Degradation and detoxification of formaline wastewater by advanced oxidation processes

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Abstract

In this study, advanced oxidation processes (AOPs) utilizing the combinations of UV/H_2O_2, Fenton, photo-Fenton and the combination of Fenton/photo-Fenton reactions were investigated in lab-scale experiments for the degradation of formaline wastewater. The studied toxic chemicals were formaldehyde and methanol in mixture solution, so-called formalin, which is the embalming agent in mortuaries. The experimental results showed that the photo-Fenton process was the most effective treatment process among the studied AOPs. Pseudo-first-order degradation rate constants of formaldehyde and methanol were obtained from batch experimental data. In the combination of Fenton/photo-Fenton reactions, the results show that applying UV light at an early stage of the reaction might not be necessary for a speedy oxidation reaction of the Fenton process. With Fenton and photo-Fenton processes, mineralization of formaline wastewater can be achieved, as no residual TOC is detected in the effluent after the reaction period. It is suggested that Fenton and photo-Fenton processes are viable techniques for the formaline wastewater treatment as they were able to provide high degradation of formaldehyde and methanol with relatively low toxicity of the by-products in the effluent.
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1. Introduction

Hospitals are one of the pollutant sources that produce a wide variety of chemical substances owing to medical, laboratory and research activities. Formaline, a mixture of 37% formaldehyde, 10% methanol and water, is frequently found in hospital waste streams. It is used as an embalming solution for preserving biological samples [1]. The direct discharges of this waste can threaten life in the receiving water. The contact of this toxic substance with aquatic ecosystems leads to a risk directly related to the existence of hazardous substances, which could have potential negative effects on the biological balance of natural environments [2,3]. The direct discharge to the biological wastewater treatment plant is also ceased the bacteria activity causing the failure of such a system [4]. However, little research work has been done to find the practical way to degrade the organic contaminants and reduce the toxicity of formaline wastewater. Advanced oxidation processes, such as UV/H_2O_2, Fenton and photo-Fenton, show promise as alternative techniques for the detoxification of wastewaters containing these toxic substances [5–7].

Photolytic oxidation with hydrogen peroxide possibly occurs if the organic or inorganic pollutants of wastewater strongly absorb UV-irradiation [8]. In this process, the contaminants to be destroyed must absorb the incident radiation and undergo degradation starting from its excited state [9]. The application of direct UV photolysis was reported that is suitable to aquatic contaminants, such as PCE and pesticides [10–12]. The high-energy

requirement for this process should be taken into account for process selection.

The Fenton process is being increasingly used in the treatment of contaminated wastewater. This process involves the use of one or more oxidizing agents, usually hydrogen peroxide and/or oxygen, and a catalyst, a metal salt or oxide (usually iron) [9,13,14]. This method is attractive due to the abundance and non-toxicity of iron. As reported by many previous works, the Fenton process in its unmodified form is efficient only in the acidic range and is usually most efficient at around pH 2.8 [15]. Uses of Fenton process can lead to the complete mineralization of some organic compounds, converting them to CO_2, H_2O and inorganic ions. However, the mechanisms of Fenton's reactions is not yet completely cleared [14,16,17].

A combination of H_2O_2 and UV radiation with ferrous ion (Fe(II)) or ferric ion (Fe(III)), the so-called photo-Fenton process, are involves irradiation with light, which increases the rate of contaminant degradation by stimulating the reduction of Fe(III) to Fe(II) [9,18,19]. This method has shown promise process due to more hydroxyl radicals in comparison with the UV/H_2O_2 and Fenton process. The efficient use of light quanta in photo reduction of ferric ion and the photolysis of Fe(III)-organic intermediate chelates are the major reasons in high efficiency of this method [20,21].

In this paper, three different advanced oxidation processes for the oxidation of formaline wastewater were compared. The degradation of both formaldehyde and methanol, which are the major components in formaline solution by each chemical oxidation method, was reported. The effects of the pH value, hydrogen peroxide and iron compounds as well as the toxicity of the treated solution were monitored. Moreover, the kinetic study of experimental results was also reported.

