Environmental Health Engineering and Management Journal 2019, 6(2), 97–104
http://ehemj.com
doi 10.15171/EHEM.2019.11

Environmental Health Engineering and Management Journal

Original Article

Open Access Publish Free

Advanced oxidation of formaldehyde in the aqueous solutions using UVC/$S_2O_8^{2-}$ process: Degradation and mineralization

Leili Tymoyrimoghadam[1], **Hossein Momeninejad**[2], **Parisa Baratpour**[3], **Fariba Gohari**[4], **Behnam Ravansalar**[2], **Mohsen Momeninejad**[2*], **Amir Adibzadeh**[5]

[1]Department of Environmental Engineering, Tendency (Water and Wastewater), Branch Bushehr, Islamic Azad University, Bushehr, Iran
[2]Yasuj University of Medical Sciences, Yasuj, Iran
[3]Department of Environmental Health Engineering, School of Public Health, Shahid Beheshti University of Medical Sciences, Tehran, Iran
[4]Department of Civil and Environmental Engineering, University of Western Ontario, Ontario, Canada
[5]Health Research Center, Lifestyle Institute, Baqiyatallah University of Medical Sciences, Tehran, Iran

Abstract

Background: As a human carcinogen, formaldehyde is a toxic chemical imposing adverse effects on public health and environment. Due to its high reactivity, colorless nature, sustainability, purity in commercial forms, and low prices, the production and consumption of this compound has expanded vastly in industries.

Methods: In this study, a UVC photoreactor with a total volume of 120 mL was used and operated in a rotary mode. To determine the residual concentration, high-performance liquid chromatography (HPLC) device was applied whose detector was set at a wavelength of 355 nm and equipped with C18 column (with dimensions of 25 × 4.6 mm i.d, and particle size of 5 μm). Total organic carbon (TOC) was determined using a TOC analyzer.

Results: The optimal condition in this study was obtained at pH=3 and formaldehyde concentration of 350 mg, so that the removal of formaldehyde and TOC was 98.2% and 95.1%, respectively, after 35 minutes reaction time. The formaldehyde removal efficiency was assessed in the presence of methanol (MeOH), tert-butyl alcohol (TBA), and salicylic acid (SA) scavengers, and it was indicated that $SO_4^{\bullet-}$ radicals were the most effective factors in formaldehyde destruction. By increasing the concentrations of MeOH, TBA, and SA to 2.5 g/L, the degradation efficiency of formaldehyde dropped from 98.02% to 69.78%, 64.68%, and 45.14%, respectively, at 35 minutes reaction time. The removal of formaldehyde in the presence of nitrate was significantly reduced and it had a significant effect on the removal of formaldehyde.

Conclusion: In this study, the removal of formaldehyde was investigated in the presence of various anions including bicarbonate, carbonate, chloride, sulfate, and nitrate. According to the results, the UVC/$S_2O_8^{2-}$ process is a convenient and cost-effective method for the removal of formaldehyde.

Keywords: Formaldehyde, Advanced oxidation, Bicarbonates, Carbonates, Sulfates, Nitrates

Citation: Tymoyrimoghadam L, Momeninejad H, Baratpour P, Gohari F, Ravansalar B, Momeninejad M, et al. Advanced oxidation of formaldehyde in the aqueous solutions using UVC/$S_2O_8^{2-}$ process: degradation and mineralization. Environmental Health Engineering and Management Journal 2019; 6(2): 97–104. doi: 10.15171/EHEM.2019.11.

Article History:
Received: 3 January 2019
Accepted: 18 March 2019
ePublished: 17 April 2019

***Correspondence to:**
Mohsen Momeninejad
Email:
momeninejad.mohsen@yums.ac.ir

Introduction

Formaldehyde is the simplest compound of the aldehyde group and is known by various names including methyl aldehyde, methanal, methyl oxide, and formic aldehyde (1). It has a pungent odor and its chemical formula is HCHO (2). The use of this compound has increased in industry due to its high reactivity, colorless nature, stability, purity in commercial forms, and low cost (3). Formaldehyde is used in the manufacture of adhesives and resins, industrial fungicides, pharmaceuticals, paper processing, chemical and petrochemical industry, plastic, polyester fiber and fiberglass industry (4). The concentration of formaldehyde in the industrial effluent has been reported to be 100 to 10 000 mg/L. Formaldehyde at low concentrations has effects such as mucosal irritation, coughing and swallowing disorders, and increases the risk of asthma over long periods of time. This compound causes chromosomal abnormalities, irritation of the eyes, nose, throat, dermatitis, and digestive system infections in children. Studies also suggest that lung, nose, and blood cancer can be increased in people who are exposed to this substance, which has been identified under “potentially carcinogenic” classification by the US Environmental Protection Agency (EPA) (5). The safe concentration of formaldehyde for the environment is 61.1 mg/L (6), therefore, any wastewater containing formaldehyde must be treated effectively before being discharged into the environment. Recent studies have been conducted on chemical and biochemical methods and the integration of biological and chemical methods for the removal of formaldehyde. Biological methods cannot be an effective and efficient way to remove formaldehyde because formaldehyde reacts with DNA, RNA, and protein, and as a result, leading to the death of microorganisms (7). Recently, advanced oxidation processes (AOPs) such as Fenton, Photo Fenton, photocatalysis (8), electrolysis, and UV-based methods (9) have been used to remove formaldehyde. Some studies have reported formaldehyde degradation at low and medium concentrations using biochemical processes, while the use of these processes alone cannot provide sufficient formaldehyde decomposition (10). UV-based methods have been widely used to decompose many organic compounds, drugs, and pesticides from drinking water for the generation of active radicals (11). Generated radicals such as hydroxyl and sulfate have been numerously used to control the contamination of drinking water and wastewater treatment due to their rapid reaction, easy application, and high reactivity (11). Nowadays, sulfate radical-based advanced oxidation processes (SR-AOPs) have been considered as a new and effective solution for the decomposition of organic compounds in drinking water (12). In general, $SO_4^{\bullet -}$ is produced by activating peroxymonosulfate (PMS) or potassium persulfate (PS) in the presence of conductive metals, heat, chemicals, and ultraviolet radiation (13). More water solubility, relatively inexpensive and easy storage, higher stability, and easier activation of PS composition compared to H_2O_2 resulted in considering this compound as an appropriate source for the active radicals production (14). The activation of PS compound by the radiation of ultraviolet rays triggers the production of $SO_4^{\bullet -}$ and $OH^{\bullet}$ radicals (15,16). These two radicals are produced through the following formulas (10):

