



Degradation of dimethyl disulfide using homogeneous Fenton's reaction

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ABSTRACT

In this work the degradation of a model odor compound (dimethyl disulfide, DMDS) using Fenton's reaction is reported. Dimethyl disulfide is present in wastewaters generated during production of poultry feather and viscera meal. Oxidation was carried out in batch reactor with temperature control. Experimental design technique was used to investigate the influence of concentration of hydrogen peroxide and Fe^{2+} , temperature and pH on degradation of DMDS. Control reactions using H_2O_2 without Fe^{2+} were carried out, but DMDS degradation could only reach 60% for a 0.025 mg L^{-1} DMDS solution, at pH 3, 60°C using $10,000 \text{ mg L}^{-1}$ H_2O_2 in 30 min of reaction. The Fenton's reaction could effectively remove DMDS, reaching 95% degradation at pH 3, 60°C , 5 mg L^{-1} H_2O_2 and 1 mg L^{-1} Fe^{2+} after only 10 min of contact. A kinetic study of the Fenton's reaction was carried out, varying the concentration of hydrogen peroxide, Fe^{2+} and temperature.

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1. Introduction

The increasing sensitivity of the population for odors and the demand for a clean and healthy environment have been pushing industries to a more effective control of the emission of odors and toxic pollutants in the air [1]. The conventional technologies for degradation of pollutants, excluding the biological processes, decisively do not solve the problem, since they are based on the phase transfer of these substances, transferring responsibility of the problem for future generations. The biological treatment is often the most cost effective conventional alternative for treatment of wastewaters since mineralization of the pollutants is often achieved. However, industrial wastewaters usually contain toxic and/or non-biodegradable organic substances, for which biological treatment is not efficient [2].

The poultry feather and viscera are the two major by-products generated during poultry meat production. These by-products are usually cooked in pressurized vessels to yield feather and viscera meals, which are used in the formulation of animal feed. The exhaust gases that leave the cooker are rich in malodorous compounds that are normally removed from the waste gases using wet scrubbers. The scrubbers require rather clean water for effective odor removal, and they generate a large amount of wastewater

that should be properly disposed of. Thus, alternatives that could decrease water consumption are of great interest to such industries.

One of the alternatives for treatment of wastewaters and residual gases is based on chemical oxidation using Fenton's reaction (hydrogen peroxide in the presence of a catalyst, like salts of iron). Fenton's reaction is known to be very effective in the degradation of hazardous organic pollutants from water. The main advantage is the complete destruction of contaminants to harmless compounds, water and inorganic salts. The Fenton's reaction causes the formation of highly reactive hydroxyl radicals [3,4]. Hydrogen peroxide is a strong oxidant, and its decomposition generates water and oxygen [5]. In homogeneous Fenton's reaction, the iron can be recovered by alkaline precipitation after the reaction.

This work aimed to study the oxidation of a model odor compound (dimethyl disulfide) using homogeneous Fenton's reaction, proposing an alternative for odor control in poultry by-product processing plants.

2. Materials and methods

2.1. Samples

A commercial standard of the dimethyl disulfide (DMDS, 99%, Aldrich) was used in all experiments. This compound was chosen, since it is found in wastewaters from the poultry by-products industry, and for its low odor threshold ($\text{sub-}\mu\text{g m}^{-3}$) [6]. A 0.025 mg L^{-1} solution of DMDS was prepared with deionized water before every experimental run. The pH of the solution was adjusted to the pH determined in the experimental design, using a NaOH 1 M or HCl 1 M solution.

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2.2. Extraction and analysis

Samples were extracted from the headspace of the standard solution by solid phase microextraction (HS-SPME) technique. The extracting fiber used was polydimethylsiloxane (PDMS), 30 μm of film thickness (Supelco, USA). The fibers were previously conditioned in the chromatograph injector for 30 min at 250 °C, according to the supplier's recommendations.

For each headspace extraction, 10 mL of sample was placed in a 20 mL amber glass vial with screw top and Teflon faced rubber septum. The vial was placed in a water bath at 50 °C. Magnetic stirring was used to increase the transfer of the volatile compound from the liquid phase to the headspace. This procedure increases the adsorption of the compounds in the SPME fibers and reduces the time necessary for the extractions [6–9]. The extraction conditions were determined in preliminary experiments (results not shown).