2. Materials and methods

2.1. Reagents

The formaline waste is composed of 37% formaldehyde and 10% methanol. Hydrogen peroxide solution (35%, w/w) and heptahydrated ferrous sulfate ($FeSO_4 \cdot 7H_2O$) were all analytical grade and purchased from Merck. Catalase was obtained from bovine liver (Fluka Biochemika). All reagents employed were not subjected to any further treatment. Water used throughout was prepared with Millipore Milli-Q water.

2.2. Experimental set-up

All experiments were performed in a batch reactor. The reactor was cylindrical with 1.1 L volume and was made from quartz glass (ACE Glass Co. 7841-06; Vineland, NJ). A 10 W germicide lamp with a principal wavelength of 254 nm was used as the light source for all experiments. The intensity of the incident light inside the photo reactor was measured as 0.50×10^{-6} Einstein s^{-1} by uranil actinometer method [22]. The UV lamp was inserted into a double-walled quartz immersion well, located at the center of the reactor. The UV lamp was kept on during the experiment. Fresh tap water was flushed

through the immersion well to prevent the lamp from overheating. The solution was fully stirred with a magnetic stirrer to ensure sufficient mixing. The reaction temperature was kept constant at 25 °C. The reaction period for all experiments in this work is 80 min unless otherwise specified.

2.3. Photodegradation procedures

2.3.1. UV and UV/H_2O_2

For each experiment, the laboratory unit was filled with 1 L of formaline wastewater containing 0.333 M of formaldehyde and 0.0079 M methanol. The solution pH was adjusted to 2.6 ± 0.1 with 0.1 M H_2SO_4 and 0.1 M NaOH prior to irradiation. In UV/H_2O_2 process, hydrogen peroxide with different initial concentrations was introduced at different amounts into the reactor before the beginning of each run. The time at which the ultraviolet lamp was turned on was considered as time zero or the beginning of the experiment which was taking place simultaneously with the addition of hydrogen peroxide. During the experiments, samples were withdrawn from the reactor at several time intervals.

2.3.2. Fenton and photo-Fenton processes

In the Fenton and photo-Fenton process, the pH value of the solution was set at 2.6 ± 0.1 by the addition of a H_2SO_4 solution before startup, then a given weight of iron salt was added. The iron salt was thoroughly mixed with the formaline waste before the addition of a given volume of hydrogen peroxide. For photo-Fenton process, the time at which the ultraviolet lamp was turned on was considered as time zero or the beginning of the experiment which was taking place simultaneously with the addition of hydrogen peroxide. As presented in the literature [23], Fenton and photo-Fenton reactions cannot occur at pH > 10. Therefore, the reaction was stopped instantly by adding NaOH to the reaction mixtures and quenched by adding Na_2SO_3 to remove H_2O_2 before analysis. During the experiments, samples were withdrawn from the reactor at several time intervals for analysis.

2.4. Analytical methods

The samples were pipetted into 2 mL glass vials. The vials were full so as to leave no headspace and sealed with Teflon-lined silicon septa and screw caps. One drop of enzyme catalase was also added to each sample to decompose any residual hydrogen peroxide and prevent hydrogen peroxide from reacting with organic substrates during the analysis. Hydrogen peroxide was measured by the standard iodometric titration method. Residues of formaldehyde and methanol were determined by gas chromatography (Perkin-Elmer SIGMA 3 equipped with an FID Detector (HP 4890)). A pack column (5% diphenyl and dimethylpolysiloxane) of 60 m and 0.53 μm was used.

For the toxicity test, all samples were diluted 16 times before analysis. Then the toxicity of the solutions was evaluated by The CellTiter 96® AQ$_{ueous}$ Non-Radioactive Cell Proliferation Assay, a colorimetric method for determining the number of viable cells in proliferation or chemosensitivity assays.

The CellTiter 96® AQ_ueous Assay is composed of solutions of a novel tetrazolium compound (3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxy-methoxyphenyl)-2-(phenazine methosulfate; PMS)). MTS is bioreduced by cells into a formazan product that is soluble in a tissue culture medium. The absorbance of the formazan at 490 nm can be measured directly from 96 well assay plates without additional processing [23]. The conversion of MTS into aqueous, soluble formazan is accomplished by dehydrogenase enzymes found in metabolically active cells. The quantity of formazan product as measured by the account of 490 nm absorbance is directly proportional to the number of living cells in the culture.

