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Advanced oxidation of high concentrations of formaldehyde in aqueous solution under fluorescent and UV light

Fatma Deniz*, Mehmet Ali Mazmancı

Department of Environmental Engineering, Mersin University, Mersin, Turkey

Abstract

Background: Formaldehyde (FA) is a carcinogen compound, which is soluble in water. FA can be removed from aqueous solution using advanced oxidation methods.

Methods: In this study, the oxidation of FA was studied under fluorescent and UV light. Hydrogen peroxide (H_2O_2) was used as an oxidant. The pH value and H_2O_2 amount of samples were optimized. The chemical oxygen demand (COD), FA concentration, and H_2O_2 consumption were followed.

Results: It was observed that the pH value of the sample was more significant under fluorescent light than UV light at oxidation of FA. The highest COD removal and H_2O_2 reduction were 18.57 and 30.90%, respectively, at pH 12.00, with a 1:1 ratio of FA:H_2O_2 under fluorescent light. 86.41% FA and 62.12% COD removal were achieved at pH 7.00, with a 1:2 ratio of FA:H_2O_2, under UV light. It was observed that H_2O_2 was consumed at all pH values under UV light. On the other hand, under fluorescent light, the concentration of H_2O_2 decreased only at pH 12. In control samples containing only H_2O_2, the H_2O_2 reduction was 92.09% at pH 11.91, while it was 2-6% at other pH levels under fluorescent light. The H_2O_2 reduction changed between 33 and 44% at different pH values under UV light. The oxidation of FA was found to be suitable for the pseudo-first-order kinetic model and Langmuir isotherm model.

Conclusion: The most effective oxidation was obtained at the original pH value (7.00) and 1:2 ratio of FA:H_2O_2 under UV light.

Keywords: Water treatment, Formaldehyde, UV light, Hydrogen peroxide

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***Correspondence to:**
Fatma Deniz,
Email: fatmadeniz@mersin.edu.tr

Introduction

Formaldehyde (FA) is a colorless, flammable gas, which is soluble in water, acetone, ethanol, benzene, diethyl ether, and chloroform. It can also be decomposed when exposed to light (1). It is dissolved in water at a rate of 40%, and its aqueous solution is called formalin (1,2). FA is used in plastic and resin production. It is also used in many medicines and cosmetic products, veterinary drugs, fungicides, embalming, and textile products (2-6). The aqueous solution containing FA occurs after producing these products and being discharged into the wastewater system from facilities (5,7,8). FA has been classified as a carcinogen by the International Agency for Research on Cancer (IARC) (3,9). Therefore, water containing FA must be treated. Biological treatment of wastewater containing FA in high concentrations is difficult due to its toxic effect on living organisms (3,10). Advanced oxidation processes (AOPs) are an alternative treatment method for organic compounds that are difficult to decompose by biological methods (11,12). In previous studies, researchers have applied various AOP methods such as electro-oxidation (13), photocatalytic degradation with nano-TiO_2 (14), composite Ag/TiO_2 (15), UV/H_2O_2, Fenton and photo-Fenton (3,16), UVC/$S_2O_8^{-2}$ (17), and photocatalytic degradation by Fe/TiO_2 (18), for FA oxidation. AOPs are a type of oxidation performed using hydroxyl radicals ($OH^{\cdot}$) (4, 19). It is known that the organics photodegradation is affected by OH radicals (20). Hydroxyl radicals react with any organic substances around thanks to their unpaired electrons, and they transform organic substances into products such as CO_2 and H_2O under suitable conditions (4,19).

AOPs are based on highly reactive radicals' on-site production to decompose organic pollutants in water. These processes include homogeneous and heterogeneous chemical and photochemical processes, such as UV photolysis, mostly performed using chemical oxidants such as O_3, H_2O_2 or catalysts like TiO_2, electrochemical oxidation, Fenton processes, supercritical water, and wet air oxidation, sonochemical processes, and various combinations of these methods (4,21).

UV-based AOPs are methods based on the use of UV light with or without different oxidants such as O_3, H_2O_2, TiO_2, and H_2O_2/Fe^{+2} (Photo-Fenton reaction) (1,2). However, the disadvantage of these methods is their cost. Therefore, the cost can be reduced by optimizing parameters such as pH, oxidant dose, and UV exposure time (4).

Using AOPs with UV has become an alternative for degradation of organic pollutants that cannot be removed by conventional methods. Among the UV-based AOPs, UV/H_2O_2 is a promising technology (22). H_2O_2 is one of the strong oxidants that reacts with UV light at wavelengths below 290 nm and forms hydroxyl radicals. The reaction equation of H_2O_2 with UV light is given in Eq. (1) (23).

$$H_2O_2 + hv \rightarrow 2OH^{\cdot} \tag{1}$$

The reaction efficiency varies according to pH level of the environment, time and intensity of UV exposure, and H_2O_2 concentration. H_2O_2 gives different reactions at different pH levels. The rate of degradation increases at basic pH under UV light (23).

This study aimed to observe the change of FA and H_2O_2 in an aqueous solution under fluorescent and UV light in the presence of H_2O_2 and to determine the most effective conditions for FA removal.

