



## Degradation of Low Concentrations of Formaldehyde in Sono Catalytic Ozonation Advanced Oxidation Processes using Zero-valent Iron

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### ABSTRACT

The purpose of the current study is to evaluate formaldehyde degradation ratio with various methods in a batch reactor. In this work, the ozonation, sonolysis (ultrasonic), and ozone sonolysis, sono catalytic ozonation (SCO), and nano zero-valent iron catalyst processes were investigated for removal of formaldehyde. In addition, the influence of important factors such as pH (5–9), ultrasonic power (60–140 W), ozone dosage (20–200 mg h<sup>-1</sup>), NZVI dosage (50–400 mg L<sup>-1</sup>), and initial HCHO concentration (1–20 mg L<sup>-1</sup>) were tested. The results demonstrated that the SCO process was the most efficient one amongst the process considered. The effect of important factors were also tested on the efficiency of the SCO process and maximum removal (99%) was found at a pH of 5, ultrasonic power of 100 W, ozone dosage of 200 mg h<sup>-1</sup>, catalyst dosage of 200 mg L<sup>-1</sup> and initial formaldehyde concentration of 15 mg L<sup>-1</sup>. The results led to the conclusion that the most effective factor was ozone dosage. Also, SCO process may be recommended for the treatment of solutions containing low formaldehyde concentrations.

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## 1. INTRODUCTION

Industrial activity results in the generation of waste streams that contain toxic and environmentally harmful compounds. Formaldehyde (HCHO) is among the most widely used chemicals in manufacturing and chemical industries that have been classified as a possible human carcinogen by the United State Environmental Protection Agency (EPA) [1, 2]. EPA has set health levels for a 1-day exposure at 10 ppm in drinking water [3]. HCHO have important applications in chemical industries for making different types of products, such as those of home furnishing, household cleaners, textiles, landscape, paper, paints, yard products, and pesticides [4, 5]. HCHO can enter drinking water supplies by leaching from polyacetal plastic fittings and discharges of it from industries in the recipient water sources. The exposure of the aquatic system to HCHO

can lead to impacts such as potential negative influences on the biological balance of the environment [3, 6, 7]. Effluents may contain 100-10,000 mg L<sup>-1</sup> of HCHO. The HCHO concentration that an aquatic environment can assimilate without harming its ecosystem is 1.61 mg L<sup>-1</sup>. Also, the results of one study show 34.1 mg L<sup>-1</sup> was the effective concentration (EC<sub>50</sub>) that inhibited 50% of microorganism respiration in a wastewater treatment plant that does not receive toxic sewages. One study was done to evaluate the degradation of high concentration of HCHO (≈8000 mg L<sup>-1</sup>) in an electro-Fenton process (EFP) in combination with biodegradation [8]. Also, in 2015, another study evaluated formaldehyde degradation by UV photolysis, ZnO catalyst and ultrasonic wave at HCHO concentration 20-100 mg L<sup>-1</sup> [6]. Conventional wastewater treatment processes (i.e., biological treatment) are only partially effective at eliminating these pollutants. Olivera and Lu et al. reported that liquid effluents with a high HCHO concentration using biological systems are difficult to treat because HCHO

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can react with DNA and damage cells and cause the death of microorganisms [5, 9]. Therefore, additional treatments are often required, including advanced oxidation processes (AOPs), due to the simplicity of application and functionality at atmospheric temperature, pressure and high degradation efficiency for various classes of organic compounds in gas and liquid streams [10]. Previous studies focused only on photolysis, such as photocatalysis with Pt/Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>, and with V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>, Fenton-like reaction, Fenton, and photo-Fenton process, UV; UV/TiO<sub>2</sub>; UV/H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>/TiO<sub>2</sub> [4, 11-18]. Nevertheless, the most of the AOPs are based on using ozone as the main component, and the literature on HCHO degradation in an aqueous solution using AOPs is limited [10, 19]. Recently, the application of sonolysis or ultrasound (US) for the treatment of chemical compounds in water has been explored [20]. The chemical effects of US are due to sound production that is passed through a liquid [21]. Ozonation and sonolysis of aqueous solutions generate highly reactive radicals (OH<sup>•</sup>, <sup>•</sup>HO<sub>2</sub>), which react with dissolved organic compounds leading to hydroxylation and oxidation reactions [22]. Also, nanocatalysis can help design catalysts with greater selectivity, high stability, and excellent activity [23]. Due to the economic reasons, the activation of molecular oxygen (O<sub>2</sub>) to produce reactive oxygen species such as hydroxyl radical (OH<sup>•</sup>), for the degradation of organic pollutants by zero-valent metals, including zero-valent iron (ZVI), is receiving increasing attention recently [24, 25]. It should be noted that few studies have evaluated the degradation of HCHO at low concentrations and in similar studies, NZVI role has not been performed HCHO degradation under sono catalytic ozonation (SCO) process in waste solution.