3. Results and discussion

3.1. UV and UV/H_2O_2

Direct UV light was used to determine the degree of photolysis of formaldehyde and methanol. It was found that the degradation percentage of formaldehyde and methanol using UV alone are 1.5 and 2%. Both substances were not well degraded with the photolysis reaction. When UV-irradiation was combined with hydrogen peroxide, the degradation of formaldehyde and methanol increased significantly compared to that when using direct photolysis. Fig. 1(a and b) show the decrease of formaldehyde and methanol as a function of irradiation time. The experimental conditions of each experiment are shown in

Table 1. As reported by previous works [24], the kinetic study of the photochemical decomposition using UV radiation follows pseudo-first-order kinetics in which the k value is determined by the following expression:

$$\ln \frac{C_0}{C} = kt \tag{1}$$

where C_0 represents the initial concentration of the organic compound and C represents the concentration of the organic compound as a function of time, t. The term $\ln(C_0/C)$ was plotted versus reaction time and the k value. The k value for formaldehyde and methanol degradation in each condition is determined as shown in Table 1.

From this work, it is obvious that the UV/H_2O_2 system enhanced the photooxidation of formaldehyde and methanol. Two effects of H_2O_2 addition can be clearly seen; first, the enhanced effect of the combination of UV and H_2O_2 in comparison to the single photodegradation by UV radiation and second the positive influence of the H_2O_2 initial concentration on the degradation of both formaldehyde and methanol. In UV/H_2O_2, hydroxyl radicals are formed according to Eq. (2) [7]:

$$H_2O_2 + h\nu \rightarrow 2OH^\bullet \tag{2}$$

The increasing of the initial H_2O_2 amount causes the increasing of the disappearance rate of both organic compounds. This trend is confirmed with the evaluation of the pseudo-first-order rate constant, k, and the percentage removal in each condition, which are also depicted in Table 1.

3.2. Fenton and photo-Fenton processes

In this step the degradation of formaldehyde and methanol in formaline waste was explored by means of the very reactive and oxidizing hydroxyl radicals generated by the Fenton and photo-Fenton processes.

In order to evaluate the effect of UV light on the degradation of formaldehyde and methanol, Fenton and photo-Fenton processes were compared at different concentrations of Fe^{2+} (6.67×10^{-3}, 2.27×10^{-2} and 6.67×10^{-2} M). Initial concentration of 0.667 M of H_2O_2 was chosen as the initial conditions. As seen in Fig. 2(a and b), the removal efficiency of formaldehyde and methanol treated by the photo-Fenton process was higher than that by the Fenton process. Results indicated that the Fe^{2+} efficiency of the photo-Fenton process with 10 W of UV light was larger than that of the Fenton process at the same concentration of Fe^{2+}.