Materials and Methods

Fluorescence/H_2O_2 and UV/H_2O_2 oxidation experiments

This study is consisted of pH optimization and FA:H_2O_2 ratio optimization under fluorescent and UV light with H_2O_2, separately.

The synthetic water samples were prepared using 37% FA solution. The pH values of synthetic water samples were adjusted as approximately 3.00, 6.00, 9.00, and 12.00 at the pH optimization. Also, the original pH of the sample (~7.00) was studied at UV experiments. The pH of the samples was adjusted using H_2SO_4 and NaOH solutions. The final FA concentration of samples was 1000 mg/L. The samples were placed in a magnetic stirrer under fluorescent and UV light, separately. H_2O_2 was added to each sample to reach the final H_2O_2 concentration of 1000 mg/L after adjusting the pH value. The FA:H_2O_2 concentration ratio was 1:1. The samples containing only FA (1000 mg/L) and only H_2O_2 (500 mg/L) were used as the control groups.

The pH of samples was adjusted as the optimum pH at the FA:H_2O_2 ratio optimization. The final FA concentration of samples was 1000 mg/L. H_2O_2 was added to each sample so that the samples' final H_2O_2 concentrations were 1000, 2000, and 3000 mg/L, respectively, and the ratio of FA:H_2O_2 were 1:1, 1:2, and 1:3, respectively.

Three different FA concentrations (500, 1000, and 1500 mg/L) were studied to examine the initial concentration of FA.

A UV-C lamp (8 W, 254 nm) was used for UV/H_2O_2 oxidation. The distance between the light source and the sample was 2 cm. The surrounding of the system was arranged to keep samples and a light source inside. The samples were collected at specific time intervals for chemical oxygen demand (COD), FA, H_2O_2 analysis, and pH measuring. All experiments were performed at room temperature.

Analytical methods

The COD analysis was performed according to Standard Methods 5220-D (24), and H_2O_2 analysis was performed according to method I^{-3} (25). Hach Lange LCK 425 kits were used for FA analysis. Colorimetric measurements were made with the Hach Lange DR3900 UV-visible spectrophotometer.

The removal efficiency (%) was calculated as follows:

$$\text{Removal efficiency, } \% = \frac{[input]-[output]}{[input]} \times 100 \tag{2}$$

Langmuir and Freundlich isotherms were calculated to compare the adsorption isotherms.

Pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic models were applied to compare adsorption kinetics.

Results

pH optimization for FA removal with H_2O_2 in water samples

It was aimed to investigate the effect of different pH levels on the oxidation of FA (1000 mg/L) with H_2O_2 (1000 mg/L) under fluorescent and UV light. For fluorescent light experiments, pH values were adjusted as 3.00, 6.02, 9.10, and 12.00. The COD removal at pH 3.00, 6.02, and 9.10 varied between 1 and 12%. At pH 12.00, the COD decrease in the first 10 minutes was 18.57% (Figure 1a). The highest COD removal was obtained at pH 12.00 in the presence of H_2O_2. For UV light experiments, pH values were arranged as 3.04, 5.92, 7.02 (original pH), 9.10, 12.24, and COD removal was obtained as 30, 34, 43, 43, and 44% in samples, respectively (Figure 1b). During the experiment, the change in the amount of H_2O_2 was followed under fluorescent light. The amount of H_2O_2 was not changed at pH 3.00, 6.02, and 9.10. However, at pH 12.00, a 20% reduction was observed in the first 10 minutes. H_2O_2 reduction reached 30.90% after 300 minutes (Figure 2a). Under UV light, it was observed that almost all of H_2O_2 (1000 mg/L) was consumed at each pH level (Figure 2b).

The changes in pH of samples were followed, and each sample's pH decreased at the end of the experiment at both light sources (Tables 1 and 2).

Sample containing only FA (1000 mg/L) and only H_2O_2 (500 mg/L) were studied as the control groups. In samples containing only FA, the COD values were followed. Under fluorescent light, the COD values remained the same. The

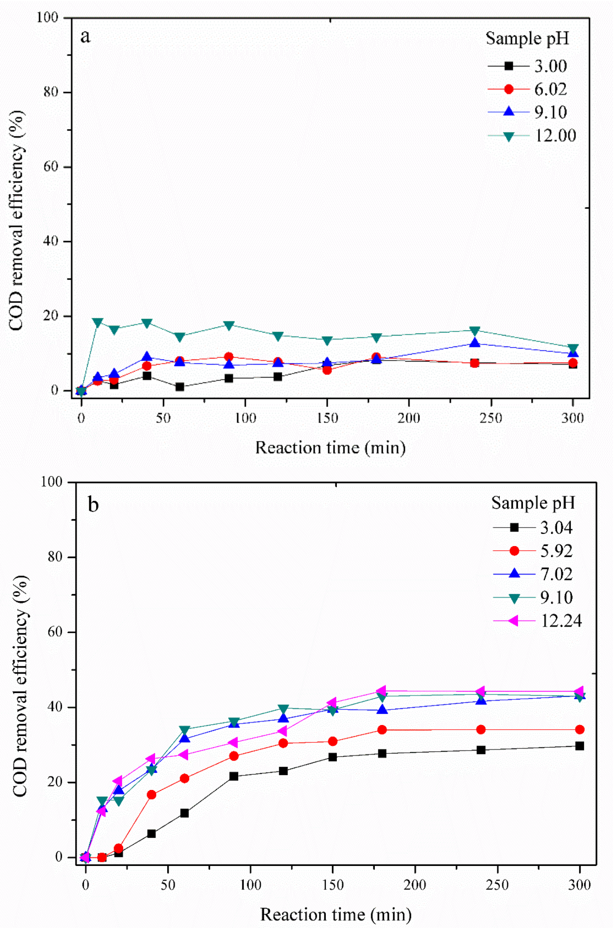

Figure 1. COD removal (%) in samples containing FA and H_2O_2 (1:1) at different pH levels, under (a) fluorescent and (b) UV light.

highest COD removal (6%) was obtained under UV light.

