

Article

Evaluation of Electrocatalytic Ozonation Process for Hydroxyl Radical Production

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Abstract: This paper seeks to evaluate the effect of reaction parameters on iron electrolysis-catalyzed ozonation (ECO) performance as a promising approach for micropollutant removal. ECO is proposed to be an environmentally and economically suitable technology for the removal of biologically recalcitrant organics in wastewater. In this process, iron ions generated via electrolysis of low-carbon steel react with dissolved ozone to produce hydroxyl radicals. The removal of tert-Butyl alcohol (TBA) was selected as a performance indicator based on its significant resistance to direct ozonation compared to hydroxyl radicals, such that TBA removal denotes catalytic breakdown of ozone. TBA removal was measured with an HS-SPME-GC-MS method for precise quantification. ECO performance ranged from 7 to 77% TBA removal (from 0.73 mM initial concentration), varying depending on the tested levels of initial pH of 5, 7, and 9, applied current between 0.065 and 0.470 A, and ozone supply rate between 3.9 and 6.4 g/h. Performance was generally increased by pH, applied current, and ozone generation, converging at high applied current rates. The most efficient use of ozone was observed at pH 9 and 0.323 A, removing 32.2% of TBA per gram of ozone supplied.

Keywords: ozonation; catalytic; advanced oxidation; advanced oxidative process; hydroxyl radical; radical oxygen species; electrocatalysis; electrocatalytic; tert-Butyl alcohol; ozone resistance



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1. Introduction

The growing presence of organic pollutants in water systems, resulting from various human activities, highlights an increasing need for effective remediation. Conventional wastewater treatment processes struggle to consistently guarantee high removal rates for many persistent pollutants [1–5]. Many metropolitan areas, and other water treatment systems subject to high regulatory standards, are increasingly pressured to adopt enhanced treatment technologies to meet stringent water quality requirements [3,6]. Advanced treatment techniques, including adsorption, advanced oxidation processes, membrane filtration, and hybrid systems, are being explored as viable solutions to the limitations of current wastewater treatment systems [1,7]. Personal care products, pharmaceuticals, polyfluoroalkyl substances, and other organic pollutants are being discharged into receiving water bodies [5,8–11]. The release of these pollutants is increasing the toxicity of receiving aquatic environments [2,3,5,8,10,12]. There is evidence that some pollutants persist long after discharge, with minimal degradation and the potential for bioaccumulation and other time-delayed consequences [3,13,14].

Ozonation is one suitable tertiary treatment method for reducing organic pollution [15]. Ozone and its breakdown products are able to oxidize a wide range of organic pollutants,

enhance the biodegradability of intermediates, improve aesthetic qualities, and maintain or enhance inactivation rates for viruses, *Giardia*, and *Cryptosporidium* [15]. Despite advancements in ozone generation technology, the high costs associated with ozonation inhibit its scalability compared to biological wastewater treatment plants [16–18]. These economic constraints have limited the widespread adoption of ozonation, despite its effectiveness.

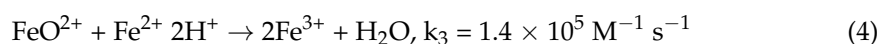
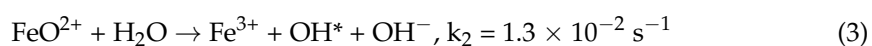
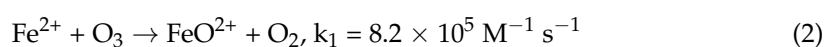
All ozonation processes involve the breakdown of ozone molecules into radical oxygen species. Catalytic ozonation is the augmentation of ozonation with the addition of a catalyst to intentionally accelerate ozone degradation for radical production. The generation of radicals enables catalytic ozonation systems to achieve extremely high removal rates for many ozone-resistant and otherwise recalcitrant contaminants, accompanied by partial or complete mineralization [19–25].

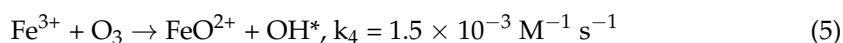
Catalytic ozonation is rarely implemented due to its unjustifiably high energy requirement for ozone generation compared to the removal rates offered, in comparison to competing advanced treatment processes that are better understood. This is largely attributed to an absence of significant regulatory or economic justification for the use of ozone as a wastewater treatment [7,16,23–26]. Where biological treatment is suitable, the high cost of ozone generation can be mitigated significantly by primary and secondary treatments that reduce the ozone demand of the water [23–25]. Where catalytic ozonation is prohibitively expensive, it is hoped that further optimization with the iron electrolysis-catalyzed ozonation (ECO) process could render it applicable to more situations.

Traditional ozonation and catalytic ozonation reactions are numerous and are dictated by the characteristics of the water matrix. Catalytic ozonation, encompassing the ECO process, can be thought of simply as the addition of a readily available substrate to an ozonated solution, increasing the rate of ozone decay. The main factors affecting the breakdown of ozone in natural waters are alkalinity and organic matter [15]. At acidic pH, the reaction is dictated predominantly by interaction with water molecules and dissolved organic matter [15,27,28]. At neutral to basic pH, the reaction can additionally be initiated by hydroxide ions [15,27,29,30]. Where alkalinity is present, the breakdown of ozone is generally inhibited, as carbonate species react quickly with hydroxyl radicals, interrupting or ending the catalytic breakdown chain of reactions which can otherwise occur [15]. The addition of organic matter increases the rate of ozone decay, as ozone molecules react preferentially with electron-rich molecules like aromatics [15,31]. This reaction typically initiates ozone breakdown, which is generally described as ozone gaining an electron from a dissolved organic molecule to become an ozonide radical which can decompose into an atomic oxygen radical and oxygen molecule, with the former reacting with a water molecule to form a hydroxyl radical and hydroxide ion [32,33].

Traditional ozonation and catalytic ozonation are intensified by electrolysis, generating catalysts on demand and in situ, as well as by providing highly reactive electrode surface areas [34]. It has long been known that certain naturally occurring transition metal ions like Fe^{2+} have been shown to exhibit enhanced ozone decomposition. By promoting ozone decomposition intentionally, researchers have consistently demonstrated extremely high removal rates of even many ozone-resistant contaminants [19–25].

In the homogeneous catalysis of ozonation with Fe^{2+} , the following reaction is accepted [35]:





Iron ions are generated by electrolysis of the anode as Fe^{2+} in Equation (1) [36]. In deionized water without additives and below pH 2.5, soluble iron ions exist as Fe^{3+} ; between pH 2.5 and 8, soluble iron is entirely Fe^{2+} while Fe^{3+} species exist as oxides and hydroxides; and above pH 8, soluble iron ions are hydrolyzed within minutes [36,37]. It has been shown that even in oxygen-saturated solutions iron electrolysis still generates Fe^{2+} preferentially, with it persisting for upwards of 1 min even at pH 7.5 [36]. The dissolved Fe^{2+} then reacts with dissolved ozone to form a ferryl ion which quickly hydrolyzes to form a hydroxyl radical (Equations (2) and (3)). The ferryl ion can also react with Fe^{2+} , which creates a parasitic drain on the reaction (Equation (4)) [19,35,38]. There is some contribution to ferryl formation by Fe^{3+} but it is kinetically negligible in comparison [39].

The heterogeneous catalytic ozonation process also contributes to the formation of hydroxyl radicals. It has been found that ozone is attracted to surface hydroxyl and Lewis acid sites [40–42]. It was recently proposed that ozone can interact with the Fe^{3+} in Fe_3O_4 and FeOOH , also referred to as magnetite and goethite, by adsorption to a surface Lewis acid site, displacing a surface hydroxyl group, forming a hydroperoxyl radical, and reducing the iron adsorption site to Fe^{2+} [42]. After the first use of low-carbon steel electrodes, surface rust is easily formed, as electrolysis and ozone scour their surfaces, allowing the oxygenated water to easily form iron hydroxides, hydroxy-oxides, and iron oxide complexes with water [36]. The natural rusting process, accelerated here within ECO, forms a highly suitable surface for catalytic ozonation with no additional preparation or cost. Repeated use of electrodes can lead to passivation, however, which can reduce the rate of iron generation and other relevant surface-level catalytic reactions [36]. The act of passing a current through any submerged electrode at elevated voltages also introduces oxygen evolution as a possible generation mechanism for hydroxyl radicals, though this is not explored here [37]. The extent to which heterogeneous or homogeneous catalytic ozonation reactions promote the decomposition of ozone in ECO is not investigated in this experiment.

