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Original Article

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Degradation of Formaldehyde From Synthetic Wastewater Using $Fe^{2+}/H_2O_2/O_3$ Process

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Abstract
Formaldehyde is used in many industries for its different chemical characteristics. The wastewater in these industries contains large amounts of formaldehyde which is dangerous and toxic for human and environment. The purpose of this study was to investigate the efficiency of $Fe^{2+}/H_2O_2/O_3$ process in degradation of formaldehyde from synthetic wastewater. This experimental bench-scale study in batch system was conducted on the synthetic wastewater in primary concentration of formaldehyde (500 mg/L). The maximum percentage of formaldehyde removal was 72.5% that was observed in molar ratio of 2.4 $[H_2O_2]/[Fe^{2+}]$. After determining optimum [H2O2]/$[Fe^{2+}]$, the effects of pH variables, function time, and ozone concentration were studied in formaldehyde removal. In this process, the maximum degradation efficiency of formaldehyde in 0.7 mg/L ozone concentration and in 2.4 of molar ratio for $[H_2O_2]/[Fe^{2+}]$ was 85.84% after 20 minutes. Moreover, the effect of pH and ozone concentration was significant in degradation efficiency ($P<0.05$). Generally, the $Fe^{2+}/H_2O_2/O_3$ process seems to be a practical and reliable method in treating the industrial wastewater contaminated with high concentrations of formaldehyde.
Keywords: Formaldehyde, Hydrogen Peroxide, Ferrous Sulfate, Ozone, Industrial Wastewater

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1. Introduction

Formaldehyde is a chemical substance with CH_2O formula, which is the simplest compound in the aliphatic aldehyde group. Concerning its diverse and complex chemical properties, formaldehyde is used nowadays enormously and extensively in different industrial, chemical, medical, and agricultural branches (1). According to Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) list, formaldehyde is a dangerous and toxic material for human and environment (2) and prevents the physiological activity of cells by binding to amino groups of proteins and causes damage to DNA, mutagenesis in cells, and carcinogenesis (3). Many studies have been done on the effects of formaldehyde on vital organs such as the nervous system, and respiratory, digestive, and cardiovascular systems (4-7). High concentrations of formaldehyde, in the range of 0.2 to 10 g/L, can be found in the effluent of industries that use this substance as one of the raw materials (8). The inhibitory effect of high concentrations of the row materials like formaldehyde on biological processes and low efficiency of conventional treatment of these toxic and non-biodegradable compounds have led us to look for a more effective method for the degradation of these compounds. Therefore, it is necessary to use a pretreatment process to decrease formaldehyde concentration to a level at which biological treatment can be achieved (3). Among pretreatment processes, advanced oxidation processes (AOPs) have attracted an enormous interest in the degradation of formaldehyde (9-12). In these processes, large amounts of hydroxyl ions ($OH^•$) are produced with high ability to oxidize organic contaminants (13). One of the AOPs that is more efficient and cost-effective is Fenton oxidation process (14). Fenton is a compound of divalent iron salt and hydrogen peroxide (H_2O_2), which is used in acidic conditions. The basis of the Fenton process is the decomposition of H_2O_2 in an acidic environment by divalent iron salt (as catalyst) and the production of hydroxyl radical (9,15,16). During Fenton process, ferrous sulfate (Fe^{2+}) catalyzes H_2O_2 decomposition with the formation of hydroxyl radicals, which are very strong and non-selective oxidizing agents.

Radical production involves a complex reaction in aqueous solution (Equation 1).

$$Fe^{2+} + H_20_2 \rightarrow Fe^{3+} + OH^- + OH^\circ \quad (1)$$

In addition, hydroxyl radicals can oxidize organic matter (RH) through the production of proton organic radicals (R) that are highly reactive.