Optimization of FA:H_2O_2 ratio in FA removal with H_2O_2 in water samples

The effect of different concentrations of H_2O_2 (1000, 2000, and 3000 mg/L) was observed for two light sources. The FA:H_2O_2 concentration ratio was adjusted as 1:1, 1:2, and 1:3. It was aimed to observe the effect of increasing H_2O_2 amount on the COD removal and to find the optimum FA:H_2O_2 rate. This experiment was performed at pH 12.00 under fluorescent light and at the sample's original pH (~7.00) under UV light. The COD removal decreased as the H_2O_2 concentration of the samples increased under fluorescent light. The highest COD removals for FA:H_2O_2 ratio of 1:1, 1:2, and 1:3 were calculated to be 18.57, 9.60, and 10.19%, respectively (Figure 3a). The COD removal efficiencies at the ratio of 1:1, 1:2, and 1:3 (FA: H_2O_2) were found to be 43.13, 62.16, and 53.78% under UV light, respectively (Figure 3b). The changes in H_2O_2 amount were followed. Under fluorescent light, H_2O_2 concentration decreased 20.39, 3.59, and 0.67% for samples with a ratio of 1:1, 1:2, and 1:3, respectively, at the 10th minute. At the end of the reaction time (300 minutes), the decrease rates in H_2O_2 were 30.90, 13.79, and 9.28% for the 1:1, 1:2, and 1:3 ratios, respectively (Figure 4a). Under UV light, the decrease in H_2O_2 concentrations were 93.69, 95.94, and 59.47% for the ratio of 1:1, 1:2, and 1:3, respectively (Figure 4b).

It was observed that under fluorescent light, the pH decreased at the end of the experiment and the highest decrease occurred at 1:1 FA:H_2O_2 sample (Table 3). Under UV light, the initial pH (7.02) in all proportions studied was measured at 2.60 levels after 300 minutes. The sample's pH change at the ratio of 1:2 was followed during the experiment. The pH value was measured as 3.88 in the 10th minute (Figure 5). During the experiment at the optimum conditions, the FA concentration decreased from 1060 to 144 mg/L, and the COD value decreased from 1380.92 to 522.58 mg/L.

The initial concentration of FA

Initial FA concentrations (500, 1000 and 1500 mg/L) were studied to calculate the kinetic and isotherm parameters containing H_2O_2 (1000 mg/L) under UV light. The results showed that COD removal efficiencies were 66.04, 34.71, and 10.85 for FA concentrations of 500, 1000, and 1500 mg/L, respectively. H_2O_2 was totally consumed at all tested FA concentrations.

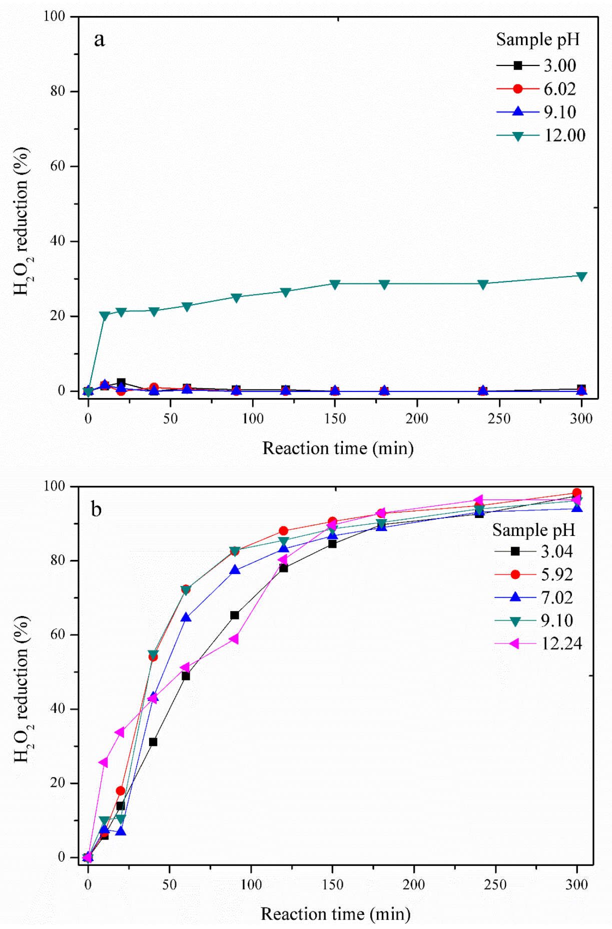

Figure 2. H_2O_2 concentration change (%) in samples containing FA and H_2O_2 (1:1) at different pH levels under (a) fluorescent and (b) UV light.