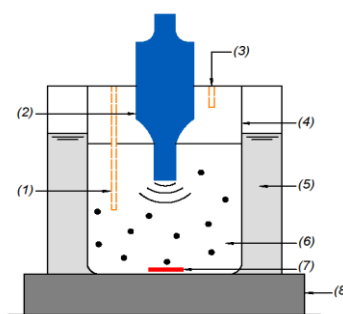
Therefore, the present study was aimed to (1) examine the HCHO degradation in the SCO and compare SCO process efficiency to several other oxidation processes, including single ozonation (O<sub>3</sub>), single sonolysis (US), ozone sonolysis (US/O<sub>3</sub>) and NZVI catalytic to remove HCHO; (2) investigate the effect of several main operational variables of the SCO – including the pH, US power, the doses of ozone and NZVI, and initial concentrations of HCHO – in a synthetic waste solution.

## 2. METHODS

**2.1. Materials** Formaldehyde solution (37%) was purchased from Merck Co. Also, the pH adjustment was carried out with concentrated solutions of sulfuric acid and sodium hydroxide (obtained from Merck Co., Germany). A powder of NZVI nanoparticles (35-45 nm) was purchased from US Research Nanomaterials Inc. and used as received.

## 2.2. Experimental set-up and Procedure

Figure 1 shows a schematic diagram of the SCO reactor. A covered cylindrical shape with an effective volume of 500 mL equipped with cooling water temperature control, to prevent the lamp from overheating was used. All experiments were the batch type and performed using ultrasonic homogenizer apparatus (BANDELIN company made in Germany), which has a fixed frequency of 23 kHz and maximum input power of 150 W. Further, an ozone generator (O & W, Japan) with a dosing capacity of 1 g O<sub>3</sub> h<sup>-1</sup> was used. The excess ozone in the outlet gas was absorbed by KI solution (2% wt). Then, the excess amount of ozone was determined according to 2350E method (potassium iodide) of the “Standard Methods for the Examination of Water and Wastewater”. A magnetic stirrer (Labinco-90-402) was located in the solution to ensure a uniform mixture. The first step was to investigate the HCHO removal rate in each process (Ozonation, US, NZVI catalyst, US/O<sub>3</sub> and SCO-US/O<sub>3</sub>/Fe<sup>0</sup>) with an initial HCHO concentration of 10 mg L<sup>-1</sup> and a reaction time of 45 min. Then, the influences of solution pH (5–9), ultrasonic power (60–140 W), ozone dosage (20–200 mg h<sup>-1</sup>), NZVI dosage (50–400 mg L<sup>-1</sup>), and initial HCHO concentration (1–20 mg L<sup>-1</sup>) were evaluated. The experiments were continued using optimal parameters obtained in the previous steps. For each SCO experiment, 400 mL of the solution containing HCHO concentration of 10 mg L<sup>-1</sup> was transferred into the reactor. All experiments were carried out at temperatures between 21 and 25 °C. After each process, NZVI was separated with a 20 cm height magnet (S BMW, 0.7 Tesla) and then filtered through a 0.2-µm pore size syringed acetate cellulose filter. Finally, the residual HCHO concentrations were measured in the filtrate. During the experiments, a control sample was applied under the same conditions without processes interference.