$$Fe^{3+} + H_20_2 \rightarrow Fe^{2+} + OH_2 + H^+ \quad (2)$$

Another advantage of the Fenton process is the short reaction time of it compared to other AOPs (17). In a study that evaluated the effect of electro-Fenton process in wastewater treatment containing high concentration of formaldehyde, the maximum degradation efficiency of formaldehyde in pH value of 10, and H_2O_2 concentration of 10 mmol/min was obtained after 6 minutes (18). In the study of Hasanbeiki et al in 2013, using AOPs, the degradation percentage of formaldehyde at pH value of 3 and after 60 minutes was obtained 47% and 70%, respectively, by adding 0.4 and 0.5 mol/L H_2O_2 (3). Kajitvichyanukul et al suggested that the Fenton and photo-Fenton processes compared to the UV/H_2O_2 process are more suitable techniques for the treatment of wastewater containing formaldehyde due to the high degree of degradation of formaldehyde as well as low toxicity of by-products. According to this study, the degradation rate of formaldehyde and methanol by photo-Fenton process was 48% and 32% in 80 minutes, respectively, which extremely increased the efficacy after adding iron ion (19). Other processes used to treat volatile organic matter are chemical oxidation methods, especially the application of ozone gas. Ozone gas has a high oxidation potential and oxidizes most volatile organic compounds (20). Ozonation has been enormously considered due to high oxidation power, lack of residue, and no increase in salt concentration (21). To the best of our knowledge, there is no research carried out simultaneously on the usage of Fenton and ozonation processes for the degradation of formaldehyde; therefore in this study, the efficiency of $Fe^{2+}/H_2O_2/O_3$ process in degradation of formaldehyde from synthetic wastewater was investigated.

2. Materials and Methods

In this experimental bench-scale study in batch system, the efficacy of $Fe^{2+}/H_2O_2/O_3$ process in degradation of formaldehyde from synthetic wastewater and the effects of initial operating variables such as molar ratio of $[H_2O_2]/[Fe^{2+}]$, pH, ozone dosage, and reaction time were investigated. For sample preparation, formalin solution (37% w/w) with chemical formula of CH_2 was used. The required chemicals were prepared from Merck Company with high purity. H_2O_2 (35%) and Fe^{2+} as $FeSO_4$ ($7H_2O$) in this study were also used. pH adjustments were performed after adding oxidants using sulfuric acid (1 N) and sodium hydroxide (0.2 N) and pH by 262 pH meter. The degradation of formaldehyde from synthetic wastewater was carried out in a Pyrex reactor with dimensions of 16×16×26 cm and a volume of 2 L. Ozone gas was generated through an ozone generator, the COG-OM model manufactured by ARDA and a maximum capacity of 10 g/h. Effective ozone distribution was accomplished through an air diffuser in the floor, as well as complete mixing with a magnetic stirrer. The study was conducted in 2 stages of optimization and main experiments. The effects of changes in molar ratio of $[H_2O_2]/[Fe^{2+}]$ were investigated by changing this factor and maintaining other factors in the experiments. At this stage, 8 molar ratios of $[H_2O_2]/[Fe^{2+}]$ including 0.5, 1, 1.2, 1.6, 2.2, 2.4, 2.8 and 3.2 were tested in constant conditions of pH value of 3 and reaction time of 40 minutes. After determining optimal ratio, the effects of 3 variables of pH (3, 5, 7, 9), reaction time (0, 5, 10, 15, 20, 30, and 40 minutes), and ozone concentration (0.3, 0.7 mg/L) were investigated in degradation of formaldehyde, totally in 192 samples (including 3 repetitions).

Hantzsch reaction method was used to measure the formaldehyde content. This method is based on color measurement at a wavelength of 412 nm visible light with a Hantzsch reagent and a specific method for measuring formaldehyde in aqueous solution. A spectrophotometer (American Hach® 2010) was used for this purpose. It should be noted that all experiments were carried out at laboratory temperature (22). In every stage, all experiments were repeated 3 times and the average of these 3 experiments for every parameter was reported as its amount.

The formula used to calculate degradation percentage is:

$$\text{Efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100 \quad (3)$$

C_0= primary concentration
C = concentration after the process

Data analysis was performed using SPSS statistical software version 16.0 (two-way ANOVA). The mean and standard deviation of formaldehyde degradation were calculated at first and at last. The effect of all revised factors on degradation of formaldehyde was calculated repeatedly using variance-analysis model.