Table 1. Initial and final pH values of samples containing FA and H_2O_2 (1:1) under fluorescent light

Initial pH	3.00	6.02	9.10	12.00
Final pH	2.91	3.60	4.00	7.53

Table 2. Initial and final pH values of samples containing FA and H_2O_2 at a ratio of 1:1 under UV light

Initial pH	3.04	5.92	7.02	9.10	12.24
Final pH	2.61	2.73	2.64	2.70	6.62

Table 3. Initial and final pH values of samples containing different ratios of FA:H_2O_2 under fluorescent light

FA:H_2O_2	1:1	1:2	1:3
Initial pH	12.00	11.99	11.99
Final pH	7.53	8.14	8.45

Kinetic and isotherm studies

According to the results, oxidation of FA with UV/H_2O_2 process was performed with pseudo-first-order kinetic and Langmuir isotherm model.

Discussion

pH optimization for formaldehyde (FA) removal with H_2O_2 in water samples

The COD removal at pH 3.00, 6.02, and 9.10 varied between 1 and 12%. At pH 12.00, the COD decrease in the first 10 minutes was 18.57% (Figure 1a). The highest COD removal was obtained at pH 12.00 in the presence of H_2O_2 under fluorescent light. A similar study was studied by Guimarães et al (3). They reported that there was a 99.3% decrease in the concentration of FA with H_2O_2. However, there was no change in the amount of dissolved organic carbon. This may be due to conversion of FA into trioxymethylene or formic acid (3). Surpateanu et al have studied three different pH values (6.80, 9.79, and 11.81) on cyanide oxidation with H_2O_2. They reported that oxidation of cyanide was more effective at basic pH. Also, they reported that after the 50th minute of the experiment, the oxidation rate increased in the sample at a neutral pH (26).

For UV light experiments, pH values were arranged as 3.04, 5.92, 7.02 (original pH), 9.10, 12.24, and COD removal was obtained as 30, 34, 43, 43, and 44% in samples, respectively (Figure 1b). The COD removal increased with increasing pH from 3.04 to 12.24. A similar result has been reported by Abbaszadeh Haddad et al (27). At pH 7.02, 9.10, and 12.24, the COD removal efficiency was close to each other. The results have shown that oxidation occurred. The COD values decreased at each pH level; however, the higher removal was obtained in neutral and basic conditions (Figure 1b). The low degradation in acidic pH can be attributed to the loss of OH ions since proton prevents the formation of OH radicals (11). Researchers have studied the UV/H_2O_2 process at different pH levels (3,16,28).

During the experiment, the change in the amount of H_2O_2 was followed under fluorescent light. The amount of H_2O_2 was not changed at pH 3.00, 6.02, and 9.10. However, at pH 12.00, a 20% reduction was observed in the first 10 minutes. H_2O_2 reduction reached 30.90% after 300 minutes (Figure 2a). It has been reported that sodium formate (HCOONa), water, and H_2 compounds are formed due to H_2O_2 and FA's reaction with NaOH in basic conditions. The reaction of H_2O_2 and FA at basic pH is explained as follows (29):

$$H_2O_2 + HCHO \rightarrow HOCH_2OOH \tag{3}$$

$$HOCH_2OOH + HCHO \rightarrow HOCH_2OOCH_2OH \tag{4}$$

$$HOCH_2OOCH_2OH + 2NaOH \rightarrow H_2 + 2HCOONa + 2H_2O \tag{5}$$

At the 10th minute of the experiment, air bubbles were observed at pH 12.00. It has been reported in the literature that air bubbles occur in the presence of H_2O_2, FA, and NaOH. The air bubbles were caused by H_2 gas given in

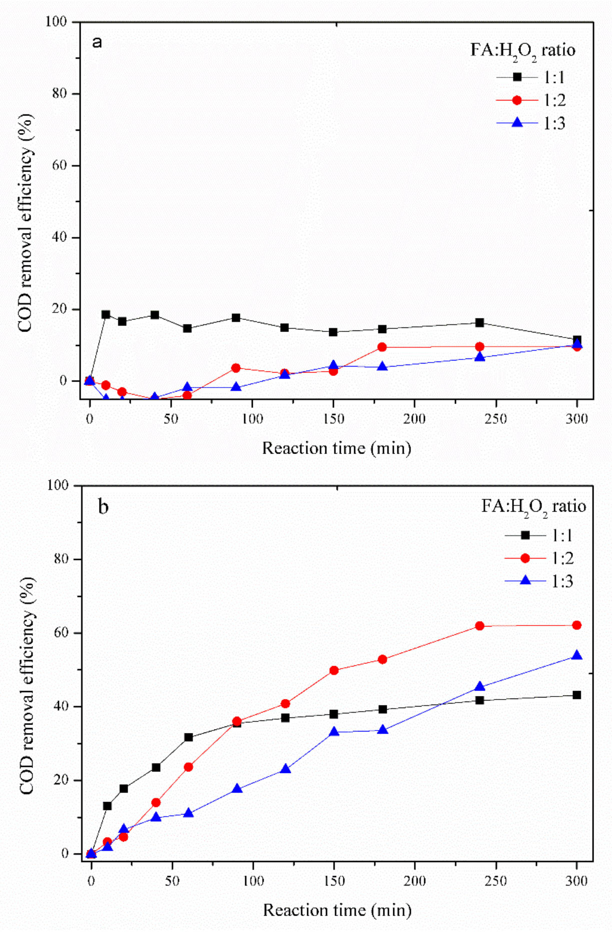

Figure 3. COD removal (%) in samples containing FA:H_2O_2 at the ratio of 1:1, 1:2, and 1:3 under (a) fluorescent and (b) UV light.

