

PHOTODECOMPOSITION OF HYDROGEN PEROXIDE IN HIGHLY SALINE AQUEOUS MEDIUM

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Abstract - The photodecomposition of hydrogen peroxide was performed in highly saline aqueous medium (60 g.L⁻¹ of NaCl). The Fe³⁺/H₂O₂/NaCl/UV system was tested at temperatures from 20 to 50 °C, while the intervals of concentration of Fe³⁺ and H₂O₂ were 1 to 2.5 mM and 230 to 630 mM, respectively. It is known from the literature that chloride is an inhibitor of the oxidation of organic compound in aqueous medium, but this effect has not been observed to be expressive for hydrogen peroxide. Despite this result, experiments were conducted in presence of high concentration of salt (60 g.L⁻¹), emulating the agrochemical process condition. The series of measurements has been evaluated and correlated. Thermal and photochemical dependencies were described satisfactorily by a simplified kinetic model. The apparent activation energy was estimated to be 27.6 kJ.mol⁻¹.

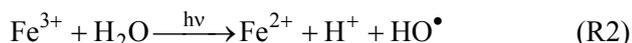
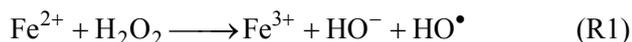
Keywords: AOT, Photodecomposition; Hydrogen peroxide; Hydroxyl radical; Chloride.

INTRODUCTION

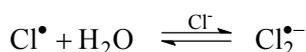
The increasing industrial demand for the re-use of water has stimulated researchers around the world to treat all the different varieties of wastewaters containing pollutants. Hazardous or bio-resistant liquid wastes have been abated with success through Advanced Oxidation Technologies (AOTs), which have as a main feature the generation of hydroxyl radical (HO[•]) during the oxidative process. This radical has been considered to be the main oxidant species, having a standard reduction potential of 2.7 V in acid solution and 1.8 V in neutral solution (Buxton et al., 1988).

One of the most useful technologies for the treatment of hazardous liquid wastes is the photo-Fenton process. In fact, this process presents a remarkable performance in the treatment of wastewater containing toxic or non-biodegradable organic compounds. The photo-Fenton process does not generate biological sludge and enables the oxidation of organic compounds in the presence of high chloride concentration. The photo-irradiated Fenton reaction has been successfully applied to the degradation of gasoline in a saline wastewater (Moraes et al., 2004). According to the authors this process may be represented by the following reactions:

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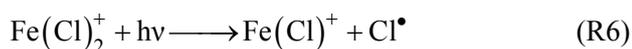
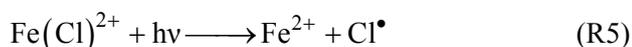


Reactions R1 and R2 are responsible for the production of the hydroxyl radical that can oxidize organic compounds, according to R3. The efficiency of the photo-Fenton process has been attributed to the reactivity of HO^\bullet , which can react with several species presented in the liquid phase. This is a problem since hydroxyl radicals are lost by undesirable reactions. The reaction with hydrogen peroxide is one way to make the hydroxyl radicals disappear from the aqueous medium, since hydrogen peroxide competes with organic compounds in reaction with HO^\bullet (Wang & Lemley, 2001). The rate of disappearance of the HO radical is increased in systems containing Cl^- or SO_4^{2-} . In presence of Cl^- , HO^\bullet reacts yielding the radical $\text{Cl}_2^{\bullet-}$.



Studies of Jayson & Parsons (1973), Pignatello (1992), Vione et al. (2005) and Machulek Jr. et al. (2006) have pointed Reaction 4 as one of the main means of scavenging HO^\bullet in organic compounds photooxidation systems containing chloride ion.

The $\text{Cl}_2^{\bullet-}$ radicals are also formed due to the reactions of Cl^\bullet with Cl^- produced during the photolysis of Fe^{3+} -Cl complexes (R5 and R6).



