

Article

Treatment of Actual Winery Wastewater by Fenton-like Process: Optimization to Improve Organic Removal, Reduce Inorganic Sludge Production and Enhance Co-Treatment at Municipal Wastewater Treatment Facilities

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Abstract: Despite many wineries being equipped with onsite wastewater treatment, winery wastewater (WWW) co-treatment at municipal wastewater treatment plants (WWTPs) remains a common practice in wine-making regions. The complex and highly variable nature of WWW can result in negative impacts on WWTP operations, highlighting a need for improved co-treatment methods. In this paper, the feasibility of using the Fenton-like process to pre-treat WWW to enhance co-treatment at municipal WWTPs is assessed. First-stage pre-treatment of the WWW, in the form of dilution and settling or aerobic biological treatment, is used prior to the Fenton-like process. A three-factor BBD experimental design is used to identify optimal reaction time and initial H_2O_2 and Fe^{3+} concentrations. Chemical oxygen demand (COD) and total organic carbon (TOC) removal rates are not able to accurately reflect the extent of reaction. Additional trials identified solubilization of particulate COD and TOC, as well as samples handling requirements prior to analysis, as factors affecting the apparent COD and TOC removal rates. Inert suspended solids (ISS) generated during the sample handling process are found to be the response variable best suited to quantifying the extent of the Fenton-like reaction. Maximum ISS generation is observed at initial H_2O_2 and Fe^{3+} concentrations of 4000 mg/L and 325 mg/L, however, results suggest that optimal concentrations exceed these values. The impact of adding pre-treated WWW, with and without Fenton-like treatment, to municipal WWTPs' primary clarifiers and aerobic bioreactors is also assessed via bench-scale trials. Challenges associated with co-treating WWW are found to remain despite the pre-treatment alternatives investigated, including negative impacts on simulated primary and secondary effluent quality. The Fenton-like AOP provides limited opportunity to optimize or enhance co-treatment at municipal WWTPs.

Keywords: advanced oxidation processes; co-treatment; Fenton-like; optimization; winery wastewater

1. Introduction

Winery wastewater (WWW), generated during the wine-making process, is a complex and highly variable waste stream [1,2]. Despite many wineries being equipped with onsite treatment, hauling WWW to municipal wastewater treatment plants (WWTPs) for co-treatment remains a common practice in wine-making regions [3–5]. Negative performance impacts on the co-treating municipal WWTPs confirm a need for improved co-treatment methods [4,6]. A pre-treatment system that reduces downstream loadings to the municipal WWTP's unit processes, that is capable of quick start-up, and that is economically viable would address these needs.

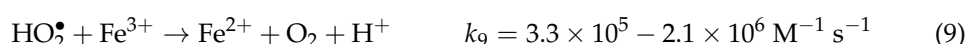
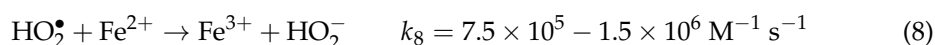
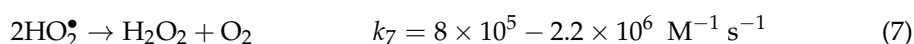
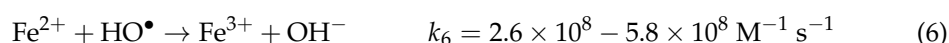
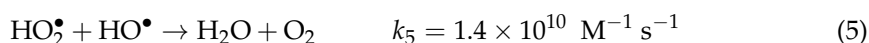
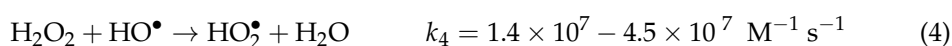
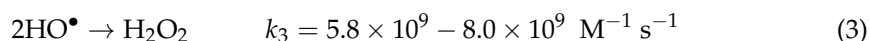
Research has been conducted into using advanced oxidation processes (AOPs) as treatment processes for WWW treatment. AOPs, which are based on the reactive characteristics of the hydroxyl radical, improve the biodegradability and reduce the ultraviolet (UV) absorbance of WWW [5]. Examples include treatment via Fenton [7–9], photo-Fenton [8,10], ozonation-based processes [11–13], and photocatalysis [11,14]. A comprehensive review of

AOP treatment of WWW by Ioannu et al. [15] concluded that Fenton and photo-Fenton were the most efficient AOPs in terms of COD and total organic carbon (TOC) removal rates, reaching values as high as 83% and 95%, respectively, for the stand-alone treatment of WWW. Disadvantages of the Fenton and photo-Fenton processes include removal of the iron catalyst and the associated inorganic sludge production, high chemical and energy costs, lack of experience at full-scale, and narrow operating pH range [5,15]. Combined AOP and biological processes have proven to be successful for the treatment of WWW; however, these studies generally utilize AOPs for the treatment of biologically treated effluents and an acclimated biomass [16–18].

Very little research has focused on the co-treatment of WWW with domestic wastewater [6,19,20]. Of these co-treatment studies, none were based on a separate AOP pre-treatment step for the WWW. In a recent investigation by Amaral-Silva et al. [21], the use of Fenton pre-treatment ahead of biological treatment was shown to be effective; however, all experimental runs were completed on pure WWW, and utilizing an acclimated activated sludge. Municipal WWTPs in Ontario that co-treat high-strength WWW during the vintage season do not have sufficient time within the short vintage season for acclimation to occur.

The Region of Niagara in Ontario, Canada is home to a significant winery industry. Volumes of WWW being hauled to regional municipal WWTPs for co-treatment are increasing and exerting a significant grey water footprint on local freshwater resources [22], requiring improved methods for WWW co-treatment [4]. AOPs may be effective methods to pre-treat WWW prior to its discharge to the main WWTP's treatment processes. Both the Fenton and Fenton-like processes occur at low pH, with reported optimal values in the range of 2.5 to 4.5 [23]. In the Fenton process, the reaction is initiated by ferrous iron (Fe^{2+}) and hydrogen peroxide (H_2O_2); in the Fenton-like process, ferric iron (Fe^{3+}) and H_2O_2 are added initially [23]. In both the Fenton and Fenton-like reactions, Fe^{2+} reacts with H_2O_2 to form $\text{HO}^\bullet$ and Fe^{3+} ; Fe^{3+} then reacts with H_2O_2 to generate $\text{HO}_2^\bullet$ and Fe^{2+} . In this way, the Fenton and Fenton-like reactions differ with respect to the form of iron added initially; however, the mechanisms associated with the generation of $\text{HO}^\bullet$ and the subsequent conversion of Fe^{3+} to Fe^{2+} are the same. Application of the Fenton-like process for WWW co-treatment in the Region of Niagara is attractive since their WWTPs utilize ferric chloride (FeCl_3) for chemical phosphorus removal, as well as H_2O_2 , at several sewage pumping stations (SPSs), for odor control in force mains.

The major reactions involved in the Fenton-like process, and their related reaction rate constants, include the following [24,25]:



where k_i is the reaction rate constant for Reaction (R2.i).

Complete mineralization (conversion of organic compounds to carbon dioxide and water) is generally not possible with the Fenton process because carboxylic and dicarboxylic acid intermediates form stable iron complexes. These iron complexes are, however, biodegradable [26], making Fenton-like pre-treatment with downstream biological treatment an attractive combined AOP–biological process for the treatment of WWW. Once

the Fenton and Fenton-like processes are complete and the pH is raised, iron sludge is generated as a byproduct [23], a disadvantage associated with these processes.

The overall objective of this study was to assess the performance of the Fenton-like treatment of WWW and to assess its feasibility for use as a pre-treatment system for the co-treatment of WWW at municipal WWTPs. This was accomplished by conducting (i) optimization of the operating parameters, including initial Fe^{3+} and H_2O_2 concentrations and reaction time, to maximize COD and TOC removal from actual WWW, and (ii) assessment and quantification of the impact of discharging Fenton-like pre-treated WWW on the liquid treatment train of the co-treating municipal WWTPs. The Design of Experiments (DOE) was used to determine optimal operating conditions using a Box–Behnken design (BBD) with response surface methodology (RSM).

