



Degradation of formaldehyde by advanced oxidation processes

José Roberto Guimarães^{a,*}, Carolina Rittes Turato Farah^a, Milena Guedes Maniero^a, Pedro Sérgio Fadini^b

^a School of Civil Engineering, Architecture and Urbanism, University of Campinas, Av. Albert Einstein, 951, PO Box 6021, 13083-852 Campinas, SP, Brazil

^b Chemistry Department, Federal University of São Carlos, PO Box 676, 13565-905 São Carlos, SP, Brazil

ARTICLE INFO

Article history:

Received 1 July 2011

Received in revised form

4 April 2012

Accepted 17 April 2012

Available online 16 May 2012

Keywords:

Anatomy lab effluent

AOPs

Formaldehyde

ABSTRACT

The degradation of formaldehyde in an aqueous solution (400 mg L^{-1}) was studied using photolysis, peroxidation and advanced oxidation processes (UV/ H_2O_2 , Fenton and photo-Fenton). Photolysis was the only process tested that did not reduce formaldehyde concentration; however, only advanced oxidation processes (AOPs) significantly decreased dissolved organic carbon (DOC). UV/ H_2O_2 and photo-Fenton AOPs were used to degrade formaldehyde at the highest concentrations ($1200\text{--}12,000 \text{ mg L}^{-1}$); the processes were able to reduce CH_2O by 98% and DOC by 65%. Peroxidation with ultraviolet light (UV/ H_2O_2) improved the efficiency of treatment of effluent from an anatomy laboratory. The effluent's CH_2O content was reduced by 91%, DOC by 48%, COD by 46% and BOD by 53% in 420 min of testing.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Formalin is an aqueous solution of approximately 37% formaldehyde gas by mass with 10–15% of methanol added to prevent polymerization of the aldehyde.

China leads the world in formaldehyde consumption, utilizing 11,990,000 tons in 2007 (Tang et al., 2009). According to the Report on Carcinogens, formaldehyde is the 25th most produced chemical in the U.S., with more than 5 million tons produced each year. It is also the most toxic organic product of 45 organic substances that cause environmental impacts (Edwards et al., 1999).

Based on large-scale human studies conducted by the International Agency for Research on Cancer (IARC), formaldehyde was classified as a human carcinogen that causes nasopharyngeal cancer and probably causes leukemia (IARC, 2005). There has been a dramatic increase in recent years in the number of reported cases of a wide range of formaldehyde-induced health effects including poisoning and cancer (Tang et al., 2009).

Formaldehyde is used in synthetic resin production (phenolic, urea and melamine resins), as a raw material in a variety of chemical products, as a sterilizing agent, as a preservative for cosmetics and cleaning products, in anatomical embalming, and as a preservative for cadavers and organs in anatomy laboratories and clinical analysis laboratories. It is a good preservative because it

causes protein denaturation, acts as an antioxidant and inhibits microbial growth.

Effluents may contain from 100 to $10,000 \text{ mg L}^{-1}$ of formaldehyde (Gonzalez-Gil et al., 1999); hence, they cannot be discharged without prior treatment, since formaldehyde is a toxic substance. According to Hohreiter and Rigg (2001), the concentration of formaldehyde that an aquatic environment can assimilate without harming its ecosystem is 1.61 mg L^{-1} , and according to Tisler and Zagorc-Koncan (1997), 34.1 mg L^{-1} was the effective concentration (EC_{50}) that inhibited 50% of microorganism respiration in a sewage treatment plant that does not receive toxic effluents. Exposure to formaldehyde causes significant health problems, potentially including development of tumors, allergic reactions and possible negative effects on fetal development (IARC, 2005). Thus, it is essential to remove CH_2O from contaminated wastewater before discharging it into the environment.

Brazilian legislation (National Environmental Council, 2005) does not cover this compound. In Poland, the discharge of effluents containing up to 0.2 mg L^{-1} formaldehyde into surface waters and up to 2 mg L^{-1} into sewage treatment plants is allowed (Kaszycki and Koloczec, 2002).

Due to their toxicity, liquid effluents with high formaldehyde concentrations ($800\text{--}1500 \text{ mg L}^{-1}$) are difficult to treat using conventional processes such as biological systems, since formaldehyde can react with DNA, RNA and protein, and can damage cells, which may cause the death of microorganisms (Lu and Hegemann, 1998).

Formaldehyde degradation has been evaluated by the following advanced oxidation processes: electrogeneration of H_2O_2 (Do and

* Corresponding author. Tel.: +55 19 3521 2378; fax: +55 19 3521 2411.
E-mail address: jorober@fec.unicamp.br (J.R. Guimarães).

Chen, 1993); electrochemical (Yi et al., 2011; Fukunaga et al., 2008; Motheo et al., 2000); photocatalysis with Pt/Fe₂O₃/TiO₂ (Yang et al., 2000); photocatalysis with V₂O₅/TiO₂ (Akbarzadeh et al., 2010); UV; UV/TiO₂; UV/H₂O₂ and UV/H₂O₂/TiO₂; Fenton and photo-Fenton (Kajitvichyanukul et al., 2006, 2008; Aranã et al., 2004; Shin et al., 1996; Shiraishi et al., 1999); Fenton-like reaction (Murphy et al., 1989); and catalytic wet oxidation (Silva et al., 2003). These processes are based on the generation of a hydroxyl radical (•OH), a powerful non-selective oxidizing agent, which can react with various types of organic and inorganic compounds (da Silva et al., 2011) such as cations and anions, generating carbon dioxide, water and inorganic anions as final products. It should be noted, however, that few studies have evaluated the degradation of formaldehyde at high concentrations.