A gas chromatograph equipped with a split/splitless injector and a mass spectrometry detector (CG/MS Shimadzu QP5050A) was used for the instrumental analysis. The injector was equipped with a 0.8 mm i.d. SPME liner. Runs were carried out with a fused silica capillary column (DB-WAX, 30 m \times 0.25 mm \times 0.25 μm – polar, polyethylene glycol; J&W Scientific).

The injection was carried out in splitless mode and desorption of the compound from the fiber was achieved after 4 min of fiber exposition inside the injection port. The temperatures of the injector and MS-interface were set at 220 °C and 250 °C, respectively. Oven temperature was programmed from 50 °C to 80 °C at 20 °C min^{-1} , then to 90 °C at 5 °C min^{-1} and finally to 155 °C at 20 °C min^{-1} . Helium was used as carrier gas at a flow rate of 0.7 L min^{-1} and the detector voltage was 1.2 kV.

2.3. Oxidation runs and analysis of the results

A control run was carried out for each experimental run of DMDS degradation. The control conditions were the same as the sample, however, without the addition of H_2O_2 and Fe^{2+} . Percent of DMDS degraded was calculated based on the blank runs.

The evaluation of the effects of the variables (H_2O_2 and Fe^{2+} concentrations, pH and temperature) on the degradation of DMDS was carried out using experimental design technique. The results were analyzed with the aid of the software Statistica 6.1 (StatSoft Inc., Tulsa, OK, USA). All the tests were carried out in duplicate, and the central points in triplicate. The statistical analyses were carried out using pure error, identifying the significant regression coefficients with a confidence level of 95%.

2.3.1. Oxidation with hydrogen peroxide

The studies of chemical oxidation of DMDS with hydrogen peroxide were carried out with aqueous hydrogen peroxide (H_2O_2) 30% (Merck, Brazil). The levels of the factors investigated are presented in Table 1, for the first complete experimental design, which consisted in a two level, three-factor experimental design (2^3), with one experimental point at the center of the cube of the experimental space. The DMDS solution (10 mL, 0.025 mg L^{-1}) was placed in 20 mL vials with magnetic stirring, and H_2O_2 was added to reach the required concentration. The vials were immediately closed and kept under the reaction conditions for 30 min.

Table 1
Levels of the factors studied in the 2^3 experimental design.

Level	H_2O_2 (mg L^{-1})	Temperature (°C)	pH
–1	500	25	3
0	5250	42.5	7
+1	10,000	60	11

Table 2

Levels of the factors studied in the second experimental design.

Level	H_2O_2 (mg L^{-1})	Fe^{2+} (mg L^{-1})	Temperature (°C)
–1	5	0.1	25
0	27.5	0.55	42.5
+1	50	1	60

2.3.2. Oxidation with homogeneous Fenton's reaction

The runs were carried out in the same way as described in the previous item, though adding a solution of ferrous sulfate (Merck, Brazil). The initial pH was kept at 3. The levels of the factors studied in the 2^3 experimental design are presented in Table 2. These levels were chosen based on the results of preliminary experiments (results not shown). The aim of the designs was to maximize the degradation of DMDS with the lowest possible amounts of H_2O_2 and Fe^{2+} .

2.3.3. Kinetic study of the oxidation of DMDS for the homogeneous Fenton's reagent

This study was carried out to determine a relationship between the reaction rate and the concentrations of H_2O_2 and of Fe^{2+} . An expression for the calculation of the rate constant of the reaction (k) was obtained following the approach proposed by Lin et al. [10]. For the kinetic study, the concentration of peroxide was kept constant (5 mg L^{-1}), while varying Fe^{2+} concentration (0.5 mg L^{-1} , 1 mg L^{-1} , 5 mg L^{-1} and 10 mg L^{-1}). Then, this latter was kept constant (1 mg L^{-1}) and peroxide amount varied (1 mg L^{-1} , 5 mg L^{-1} , 10 mg L^{-1} and 50 mg L^{-1}). DMDS concentration was monitored as a function of time of reaction.