From this experiment set, the degradation of both formaldehyde and methanol with Fenton process is the results of the reactions between ferrous ion and hydrogen peroxide. Several reactions can take place in degradation of formaldehyde and methanol. However, the mechanisms of these reactions in Fenton's process are not yet completely clear and there is much disagreement in the literature on the exact intermediates that form including whether or not the hydroxyl radical itself forms [14,16,17,25]. More recent studies have confirmed the existence of the ferryl ion (Fe^{VI}O^{2+}) as an intermediate and shown evidence that disfavours the hydroxyl radical as an intermediate
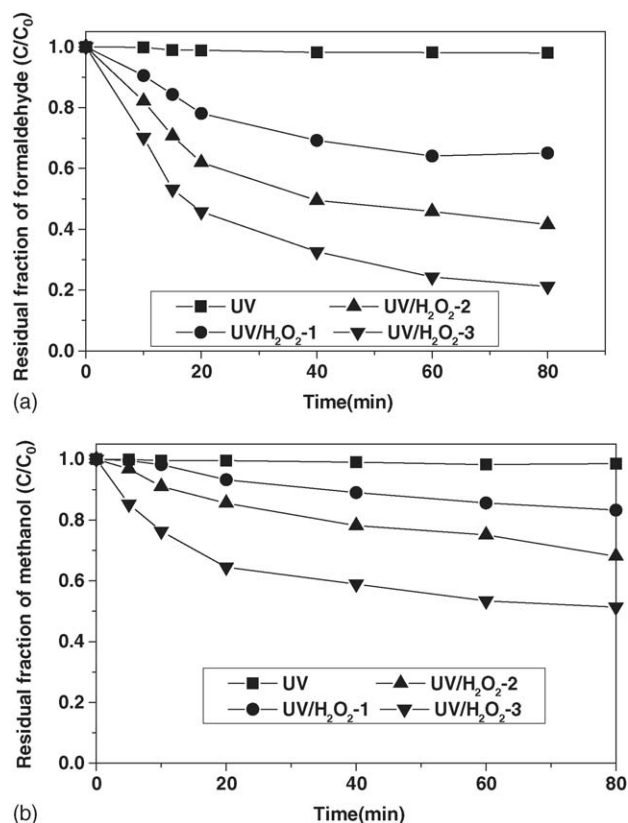

Fig. 1. Degradation of formaldehyde (a) and methanol (b) by UV radiation and UV/H_2O_2 processes. Experimental conditions are given in Table 1.

Table 1
Pseudo-first-order rate constants and removal percentage for the degradation of formaldehyde and methanol by UV radiation and UV/H_2O_2 processes during 80 min reaction period

Experiments	$[H_2O_2]_0$ (M)	Formaldehyde (CH_2O)		Methanol (CH_3OH)	
		k (min^{-1})	% removal	k (min^{-1})	% removal
UV	–	0.0003	1.99	0.0002	1.45
UV/H_2O_2-1	0.165	0.0054	34.88	0.0025	16.74
UV/H_2O_2-2	0.333	0.0104	58.42	0.0047	31.91
UV/H_2O_2-3	0.666	0.0185	78.80	0.0079	48.63

[26,27]. As reported by several previous works [14,25], the first step in the reaction of metal complexes with H_2O_2 in most case is the formation of a transient complex of metals (or a transient ferrous peroxide complex for iron catalyst as specified by Winterbourn [28]) which may decompose to the hydroxyl radical or a higher oxidation state of the metal or it may yield an organic free radical in the presence of organic substrates. The forming of hydroxyl radicals via Fenton reaction is based on the relative rates of the decomposition reactions of metal-peroxide complex and that of its reaction with organic substrates. By applying

[Fe^{2+}]=6.67x10^{-3} M, —■— Fenton 1 —□—, photo-Fenton 1
[Fe^{2+}]=2.27x10^{-2} M, —▲— Fenton 2 —△—, photo-Fenton 2
(a)   [Fe^{2+}]=6.67x10^{-2} M, —●— Fenton 3—○—, photo-Fenton 3

[Fe^{2+}]=6.67x10^{-3} M, —■— Fenton 1 —□—, photo-Fenton 1
[Fe^{2+}]=2.27x10^{-2} M, —▲— Fenton 2 —△—, photo-Fenton 2
(b)   [Fe^{2+}]=6.67x10^{-2} M, —●— Fenton 3 —○—, photo-Fenton 3

Fig. 2. Degradation of formaldehyde (a) and methanol (b) by Fenton and photo-Fenton processes. Experimental conditions are given in Table 2.

UV light in photo-Fenton process, the previous works [29,30] indicated that the classical Fenton reaction is assisted by the photoreduction process which takes place in the near UV region and results in the regeneration of metal catalysts and production of hydroxyl radical.