2. Materials and Methods

2.1. Overview of Fenton-like Pre-Treatment Concept

The Fenton-like pre-treatment concept is shown visually in Figure 1. Pre-treatment would consist of two stages: preliminary treatment of the WWW followed by the Fenton-like AOP. The pre-treated WWW could then be discharged to two potential addition points: (1) upstream of the WWTP's primary clarifiers, and (2) upstream of the WWTP's bioreactors (Figure 1). By discharging the iron-rich Fenton-like pre-treated WWW to the municipal WWTP's main treatment process, it may be possible to “reuse” this iron for chemical phosphorus removal, reducing or eliminating the need for dedicated FeCl_3 addition in the liquid treatment train. If feasible, this would eliminate one of the biggest limitations associated with Fenton and Fenton-like treatment processes, namely the generation of large quantities of chemical sludge.

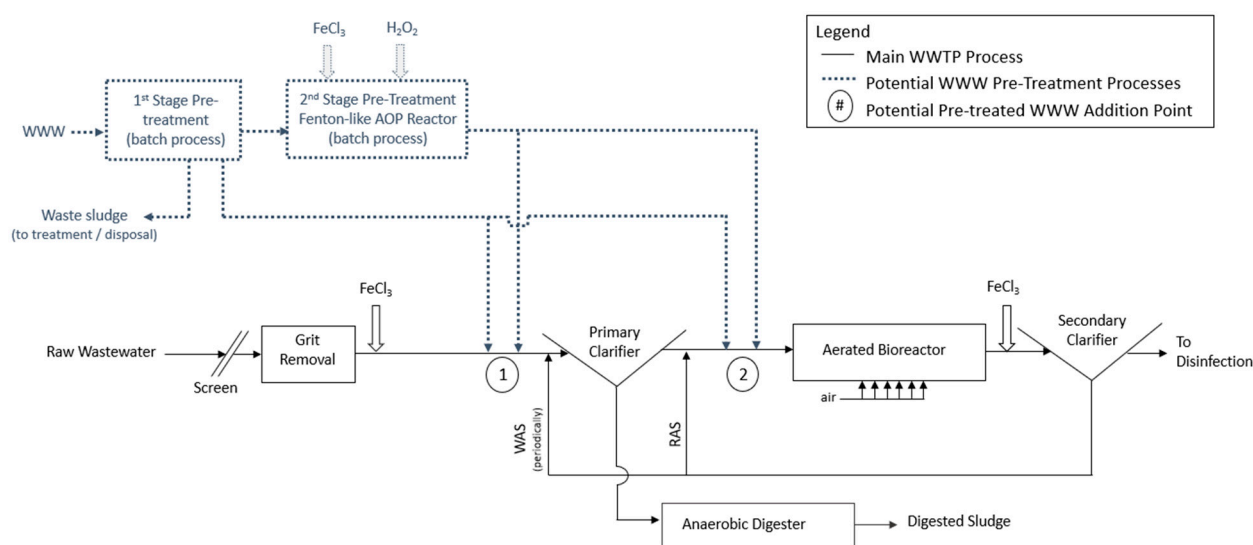


Figure 1. Process flow diagram illustrating potential incorporation of Fenton-like pre-treatment of WWW at a municipal WWTP.

Four WWW pre-treatment schemes were evaluated as part of this study (Figure 2). Settling alone was inefficient since the solids blanket remained at as much as 90% or more of the total WWW sample volume, even after over 24 h of settling. Despite this, it was evident that the solids could readily settle under quiescent conditions. It was therefore determined that dilution of the WWW would be required prior to any subsequent pre-treatment step. The purpose of the first pre-treatment stage was to remove a portion of the WWW solids. Filtration was discarded as the first-stage pre-treatment option. Lofrano and Meric [5] report that colloidal particles can cause clogging of filtration systems, reducing the suitability of these processes for WWW treatment, a finding which was confirmed during preliminary trials conducted as part of this study. Therefore, two alternative first stage

pre-treatment options ((1) dilution and settling; (2) biological) were chosen for their ability to be implemented at full-scale. These first-stage pre-treatment options were followed by either (A) Fenton-like treatment, or (B) no additional treatment (Figure 2).

WWW Pre-Treatment Scheme	Pre-Treatment Steps		Experimental Methods (Objectives)		
	1 st Stage	2 nd Stage			
1A	Dilution and Settling	Fenton-like Treatment	BBD Trials (Optimize Fenton-like parameters)	Time Series Trials (Investigate impact of WWW solids on Fenton-like process)	Co-Treatment Feasibility Trials (Evaluate feasibility of pre-treatment schemes at full-scale)
2A	Biological	Fenton-like Treatment			
1B	Dilution and Settling	None	1 st Stage Pre-Treatment Trials (Evaluate performance of 1 st stage pre-treatment methods)		
2B	Biological	None			

Figure 2. Alternative WWW pre-treatment schemes evaluated as part of this study.

Scheme 1A was conducted with the objective of optimizing Fenton-like operating parameters utilizing BBD. Schemes 1A and 2A were used to investigate the impact of the presence of WWW solids on the Fenton-like process utilizing time series trials. Schemes 1B and 2B, which consist of only one pre-treatment stage, were conducted to confirm the performance of this first pre-treatment step. Schemes 1A to 2B were used to evaluate the feasibility of utilizing these various pre-treatment procedures at full-scale by conducting co-treatment feasibility trials, simulating the impact of adding pre-treated WWW to either of the two potential additional points (Figure 1). By comparing Schemes 1A and 2A to Schemes 1B and 2B, respectively, it was also possible to evaluate the benefit, if any, provided by the Fenton-like pre-treatment step on downstream WWTP performance.

2.2. Chemicals

Industrial grade ferric chloride (FeCl_3) was taken from bulk deliveries supplied by Kemira Water Solutions Canada Inc. (Varenes, QC, Canada) and was received at one of Niagara Region's municipal WWTPs. Thirty percent *w/w* Hydrogen peroxide (H_2O_2) solution was supplied by HACH Canada (London, ON, Canada). Catalase from *Micrococcus lysodeikticus* with a concentration of $\geq 100,000$ U/mL, to quench residual H_2O_2 in Fenton-like treated samples, was supplied by MilliporeSigma Canada Ltd. (Oakville, ON, Canada).

2.3. Winery Wastewater

The characteristics of WWW accepted for co-treatment at the Niagara Region's municipal WWTPs can vary significantly from load to load, reaching COD and TSS concentrations in excess of 300,000 mg/L and 80,000 mg/L [1]. To assess the feasibility of utilizing the Fenton-like process for initial treatment of WWW, all experiments were conducted on a sample of high-strength WWW collected during the vintage period.

Samples of actual WWW were collected directly from loads hauled by truck to municipal WWTPs in the Niagara Region. Samples were collected during the vintage period (September to December) of 2019. Preliminary experiments were conducted on WWW samples collected during the vintage periods of 2017 and 2018.

2.4. Mixed Liquor

Mixed liquor samples were collected directly from the aerobic bioreactors of a municipal conventional activated sludge plant equipped with mechanical aerators for use in the

aerobic biological treatment tests. Samples were collected no more than 4 h prior to the start of the biological treatment tests to best simulate the treatment levels anticipated in full-scale aerobic bioreactors.

2.5. Experimental Methods

2.5.1. First Stage Pre-Treatment Trials

Two first stage pre-treatment options were evaluated, namely:

- Dilution and settling;
- Biological.

Dilution and Settling

Pre-treatment via dilution and settling was selected to simulate a simple batch settling process and was accomplished by diluting the WWW with distilled H₂O (dH₂O) (4% WWW *v/v*), mixing well, and allowing the diluted WWW to settle via gravity for 1 h. The supernatant was then carefully removed via siphoning.