**Figure 1.** Schematic diagram of SCO reactor: (1) ozone generator; (2) ultrasonic homogenizer; (3) KI solution; (4) reactor; (5) temperature-controlled bath; (6) sample content NZVI; (7) magnet; and (8) magnetic stirrer.

**2. 3. Analytical Methods** In order to assess the performance of the considered processes for HCHO removal, spectrophotometer method (DR-5000, HACH model) was used in accordance with 8110 colorimetric methods with a visible light detector operating at a wavelength of 630 nm. Removal efficiency (RE %) of HCHO in US/O<sub>3</sub>/Fe<sup>0</sup> process was calculated by Equations (1):

$$RE\% = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where C<sub>0</sub> and C, (mg L<sup>-1</sup>) are concentrations of HCHO before and after the reaction, respectively.

### 3. RESULTS AND DISCUSSION

#### 3. 1. Degradation of HCHO in Different Comparable Systems

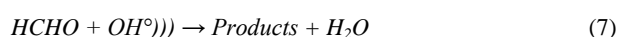
Five series of systems were investigated, i.e. ozone, US, Fe<sup>0</sup>, US/O<sub>3</sub>, US/O<sub>3</sub>/Fe<sup>0</sup> under a natural pH, same experimental conditions and with an initial HCHO concentration of 10 mg L<sup>-1</sup> in order to evaluate and compare their ability to remove HCHO from a waste solution (Figure 2). As indicated, the maximum HCHO removal for single ozonation, ultrasonic wave, and NZVI catalyst processes were around 30%, 28%, and 46%, respectively. Since the HCHO is a saturated compound, reactivity of this compound with ozone is very low [10]. Furthermore, the single ozonation did not significantly contribute to the removal of HCHO. Also, the degradation of HCHO mechanisms by ultrasonic wave performance may be associated to sound waves that break chemical bonds in solution using shear force caused by energy release [26]. These results are likely due to a low concentration of OH radicals formed in both ozonation and US processes. However, the results reveal that NZVI catalyst process is a rather suitable method for the removal of HCHO. The electron transfer from Fe<sup>0</sup> to dissolved oxygen initiates the NZVI reaction and the mass transfer of oxygen molecule onto the NZVI surface is critical. The ZVI nanoparticles can attract O<sub>2</sub>, which speeds up the mass transfer process. The higher reduction of oxygen on ZVI nanoparticles leads to the enhanced production of OH<sup>•</sup> [27, 28]. Similar results reported by Amin et al.'s study on the effect of ultrasonic waves and nZnO catalyst process on HCHO solution with a concentration of 50 mg L<sup>-1</sup>, showed that the HCHO degradation efficiency was approximately 34 and 44%, respectively [6]. Additionally, they stated the application of sonolysis could slightly degrade low concentrations of HCHO. Therefore, the OH<sup>•</sup> produced by ultrasound process is the main factor responsible for the degradation of the HCHO. Generally, the following mechanisms are proposed for the hydroxyl radical

formations for the ozonation, sonolysis, and NZVI catalyst processes [Equations (2)-(9)] [10, 27, 29-32]:

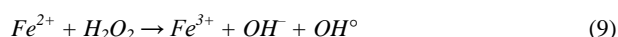
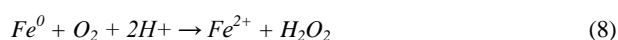
Ozonation



Sonolysis



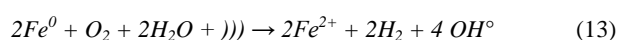
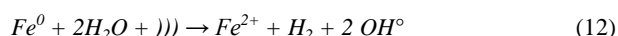
NZVI catalyst process



where US denotes the ultrasonic wave and the subscript  $\cdot$  denotes the products generated by the ultrasonic process. Cavitation bubble is able to support radical species not only from sonolysis of water but also from the gas involved. For instance, O<sub>2</sub> gas promotes parallel reactions and OH radical species via Equations (10) and (11) [30].