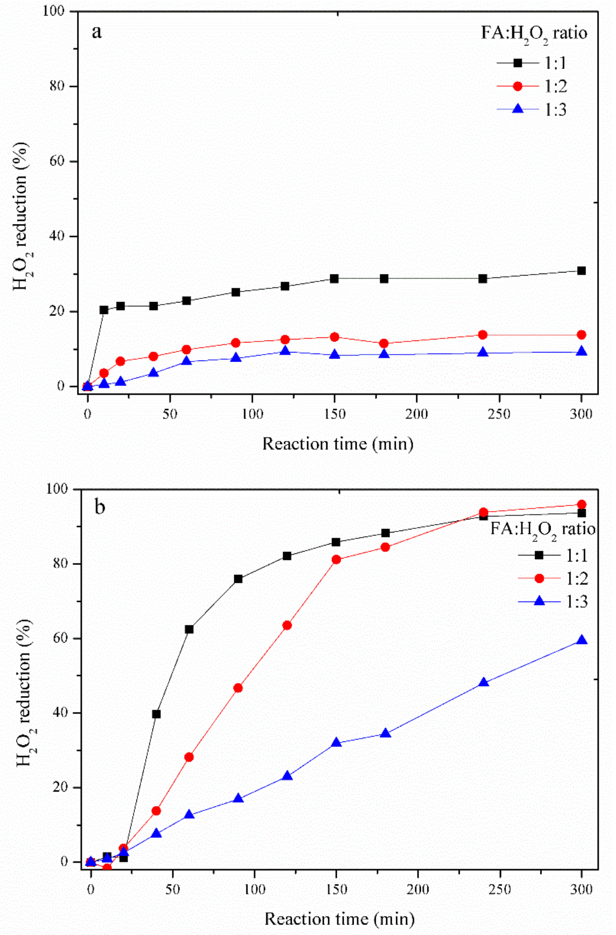

Figure 4. Change in H_2O_2 concentration (%) in samples containing 1:1, 1:2, and 1:3 FA:H_2O_2 ratio under (a) fluorescent and (b) UV light.

Eq. (5) (29).

H_2O_2 is one of the strong oxidants that reacts with UV light at wavelengths below 290 nm. In the UV/H_2O_2 process, UV light catalyzes the decomposition of H_2O_2 into hydroxyl radicals through chain reactions. These radicals are strong oxidants that react with organic compounds in water (23).

$$H_2O_2 + hv \rightarrow 2OH^{\cdot} \qquad (6)$$

When the organic pollutant reacts with OH radicals, CO_2, H_2O, etc. (Equation 7) (30,31), it provides the COD removal. In this study, FA was transformed into CO_2, H_2O, and intermediates.

$$\text{Organic pollutant} + OH^{\cdot} \rightarrow CO_2 + H_2O + \text{etc.} \qquad (7)$$

These reactions' efficiencies depend on the pH level of the environment, duration of UV exposure, intensity of UV exposure, and H_2O_2 concentration (23). In this study, OH radicals formed by the effect of UV light carried out FA oxidation. As a result, up to 44% of COD removal was achieved.

Under UV light, it was observed that almost all of H_2O_2 (1000 mg/L) was consumed at each pH level (Figure 2b). The findings show that different pH levels did not affect the change of H_2O_2, and H_2O_2 reduction occurred at the same rate at each pH level. However, the fastest H_2O_2 consumption was at pH 12.00 in the first minutes of the experiment, as in the fluorescent light experiments. Under fluorescent light, the pH levels of samples affected the decomposition of H_2O_2. The most effective pH level was 12.00.

Under UV light, COD removal and H_2O_2 consumption increased until the 180th minute, and then, remained approximately the same. At 180th minute, at pH 3.04, 5.92, 7.02 (original pH), 9.10 and 12.24, COD removal was 28, 34, 39, 43, and 44%; H_2O_2 consumption was 90, 93, 89, 90, and 93%, respectively (Figure 1b and 2b). The results show that since the H_2O_2 concentration decreased to 10%, the COD removal slowed down. Therefore, if the amount of H_2O_2 increases, COD removal will increase.

The pH change of samples was followed, and each sample's pH decreased at the end of the experiment at both light sources (Tables 1 and 2). The decrease in pH values was explained by converting FA to formic acid in the medium (3). Under UV light, the pH values dropped more than that under fluorescent light. Similar results were reported in previous studies (3,27,32).

In the control samples containing only FA (1000 mg/L), the COD value was followed. Under fluorescent light, the COD values remained the same. The highest COD removal (6%) was obtained under UV light.

