Decolorization of alkaline TNT hydrolysis effluents using UV/H$_2$O$_2$

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Abstract

Effects of H$_2$O$_2$ dosage (0, 10, 50, 100 and 300 mg/l), reaction pH (11.9, 6.5 and 2.5) and initial color intensity (85, 80 and 60 color unit) on decolorization of alkaline 2,4,6-trinitrotoluene (TNT) hydrolysis effluents were investigated at a fixed UV strength (40 W/m^2). Results indicated that UV/H$_2$O$_2$ oxidation could efficiently achieve decolorization and further mineralization. Pseudo first-order decolorization rate constants, k, ranged between 2.9 and 5.4 h^{-1} with higher values for lower H$_2$O$_2$ dosage (i.e., 10 mg/l H$_2$O$_2$) when the decolorization occurred at the reaction pH of 11.9, whereas a faster decolorization was achieved with increase in H$_2$O$_2$ dosage at both pH 6.5 and 2.5, resulting in the values of k as fast as 15.4 and 26.6 h^{-1} with 300 mg/l H$_2$O$_2$ at pH 6.5 and 2.5, respectively. Difference in decolorization rates was attributed to the reaction pH rather than to the initial color intensity, resulting from the scavenging of hydroxyl radical by carbonate ion. About 40% of spontaneous mineralization was achieved with addition of 10 mg/l H$_2$O$_2$ at pH 6.5. Efficient decolorization and extension of H$_2$O$_2$ longevity were observed at pH 6.5 conditions. It is recommended that the colored effluents from alkaline TNT hydrolysis be neutralized prior to a decolorization step.
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Keywords: Alkaline hydrolysis; Carbonate; Decolorization; Hydroxyl radical ($^•$OH); TNT

1. Introduction

Environmental contamination with high explosives (HEs) has been posing a significant threat due to their toxic effects to humans, animals, agricultural produce, and other natural receptors [1,2]. 2,4,6-Trinitrotoluene (TNT) had been the predominant HE for military purposes before its production was ceased in the mid 1980s in the United States. TNT environmental contamination still exists because of both military activities before that time and demilitarization afterwards. For example, 28% of 1155 soil samples from 46 sites were found to be contaminated with one or more explosives. Of those samples, 97% contained TNT, hexahydro-1,3,5-trinitro-1,3,5-triazine and/or 2,4-dinitrotoluene [3].

Alkaline hydrolysis has recently been reported as an alternative remediation technology for TNT-contaminated water

[4,5]. An intriguing feature in alkaline TNT treatment is the production of color-forming intermediates/by-products [5,6]. A redish color production in TNT reaction with alkali is from Meisenheimer complexes that result from the nucleophilic attack by a hydride ion on the aromatic ring [5,7]. Azo- and azoxy-compounds are also generated by spontaneous intermolecular condensation of nitroso- and hydroxylamino-intermediates of TNT [8], resulting in the appearance of varying colors in the visible range. Together with potential environmental concerns due to unknown properties of the color-forming compounds, the colored effluents can pose aesthetic problems.

Advanced oxidation processes (AOP) such UV/hydrogen peroxide (H$_2$O$_2$), UV/ozone (O$_3$) and O$_3$/H$_2$O$_2$ utilize hydroxyl radical ($^•$OH) generated, which has a very high oxidizing capacity with the redox potential of 2.8 V and has very fast reaction rate with organic compounds in the range of 10^8–10^{10} M^{-1} s^{-1} [9]. UV/H$_2$O$_2$ combination is the simplest method of $^•$OH generation (H$_2$O$_2$ + $h\nu$ → 2$^•$OH) [10] and is capable of destroying a wide variety of hazardous compounds in water [11–13]. Furthermore, studies with UV/H$_2$O$_2$ oxidation for the remediation of colored wastewater (mainly, textile wastewater) have

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shown great potential to yield efficient decolorization [14–16].

Therefore, the purpose of this study was to evaluate the applicability of UV/H_2O_2 advanced oxidation, as a polishing step, to the decolorization of the effluents from alkaline TNT hydrolysis. To this end, a batch UV/H_2O_2 system was employed to investigate relationships between the decolorization rate and the operating variables such as reaction pH, initial color intensity and H_2O_2 dosage. The findings from the current study are valuable in the attempt to optimize alkaline remediation and process control for TNT-contaminated water.