Biological

Biological pre-treatment was accomplished using bench-scale biological treatment reactors consisting of 20 L, flat bottomed, 29 cm diameter, open topped containers. Aerobic conditions were maintained with 2.5 L/min of air provided per container via a 9 cm diameter ceramic fine bubble diffuser and an 8-outlet ActiveAQUA AAPA25L air pump (Hydrofarm, Petaluma, CA, USA).

The reactor was seeded with 14 L of mixed liquor from a municipal WWTP's aerobic bioreactor. The mixed liquor was allowed to settle for 30 min and 7 L of supernatant was removed. The reactor was then fed with 560 mL of WWW and 6.44 L of primary effluent and was allowed to react for 6 h, at which time the aeration was suspended, the mixed liquor was allowed to settle, and the biologically pre-treated WWW was removed as supernatant.

2.5.2. BBD Fenton-like Trials

First stage pre-treated WWW was diluted with dH₂O to achieve the target of an initial COD (COD₀) concentration of 1460 mg/L, and pH adjusted to 3.3 using 1 N NaOH or 1 N HCl. A jar testing apparatus (Phipps and Bird 8-jar tester) was used for all Fenton-like treatment trials. Each jar was loaded with an initial volume of 225 mL of diluted and settled WWW. Rapid mixing (150 rpm) was used during the addition of FeCl₃ and H₂O₂, while slow mixing (30 rpm) was used during the reaction phase. FeCl₃ was added to each jar and the pH was, again, adjusted to 3.3, as needed. The addition of H₂O₂ marked reaction time zero. The pH of each jar was noted every 15 min throughout the Fenton-like trial, and was adjusted with 1 N NaOH as necessary to maintain the pH within the range 3.3 to 3.5. All runs were conducted at room temperature, which varied from 14.8 °C to 16.2 °C. Contents of the jars were mixed during sample collection to ensure representative samples were collected throughout testing.

The pH of collected samples was adjusted to >9 using 1 N NaOH to terminate the Fenton-like reaction. Catalase was added (0.1 mL per 100 mL of collected sample) to quench the remaining H₂O₂ to eliminate potential interferences with subsequent COD testing. After 60 min of reaction time with the catalase, the sample was filtered using 0.45 micron Whatman glass filter paper. The filtered sample was analyzed for COD and TOC, while the residue on the filter paper was analyzed for TSS and volatile suspended solids (VSS). This allowed for the calculation of the inert suspended solids (ISS) concentration.

2.5.3. Fenton-like Time Series Trials

The methodology used for the time series trials followed that outlined in Section 2.5.2, with the following exceptions: initial volumes of 1500 mL; samples collected every 30 to 60 min over a 5 h reaction time; all runs used H₂O_{2,0} of 2500 mg/L and Fe₀³⁺ of 325 mg/L; trials were run on first stage pre-treated WWW (both diluted and settled, and biological,

see Figure 2). The diluted and settled WWW was diluted to a COD_0 of 1460 mg/L while the biologically pre-treated WWW was diluted to a COD_0 of 1330 mg/L. For each type of first stage pre-treated WWW, a separate time series trial was run using an unfiltered and filtered sample to assess the impact of particulate fractions on the performance of the Fenton-like process. Samples were filtered using 0.45 micron Whatman glass filter papers.

Samples collected at 5 h of reaction time were also used as influent in the co-treatment trials. For these samples, the pH was adjusted to >9 using 1 N NaOH to ensure the Fenton-like reaction had terminated while the samples were being transported to the bench-scale equipment used to simulate co-treatment (Section 2.5.3). In addition, previous studies completed by the authors concluded that pH inhibition is a limiting factor associated with the co-treatment of WWW in aerobic bioreactors. Thus, adjusting the pH prior to its addition to the co-treatment trials eliminates potential pH inhibition. No catalase was added to quench the remaining H_2O_2 residual. This was done to simulate the full-scale implementation of Fenton-like pre-treatment which would not include a step to quench the H_2O_2 (Figure 1). Samples used in the co-treatment trials were added to the bench-scale primary clarifier and aerobic bioreactors within 30 min of collection and pH adjustment.

2.5.4. Co-Treatment Trials

Two co-treatment alternatives were evaluated, namely:

- Simulated primary clarification, to simulate discharging pre-treated WWW to addition point (1) (Figure 1);
- Simulated secondary treatment, to simulate discharging pre-treated WWW to addition point (2) (Figure 1).

Simulated Primary Clarification

The primary clarification was simulated using 1 L glass beakers containing 675 mL of raw wastewater collected from the primary clarifier influent channel of a municipal WWTP. Beakers were then fed with 75 mL of pre-treated WWW (Schemes 1A to 2B, Figure 2). Using the FeCl_3 solution, additional Fe was dosed to beakers fed with pre-treated WWW for Schemes 1B and 2B so that all beakers received the same Fe dosage (32.5 mg Fe/L). Two control beakers contained 750 mL of raw wastewater only. FeCl_3 was added to one of the control reactors to achieve a target dosage of 32.5 mg Fe/L.

All beakers were subjected to a 3 min rapid mix phase, using a magnetic stir plate and bar set to induce a vortex that reached the bottom of the beaker when fed with the pretreated WWW and/or FeCl_3 . A 3 min rapid mix phase was also used on the control beaker, although nothing was fed to the beaker during this time.

Following the rapid mix phase, all mixing was suspended and the contents of the beakers were allowed to settle for 2 h. At the end of the settling period, supernatant was removed using a syringe to draw liquid from below the water surface to avoid the scum layer, if any, that had accumulated.

Simulated Secondary Treatment

The aerobic biological treatment reactors were 8 L, flat bottomed, 24 cm diameter, open topped containers. Aerobic conditions were maintained with 2.5 L/min of air provided per container via a 9 cm diameter ceramic fine bubble diffuser and an 8-outlet ActiveAQUA AAPA25L air pump (Hydrofarm, Petaluma, CA, USA). Each test reactor was seeded with 2 L of mixed liquor which was allowed to settle, and 0.2 L of supernatant was removed, retaining 1.8 L of settled, mixed liquor. The reactors were fed with 0.2 L of pre-treated WWW (Schemes 1A to 2B, Figure 2). Using the FeCl_3 solution, additional Fe^{3+} was dosed to reactors fed with WWW pre-treated using Schemes 1B and 2B so that all reactors received the same Fe dosage (32.5 mg Fe/L). Two control reactors were seeded with 2 L of mixed liquor. No supernatant was withdrawn nor was pre-treated WWW added to the control reactors. FeCl_3 was added to one of the control reactors to achieve a target dosage of 32.5 mg Fe/L.

The reactors were aerated for 3 h. At the end of the reaction period, samples of mixed liquor were collected, then aeration was suspended and the reactor contents were allowed to settle for 30 min. Samples of supernatant, representing simulated secondary effluent quality, were then collected for subsequent analysis.

2.6. Analytical Methods

Instantaneous measurements were conducted as follows: turbidity was measured using a handheld 2100P Turbidimeter (HACH, London, ON, Canada); pH and temperature were measured by an Orion Versa Star Pro (Thermo Fisher Scientific, Waltham, MA, USA) during Fenton-like treatment trials, and by portable PHC101 pH electrode equipped HQ30d Meter (HACH, London, ON, Canada) during biological reactor trials.

Section 2540 of [27] was followed for the measurement of TSS and VSS, while US EPA method 200.7 was used to measure total iron (Fe). A Skalar SAN Plus 3000/5000 Segmented Flow Analyzer was used to measure total phosphorous (TP) (method 503-324w/r). A HACH colorimeter (HACH, London, ON, Canada) was used to measure chemical oxygen demand (COD), following HACH Method 8000. A Shimadzu TOC-500A was used to analyze TOC following US EPA method 415.1. Finally, 0.45 micron glass Whatman filter papers were used for sample filtering.