The effect of the temperature in the oxidation of DMDS with the homogeneous Fenton's reagent was evaluated at 1 mg L^{-1} of Fe^{2+} and 5 mg L^{-1} of H_2O_2 , pH 3 and time of reaction of 30 min. Temperatures studied were 25 °C, 40 °C, 55 °C and 60 °C.

3. Results and discussion

3.1. Oxidation with hydrogen peroxide

The matrix of the first experimental design and the respective responses in terms of degradation percentage (oxidation) of DMDS, using H_2O_2 is presented in Table 3.

The results of the analysis of variance validated the coded empiric model presented in Eq. (1), since the calculated F -test (Fisher distribution) is 6.8 times higher than the tabulated F , with a correlation coefficient $R=0.90$, for the analysis of the regression in relation to the residues.

$$\% \text{Removal} = 31.7 + 14.8 \times T - 6.1 \times \text{pH} + 1.4 \times \text{per} + 4.4 \times T \times \text{per} - 4.5 \times \text{pH} \times \text{per} \quad (1)$$

where T is the reaction temperature, pH is the pH of the solution and per is the concentration of H_2O_2 .

Table 3

Matrix of the 2^3 experimental design (real and coded values) and the respective responses in terms of degradation of DMDS. Runs without addition of Fe^{2+} .

Run	Temperature (°C)	pH	H_2O_2 (mg L^{-1})	% Degradation
1	25 (–1)	3 (–1)	10,000 (+1)	22.4 \pm 4.0
2	60 (+1)	3 (–1)	10,000 (+1)	59.7 \pm 0.2
3	25 (–1)	11 (+1)	10,000 (+1)	0
4	60 (+1)	11 (+1)	10,000 (+1)	39.5 \pm 1.4
5	25 (–1)	3 (–1)	500 (–1)	19.3 \pm 2.0
6	60 (+1)	3 (–1)	500 (–1)	39.2 \pm 1.6
7	25 (–1)	11 (+1)	500 (–1)	15.0 \pm 1.6
8	60 (+1)	11 (+1)	500 (–1)	37.0 \pm 1.6
9	42.5 (0)	7 (0)	5250 (0)	53.3 \pm 2.2

The statistical analysis shows that all the variables presented a significant effect in the removal of the DMDS ($p < 0.05$). Only the interaction between the temperature and pH did not present statistically significant effect ($p < 0.05$), and was then added to the model's lack of fit. Temperature and pH are the factors that most influenced DMDS degradation. Both temperature and the concentration of peroxide have a positive influence in the degradation, i.e., the increase in temperature and the increase in concentration of H_2O_2 cause an increase in degradation. On the other hand, the pH showed a negative effect on the response. Kremer [11] observed an increase in the concentration of O_2 with the increase of the pH in a reaction with H_2O_2 . This fact consequently reduces the power of reaction of the oxidizer, since the H_2O_2 is degrading into non-reactive species.

The conditions of run 2 yielded the highest degradation (59.7%) in 30 min. The increase in the temperature increases the reaction rate, improving degradation. Gogate and Pandit [3] agree that the oxidation for H_2O_2 is accelerated by the increase of the temperature, but they recommend a maximum reaction temperature of 40°C , because the H_2O_2 is very quickly degraded above this temperature. Conversely, Chen et al. [12] verified that the use of H_2O_2 in oxidative processes is efficient up to 100°C , alleging that the fast decomposition only occurs after 120°C . The effects of the studied factors on DMDS degradation can be better visualized in Fig. 1.

The binary interactions between temperature and H_2O_2 and between pH and H_2O_2 were statistically significant, showing that the studied factors have synergistic effects. For instance, if the concentration of H_2O_2 and pH are increased at the same time, this will negatively affect the degradation of DMDS. The highest removal of DMDS (59.7%) occurs in the direction of the higher level of temperature (60°C), lower level of pH (3) and higher level of concentration of H_2O_2 . The oxidation using only H_2O_2 is not effective enough to guarantee a high degradation of DMDS. This result is also reported by other authors [4].