The US/O<sub>3</sub> process gave a maximum removal efficiency of 38%, also indicating a low HCHO removal. The enhancing effects of zero-valent iron nanoparticle on the HCHO degradation can be observed from experimental data obtained from the US/O<sub>3</sub> and US/O<sub>3</sub>/Fe<sup>0</sup> processes as shown in Figure 2. According to the change during 45 min ultrasonic irradiation, the degradation of HCHO by the US/O<sub>3</sub> process was slower than those by US/O<sub>3</sub>/Fe<sup>0</sup>. When NZVI was introduced into the US/O<sub>3</sub> process, the removal ratios of HCHO were increased. As seen, the HCHO removal rate was observed after 45 min reaction time, which was as high as 60%. These results indicate that NZVI plays a key role in the SCO system. With the addition of NZVI to the system, additional hydroxyl radicals can be obtained from the reaction between NZVI and ultrasonic waves, as shown in Equations (12) and (13).

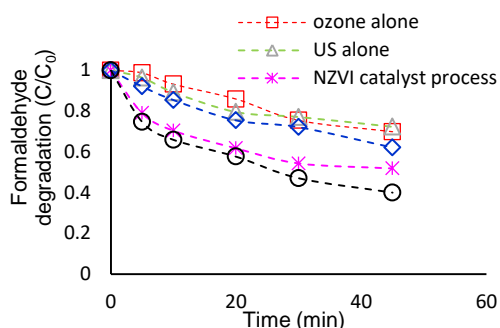


Wen et al. [33] studied the oxidation capacity of different zero valent metals for degradation of diethyl

phthalate (DEP), ZVI, zero valent aluminum (ZVAL), zero valent copper (ZVC) and zerovalent zinc (ZVZ). Their results indicated that ZVI, ZVC, and ZVAL showed excellent degradation efficiency towards DEP. Also, Son et al. reported that when  $\text{Fe}^0$ ,  $\text{Fe}^{2+}$ , and  $\text{S}_2\text{O}_8^{2-}$  were individually combined with sonication, the degradation efficiency of 1, 4-dioxane (1, 4-D) increased [34]. From the above explanation, it follows that the SCO process could be more efficient in HCHO removal than other processes in this study. Pseudo-first-order rate constants ( $k$ ) and removal percentage obtained from all processes during 45 min reaction period are shown in Table 1. The value of  $k$  in SCO degradation is higher than those obtained from other processes. These findings confirm the significant influence of the radical pathway due to the additional generation of  $\text{OH}^\circ$  radicals in the SCO process. In other words, the SCO process provides five sources of  $\text{OH}^\circ$ : i) chemical degradation of ozone, ii) ultrasonic decomposition of water, iii) decomposition of ozone in the acoustic cavitation bubble, and iv) NZVI reaction to products of ozone decomposition and v) reaction between NZVI and ultrasonic waves.

### 3. 2. Effect of Operational Parameters

**3. 2. 1. Effect of Initial Solution pH** In Figure 3 the pH effect on the HCHO degradation is depicted.



**Figure 2.** HCHO degradation efficiencies in different comparable systems.

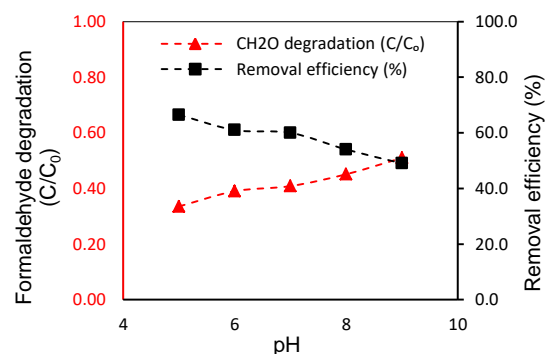
**TABLE 1.** Pseudo-first-order rate constants and removal percentage for HCHO degradation by different oxidation processes

Processes	HCHO	
	$k$ ( $\text{min}^{-1}$ )	Removal efficiency (%)
Ozone alone	0.0086	30
US alone	0.0074	28
NZVI	0.0135	46
US/O <sub>3</sub>	0.0102	38
SCO	0.0187	60