Many articles have been published covering catalytic ozonation enhanced by iron [24,34,39,42–48]. It has been found, however, that iron produced electrolytically can be used more effectively than the addition of iron salts, especially when iron salts are not supplied throughout the reaction [49]. This is one of many distinctions between catalytic ozonation with iron and the ECO process. Due to the recency of the field of ECO research, few papers were found that presented optimization of parameters using steel electrodes for catalytic ozonation. The first study conducted with this reactor optimized the removal of 84 mg/L TOC from a tap water and dextrose solution. With ozonation fixed at 10 L/min and approximately 4 g/h supplied over one hour, removal increased steadily from 4 mA/cm² to 12 mA/cm² (approximately 0.5–1.5 A, with nearly equivalent electrode size and separation used here) peaking at 63% at pH 9 and the highest current [49]. The highest improvement in effectiveness was always found when comparing ozonation and the lowest level of applied current [49]. One research team led by Perumal Asaithambi and associates has published multiple relevant and influential ECO studies [50–55]. Their first paper on ECO removal of 2500 ppm COD from distillery effluent found that at a fixed 15 L/min and 2 g/h ozone supply for 4 h, removal improvements reduced beyond 3 A/dm² (approximately 0.67 A applied current, or equivalent to 1.04 A in the current system due to larger electrodes) [50]. Their next paper on the ECO system evaluated the removal of COD from distillery effluent using a response surface methodology and found that removal of ~2000 ppm COD was optimized at the same ozone supply, 3.85 A/dm² applied current with electrodes 1.2 cm apart (approximately 0.97 A applied current or equivalent to 1.38 A here), initial pH of 6.15, and a reaction time of 2.2 h. Their research

now pursues ECO systems enhanced with UV, hydrogen peroxide and other developments in catalytic ozonation.

The comparison of performance and reactor setups between articles is fraught by inconsistent units, different design elements like aerators, measurement systems and methodologies, temperatures, water parameters, and more factors that affect catalytic ozonation and ECO. Most articles found that used ECO systems had little to no optimization of parameters or insufficient detail to be comparable. In addition to the articles discussed above, the following twenty-five articles all contain some level of investigation into the iron-ECO system [18,56–78].

This study builds upon the work of Heebner and Abbassi (2022) and advances the objectives outlined in the authors' NSERC Proposal [49]. The previous investigation into ECO required some estimation and conversion of ozone gas flow or current density values. Multiple publications were chosen that reported optimization of iron-catalyzed ozonation reactions near concentration ratios of 0.25 to 2 M Fe^{2+} to 1 M O_3 [79–82]. The previous work tested ECO performance between ratios of average molar concentrations of total iron and DO_3 of 1:1 and 7:1 (0.083 mM to 0.58 mM) [83]. The current study expands on this range and bases its selection of values on molar generation rates of iron and ozone rather than average concentrations. Six values were tested between a range of molar generation rate ratios of 62:1 to 12:1 supply rate of ozone to generation rate of iron. The ozone supply rates chosen kept the range of measured DO_3 within 4 to 9 mg/L, which conforms with most ozonation tests in the literature and keeps the rate of the absorption of gaseous ozone high. Experiments were conducted across a range of dissolved iron concentrations and initial pH values to identify conditions for optimized catalytic performance. Each trial was sampled after 30 min. The rationale is described further in Methodology Section 2.2. The primary objective is to determine the optimal ratio between dissolved iron and ozone to improve the design and efficiency of a novel electrocatalytic ozonation process.

2. Materials and Methods

2.1. Materials and Experimental Setup

The ECO setup used to carry out this investigation is shown in Figure 1. The reactor is constructed of a 3.5 L section of a clear PVC cylinder with PVC bottom and top. The bottom has a bulkhead connecting the ozone flow to a 3-inch ceramic air stone, producing medium bubbles. Two other bulkheads at the bottom and middle of the tank allow for a constant 1.5 L/min recirculation of reactor water through chemically resistant Tygon tubing and a peristaltic pump. This mixes the bulk while allowing for the separation of a DO_3 electrode from the iron electrodes housed in a custom PVC flow cell [38]. The top has an outlet for gas to flow through an ozone destructor before venting and two holes for steel rods to pass through, connecting the DC power supply to the submerged electrodes.

Low-carbon iron bar stock (AISI grade 1018, 2 in. by 1/8th in.) was used as electrode material. The submerged volume of each electrode was approximately 12.6 cm by 5.1 cm by 0.32 cm and the geometric surface area of one electrode face is 64.0 cm². A BK Precision 9110 60 V DC power supply was used for trials including electrolysis. Total iron was measured with the 1,10 phenanthroline spectrophotometric method, via Hach pre-packaged reagents and Hach method 8008 [84].

Reaction water was prepared in batches to maximize the consistency of tertiary butanol (TBA) concentrations between runs. Deionized water was used exclusively in this experiment. The pH of the reaction water was adjusted with 1 M solutions of hydrochloric acid and sodium hydroxide. Batches were prepared with 1.30 mM sodium chloride to provide the necessary conductivity for the pH and the dissolved ozone probe's electrochemical sensors. TBA was added from a prepared 1 M solution to 0.73 mM. The first three batches

of reaction water were made in a 65 L drum while the remaining batches were prepared in a 25 L Nalgene carboy. All batches were prepared by diluting the required TBA and sodium chloride to a 5 L solution, then adding measured transfer pails of deionized water to the required volume. When a batch had been sitting for more than three hours, the containers were mixed by pump for at least 15 min to ensure a uniform product. Reaction water was stored at room temperature (21 °C) away from direct light. TBA concentration was monitored and found to be constant while reaction water was stored between experiments.

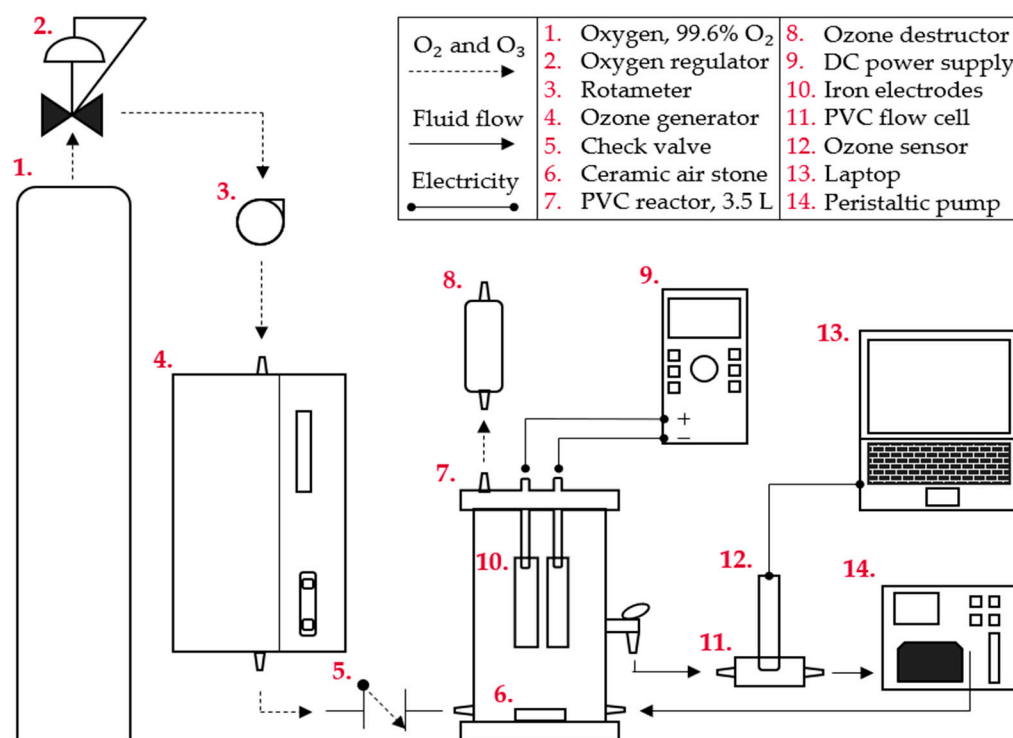


Figure 1. Experimental layout showing reactor and data collection equipment.

2.2. Experimental Design Process

The experimental methodology is laid out in Table 1. A total of 88 trials were performed, including 54 unique combinations of ECO factors, 4 center point replicates, 12 using oxygenation and ozonation without electrolysis, and 12 using electrolysis without ozone. The non-ECO trials were all repeated in triplicate. A further 6 samples were taken over a week to evaluate whether any TBA was lost during the storage of reaction water. All trial combinations were sampled in triplicate upon creation, yielding approximately 372 individual samples.

The planned experimental design had 3 levels of applied ozone and 6 levels of applied current each. The applied current levels were increased proportionally to the increased output ozone concentration, resulting in 18 individual applied currents. The chosen levels of applied current are shown in Table 2.