2.7. BBD Experimental Design and Optimization

A three-factor BBD experimental design was used to evaluate the impact of, and optimize operating parameter values associated with the BBD Fenton-like trial. Response variables were the percentage of COD and TOC removal, and the generation of ISS sludge from the Fenton-like process sample handling procedures (Section 2.5.2). Independent variables were reaction time (X_1), initial H_2O_2 ($H_2O_{2,o}$) concentration (X_2), and initial Fe^{3+} (Fe_o^{3+}) concentration (X_3), with coded values as presented in Table 1.

Table 1. Independent Variable Actual and Coded Values Used for Three-Factor, Three-Level BBD.

Independent Variable	Units	Symbol	Coded Levels		
			−1	0	+1
Reaction Time	h	X_1	2	3	4
$H_2O_{2,o}$	mg/L	X_2	1000	2500	4000
Fe_o^{3+}	mg/L	X_3	75	200	325

$H_2O_{2,o}$ and Fe_o^{3+} were chosen as independent variables since these operational parameters are known to have a significant impact on the performance of the Fenton-like process. The range of Fe_o^{3+} was developed based on achieving a minimum range of $Fe_o^{3+}:H_2O_{2,o}$ of 0.01875 to 0.3250, based on optimal values for the Fenton reaction determined by others [28–30]. A maximum Fe_o^{3+} value of 325 mg/L was selected based on: projected pre-treated WWW discharge rates to full-scale municipal WWTPs (Figure 1); and, an appropriate Fe dosage range of 6 to 30 mg/L on the downstream liquid treatment train [31]. Reaction time, X_3 , is also a key consideration, impacting both the extent of the reaction as well as required reactor sizing. A range of 2 h to 4 h was selected based on the results of preliminary tests.

The relationships between independent variables and process responses were assessed using a quadratic model and least-squares regression to allow for the determination of optimal operating conditions [32,33] of the general form:

$$Y_i = \beta_o + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^k \beta_{ij} X_i X_j + c \quad (10)$$

where Y_i is the predicted response, β_o , β_i , β_{ii} , and β_{ij} are coefficients representing the intercept, linear, quadratic, and cross-factor interaction terms, X_i and X_j are independent variables, k is the number of factors, and c is the residual term.

The Design Expert version 13.0.8.0 software package was used for design of experiments (DOE), to develop the quadratic model equations using least squares regression and Analysis of Variance (ANOVA) to a 95% confidence interval ($\alpha = 0.05$), and to navigate the 3-dimensional (3D) response surface.

3. Results and Discussion

3.1. Assessment of First Stage WWW Pre-Treatment Options

Characteristics of the WWW before and after first stage pre-treatment are shown in Table 2, along with the calculated removal rates of key parameters.

Table 2. Characteristics of actual WWW before and after pre-treatment via dilution and settling, and aerobic biological pre-treatment.

Parameter	Units	WWW		Pre-Treated WWW	
		Raw	Diluted (4% v/v)	Scheme 1B	Scheme 2B
COD	mg/L	163,000	6520	4850	2970
Filtered COD	mg/L	103,200	4128	4550	2020
TOC	mg/L	57,300	2292	1300	678
Filtered TOC	mg/L	27,600	1104	994	595
TSS	mg/L	71,600	2864	575	440
VSS	mg/L	51,600	2064	560	419
TP	mg/L	30.2	1.21	7.34	6.40
Filtered TP	mg/L	-	-	2.61	1.37
pH	-	3.78	-	-	-
COD Removal	%	-	-	26	54
Filtered COD Removal	%	-	-	-10	51
TOC Removal	%	-	-	43	70
Filtered TOC Removal	%	-	-	10	46
TSS Removal	%	-	-	80	85
VSS Removal	%	-	-	73	80
TP Removal	%	-	-	-513	-429

Scheme 1B resulted in COD, TOC, and TSS removal of 26%, 43%, and 80%, respectively, while Scheme 2B provided COD, TOC, and TSS removal of 54%, 70%, and 85%, respectively. While the biological pre-treatment provides better removal efficiencies, this process is more complex than simple dilution and settling and would, therefore, be more difficult to implement at full-scale. For both pre-treatment methods, a negative TP removal rate was observed. This was also observed during earlier biological co-treatment trials, suggesting potential solubilization of particulate phosphorus that had been present in the WWW in a form that was not captured in the analytical method for TP. A negative removal rate for filtered COD was also observed during dilution and settling, suggesting the conversion of particulate COD to soluble COD.

In addition, both pre-treatment methods yield a waste stream: for dilution and settling, a liquid sludge is produced that consists of the settled particulate matter from the WWW; for biological pre-treatment, the settled mixed liquor waste contains both the biomass as well as WWW constituents that have sorbed onto the floc. Therefore, full-scale implementation of either of these pre-treatment processes would require a method to appropriately handle and treat these waste streams.

3.2. Box-Behnken Design Fenton-like Trials

3.2.1. Experimental Results and Model Development

The overall objective was to determine the feasibility of using the Fenton-like treatment process to minimize organic loadings to the downstream liquid treatment train of the WWTP (Figure 1). Therefore, COD removal rate (Y_1) and TOC removal rate (Y_2) were selected as two key response variables. The generation of ISS due to the precipitation of iron hydroxides and other non-soluble iron precipitates during post-reaction pH adjustment was also selected as a response variable (Y_3). The rationale for the selection of this response parameter is discussed in more detail in Section 3.3. To improve model fit, the ISS concentration response variable, Y_3 , was log-transformed, as follows:

$$Y'_3 = \ln(1 + Y_3) \quad (11)$$

where Y'_3 is the transformed response parameter.

The quadratic models developed to predict the response parameters, in terms of the coded independent variables reaction time (X_1), $H_2O_{2,o}$ (X_2), and $Fe_{o^{3+}}$ (X_3), are presented in Equations (12) to (14).

$$Y_1 = 51.83 + 3.39X_1 + 0.950X_2 + 5.25X_3 - 0.413X_1X_2 - 2.16X_1X_3 + 1.04X_2X_3 - 6.54X_1^2 - 3.27X_2^2 - 0.187X_3^2 \quad (12)$$

$$Y_2 = 42.85 + 0.895X_1 + 0.0448X_2 + 3.84X_3 - 0.767X_1X_2 + 0.384X_1X_3 + 0.512X_2X_3 - 4.52X_1^2 - 3.24X_2^2 + 0.341X_3^2 \quad (13)$$

$$Y'_3 = 5.10 - 0.0545X_1 - 0.116X_2 + 2.38X_3 + 0.130X_1X_2 + 0.209X_1X_3 + 0.743X_2X_3 - 0.0014X_1^2 - 0.207X_2^2 - 1.60X_3^2 \quad (14)$$

Table 3 presents the observed and predicted values of the three response variables. The reported observed and predicted values of ISS generation presented in Table 3 represent the untransformed values. Table 4 presents the results of the ANOVA for the overall models and their individual terms. Coefficients with p -values < 0.05 were considered significant, while those with $p > 0.10$ were considered not-significant.

Table 3. Observed and predicted COD removal, TOC removal, and ISS generation for the three-factor BBD used to assess performance of the Fenton-like process for the treatment of actual WWW pre-treated via dilution and settling.

Run	Independent Coded Variables			COD Removal (%)		TOC Removal (%)		ISS Generation (mg/L)	
				Y_1		Y_2		Y_3	
	X_1	X_2	X_3	Observed	Predicted	Observed	Predicted	Observed	Predicted
1	−1	−1	0	36.58	37.27	33.04	32.98	146	178
2	1	−1	0	45.55	44.87	35.35	36.3	119	123
3	−1	1	0	39.32	40.00	36.37	35.41	112	109
4	1	1	0	46.64	45.95	35.6	35.66	154	127
5	−1	0	−1	33.84	34.31	33.81	34.32	3	3
6	1	0	−1	43.56	45.4	35.86	35.35	1	1
7	−1	0	1	50.96	49.12	40.72	41.23	354	304
8	1	0	1	52.05	51.58	44.3	43.79	409	415
9	0	−1	−1	44.38	43.22	36.62	36.18	6	5
10	0	1	−1	44.18	43.03	35.6	36.05	0	0
11	0	−1	1	50.48	51.63	43.27	42.83	161	153
12	0	1	1	54.45	55.61	44.3	44.74	451	544
13	0	0	0	50.48	51.83	42.51	42.85	176	163
14	0	0	0	51.99	51.83	42.76	42.85	165	163
15	0	0	0	53.01	51.83	43.27	42.85	147	163

Table 4. ANOVA results for the development of quadratic models to predict COD removal, TOC removal, and ISS generation.