Similar results with this work have been reported by Li et al. [31] in that photo-Fenton oxidation under UV light conditions would accelerate mineralization faster than under dark conditions. The photo-Fenton process exhibited a good decomposition ability on the degradation of organic contaminants in this work due to the fact that Fe^{2+} can be regenerated through the photoreduction of Fe^{3+} to produce highly reactive hydroxyl radicals.
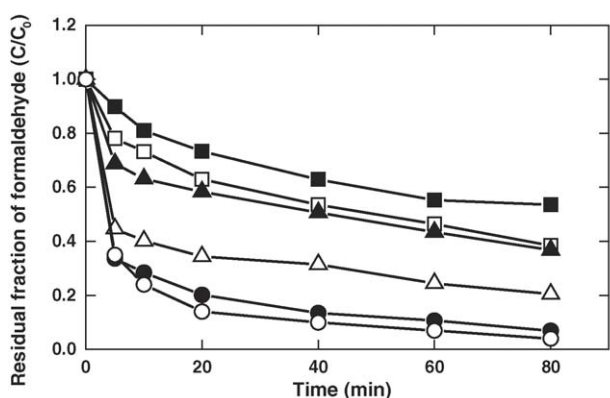
Starting photo-Fenton reaction at higher Fe^{2+} concentrations (higher than 6.67×10^{-2} M) led to the formation of a brown turbidity in the reaction system as a consequence of pH increasing by NaOH addition and no more advancement in the degradation was seen. This phenomenon is in a good agreement with Al Momani et al. [20] and Perez et al. [32]. The explanation of this behavior can be rationalized that this turbidity is due to the precipitation of iron hydroxides. The oxidation of Fe^{2+} to Fe^{3+} in form of iron hydroxides in this system leads to the stagnation of the reaction. It was reported that this turbidity decreased the absorption of UV-light and promoted the recombination of hydroxyl radicals [8].

Following the suggestions of several authors [33–36], the Fenton and photo-Fenton reaction is well represented by using pseudo-first-order kinetics for the initial times. The pseudo-first-order rate constants, k, obtained from both Fenton and photo-Fenton processes are shown in Table 2. These values of k in formaldehyde and methanol degradations are much higher than those obtained for the former oxidation processes (k for the UV and UV/H_2O_2). These findings confirm the significant contribution of the radical pathway due to the additional generation of hydroxyl radicals in the Fenton and photo-Fenton processes.
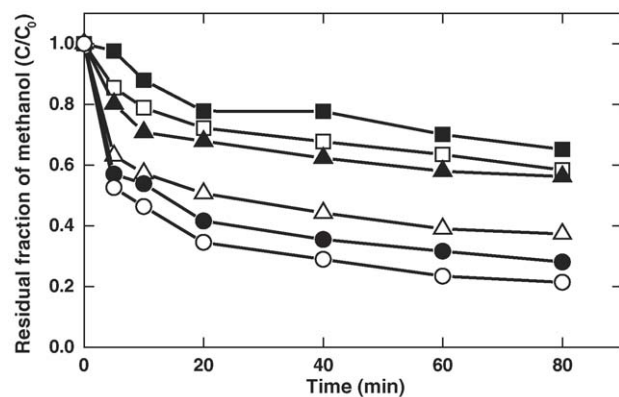
The role of UV light in promoting the efficiency of formaldehyde and methanol oxidation could be clearly illustrated with the values obtained in Table 3. The ratios of UV light promoting the efficiency on the initial rates of formaldehyde could be obtained as follows:

$$\frac{r_p}{r_f} = \frac{\text{Initial rate of photo-Fenton process}}{\text{Initial rate of Fenton process}} \qquad (3)$$

where r_p represents the initial rate of the photo-Fenton process and r_f represents the initial rate of the Fenton process. The initial oxidation rate by hydroxyl radicals of organic compounds in the Fenton and photo-Fenton process can be expressed as (4) and

Table 2
Pseudo-first-order rate constants and removal percentage for the degradation of formaldehyde and methanol by Fenton and photo-Fenton processes during 80 min reaction period