The scaled applied current values were intended to be condensed and form three data points for each combination of initial pH and ratio of ozone to iron generation, referred to as excess ozone supply (EOS). EOS ratio denotes the ratio between the molar generation rate of ozone divided by the molar generation rate of iron. The ECO trial factor levels were initially selected to maintain a consistent ratio of excess ozone supply across each initial pH and ozone supply combination, while covering an increasing range of applied current and ozone values. The applied currents were first chosen relative to ozone generator level 4, based on the results of the previous study [83]. The applied currents for ozone generator

levels 5 and 6 were chosen by increasing the first values in proportion to the 24.5% and 46.4% increases in respective ozone mass generation rates. Choosing to scale the applied currents with ozone production allowed for the grouping of points by EOS. This created a new category of data, transforming the 18 individual combinations of ozone generation intensity and applied current, multiplied by three pH values, into 6 points of EOS data, with three replicates each, per pH value. The intention was to explore a new way to model and analyze ECO trials using EOS as a descriptor for catalytic performance.

Table 1. Data collection procedure for the combination of each factor, 3 levels of ozone supply rate, and 18 levels of applied current at 3 levels of initial pH.

Reaction Water Batch	Purpose	Ozone Level	Applied Current Levels	Repetitions	Calibration Samples	Actual Sample Quantity
1	ECO Trials, pH 5	4, 5, 6	18	1	9	67
2	ECO Trials, pH 7	4, 5, 6	18	1	18	73
3	ECO Trials, pH 9	4, 5, 6	18	1	9	67
4	Three Oxygen, Ozone, pH 7	0, 5	0	3	9	27
5	Ozone only, pH 5 and pH 9	5	0	3	9	27
6	Coagulation, pH 5	NA	2	3	9	27
7	Coagulation, pH 9	NA	2	3	9	27
8	ECO at mid-point, pH 7	5	1	4	9	24
9	Testing TBA decay in storage	NA	N/A	6	15	33

Table 2. Ozone generator levels and corresponding levels of applied current tested in the ECO factor trials.

Ozone Generator Level	Planned Ozone Generation Rate (g/h)	Actual Ozone Generation Rate (g/h)	Applied Current Level (Amps)					
			1	2	3	4	5	6
4	3.62	4.10 (3.94–4.64)	0.065	0.108	0.151	0.194	0.237	0.323
5	4.51	5.43 (5.09–5.96)	0.080	0.130	0.190	0.240	0.300	0.400
6	5.30	6.23 (6.02–6.44)	0.100	0.160	0.22	0.280	0.350	0.470

2.3. Estimating Ozone Production

Three levels of applied ozone were tested, corresponding to the ozone generator's settings of 4, 5, and 6 out of 10. The corresponding ozone concentration and production are estimated from values made publicly available by Oxidation Technologies LLC., Inwood, IA, USA, based on their independent test results [85]. Their data may not be representative of current system performance due to different oxygen concentration, pressure, and flow rates, as well as materials and implementation. The ozone supply rate of this VMUS-4 unit was verified manually using the Indigo method [86]. The performance of each generator setting as measured was found to be within 10% of the values reported by Oxidation Technologies and were therefore considered similar enough to this unit to be used in estimations of ozone supply and concentration without a direct measurement device.

An AquaSensors DataStick Dissolved Ozone Measurement System was used to record DO_3 values for each trial. The DO_3 concentration reported digitally was verified using the Indigo Method as within 0.1 mg/L [87]. The DO_3 value reported by the probe seemed to change as air or ozone accumulated in its flow cell throughout testing, which caused swings up to 2 ppm after shaking the bubbles free from the flow cell. The DO_3 probe values were not validated to be accurate throughout the length of the ECO trials in this system. Comparison between shaking and not shaking the flow cell throughout testing seemed to show that reported DO_3 concentrations varied by less than 0.5 ppm.

To estimate ozone production in experimental conditions, the ozone generator performance curves for output concentration based on flow rate were found for each setting. The equations were then used to convert incoming moles of oxygen to moles of ozone output, specific to incoming flow and generator setting. Oxygen flow rates were then converted to standard liters per minute using room temperature and recorded gauge and nearby atmospheric pressure, then to molar oxygen flow, and finally to molar ozone flow. Data were reported and analyzed using ozone generation rate in grams per hour, as well as ozone dose in grams.

2.4. Estimating and Measuring Iron Production

Total dissolved iron was measured once at the end of each trial using Hach prepackaged reagents and spectrophotometric methods. These methods were used for the previous study and found to be precise and accurate, although measured iron concentrations during reactions usually varied from the amount predicted by Faraday's law of electrolysis, which was also observed previously [83]. The amount of iron measured was 8.8% lower than predicted on average. This was attributed to the settling of heavy iron hydroxides near the outside edges of the bottom of the reactor. Since the dissolved iron testing methodology withdrew between 10 mL and 250 μL of reactor water, it is likely that variations in sampling methodology and settling of hydroxides impacted the observed concentration. It is also possible that electrode passivation contributed, though this was not investigated. Measurement discrepancy is mitigated by using the exact amount of electrolytic iron predicted in calculations and modeling.

2.5. Measurement of Performance with Tert-Butyl Alcohol by Headspace Gas Chromatography Mass Spectrometry

The performance of the ECO system was defined as its capacity to degrade tert-Butyl Alcohol (TBA). TBA has been used as a hydroxyl radical probe and scavenger in many studies to estimate the quantity of hydroxyl radicals being produced [27,88–92]. TBA reaction rates with ozone and hydroxyl radicals are $k_{\text{O}_3} = 1.1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ [15,92] and $k_{\text{OH}\cdot} = 6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [93]. Due to this disparity in rate constants, the degradation of TBA is often attributed nearly exclusively to hydroxyl radical exposure, and has been used frequently to investigate hydroxyl radical production in advanced oxidation systems [90,94–96]. It was assumed that most of the degradation of TBA in this reaction not described by physical or chemical removal processes is the product of hydroxyl radical degradation. The concentration of TBA was chosen to be 0.73 mM to produce accurate and linear chromatographic responses to TBA at high removal percentages. Testing of the measurement method was conducted prior to data collection and found that ion response was linearly correlated with $R^2 \geq 0.99$ between 0.0091 and 0.728 mM.

Headspace Gas Chromatography Mass Spectrometry (HS-GC-MS) was used to evaluate concentrations of TBA [97–100]. The previous study required the adaptation of some existing chromatographic methods to the equipment available and used solid phase microextraction-enhanced GC-MS to better capture the small molecules resulting from the catalytic breakdown of TBA [83]. The current study chose direct HS-GC-MS instead, for its

improved process and data consistency alongside reduced cost and complexity. The HS-GC-MS analysis parameters are included below in Supplementary Materials (Section S1).

The data points discussed in this study were developed from chromatographic signals (the identified TBA peak area) into removal rates associated with each combination of ECO factors. Fresh samples, all having the same initial TBA concentration, and their respective chromatographic processing order, were used to generate a curve representing the initial TBA concentration signal for all samples. This compensated for the GC-MS system's declining response to TBA throughout chromatographic data collection. Using each triplicated sample's average signal and sample order, an average signal was developed for each trial, which was then subtracted from and divided by the initial TBA concentration curve at that sample order to generate a removal rate for that trial. The data collection and correction process is elaborated on in Supplementary Materials (Section S1).

3. Results

3.1. Stability of TBA in Prepared Reaction Water

Since each trial took approximately 50 min from set up to reset, sampling took place over three weeks. It was investigated whether some evaporation of TBA could take place during the longest storage period of 5 days. Samples were taken immediately after the creation of a 60 L batch, treated and stored in the same fashion as all other batches (described in Section 2.1) as well as daily for 6 days. Fresh and aged samples were compared three ways with ANOVA tests. Comparing all fresh samples against both each day's aged samples and all aged samples grouped showed no significant difference between any group of samples stored for 0, 1–5, and >0 days. A summary of the ANOVA results is included in Supplementary Materials (Section S2.1). Given the absence of any significant effect, the comparison between the initial TBA concentration of the batch and each subsequent sample measured is considered a reasonably accurate measurement of TBA removal.

3.2. Effect of Oxygen and Ozone on TBA Removal

3.2.1. Experimental Results of Oxygenation and Ozonation Trials

Oxygenation and ozonation were tested on their own to determine whether either factor had a significant effect on TBA removal in the absence of dissolved iron. Bubbling oxygen at pH 7 and bubbling ozone at each pH level were tested with three replicate trials each. The percentage TBA removal rates and removal rates per gram of ozone supplied for each group are listed in Figure 2. Bubbling oxygen was used to determine whether there was any significant removal of TBA associated with the physical bubbling of the solution by gas stripping or any other baseline loss. The average removal of the oxygenation trials was -0.55% removal, with a standard deviation of 2.65% . Since no TBA could be created and no notable changes were found in the chromatograph, this result is assumed to be zero, and all TBA removal figures are believed to result from ozonation or catalytic ozonation reactions.