3.2. Oxidation with H_2O_2 and Fe^{2+} (homogeneous Fenton's reagent)

Several authors [2,3,11,13,14] claim that the oxidation process using the Fenton's reaction presents its highest effectiveness in pH between 3 and 4. Since our previous results showed that the largest degradations are obtained at the lower level of pH, the oxidation runs with Fenton's reaction were carried out at pH 3. This will avoid

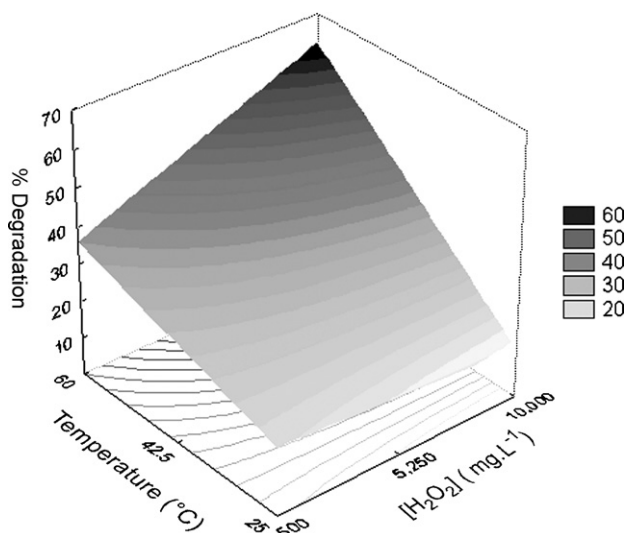


Fig. 1. Response surface for the study of the effect of the variables in the degradation of DMDS using hydrogen peroxide.

Table 4

Matrix of the 2^3 complete experimental design (real and coded values) and the respective responses in terms of degradation of DMDS. Runs using Fenton's reaction.

Run	Fe^{2+} (mg L^{-1})	H_2O_2 (mg L^{-1})	Temperature ($^\circ\text{C}$)	% Degradation
1	0.1 (-1)	5 (-1)	25 (-1)	8.16 ± 1.46
2	1 (+1)	5 (-1)	25 (-1)	73.81 ± 1.28
3	0.1 (-1)	50 (+1)	25 (-1)	21.82 ± 2.49
4	1 (+1)	50 (+1)	25 (-1)	93.89 ± 0.38
5	0.1 (-1)	5 (-1)	60 (+1)	79.89 ± 1.58
6	1 (+1)	5 (-1)	60 (+1)	95.77 ± 0.09
7	0.1 (-1)	50 (+1)	60 (+1)	95.41 ± 3.63
8	1 (+1)	50 (+1)	60 (+1)	100.00 ± 1.45
9	0.55 (0)	27.5 (0)	42.5 (0)	97.04 ± 0.71

the formation of Fe^{3+} complexes, which are able to reduce the reaction performance. Also, the H_2O_2 degrades faster into H_2O and O_2 at high pH [11].

The matrix of the 2^3 experimental design for the study of oxidation of DMDS with Fenton's reaction is presented in Table 4, with the respective responses in terms of DMDS degradation.

The analysis of variance validates the model presented in Eq. (2), since the calculated F -test was 20 times higher than the tabulated value, and $R = 0.96$.

$$\% \text{Removal} = 73.7 + 21.3 \times T + 20.2 \times \text{Fe} + 6.3 \times \text{per} - 14.3$$

$$\times \text{Fe} \times T - 2.1 \times \text{per} \times T \quad (2)$$

where T is the reaction temperature, Fe is the concentration of Fe^{2+} and per is the concentration of H_2O_2 .

As in the previous study, without addition of Fe^{2+} , all the factors influenced significantly the degradation of DMDS. All the primary effects were positive. The temperature and the concentration of Fe^{2+} presented positive significant effects much larger than the effect of the concentration of H_2O_2 . The validated model was used to plot the response surfaces presented in Fig. 2. As already discussed, the increase in the reaction temperature causes the increase in reaction rates, according to the Arrhenius model. The increase in the concentration of Fe^{2+} and in the concentration of H_2O_2 leads to the rise in the formation rates of hydroxyl radicals, thus improving the degradation of DMDS.