The objective of this work was to evaluate the capability of photolysis (UV), peroxidation (H₂O₂) and advanced oxidation processes (UV/H₂O₂, Fenton and photo-Fenton) to degrade formaldehyde (400–12,000 mg L⁻¹) and in the treatment of a real effluent from an anatomy laboratory.

2. Materials and methods

2.1. Chemical reagents and effluent

Formaldehyde (37%), concentrated H₂SO₄ and hydrogen peroxide (30% v/v) were supplied by Synth. Ferrous sulfate (FeSO₄·7H₂O) was supplied by Merck.

The effluent from the University of Campinas Anatomy Laboratory of the Institute of Biology, (IB UNICAMP, Brazil), contained 2152 mg L⁻¹ formaldehyde, 2128 mg L⁻¹ dissolved organic carbon (DOC), 6125 mg O₂ L⁻¹ chemical oxygen demand (COD), 3766 mg O₂ L⁻¹ biochemical oxygen demand (BOD) and had a pH of 3.6.

2.2. Procedure

The experimental system consisted of a reservoir, a pump, a Trojan Technologies UVMAX F ultraviolet sterilizer with an effective volume of 5 L, and a 102 W low-pressure mercury-vapor lamp (Fig. 1). A cooling system (Refrisa Santana Brasil) was

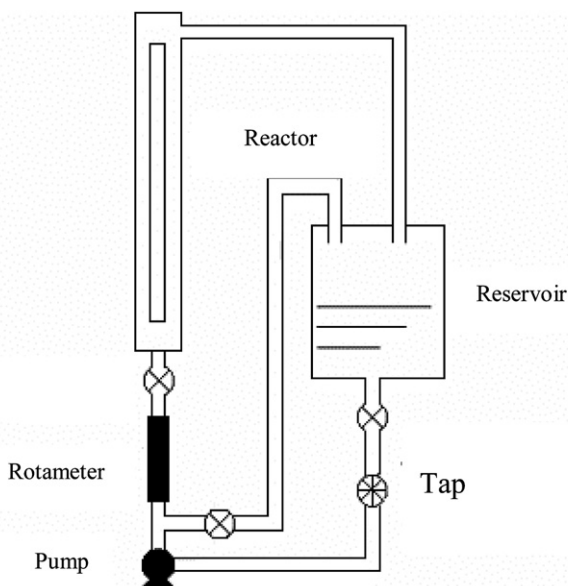


Fig. 1. Experimental setup.

attached to this system to maintain constant temperature during the tests.

In all the tests with synthetic effluent, 12 L of formaldehyde solution were used. There was a formaldehyde-to-hydrogen peroxide mass ratio of 1:2.27 or a DOC:H₂O₂ ratio of 1:5.68, and 25 or 50 mg L⁻¹ of ferrous ion (Fe²⁺) in the form of FeSO₄·7H₂O. The same mass ratio used with synthetic effluent was employed in the tests of the real effluent, i.e., a CH₂O:H₂O₂ ratio of 1:2.27 and a ferrous ion concentration of 50 mg L⁻¹. Tests were performed in batches and samples were circulated for a given time.

Degradation tests by photolysis, peroxidation and UV/H₂O₂ were performed at the original pH of the solution (6.0–7.0), while the Fenton and photo-Fenton tests were performed at pH 3.0, which was adjusted with concentrated sulfuric acid. The flow used in the experiments was 1600 L h⁻¹, and the temperature was kept at 22 °C.

During the degradation experiments, a control test was performed under the same conditions as the other processes: the sample was circulated in the reactor for 2 h without adding the reagent and without UV radiation.

Note that the time shown on all the x-axes of the graphs in this paper represents total reaction time, which differs from irradiation time, as the volumes of the reactor (5 L) and solution under treatment (12 L) are not the same. Irradiation time was calculated according to Equation (1).

$$t_{\text{irradiation}} = t_{\text{reaction}} \times \frac{V_{\text{reactor}}}{V_{\text{total}}} \quad (1)$$

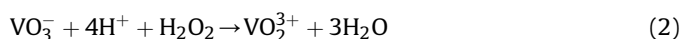
in which $t_{\text{irradiation}}$ is exposure time, t_{reaction} is reaction time, V_{reactor} is reactor volume and V_{total} is sample volume.

2.3. Analytical methods

To characterize the effluent and monitor degradation of the formaldehyde solution during these tests, aliquots of the samples were collected at predetermined times to evaluate the following parameters: pH, H₂O₂ concentration, formaldehyde concentration, DOC, COD and BOD.

Formaldehyde concentrations were analyzed according to EPA method 8315A. This method involves determining free carbonyl compounds with 2,4-dinitrophenylhydrazine (DNPH) using high performance liquid chromatography (HPLC, HP 1100) with an ultraviolet detector operating at a wavelength of 365 nm and a Supelco LC-18 column (4 mm internal diameter and 12.5 cm length). The mobile phase was composed of 34%A/66%B, where eluent A is acetonitrile and eluent B is a 1:1 mixture of methanol and water. Isocratic elution was performed at a flow rate of 0.8 mL min⁻¹. Retention time was approximately 2.5 min, and the detection limit was less than 0.5 mg L⁻¹.