The ozonation trials showed moderate removal scaling from 8.2% to 44.8% from pH 5 to pH 9. Comparing TBA removal by pH group, only the ozonation trials at pH 9 were found to be significantly different than pH 5 and pH 7. When comparing ozone-normalized removal rates, all three groups were found to be significantly different. A summary of the ANOVA results is included in Supplementary Materials (Section S2.2). The small change between initial pH groups 5 and 7 followed by the significant uplift between pH 7 and 9 shows that the mechanism for increased removal increases exponentially in this pH range. This removal is assumed to be hydroxide-induced ozone decay, due to the absence of any other factors in the solution. The reaction rate kinetics of ozone decay were not measured in this study.

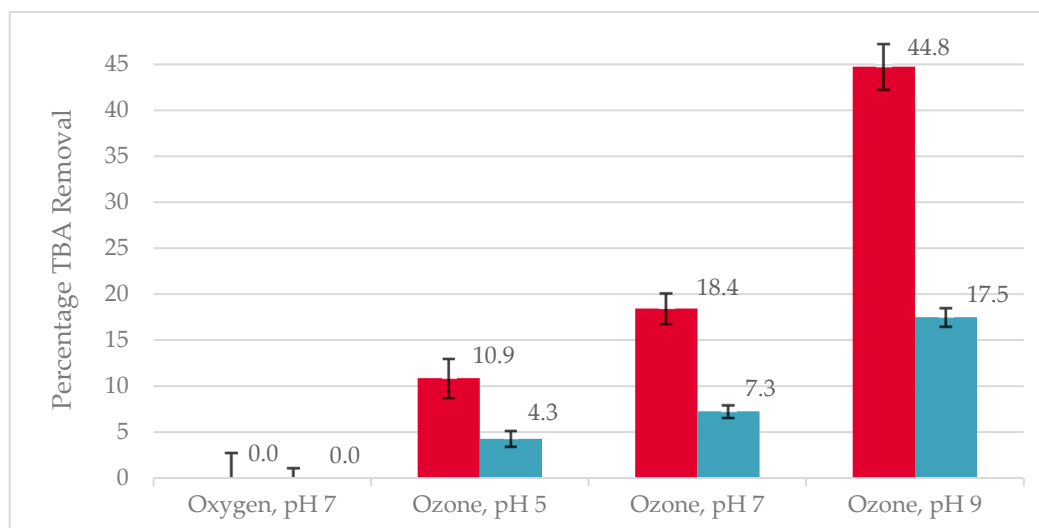


Figure 2. Average percentage removal (in red) and ozone-normalized percentage removal (in blue) of TBA by oxygenation at pH 7 then ozonation at pH 5, 7, and 9.

3.2.2. Estimating TBA Removal by Direct Ozonation

The average dissolved ozone concentrations for each trial were used to determine the fraction of TBA removal attributable to direct ozonation. The direct reaction between TBA and ozone was calculated using a second order rate equation, first order with respect to both compounds [92,101,102]. The reaction rate constant was calculated from the Arrhenius coefficient $K_{\text{TBA-O}_3} = 1.52 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 23 °C from [15,92]. The average DO_3 concentrations for the pH 5, 7, and 9 trials were 8.42, 8.74, and 4.99 ppm, resulting from all trials receiving an estimated 2.54 to 2.56 g of Ozone. The average DO_3 concentration for each trial is included alongside all collected trial data in Supplementary Materials (Section S3). Using the average DO_3 concentration recorded for each pH level, the removal of TBA by direct ozonation was estimated with Equation (6) to be less than 0.05%. The direct reaction between TBA and ozone is negligible compared to the removal rates observed.

$$\text{TBA removed} = k_{\text{TBA-O}_3} \times [\text{TBA}]_{\text{avg}} \times [\text{DO}_3]_{\text{avg}} \times (\text{Time elapsed}) \quad (6)$$

The difference in pH 9 ozone concentration is a response to the increased concentration of hydroxide ions present initiating the decomposition of ozone. It was observed that at pH 9, the first 5–20 min of each 30 min trial recorded very low concentrations of DO_3 compared to the other initial pH groups, which increased with trial duration as pH decreased. Using the observed concentration of DO_3 in the modeling equation seems to misrepresent the actual amount of ozone available to the ongoing reaction at steady state, since the same amount of ozone was supplied for each reaction. The consumption rate of DO_3 at pH 9 appeared much higher than in the other trials, which supports the observed differences in TBA removal rates. Both the reported concentration and an average concentration from the lower pH trials will be used in modeling and the results provided for discussion.

3.2.3. Estimating the Ozone Decay and Comparison with Observations

The decomposition of ozone in water is particularly challenging to model and is required to be measured specifically for each water source prior to any work attempting to estimate ozonation kinetics [103]. The rate of decay of ozone in water is highly dependent on the water characteristics [103]. A review of ozone decay kinetics found that published ozone decay estimates varied significantly, with ozone half-life estimates ranging from 1000–20,000 s at pH 5, shrinking to 20–400 s at pH 9 [103]. Their conclusion was that initial

pH, alkalinity, temperature, other inorganic or organic constituents, movement and mixing all effect the rate of ozone transfer observed decay [103].

TBA is extremely resistant to ozonation, as shown above, so its reaction rate with hydroxyl radicals $k_{OH\bullet} = 6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ is the primary degradation pathway in ozonation reactions [90]. It was assumed initially that the decomposition of ozone by hydroxide ions would account for the majority of TBA, but the previous estimation is an oversimplification of the reaction mechanism. The initiation step of the ozone–hydroxide interaction is often reported as having a rate of $k_{O_3-OH^-} = 70 \text{ M}^{-1} \text{ s}^{-1}$ [15,101]. An estimation of hydroxide-induced decay was conducted using Equation (7), with the average hydroxide concentration and DO_3 concentrations recorded during the pH 7 ozonation trials. The amount of ozone decay estimated accounts for less than 0.1% of removal.

$$\text{Ozone Degraded} = k_{O_3-OH^-} \times [\text{DO}_3] \times [\text{OH}^-], k = 70 \text{ M}^{-1} \text{ s}^{-1} \quad (7)$$

An equation posited by Sotelo et al., 1987, was used to estimate ozone decay including temperature and pH as factors, included below as Equation (8) [104]. The estimated rates were 3.45×10^{-6} , 5.92×10^{-6} and $1.17 \times 10^{-6} \text{ M/min}$ at 23°C and the average pH values for the ozonation trials. These molar decay rates corresponded to roughly 0.104, 0.178, and 0.351 mM of ozone decayed over the duration and volume of the reactions. These values are comparable to the observed TBA removed of 0.082, 0.138, and 0.336 mM, respectively. The ratio of modeled ozone decay to observed TBA removal was 1.27, 1.28, and either 0.50 or 1.04, whether the lower observed DO_3 concentration for pH 9 is used, or if the DO_3 is taken to be the same as the previous two trials, since the ozone supply rate was unchanged. The difference between those two values highlights the need for increased data density with respect to time, in order to more accurately integrate these kinetic estimates. The similarity between the rate of increase of the estimated ozone decay and observed TBA removal suggests that the faster rate of ozone decay is responsible for increased TBA removal. The ratio between the observed ozone decay and TBA removal is unchanged at pH 5 and 7 but drops significantly at pH 9. TBA removal at pH 9 becomes 23% or 156% more efficient per mol of ozone supplied (depending on which ozone concentration is more appropriate in Equation (8)). Beyond the obviously higher removal rate achieved, this shows that more efficient removal took place. There were insufficient data collected on the decay kinetics of ozone in the reaction water to comment further on the exact reaction pathways involved. There could have been other confounding effects participating, like the effect of carbonate diffusing into higher pH solutions, or the effect of pH on the ozone breakdown pathway and its overall hydroxyl radical yield, or simply that the increased removal rate led to a higher concentration of TBA breakdown products, which allowed ozone to more efficiently or rapidly decay in the system.

$$\begin{aligned} &\text{Rate of Ozone Decay (mol/L} \times \text{min)} \\ &= 3.26 \times 10^5 \times e^{(-4964/T)} \times [\text{O}_3] + 5.69 \times 10^{18} \times e^{(-10130/T)} \times [\text{OH}^-]^{0.5} \times [\text{O}_3]^{1.5} \quad (8) \end{aligned}$$

3.3. Effect of Electrolysis on TBA Removal

The potential effect of electrolysis on TBA removal was investigated. Three replicates of four trial combinations were selected to represent the near-corner values of each condition: pH 5 and pH 9, and 0.080 A and 0.400 A applied current. Testing was conducted with oxygen bubbling to provide a similarly turbulent hydraulic and electrical environment to the ECO testing data, as well as a similar oxygen-saturated solution for the oxidation of iron produced. Removal was expected to be near zero or slightly positive due to the potential for hydrated electrons or water oxidation at the electrodes reducing TBA. Removal values for all trials were below 3%, as shown in Figure 3, except for one outlier which was removed.