3. Results and Discussion

In the optimization phase, to determine the optimal molar ratio of $[H_2O_2]/[Fe^{2+}]$, the experiments were carried out in 8 proportions. The average percentage of degradation of formaldehyde in terms of $[H_2O_2]/[Fe^{2+}]$ is presented in Fig. 1 in pH 3 and the contact time of 40 minutes. Regarding the diagram, maximum degradation efficiency of formaldehyde in optimal molar ratio of $[H_2O_2]/[Fe^{2+}]$ was obtained 2.4. The average degradation percentage of formaldehyde observed in this ratio was 72.5%. The degradation efficiency in $[H_2O_2]/[Fe^{2+}]$ ratio of 0.5 was low. This is due to the excessive absorption of hydroxyl radical by iron. The degradation percentage of

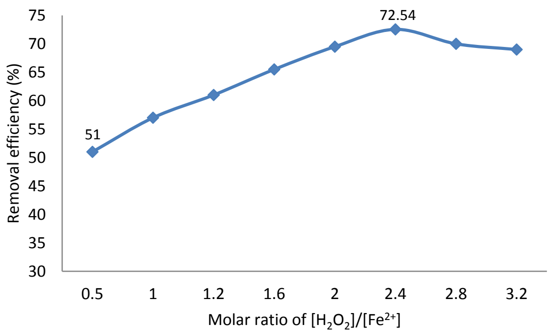

Fig. 1. Degradation Efficiency of Formaldehyde Versus Molar Ratio of $[H_2O_2]/[Fe^{2+}]$.

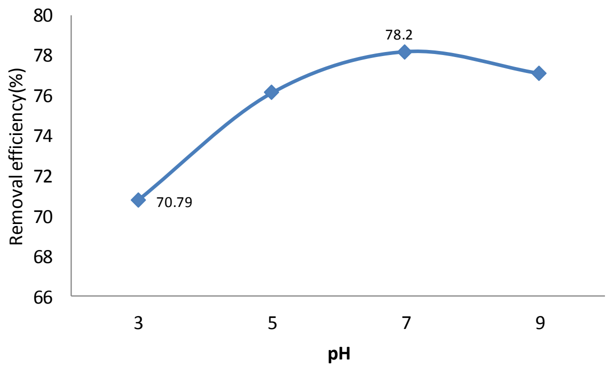

Fig. 2. Degradation Efficiency of Formaldehyde Versus pH Level.

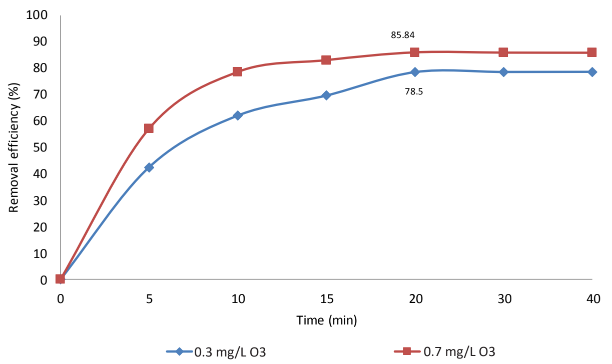

Fig. 3. The Degradation Efficiency of Formaldehyde Versus Ozone Concentration and Reaction Time.

formaldehyde was increased from 51% to 72.54% when $[H_2O_2]/[Fe^{2+}]$ concentration increased from 0.5 to 2.4. The molar ratio of higher than 2.4 in degradation of formaldehyde causes a decrease in efficiency. In Fenton optimization, the role of H_2O_2 is very significant because the excess amount of H_2O_2 causes one-way reactions. This occurs since H_2O_2 acts as a strong remover of hydroxyl radicals and converts them to hydroxyl radicals with lower potential. According to the study of Riano et al, the optimal concentrations of H_2O_2 and Fe^{2+} were 400 and 100 mg/L in Fenton process, respectively. In this study, the degradation efficiency in concentrations of 200, 400, and 800 mg/L H_2O_2 was 75%, 80%, and 77%, respectively, which was stable by increasing the H_2O_2 concentration to 800 mg/L. In addition, in optimizing Fe^{2+}, with increasing the concentration from 100 to 400, the efficiency decreased from 88% to 80%, and this decrease continued. The results of this study were consistent with the results of our study (23).