Source	Sum of Squares	DF	Mean Square	F Value	p-Value	Remark
COD _{removal} model (Y_1)	530.1	9	58.90	16.67	0.0032	Significant
X_1	91.80	1	91.80	25.98	0.0038	Significant
X_2	7.220	1	7.220	2.043	0.2123	Not significant
X_3	220.3	1	220.3	62.35	0.0005	Significant
X_1X_2	0.681	1	0.681	0.193	0.6791	Not significant
X_1X_3	18.62	1	18.62	5.270	0.0702	
X_2X_3	4.347	1	4.347	1.230	0.3178	Not significant
X_1^2	157.8	1	157.8	44.66	0.0011	Significant
X_2^2	39.41	1	39.41	11.15	0.0206	Significant
X_3^2	0.129	1	0.129	0.037	0.8559	Not significant
Residual	17.67	5	3.533			
Lack of fit	14.43	3	4.809	2.968	0.2621	Not significant
Pure error	3.240	2	1.620			
Corrected total SS	547.8	14				
R^2	0.968					
Adjusted R^2	0.910					
Adequate precision	13.88					
TOC _{removal} model (Y_2)	239.2	9	26.58	33.21	0.0006	Significant
X_1	6.410	1	6.410	8.011	0.0367	Significant
X_2	1.603	1	1.603	2.003	0.2162	Not significant
X_3	117.7	1	117.7	147.1	<0.0001	Significant
X_1X_2	2.355	1	2.355	2.943	0.1469	Not significant
X_1X_3	0.589	1	0.589	0.736	0.4302	Not significant
X_2X_3	1.047	1	1.047	1.308	0.3046	Not significant
X_1^2	75.38	1	75.38	94.20	0.0002	Significant
X_2^2	38.75	1	38.75	48.43	0.0009	Significant
X_3^2	0.429	1	0.429	0.537	0.4967	Not significant
Residual	4.001	5	0.800			
Lack of fit	3.696	3	1.232	8.071	0.1122	Not significant
Pure error	0.305	2	0.153			
Corrected total SS	243.2	14				
R^2	0.984					
Adjusted R^2	0.954					
Adequate precision	16.11					
ISS _{generation} model (Y_3')	57.57	9	6.397	149.7	<0.0001	Significant
X_1	0.024	1	0.027	0.556	0.4894	Not significant
X_2	0.107	1	0.107	2.513	0.1738	Not significant
X_3	45.43	1	45.43	1063	<0.0001	Significant
X_1X_2	0.067	1	0.067	1.576	0.2649	Not significant
X_1X_3	0.175	1	0.175	4.100	0.0988	
X_2X_3	2.208	1	2.208	51.67	0.0008	Significant
X_1^2	7.239×10^{-6}	1	7.239×10^{-6}	1.694×10^{-4}	0.9901	Not significant
X_2^2	0.1575	1	0.1575	3.685	0.113	Not significant
X_3^2	9.473	1	9.473	221.68	<0.0001	Significant
Residual	0.214	5	0.043			
Lack of fit	0.197	3	0.066	8.000	0.1131	
Pure error	0.016	2	0.008			
Corrected total SS	57.79	14				
R^2	0.996					
Adjusted R^2	0.990					
Adequate precision	37.04					

Figures 3 and 4 present 3D plots of the cross-factor interaction effects between influent H_2O_2 and reaction time (X_1X_2) on COD and TOC removals, respectively. Figure 5 presents

a 3D plot of the cross-factor interaction effects between $\text{H}_2\text{O}_{2,o}$ and Fe_0^{3+} (X_2X_3) on ISS generation.

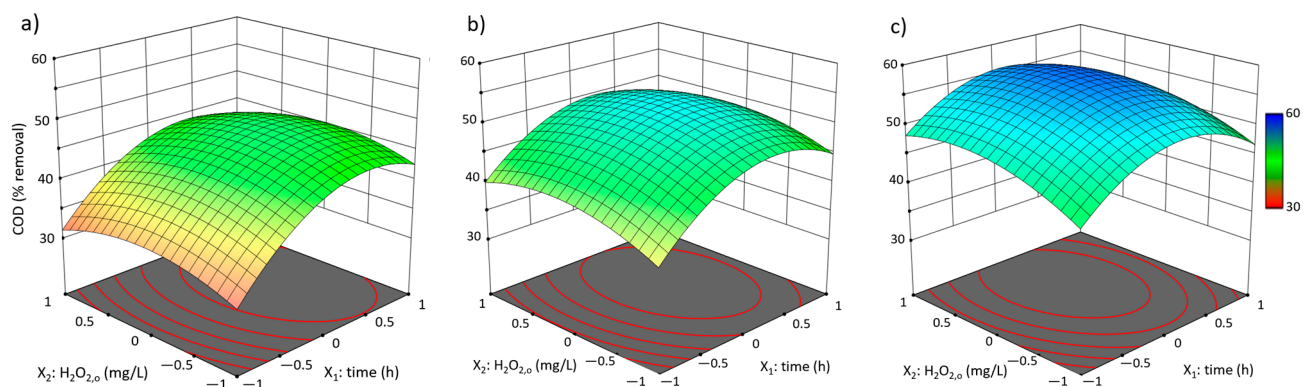


Figure 3. 3D plots of the cross-factor interaction effects between $\text{H}_2\text{O}_{2,o}$ and reaction time (X_1X_2) on COD removal (Y_1) at Fe_0^{3+} (X_3) concentration of (a) 75 mg/L; (b) 200 mg/L; (c) 325 mg/L.

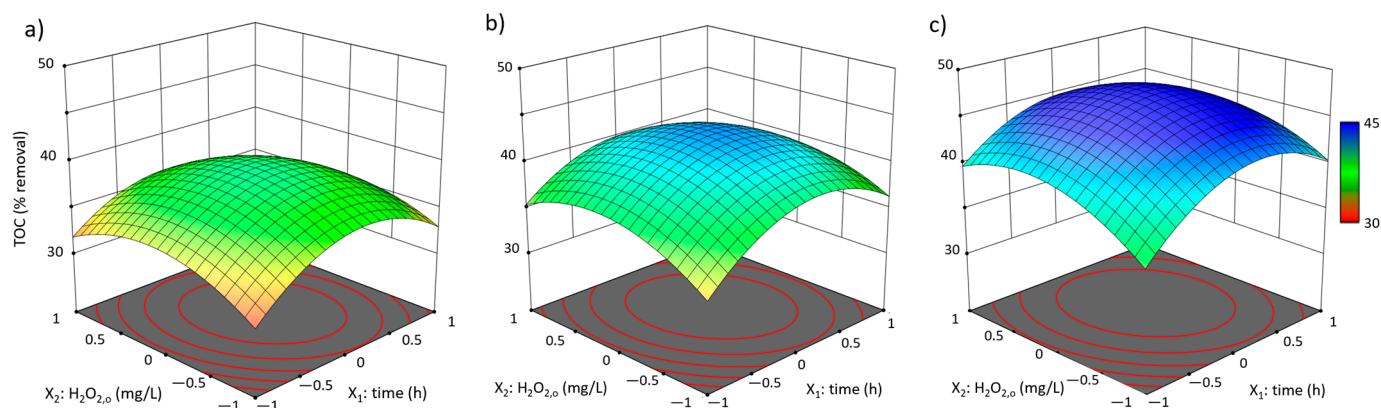


Figure 4. 3D plots of the cross-factor interaction effects between $\text{H}_2\text{O}_{2,o}$ and reaction time (X_1X_2) on TOC removal (Y_1) at Fe_0^{3+} (X_3) concentration of (a) 75 mg/L; (b) 200 mg/L; (c) 325 mg/L.

