

Resumo: Um método de correção de interferência espectral e de transporte é proposto, e foi aplicado para minimizar interferências por moléculas de PO produzidas em chama ar-acetileno e de transporte causada pela variação da concentração de ácido fosfórico. Átomos de Pb e moléculas de PO absorvem a 217,0005 nm, então $A_{\text{total}}^{217,0005 \text{ nm}} = A_{\text{Pb}}^{217,0005 \text{ nm}} + A_{\text{PO}}^{217,0005 \text{ nm}}$. Monitorando o comprimento de onda alternativo de PO em 217,0458 nm, é possível calcular a contribuição relativa de PO na absorvância total a 217,0005 nm: $A_{\text{PO}}^{217,0005 \text{ nm}} = A_{\text{total}}^{217,0005 \text{ nm}} - A_{\text{Pb}}^{217,0005 \text{ nm}}$. O fator de correção k é a razão entre os coeficientes angulares de duas curvas analíticas para P obtidas a 217,0005 e 217,0458 nm ($k = b^{217,0005 \text{ nm}} / b^{217,0458 \text{ nm}}$). Fixando-se a taxa de aspiração da amostra em 5,0 ml min⁻¹, e integrando-se a absorvância no comprimento de onda a 3 pixels, curvas analíticas para Pb (0,1 - 1,0 mg L⁻¹) foram obtidas com coeficientes de correlação típicos $\geq 0,9990$. As correlações lineares entre absorvância e concentração de P nos comprimentos de onda 217,0005 e 217,0458 foram $\geq 0,998$. O limite de detecção de Pb foi 10 µg L⁻¹. O método de correção proposto forneceu desvios padrão relativos ($n=12$) de 2,0 a 6,0%, ligeiramente menores que os obtidos sem correção (1,4-4,3%). As recuperações de Pb adicionado às amostras de ácido fosfórico variaram de 97,5 a 100% (com correção pelo método proposto) e de 105 a 230% (sem correção).

Palavras-chave: método de correção por equação matemática; espectrometria de absorção atômica com fonte contínua e de alta resolução; chumbo; ácido fosfórico.

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PHOTO-FENTON PROCESS FOR TREATING BIOLOGICAL LABORATORY WASTEWATER CONTAINING FORMALDEHYDE

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Abstract: Laboratories consume great amounts of hazardous chemicals substances and consequently generate wastewater containing them, for example formaldehyde. This substance is widely utilized to preserve biological samples generating many liters of this residue every year. The present work proposes the use of the photo-Fenton process to treat formaldehyde wastewater using sunlight irradiation. Some aspects were investigated such as the iron source, sample and hydrogen peroxide concentration and also the use of stirred systems. The use of ferrioxalate (0.5 mmol L⁻¹) improved the efficiency of the process in relation to the use of iron nitrate, while at least 1.0 mol L⁻¹ H₂O₂ is necessary to treat the sample of the 500 mg C L⁻¹. Under these conditions, every formaldehyde detectable was degraded and 89% of the dissolved organic carbon was removed in two hours of exposure to sunlight. These results are satisfaction considerable for São Paulo State Environmental Agency.

Keywords: laboratory wastewater treatment, formaldehyde, photo-Fenton

Introduction

A large number of biological laboratories use solutions of formaldehyde to preserve anatomic pieces, generating many liters of formaldehyde waste every year. In according to the literature formaldehyde is genotoxic in exposed cells in vitro or exposed tissues in vivo [1,2,3]

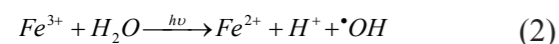
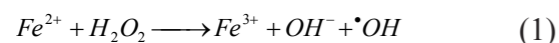
Although the concentration of formaldehyde is just 3.7% w/w, discharging formaldehyde without treatment can cause serious damage from aquatic environment, due to its carcinogenicity [4] and there is no safe limit to exposition for this class (carcinogenic). Hence, these wastes require an appropriate treatment to avoid risks to the environment and human health.

The adequate treatment of wastes generated by industrial, agricultural or domestic activities is regulated by environmental agencies throughout the world, [5,6] which the levels of specific parameters are limited and checked in the discharged wastes. This is necessary due to large volumes of toxic generated wastes and consequently to the impacts that this cause. The formaldehyde, for example, is able to react with DNA, RNA and proteins, damaging cells and causing the death of microorganisms present in biological wastewater treatment plants [7,8].