$$S_2O_8^{2-} \overset{hv}{\rightarrow} 2SO_4^{\cdot -} \tag{1}$$

$$S_2O_8^{2-} + M^{n+} \rightarrow S2O_4^{2-} + S_2O_4^{\cdot -} + M^{(n+1)+} \tag{2}$$

$$S_2O_4^{2-} + H_2O + S_2O_4^{2-} + \cdot OH + H^+ \tag{3}$$

$$S_2O_4^{2-} + \cdot OH + \text{organic pollutant} \rightarrow \text{intermediate} \rightarrow CO_2 \tag{4}$$

Sulfate and hydroxyl radicals can produce resistant organic compounds by chain oxidation reactions and mineralization. The aim of this study was to investigate the ability of the UVC/PS process to decompose formaldehyde in a synthetic wastewater contaminated with this compound. The effects of process parameters including pH, formaldehyde concentration, input persulfate, reaction time, and domestic water characteristics were investigated.

The aim of this study was to decompose and mineralize formaldehyde, which is widely used in various industries, especially wood, pharmaceutical, and petrochemicals, using UVC/$S_2O_8^{2-}$ process by a high yield and low cost method. The effect of various anions has been investigated, which is the innovation of this study.

Materials and Methods

Materials

The materials prepared for this study including potassium persulfate ($K_2S_2O_8$) 99%, methanol (CH_3OH) 99.8%, butyl alcohol ($C_4H_{10}O$) 99.5%, and salicylic ($C_7H_6O_3$) 99%, were purchased from Sigma-Aldrich.

Sodium salts including Na_2SO_4, $NaNO_3$, Na_3PO_4, Na_2CO_3, $NaHCO_3$, and NaCl were purchased from Merck. Paraformaldehyde (CH_2O) was also purchased from Merck, which its properties are shown in Table 1.

Experiment settings

Formaldehyde solution was prepared by dissolving 1 g of paraformaldehyde in 1 L of distilled water. Then, the initial concentration of the samples was extracted from a stock solution. To obtain the desired pH, sodium hydroxide and sulfuric acid 0.1 N were used and experiments were performed using a pH meter (Metrohm) in a Pyrex cylindrical photoreactor (350 mm height × 24 mm diameter), and operated in a circular mode. A low-pressure mercury lamp (4 W) is placed in the center of the photoreactor, and a quartz coat (150 mm height × 15 mm diameter) is employed for the lamp protection. The UVC lamp (Boston Electronic Co.) radiates the wavelengths of 254 and 185 nm. The schematic of the UVC photoreactor is shown in Figure 1. A peristaltic pump (Heidolph Co.) was used to create flow in the photoreactor. The injection rate of this pump was set to be 1 L/min for all experiments. The effect of pH (3-12), initial concentration of formaldehyde (200-500 mg/L), reaction time, mineralization rate, water anion, and scavengers were evaluated in this study. Also, the effects of common water anions including sulfate, nitrate, chloride, carbonate, bicarbonate, and phosphate were assessed. A set of experiments were also performed with tap water with the following characteristics: $Cl^- = 59$ mg/L, $SO_4^{2-} = 19$ mg/L, $NO_3^- = 10$ mg/L , and alkalinity = 67 mg $CaCO_3$/L. All experiments were performed

Table 1. Paraformaldehyde (CH_2O) purchased from Merck

Structure Formula Image	$H_2C=O$ OH2
Boiling point	93-96°C (1013 hPa)
pH value	2.8-4.0 (H_2O, 20°C)

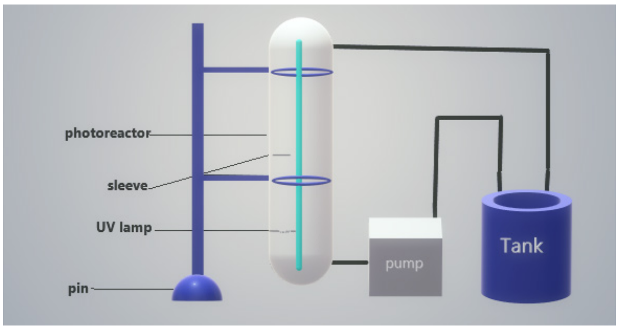

Figure 1. Schematic of UVC-photoreactor.

twice for validation and samples were analyzed by high-performance liquid chromatography (HPLC) to determine the concentration of residual formaldehyde. The formaldehyde degradation and mineralization efficiency were calculated by Eq. (5) and (6):

$$\text{Formaldehyde degradation (\%)} = \frac{(C_o - C_t)}{C_o} \times 100 \qquad (5)$$

$$\textit{Formaldehyde minerilazation efficiency } (\%) = \frac{(TOC_0 - TOCC_t}{TOC_{in}} \qquad (6)$$

