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Photo-Fenton process for treating biological laboratory wastewater containing formaldehyde

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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 absorbância total a 217,0005 nm: $A_{\text{Pb}}^{217,0005 \text{ nm}} = A_{\text{total}}^{217,0005 \text{ nm}} - A_{\text{PO}}^{217,0005 \text{ nm}}$. 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 absorbância 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 absorbância 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).

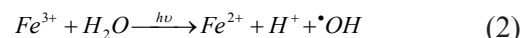
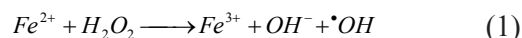
Palavras-chave: método de correção por equação matemática; espectrometria de absorção atômica com fonte contínua e de alta resolução; chumbo; ácido fosfórico.

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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 H_2O_2 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 H_2O_2 , 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 H_2O_2 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 $Fe(NO_3)_3 \cdot 9H_2O$ (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 H_2SO_4 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 H_2SO_4 . The reaction was initiated after H_2O_2 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 ($21^\circ \text{ S } 48^\circ \text{ W}$) 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

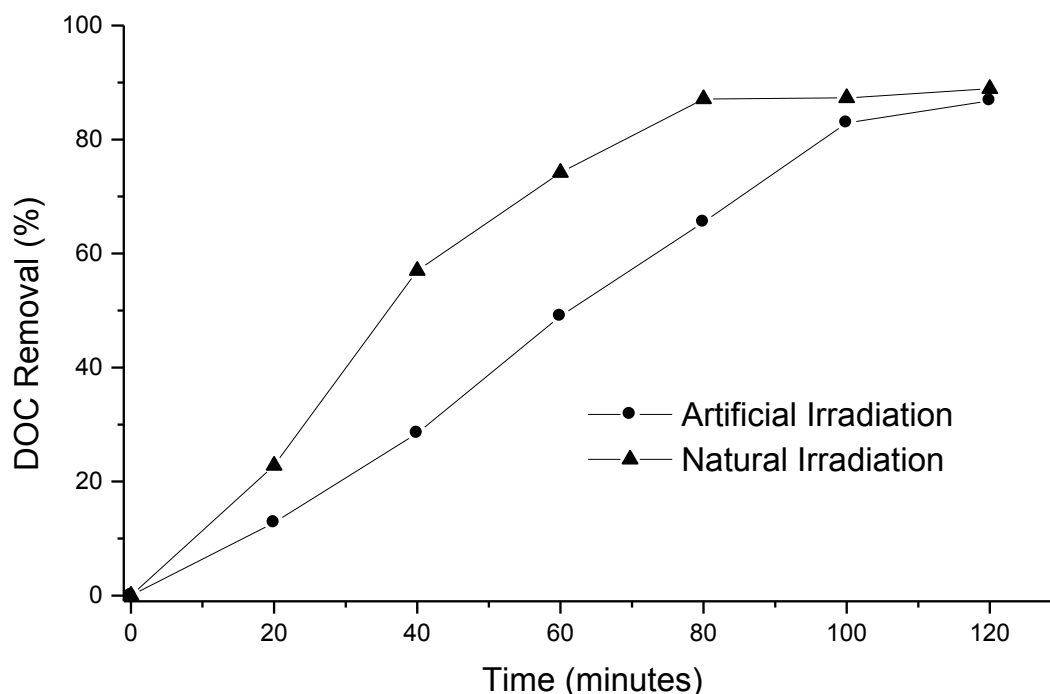
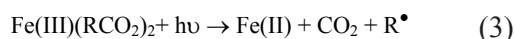


Figure 1. DOC removal from formaldehyde waste during using different irradiation sources. Conditions: 500 mg L⁻¹ C formaldehyde sample; 0.5 mmol L⁻¹ FeOx; 1.0 mol L⁻¹ H₂O₂, magnetic stirring.

3.2. Determination of the optimum conditions

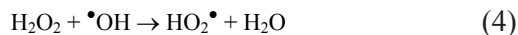
3.2.2. Influence of iron source and hydrogen peroxide concentration

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

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.



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).