H_2O_2 change was followed in the control samples containing only H_2O_2 (500 mg/L). Under fluorescent light, H_2O_2 concentration decreased 63.62% in the 5th minute and 92.09% at the end of 120 minutes at pH 11.91, but limited decomposition was found at other pH levels (2-6%). The findings showed that H_2O_2 was decomposed rapidly in basic conditions. A similar result

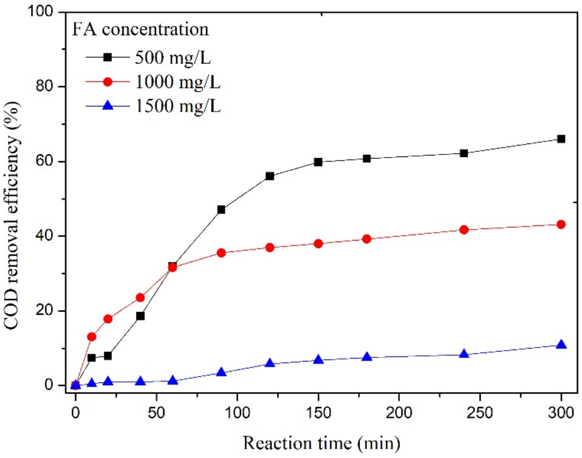

Figure 5. COD removal (%) in samples containing 500, 1000, and 1500 mg/L FA and 1000 mg/L H_2O_2 under UV light.

was reported by Yazıcı and Deveci (33). Under UV light, H_2O_2 concentration decreased 42, 39, 33, and 44% at pH 3.04, 6.04, 9.00, and 12.35, respectively. H_2O_2 decreased 33-44% under UV light in samples with pH values below 12.00 under the contrary fluorescent light. The results show that H_2O_2 can be decomposed under UV light at all pH. However, pH is a significant parameter for H_2O_2 and FA's reactions under fluorescent light.

Optimization of FA:H_2O_2 ratio in FA removal with H_2O_2 in water samples

The results obtained under UV light in pH optimization showed that COD removal can increase by adding H_2O_2. So, the effect of different concentrations of H_2O_2 (1000, 2000, and 3000 mg/L) was observed for two light sources. The FA:H_2O_2 concentration ratio was adjusted as 1:1, 1:2, and 1:3. It was aimed to observe the effect of increasing H_2O_2 amount on the COD removal and to find the optimum FA:H_2O_2 rate. This experiment was performed at pH 12.00 under fluorescent light and at the sample's original pH (~7.00) under UV light.

The COD removal decreased as the H_2O_2 concentration of the samples increased under fluorescent light. The highest COD removals for FA:H_2O_2 ratio of 1:1, 1:2, and 1:3 were calculated as 18.57, 9.60, and 10.19%, respectively (Figure 3a). But, there are opposite results obtained for different contaminants (26).

The COD removal efficiencies at the ratio of 1:1, 1:2, and 1:3 (FA:H_2O_2) were found to be 43.13, 62.16, and 53.78% under UV light, respectively (Figure 3b). COD removal increased when the H_2O_2 concentration was increased from 1000 to 2000 mg/L. However, when it was increased to 3000 mg/L, the COD removal decreased. This situation is attributed to the scavenging effect of excess H_2O_2 in the sample. The scavenging effect is realized by the reaction of the excess amount of H_2O_2 with the OH· radicals. Thus, HO_2· radicals are formed (Equation 8). The HO_2· radicals also react with the OH· radicals (Equation 8). Therefore, OH· radicals decrease (34).

$$H_2O_2 + \cdot OH \rightarrow H_2O + HO_2\cdot \quad (8)$$

$$HO_2\cdot + \cdot OH \rightarrow H_2O + O_2 \quad (9)$$

In a similar study, Kajitvichyanukul et al reported that they achieved 34.88%, 58.42%, and 78.80% removal in samples containing 1:0.5, 1:1, and 1:2 FA:H_2O_2, respectively, under UV light (16). Guimarães et al used a similar ratio and reported that 100% FA and 99% dissolved organic carbon removal were obtained (3). Giri et al also investigated the removal of pharmaceutical compounds by UV/H_2O_2. They have reported that as H_2O_2 concentration increased, the removal efficiency decreased for some pharmaceutical compounds (Fenoprofen and Clofibric acid). But, as H_2O_2 concentration increased for many compounds, the removal efficiency increased (35).

The change in H_2O_2 amount was followed. Under fluorescent light, H_2O_2 concentration decreased 20.39%, 3.59%, and 0.67% for samples with a ratio of 1:1, 1:2, and 1:3, respectively, in the 10th minute. At the end of the reaction time (300 minutes), the decrease in H_2O_2 were 30.90% (309 mg/L), 13.79 (275.8 mg/L), and 9.28 (278.4 mg/L) for the 1:1, 1:2, and 1:3 ratio, respectively (Figure 4a). The most effective ratio for H_2O_2 decomposition was 1:1. COD removal also supports this situation. It was seen that excess H_2O_2 amount could not increase FA removal under fluorescent light.

Under UV light, the decrease in H_2O_2 concentrations were 93.69, 95.94, and 59.47% for the ratio of 1:1, 1:2, and 1:3, respectively (Figure 4b). Although the amount of H_2O_2 decomposed at the ratio of 1:2 and 1:3 was close (about 1900 mg/L), the ratio of 1:2 was more effective in COD removal. The medium with the FA: H_2O_2 ratio of 1:2 was found to be the optimum ratio.