Where C_0 and C_t are respectively the concentrations of Formaldehyde before and after each experimental step and TOC is the total organic carbon concentration. TOC was measured by a TOC analyzer before and after the reaction. The kinetics of formaldehyde degradation and mineralization was calculated by the pseudo-first-order kinetic model using the experimental data according to the Eq. (7). Moreover, the formaldehyde degradation rate in UVC/$S_2O_8^{2-}$ was determined by the first-order linear reaction model using Eq. (8):

$$\ln\left(\frac{C_t}{C_0}\right) = -k_1 \times t \qquad (7)$$

$$r_1 = -k_1 \times C_0 \qquad (8)$$

Where k_1 is the rate constant for the first-order reaction (min^{-1}) and r_1 is the rate of formaldehyde degradation and mineralization (mg/L.min).

Analytical methods

The HPLC was equipped with two pumps and a double-Beam UV-Vis spectrophotometers for formaldehyde measurement. This study was performed at room temperature in a phase with C18 column (with dimensions 25 × 4.6 mm i.d, 5 µm particle size) using a SPD-M20A photodiode array detector (both manufactured by Shimadzu, Kyoto, Japan). The volume of each injection of 20 µL and mobile phase (mobile phase) of water and methanol (35:65) were performed with isocratic program. The mobile phase flow rate was adjusted to 1 mL/min and injected into a volume of 20 µm and each run lasted for 12 minutes. The moving phase was filtered by a syringe filter and its gas was taken out before usage. The wavelength of the detector was set at 355 nm. To calibrate, the formaldehyde standard solution was first prepared and several concentrations of formaldehyde (50 to 150 mg/L) were made by dilution of the solution and injected into the HPLC. For the calibration curve, a peak of formaldehyde concentration was plotted. The total organic carbon (TOC) concentration was measured by the TOC analyzer (TOC-V-CPN, Shimadzu Ltd, Japan).

Determination of the dominant radicals

To understand the oxidation reaction, radicals were used for the formaldehyde degradation in UVC/$S_2O_8^{2-}$ photoreactor, and methanol (MeOH), tert-butyl alcohol (TBA), and salicylic acid (SA) were used as scavenging agents. The concentration of scavengers was 250 mg/L and the dominant scavenger radical was determined at the optimum pH of 3. The concentration of formaldehyde was 200 mg/L and the concentration of $S_2O_8^{2-}$ was equal to 0.25 g/L at reaction times of 20 and 35 minutes.

Results

The effect of pH on the formaldehyde degradation in UVC/$S_2O_8^{2-}$ photoreactor

As shown in Figure 2, the optimum pH was determined to be 3 to 10. At pH 3 to 10, the rates of formaldehyde removal were 47.51, 33.6, 25.1, 23.3, 15.83, 17.18, and 26.15%, respectively, at 15 min reaction time. Whereas at 30 min reaction time, formaldehyde removal efficiencies raised up to 87.8, 81.5, 81.4, 53.4, 08.08, 28.18, 20.31, 21.11, and 29.41%, respectively. According to the results, the highest formaldehyde removal efficiency was obtained at pH 3 and it was selected as the optimal pH. Additionally, the final pH value is shown at 15 and 30 min (Figure 2). At reaction time of 30 minutes, the initial pH of 3 to 10 dropped to 2.91, 3.58, 4.76, 5.59, 6.6, 7.2, 8.23, and 9.16, respectively.

The effect of initial formaldehyde concentration on the removal efficiency in the UVC/$S_2O_8^{2-}$ photoreactor

As shown in Figure 3, formaldehyde concentrations of 200, 350 and 500 mg/L at 20, 35, and 50 min, with PS concentration of 0.25 mg were investigated. At formaldehyde concentration of 200 mg/L and reaction time of 20, 35, and 50 min, formaldehyde removal efficiencies of 57.65, 100, and 100% were achieved respectively. At $S_2O_8^{2-}$ concentration of 0 to 200 mg and reaction time of 20 minutes, the rate of removal efficiency was 25 and 57.65%, respectively. Also at concentration of 350 mg/L and reaction time of 20, 35, and 50 minutes, the removal efficiencies were 53.20, 98.03, and 100%, respectively. At concentration of 500 mg/L and the aforementioned times, formaldehyde removal efficiencies were equal to 43.25%, 74.96%, and 93.40%, respectively.

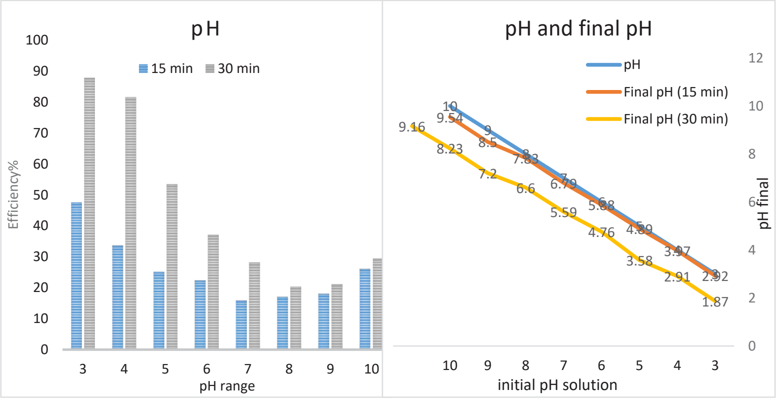

Figure 2. The effect of pH on the formaldehyde degradation in UVC/$S_2O_8^{2-}$ (formaldehyde concentration = 200 mg/L, persulfate concentration = 0.25 g/L, pH = 3 to 10, and reaction time = 15 and 30 minutes).