Experiments	$[H_2O_2]_0$ (M)	$[Fe(II)]_0$ ($\times 10^{-2}$ M)	Formaldehyde (CH_2O)		Methanol (CH_3OH)	
			k (min^{-1})	% removal	k (min^{-1})	% removal
Fenton 1	0.667	0.667	4.04×10^{-3}	46	2.91×10^{-3}	35
Fenton 2	0.667	2.27	7.49×10^{-3}	62	3.20×10^{-3}	44
Fenton 3	0.667	6.67	1.14×10^{-2}	90	6.48×10^{-3}	72
Photo-fenton 1	0.667	0.667	8.25×10^{-3}	62	4.85×10^{-3}	44
Photo-fenton 2	0.667	2.27	9.01×10^{-3}	79	5.24×10^{-3}	63
Photo-fenton 3	0.667	6.67	1.45×10^{-2}	94	8.25×10^{-3}	79

Table 3
UV light promoting the efficiency of formaldehyde oxidation

Experiments	$[H_2O_2]_0$ ($\times 10^{-2}$ M)	$[Fe(II)]_0$ ($\times 10^{-2}$ M)	Formaldehyde (CH_2O)			Methanol (CH_3OH)		
			r_p	r_f	r_p/r_f	r_p	r_f	r_p/r_f
1	0.667	0.667	1.46×10^{-2}	1.74×10^{-2}	0.8	3.98×10^{-4}	2.31×10^{-3}	0.17
2	0.667	2.27	3.69×10^{-2}	2.06×10^{-2}	1.79	5.89×10^{-3}	3.15×10^{-3}	1.87
3	0.667	6.67	4.33×10^{-2}	4.40×10^{-2}	0.98	7.55×10^{-3}	6.85×10^{-3}	1.10

(5), respectively [35]:

$$-\frac{d[C_f]}{dt} = k_{OH}[OH^\bullet][C_f] = r_f \tag{4}$$

$$-\frac{d[C_p]}{dt} = k_{OH}[OH^\bullet][C_p] = r_p \tag{5}$$

where C_p and C_f are the concentration of organic compounds in the photo-Fenton and Fenton processes and k_{OH} represents the rate constants for the reaction between $OH^\bullet$ and the organic compound.

The ratios (r_p/r_f) of UV light promoting the efficiency on the initial rates of formaldehyde were 0.84, 1.79 and 0.98 while the initial concentrations of Fe^{2+} increased from 6.67×10^{-3} to 2.27×10^{-2} and 6.67×10^{-2} M, respectively. Similarly, when the Fe^{2+} concentration increased, the fraction of UV light promoting the efficiency on initial rates of methanol changed from 0.17 to 1.87 and 1.10, respectively. It can be concluded that the highest benefit of UV light was achieved at 2.27×10^{-2} M of Fe^{2+}; with higher concentrations of Fe^{2+}, the benefit of UV light decreased.

3.3. Combinations of Fenton and photo-Fenton processes

Due to the fast reaction of H_2O_2 with Fe^{2+} in the beginning stage of the oxidation reaction as shown earlier in Fig. 2(a and b), applying UV light in the early stages may not be necessary. Therefore, Fenton and photo-Fenton processes were combined in this part of the experiment in order to compare the efficiencies of photo-Fenton and combined Fenton/photo-Fenton processes. The initial concentrations of H_2O_2 and Fe^{2+} were set as follows: $[H_2O_2] = 0.667$ M, $[Fe^{2+}] = 6.67 \times 10^{-2}$ M. The reaction was started with a Fenton reaction for 15 min before the UV lamp was turned on.

As illustrated in Fig. 3(a and b) for formaldehyde and methanol degradations, a similar degradation pattern of both contaminants was seen. Organic contaminant degradations in photo-Fenton and the combined Fenton/photo-Fenton process occurred in the early stage with an approximately similar initial rate (4.41×10^{-2} M min^{-1} for formaldehyde and 6.85×10^{-3} M min^{-1} for methanol) from both systems. Prior to UV light being applied to the combined Fenton/photo-Fenton process, a higher amount of residual hydrogen peroxide was detected as compared to that from the photo-Fenton reaction, as shown in Fig. 3(c). The oxidation reaction occurred progressively with lower efficiency of formaldehyde and methanol degradations in the combined Fenton/photo-Fenton process. The lower amount of generated hydroxyl radicals in the beginning of the combined process is anticipated to be the reason of this slower degradation. However, after 80 min reaction period, the degradation efficiency of both systems were equal. Findings from this experiment may suggest that applying UV light at the early stage might not be necessary for a fast oxidation reaction of the Fenton process.