The low standard deviation and the lack of a trend in standard deviation associated with these removals suggest that changing applied current or initial pH has no effect on the data quality as gathered by HS-GC-MS, as expected.

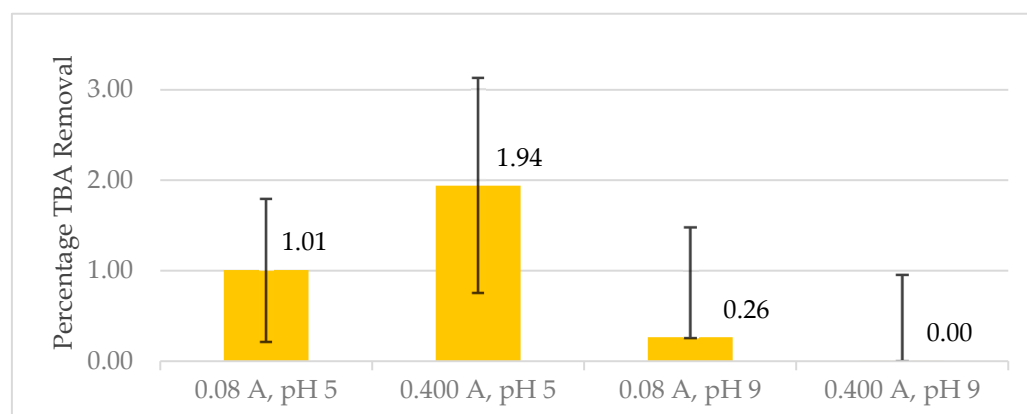


Figure 3. Measuring TBA removal at pH 5 and pH 9 at the second lowest and highest applied current values.

Three ANOVA tests were conducted to compare the effects of pH and applied current on TBA removal. A Games–Howell means confidence interval comparison showed no significant differences in TBA removal. The least insignificant difference was a 1.24% reduction in removal between the pH 5 and 9 groups with $p = 0.064$. No significant difference in TBA removal was expected between groups since TBA is completely miscible with water [105]. A summary of the ANOVA tests is included in Supplementary Materials (Section S2.3). These findings support the idea that essentially all removal observed is obtained by some degradation pathway ozone.

3.4. Electrolysis-Catalyzed Ozonation for TBA Removal

3.4.1. Results of the ECO Trials

This study evaluated the capacity for catalytic activity in ECO trials by their rates of TBA removal. The experimental data collected for each trial are included for reference in Supplementary Materials (Section S3). The results are presented below, sorted by initial pH levels 5, 7, and 9, in Figure 4. Elevated removal was seen in almost all ECO trials compared to those only featuring ozone, oxygen, or electrolysis separately. ECO removal of TBA was observed at rates between 7% and 77% of the initial 0.73 mM TBA concentration. Removal trended upwards with the increase in applied ozone, current, and pH. The highest and lowest removal rates always corresponded to the combinations of the highest and lowest supplied ozone and applied current rates, respectively.

The highest removal rates were 76.5%, 72.3%, and 79.0% for pH 5, 7, and 9 groups, respectively. The average of those points (75.9%) corresponds to 0.55 mM TBA removed. Since TBA is highly resistant to ozonation and unaffected by electrolysis, these removal rates present a reasonable approximation of the system's minimum capacity to remove substances with similar resistances to ozone [80].

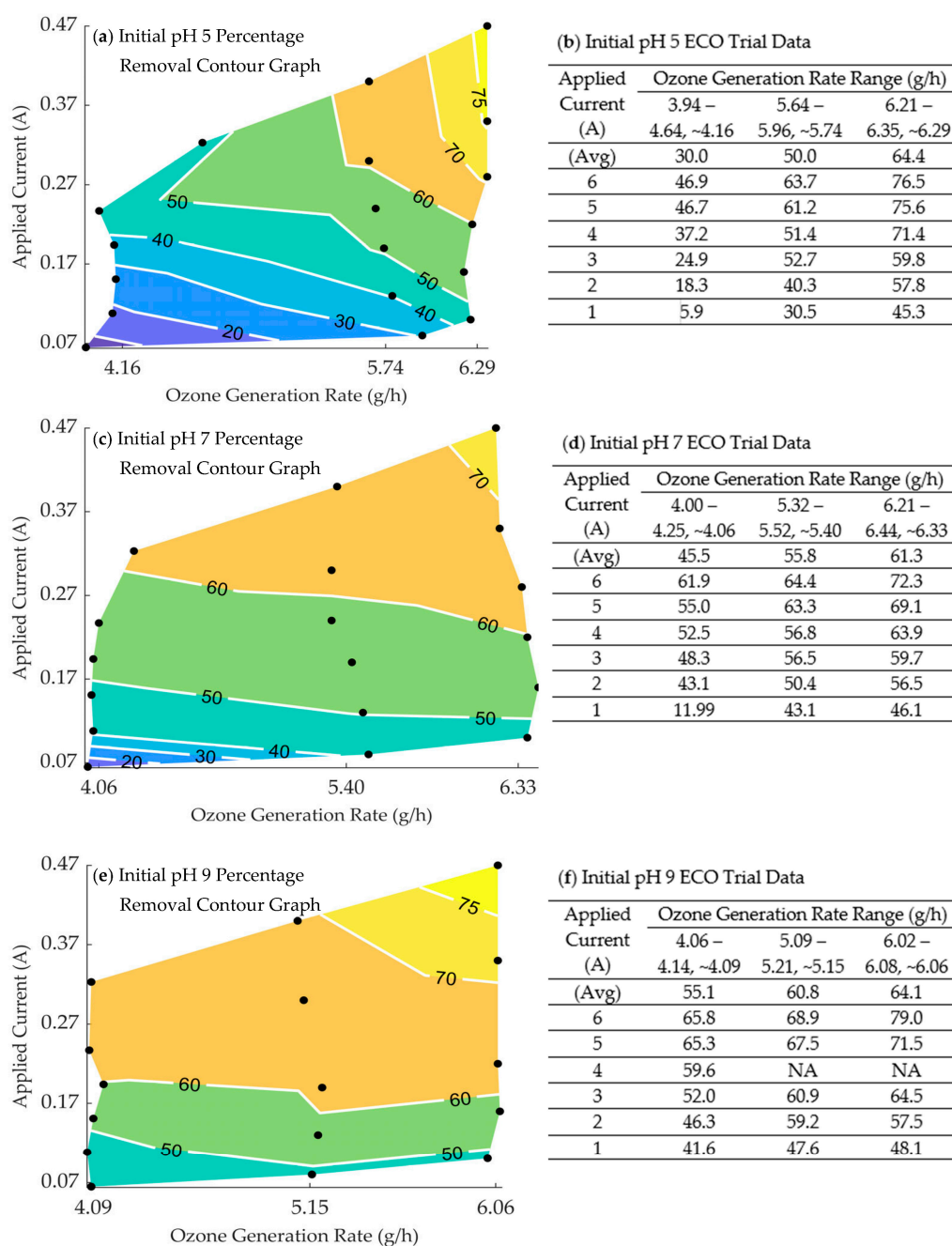


Figure 4. Contour graphs and tables presenting percentage TBA removal results from the ECO trials. (a,b) show initial pH 5 results, (c,d) show initial pH 7 results, and (e,f) show initial pH 9 results.

The lowest removal rate of 5.9% was observed at pH 5 and 0.065 A, followed by 12% at pH 7 and 0.065 A. The first pH 5 point was the first trial sample measured after the initial set of calibration points and is believed to be skewed low due to an increased GC-MS response to TBA observed after the system was allowed to rest, referred to in Supplementary Materials (Section S1). Taking only the final triplicate to represent this trial results in a removal rate of 9.9%, which appears more consistent with the other data points nearby. The pH 7 point appears to have been affected similarly. Compounding this, the initial supply rate of ozone was constrained to a greater extent than in subsequent trials due to a faulty oxygen regulator which was unable to accurately constrain the initial high pressure of the fresh oxygen cylinder. This caused the variation in observed ozone generation rates, as shown on the x-axes of Figure 4a,c,e.

The results of the ECO trials with an initial pH of 7 are shown in Figure 4c,d. The highest removal rates were similar to the pH 5 results, as were the lowest. The lower levels of applied current at pH 7 had significantly higher removal rates compared to the pH 5 trials. The rising minimum removal rate is also seen comparing the pH 9 trials to those from the lower two pH groups. This effect is attributed to the increased pH itself, as the increase in hydroxide ion concentration increased the rate of ozone decomposition (discussed in Section 3.2.2) [103,104].