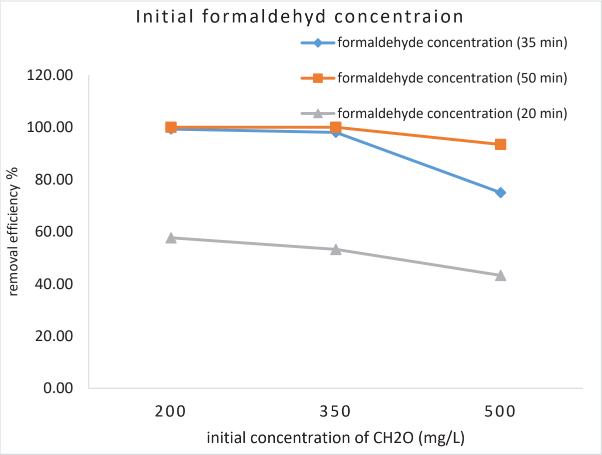

Figure 3. The Effect of initial formaldehyde concentration on removal efficiency (formaldehyde concentration = 200, 350, and 500 mg/L, persulfate concentration = 0.25 mg/L, pH = 3, and reaction time = 20, 30, and 50 min).

The effect of initial formaldehyde concentration on the kinetics in the UVC/$S_2O_8^{2-}$ photoreactor

To study the kinetics of this process, pseudo-first-order and pseudo-second order kinetic models were used to describe the experimental data. As shown in Table 2, the first-order model has a better fit with the experimental data. The kinetic result of this study, based on the previous studies, has been reported as the first kinetic model in AOPs processes. According to Table 2, the constant (1) at different formaldehyde concentrations of 200, 350, and 500 mg/mL was found to be 0.08, 0.033, and 0.066 L/min, respectively. The increase of *k* and stability of the reaction is due to the high reaction between formaldehyde molecules and active radicals species. Also, by increasing formaldehyde concentration, the low capacity of pollutant molecules in the reaction with radicals reduces the formation of reactive radicals and the *k* value of the reaction.

Effect of reaction time on formaldehyde decomposition in the UVC/$S_2O_8^2$ photoreactor

Figure 4 demonstrates 5 to 50 minutes reaction time, with concentrations of formaldehyde (350 mg/L) and $S_2O_8^2$ (0.25 g/L) in UVC/$S_2O_8^{2-}$ photoreactor. At 5 minutes, the rate of formaldehyde degradation was 25% and at 10, 15, 20, 25, and 30 minutes, it reached up to 37, 44.8, 53.2, 74.57, and 89.14%, gradually. At 35 and 40 minutes, almost complete removal occurred and 98.8 and 99.79% of decomposition were achieved, respectively. And at the time of 45 minutes, complete decomposition (100%) occurred.

Table 2. Kinetics of formaldehyde degradation in UVC/$S_2O_8^{2-}$

CH_2O concentration (mg/L)	Formaldehyde Removal		TOC Removal	
	R^2	k_1	R^2	k_1
200	0.990	0.088	0.984	0.06
350	0.979	0.053	0.970	0.039
500	0.982	0.041	0.968	0.028

Formaldehyde concentration = 200, 350, and 500 mg/L, $S_2O_8^{2-}$ concentration = 0.25 g/L, solution pH = 3, and reaction time = 5 to 90 min.

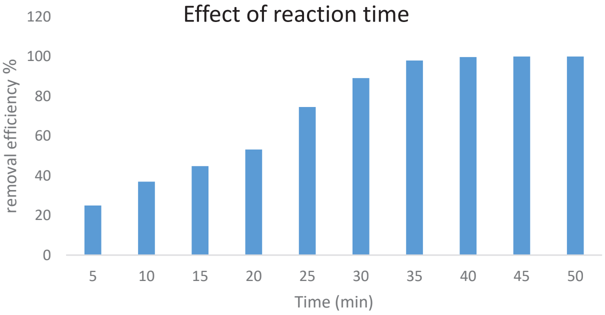

Figure 4. Effect of reaction time on the formaldehyde degradation in UVC/$S_2O_8^2$ (formaldehyde concentration = 350 mg/L, $S_2O_8^2$ concentration = 0.25 g/L, pH = 3, and reaction time = 5 to 50 min).

Effect of PS concentration on $S_2O_8^{2}$ photoreactor

As shown in Figure 5, the effect of persulfate concentration on UVC/$S_2O_8^{2}$ photoreactor was investigated. In this figure, the effect of different concentrations of persulfate (0.05, 0.1, 0.15, 0.2, 0.25, and 0.3 g/L) at 20, 35 and 50 minutes reaction time, with initial formaldehyde concentration of 200 mg/L was studied in UVC/$S_2O_8^{2}$ photoreactor. At persulfate concentrations of 0.25 and 0.3 g/L at 20 minutes, formaldehyde decomposition was 57.65% and 60%, respectively, at 35 minutes, formaldehyde decomposition at both concentrations of persulfate was almost complete, therefore, the concentration of 0.25 g/L was selected as the optimal concentration of persulfate.

The effect of anionic water content on the removal efficiency and mineralization of formaldehyde in UVC/$S_2O_8^{2}$ photoreactor

In this study, the effect of a number of water anions on the mineralization of formaldehyde was investigated. The samples including nitrate, sulfate, carbonate, and sodium chloride were synthesized to determine their effect on the UVC system efficiency. As shown in Figure 6, the removal efficiency of formaldehyde was increased to 35.54% and 50% when nitrate was added at 20 and 35 minutes reaction time. According to this figure, all anions had an impact on the removal efficiency of TOC and nitrate> carbonate> chloride> sulfate had respectively the greatest effect. A number of domestic water anions, such as SO_4^{2-}, Cl^-, CO_3^{2-}, HCO_3^-, and NO_3^-, were investigated.