Furthermore, the residues generated by Universities and Research Centers offers a special challenge: present specific treatments of different wastes. The ideal solution would be an *in situ* treatment of these wastes, avoiding storage and

transportation risks and reducing the number of people in contact with toxic products. It would be also relatively easy and cheap to treat the residues if their compositions are known.

Advanced Oxidation Processes (AOP) can be applied *in situ* to degrade a great variety of organic pollutants such as pesticides [9,10,11,12], dyes [13,14,15] and chlorophenols [16]. Among the various AOPs, the so-called photo-Fenton process has attracted great interest due to its high efficiency to generate hydroxyl radicals during the decomposition of H₂O₂ by Fe (II) in acid medium. Associated to UV-Vis irradiation, a considerable increase in the oxidation power is observed mainly due to the photo-reduction of Fe(III) to Fe(II), which can react with H₂O₂, establishing a cycle and generating hydroxyl radicals, as shown in equations 1 and 2 [17,18].



Many researchers have studied the degradation of formaldehyde in aqueous medium using different Advanced Oxidative Processes [8,19,20,21]. However, the difficulty is much greater when, along with the aqueous solution of formaldehyde, the residue presents a high concentration of organic compound and interferences, as was the case described above.

Besides the high efficiency of the photo-Fenton process to oxidize a variety of organic compounds, the simplicity of operation and the possibility of using solar light are advantages which can make the implementation easier of *in situ* and small scale treatment processes, adequate for laboratory wastes.

In this work, the photo-Fenton process was studied for the treatment of aqueous wastes containing formaldehyde generated in a biological laboratory of the Bioscience Institute of the São Paulo State University. The influence of the concentration of the H₂O₂ and the sample, the iron source (potassium ferrioxalate or ferric nitrate), and the use of stirred systems were evaluated as to their effect on the mineralization of the waste.

2 Materials and methods

2.1 Chemicals

Potassium ferrioxalate (FeOx) was prepared and purified as described previously [22]. The aqueous stock solution of FeOx and Fe(NO₃)₃·9H₂O (Mallinckrodt) were prepared using Millipore Milli-Q water, at a concentration of 0.25 mol L⁻¹ and stored in the dark at room temperature for a maximum of one week. Hydrogen peroxide 30% (w/w) (Synth) was used. Ammonium metavanadate (Vetec) solution was prepared to have a final concentration of 0.060 mol L⁻¹ in H₂SO₄ at 0.58 mol L⁻¹ (Synth).

The formaldehyde waste sample was collected in a biological laboratory at the University campus having a concentration of 1.2 mol L⁻¹ of formaldehyde and pH value of 6.8. For all experiments, the pH of the samples was adjusted to 2.5 by adding H₂SO₄. The reaction was initiated after H₂O₂ and iron solutions were added, and when they were exposed to irradiation.

2.2. Experimental conditions

All experiments were realized under magnetic stirring and in batch mode. The sample was exposed to irradiation in open dark glass vessels having a diameter of 9.5 cm, height of 4.5 cm and a total volume of 250 mL [23] under magnetic stirring unless otherwise stated.

2.2.1. Photo-Fenton Process

The experiments were carried out in Araquara, SP, Brazil (21° S 48° W) under clear sky conditions. The vessels were covered with PVC film to avoid wastage by evaporation. The absorption/reflection of such film is approximately 10% of the solar irradiation in the UVA region. All the experiments were undertaken in winter (July and August), between 10 a.m. and 2 p.m. The solar

energy dose accumulated during exposure time and solar irradiance was measured every 20 minutes using a Solar Light CO radiometer (model PMA 2100) in the UVA region (320 and 400 nm) during the experiments. The sensor was positioned horizontally and covered with the same film of the sample to equal the solar energy reception. The total energy dose was also measured during the experiment, which ranged from 13 to 18 J cm⁻² for a total exposure period of 2 h.

In the experiments using artificial irradiation two 15 W germicide lamps with a wavelength of 254 nm were used. In this case, the samples were submitted a two hours of irradiation too.

2.3 Chemical analysis

The photodegradation process was monitored by measuring the Total Organic Carbon (TOC) concentration using an organic carbon analyzer (TOC 5000A Shimadzu). Samples were collected at various times during the experiment. These collections were done: before the vessels were exposed to the irradiation; every twenty minutes and once the full 120-minute interval was complete. Then the samples were immediately filtered through a 0.45 μm membrane and analyzed. The results are denoted as Dissolved Organic Carbon (DOC). Residual H₂O₂ was determined using the

metavanadate spectrophotometric method [11]. The formaldehyde concentration - before and after photo-Fenton treatment - was determined by colorimetric method using chromotropic acid [24].