3.4. Comparison of the toxicity for degradation products of formaline waste using AOPs

In this part, three experiments using UV/H_2O_2, Fenton and photo-Fenton processes were conducted for 240 min to investigate the toxicity of the effluent supernatant of real formaline wastewater containing 0.333 M of CH_2O, 0.0796 M of CH_3OH (analyzed by gas chromatography). A concentration of 0.667 M of H_2O_2 was chosen for wastewater treatment in the UV/H_2O_2 process. In addition, 6.67×10^{-2} M of Fe^{2+} was selected for Fenton and photo-Fenton processes. The effluent supernatants from those three processes were diluted 16 times before analysis.
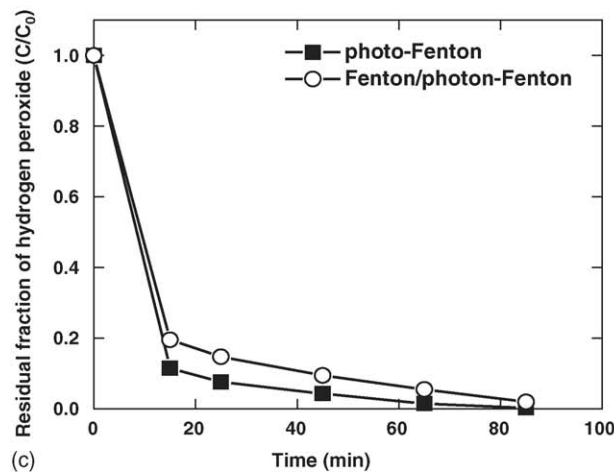
As represented in Fig. 4, by applying Fenton and photo-Fenton processes, the inhibition ratios of formaline wastewater were drastically reduced within 20 min of the oxidation reaction. This information informs that Fenton and photo-
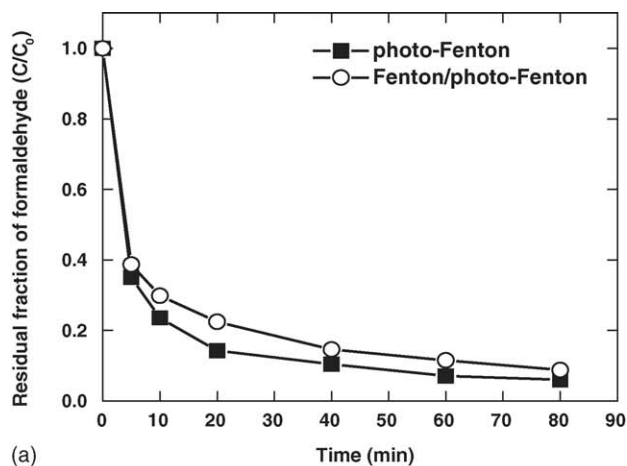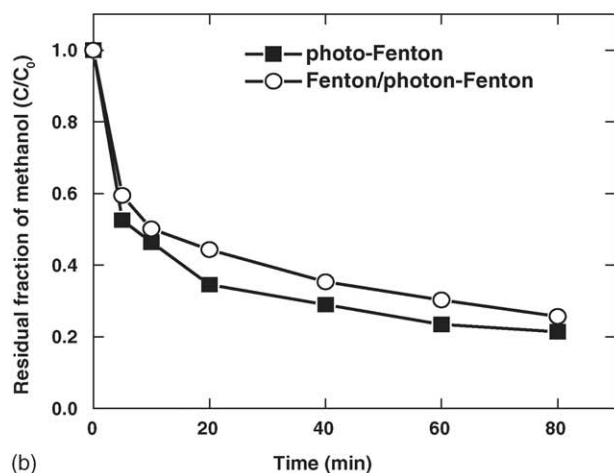
Fig. 3. Degradation of formaldehyde (a), methanol (b) and hydrogen peroxide residues (c) in photo-Fenton and Fenton/photo-Fenton processes.
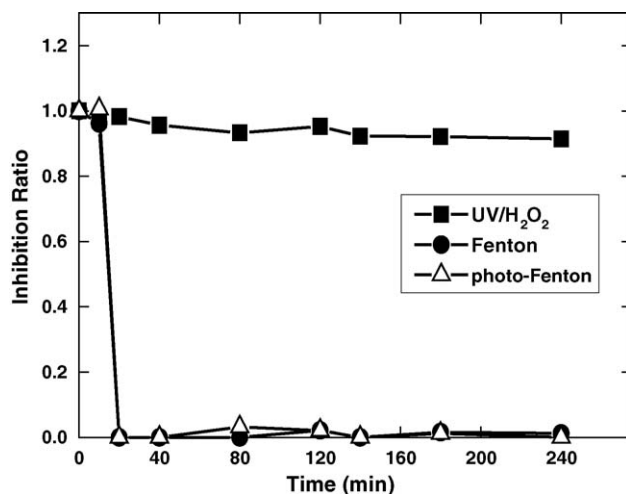