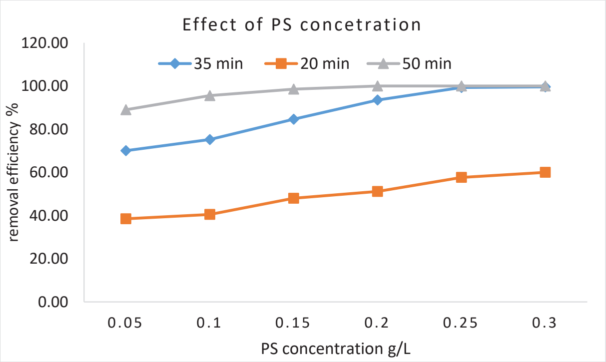

Figure 5. Effect of PS concentration on UVC/$S_2O_8^{2}$ photoreactor (formaldehyde concentration = 200 mg/L, persulfate concentration = 0.05 to 0.3 g/L, pH = 3, and reaction time = 20, 35, and 50 min).

Effect of scavenger on the formaldehyde decomposition efficiency in UVC/$S_2O_8^{2}$ photoreactor

Active radicals have great influence on the decomposition and mineralization of organic pollutants. In this study, MeOH, TBA, and SA radicals were used to better understand the radical mechanism in the decomposition of formaldehyde. The effect of scavengers on the formaldehyde decomposition and mineralization was investigated at initial formaldehyde concentration of 350 mg/L, solution pH of 3, $S_2O_8^{2-}$ concentration of 0.25 g/L, and reaction times of 20 and 35 min. As shown in Figure 7, with increasing concentrations of MeOH, TBA, and SA to 2.5 g/L, the efficiency of formaldehyde degradation dropped from 53.2% to 47.71%, 43.91, and 31.7%, respectively, at 20 minutes reaction time. The same trend was observed at 35 min reaction time where efficiency declined from 98.02% to 69.78%, 64.68%, and 45.14%, respectively, and the concentration of residual formaldehyde increased. MeOH can be a scavenger for both $SO_4^{\bullet-}$ ($k = 1.1\times10^7\ M^{-1}s^{-1}$) and $^{\bullet}OH$ ($k = 9.7\times10^8\ M^{-1}s^{-1}$) radicals while the TBA is more effective in eliminating the effects of $^{\bullet}OH$.

Discussion

According to the results, the solution pH, affects persulfate activity and formaldehyde degradation. When pH is lower than 7, $SO_4^{\bullet-}$ is dominated based on the Eq. (9) and (10), and when pH is higher than 7, two reasons for this increase can be considered:

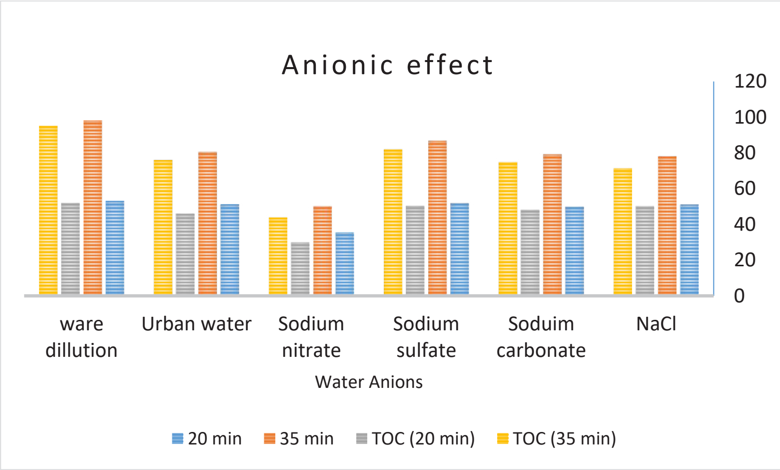

Figure 6. The effect of anionic water content on the removal efficiency and mineralization of formaldehyde (formaldehyde concentration = 350 mg/L, $S_2O_8^{2}$ concentration = 0.25 g/L, pH = 3, and reaction time = 20 to 35 min).

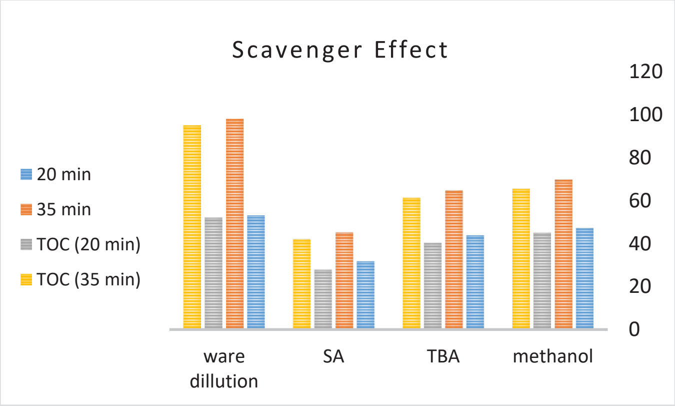

Figure 7. Effect of scavenger on the formaldehyde decomposition efficiency (formaldehyde concentration = 350 mg/L, $S_2O_8^{2}$ concentration = 0.25 g/L, pH = 3, and reaction time = 20 to 35 min).

The first reason can be attributed to the fact that, when pH is higher than 7, according to Eq. (11) and (12), with increasing $S_2O_8^{2-}$ concentration, the activity of persulfate is increased and consequently, it produces more SO_4 radicals (11).