3 Results and discussion

3.1 Preliminary experiments

Control experiments (residue, residue + FeOx and residue + H₂O₂) in dark and sunlight were done to determine the rate of photolysis of wastewater in study. It was found that the residue and residue + FeOx did not present removal. Even when H₂O₂ was added the degradation was only 0.5%.

In this preliminary study artificial and sunlight photo-Fenton were utilized for evaluated the degradation of formaldehyde waste. And it was possible to note that using the artificial and solar irradiation was removed 88.8% and 89% of DOC, respectively, see **Figure 1**. As the results obtained did not present relevant differences, in the rest of the work was used natural irradiation, it could be simpler to make *in situ*.

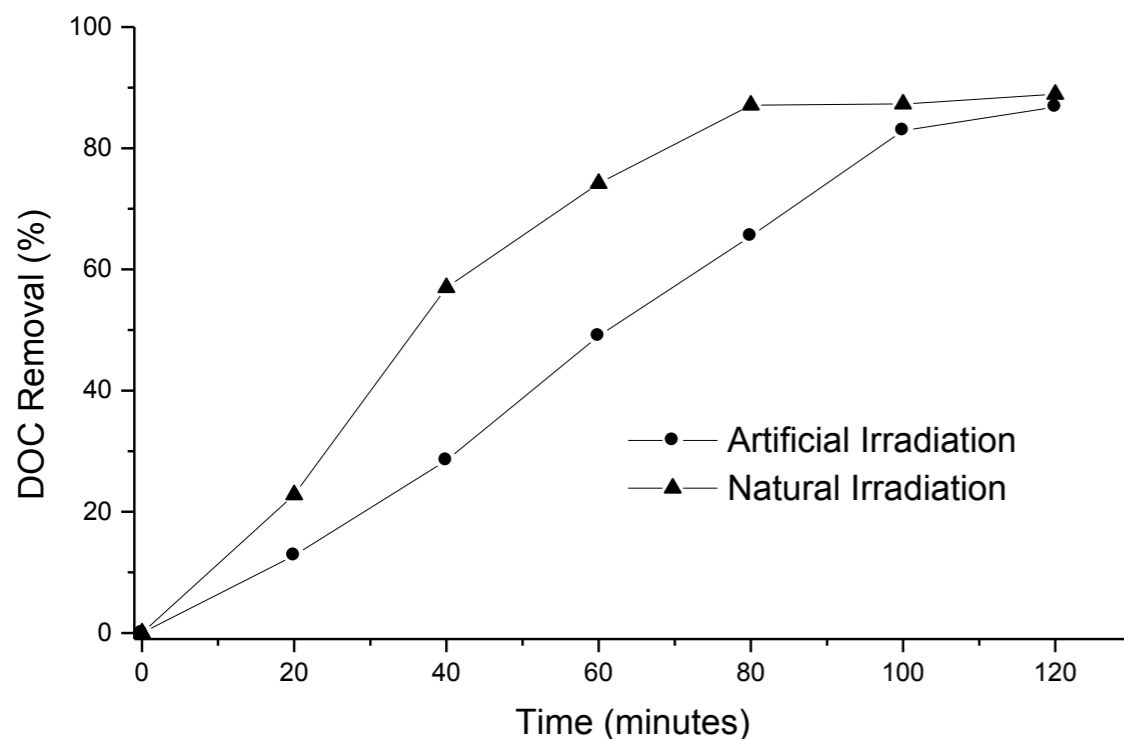


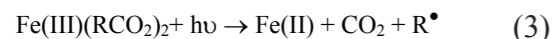
Figure 1. DOC removal from formaldehyde waste during using different irradiation sources. Conditions: 500 mg L⁻¹ C formaldehyde sample; 0.5 mmol L⁻¹ FeOx; 1.0 mol L⁻¹ H₂O₂, magnetic stirring.