In the trials using only ozonation, the average removal rates of the pH 5, 7, and 9 groups were 10.9%, 18.4%, and 44.8%, respectively. The ECO trials' removal rates improved far less with increased pH, with average removal rates by pH group of 48.1%, 54.1%, and 60.0%, respectively. This is thought to be the result of the generated Fe^{2+} competing with ozone for hydroxide ions and forming iron(II) hydroxide [106].

The results of the ECO trials with an initial pH of 9 are shown in Figure 4e,f. The highest removal rate is similar to that from the pH 7 and 5 trials, but the minimum removal rate was improved significantly. This is assumed to be the result of the higher hydroxide concentration, discussed above and in Section 3.2.2. The minimum removal values reported at pH 9 overlap with those reported at pH 7, ignoring the lowest point.

3.4.2. Observation of Removal Rate Trends in ECO

The results of the ECO trials were studied for trends that might reveal areas of higher or lower catalytic removal, with respect to the combination of iron and ozone supply rates at each pH level. Analysis of the removal rate data and estimated ozone supply revealed that variance in the ozone supply rate increased the variance associated with the final removal rate data. To better compare the removal rates between trials, removal rates were divided by the estimated supplied ozone dose, referred to as ozone normalization.

Figure 5 shows the individual values and average pH group trends of ozone-normalized removal rates. The individual values are poorly correlated above the pH 5 trial, reducing in correlation with increased initial pH. A slight trend is visible in the individual data at pH 7 and pH 9, showing that ozone-normalized removal rates were generally decreased with increasing ozone generation. The highest ozone-normalized removal rates occurred at ozone level 4 for both pH 7 and pH 9, with 29.1% at 0.323 A for pH 7, and 32.1% and 32.2% at 0.237 A and 0.323 A at pH 9. At elevated pH, either the incremental addition of ozone or increase of applied current associated generally resulted in lower ozone utilization efficiency. This shows that increasing the rate of ozone application does not accelerate the rate of removal, which was already known based on the reaction kinetics described in Section 3.2. At pH 5, this trend was not present, with the highest ozone-normalized removal rate occurring at ozone level 6 and 0.47 A, as 24.1% per gram of ozone supplied. The ozone-normalized removal at pH 5 was almost always less effective than at pH 7 or 9 at the applied current values tested. The lack of correlation in the pH 7 and 9 trials makes speculation difficult, as it suggests there were likely other factors or experimental errors influencing results. All pH groups exhibited similar behavior trends when all ozone generation levels were averaged, with increasing pH corresponding to between 2 and 4% increased removal per gram of ozone supplied. The increased correlation between the averaged data points is likely due to the reduced number of points used rather than revealing a trend.

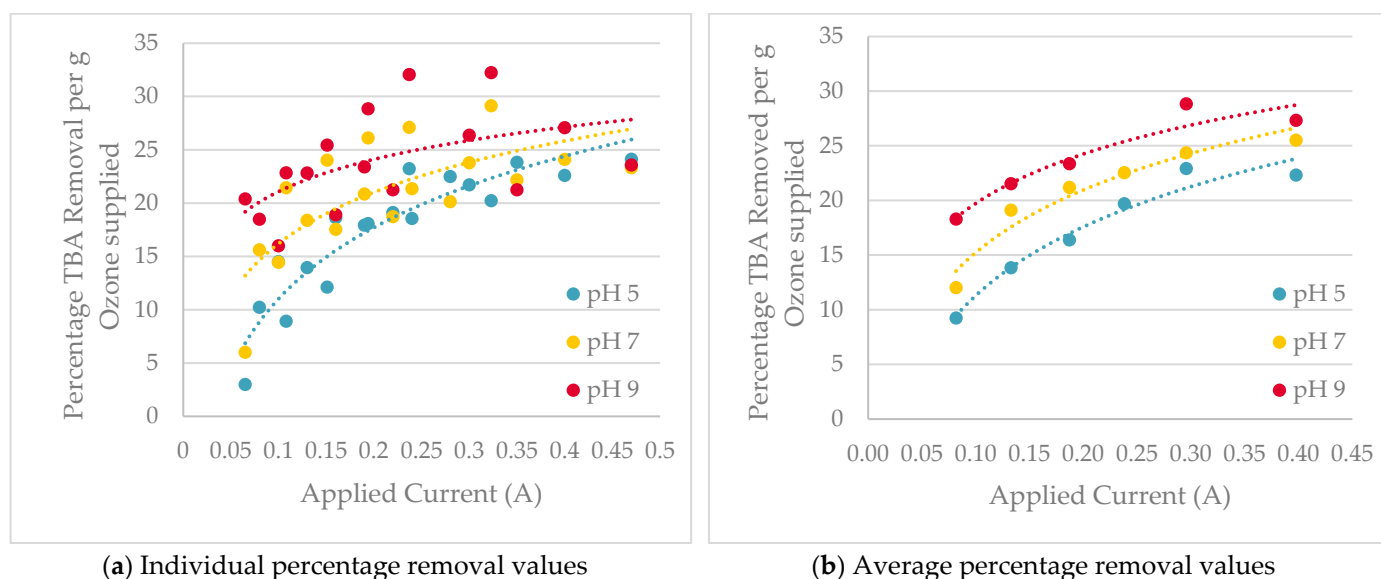


Figure 5. Plots of ozone-normalized % TBA removal and associated trends, grouped by initial pH level (pH 5 in blue, pH 7 in yellow, pH 9 in red). (a) Plotted individual values and (b) the averages of the three levels of ozone generation tested.

3.4.3. The Effect of ECO Factors on pH

A change in pH was observed during the ozonation and ECO trials, but not during electrolysis. The change in pH for each ECO trial pH group is recorded below in Table 3. During the oxygenation trials, an average decrease in pH was observed of 0.77 due to an outlying final pH value of 5.3 recorded during one repetition. Since dissolved oxygen has a negligible impact on pH, this result is assumed to be skewed, compared to the other two repetitions' values of 6.86 and 6.95, which align with expectations. Due to the lack of buffer in the tested solution, it is also possible that the pH was poorly adjusted or not properly mixed during that outlying result.

The ozonation trials saw pronounced acidification of the reaction water. It has been observed that high doses of ozone can result in acidification of deionized water, citing the belief that ozone continues to react preferentially with hydroxide ions [107]. The average mass of supplied ozone during the ozonation trials was 2.55 g, corresponding to 17.7 mM (850 mg) O_3 per liter, or, with respect to the 0.73 mM (54 mg) TBA per liter, the ratio of supplied ozone to TBA was 24.3:1 by molarity or 15.7:1 by mass. Since all TBA is dissolved, the ozone dose by dissolved organic carbon was 850 mg O_3 by 35 mg DOC, or 24.3 mg/mg. Testing was not performed separately to determine the amount of pH change resulting from ozonation of each reaction water pH.

The electrolysis trials were conducted at pH 5 and pH 7 with applied currents of 0.08 and 0.400 A, respectively. A basifying effect was observed in the initial pH 5 group, with an average pH change of +0.23 at 0.08 A and +3.8 at 0.400 A. This was not observed in the initial pH 9 group, where both low and high levels of applied current rose by +0.25 and +0.16 units, respectively. The change cannot be attributed to an outlying replicate, all tested samples conformed to those averages. The strong upwards shift in the pH 5, 0.400 A group is likely the product of multiple phenomena. A thorough review was recently published on the effect of iron electrocoagulation on pH, and at similar levels of applied current it was found that carbonate-stripping accounted for the majority of the observed pH changes [108,109]. A mechanism was also suggested for the formation of iron hydroxide complexes with chloride that would have a net release of hydroxide ions in solution, which was secondary to the effect of carbonate in their experiments. Due to the lack of any intentional buffering of the current reaction water, combined with the minimum of 1.3 mM sodium chloride

(increased chloride present at pH 5 from adjustment with hydrochloric acid), it may be possible that an increased amount of chloride complexing is affecting our observed pH more strongly [108]. It may also be that at the higher voltages required by the high level of applied current, the rate of hydroxide production is outpacing the rate at which iron ions are forming hydroxides, given the duration of the experiment [108].

The ECO trials showed varying pH changes according to their initial pH. There was a negligible pH change observed in the initial pH 5 group, while the pH 7 and 9 groups dropped by averages of 1.90 and 3.23 units. On average, all trials' final pH values only differed by ~0.3 pH units between groups, converging at 5.0, 5.4, and 5.7, respectively, for the initial groups. This points towards the formation of a buffered system between soluble iron ions, hydrolyzed iron complexes (that may or may not be affected by chloride, as described above), the small organic molecules present from ongoing TBA degradation, and any remaining or actively diffusing carbonate species. The data collected in this study are insufficient to speculate further on the exact reasoning as to the pH changes observed throughout the experiment. The initial and final pH values recorded for all trials are included in Supplementary Materials (Section S3).

Table 3. Changes in pH observed in ozonation and ECO Trials.