Fig. 2 shows the average percentage of degradation of formaldehyde in terms of pH level. According to the diagram, with increasing the pH, the degradation efficiency increased and maximum efficiency was obtained as 78.2% in pH value of 7. As shown in Fig. 2, the maximum degradation efficiency of formaldehyde was in pH value of 7. According to the conducted studies, if H_2O_2 is used as an oxidation factor, the degradation efficiency of aldehyde compounds will increase in higher pH values. On the other hand, because of the presence of Fe in high pH values in the form of $Fe(OH)_2$ compared to more acidic pH values, the mechanism of hydroxyl radical production by reaction of $Fe(OH)_2$ with H_2O_2, is based on the following reaction:

$$Fe(OH) + 2H_20 \rightarrow 2OH^{\circ} + Fe_2O_3 + 3H_2O \quad (4)$$

In the study of Lei et al, the degradation efficiency of formaldehyde increased as sample pH increased. According to the study, if H_2O_2 is used as an oxidant, the degradation efficiency of aldehyde compounds in high pH values will increase (24).

Fig. 3 shows the average percentage of degradation of formaldehyde in terms of ozone concentration and reaction time. According to the diagram, the maximum efficiency was obtained in ozone concentration of 0.3 mg/L and after 20 minutes of reaction time. Moreover, with an increase in reaction time from 0 to 20 minutes, the average percentage of degradation of formaldehyde increased and after this time, no significant increase was observed, to such a degree that the maximum efficiency was observed in concentrations of 0.3 and 0.7 mg/L by 20 minutes. According to Fig. 3, with increasing the reaction time from 0 to 20 minutes, the degradation efficiency of formaldehyde increased and reached the maximum level of 85.84%. By increasing the reaction time to more than 20 minutes, no significant increase was observed due to the consumption of H_2O_2 added to the system. In general, the reaction time is affected by the amount of H_2O_2. It can also be justified by the fact that with the reaction time, the intermediate compounds are produced. It is itself a competitor of primary compounds that react with hydroxyl radicals and act as a hydroxyl escape agent. According to Bahmani et al, formaldehyde oxidation was conducted by increasing the reaction time in the Fenton oxidation process in the first 15 minutes, and then, until 60 minutes, the diagram gradient was almost constant. This process removes more than 95% of color compounds in 15 minutes. On the other hand, Moussavi et al supposed that increasing the reaction time from 1 to 10 minutes, increases the efficiency of formaldehyde oxidation to the maximum value of 70%. By increasing the reaction time to more than 10 minutes, no significant changes were found in the efficiency of formaldehyde oxidation. The results of mentioned study corresponded our obtained results (25). In evaluating the effect of ozone dose on the degradation efficiency of formaldehyde , increasing ozone concentration resulted in increasing the efficiency. By increasing the ozone concentration from 0.3 to 0.7 mg/L, the degradation efficiency of formaldehyde was significantly increased ($P<0.015$). According to Moussavi et al, there is a linear relationship between ozone dose and degradation efficiency of formaldehyde . In addition, the presence of certain concentration of H_2O_2 causes the available ozone to react more quickly because it causes radical formation. On the other hand, with increasing ozone concentration, turbulence in the suspension is increased and this increase in velocity of ozone gas in the reactor improves its penetration in liquid phase. This will increase the performance of ozone (2). Moreover, in the study of Hong et al, by increasing ozone concentration from 49 to 141 mg/m^3 through UV/TiO_2/O_3 process, degradation of formaldehyde was increased from 72% to 94% (26).

4. Conclusion

Investigating the performance of $Fe^{2+}/H_2O_2/O_3$ process in degradation of formaldehyde from a solution containing high concentration of this material shows that this method depends on the reaction time, sample pH, and ozone concentration. In this process, the reaction time of 20 minutes was considered as the optimal time of the process. Other optimal conditions of operation were pH value of 7, and ozone concentration of 0.7 mg/L in which 85.84% of formaldehyde was degraded. It seems that this process can be a practical and reliable pretreatment method in treating industrial wastewater contaminated with high concentration of formaldehyde.

Conflict of Interest Disclosures

The authors declare that they have no conflict of interests.

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