3.2. Determination of the optimum conditions

of iron such as iron nitrate could be simpler, so the use of iron nitrate at a concentration of 0.5 mmol L⁻¹ was compared to ferrioxalate for the removal of DOC in formaldehyde wastes. Although the use of ferrioxalate implies an increase in the carbon content, at the concentration used in this work, it represents an increase of only 36 mg C L⁻¹, which is very small when compared to the high amount of organic matter present in the sample, 500 mg C L⁻¹. Furthermore, the use of this iron source is more efficient when compared to iron nitrate as can be seen in **Figure 2**. The results with iron nitrate presented a lower efficiency of DOC removal reaching only 55% in 80 minutes, while 87% of DOC removal is obtained for the same experiment time, when FeOx was used.

3.2.2. Influence of iron source and hydrogen peroxide concentration

Literature indicates ferrioxalate as a suitable candidate for capturing solar energy since it absorbs at between 250-500 nm and the quantum yield for ferrous-ion photo-generation (equation 3) can reach values higher than 1 [25].



The improvement of the photo-Fenton degradation of different contaminants such as toluene, 2-butanone and urea herbicides by using the ferrioxalate complex compared to that of Fe³⁺/H₂O₂ under solar irradiation has been previously reported [18, 20, 25]. In this work, a commercial source

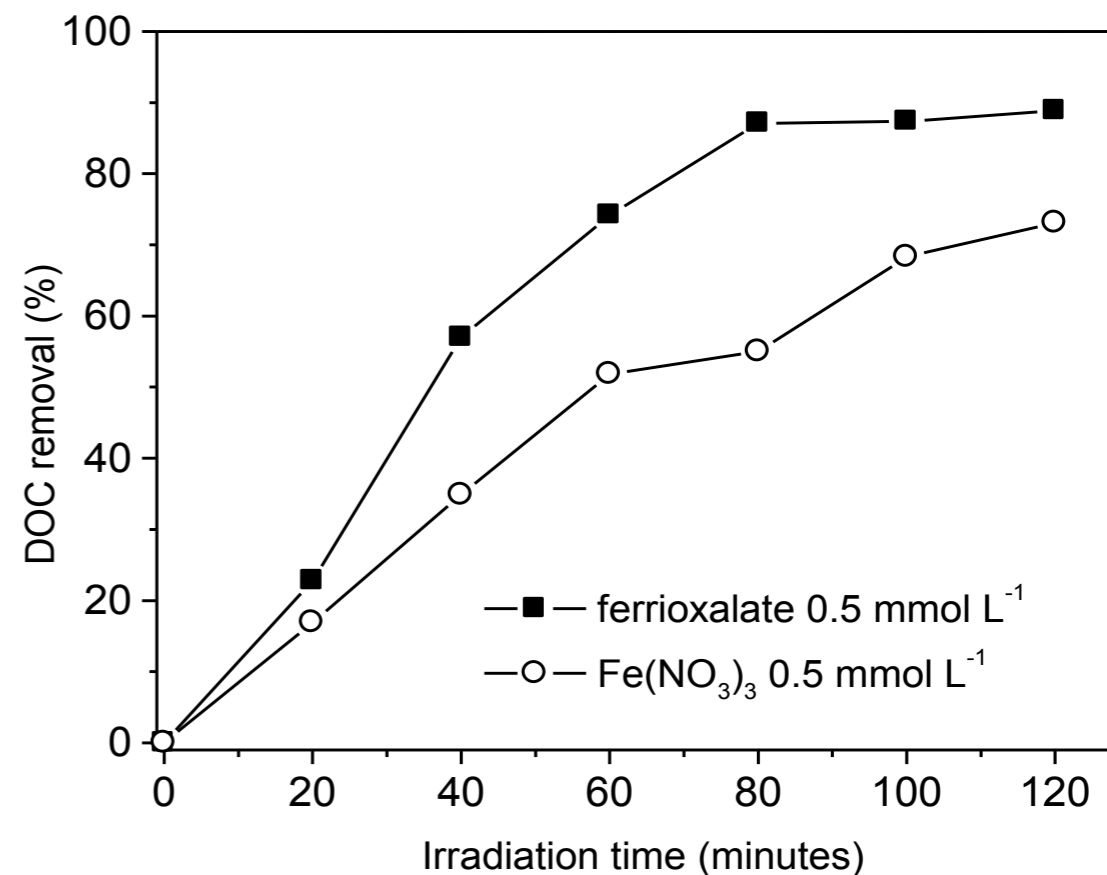


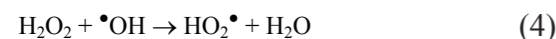
Figure 2. DOC removal from formaldehyde waste during solar irradiation using different iron sources. Conditions: 500 mg L⁻¹ C; 1.0 mol L⁻¹ H₂O₂ and magnetic stirring.