Hydrogen peroxide concentrations were determined using a colorimetric method based on the redox reaction of the solution containing H₂O₂ with a yellow metavanadate ion acid solution. This reaction turns the solution red due to the formation of peroxovanadium cations (Equation (2)) with maximum absorbance at 450 nm, which can be determined by UV-Visible spectrophotometry (Nogueira et al., 2005).



Dissolved organic carbon (DOC) was determined using the standard method from APHA/AWWA/WEF section 5310 B (1998), using a Shimadzu TOC 5000 total organic carbon analyzer. BOD tests used APHA/AWWA/WEF sections 5210 B and COD tests used APHA/AWWA/WEF section 5220 D (1998). Hydrogen ionic potential (pH) was measured with an Orion model 250A pH meter.

3. Results and discussion

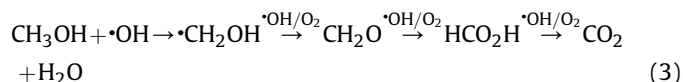
3.1. Degradation of low concentration formaldehyde solution

The initial concentration of the formaldehyde solution was 400 mg L⁻¹. The solution was subjected to photolysis, hydrogen peroxide oxidation, UV/H₂O₂, Fenton reagent and photo-Fenton for a 120-min test with 50 min of exposure to ultraviolet radiation. Initial formaldehyde concentrations of the solutions evaluated in the various processes were 350 ± 46 mg L⁻¹, DOC was 166 ± 8 mg L⁻¹ and pH was in the range of 6.2–7.0.

In the control experiment, CH₂O and DOC concentrations were found to remain constant when the formaldehyde sample was kept in the reactor without reagents. This was similar to what took place in photolysis, as shown in the data presented in Fig. 2A and B. It can be seen that there was no photodegradation of formaldehyde because the compound did not absorb ultraviolet light in the wavelength emitted by the lamp. Similar results were reported by Shiraishi et al. (1999), who also found that formaldehyde (7 mg L⁻¹) was not degraded when subjected to the photolytic process using a 254 nm wavelength, 6 W germicidal lamp; however, the compound was destroyed in a photocatalytic test. In addition, Kajitvichyanukul et al. (2006) obtained 1.5% formaldehyde degradation using UV alone (using a 10 W germicidal lamp with a main wavelength of 254 nm). However, Shin et al. (1996) reported that 20% of CH₂O (at an initial concentration of 100 mg L⁻¹) was removed during photolysis when they used a 400 W medium pressure Hg lamp.

During the peroxidation test, the DOC value did not vary, hydrogen peroxide concentration changed significantly and pH variation was less than 0.5. The addition of hydrogen peroxide caused an instantaneous reaction in CH₂O concentration: the CH₂O concentration dropped from 427.3 to 123.2 mg L⁻¹, a reduction of 71.2%. In the two hours of the test, the CH₂O concentration was reduced by 99.3%. DOC concentration did not change during the degradation test; this may have been due to formation of the compound trioxymethylene. This compound is a polymer composed of three molecules of formaldehyde. According to Kaszycki and Koloczec (2002), this polymer is nontoxic but is bio-recalcitrant. Another possibility would be the oxidation of a small quantity of formaldehyde to formic acid, as there was a small decrease in the pH in response to the addition of hydrogen peroxide.

During UV/H₂O₂ degradation, there was a marked drop in the values of pH up to 60 min, after which pH returned to the initial level and remained stable until the end of the experiment. This is likely because of mineralization of organic compounds in the solution. These results were confirmed by the DOC and CH₂O concentration monitoring data (Fig. 2A and B). Methanol and formaldehyde are oxidized to formic acid and then to CO₂ and water. These compounds are responsible for the drop in the pH of the solution. As CO₂ was liberated from the solution, pH increased. Equation (3) illustrates these reactions.



In the oxidation of a formaldehyde solution, formic acid is expected to form because its oxidized state is higher than that of formaldehyde, as has been observed by Moussavi and Heidarizad (2011), Pereira and Zaiat (2009) and Silva et al. (2003).

During the degradation of an aqueous solution of 1,4-dioxane by UV/H₂O₂, Stefan and Bolton (1998) also found a drop in pH from 5.0 (at the initial time) to 3.1 after 23 min. This value gradually increased to 4.2 (after 60 min), when irradiation stopped. According to these authors, this variation is consistent with the formation of organic acids and their subsequent total removal through oxidation reactions. The fact that the pH was lower at the end of the experiment than at the beginning may be explained by the generation of dissolved carbon dioxide gas during the mineralization of the compounds.

In the UV/H₂O₂ process, H₂O₂ was consumed and DOC reduced. Like in the peroxidation process, it was found that adding hydrogen peroxide led to an immediate decrease of approximately 72% in the concentration of CH₂O. At the end of 60 min of testing, CH₂O had decreased by 99 and DOC had decreased by 97.9%. Similar results were reported by Kajitvichyanukul et al. (2006), who observed that formaldehyde degradation increased significantly over direct photolysis when UV radiation was combined with hydrogen peroxide.