3.2.2. Analysis and Discussion

Increasing Fe_0^{3+} (X_3) increased the removal rates of both COD and TOC. This can be seen visually by comparing Figure 3a–c for the COD removal rate, and Figure 4a–c for the TOC removal rate. The significance of the quadratic terms for X_1 and X_2 suggest an optimal value for each of these parameters over the ranges tested. These optima can be visualized in Figures 3 and 4, with maximum COD and TOC removals at approximately the mid-point of the parameter ranges tested: reaction time (X_1) of 3 h, and $\text{H}_2\text{O}_{2,o}$ (X_2) of 2500 mg/L. Optimal $\text{H}_2\text{O}_{2,o}$ in H_2O_2 -based AOPs is an established phenomenon due to its role as a known radical scavenger [34]. However, an optimal reaction time is a paradoxical result, since the reactions that lead to COD and TOC removal are expected to be irreversible and, therefore, removal rates are expected to increase with increasing reaction time.

It is possible that the solubilization of particulate COD and TOC fractions present in the pre-treated WWT could explain the apparent decrease in removal rates at longer reaction times. Sample handling procedures (see Section 2.5.2) necessitated filtration of samples prior to COD and TOC analysis. This filtering could remove particulate fractions of the WWT, resulting in an overestimate of the COD and TOC removal rates, particularly early in the trials. In addition, the coagulation of iron oxide precipitates during sample pH adjustment prior to filtering has the potential to promote the coagulation and subsequent removal of compounds that contribute to the COD and TOC, a mechanism known to contribute to reported removal rates during Fenton treatment of wastewaters, including

WWW [35]. In fact, a sample of the pre-treated WWW was subjected to the same handling procedures as those samples that underwent Fenton-like treatment, including a reaction time of 3 h and Fe_0^{3+} of 200 mg/L; however, no H_2O_2 was added. Therefore, this “blank” did not undergo Fenton-like treatment. The apparent COD and TOC removal rates in this “blank” run, after sample handling (Section 2.5.2) and analysis, were 41.2% and 37.9%, respectively, confirming that coagulation and/or filtration impacted apparent COD and TOC removal rates. As the reaction progressed, the solubilization of particulate fractions would result in underestimates of COD and TOC removal, resulting in an apparent optimal reaction time. Kotta et al. [36] observed solubilization of particulate COD during the electrochemical treatment of olive mill effluents, resulting in apparent negative soluble COD removal rates.

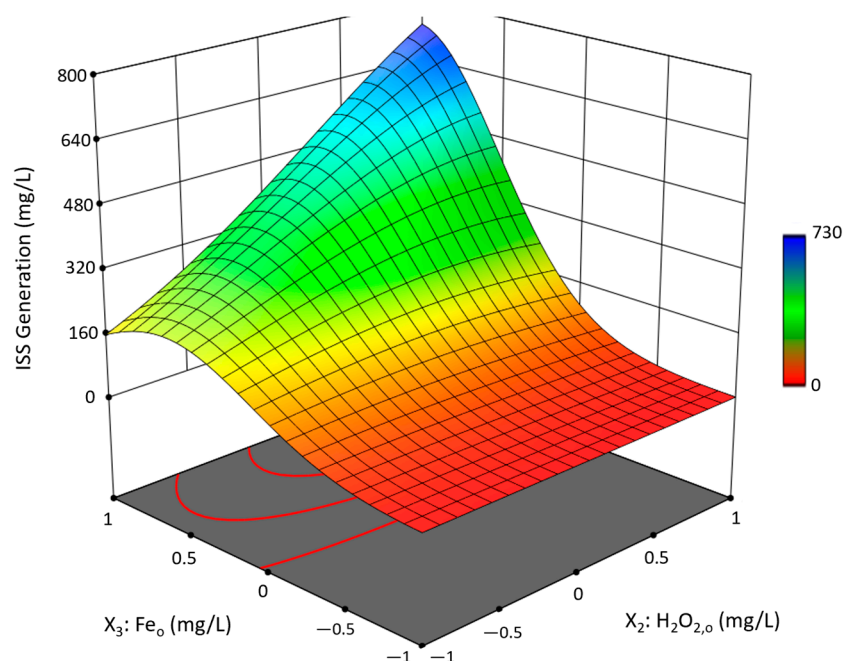


Figure 5. 3D plot of the cross-factor interaction effects between $\text{H}_2\text{O}_{2,o}$ and Fe_0 (X_2X_3) on ISS generation (Y_3) at reaction time of 4 h.

3.3. Time Series Treatment Trials

Time series Fenton-like treatment trials were conducted to determine if solubilization of particulate fractions could explain the decreasing COD and TOC removal rates as reaction time progressed during the BBD treatment trials.

The evolution of COD concentrations during the time series Fenton-like treatment trials are presented in Figure 6. For the samples that were not initially filtered, there is a significant initial decrease in COD concentrations, followed by a period of variable concentrations with no significant downward trend. At 5 h of reaction time, COD removal rates ranged from 21% (first stage pre-treatment dilution and settling) and 27% (first stage pre-treatment biological). Conversely, the samples that were initially filtered saw a gradual decrease in COD concentrations as the reaction progressed, reaching 17% (first stage pre-treatment dilution and settling) and 25% (first stage pre-treatment biological) after 5 h of reaction time. These results are consistent with the COD removal rates being affected by particulate fraction ratios. This also makes direct comparison of these results to the results of other published studies difficult since the impact of sample handling procedures (coagulation during pH adjustment, filtration prior to sample analysis) are generally not accounted for; rather, these are considered intrinsic components of Fenton and Fenton-like treatment processes [35]. When considering a pre-treatment scheme that does not incorporate removal of coagulated and/or particulate fractions from the Fenton-like

wastewater prior to its discharge into a municipal WWTP (Figure 1), it is necessary to ensure that the impacts of sample handling on apparent organic removal rates are understood.

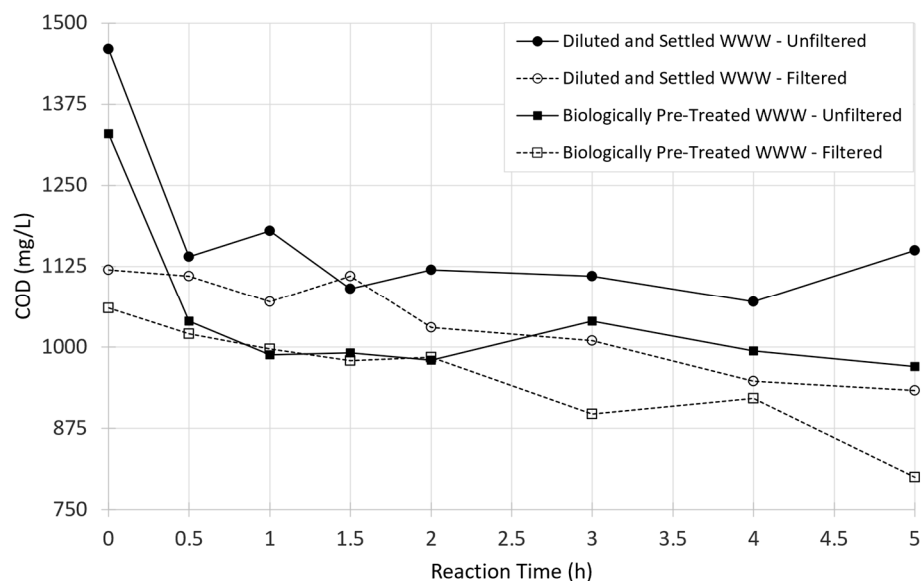


Figure 6. Evolution of COD concentrations during the Fenton-like treatment at $\text{H}_2\text{O}_{2,0}$ 2500 mg/L and Fe_0^{3+} 325 mg/L of filtered and unfiltered WWW that had undergone first stage pre-treatment via settling and dilution or aerobic biological treatment.