The higher efficiency of ferrioxalate in relation to iron nitrate may be a consequence of the higher quantum yield of Fe(II) photo-generation when compared to iron nitrate [26]. This result was also observed for the mineralization of formaldehyde present however in a much lower concentration (1 mmol L⁻¹; 12 mg C L⁻¹) under solar photo-Fenton degradation [20]. This indicates that besides to degrade the formaldehyde, the organic matter present in the waste is also more efficiently oxidized when ferrioxalate is used as iron source. The enhancement of the photo-generation of Fe²⁺ improves the formation of the hydroxyl radical by establishing an iron oxidation cycle (equations 1 and 2), which improves the organic matter degradation. Besides the OH radical, the organic radical R[•] (equation 3) may also react with oxygen and

promote the degradation of organic contaminants [27].

Another parameter to be analyzed is the hydrogen peroxide consume. When the H₂O₂ is completely consumed in the photo-Fenton process, the degradation reaction practically stops, and new additions of the oxidant is necessary. On the other hand, H₂O₂ can also act as •OH scavenger when high concentrations are present, hindering the photodegradation reaction due to the lower oxidation power of the HO₂[•] radical formed (equation 4) [28]

Hence is very important to guarantee that it been utilized H₂O₂ enough to supply the demand, that depends on the organic matter concentration, which is high in this work. Therefore it does not work as hydroxyl radical scavenger.



When the iron source was evaluated it was used $1.06 \text{ mol L}^{-1} \text{H}_2\text{O}_2$, which is a quite high concentration and it resulted in 87% of DOC removal in 80 minutes of irradiation. After measuring the residual H_2O_2 concentration, it was observed that only 31% of the initial peroxide was consumed after 80 minutes irradiation. Thus the study was done decreasing the H_2O_2 concentration from 1.06 to 0.73 mol L^{-1} (Figure 3).