Supplied Ozone Level	Initial pH 5	Initial pH 7	Initial pH 9
Oxygen Only	NA	−0.16	NA
O3 Only	−0.61	−2.05	−3.48
Electrolysis—0.08 A	+0.23	NA	+0.25
Electrolysis—0.40 A	+3.82	NA	+0.16
ECO—Level 4	+0.08	−2.13	−3.39
ECO—Level 5	+0.15	−1.94	−3.29
ECO—Level 6	−0.07	−1.65	−3.27
ECO—Average Initial pH	4.98	7.28	9.05
ECO—Average Final pH	5.03	5.38	5.73
ECO—Average pH change	+0.05	−1.90	−3.32
ECO—Average Ozone Supply (g)	2.70	2.63	2.52

3.4.4. The Effect of Initial pH on ECO Performance

Comparing ECO removal results by pH level without normalizing for ozone, no significant difference was found between any pH level. The same comparison using ozone-normalized removal rates found that only pH 5 and pH 9 showed significant differences. The group average rates were 8.7%, 10.4%, and 12.0%, with the increase by pH group showing a steady, linear increase of 1.70% between the mean confidence intervals of the pH 5 and 7 groups, and 1.66% between the pH 7 and 9 groups. Both ANOVA tests are summarized in Supplementary Materials (Section S2.4).

The pH affects the ECO reaction in at least three ways; by hydroxide ions catalyzing ozone regardless of electrolysis, by affecting the ongoing reaction pathways of ozone, and by affecting the iron species available and their solubility. The effect of hydroxide ions on ozonation was discussed above. The effect on ozone breakdown was not determined here, as the hydroxyl radical output was the sole concern. The effect on iron as it pertains to catalytic ozonation is separated into two categories below, homogeneous and heterogeneous catalytic processes.

On homogeneous ozonation catalyzed by iron ions, the majority of research suggests that catalytic ozonation proceeds by reaction with the soluble iron ions described above [34,47,68]. The formation of FeO^{2+} (ferryl ions) and their rapid decay into hydroxyl radicals is initiated by the electrolytic supply of Fe^{2+} ions reacting with DO_3 [35]. The determination of rate constants for homogeneous catalysis of ozone by iron is inhibited by the rapid oxidation of Fe^{2+} above pH 3 [15,35]. The half-life of Fe^{2+} ions in an oxygenated solution post electrolysis is greater than 5 min at pH 6.5, but less than 2 min above pH 7.5 [36]. As the pH of an ECO process increases, the persistence of Fe^{2+} ions will decrease significantly, reducing the iron available to form ferryl ions. The accompanying increase in Fe^{3+} is a much less effective catalyst [35,110–112]. The lower lifetime of Fe^{2+} did not reduce performance in this study, likely due to a combination of continuous production and the convergence of pH towards 5–6. Similar findings were reported by Psaltou et al. in testing the degradation of another ozone resistant compound by Fe^{2+} , as iron sulphate, where the initial pH had a dramatic improvement on removal, rising from pH 3 to 6, which was roughly equal to 7, and another significant uplift at pH 8 [80]. This emphasizes the importance of the decay rate of ozone on radical production, as discussed above.

The formation of various iron oxide and hydroxide complexes enables heterogeneous processes, as described below. No articles were found specifically describing ozone interactions with insoluble iron hydroxides as a homogeneous process, although adsorption of ozone or their target compounds is often mentioned as a heterogeneous pathway for degradation [34,47,68]. Due to the breadth of possible iron species and difficulty in selectively generating them, as well as their insolubility compared to Fe^{2+} and Fe^{3+} ions, there seems to be little value in describing the exact impact of iron hydroxide species on the homogeneous ECO process. There is significant value to studies as they pertain to electrocoagulation, but this was not observed to affect TBA removal [60,68].

The pH of a solution dictates the surface hydroxylation of a catalyst based on its point of zero charge. The point of zero charge of a material is the pH where a catalyst surface is electrically neutral [113,114]. When a solution's pH exceeds the surface's point of zero charge, surface hydroxyl groups become positively charged and act as a Lewis acid [114,115]. Ozone, being attracted Lewis acids and surface hydroxyl groups, exhibits higher catalytic performance in the presence of catalysts with favorable surface hydroxylation [113,114]. Unfortunately, this study did not employ the tools required to study the exact crystal structures of both the electrodes as well as the dissolved species, or to be able to comment on the exact points of zero charges and speculate on their performances across the range of pH values tested. The iron electrodes, being carbon steel, are initially structured predominantly of ferrite with cementite inclusions known as pearlite [116]. Ferrite species are rapidly oxidized to iron hydroxide and oxyhydroxides [36,117]. These species can have points of zero charge between 4.5 and 9.5 [118]. Catalytic ozonation is most effective at pH values near or above this point, where Lewis acid sites remain available for bonding to either ozone or the compound targeted for degradation [34]. The dissociation constant of the target compound is also affected by pH, where the ionization of certain compounds can affect their adsorption affinity and therefore degradation rate [34]. Given that the pK_a of TBA is approximately 19.2, this does not affect the current study but remains noteworthy for many other ozone-resistant micropollutants [105].

3.4.5. The Effect of TBA Breakdown Products on TBA Removal

The improved TBA removal observed at increasing pH should be attributed to the increased initial rate of ozone decay present. The higher concentration of hydroxide, though initiation is slow, allows for the system of reactions to begin to self-catalyze much faster than at lower pH values. Due to the relative concentration of TBA (0.2–0.73 mM) with

respect to iron (0–1.4 mM) in this system, TBA breakdown products must interact with ozone at a rate similar or greater than with Fe^{2+} ions. The limiting factor for TBA removal in this reaction is the generation of a hydroxyl radical near enough to react with a molecule of TBA. Thorough investigation into the breakdown of TBA initiated by hydroxyl radicals has been conducted [88–92,119]. As TBA is broken down, it forms various organic radical species which can participate in further destruction of TBA breakdown products, leading to unstable and uncertain yields of smaller molecules. It has been observed experimentally that the breakdown of TBA in ECO can exhibit an acceleration in removal rate as reaction time increases. Previous investigations took reaction samples in the middle of the reaction duration, and it was generally found that the second half of the reaction time accounted for significantly more TBA removal compared to the first half during ECO reactions [83]. Either the increase in the number of organic molecules present, as TBA is broken down, or the increased concentration of iron, appears to accelerate removal in the context of this otherwise minimally buffered and low-dissolved carbon water matrix.

The increase in total organic molecules provides more potential sites for ozone to react with, potentially resulting in more hydroxyl radical production, but the increased scavenging of ozone and hydroxyl radicals most likely nullifies any benefit once the concentration of breakdown products exceeds that of TBA. The breakdown of TBA by hydroxyl radicals commonly produces formaldehyde and acetone, which have ozonation reaction rate constants one and two orders of magnitude larger than TBA, but remain seven orders of magnitude smaller than the initiation with Fe^{2+} described in the introduction [90,101]. The increase in breakdown products is therefore unlikely to decrease the rate of ozone reacting with iron, although they will compete with TBA for hydroxyl radicals. The reaction rate constants between hydroxyl radicals and formaldehyde (and its ions) and acetone are within an order of magnitude of that of TBA [93]. There is likely some short-lived competition between TBA and its breakdown products, as they are likely to persist for some time prior to ozonation. It has also been speculated that the increased breakdown products accelerate ozone breakdown, which would partially offset their consumption of hydroxyl radicals [95].

No further comment on the contribution of TBA breakdown products to the further breakdown of TBA can be made here without a higher temporal density of sampling, preferably supplemented with full-scan mass spectrometry to determine the prevalence of certain breakdown products as the reaction progresses. The previous work almost always found acetone present in the final products, using SPME-enhanced HS-GC-MS, though the column and process used did not allow for the separation of acetone from other light molecules that tended to elute alongside it [83].

3.4.6. The Effect of Other Ions on ECO Performance

In this instance, it is likely that the effect of chloride and carbonate ions exerted some effect on ozone decay within the solution. It is unlikely that iron was present in a solution after cleaning the reactor multiple times between trials as well as performing three oxygenation repetitions prior to ozonation. A significant amount of sodium chloride was added to the solution to provide conductivity to promote electrolysis, as well as allowing the electrochemical probes to function. It has been found that similar concentrations of chloride in deionized water below neutral pH have accelerated the rate of ozone decomposition [109,120,121]. Despite ozone having a slow initiating reaction with chloride, this process produces chlorate and chlorites, as well as halogen–oxygen radicals that may accelerate ozone degradation [15,109,122]. These products were not tested for, so their generation or impact can only be speculated on, although it is unlikely they were generated and remained in solution in an impactful concentration. It is also possible that a

quantity of carbon dioxide diffused into the reaction water samples prior to ozonation or ECO. Inorganic carbon species are generally considered to be hydroxyl radical scavenging species, contributing to ozone stability in solution [103]. The reaction water stored at pH 9 is likely to have absorbed more carbonic acid than the neutral and acidic samples. It would be expected that decreased ozone decay would be observed, resulting in decreased TBA removal, yet the pH 9 trials were generally the highest performing as well as the most efficient by ozone use. It may be that carbonate was present in such a low amount that the reaction was not significantly impeded, or that other factors accelerated the pH 9 hydroxyl radical production above and beyond the increased radical scavenging potential. Unfortunately, alkalinity was not measured during this study, so the effect of carbonate on these ECO trials was not discerned.