The results show that the complete degradation of DMDS in 10 min of reaction can be achieved with 1 mg L^{-1} of Fe^{2+} , 50 mg L^{-1} of H_2O_2 at 60°C . However, high degradations (above 95%) can also be obtained using a concentration 5 mg L^{-1} H_2O_2 for the same concentration of Fe^{2+} at 60°C . Thus, Fe^{2+} concentration could be kept below 15 mg L^{-1} , which is a level required by the main Brazilian legislation on water resources (Resolution No. 357 issued on March 17, 2005, by the National Environment Council – CONAMA). Analysis of the aqueous phase by ionic chromatography (results not shown) showed a slight increase in the sulfate (SO_4^{2-}) concentration in the solution, suggesting that SO_2 is produced and partly solubilized, yielding sulfuric acid. However, the amount of sulfate detected was in average only 8% of the theoretical value, obtained by the mass balance. This result suggests that most of the SO_2 produced is volatilized.

Some reports on degradation of organic compounds by Fenton's reaction could be found elsewhere. Lin et al. [10] studied the degradation of two surfactants, anionic alkylbenzene sulfonate (ABS) and linear alkylbenzene sulfonate (LAS), in the concentration of 10 mg L^{-1} each with the Fenton's reagent. They achieved degradations higher than 95%, using 60 mg L^{-1} of H_2O_2 and 60 mg L^{-1} of Fe^{2+} , in 90 min and 60 min of reaction for ABS and LAS, respectively. Ksibi [14] studied the application of Fenton's reaction for domestic wastewater treatment, reaching 85% of chemical oxygen demand (COD) removal using 450 mg L^{-1} H_2O_2 and 22.4 mg L^{-1} Fe^{2+} in 3 h of reaction. Fenton's reaction was also proposed for the treatment of landfill leachate, yielding 75% removal of COD by treatment with

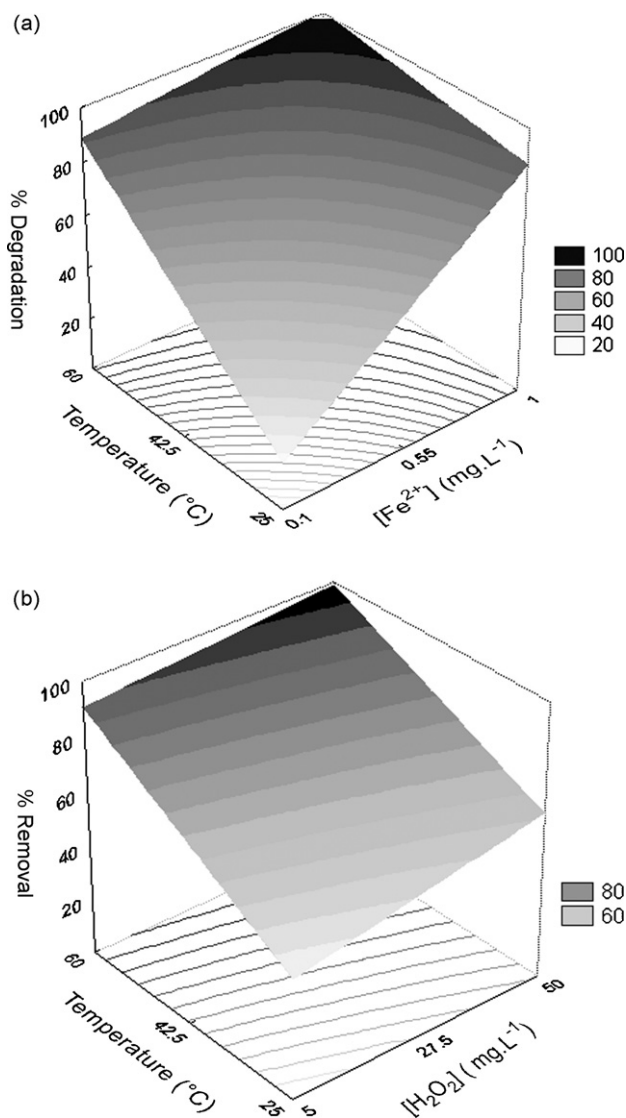


Fig. 2. Response surfaces showing the effect of factors on the degradation of DMDS using Fenton's reaction.