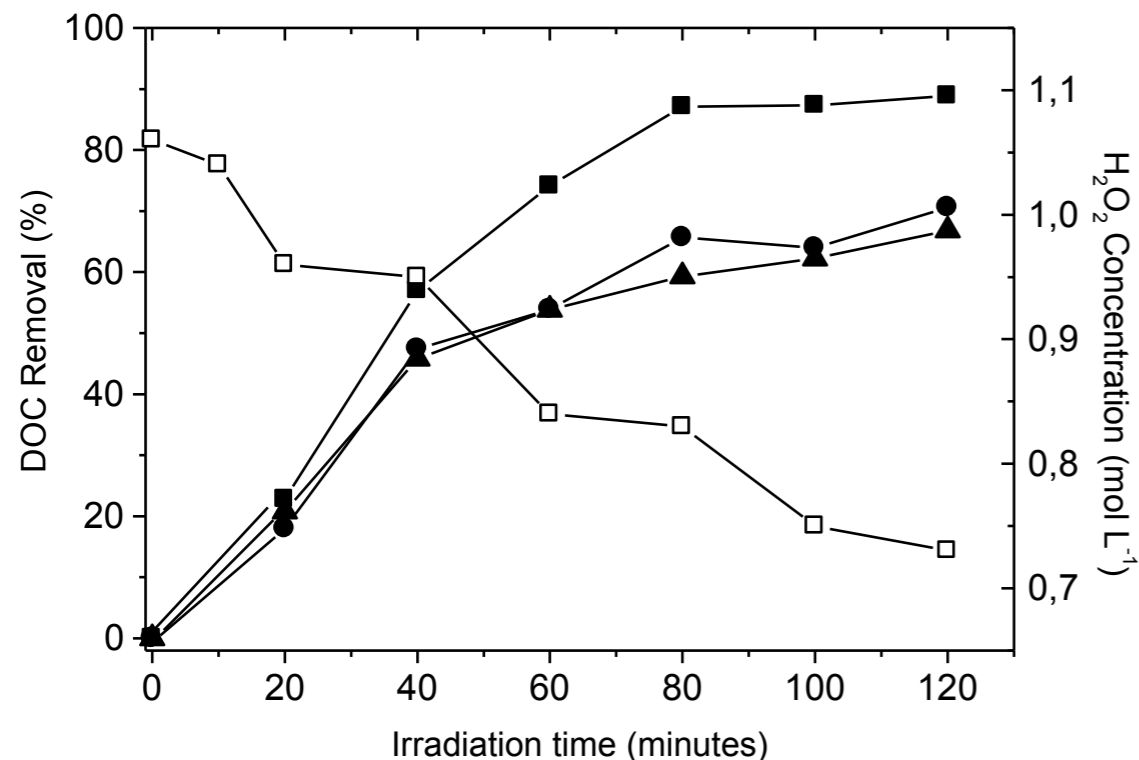


Figure 3. Influence of hydrogen peroxide concentration on DOC removal from formaldehyde waste. Initial concentrations: 500 mg L^{-1} DOC; 0.5 mmol L^{-1} ferrioxalate; (■) $\text{H}_2\text{O}_2 = 1.0 \text{ mol L}^{-1}$; (●) $\text{H}_2\text{O}_2 = 0.9 \text{ mol L}^{-1}$; (▲) $\text{H}_2\text{O}_2 = 0.8 \text{ mol L}^{-1}$ (□); Residual hydrogen peroxide for 1.0 mol L^{-1} initial concentration is also shown.

It supposes that similar mineralization can be achieved with a lower H_2O_2 concentration. However, a small decrease in the initial H_2O_2 concentration to 0.9 and 0.8 mol L^{-1} resulted in a significant decrease in DOC removal, reaching 71% and 67%, respectively. Although a considerable amount of H_2O_2 was still present in the reaction medium, this did not hinder the reaction by scavenging OH radicals. In contrast, this was necessary to achieve the higher degradation efficiency.

3.2.3. Influence of concentration of sample

For determined the ideal concentrations of the formaldehyde waste had been studied: 500, 800 and 1100 mg L^{-1} and the solutions were irradiated in the presence of 0.5 mmol L^{-1} ferrioxalate and $1 \text{ mol L}^{-1} \text{H}_2\text{O}_2$ (due to results presents using this iron source) As can be seen in Figure 4, higher DOC removal was found for the 500 mg L^{-1} sample, reaching 89% in 2 h irradiation while

only 19% was obtained for the sample containing 1100 mg L^{-1} organic carbon for the same exposure same time.