Fig. 4. Inhibition ratio of effluent from formaline wastewater treatment using UV/H_2O_2, Fenton and photo-Fenton processes.
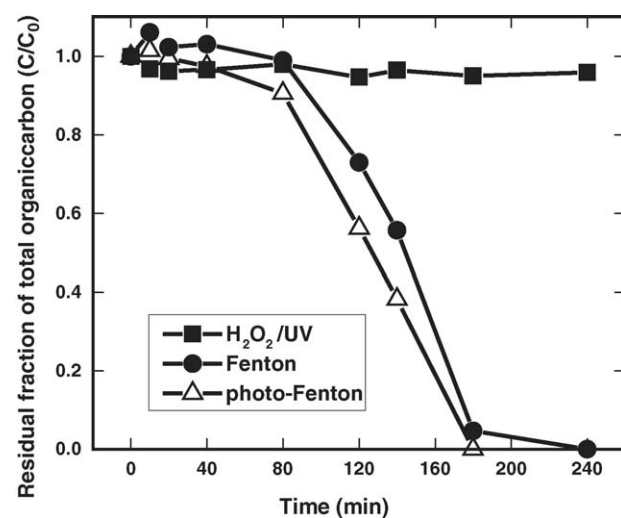

Fig. 5. Residual fraction of total organic carbon from formaline wastewater treatment using UV/H_2O_2, Fenton and photo-Fenton processes.

This may be the result of CH_2O oxidizing to other toxic intermediates by the UV/H_2O_2 process as represented by the TOC residuals of this process in Fig. 5.

For real applications of advanced oxidation processes in treating formaline wastewater, it is recommended that the combined Fenton and photo-Fenton process is a viable technique for formaldehyde and methanol degradation with relatively low toxicity of the by-products in the effluent.

4. Conclusion

In this experimental work, degradations of formaldehyde and methanol were investigated using several advanced oxidation processes, which were UV/H_2O_2, Fenton, photo-Fenton and the combination of Fenton and photo-Fenton. Of all the applied processes, photo-Fenton was found to be the most effective method for formaldehyde and methanol degradations. In this process pseudo-first-order degradation rate constants were found to increase with the increasing of the initial concentration

Fenton processes can efficiently reduce the toxicity of the solution.

Whereas, in the UV/H_2O_2 process, the toxicity reduction was not observed within 240 min of the reaction; even though formaldehyde and methanol were almost completely reduced at the end of the reaction. For this reason, the UV/H_2O_2 process could not decrease the toxicity of formaline wastewater.

of ferrous ions. It was also found that the Fenton process provided the highest efficiency as the second most effective process on the degradation of both toxic contaminants. From the combination of Fenton and photo-Fenton processes, it is suggested that applying UV light at an early stage might not be necessary for a speedy oxidation reaction of the Fenton process. With Fenton and photo-Fenton processes, mineralization of formaline wastewater can be achieved, as no residual TOC is detected in the effluent after 180 and 240 min reaction period. In addition, toxicity reduction was determined for final effluents from each process. The effluents of the Fenton and photo-Fenton applications after 120 min treatment can be safely disposed of with relatively low toxicity to environment.

Acknowledgements

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