In the Fenton process, there was an immediate 46% reduction in DOC. After this reduction, the concentration of carbon remained constant despite the high concentration of peroxide in the medium. The reaction may stabilize due to capture of ferrous ions by excess hydroxyl radicals, forming ferric ions (Equation (4)) (Tekin et al., 2006) which do not contribute to the generation of OH· radicals, the formation of intermediate compounds resistant to degradation processes, or the reaction of ferric ions with intermediate products, thus forming stable organic compounds that are difficult to degrade (Equation (5)) (Maciel et al., 2004).

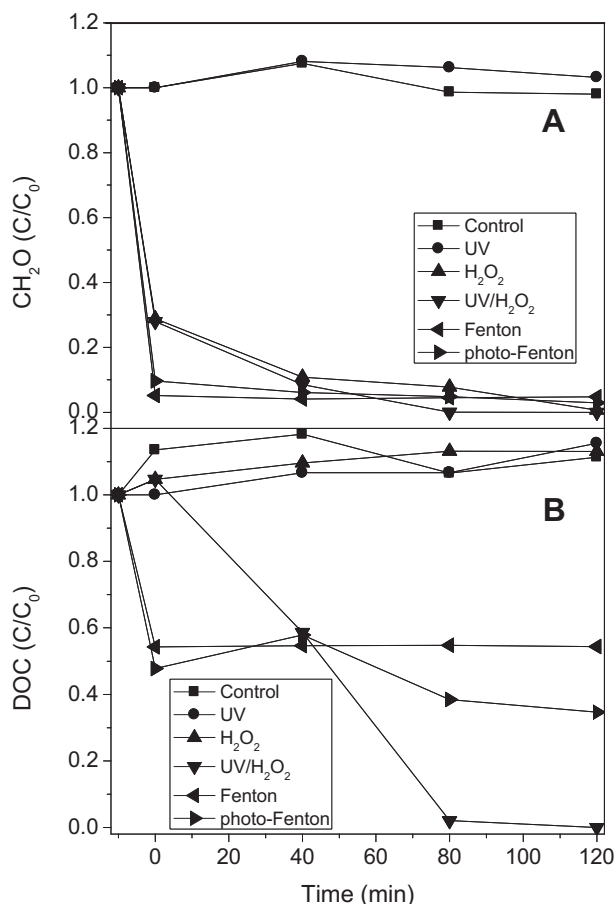


Fig. 2. Variation of normalized concentration of (A) CH₂O and (B) DOC as a function of test time for degradation of 400 mg L⁻¹ of formaldehyde.

Just as in the Fenton reaction, addition of the reagents in the photo-Fenton process ($\text{UV}/\text{Fe}^{2+}/\text{H}_2\text{O}_2$) led to an instantaneous reduction of about 90% of CH_2O concentration. At the end of the test, DOC concentration was reduced by 65%.

It was found that after 120 min, photolysis was the only process evaluated that was not efficient at removing CH_2O ; the other processes were able to degrade of more than 95%. The order of efficiency of the processes in removing DOC was: $\text{UV}/\text{H}_2\text{O}_2 > \text{photo-Fenton} > \text{Fenton}$. Peroxidation and photolysis processes did not reduce the concentration of dissolved organic carbon, indicating that these processes are not suitable for the removal of organic matter from wastewaters; however, peroxidation is able to modify formaldehyde molecules.

3.1.1. Contribution of ultraviolet radiation to peroxidation and Fenton processes

Because the results were similar for CH_2O and DOC removal by Fenton reagent and photo-Fenton reaction in the initial minutes of reaction, as shown in Fig. 2, it may not be necessary to apply UV light in the early stages. To verify this, the 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 at degrading formaldehyde (initial concentration of 400 mg L^{-1}). The reaction was started with a 60-min Fenton reaction, after which the UV lamp was turned on. A similar experiment was performed in which the peroxidation process was initially applied for 60 min, after which the UV lamp was turned on to trigger the $\text{UV}/\text{H}_2\text{O}_2$ process.

As can be seen in Fig. 3A, adding hydrogen peroxide solution reduced the concentration of CH_2O by about 70%, with ferrous ions

(Fenton process) contributing approximately 20% to this reduction. Both reductions occurred instantaneously and did not vary over time despite the significant residual amount of H_2O_2 in the reaction medium. However, hydrogen peroxide did not change DOC, although the addition of ferrous ions caused an immediate reduction of 50% in this parameter (Fig. 3B).

Use of the UV lamp caused no variation in the concentration of CH_2O in the photo-Fenton process but decreased concentration over time in the $\text{UV}/\text{H}_2\text{O}_2$ process, as shown in Fig. 3A. The remaining DOC was only reduced in response to photolization of residual hydrogen peroxide (Fig. 3B). It should be noted that in 100 min of testing, both photo-Fenton and $\text{UV}/\text{H}_2\text{O}_2$ processes reduced CH_2O concentration by 94% and DOC concentration by 70%.

After 100 min, $\text{UV}/\text{H}_2\text{O}_2$ reduced CH_2O concentration by 100 and DOC concentration by 99%, and photo-Fenton reduced CH_2O concentration by 95% and DOC concentrations by 63%. The combined H_2O_2 – $\text{UV}/\text{H}_2\text{O}_2$ and Fenton–photo-Fenton processes reduced the CH_2O concentration by 94% and DOC concentration 70%. The efficiency of the combined Fenton-photo-Fenton process in removing CH_2O and DOC was found to be similar to that of the photo-Fenton process; therefore applying UV light in the early stage of the process may not be necessary to achieve a higher degradation.