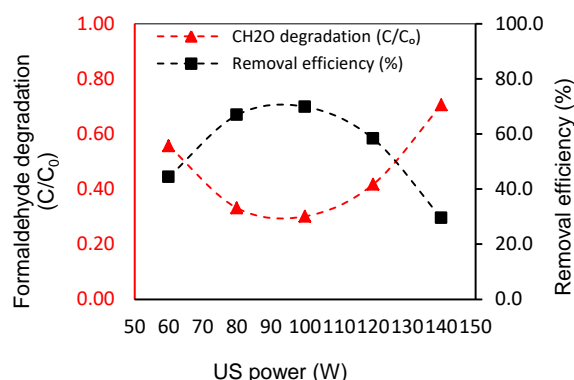
As can be seen, an increase in the degradation rate of HCHO under acidic media was observed. The HCHO degradation decreases from 66.5% to 49% for pH 5 and 9, respectively. The possible reasons for the decrease in HCHO degradation with increasing pH are: (i) rapid consumption of  $\text{OH}^\circ$ , and (ii) decreasing oxidation potential of  $\text{OH}^\circ$  [21]. Moreover, the results may be associated with the effect of pH on surface properties of NZVI and contaminant properties. On the other hand, the acidic condition leads to a reduction of the NZVI particle size, leading to an increase in reaction rate. Zhou et al. observed similar results. They found that lower initial pH would favor reactive black 5 (RB5) and oxalate degradation efficiencies in an ultrasound/UV/ferric system [35]. Wang et al. examined the ultrasonic degradation of p-nitrophenol (p-NP) in aqueous solution with  $\text{CCl}_4$  enhancement. They reported that p-NP degradation increases with decreasing the initial pH of the solution [36]. Another reason may be that the occurrence of a competitive reaction led to limiting the rate of HCHO degradation in the alkaline pH. Moussavi et al reported that the HCHO removal in the alkaline pH relates to the type of iron species that dominated at these conditions [8]. In other words, the rate constant of the  $\text{H}_2\text{O}_2$  reaction with the  $\text{Fe}(\text{OH})^+$  is greater than that with  $\text{Fe}^{2+}$ , the higher amount of  $\text{OH}^\circ$  was produced at an alkaline pH level compared to the acidic solutions in which  $\text{Fe}^{2+}$  is the dominant species of iron. Bagheri et al. reported that the performance of the electro-Fenton process in alkaline pH could improve HCHO degradation rate of industrial wastewater [4]. Therefore, in this study, pH of 5 was used as optimum for the next experiments.

### 3 .2. 2. Effect of the Applied Ultrasonic Power

The most important factors for application of sonolysis is the power employed [30]. Figure 4 shows the effect of the applied ultrasonic power on the degradation of HCHO.



**Figure 3.** Effect of pH on HCHO degradation ( $[\text{HCHO}] = 10 \text{ mg L}^{-1}$ ,  $\text{O}_3$  dosage =  $100 \text{ mg h}^{-1}$ ,  $[\text{NZVI}] = 200 \text{ mg L}^{-1}$ , US power =  $60 \text{ W}$ , and reaction time = 45 min)

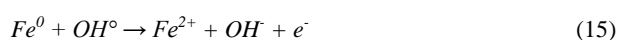


**Figure 4.** Effect of US power on HCHO degradation ( $[\text{HCHO}] = 10 \text{ mg L}^{-1}$ ,  $\text{O}_3$  dosage =  $100 \text{ mg h}^{-1}$ ,  $[\text{NZVI}] = 200 \text{ mg L}^{-1}$ ,  $\text{pH} = 5$ , and reaction time = 45 min).