According to Eq. (1-4), under UVC irradiation, $S_2O_8^{2-}$ converts to $SO_4^{\bullet-}$ radicals, which can react with formaldehyde molecules. Therefore, $SO_4^{\bullet-}$ can oxidize formaldehyde through the following reactions presented as Eq. (9-11) (11):

$$formaldehyde + SO_4^{\bullet-} \rightarrow formaldehyde^{\bullet+} + SO_4^{2-} \quad (9)$$

$$formaldehyde^{\bullet+} + H_2O \rightarrow (OH)formaldehyde + H^+ \quad (10)$$

$$(OH)formaldehyde \rightarrow Intermediates \rightarrow CO_2 + H_2O \quad (11)$$

And the second reason is the high OH^- level for producing $OH^\bullet$ that tends to react with $SO_4^{\bullet-}$. However, due to the low redox potential of $OH^\bullet$ (1.9-2.7 V), compared to $SO_4^{\bullet-}$ (2.5-3.1 V), it may reduce the efficiency of formaldehyde removal at high pHs (9).

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^- \quad (12)$$

$$HS_2O_8^- + SO_4^{-\cdot} + SO_4^{2-} + H^+ \quad (13)$$

$$\text{Alkaline pH: } SO_4^{-\cdot} + OH^- \rightarrow SO_4^{2-} + {}^\bullet OH \quad K = 7 \times 10^7 M^{-1}S^{-1} \quad (14)$$

$$\text{Alkaline pH: } {}^\bullet OH + OH^- \rightarrow H_2O \ (K = 1.2 \times 10^{10} M^{-1}S^{-1}) \quad (15)$$

In a study by Lee et al, perfluorooctanoic acid (PFOA) decomposition in the presence of persulfate at different pHs was conducted and PFOA decomposition at different pHs in radical reactions was investigated. In acidic condition, PFOA degradation was more than that in alkaline condition, because hydroxyl anions could play a role in scavenging radicals, consequently, the produced $OH^\bullet$ radical had little reactivity with PFOA (17). Also, in another study by Ou et al, the photo degradation of tris (2-chloroethyl) phosphate by the UVC/PS system can transfer $SO_4^{\bullet-}$ to SO_4^{2-} when pH ≤ 9, and at pHs above 9, all $SO_4^{\bullet-}$ is converted to SO_4^{2-} (18).

Due to the constant amount of $SO_4^{\bullet-}$ radicals production by a certain amount of $S_2O_8^{2-}$, as shown in Figure 3, by increasing formaldehyde concentration, the formaldehyde degradation efficiency decreased and during the reaction time, the formaldehyde molecules were decomposed which was followed by the generation of a large number of intermediates that had not been destroyed by $SO_4^{\bullet-}$, which is consistent with the results of previous reports (12).

In the other study conducted by Sharma et al on the degradation of bisphenol A (BPA) by UVC/PMS, it is reported that an increase in the concentration constant of BPA, yields a greater number of BPA molecules to oxidize free radicals, therefore, the reaction rate increases. In the present study, it was observed that by increasing formaldehyde concentration to 350 mg/L, the k-value decreased to 0.053/min, indicating that formaldehyde and interfering molecules cannot be completely decomposed by active radicals, hence, the formaldehyde decomposition and k-value decrease (19).

As shown in Figure 4, with increasing reaction time from 5 to 60 minutes, the rate of formaldehyde degradation also increased, which is due to the fact that a large number of formaldehyde molecules are available over time for free radicals, and the rate of reaction was increased (19).

As can be seen, the percentage of formaldehyde decomposition at $S_2O_8^{2-}$ concentration of 0.25 g/L and 0.3 g/L is almost the same and its further use is not cost effective, because this excess dose causes excessive sulfur anion decomposition, and at higher concentrations, re-destruction of $SO_4^{\bullet-}$ radicals may also occur, although the inhibitory effect of $S_2O_8^{2-}$ was not observed in this study (11).

It has been reported that these anions can be effective in the decomposition efficiency in water. These contents can act as scavengers in the AOP processes and interfere with radicals' activity, therefore, these anions have significant effects on the formaldehyde degradation by the UVC/ $S_2O_8^{2-}$ process in order to apply this method for formaldehyde degradation (20). In fact, due to its strong UVC absorption, nitrate reduced the efficiency of UVC processes. By absorbing ultraviolet radiation, nitrate eliminates both formaldehyde and persulfate direct photolysis (forming $SO_4^{\bullet-}$) and hemolysis of water (forming $^{\bullet}OH$) through which process efficiency is reduced. The relevant reactions are as follows (21):

$$NO_3^- \xrightarrow{hv>200\ nm} NO_2^- + 1/2\ O_2 \quad (16)$$

$$NO_2^- + O_3 \rightarrow NO_3^- + O_2 \quad (17)$$

The reaction of $OH^{\bullet}$ with carbonate and bicarbonate leads to carbonate radical formation, whose oxidation potential (~ 1.63 V) is much less than that of hydroxyl radical (22). In addition, in comparison with bicarbonate, the carbonate has a higher rate of reaction with hydroxyl (22):

$$OH^{\bullet} + HCO_3^{\bullet-} \rightarrow CO_3^{\bullet-} + H_2O \quad K= 8.5 \times 10^6\ M^{-1}S^{-1} \quad (18)$$

$$OH^{\bullet} + CO_3^{2-} \rightarrow + OH^- \quad K= 3.9 \times 10^8\ M^{-1}S^{-1} \quad (19)$$