On the other hand, when the $\text{UV}/\text{H}_2\text{O}_2$ and combined H_2O_2 – $\text{UV}/\text{H}_2\text{O}_2$ processes are compared, the combined process was less effective in the removal of formaldehyde and dissolved organic carbon concentrations.

Kajitvichyanukul et al. (2006) evaluated formaldehyde degradation in the photo-Fenton and combined Fenton–photo-Fenton processes and found that degradation occurred in the early stage at a similar initial rate ($4.41 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$) in both systems. They suggested that applying UV light in the early stage may not be required for a fast oxidation reaction in the Fenton process.

3.2. Degradation of formaldehyde solutions in concentrations of 1200 to $12,000 \text{ mg L}^{-1}$

Formaldehyde solutions with high initial concentrations (1200, 3000, 6000 and $12,000 \text{ mg L}^{-1}$) were degraded using the processes that were most efficient at low concentrations (400 mg L^{-1}), the $\text{UV}/\text{H}_2\text{O}_2$ and photo-Fenton processes.

It can be concluded that the efficiency of the $\text{UV}/\text{H}_2\text{O}_2$ process in terms of the reduction of DOC concentration declined as the concentration of formaldehyde increased, requiring more time for the reduction to occur, as shown in Fig. 4A. DOC reductions were 91, 78, 62 and 21% at the end of 210 min for formaldehyde solutions with initial concentrations of 1200, 3000, 6000 and $12,000 \text{ mg L}^{-1}$, respectively.

CH_2O concentration was shown to degrade easily. At all of the formaldehyde concentrations evaluated here, final CH_2O concentration was closer to or lower than 100 mg L^{-1} (Figure not shown).

It should be noted that the $\text{UV}/\text{H}_2\text{O}_2$ process was very efficient, considering that the initial formaldehyde content was very high. This suggests that this process is an option for the treatment of effluents containing high concentrations of formaldehyde which cannot be treated by traditional biological processes, according to Lu and Hegemann (1998).

The photo-Fenton process reduced DOC concentration by approximately 60%, regardless of the initial concentration of formaldehyde (Fig. 4B). However, the higher the initial concentration, the longer the time required for its degradation. Reaction times required to achieve this level of degradation were 90, 120, 180 and 390 min for formaldehyde solutions with initial concentrations of 1200, 3000, 6000 and $12,000 \text{ mg L}^{-1}$, respectively.

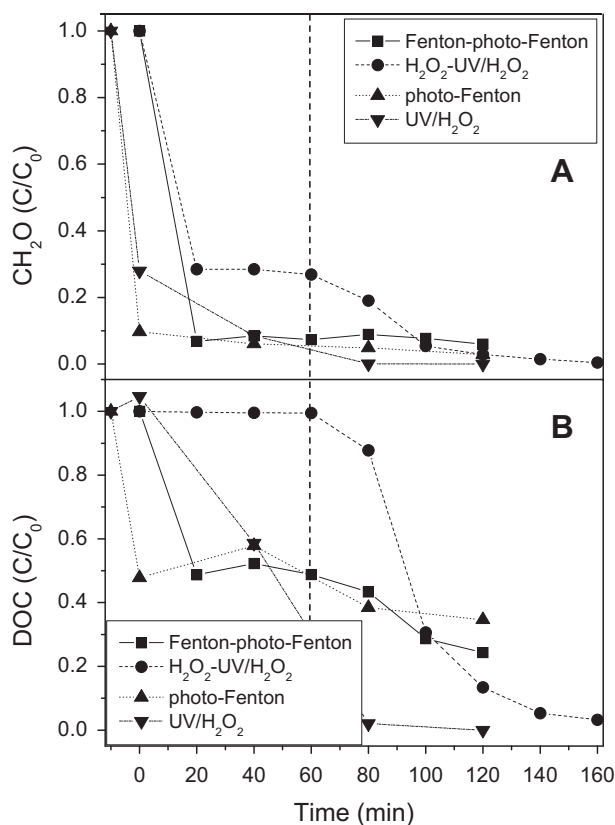


Fig. 3. Variation of normalized concentration of (A) CH_2O and (B) DOC as a function of test time for degradation of 400 mg L^{-1} of formaldehyde. UV light was employed after 60 min.