4 g L⁻¹ H₂O₂, 1 g L⁻¹ Fe²⁺ in 1 h reaction [15]. The treatment of textile wastewaters with Fenton's reagent was able to decrease only 45% of COD in 4 h using 30 mg L⁻¹ H₂O₂ and 40 mg L⁻¹ Fe²⁺ [16].

In contrast to the other reports from literature, the small H₂O₂ and Fe²⁺ concentrations as well as the short time of reaction found in the present work can be justified by the fact that the molecule of DMDS is simpler and consequently easier degrading. More complex organic compounds may lead to expressively smaller reaction rates [4].

3.3. Kinetic study of the oxidation of DMDS using the homogeneous Fenton's reagent

The degradation of DMDS obtained at different concentrations of Fe²⁺ and a fixed concentration of H₂O₂ (5 mg L⁻¹) is shown in Fig. 3.

In most conditions the degradation increases sharply in the first 30 min of reaction, decelerating until stabilization. Similar behavior is observed by other authors [10,15]. It is clearly observed that the increase in Fe²⁺ causes an increase in reaction rate.

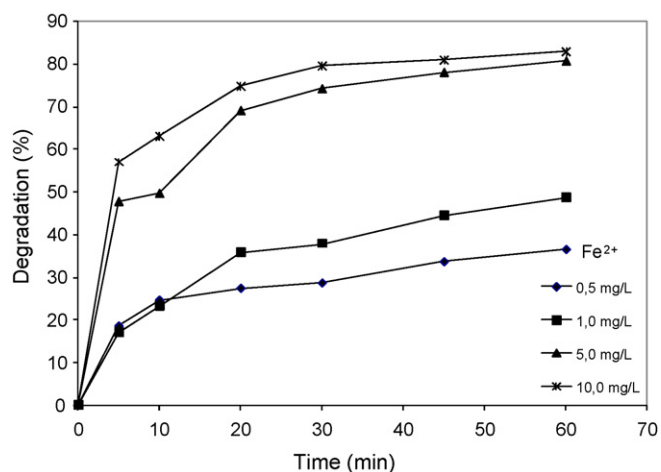


Fig. 3. Effect of the [Fe²⁺] in the degradation of DMDS with 5 mg L⁻¹ of [H₂O₂].

The oxidation with the Fenton's reagent can be represented by the following kinetic equation of order x [10]:

$$\frac{dC_A}{dt} = r_A = -k \times C_A^x \quad (3)$$

where C_A represents the concentration of DMDS, x the order of the reaction, k the coefficient of speed of the reaction and t the time.

The oxidations using the reaction of Fenton follows, in most of the cases, first order kinetics [2,10,17]. Thus, considering first order reaction rate:

$$-\ln\left(\frac{C_A}{C_{A0}}\right) = kt \quad (4)$$

where C_{A0} is the initial concentration of DMDS.

According to Eq. (4), plotting $\ln(C/C_0)$ versus t , it is possible to determine the rate constant (k). Since Fenton's reaction is still dependent on the initial concentrations of H₂O₂ and Fe²⁺, these dependencies can be included in the expression for the rate constant (k) according to Eq. (5), as suggested by Lin et al. [10].

$$k = A \times [H_2O_2]_0^n \times [Fe^{2+}]_0^m \times \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

where A is the frequency factor, $[H_2O_2]_0$ and $[Fe^{2+}]_0$ are the initial concentrations of hydrogen peroxide and ferrous ion, respectively. The exponents n and m stand for the orders of the concentration dependence, E_a is the apparent activation energy, T is the absolute temperature (K) and R is the constant of the gases (8.314 J/(mol K)).

Thus, the order of dependence of the rate constant on the concentration of Fe²⁺ was determined by fitting the data from Fig. 3 after logarithmic linearization. This procedure yielded $m = 0.457$ ($R^2 = 0.94$), valid for the concentration range of Fe²⁺ from 0.5 mg L⁻¹ to 10 mg L⁻¹. The same procedure was carried out to find the order of dependence of the rate constant on the concentration of the oxidizer, fitting data from Fig. 4. The order of dependence of the rate constant on the concentration of H₂O₂ (n) was found to be 0.238 ($R^2 = 0.99$), valid for the concentration range of H₂O₂ from 1 mg L⁻¹ to 50 mg L⁻¹. These results then show that the reaction rate is more dependent on the concentration of Fe²⁺ than on the concentration of hydrogen peroxide. Similar findings are reported for surfactant degradation by Fenton's reaction [10]. These data confirm the results obtained in the stage of optimization of the conditions of the oxidation by the Fenton's reagent, which showed that the effect of the concentration of Fe²⁺ was always stronger than the effect of the concentration of H₂O₂.

