in E1, although E1 and E2 were both collected at the outlet of the same WWTP. These results reflect the different compositions of the urban wastewater reaching the WWTP over time and likely indicate the occurrence of a higher share of substances of industrial origin when the E2 sample was collected.

The tannery effluent (E3) under investigation initially contained 62% of  $X_I$ . This is slightly higher than values reported in previous scientific studies, indicating that the particulate inert COD fraction of a typical tannery wastewater may range from 13 to 52% of the total COD [35]. Although E3 samples had already undergone pretreatment, it should be highlighted that the vegetable tannins often used to replace the metal-based tanning solutions may turn to be poorly biodegradable, accounting for the highest share of the inert fraction of the tCOD.

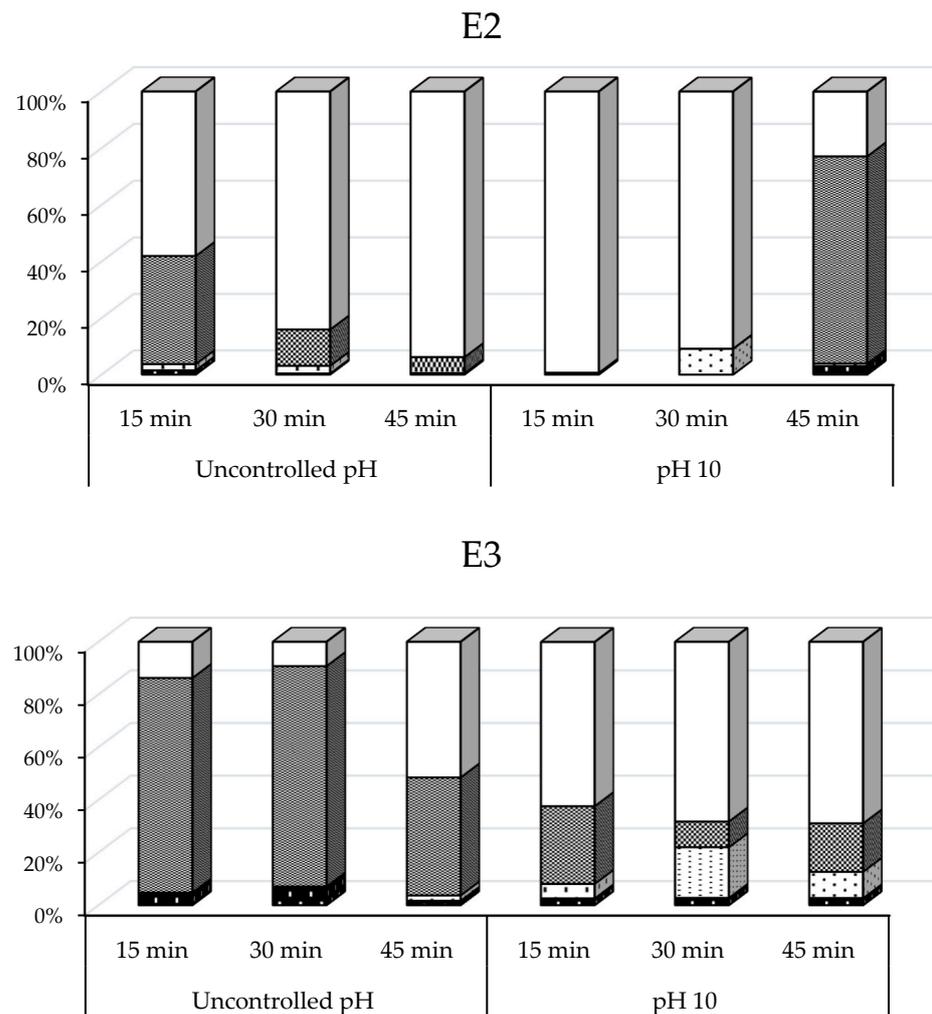
Figure 5 shows the different COD fractions as the contact time changes. An ozone contact time of 15 min resulted in a significant decrease in the  $S_S$  component under both pH conditions ( $p < 0.05$ ). At an uncontrolled pH, the  $S_S$  fraction decreased by 84, 32, and 50% for E1, E2, and E3, respectively. Prolonged ozone applications, i.e., up to 45 min, resulted in almost complete removal of the biodegradable fraction with consequent relative increases in the inert  $S_I$  and  $X_I$  fraction percentages in all samples. This may also have been amplified by the generation of less biodegradable organic by-products, as reported by Orhon et al. [36]. This evidence suggests that applying ozonation under the investigated conditions would make further biological treatment of E3 ineffective.



**Figure 4.** Initial COD fractionation of wastewater samples of the Mercato San Severino (E1 and E2) and leather tanning (E3) wastewater treatment plants.