2. Materials and method

2.1. Source of colored wastewater

Alkaline TNT hydrolysis was carried out in a continuously stirred tank reactor (CSTR) to generate an effluent stream of colored water for this study. Briefly, the pure water in a CSTR was initially dosed with 50% sodium hydroxide (NaOH) solution to raise the starting solution pH to 11.9. Ten mg/l of TNT solution was then continuously added to the reactor at 2-day hydraulic retention time (i.e., at the flow rate of 5 l per day to 10 l CSTR). During the experiment, a pH controller maintained a constant reaction pH by the automatic addition of 0.1N sulfuric acid (H_2SO_4) and 0.2 N NaOH solutions. The reaction temperature was kept constant at 25 °C.

2.2. UV/H_2O_2 decolorization

For the current decolorization study, 1 l of the colored water was initially placed in a UV/H_2O_2 photochemical reaction vessel purchased from ACE Glass Co. A 12 W low-pressure immersion lamp (Arc length 16.5 cm, Canrad-Hanovia, Inc., ACE Glass Co.) fabricated from Suprasil was used as the light source. UV output at principal wavelength of 254 nm was 3.5 W. The UV lamp was inserted into a double-walled quartz immersion well located at the center of reactor. The UV lamp was kept on during the experiment. Fresh tap water was flushed through the immersion well to prevent the lamp from overheating. The solution was fully stirred with a magnetic stirrer to ensure sufficient mixing. Reactions were performed at ambient temperature (20–22 °C).

Experiments were carried out with three different pHs of nominal 11.9, 6.5, and 2.5, corresponding to initial color intensities of nominal 85, 80, and 60, respectively. The lower pHs of 6.5 and 2.5 were obtained by adding concentrated H_2SO_4 dropwise to the original pH 11.9 solution. This acid addition decreased the color intensity. Four different initial H_2O_2 concentrations (10, 50, 100, and 300 mg/l) were also investigated. Control experiments without UV irradiation (i.e., H_2O_2 oxidation only) were conducted at 100 mg/l

H_2O_2 concentration at the pHs of 11.9 and 2.5. Blank experiments without H_2O_2 dosage (i.e., UV photolysis only) were also carried out at the three pH levels (11.9, 6.5 and 2.5).

2.3. Sample analysis

Samples ($\sim$5 ml) were collected at predetermined times and immediately analyzed for color intensity, H_2O_2 concentration and pH. After the analyses were done, the samples were returned to the reactor so that the change in total volume in the reactor throughout the experiment was less than 1%. Since color removal was the principal objective of this study, color intensity was the main parameter monitored. In this regard, "apparent" color without filtering or centrifuging the samples was measured spectrophotometrically with the HACH Platinum-Cobalt Standard Method [17]. H_2O_2 concentration was measured with an RQflex 2 reflectometer (EM Science, Gibbstown, NJ). The value of pH was measured with an OAKTON pH 6 Acorn Series Meter. Despite unbuffered reaction pH, the pH did not change significantly throughout the experiments (i.e., ±0.1 unit). A short-wave UV meter (Model J-225 BLAK-RAY, UVP, Upland, Ca) was used to measure the UV radiation intensity, which was 40 W/m^2. Alkalinity was determined by titration [18].

High pressure liquid chromatography (HPLC) was used for analysis of TNT and potential TNT-related by-products by comparing retention times of degradation products to authentic standards (EPA 8330 Energetic Materials Kit (Supelco)) of TNT, 2-amino-4,6-dinitro-toluene, 4-amino-2,6-dinitrotoluene, 2,4-dinitrotoluene, 2, 6-dinitrotoluene, 2-nitrotoluene, 3-nitrotoluene, 4-nitrotoluene, 1,3,5-trinitrobenzene, 1,3-dinitrobenzene, and nitrobenzene. Total organic carbon (TOC) concentrations (Tekmar-Dohrmann Phoenix 8000 TOC Analyzer, Mason, OH) were measured at reaction pH of 6.5 to investigate the portion of TNT mineralized during UV only treatment and UV/H_2O_2 treatment (10 mg/l H_2O_2).