This behaviour could also explain the apparent decrease in removal rates at reaction times exceeding the apparent optimal value observed during the BBD trials. This also confirms that COD and TOC removal rates do not accurately reflect the extent of reaction and, thus, are not useful response parameters for the Fenton-like treatment of the pre-treated WWW.

It was also observed that a large fraction of the Fe remained in the solution after samples were quenched and pH was raised (see Section 2.5.2), and that the fraction of Fe remaining in the solution varied considerably over time. Figure 7 presents a qualitative summary of the solids that were removed after filtering 25 mL of the samples of quenched, pH adjusted wastewaters collected over 0.5 to 5 h of reaction time.

Over the course of the treatment of non-filtered, first-stage, and pre-treated WWW (Figure 7a,c), small, disperse, and medium to dark brown solids were retained on the filter paper during the early reaction period, reducing in quantity as the reaction time increased. At the same time, the generation of iron sludge during post-Fenton-like sample pH adjustment was visually observed to increase at longer reaction times, characterized as orange, rust colored solids. The resulting iron sludge could be seen on the filter papers as the reaction progressed. This is most easily observed in Figure 7a,b.

WWW has high concentrations of sugar from grape pulp [1], which can create complexes with Fe^{3+} that remain soluble at alkaline pH [37]. Therefore, the presence of sugar and, potentially, other iron-complexing organic compounds in the WWW could explain the observed limited iron sludge generation during post-Fenton-like pH adjustment. Visual observations support this hypothesis, with little to no visible iron sludge having been generated after pH adjustment to >9 ; however, distinct sludge and clear supernatant layers formed when allowing samples undergoing Fenton-like treatment at pH at 3.3 to settle quiescently. This suggests that, at the low pH necessary for the Fenton-like AOP, iron is present in complexes and not available as the dissolved Fe^{2+} / Fe^{3+} ions which are necessary to generate hydroxyl radicals; however, as the pH is increased, these iron-organic compound complexes solubilize. As the AOP treatment progresses, it would be expected that less iron-complexing compounds would remain, resulting in more iron hydroxide sludge being generated during pH adjustment (>9), which was observed (Figure 7). A

limitation of this study, however, is that the neither the organic constituents of the WWW nor any iron-organic complexes were identified or quantified; therefore, this hypothesis could not be confirmed.

Preliminary treatment method	Fenton-like Treatment Reaction Time						
	0.5 h	1.0 h	1.5 h	2.0 h	3.0 h	4.0 h	5.0 h
a) Diluted and settled WWW							
b) Diluted, settled and filtered WWW							
c) Biologically treated WWW							
d) Biologically treated and filtered WWW							

Figure 7. Residue left on 0.45 micron glass filter papers after filtering 25 mL of sample collected, quenched, and pH adjusted to >9 at various reaction times during Fenton-like treatment of WWW samples at $\text{H}_2\text{O}_{2,0}$ 2500 mg/L and Fe_0^{3+} 325 mg/L that had undergone first-stage pre-treatment consisting of (a) dilution and settling, (b) dilution and settling followed by filtration, (c) biological treatment, and (d) biological treatment followed by filtration.

Despite this, it can be concluded that the extent of treatment of WWW by Fenton-like reaction can likely be best assessed by quantifying the ISS generation rate in the quenched, pH-adjusted samples. Directly measuring the COD and/or TOC remaining in the solution is not accurate as it is affected by the removal of particulate wastewater fractions during sample filtering and the solubilization of particulate matter in the wastewater as the reaction progresses.

At low Fe_0^{3+} concentrations (approximately <150 mg/L), very little ISS was generated, regardless of $\text{H}_2\text{O}_{2,0}$ (Figure 4). This is consistent with the presences of iron-complexing compounds in the pre-treated WWW that shield the Fe^{3+} , effectively inhibiting the ability for its conversion to Fe^{2+} (Reaction 1) and acting as the catalyst for the Fenton-like process. Over the ranges tested, the ISS generation rate was maximized at an $\text{H}_2\text{O}_{2,0}$ of 4000 mg/L, reaction time of 4 h, and Fe_0^{3+} of 325 mg/L; these differ significantly from those determined based on COD and TOC removal ($\text{H}_2\text{O}_{2,0}$ of 2500 mg/L, reaction time 3 h, and Fe_0^{3+} 325 mg/L). Furthermore, the results from Figure 5 suggest that the optimal $\text{H}_2\text{O}_{2,0}$ and Fe_0^{3+} concentrations exceed 4000 mg/L and 325 mg/L, respectively.

Because the WWW requires pre-treatment ahead of the Fenton-like process, any treatment scheme that incorporates this AOP will be complex to operate. The performance of biological pre-treatment as a stand-alone pre-treatment option was studied in more detail as part of other studies by the authors. Ultimately, these investigations led to the development of a novel pre-treatment system that can be utilized to improve co-treatment of WWW and other high-strength wastewaters at municipal WWTPs [38].

3.4. Co-Treatment Feasibility Trials

3.4.1. Impact on Primary Clarification Performance

The results of the simulated primary clarification trials are shown in Table 5. The purpose of these trials was to evaluate the potential impact of discharging pre-treated WWTP, both with and without subsequent Fenton-like treatment, upstream of a municipal WWTP's primary clarifiers (Figures 1 and 2). In addition to determining the impact on primary effluent quality, qualitative impacts on clarifier performance were also considered. These factors are all considerations for the full-scale implementation of WWTP pre-treatment schemes. All trial runs, with the exception of the Control—No FeCl₃, had equivalent Fe dosages of 32.5 mg/L. For trials involving Fenton-like treated WWTP (Schemes 1A and 2A), it was not necessary to add Fe to the bench-scale clarification unit, since they contained sufficient Fe to provide an equivalent dose of 32.5 mg/L.

Table 5. Simulated primary effluent concentrations and removal rates for actual domestic WWTP raw influent plus WWTP after undergoing various types of pre-treatment.

Parameter	Raw Wastewater ¹	Control—No WWTP		Pre-Treatment Scheme			
		No FeCl ₃ ²	Plus FeCl ₃ ³	1A ^{4,5}	2A ^{4,5}	1B ³	2B ³
COD (mg/L)	537	221	94	327	306	323	311
TOC (mg/L)	110	60.0	22.4	81.5	79.0	77.8	79.4
TSS (mg/L)	338	69	17	63	56	132	139
TP (mg/L)	9.52	4.01	0.40	2.29	2.11	3.38	3.58
Fe (mg/L)	8.54	0.83	2.85	4.66	3.79	27.1	27.9
COD Removal ⁶ (%)	-	59	82	45	47	49	50
TOC Removal ⁶ (%)	-	45	80	37	38	44	39
TSS Removal ⁶ (%)	-	80	95	80	83	58	57
TP Removal ⁶ (%)	-	58	96	74	76	61	60
Fe Removal ⁶ (%)	-	90	93	88	91	33	31

¹ Raw wastewater sample collected upstream of the primary clarifiers at a municipal WWTP. ² No Fe dosed. Represents settled raw wastewater characteristics. ³ Supplemental Fe added to provide an equivalent dose of 32.5 mg/L as Fe. ⁴ For the pre-treatment schemes involving a Fenton-like treatment step (Schemes 1A and 2A), the Fe was present in the Fenton-like pretreated WWTP. The WWTP:raw wastewater ratio was selected to achieve an equivalent Fe dose of 32.5 mg/L as Fe. ⁵ Fenton-like operating parameters were H₂O₂ of 2500 mg/L, Fe₀ of 325 mg/L, and reaction time of 5 h. ⁶ Removal rates calculated based on overall influent concentrations of the raw wastewater plus pre-treated WWTP as applicable.