It was observed that under fluorescent light, the pH decreased at the end of the experiment, and the highest decrease occurred at 1:1 FA:H_2O_2 sample (Table 3). As in the previous experiment, the increase in acidity can be explained by forming formic acid.

Under UV light, the initial pH (7.02) in all proportions studied was measured at 2.60 levels after 300 minutes. The sample's pH change in the ratio of 1:2 was followed during the experiment. The pH value was measured as 3.88 in the 10th minute. This result showed that acidic compound formation, which causes a reduction in the pH, occurs in the first minutes of the experiment.

During the experiment at the optimum conditions, while the FA concentration decreased from 1060 to 144 mg/L, the COD value decreased from 1380.92 to 522.58 mg/L. The change in pH shows that the medium's acidification occurs in the first minutes. The COD removal was 62.12%, and the reduction in FA was 86.41%. The COD caused by the remaining FA (144 mg/L) was calculated at approximately 201 mg/L. This result indicates that the measured COD in the medium is due to FA and intermediates such as formic acid, and also, acidic compounds formed in the sample caused a decrease in the pH value. Abbaszadeh Haddad et al reported that the C–H bond in FA is a relatively stronger bond than the C=O bond. Breaking the C–H bond is more difficult than the C=O bond. Thus, the remaining organic content may be in the form of C–H (27,36).

Temperature control was not performed in this study. During the experiment, the temperature change in the samples was followed. The studies were conducted with an initial temperature of 20°C and temperature changes were followed. After 300 minutes, an increase of 5-6°C under fluorescent light and 8-9°C under UV light was observed at the sample temperature. The oxidation efficiency, which decreased up to the end of the experiment, was attributed to the decreasing amount of H_2O_2 in the sample. There are studies conducted under temperature-controlled conditions and at different temperatures to investigate the effect of temperature (37,38). Researchers stated that temperature change (25-70°C) increased the reaction rate in the photocatalytic oxidation of oxalic acid in the first minutes but did not affect the total yield (37). Temperature changes affect chemical oxidation systems in different ways. For example, increasing temperature leads to higher reaction rates for all chemical reactions involved in heterogeneous oxidations while reducing the solubility of oxygen and ozone in an aqueous solution. Therefore, its effect on the oxidation process will vary depending on these two conditions (37).

The initial concentration of FA

To examine the effect of initial FA concentration and calculate the kinetic and isotherm parameters, different FA concentrations (500, 1000, and 1500 mg/L) were studied for oxidation of FA with UV light and 1000 mg/L H_2O_2, at original pH. The results showed that COD removal efficiencies were 66.04, 43.13, and 10.85% for FA concentrations of 500, 1000, and 1500 mg/L, respectively (Figure 5). At three FA concentrations, all H_2O_2 amounts were consumed. Maximum COD removal was obtained at FA concentration of 500 mg/L. In the previous experiment, the optimum FA:H_2O_2 ratio was found to be 1:2 (Figure 3). This experiment proved that as FA concentration increased, a decrease in the COD removal efficiency was observed. While the amount of oxidized COD in mg/L was almost the same in the samples containing 500 and 1000 mg/L FA, this amount decreased in the sample containing 1500 mg/L FA. In this case, it can be concluded that increasing the organic compound amount decreases oxidation efficiency.

Similar and different studies conducted on FA removal from water and wastewater are given in Table 4.

Kinetic and isotherm studies

Pseudo-first-order, pseudo-second-order, and intraparticle diffusion model kinetic parameters were calculated to compare the kinetic models. Different initial FA concentrations (500, 1000, and 1500 mg/L) were studied. pH value and H_2O_2 concentration of sample were 7.00 and 1000 mg/L, respectively. COD values were measured at certain time intervals for 300 minutes.

The equations of kinetic models used were given in Eqs. (10-12).

Pseudo-first-order

$$Log\left(q_e - q_t\right) = Log\, q_e - k_1 \times t / 2.303 \qquad (10)$$

where q_t and q_e are the oxidized amounts at a given time t and equilibrium (mg/g), respectively, and k_1 (min^{-1}) is the pseudo-first-order rate constant. The parameters were calculated using the graph of Log (q_e-q_t) versus t (39, 40).

Pseudo-second-order

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad (11)$$

where K_2 (min^{-1}) refers to the pseudo-second-order rate constant. The parameters were calculated using the graph of t/q_t versus t (40,41).