3. Results and discussion

3.1. Characteristics of colored effluents from alkaline TNT hydrolysis

The characteristics of the colored water produced from alkaline hydrolysis of TNT are shown in Table 1. The presence of high carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) species is known to impede AOP performance due to the scavenging of $^\bullet OH$ [19]. An initial hypothesis from the high CO_3^{2-} alkalinity in the original colored water (Table 1), is that lower decolorization efficiencies were expected in the experiments at pH 11.9.

As shown in Fig. 1, the UV-Vis spectra during alkaline TNT hydrolysis in a CSTR indicated the presence of dissimilar color-forming intermediates that adsorbed light over a specific wavelength range and thereby produced different

Table 1
Characteristics of colored effluent collected from alkaline TNT hydrolysis

	Values
pH	11.9
Color intensity (color unit[a])	85
Total organic carbon (TOC) (mg/l)	2.1
Hydroxide (OH^-) alkalinity (mg/l as calcium carbonate ($CaCO_3$))	445
Carbonate (CO_3^{2-}) alkalinity (mg/l as $CaCO_3$)	340
Bicarbonate (HCO_3^-) alkalinity (mg/l as $CaCO_3$)	0
2,4,6-Trinitritoluene (TNT) (μg/l)	90

[a] One color unit is equivalent to 1 mg/l platinum as chloroplatinate ion.

visual colors. Yellow, orange, and red colors are observed over the wavelength range of 380–460 nm, 380–500 nm, and 440–560 nm, respectively [20]. A gradual increase in absorbance was observed at these wavelengths (Fig. 1) as alkaline TNT hydrolysis proceeded in the CSTR. The spectral mound over a wide range of visual wavelengths suggests the effluent contained a variety of color-forming compounds.

3.2. Effect of initial H_2O_2 concentration

Different H_2O_2 concentrations (0, 10, 50, 100, and 300 mg/l) were dosed to determine the effect of H_2O_2 concentration on the decolorization rate by UV/H_2O_2. A pseudo first-order rate constant, k, was calculated by simple least-squares regression of the natural log of color intensities versus time. The $^{\bullet}OH$ concentration was then estimated by assuming a second-order rate constant, K, of 5×10^9 M^{-1} s^{-1} and using $[^{\bullet}OH] = k/K$ according to the procedure of Beltran et al. [21]. This assumed K value lies within the reported range of 10^8–10^{10} M^{-1} s^{-1} [9].

In general, the best UV/H_2O_2 decolorization was achieved at the lowest reaction pH of 2.5, whereas a relatively less effective decolorization was observed in the solutions of pH 11.9 (Fig. 2 and Table 2). At both pH 6.5 and 2.5, a faster decolorization was achieved with the higher H_2O_2 dosage, whereas the decolorization rate was hindered by the increase of H_2O_2 dosage at pH 11.9. Blank experiments in the absence of H_2O_2 (i.e., UV only) showed a quicker decolorization at a lower pH, although decolorization rates were slower than those for UV/H_2O_2 systems. Control experiments with H_2O_2 only achieved negligible decolorization. The observation in the blank experiments was consistent with the results by Ince et al. [22], who reported that the chemical bond of azo compounds could be directly but slowly photolyzed by UV irradiation and that the process could be substantially improved by the addition of H_2O_2.

The excess H_2O_2 dose can reduce the oxidation rate by acting as a $^{\bullet}OH$ radical scavenger itself as follows [9,23]:

$$^{\bullet}OH + H_2O_2 \rightarrow {}^{\bullet}HO_2 + H_2O \tag{1}$$

$$^{\bullet}OH + H_2O_2 \rightarrow {}^{\bullet}O_2^- + H^+ \tag{2}$$
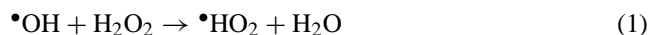
Wang et al. [19] reported decreased humic acid oxidation rates with the increase of H_2O_2 concentration greater than 0.01%. Huling et al. [24] also found a decreased oxidation of adsorbed 2-chlorophenol to granular activated carbon containing fixed iron oxide at the high H_2O_2 concentration due to increased scavenging by excess H_2O_2. Also, the excess H_2O_2 can absorb most of the light. It is also important to account for a greater CO_3^{2-} alkalinity in the colored water at pH 11.9. The presence of HCO_3^- and CO_3^{2-} species had a negative effect due to the scavenging of $^{\bullet}OH$ as follows [19]:

$$HCO_3^- + {}^{\bullet}OH \rightarrow {}^{\bullet}CO_3^- + H_2O \tag{3}$$

$$CO_3^{2-} + {}^{\bullet}OH \rightarrow {}^{\bullet}CO_3^- + OH^- \tag{4}$$
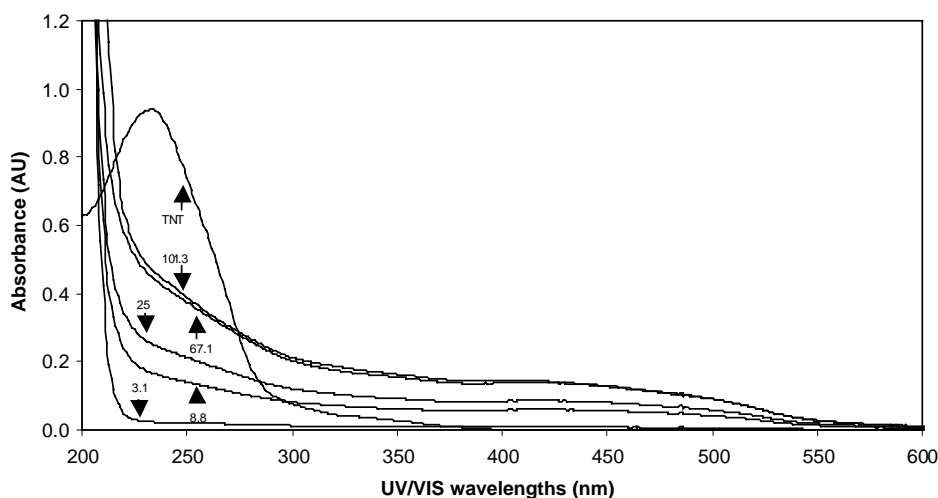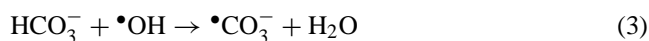