A higher degradation rate was reached around 70% for 100 W of applied power. In fact, when ultrasonic power reaches 100 W, the formation rate of hydrogen peroxide increased. Therefore, ultrasonic waves generate  $\text{OH}^\circ$  radicals by cleavage of HCHO in the solution. Also, concerning these results, it can be assumed that the influence of NZVI nanocatalyst is predominantly of mechanical nature. This can be explained by the fact that the spherical shape of the bubbles is distorted to an asymmetric one. Therefore, the larger surface of these asymmetric bubbles leads to a higher reaction rate of HCHO at the liquid-gas interface of the bubbles. This effect depends on the particle size. Thus, due to the presence of ZVI nanoparticles as a catalyst, the rate of HCHO elimination was better, and chemical effects with an increasing rate of  $\text{OH}^\circ$  can be excluded. These results were in good agreement with Hartmann et al. study [31]. However, the HCHO degradation decreased from 70 to 30% for an ultrasonic wave power of 100 to 140 W, respectively. The reasons for this result are probably depletion of dissolved air in the solution and reducing the  $\text{OH}^\circ$  generation during the period of the process. Moreover, it should be noted that both protons and  $\text{O}_2$  molecules are competing for electron acceptors of NZVI [Equations (8), (9) and (14)] [27]. Therefore,  $\text{O}_2$  molecules are oxidants for NZVI at ultrasonic power over 100 W.



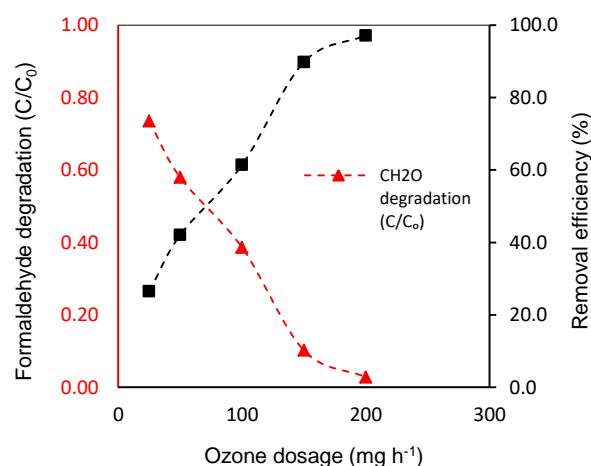
Also,  $\text{Fe}^0$  could be oxidized to  $\text{Fe}^{2+}$  by  $\text{OH}^\circ$  radical and therefore the presence of  $\text{Fe}^0$  inhibited the sonication of HCHO at ultrasonic powers above 100 W as shown in Equation (15) [34]:



With this description, the ultrasonic power of 100 W is useful and more effective for HCHO degradation.

**3. 2. 3. Effect of Ozone Dosage** The HCHO decomposition with different ozone dosages of 20, 50, 100, 150, and  $200 \text{ mg h}^{-1}$  using SCO process is shown in Figure 5. As expected, the rate of compound degradation, increased with increasing ozone dosage. In this case, HCHO removal increases from 26.5 to 97.2% as the ozone concentration increases from 20 to  $200 \text{ mg h}^{-1}$ . Therefore, the maximum HCHO removal efficiency is 97.2% for  $200 \text{ mg h}^{-1}$  ozone dosage. It is reported that, as the ozone served as the initiator for the production of radical species, an increased amount of ozone in the presence of a given concentration of NZVI makes more ozone available to contribute to the reaction and enhancement of the radical species formation, thus improving the HCHO degradation rate [37, 38]. On the other hand, an increase in ozone dosage is expected to correspond with an increase in the  $\text{OH}^\circ$  generation [39]. Also, since ozone would not consume the produced  $\text{OH}^\circ$ , therefore, the more ozone introduced in the solutions, the more  $\text{OH}^\circ$  would be produced [38]. Another reason may be the increase of turbulence in suspension with the increase of ozone-containing gas flow rate to the reactor, and in turn, improved the mass transfer of ozone to the HCHO solution [40, 41]. Figure 5 shows that the most important variable for the enhancement of HCHO degradation was ozone dosage.

**3. 2. 4. Effect of NZVI Catalyst Dosage** The performance of SCO for HCHO removal was studied in the presence of various dosages of the NZVI ( $50 - 400 \text{ mg L}^{-1}$ ) and the results are shown in Figure 6. As illustrated in Figure 6, the increase in the NZVI amount from causes an increase in HCHO oxidation efficiency to 97.2%. It could be related to oxidation mechanisms of NZVI that have been described in previous stages.