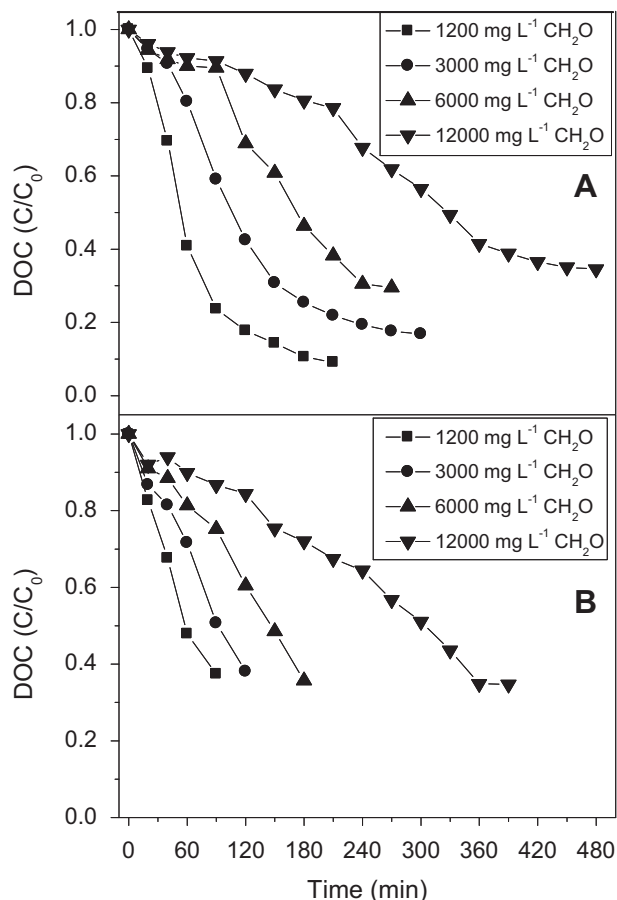


Fig. 4. Variation of normalized concentration of DOC as a function of test time for degradation of high concentrations of formaldehyde by (A) UV/H₂O₂ and (B) photo-Fenton.

As with degradation by UV/H₂O₂, formaldehyde was easily degraded by the photo-Fenton process at the concentrations evaluated. This process was efficient, indicating that it can be considered for the treatment of effluents with high concentrations of formaldehyde (Figure not shown).

3.2.1. Comparison of photo-Fenton and UV/H₂O₂ processes in degradation of high concentrations of formaldehyde (12,000 mg L⁻¹)

The photo-Fenton and UV/H₂O₂ processes produced very similar results for the degradation of high concentrations of formaldehyde (12,000 mg L⁻¹): the CH₂O and DOC levels were reduced by 98 and 65%, respectively, in the two processes. The difference lies in the time required for the degradation of the target compound, which took 480 min in the UV/H₂O₂ process and 390 min in the photo-Fenton process. The degradation rate constant of the reactions in the UV/H₂O₂ process was 0.0024674 min⁻¹ and the photo-Fenton process yielded 0.0026706 min⁻¹. It should be noted that after 390 min of reaction in the UV/H₂O₂ process, DOC was reduced by 61%, which is very similar to the result obtained with the photo-Fenton process.

pH values were also very similar: the pH decline in the photo-Fenton process was due to adjusting the pH to 2.8 by adding sulfuric acid. In the UV/H₂O₂ process, a pH of 2.6 was detected after 20 min of testing, undoubtedly due to the presence of formic acid, which is an intermediate in the formaldehyde oxidation reaction. So at the end of the test in both processes, the pH must be adjusted prior to discharging the effluent into surface waters and into the sewage system.

There is local legislation for the discharge of effluents containing iron that must be observed for the photo-Fenton process. The concentration of Fe²⁺ ion used in this work was higher than 15 mg L⁻¹, which is the maximum value for effluent discharges into both surface waters and sewage systems allowed by the legislation of the state of São Paulo, Brazil. However, this metal could be used as a coagulant after adjusting the pH of the medium, thus further improving the quality of the effluent generated.

Degradation tests with 12,000 mg L⁻¹ of formaldehyde were performed using 25 and 50 mg L⁻¹ of ferrous ion to verify if an increase in the concentration of ferrous ions during the photo-Fenton process would increase the removal of DOC. Formaldehyde was found to degrade faster with a higher concentration of Fe²⁺: degradation rate constants were 0.00267 min⁻¹ for 25 mg L⁻¹ and 0.00301 min⁻¹ for 50 mg L⁻¹ of ferrous ions. These results are consistent with those of Kajitvichyanukul et al. (2008), who found that increasing the concentration of ferrous ions enhanced the degradation of formaldehyde by the photo-Fenton process.

3.3. UV/H₂O₂ and photo-Fenton process degradation tests of effluent from an anatomy laboratory

During degradation of effluent from an anatomy laboratory, it was found that part of the DOC is difficult to degrade. It was not removed by the UV/H₂O₂ and photo-Fenton processes (Fig. 5). The carbon that was not degraded does not come from the formaldehyde present in the solution, as the CH₂O was almost completely removed by the AOPs in the first few minutes of reaction, a degradation efficiency of more than 90% (Figure not shown). Undoubtedly, these were organic compounds that leached from biological material, making them difficult to characterize.

As previously reported, it was seen that in terms of reduction of DOC concentration for the synthetic effluent, efficiency declined as the concentration of formaldehyde increased. Comparing results obtained for the treatment of real effluent containing 2152 mg L⁻¹ formaldehyde by UV/H₂O₂ with those from synthetic wastewater containing formaldehyde in high concentrations (1200–12,000 mg L⁻¹) (Fig. 4A), it can be seen that maximum DOC removed from the real effluent was 46%, while for high concentrations of formaldehyde solutions, 3000 and 12,000 mg L⁻¹, it was 83 and 65%, respectively. Thus DOC removed from the anatomy laboratory effluent was lower than DOC removed from the synthetic effluent, even for the highest concentration of formaldehyde evaluated, 12,000 mg L⁻¹, due to organic