Fig. 1. UV-Vis spectra of the colored effluent in the time course of alkaline TNT hydrolysis at pH 11.9. TNT: TNT solution before alkaline hydrolysis; 3.1, 8.8, 25, 67.1 and 101.3: alkaline hydrolysis effluents at 3.1, 8.8, 25, 67.1 and 101.3 h, respectively. The analysis was done with an HP-8453 diode array spectrophotometer.
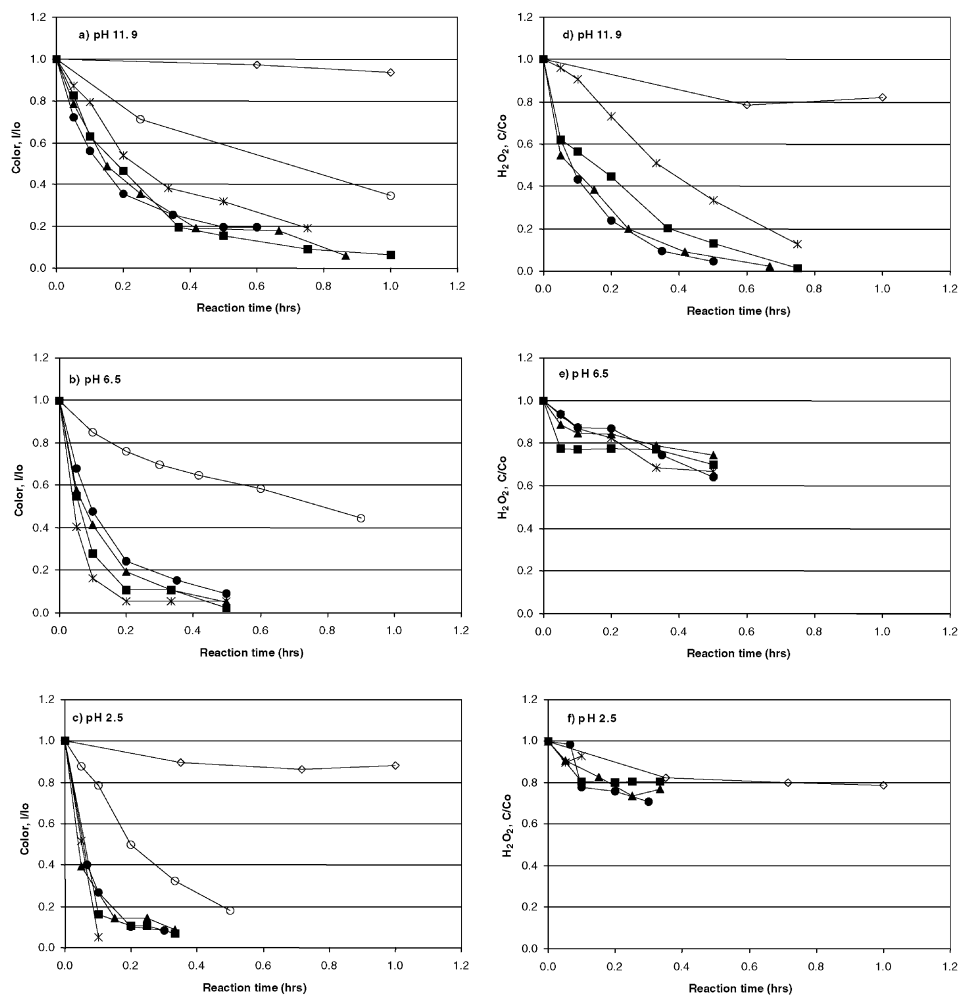
Fig. 2. Trends of decolorization depending on H_2O_2 dosage at different reaction pH (a–c) and residual H_2O_2 concentration depending on initial H_2O_2 dosage at different reaction pH (d–f). (●) UV + H_2O_2 10 mg/l; (▲) UV + H_2O_2 50 mg/l; (■) UV + H_2O_2 100 mg/l; (*) UV + H_2O_2 300 mg/l; (○) UV only; and (◇) H_2O_2 100 mg/l only.

Since CO_3^{2-} is not prevalent in the lower pH solutions, especially at pH 2.5, free radical scavenging effects by CO_3^{2-} was nearly absent. Therefore, the decrease in decolorization rate at the highest pH 11.9 could be attributed to an increased scavenging by both H_2O_2 itself and CO_3^{2-} species. The scavenging effect of H_2O_2 at pH 11.9 was also supported by the noticeable decreasing trend of the residual H_2O_2, (Fig. 2).

Table 2
Pseudo first-order decolorization rate constants (k) and calculated hydroxyl radical ($^\bullet$OH) concentrations

pH	H_2O_2 dosage (mg/l)									
	0		10		50		100		300	
	k^a	[$^\bullet$OH]^b	k	[$^\bullet$OH]	k	[$^\bullet$OH]	k	[$^\bullet$OH]	k	[$^\bullet$OH]
11.9	1.3 (0.99^c)	–^{d}	5.4 (0.98)	1.1	4.8 (0.98)	1.0	4.0 (0.99)	0.8	2.9 (0.99)	0.6
6.5	1.4 (0.98)	–^{d}	7.2 (0.99)	1.4	8.4 (0.98)	1.7	11.4 (0.99)	2.3	15.4 (0.97)	3.1
2.5	3.2 (0.96)	–^{d}	12.0 (0.97)	2.4	13.5 (0.96)	2.7	18.3 (0.99)	3.7	26.6 (0.89)	5.5