Sulfate and chloride have less inhibitory effect on formaldehyde removal and mineralization. In the presence of sulfate, the removal of relatively high concentration of formaldehyde increased, but TOC removal decreased from 95.1% to 81.94%. In the presence of chloride, the removal efficiency of formaldehyde and its mineralization decreased from 95.1% to 77.98% and 71.31%, respectively. This can be explained by the formation of $ClOH^{\bullet-}$ as a result of the reaction of chloride and hydroxyl radical (23).

$$Cl^- + OH^{\bullet} \rightarrow ClOH^{-\cdot}\ K= 4.3 \times 10^9\ M^{-1}S^{-1} \quad (20)$$

$$ClOH^{\bullet} \rightarrow Cl^- + HO^{\cdot}\ K= 6.1 \times 10^9\ M^{-1}S^{-1} \quad (21)$$

$$ClOH^{\bullet} + H^+ \rightarrow Cl^{\cdot} + H_2O\ K= 2.1 \times 10^{10}\ M^{-1}S^{-1} \quad (22)$$

$$Cl^{\cdot} + Cl^- \rightarrow Cl_2^{\bullet-}\ K= 2.1 \times 10^{10}\ M^{-1}S^{-1} \quad (23)$$

As shown in Figure 7, the SA effect on radical scavenging is much greater than that of MeOH and TBA at the same concentration. SA has a high reaction rate with $^{\bullet}OH$ and can produce $SO_4^{\bullet-}$ in an acidic pH, thus, decreased formaldehyde degradation by SA could be due to its scavenging effect on both other active radicals. Comparison of the effect of MeOH and TBA shows that the removal efficiency of formaldehyde in the presence of TBA is greater than that in the presence of MeOH.

This is due to the fact that MeOH can have a scavenger function for both active radicals, however, TBA is a good $OH^{\bullet}$ scavenger. It is noteworthy that in the case of formaldehyde degradation in this study, the role of $SO_4^{\bullet-}$ is more important than $^{\bullet}OH$. The reason for low formaldehyde removal efficiency in the presence of TBA is that, due to acidic conditions, $S_2O_8^{2-}$ can convert to $SO_4^{\bullet-}$, and the $^{\bullet}OH$ radicals produced under these conditions, are affected by TBA scavengers (24-26).

Conclusion

According to the results, pH can significantly affect formaldehyde degradation and pH = 3 was selected as the optimum pH. The initial concentration of $S_2O_8^2$ was obtained by the degradation rate of contaminants by the UVC/$S_2O_8^2$ system. Increasing the initial concentration of $S_2O_8^{2-}$ can lead to an increase in formaldehyde degradation. The increases in k-value and stability of the reaction rate at concentration ratio of 50 to 25 have been shown to provide an appropriate contribution to the interaction between the formaldehyde molecules and active radicals species. In other words, due to the low capacity of pollutant molecules in the reaction with radicals, the reformation of reactive radicals is reduced and the constant of the reaction rate is reduced as well. Furthermore, with increasing the reaction time from 5 to 50 minutes, the rate of formaldehyde removal in the photoreactor is significantly increased, so that a high amount of this compound is removed in this period of time. Accordingly, the UVC/$S_2O_8^{2-}$ process is a suitable method for the degradation of formaldehyde in contaminated water and is capable of removing great amount of this compound at high concentrations over a short period of time.

Acknowledgments

The authors would like to gratitude Yasuj University of Medical Sciences (YUMS) for supporting this study.

Ethical issues

The author hereby certifies that all data collected during the study is as stated in the manuscript, and no data from the study has been or will be published separately elsewhere.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

The authors contributed and were involved in the suggestion of the problem, design of experiments, data collection, analysis, and interpretation, and manuscript approval.

References

1. Trivedi D, Crosse J, Tanti J, Cass AJ, Toghill KE. The electrochemical determination of formaldehyde in aqueous media using nickel modified electrodes. Sens Actuators B Chem 2018; 270: 298-303. doi: 10.1016/j.snb.2018.05.035.
2. Moussavi G, Yazdanbakhsh A, Heidarizad M. The removal of formaldehyde from concentrated synthetic wastewater using O3/MgO/H2O2 process integrated with the biological treatment. J Hazard Mater 2009; 171(1-3): 907-13. doi: 10.1016/j.jhazmat.2009.06.090.
3. Moussavi G, Heidarizad M. The performance of SBR, SCR, and MSCR for simultaneous biodegradation of high concentrations of formaldehyde and ammonia. Sep Purif Technol 2011; 77(2): 187-95. doi: 10.1016/j.seppur.2010.11.028.
4. Oliveira SV, Moraes EM, Adorno MA, Varesche MB, Foresti E, Zaiat M. Formaldehyde degradation in an anaerobic

packed-bed bioreactor. Water Res 2004; 38(7): 1685-94. doi: 10.1016/j.watres.2004.01.013.