Table 4. Similar and different studies conducted on formaldehyde removal from water and wastewater

The method	The initial FA or COD concentration (mg/L)	Time (min)	H_2O_2 and other chemicals used amount	Removal efficiency (%)	pH	References
UV/H_2O_2	1000 mg/L	300	2000 mg/L	86.41 (FA) 62.12 (COD)	7	This study
UV/H_2O_2	400 mg/L	100	CH_2O:H_2O_2 ratio of 1:2.27	99 (DOC) 100 (FA)	6-7	(3)
UV/H_2O_2	1200 mg/L 3000 mg/L 6000 mg/L 12000 mg/L	210	CH_2O:H_2O_2 ratio of 1:2.27	91 78 62 21 (DOC)	6-7	(3)
UV+TiO_2	500 mg/L	300	-	50 (COD)	7	(28)
UV+ZnO	500 mg/L	300	-	86 (COD)	7	(28)
The chemical-less UVC/VUV process	200 mg/L	60	-	94 (COD)	7	(27)
The catalytic advanced oxidation process (CAOP) of O_3/MgO/H_2O_2	7000 mg/L	120	0.09 mole/L H_2O_2 5 g/L MgO 0.153 g/L.min O_3	79 (FA) 65.6 (COD)	8	(43)
UV/H_2O_2	0.333 M	80	0,165 M 0.333 M 0.666 M	34.88 (FA) 58.42 (FA) 78.80 (FA)	2.6	(16)
UV and ferrate(VI)	1102 mg/L COD	35	-	100 (FA)	2	(47)

Table 5. Parameters of pseudo-first-order kinetic model

Initial Concentration (mg/L)	k_1 (min-1)	qe (mg/g) exp.	qe (mg/g) cal.	R^2
500	0.0136	652.71	671.58	0.9529
1000	0.0124	479.26	473.15	0.9743
1500	0.00714	253.25	263.87	0.9717

Intra particle diffusion

$$q_t = k_d t^{1/2} + C \qquad (12)$$

where *C* (mg/g) and k_d (mg/g.min) are the constants depending on the boundary layer thickness and the intraparticle diffusion rate constant, respectively (42).

When the parameters of three different kinetic models were evaluated, R^2 values closest to 1 were obtained with pseudo-first-order kinetic model. The pseudo-first-order kinetic curve for 500 mg/L FA and parameters for three FA concentrations are given in Figure 6 and Table 5, respectively. Similar results were reported by other researchers (16,27,3).

The highest removal at equilibrium was obtained at 500 mg/L FA concentration. The rate constant of the COD in this study was found to be 0.0136 min^{-1}. As the FA concentration increased, the COD removal decreased. Abbaszadeh Haddad et al reported that they found the rate constant as 0.026 min^{-1} with UVC/VUV process (27)

To calculate the isotherm constants, Langmuir (44) and Freundlich (45) isotherms were applied.

The equations of Langmuir and Freundlich isotherm models were given in Eqs. (13) and (14), respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \qquad (13)$$

where q_{max} (mg/g) and K_L are the maximum oxidation capacity and the Langmuir constant, respectively [26].

$$Log q_e = Log K_F + \frac{1}{n} Log C_e \qquad (14)$$

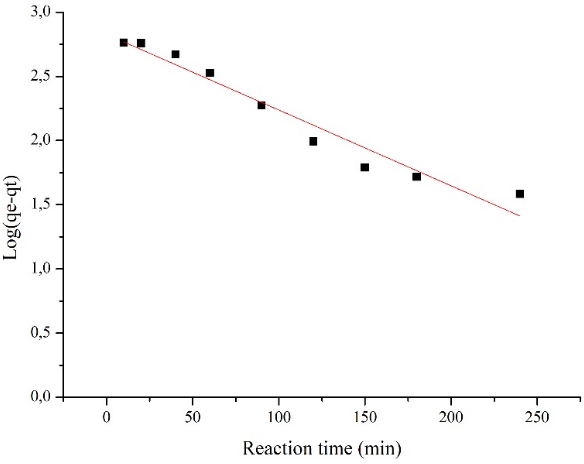

Figure 6. Pseudo-first-order chart.

where K_F (L/g) and *1/n* are the Freundlich constant and heterogeneity factor, respectively (46).

R^2 values were 0.9624 and 0.9133 for Langmuir and Freundlich isotherms, respectively. The reaction was carried out according to the Langmuir isotherm model.

Conclusion

Under fluorescent light, in samples containing FA and H_2O_2 (1:1), the highest COD removal and H_2O_2 reduction were 18.57 and 30.90%, respectively, at pH 12. In samples containing only H_2O_2 (500 mg/L), the H_2O_2 reduction was 92.09% at pH 11.91, while it was 2-6% at other pH levels. There was no change in COD caused by FA. It was observed that as H_2O_2 concentration increased, the COD removal did not increase.

Under UV light, 43-44% COD removal was achieved in the sample containing FA and H_2O_2 (1:1) at pH 7.02, 9.10, and 12.24. Almost all H_2O_2 (1000 mg/L) was consumed at each pH level. COD removal efficiencies at FA:H_2O_2 ratios of 1:1, 1:2, and 1:3 were 43.13, 62.16, and 53.78%, respectively, at pH 7.02. In samples containing only H_2O_2 (1000 mg/L), the H_2O_2 concentration decreased regardless of the pH level.

Kinetic and isotherm studies showed that the reaction was carried out according to pseudo-first-order kinetic and Langmuir isotherm models.

For the oxidation of FA, the most effective conditions were pH 7.00 (original pH) and 1:2 of FA:H_2O_2 ratio under UV light. Under these conditions, FA and COD removal were 86.41 and 62.12%, respectively.

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Ethical issues

All authors certify that all data obtained during the study are presented in this manuscript and no data from the study has been or will be published elsewhere separately.

Competing interests

The authors declare that they have no conflict of interests.

Authors' contributions

All authors were involved in the planning, experiments, and manuscript preparation of this study.

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