[a] Unit: h^{-1}.
[b] Unit: mol/l.
[c] Values in parenthesis are the correlation efficiency (R^2).
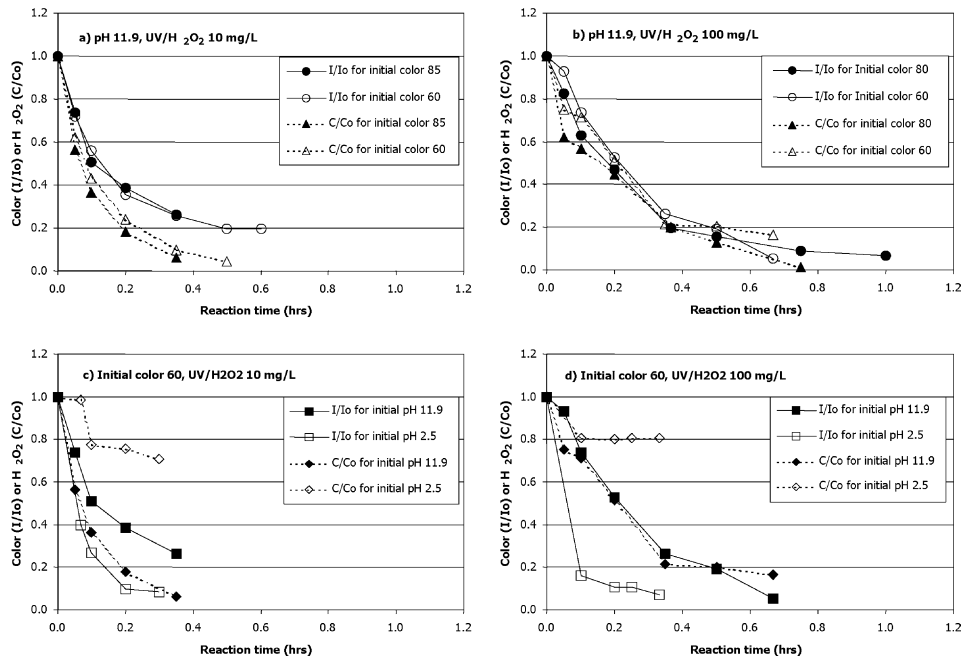[d] Not applicable for the UV only system.

Fig. 3. Effect of different initial color intensity on decolorization in the solution that had the same pH of 11.9 (a and b) and effect of different reaction pH on decolorization in the solution that had the same initial color intensity of 60 (c and d).

3.3. Effects of initial color intensity and reaction pH

As mentioned previously, the efforts to decrease the initial reaction pH to 6.5 and 2.5 weakened the color intensity from 85 to 80 and 60, respectively. Hence, different decolorization rates could be attributed to the confounding effect of both the reaction pH and the initial color intensity, unless one of those variables is ruled out. In this regard, the sole effect of initial color intensity on decolorization efficiency was further investigated. The original colored water with color intensity of 85 was diluted with pure water to decrease the color intensity to 60. This dilution decreased the pH to 11.3, and a couple of drops of 50% NaOH were added to restore the pH to 11.9. The decolorization rates were compared in these two initial solutions at pH 11.9 and different initial color intensity (85 versus 60). No significant
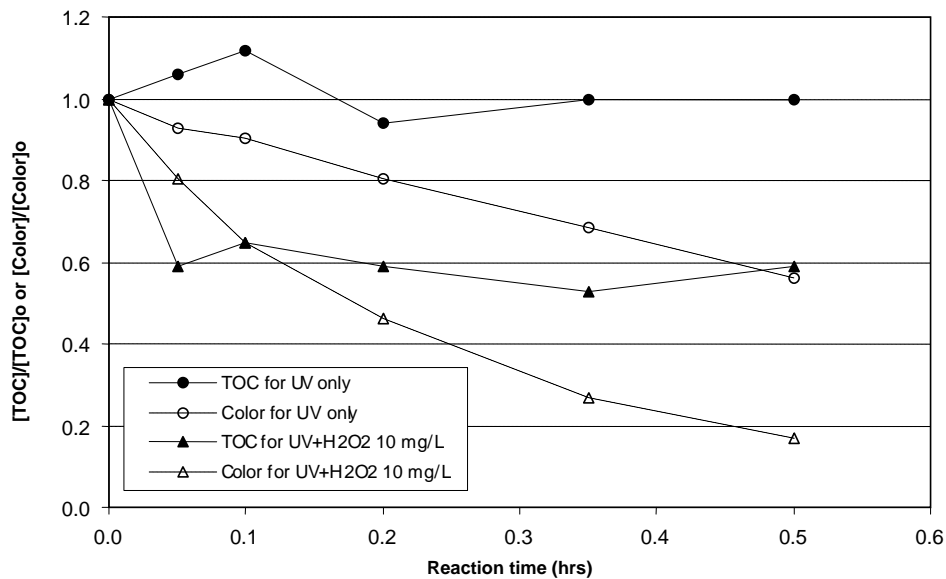