5. Moteleb MA, Suidan MT, Kim J, Maloney SW. Pertubated loading of a formaldehyde waste in an anaerobic granular activated carbon fluidized bed reactor. Water Res 2002; 36(15): 3775-85.
6. Gamelas JA, Oliveira F, Evtyugina MG, Portugal I, Evtuguin DV. Catalytic oxidation of formaldehyde by ruthenium multisubstituted tungstosilicic polyoxometalate supported on cellulose/silica hybrid. Appl Catal A Gen 2016; 509: 8-16. doi: 10.1016/j.apcata.2015.10.003.
7. Guimaraes JR, Farah CR, Maniero MG, Fadini PS. Degradation of formaldehyde by advanced oxidation processes. J Environ Manage 2012; 107: 96-101. doi: 10.1016/j.jenvman.2012.04.024.
8. Huang C, Ding Y, Chen Y, Li P, Zhu S, Shen S. Highly efficient Zr doped-TiO_2/glass fiber photocatalyst and its performance in formaldehyde removal under visible light. J Environ Sci (China) 2017; 60: 61-9. doi: 10.1016/j.jes.2017.06.041.
9. Moussavi G, Bagheri A, Khavanin A. The investigation of degradation and mineralization of high concentrations of formaldehyde in an electro-Fenton process combined with the biodegradation. J Hazard Mater 2012; 237-238: 147-52. doi: 10.1016/j.jhazmat.2012.08.022.
10. Abbaszadeh Haddad F, Moussavi G, Moradi M. Advanced oxidation of formaldehyde in aqueous solution using the chemical-less UVC/VUV process: Kinetics and mechanism evaluation. Journal of Water Process Engineering 2019; 27: 120-5. doi: 10.1016/j.jwpe.2018.11.017.
11. Moussavi G, Momeninejad H, Shekoohiyan S, Baratpour P. Oxidation of acetaminophen in the contaminated water using UVC/$S_2O_8^{2-}$ process in a cylindrical photoreactor: efficiency and kinetics of degradation and mineralization. Sep Purif Technol 2017; 181: 132-8. doi: 10.1016/j.seppur.2017.03.022.
12. Moussavi G, Rezaei M. Exploring the advanced oxidation/reduction processes in the VUV photoreactor for dechlorination and mineralization of trichloroacetic acid: parametric experiments, degradation pathway and bioassessment. Chem Eng J 2017; 328: 331-42. doi: 10.1016/j.cej.2017.07.006.
13. Thanekar P, Panda M, Gogate PR. Degradation of carbamazepine using hydrodynamic cavitation combined with advanced oxidation processes. Ultrason Sonochem 2018; 40(Pt A): 567-76. doi: 10.1016/j.ultsonch.2017.08.001.
14. Ye J, Shang J, Li Q, Xu W, Liu J, Feng X, et al. The use of vacuum ultraviolet irradiation to oxidize SO^2 and NOx for simultaneous desulfurization and denitrification. J Hazard Mater 2014; 271: 89-97. doi: 10.1016/j.jhazmat.2014.02.011.
15. Ayoub G, Ghauch A. Assessment of bimetallic and trimetallic iron-based systems for persulfate activation: application to sulfamethoxazole degradation. Chem Eng J 2014; 256: 280-92. doi: 10.1016/j.cej.2014.07.002.
16. Ghauch A, Tuqan AM, Kibbi N. Naproxen abatement by thermally activated persulfate in aqueous systems. Chem Eng J 2015; 279: 861-73. doi: 10.1016/j.cej.2015.05.067.
17. Lee YC, Lo SL, Kuo J, Lin YL. Persulfate oxidation of perfluorooctanoic acid under the temperatures of 20-40°C. Chem Eng J 2012; 198-199: 27-32. doi: 10.1016/j.cej.2012.05.073.
18. Ou HS, Liu J, Ye JS, Wang Ll, Gao NY, Ke J. Degradation of tris(2-chloroethyl) phosphate by ultraviolet-persulfate: kinetics, pathway and intermediate impact on proteome of *Escherichia coli*. Chem Eng J 2017; 308: 386-95. doi: 10.1016/j.cej.2016.09.076.
19. Sharma J, Mishra IM, Dionysiou DD, Kumar V. Oxidative removal of bisphenol A by UV-C/peroxymonosulfate (PMS): kinetics, influence of co-existing chemicals and degradation pathway. Chem Eng J 2015; 276: 193-204. doi: 10.1016/j.cej.2015.04.021.
20. Kanakaraju D, Motti CA, Glass BD, Oelgemoller M. TiO2 photocatalysis of naproxen: effect of the water matrix, anions and diclofenac on degradation rates. Chemosphere 2015; 139: 579-88. doi: 10.1016/j.chemosphere.2015.07.070.
21. Peng J, Wang G, Zhang D, Zhang D, Li X. Photodegradation of nonylphenol in aqueous solution by simulated solar UV-irradiation: the comprehensive effect of nitrate, ferric ion and bicarbonate. J Photochem Photobiol A Chem 2016; 326: 9-15. doi: 10.1016/j.jphotochem.2016.04.015.
22. Yang S, Yang X, Shao X, Niu R, Wang L. Activated carbon catalyzed persulfate oxidation of Azo dye acid orange 7 at ambient temperature. J Hazard Mater 2011; 186(1): 659-66. doi: 10.1016/j.jhazmat.2010.11.057.
23. Grebel JE, Pignatello JJ, Mitch WA. Effect of halide ions and carbonates on organic contaminant degradation by hydroxyl radical-based advanced oxidation processes in saline waters. Environ Sci Technol 2010; 44(17): 6822-8. doi: 10.1021/es1010225.
24. Yang L, Yu LE, Ray MB. Photocatalytic oxidation of paracetamol: dominant reactants, intermediates, and reaction mechanisms. Environ Sci Technol 2009; 43(2): 460-5.
25. Zhou L, Ferronato C, Chovelon JM, Sleiman M, Richard C. Investigations of diatrizoate degradation by photo-activated persulfate. Chem Eng J 2017; 311: 28-36. doi: 10.1016/j.cej.2016.11.066.
26. Tan C, Fu D, Gao N, Qin Q, Xu Y, Xiang H. Kinetic degradation of chloramphenicol in water by UV/persulfate system. J Photochem Photobiol A Chem 2017; 332: 406-12. doi: 10.1016/j.jphotochem.2016.09.021.