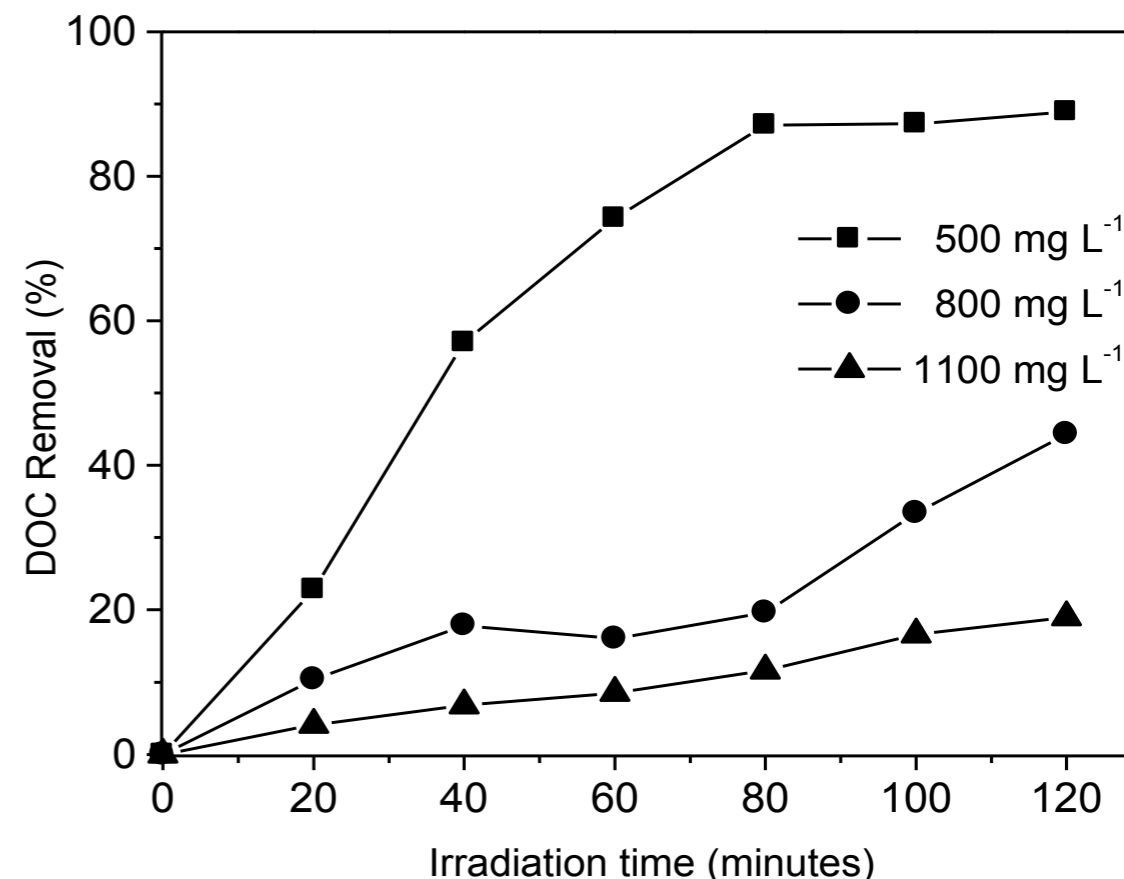


Figure 4. Influence of sample concentration on the organic carbon removal using $1.0 \text{ mol L}^{-1} \text{H}_2\text{O}_2$; $0.5 \text{ mmol L}^{-1} \text{FeOx}$ and system with magnetic stirring.

The Brazilian Environmental legislation recommends an efficiency of COD reduction of the 80% or maxim organic matter of 60 mg L^{-1} for treated effluent [5], in this case is 55 mg L^{-1} . Although mineralization of organic matter was not reached all formaldehyde was removed, which it was observed using the colorimetric method with chromotropic acid. The results showed that after 120 minutes of the solar irradiation, the formaldehyde levels were below the detection limit of the method ($3.3 \mu\text{mol L}^{-1}$). Considering that the high toxicity of such wastes is mainly due to the presence of formaldehyde, the proposed method represents a significant hazard reduction, although total mineralization of the organic material was not achieved within two hours irradiation.

In agreement with this work Pereira and Zaiat [29] observed COD removal was around 70% when the formaldehyde concentrations ranging 110 to 1104 mg L^{-1} . And in according with Aranã and co-workers [30] treating formaldehyde waste not is a simple task due to the diversity of organic and inorganic compounds that they may contain and due to high demand for H_2O_2 .

Considering the simplicity and easily application of a non-stirred system, the results obtained under magnetic stirring were compared to the results of a system without stirring maintain the conditions early defined. It was observed that in the unstirred system, a white solid was formed and precipitated. Considering that the original sample did not presented solid material, this pre-

precipitate can be related to either the formation of insoluble degradation products or to the precipitation of proteins and lipids extracted from the anatomic pieces [30]. These long-chain organic compounds may precipitate due to the increase of the ionic strength of the medium since organic acids and various ions can be formed during oxidation. The further degradation of the precipitate was favored at the stirred system probably due to a better absorption of the irradiation which improved the degradation, as previously observed for high absorbance samples [23]. The results in **Figure 5** show a slight improvement in the degradation process in the dissolved fraction of the stirred system. This is the reason why subsequent experiments were carried out under stirring.