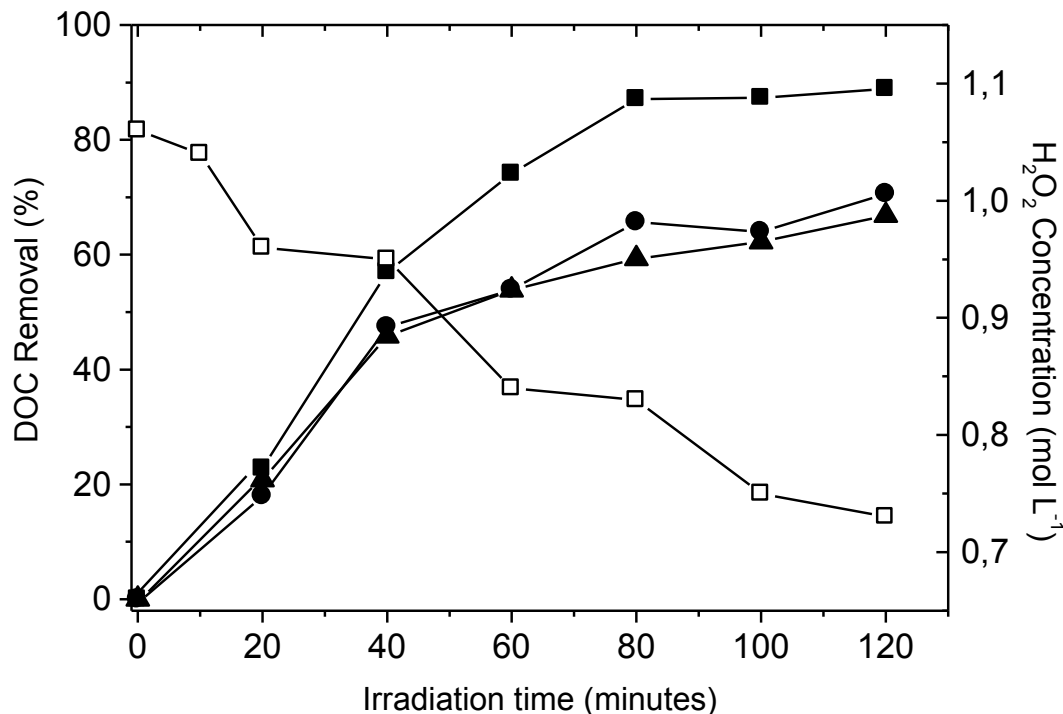


Figure 3. Influence of hydrogen peroxide concentration on DOC removal from formaldehyde waste. Initial concentrations: 500 mg L^{-1} DOC; 0.5 mmol L^{-1} ferrioxalate; (■) $\text{H}_2\text{O}_2 = 1.0 \text{ mol L}^{-1}$; (●) $\text{H}_2\text{O}_2 = 0.9 \text{ mol L}^{-1}$; (▲) $\text{H}_2\text{O}_2 =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

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.

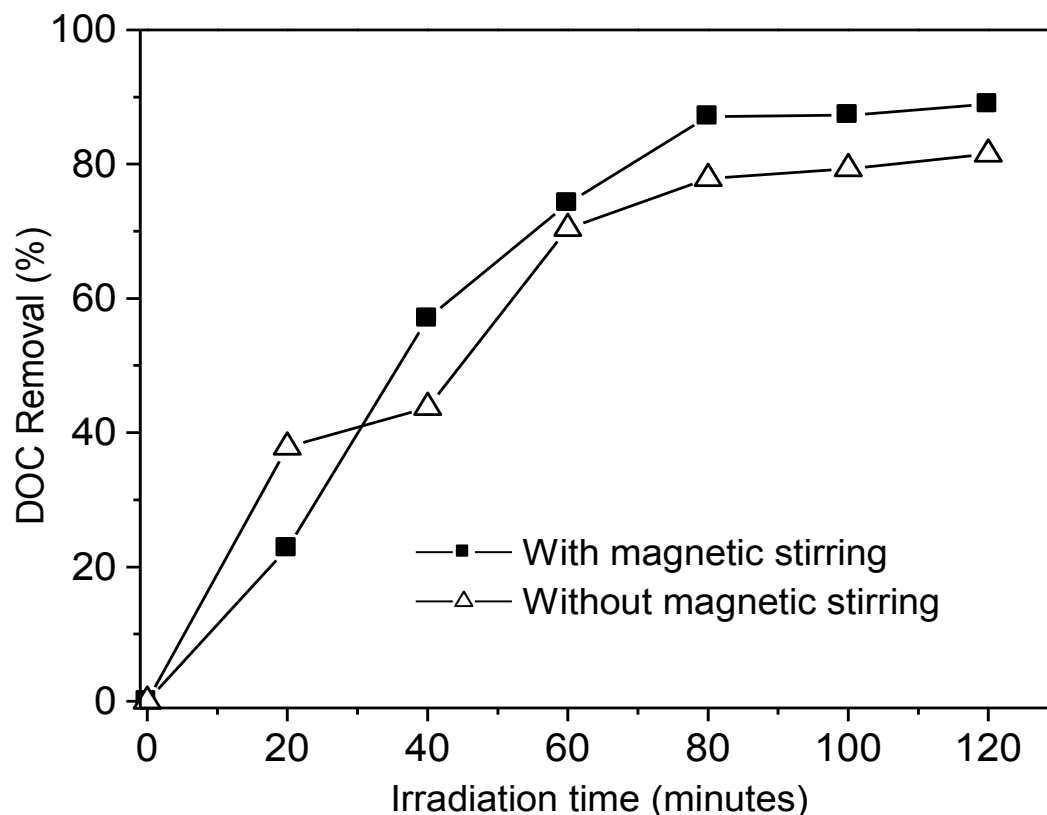


Figure 5. Influence of magnetic stirring. 500 mg L⁻¹ C; 0.5 mmol L⁻¹ FeOx; 1.0 mol L⁻¹ H₂O₂.

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 to 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