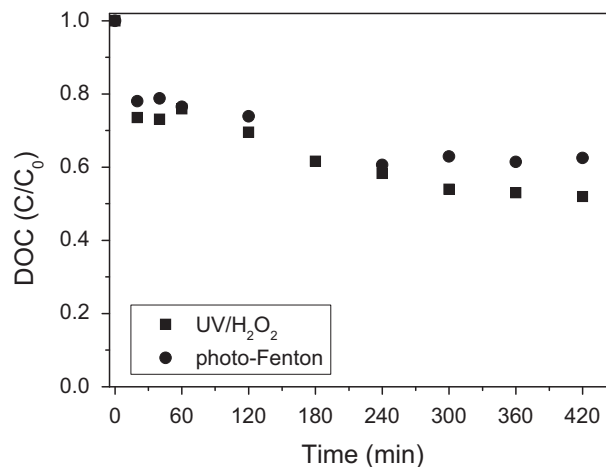


Fig. 5. Variation of normalized concentration of DOC as a function of test time for treatment of anatomy lab effluent by the UV/H₂O₂ and photo-Fenton processes.

Table 1

Reduction of CH₂O, DOC, BOD and COD in effluent from an anatomy laboratory by UV/H₂O₂ and photo-Fenton processes.

Parameter	Process	
	% Removal (UV/H ₂ O ₂)	% Removal (photo-Fenton)
CH ₂ O	91	94
DOC	48	38
BOD	53	43
COD	46	38

compounds leached from biological material. Real wastewater also had high DOC reduction rate in the first 20 min of reaction; after this period, this rate decreased over time, stabilizing at 300 min.

The photo-Fenton process was similar, that is, the maximum DOC removed from the anatomy laboratory effluent (38%) was lower than DOC removed from the synthetic wastewater that contained 12,000 mg L⁻¹ of formaldehyde (65.3%).

Table 1 shows reductions in the values of the parameters analyzed (CH₂O, DOC, BOD and COD) over 420 min of testing. The UV/H₂O₂ process was slightly more efficient at degradation than the photo-Fenton process for all the parameters analyzed, except for the formaldehyde concentration.

4. Conclusions

There was no photodecomposition of formaldehyde.

Although the peroxidation process was able to degrade formaldehyde, it was not able to remove DOC, which may be caused by the formation of formic acid, an intermediate in the oxidation reactions of formaldehyde and/or trioxymethylene.

All the processes were efficient at removing CH₂O (degradation higher than 95% in 120 min of testing) except for photolysis. DOC removal efficiency was as follows: UV/H₂O₂ > photo-Fenton > Fenton.

The UV/H₂O₂ and photo-Fenton processes are capable of degrading high concentrations of formaldehyde (12,000 mg L⁻¹). The degradation rate constant of the photo-Fenton process was the highest. The UV/H₂O₂ process took 480 min to reduce DOC by 65% while the photo-Fenton process took 390 min.

For the anatomy laboratory effluent, the degradation efficiency of the UV/H₂O₂ process was slightly higher than that of the photo-Fenton process. The UV/H₂O₂ process reduced CH₂O by 91% and DOC by 46% in 420 min; in that time, the photo-Fenton process reduced CH₂O by 94% and DOC by 38%.

From this data, it can be concluded that the advanced oxidation processes of UV/H₂O₂ and photo-Fenton are recommended for the treatment of effluents containing high concentrations of formaldehyde.

Acknowledgments

The authors would like to thank the research funding agencies of the Brazilian Federal Agency for Support and Evaluation of Graduate Education (CAPES) for granting a scholarship and São Paulo Research Foundation (FAPESP) (02/12017-0) for its financial support of this project.

References

- Akbarzadeh, R., Umbarkar, S.B., Sonawane, R.S., Takle, S., Dongare, M.K., 2010. Vanadia–titania thin films for photocatalytic degradation of formaldehyde in sunlight. *Appl. Catal. A: General* 374, 103–109.