The investigation of the dependence of reaction rate with temperature was obtained by fitting the Arrhenius model to the data. The model fit yielded an activation energy of 57.081 kJ mol⁻¹

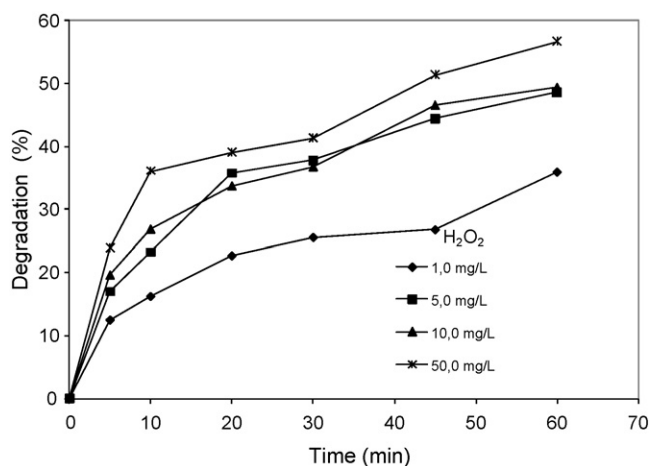


Fig. 4. Effect of the $[H_2O_2]$ in the degradation of DMDS with 1 mg L^{-1} in $[Fe^{2+}]$.

($R^2 = 0.98$). The value found for the activation energy was higher than that found by Maass et al. [18] (29.7 kJ mol^{-1}) in the study of the oxidation of hydrogen sulfite using only H_2O_2 . Lin et al. [10] found $10.62 \text{ kJ mol}^{-1}$ and 8.08 kJ mol^{-1} for degradation of two surfactants using homogeneous Fenton.

Finally, the expression for the calculation of the constant of speed (k) for this process is found:

$$k = 6.34 \times 10^7 [H_2O_2]_0^{0.238} \times [Fe^{2+}]_0^{0.457} \times \exp\left(\frac{6.856}{T}\right) \quad (6)$$

4. Conclusions

In the oxidation of a model odor compound (dimethyl disulfide) only with H_2O_2 , a maximum degradation of 59.7% for an aqueous solution with 0.025 mg L^{-1} of DMDS could be obtained, using pH 3, 60°C and concentration of H_2O_2 of $10,000 \text{ mg L}^{-1}$ in 30 min of reaction.

The oxidation of DMDS by Fenton's reaction proved to be much more effective than the oxidation only with hydrogen peroxide. For a solution with 10 mg L^{-1} , in 10 min of reaction, degradations higher than 95% could be achieved in the following conditions:

- pH 3, $T = 60^\circ\text{C}$, $[H_2O_2] = 5 \text{ mg L}^{-1}$ and $[Fe^{2+}] = 1 \text{ mg L}^{-1}$
- pH 3, $T = 60^\circ\text{C}$, $[H_2O_2] = 50 \text{ mg L}^{-1}$ and $[Fe^{2+}] = 0.1 \text{ mg L}^{-1}$
- pH 3, $T = 42.5^\circ\text{C}$, $[H_2O_2] = 27.5 \text{ mg L}^{-1}$ and $[Fe^{2+}] = 0.55 \text{ mg L}^{-1}$
- pH 3, $T = 60^\circ\text{C}$, $[H_2O_2] = 50 \text{ mg L}^{-1}$ and $[Fe^{2+}] = 1 \text{ mg L}^{-1}$

Through the kinetic study of the Fenton's peroxidation, the influence of the concentration of H_2O_2 , Fe^{2+} and temperature were

investigated. The results showed that the reaction is more dependent on the ferrous ion than on the peroxide, confirming the results obtained using the experimental design technique. A kinetic model for the reaction rate, based on the initial concentration of catalyst, oxidizer and temperature, was proposed.

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