3.4.7. The Effect of Ozone on ECO Performance

Despite each trial having the same ozone generator setting and similar flow rate, different ozone supply rates had occurred due to an insufficient pressure regulation setup. At the maximum pressure supplied by the fresh oxygen cylinder used, small fluctuations in pressure and small percentage error values compounded to result in significant impacts on the final amount of gas supplied at standard temperature and pressure. This issue started with the first, initial pH 5 trials and persisted through some of the pH 7 trials. The variance is noted in Figure 4, including the range of ozone supply rates as well as the average. Trial specific ozone generation rates are provided in Supplementary Materials (Section S3). The average generation rate corresponding to the ozone generator settings of 4, 5, and 6 out of 10 (unitless settings) were 4.10, 5.43, and 6.23 g/h for the ECO trials, with individual values falling within 17%, 16%, and 6% of those figures, respectively.

Comparison between each level of ozone generation was performed by ANOVA with Games–Howell mean confidence interval difference testing post hoc. Testing showed that levels 4 and 5 were statistically significant by 12.26% mean removal ($p = 0.040$), levels 5 and 6 differed by 7.36% mean removal, but not significantly ($p = 0.086$), and levels 4 and 6 differed significantly by the sum difference of 19.62% ($p = 0.001$). It was found that the increase in TBA removal increased linearly with supplied ozone. The removal rate increase, divided by the increase in (average) applied ozone rate (mentioned above), was found to be by 9.22% per gram from level 4 to 5, and 9.20% per gram from level 5 to 6. Examining ozone-normalized removal rates further, it was found that the average TBA removal per gram of ozone supplied, by each level of ozone generation and across all pH levels, was 10.6%, 10.3%, and 10.2%. These values were not found to be significantly different. The ANOVA test is summarized in Supplementary Materials (Section S2.4). It appears that over the range of factors tested, the addition of ozone caused a consistent, linear improvement in ECO performance.

3.4.8. The Effect of Applied Current on ECO Performance

Evaluating the effect of applied current was made complicated by structuring the test as a response surface based on EOS. Except for the three valid center point runs, no applied current value was tested with the same pH and ozone generation level. Analysis on the effect of applied current in this study is limited to the level of applied current (or EOS category, as intended) while using ozone-normalized results to make comparison between trials possible. Normalizing removal rate by applied current was not performed. The range of current values spanning an order of magnitude, while not affecting the final “cost” of the system as significantly as ozone supply, seemed to generate a parameter skewed heavily in favor of minimizing applied current, while the goal should be to maximize removal per unit ozone. The electrolysis trials found that applied currents up to 0.400 A contributed

less than 3% to TBA removal; therefore, the discussion on applied current values regards catalyst supply and the efficient use of current and added iron.

It was found that increasing applied current always improved TBA removal, though not always at a significant level. Table 4, below, summarizes the average ozone-normalized removal rates for each initial pH group. The average increases from the first to sixth level of applied current were 13.0%, 13.5%, 10.2%, at pH 5, 7, and 9, respectively. Some of this trend is obscured by lower-than-expected minimums in the pH 5 and 7 trials, as mentioned in the previous section. At high rates of applied current, all pH groups' performances largely overlapped, likely since each trial tended to converge towards the same pH. Examining the rates of change in ozone-normalized removal in Table 4, at pH 5 the removal by ozonation was negligible, while a significant increase was observed at the minimum amount of applied current. At pH 7, there is higher removal by ozonation, but the addition of applied current has a similar improvement on performance to pH 5. At pH 9, there was negligible change in removal rate between ozonation and the minimum level of applied current, and additional applied current had reduced improvement compared to the lower pH groups.

Each pH group's ozone-normalized removal rates converged somewhat with increasing applied current. The similar end point is believed to be reached by two different reaction pathways, based on the differing rates of change with respect to applied current. At acidic and neutral pH, the ECO reaction starts and proceeds at a relatively linear pace, with incremental applied current being used at a similar rate of efficiency, since the pH remains below 5.4 in every trial. At basic pH, there are two factors describing removal. At first, catalytic ozonation is mostly initiated by interaction with hydroxide ions, partly due to lower initial concentrations of iron. Once the pH has been sufficiently lowered for iron to remain soluble ion for a prolonged time, or otherwise once a sufficient concentration of iron is reached, catalytic degradation becomes predominantly initiated by iron. This speculated is based on the rate of change of the ozone-normalized removal rates, since the addition of applied current is immediately effective compared to ozonation at pH 5 and pH 7 but shows little effect at pH 9.

Table 4. Ozone-normalized removal rates and rates of change for all ECO groups.

Initial pH 5	9.23	13.83	16.38	19.7	22.92	22.31
Rate of change	5.92 ¹	4.6	2.55	3.32	3.22	−0.61
Initial pH 7	12.02	19.11	21.19	22.53	24.35	25.51
Rate of change	8.84 ¹	7.09	2.08	1.34	1.82	1.16
Initial pH 9	18.28	21.52	23.35	28.83	27.32	28.44
Rate of change	0.79 ¹	3.23	1.84	5.48 (1.99) ²	−1.51 (1.99) ²	1.12
Avg. of all pH groups	13.18	18.15	20.31	22.22	24.86	25.42
Rate of change	5.18 ¹	4.97	2.16	1.91 (2.21) ²	2.65 (2.34) ²	0.56

¹: Rate of change for the first step was compared against the ozone-only average removal rate. ²: Rate of change in brackets uses the average of the higher and lower average removal rates for level 4, since initial pH 9 at ozone levels 5 and 6 had missing data.

4. Conclusions

The ECO process is an iterative improvement to ozonation and catalytic ozonation systems. The process is intended to have three major benefits over ozonation, including higher removal rates of ozone-resistant compounds, higher mineralization rates of all organic compounds, and lower ozone requirements.

Three main effects on ECO performance were investigated by a series of batch reactions. TBA was used to measure hydroxyl radical generation, since it is negligibly affected by ozonation. Initial pH levels of 5, 7 and 9 were chosen, ozonation rates of 4–6 g/h were used

(corresponding to ozone doses between 2–3 g), and applied current values between -0.065 and 0.470 A were used to generate between 10 and 85 mg of iron per trial.

It was found that oxygenation and electrolysis of TBA never resulted in more than 3% removal and were disregarded as mechanisms of physical removal of TBA. Ozonation trials revealed that initial pH had a significant, nonlinear impact on TBA removal, with removal rates ranging from 11% at pH 5 to 45% at pH 9. The effect of hydroxide ions on the system was explored, although increased testing time-density and accuracy is required to fully describe the complex effect of pH on this system.

The ECO system's performance was explored by 54 combinations of initial pH, ozone generation rate, and applied current. Broadly, increasing every factor contributed to increased rates of TBA removal. The rate of increase of removal with respect to each factor was investigated. It was found that the rate of improvement with increased pH was consistently 6% between the single average value of each trial, suggesting that including electrolysis reduced the impact of initial pH on final removal. The effect of each factor on the observed pH was discussed, as well as the mechanisms responsible for the changing removal rate with pH. The rate of improvement with increased ozone was most significant at initial pH 5, while the higher pH trials showed decreasing improvement. Dividing removal rates by estimated ozone dose to compare ozone-normalized removals was performed to make trials more comparable, which also showed that incremental ozone addition was most effective at pH 5. The rate of improvement of ozone-normalized removal by applied current was the same for pH 5 and pH 7 and about 20% reduced at pH 9. It appeared that the incremental improvement with increased applied current generally slowed around the fourth or fifth levels in most trial groups, which is between 0.2 and 0.35 A, varying with ozone level.

Supplementary Materials: The supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/pr13030784/s1>, Section S1: Chromatography Data Correction Process; Section S2: ANOVA Test Result Summaries; Section S3: Experimental Data Compilation.

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Abbreviations

The following abbreviations are used in this manuscript:

ECO	Electrolysis Catalyzed Ozonation
EOS	Excess Ozone Supply
DO ₃	Dissolved Ozone
HS-GC-MS	Headspace–Gas Chromatography–Mass Spectrometry

MDPI Multidisciplinary Digital Publishing Institute
TBA Tert-Butyl Alcohol

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