- APHA/AWWA/WEF, 1998. *Standard Methods for the Examination of Water and Wastewater*, 21st ed. American Public Health Association, Washington D.C.
- Aranã, J., Martínez Nieto, J.L., Melián, J.A.H., Rodríguez, J.M.D., Díaz, O.G., Pena, J.P., Bergasa, O., Alvarez, C., Méndez, J., 2004. Photocatalytic degradation of formaldehyde containing wastewater from veterinarian laboratories. *Chemosphere* 55, 893–904.
- da Silva, C.R., Maniero, M.G., Rath, S., Guimarães, J.R., 2011. Antibacterial activity inhibition after the degradation of flumequine by UV/H₂O₂. *J. Adv. Oxid. Technol.* 14, 106–114.
- Do, J.-S., Chen, C.-P., 1993. In situ oxidative degradation of formaldehyde with electrogenerated hydrogen peroxide. *J. Electrochem. Soc.* 140, 1632–1637.
- Edwards, F.G., Egemen, E., Brennan, R., Nirmalakhandan, N., 1999. Ranking of toxics release inventory chemicals using a level III fugacity model and toxicity. *Water Sci. Technol.* 39, 83–90.
- Fukunaga, M.T., Guimarães, J.R., Bertozzoli, R., 2008. Kinetics of the oxidation of formaldehyde in a flow electrochemical reactor with TiO₂/RuO₂ anode. *Chem. Eng. J.* 136, 236–241.
- Gonzalez-Gil, G., Kleerebezem, R., van Aelst, A., Zoutberg, G.R., Versprille, A.I., Lettinga, G., 1999. Toxicity effects of formaldehyde on methanol degrading sludge and its anaerobic conversion in biobed expanded granular sludge bed (EGSB) reactors. *Water Sci. Technol.* 40, 195–202.
- Hohreiter, D.W., Rigg, D.K., 2001. Derivation of ambient water quality criteria for formaldehyde. *Chemosphere* 45, 471–486.
- IARC. International Agency for Research on Cancer, 2005. In: List of IARC Evaluations. <<http://www-cie.iarc.fr/monoeval/grlist.html>> (accessed 12.07.05.).
- Kajitvichyanukul, P., Lu, M.-C., Jamroensan, A., 2008. Formaldehyde degradation in the presence of methanol by photo-Fenton process. *J. Environ. Manage.* 86, 545–553.
- Kajitvichyanukul, P., Lu, M., Liao, C., Wirojanagud, W., Koottatep, T., 2006. Degradation and detoxification of formaline wastewater by advanced oxidation processes. *J. Hazard. Mater. B* 135, 337–343.
- Kaszycki, P., Koloczek, H., 2002. Biodegradation of formaldehyde and its derivatives in industrial wastewater with methylotrophic yeast *Hansenula polymorpha* and with the yeast-bioaugmented activated sludge. *Biodegradation* 13, 91–99.
- Lu, Z., Hegemann, W., 1998. Anaerobic toxicity and biodegradation of formaldehyde in batch cultures. *Water Res.* 32, 209–215.
- Maciel, R., Sant'Anna Jr., G.L., Dezotti, M., 2004. Phenol removal from high salinity effluents using Fenton's reagent and photo-Fenton reactions. *Chemosphere* 57, 711–719.
- Motheo, A.J., Gonzalez, E.R., Tremiliosi-Filho, G., Olivi, P., de Andrade, A.R., Kokoh, B., Léger, J.-M., Belgsir, E.M., Lamy, C., 2000. The oxidation of formaldehyde on high overvoltage DSA type electrodes. *J. Braz. Chem. Soc.* 11, 16–21.
- Moussavi, G., Heidarizad, M., 2011. The performance of SBR, SCR, and MSCR for simultaneous biodegradation of high concentrations of formaldehyde and ammonia. *Sep. Purif. Technol.* 77, 187–195.
- Murphy, A.P., Boegli, W.J., Price, M.K., Moody, C.D., 1989. A Fenton-like reaction to neutralize formaldehyde waste solutions. *Environ. Sci. Technol.* 23, 166–169.
- National Environmental Council, 2005. (Ministério do Meio Ambiente, Conselho Nacional do Meio Ambiente) (CONAMA) 2005. Resolution No 357, 03/17/2005. Available at: <http://www.mma.gov.br/port/conama/res/res05/res35705.pdf> (accessed 14.06.11.).
- Nogueira, R.F.P., Oliveira, M.C., Paterlini, W.C., 2005. Simple and fast spectrophotometric determination of H₂O₂ in photo-Fenton reactions using metavanadate. *Talanta* 66, 86–91.
- Pereira, N.S., Zaiat, M., 2009. Degradation of formaldehyde in anaerobic sequencing batch biofilm reactor (ASBBR). *J. Hazard. Mater.* 163, 777–782.
- Shin, E.-M., Senthurichelvan, R., Munoz, J., Basak, S., Rajeshwar, K., 1996. Photolytic and photocatalytic destruction of formaldehyde in aqueous media. *J. Electrochem. Soc.* 143, 1562–1570.
- Shiraishi, F., Toyoda, K., Fukinbara, S., Obuchi, E., Nakano, K., 1999. Photolytic and photocatalytic treatment of an aqueous solution containing microbial cells and organic compounds in an annular-flow reactor. *Chem. Eng. Sci.* 54, 1547–1552.
- Silva, A.M.T., Castelo-Branco, I.M., Quinta-Ferreira, R.M., Levec, J., 2003. Catalytic studies in wet oxidation of effluents from formaldehyde industry. *Chem. Eng. Sci.* 58, 963–970.
- Stefan, M.L., Bolton, J.R., 1998. Mechanism of degradation of 1,4-Dioxane in dilute aqueous solution using the UV/Hydrogen peroxide process. *Environ. Sci. Technol.* 32, 1588–1595.
- Tang, X., Bai, Y., Duong, A., Smith, M.T., Li, L., Zhang, L., 2009. Formaldehyde in China: production, consumption, exposure levels, and health effects. *Environ. Inter.* 35, 1210–1224.
- Tekin, H., Bilkay, O., Ataberk, S.S., Balta, T.H., Ceribasi, I.H., Sanin, F.D., Dilek, F.B., Yetis, U., 2006. Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater. *J. Hazard. Mater. B* 136, 258–265.
- Tisler, T., Zagorc-Koncan, J., 1997. Comparative assessment of toxicity of phenol, formaldehyde, and industrial wastewater to aquatic organisms. *Water Air Soil Pollut.* 97, 315–322.
- Yang, J., Li, D., Zhang, Z., Li, Q., Wang, H., 2000. A study of the photocatalytic oxidation of formaldehyde on Pt/Fe₂O₃/TiO₂. *J. Photochem. Photobiol. A: Chem.* 137, 197–202.
- Yi, Q., Niu, F., Yu, W., 2011. Pd-modified TiO₂ electrode for electrochemical oxidation of hydrazine, formaldehyde and glucose. *Thin Solid Films* 519, 3155–3161.