**Figure 5.** Effect of ozone dosage on HCHO degradation ( $[\text{HCHO}] = 10 \text{ mg L}^{-1}$ ,  $[\text{NZVI}] = 200 \text{ mg L}^{-1}$ ,  $\text{pH} = 5$ , US power = 100 W, and reaction time = 45 min).

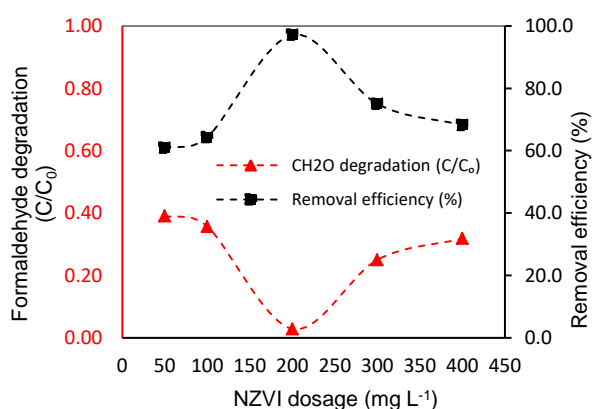


Also, increasing the amount of nanoparticles leads to increasing HCHO removal rate due to the creation of more surface area and active sites in ZVI nanoparticles. Therefore, more oxidation agents such as the OH radicals were formed. Although there is a lack of information regarding the nanocatalysis effect of ZVI on US/O<sub>3</sub>, other researchers have found increased oxidation efficiency in metal-based AOPs with increased catalyst dosage [10, 39, 42]. However, upon increasing the ZVI dosage to above 200 mg L<sup>-1</sup>, HCHO removal efficiency decreased to 68%. This can be explained that dissolved air in the solution exhausted faster, and thus OH<sup>•</sup> generation in reduced time decreased during the process.

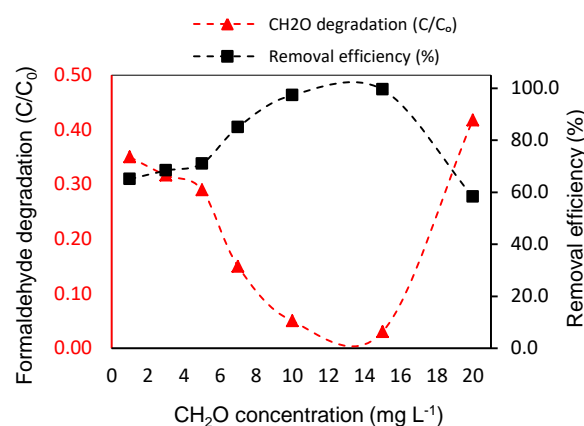
### 3. 2. 5. Effect of Initial HCHO Concentration

The effect of initial HCHO concentration (1–20 mg L<sup>-1</sup>) on the SCO process was investigated (Figure 7). This Figure shows that increasing the initial HCHO concentration from 1 to 15 mg L<sup>-1</sup> led to the increase of degradation. When the initial HCHO concentration increased, the number of HCHO molecules exposed to reactive radicals for degradation also increased, which subsequently led to higher degradation efficiency. But, for 20 mg L<sup>-1</sup> HCHO concentration, the removal efficiency decreased to 58%. Since, the initial oxidant concentration has been fixed, high concentration of HCHO resulted in increased formation of intermediate products, which, in turn lowered the reaction rate of radicals towards HCHO. Also, another reason may be that since HCHO is a polar compound and hydrophilic and at low concentrations, it has less access to NZVI catalyst for reforming. It may be explained that upon increasing HCHO concentrations, it is more soluble in solution, and therefore NZVI could reform it better [43].

But, HCHO removal efficiency decreased to 58% with increasing initial concentration that could be



**Figure 6.** Effect of NZVI dosage on HCHO degradation ([HCHO] = 10 mg L<sup>-1</sup>, pH = 5, US power = 100 W, O<sub>3</sub> dosage = 200 mg h<sup>-1</sup>, and reaction time = 45 min).