**Figure 5.** Cont.



**Figure 5.** Different fractions of COD depending on the contact time and pH of the wastewater samples of the Mercato San Severino (E1 and E2) and tanning wastewater treatment plants (E3).

### 3.3. Preliminary Cost Evaluation

After comparing the experimental results obtained in this study, ozonation seems to be more suitable for treating the urban effluent from the Mercato San Severino WWTP (E1–E2) than the pretreated leather tanning wastewater (E3). Furthermore, the limited and nonsignificant ( $p > 0.05$ ) increases in both color and COD RE achieved at pH 10 do not justify the increased treatment costs associated with the NaOH dosage. Therefore, a cost evaluation was carried out considering the ozonation of the effluent from the Mercato San Severino WWTP at an uncontrolled pH. It is worth highlighting that, although the effluent of Mercato San Severino WWTP fulfils the color threshold limits set by the Italian legislation, the plant operators aim to ensure complete color removal.

For a contact time of 45 min, the estimated ozone dose per  $\text{m}^3$  of treated effluent was calculated to be  $18.75 \text{ g O}_3 \cdot \text{m}^{-3}$ . Accordingly, considering an average influent wastewater flow rate of  $2000 \text{ m}^3 \cdot \text{h}^{-1}$ , the evaluated ozone dose was equal to  $37.5 \text{ kg O}_3 \cdot \text{h}^{-1}$ . To provide such treatment, according to the more innovative technologies currently available on the market, it would be necessary to consider an ozone system equipped with two ozone generators including a diffuser and residual ozone destroyer to give a total capital cost of approximately 3,000,000 €.

The operation of such system is estimated to be around  $480 \text{ kWh} \cdot \text{h}^{-1}$ . Based on the price of the energy supplied by Italian Regulatory Authority for Energy Networks and Environment (ARERA) in March 2023, which is equal to  $0.361 \text{ €} \cdot \text{kWh}^{-1}$ , and assuming the

continuous operation of the ozonation system, the annual operating costs would amount to about 1,500,000 €.

Based on Equation (7), the total capital cost of a WWTP, such as that of Mercato San Severino, is about 25,000,000 €. Therefore, the capital cost of the ozone system would result in an increase of about 12% compared to the capital cost of the whole WWTP. Regarding energy consumption, its cost for ozone treatment would increase the total energy cost of the target WWTP by 69%. Additional costs would be those related to (i) the supply of an oxygen flow rate of 500 kg/h, as well as (ii) the skilled labor required for the maintenance of the ozonation system.

These preliminary economic considerations, which confirm that the main limitation of ozonation lies in the operating costs, were developed based on the results of a lab-scale experimental activity performed on samples (i.e., E1 and E2) collected at the outlet of the sedimentation tank before sand filtration so that a reduction in the ozone dose could be expected if sand-filtered samples were treated. Furthermore, an ozone dose decrease can be pursued by optimizing the ozone transfer efficiency. To this end, a pilot-scale activity could provide more reliable test conditions.

It is worth highlighting that a reduction in the energy consumption cost could also be sought by maintaining the ozonation at a lower flow rate. In this regard, acting on the tanning wastewater with the sole aim of color removal may represent a suitable option. This need, in turn, calls for a detailed characterization of the leather tanning wastewater throughout the processing line, with particular regard to the content of dyes, in order to better integrate the ozonation step within the existing pretreatment plant.

#### 4. Conclusions

This paper investigated and compared the effects of ozonation at different contact times (15, 30, and 45 min) and under two pH conditions (uncontrolled and pH 10) on the decolorization of both urban and leather tanning wastewaters with a view of a future full-scale application of ozonation in both WWTPs considered. The experimental results illustrate that the highest color REs of 100, 90, and 26% were obtained for E1, E2, and E3, respectively, after 45 min and at pH 10, suggesting the need for intense ozonation to gain efficient decolorization of real tannery wastewater. Under the same conditions, COD REs of 51, 31, and 33% were achieved for E1, E2, and E3, respectively. When the initial pH was not adjusted, color REs of 92, 81, and 21% were reached for E1, E2, and E3, respectively, indicating that an ozonation stage could be proposed as a post-treatment for a biologically processed effluent within the urban WWTP without any alkali dosage. The preliminary cost analysis for such a scenario showed that the capital and energy cost of ozone treatment would account for 12 and 69% increases, respectively, in the corresponding overall costs of the WWTP. This evidence confirms that the energy expenses represent a limit for ozone-based processes, whose application calls for further studies on either the optimization of the ozone transfer efficiency or the treatment of lower flow rates with the main aim of promoting color removal.

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