Fig. 4. Reduction in the total organic carbon concentrations in comparison with decrease in color intensities. Reaction pH 6.5; $[TOC]_o = 1.7$ mg/l; and $[color]_o = 60$.

effect of initial color intensity on the decolorization rate was observed as long as the reaction occurred at the same pH (Fig. 3a and b).

Another experimental set involved comparison of decolorization rates in two solutions at pH 11.9 and 2.5 with the same color intensity of 60. The decrease in reaction pH significantly enhanced the decolorization rate (Fig. 3c and d). Also, a lesser amount of H_2O_2 was consumed at pH 2.5 than pH 11.9, despite a more enhanced decolorization at pH 2.5. Consequently, the data in Fig. 3 indicate that the decolorization rate is controlled by reaction pH rather than the initial color intensity. This is consistent with the greater carbonate alkalinity in the pH 11.9 solution which scavenges the $^\bullet$OH and reduces decolorization reactivity.

3.4. Total organic carbon removal

For the UV only treatment, a reduction in TOC concentration was not achieved, despite attaining nearly 40% decolorization after 0.5 h (Fig. 4). Consequently, UV oxidation partially destroyed the color-forming compounds, but was not able to mineralize the organic carbon.. When UV oxidation was coupled with 10 mg/l H_2O_2 (i.e., advanced oxidation), a 40% reduction in TOC concentration and 80% reduction in color intensity were observed after 0.5-h reaction time. These data are consistent with the results of Ince et al. [22], who reported that UV irradiation could directly photolyze the chemical bond of color-forming azo compounds, and the presence of H_2O_2 significantly enhanced this process.

In the time course of the decolorization experiments, no compounds were detected with HPLC even in the UV only experiment. The colored water was determined to have an initial TNT concentration of 90 μg/l and no detectable intermediates. Therefore, the absence of TNT and any detected aromatic intermediates in the UV/H_2O_2-treated water indirectly indicated reactions involving aromatic-ring cleavage. An ion chromatography was employed in an attempt to detect formation of organic/inorganic intermediates such as acetate, formate, nitrite, nitrate, citrate and oxalate during the decolorization reactions. None of these compounds were detected during the experiments.

4. Conclusions

This study employed UV/H_2O_2 advanced oxidation for the treatment of colored wastewater produced from alkaline hydrolysis of TNT-contaminated water. The influence of pH, H_2O_2 dosage, and initial color intensity on decolorization rates were investigated. The UV/H_2O_2 treatments were capable of decolorizing the colored wastewater at the pHs investigated (11.9, 6.5, and 2.5) within feasible treatment duration of less than 1 h. Enhanced decolorization was

achieved with an increase in H_2O_2 dosage and decrease in pH. The only exception to this trend was at pH 11.9 where less decolorization was observed with an increase in H_2O_2 dosage. The behavior with pH was due to the scavenging of $^\bullet$OH by CO_3^{2-}.

Efficient decolorization and use of H_2O_2 were observed at pH 6.5 conditions. It is recommended that the colored effluents from alkaline TNT hydrolysis be neutralized prior to a decolorization step by UV/H_2O_2 advanced oxidation. The lack of detectable intermediates using HPLC suggests aromatic-ring cleavage of the colored compounds during UV/H_2O_2 treatment. Furthermore, the TOC mass balance indicated 40% mineralization of the initial organic matter. Future work should study the toxicity of the UV/H_2O_2 treated water to ensure safe discharge of the effluent from this process.

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