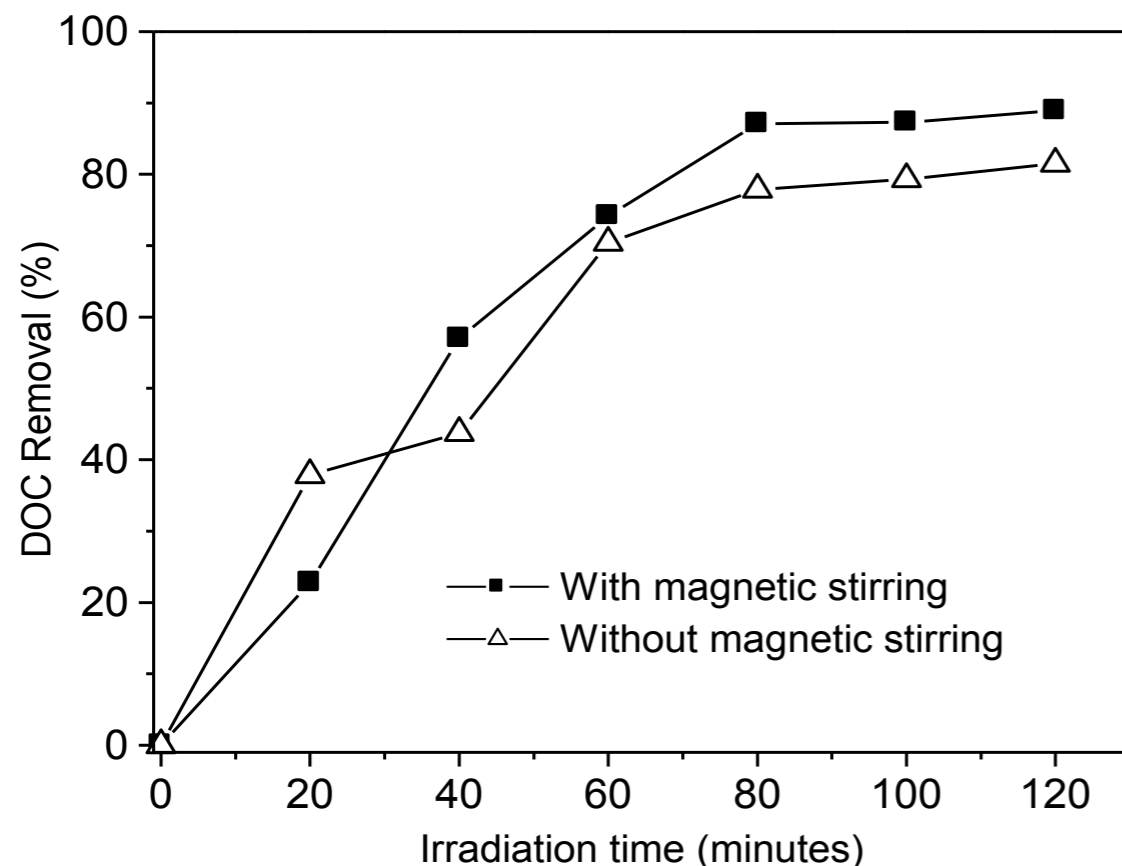


Figure 5. Influence of magnetic stirring. 500 mg L⁻¹ C; 0.5 mmol L⁻¹ FeOx; 1.0 mol L⁻¹ H₂O₂.

4 Conclusions

The present work proposes the application of the photo-Fenton process as an alternative to incineration, which is currently applied to eliminate biological laboratory wastewaters containing formaldehyde. This treatment applies an AOP that can easily be applied *in situ*, avoiding storage and transportation risks. The method uses sunlight in order to provide a simple and feasible procedure for the decontamination of this kind of waste.

The results suggested that in the presence of 0.5 mmol L⁻¹ potassium ferrioxalate, 1 mol L⁻¹ H₂O₂, and two hours of exposure to sunlight is sufficient to remove at least 85% of the carbon content and also completely oxidize the formaldehyde present in the sample. Considering that the experiments were carried out in the winter, it is expected that better results can be obtained in the summer when solar irradiance is higher. The suggested procedure is simple and feasible to carry out and can be done by the personnel who work

in biological laboratories avoiding the storage of waste and its inappropriate discharge.

5 Acknowledgements

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Resumo: Laboratórios e centros de pesquisa consomem uma grande variedade de substâncias químicas perigosas e, conseqüentemente, geram resíduos contendo-as, como por exemplo: resíduo de formaldeído. O formol é bastante empregado na conservação de peças anatómicas, gerando muitos litros desse resíduo por ano. O presente trabalho sugere o uso do processo foto-Fenton com irradiação solar para tratar resíduo contendo formaldeído. Alguns aspectos foram estudados como a concentração da fonte de ferro, da amostra e do peróxido de hidrogênio, além da aplicação de agitação magnética. O uso de ferrioxilato (0,5 mol L⁻¹) mostrou ser mais eficiente na degradação da matéria orgânica quando comparado ao nitrato férrico. Já a concentração de peróxido necessária para tratar 500 mg C L⁻¹ foi de 1 mol L⁻¹. Sob essas condições todo formaldeído detectável foi degradado e foi possível remover 89% da matéria orgânica dissolvida na amostra em duas horas. Tais resultados são considerados satisfatórios para descartar na rede de esgoto, segundo a agência paulista de controle ambiental.

Palavras-chave: tratamento de resíduo de laboratório, formaldeído e foto-Fenton

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