**Figure 7.** Effect of HCHO concentration on HCHO degradation (pH = 5, US power = 100 W, ozone dosage = 200 mg h<sup>-1</sup>, [NZVI] = 200 mg L<sup>-1</sup>, and reaction time = 45 min).

explained by active sites of the catalyst surface area completely filled, and for more initial HCHO concentrations, the more NZVI catalyst may be needed [6]. Therefore, the optimal initial concentration of HCHO in these experiments is 15 mg L<sup>-1</sup>. Guimarães et al. evaluated UV/H<sub>2</sub>O<sub>2</sub> and photo-Fenton processes to degrade HCHO at the highest concentrations (1200–12000 mg L<sup>-1</sup>). They observed that the efficiency of the UV/H<sub>2</sub>O<sub>2</sub> and photo-Fenton declined as the concentration of HCHO increased [44].

## 4. CONCLUSION

In this study, degradation of low concentration of HCHO was investigated using several processes. Different processes were performed under same conditions in order to evaluate and compare their ability to remove HCHO. The removal efficiency was as follows:

SCO > NZVI catalytic process > US/O<sub>3</sub> > ozonation > sonolysis

In SCO process, pseudo-first-order degradation rate constant was found, and this process provided the highest degradation rate constants. The degradation rate constant of the SCO process was calculated as 0.0187 min<sup>-1</sup>. Also, the experiments were carried out by determining appropriate conditions for HCHO removal with SCO process. Optimum pH, ultrasonic power, ozone dosage, NZVI dosage and HCHO concentration for efficient removal of HCHO were 5, 100 W, 200 mg h<sup>-1</sup>, 200 mg L<sup>-1</sup> and 15 mg L<sup>-1</sup>, respectively. It was found that the oxidation by hydroxyl radicals was the dominant removal mechanism. From this data, it can be concluded that the catalytic AOP of SCO is recommended for the treatment of effluents containing low concentrations of HCHO.

## 5. ACKNOWLEDGEMENT

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## Degradation of Low Concentrations of Formaldehyde in Sono Catalytic Ozonation Advanced Oxidation Processes using Zero-valent Iron

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هدف از مطالعه حاضر، بررسی میزان حذف فرمالدهید با استفاده از روش‌های مختلف در سیستم‌های ناپیوسته می‌باشد. در این پژوهش، به منظور بررسی میزان حذف فرمالدهید، فرایندهای ازن زنی، اولتراسونیک، ازن زنی به همراه اولتراسونیک، ازن زنی کاتالیزوری به همراه اولتراسونیک (SCO) و فرایند کاتالیزوری آهن صفر ظرفیتی بررسی شد. همچنین، تأثیر پارامترهای عملیاتی از جمله pH= 5-9، توان اولتراسونیک (۶۰-۱۴۰ وات)، دوز ازن (۲۰-۲۰۰ mg h<sup>-1</sup>)، دوز (۴۰۰-۵۰۰ mg L<sup>-1</sup> =NZVI) و غلظت اولیه فرمالدهید (۱-۲۰ mg L<sup>-1</sup>) ارزیابی شد. نتایج نشان می‌دهد که فرایند SCO در مقایسه با سایر فرایندها راندمان بهتری دارد. تأثیر فاکتورهای مهم بر فرایند SCO نیز بررسی شد و در pH ۵، توان اولتراسونیک ۱۰۰ وات، دوز ازن ۲۰۰ mg h<sup>-1</sup>، دوز کاتالیزور ۲۰۰ mg L<sup>-1</sup> و غلظت اولیه فرمالدهید ۱۵ mg L<sup>-1</sup> حداکثر راندمان ۹۹ درصد به دست آمد. با توجه به نتایج به دست آمده می‌توان چنین نتیجه گیری کرد که دوز ازن مهم‌ترین فاکتور می‌باشد. همچنین فرایند SCO جهت تصفیه محلول‌های آبی حاوی غلظت پایین فرمالدهید پیشنهاد می‌گردد.

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