Iron salts are added to municipal WWTPs for phosphorus removal and improved coagulation and sedimentation performance [31]. The beneficial impact of FeCl₃ addition on the removal rates of COD, TOC, TSS, and TP can be seen in the Control trials (Table 4). The most significant improvement was in terms of TP removal, increasing from 45% to 80%. It was hypothesized that the iron present in the Fenton-like treated WWTP (Schemes 1A and 2A) would also be available to improve phosphorus removal and enhance coagulation in the primary clarification process. However, after the addition of WWTP pre-treated using Schemes 1A or 2A, the removal rates for COD, TOC, and TSS were consistent with or less than those observed for raw wastewater alone (Control—No FeCl₃, Table 5), suggesting little to no benefit associated with the addition of this iron source on primary settling performance. Furthermore, there was no improvement in COD or TOC removal rates when adding WWTP having undergone pre-treatment that included a Fenton-like step (Schemes 1A and 2A) vs. single stage pre-treatment (Schemes 1B and 2B). Improvements were observed in terms of TSS, TP, and Fe removal, likely due to the lower concentration of iron-complexing compounds present post-Fenton-like treatment. However, TP concentrations for all pre-treatment schemes were considerably higher than that associated with the Control—Plus FeCl₃ trial, despite 32.5 mg/L Fe being added to each of these trials.

Qualitatively, the addition of WWTP resulted in more turbid supernatant regardless of the pre-treatment scheme. The decomposition of the residual peroxide present in the post-Fenton-like WWTP samples resulted in the generation of small gas bubbles, negatively

impacting sludge settling and resulting in a less dense sludge blanket and an accumulation of a scum layer on the surface of the bench-scale units.

3.4.2. Impact on Aerobic Biological Treatment Performance

The results of the aerobic biological treatment trials are shown in Table 6. The purpose of these trials was to evaluate the potential impact of discharging pre-treated WWW, both with and without subsequent Fenton-like treatment, upstream of a municipal WWTP's aerobic bioreactors (Figure 1). All trial runs, with the exception of the Control—No FeCl₃, had equivalent Fe dosages of 32.5 mg/L. For trials involving Fenton-like treated WWW, it was not necessary to add Fe to the bench-scale bioreactor unit, since these WWWs contained sufficient Fe to achieve an equivalent dose of 32.5 mg/L.

Table 6. Simulated secondary effluent concentrations and mixed liquor characteristics after 3 h of aerobic oxidation using mixed liquor from a municipal WWTP treating WWW after undergoing various types of pre-treatment.

Parameter	Control—No WWW ¹		Pre-Treatment Scheme ²			
	No FeCl ₃ ³	Plus FeCl ₃ ⁴	1A ^{5,6}	2A ^{5,6}	1B ⁴	2B ⁴
COD (mg/L)	111	89	127	123	93	146
Filtered COD (mg/L)	43	46	66	77	59	62
TOC (mg/L)	16.7	12.5	23.6	24.5	14.6	23.6
Filtered TOC (mg/L)	9.7	7.7	12.6	13.0	8.7	12.1
TSS (mg/L)	35	24	46	50	44	52
TP (mg/L)	1.45	0.78	1.53	1.49	1.16	1.48
Filtered TP (mg/L)	0.28	0.08	0.26	0.25	0.13	0.24
Fe (mg/L)	1.68	2.89	6.27	5.69	7.42	10.5
Filtered Fe (mg/L)	0.08	0.08	0.15	0.21	1.29	2.8
MLSS _o (mg/L)	1129	1129	1129	1129	1129	1129
MLSS _{final} (mg/L)	991	1220	1169	1140	1199	1185

¹ No feed was added to the “Control” reactors. Reactors contained mixed liquor from the municipal WWTP's aerobic bioreactor. ² Reactors initially contained mixed liquor from the municipal WWTP's aerobic bioreactor. The reactor contents were allowed to settle and 10% of the volume was removed as supernatant. Pre-treated WWW was then added at a volumetric loading rate of 10% v/v. ³ No Fe dosed to this control reactor. ⁴ Supplemental Fe added to provide an equivalent dose of 32.5 mg/L as Fe. ⁵ For the pre-treatment schemes involving a Fenton-like treatment step (Schemes 1A and 2A), the Fe was present in the Fenton-like pretreated WWW. The volumetric loading of Fenton-like pre-treated WWW resulted in an equivalent Fe dose of 32.5 mg/L as Fe to the bioreactors. ⁶ Fenton-like operating parameters were H₂O_{2,o} of 2500 mg/L, Fe_o of 325 mg/L and reaction time of 5 h.

The addition of FeCl₃ to the control trials improved effluent quality in terms of COD, TOC, TSS, and TP. The addition of WWW that was pre-treated using Scheme 1A or 2A degraded the simulated secondary effluent compared to the Control—no FeCl₃ trial for all parameters. Furthermore, there was no apparent benefit associated with Fenton-like pre-treatment of the biologically pre-treated WWW (Scheme 2A vs. Scheme 2B), and an apparent negative impact of Fenton-like treatment of the diluted and settled WWW (Scheme 1A vs. Scheme 1B). Furthermore, the Fe present in the Fenton-like treated WWW (Schemes 1A and 2A) did not improve TP removal, which is consistent with the results of the primary clarification trials. This suggests that the Fe remaining in the Fenton-like treated WWW cannot be used as an effective coagulant in either primary or secondary municipal WWTP treatment units. High effluent TP concentrations were also observed in the trials with WWW pre-treated using Schemes 1B and 2B compared to the Control—Plus FeCl₃ trial, despite 32.5 mg/L of Fe being added to all of these trials. It is possible that this is due to the presence of iron-complex-forming compounds in the pre-treated WWW samples (see Section 3.3).

Qualitatively, there were no differences observed in bioreactor performance or the settleability of the mixed liquor between the various treatment trials.

4. Conclusions

Options for the pre-treatment of WWW were evaluated at a high level. Two options (dilution and settling; aerobic biological treatment) were identified as feasible for full-scale implementation. A three-factor BBD experimental design was used to evaluate the Fenton-like AOP for the treatment of pre-treated WWW. COD and TOC removal rates were selected as response variables; however, it was concluded that these variables do not accurately reflect the extent of the reaction. This may be due to the solubilization of particulate COD and TOC fractions during Fenton-like treatment, which, when combined with sample handling protocols prior to parameter analysis, affects apparent removal rates. The ISS generation rate, as measured in the quenched and pH adjusted samples post-Fenton-like treatment, was determined to be an alternative response variable that could be used to assess the extent of the Fenton-like reaction. Using this response variable, optimal operating conditions over the ranges evaluated were determined to be $\text{H}_2\text{O}_{2,0}$ of 4000 mg/L, Fe_0 of 325 mg/L, and reaction time of 4 h for diluted and settled WWW with a COD of 1460 mg/L. RSM results suggest that the optimal $\text{H}_2\text{O}_{2,0}$, and Fe_0 concentrations exceed these concentrations.

The impact of adding pre-treated WWW, with or without Fenton-like treatment, and upstream of a municipal WWTP's primary clarifiers or aerobic bioreactors, was also assessed. The decomposition of residual H_2O_2 in the Fenton-like treated WWW is likely to negatively impact the primary clarifier sludge settling performance and promote the generation of scum on the clarifier surface. Co-treating WWW negatively impacted both the simulated primary effluent and simulated secondary effluent quality, regardless of the pre-treatment method used. In addition, the Fe present in the pre-treated WWW, both with and without Fenton-like treatment, was not effective at enhancing TP removal. Therefore, challenges associated with co-treating WWW in municipal WWTPs remain despite the pre-treatment alternatives investigated as part of this study. Further optimization of the Fenton-like treatment could improve co-treatment in the aerobic bioreactors; however, the pre-treatment system would be complex to operate. Overall, it can be concluded that the Fenton-like AOP provides limited opportunity to optimize or enhance co-treatment at municipal WWTPs.

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