According to studies developed by Nadtochenko & Kiwi (1998 a,b) and Machulek Jr. et al. (2006), a photo-Fenton reaction system containing chloride tends to produce Cl^\bullet in instead of HO^\bullet by the following reasons: (1) the formation equilibrium constants of $\text{Fe}(\text{Cl})^{2+}$ and $\text{Fe}(\text{Cl})_2^+$ at 25°C are higher than hydrolysis constants of $\text{Fe}(\text{OH})^{2+}$ and

$\text{Fe}(\text{OH})_2^+$, i.e., respectively, 5.34 M^{-1} , 1.82 M^{-2} , $1.9 \times 10^{-3} \text{ M}$ and $2.5 \times 10^{-9} \text{ M}^2$; (2) in pH lower than 3, $\text{Fe}(\text{Cl})^{2+}$ and $\text{Fe}(\text{Cl})_2^+$ are the most chromophore species at 347 nm, with the molar absorption coefficients of $2300 (\text{M cm})^{-1}$ and $2740 (\text{M cm})^{-1}$, against $800 (\text{M cm})^{-1}$ and $550 (\text{M cm})^{-1}$ related to $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})_2^+$ hydro-complexes; (3) the quantum yield, measured at 247 nm, is also favorable to formation of Cl^\bullet with a value of 0.5 against 0.21 obtained for the $\text{Fe}(\text{OH})^{2+}$.

Investigating the photodegradation of 2,4-dichlorophenoxyacetic acid in saline medium, Pignatello (1992) carried out the photodecomposition of hydrogen peroxide in the absence of 2,4-D, conducted in a climate-controlled room at 21 °C. In this medium, there was a source of light with irradiance of $0.034\text{-}0.036 \text{ mW/cm}^2$ in the near-UV (290-385 nm) and $1.2\text{-}1.3 \text{ mW/cm}^2$ in the visible region (400-700 nm) spectra. In relation to the hydrogen peroxide photodecomposition the following observations were pointed out: (1) part of the H_2O_2 is consumed in the reaction with Cl^- , which reacts with the HO^\bullet radical, scavenging it; (2) the decomposition of H_2O_2 is accelerated by irradiation; (3) the pseudo-first-order rate constant when $[\text{Fe}^{3+}] = 1 \text{ mM}$ and $[\text{H}_2\text{O}_2] = 100 \text{ mM}$, determined in the photo-irradiated system, was verified as being 1.35 times greater than a similar dark reaction, and; (4) in the presence of excess hydrogen peroxide, $[\text{Fe}^{2+}]$ is small in relation to $[\text{Fe}^{3+}]$.

The thermal dependency of the degradation of 2,4-D in a $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system has also been studied by Lee et al. (2003). These authors elaborated a simplified mechanism based on Barb et al. (1951) and Walling and Weil (1974) whereby the decomposition of hydrogen peroxide may be expressed as a pseudo-first-order reaction in which the kinetic constant is a function of $[\text{Fe}^{3+}]$. The mechanism was proposed considering a steady-state regime for the formation of HO^\bullet . The consequence of this hypothesis is that the concentrations of Fe^{2+} and Fe^{3+} exist in a constant ratio during most of the reaction. This result is in accordance to what Pignatello (1992) observed for a photo-irradiated system with peroxide in excess. Therefore, the objective of this work is to study the process of the photodecomposition of H_2O_2 in the presence of Fe^{3+} and a high concentration of Cl^- . Furthermore, a simple kinetic model based in the concentrations of $\text{Fe}(\text{III})$, H_2O_2 and temperature is applied to describe the decomposition behavior. The photochemical

reaction was conducted in presence of salt at concentration of 60 g.L^{-1} because similar values are often found in specific streams of some agrochemical industries (Luna, 2005).

EXPERIMENTAL SECTION

Apparatus

Experiments were carried out in a 1000 cm^3 jacketed stirred glass tank with an inner diameter of 10 cm (Figure 1). The system temperature was

controlled by a thermostatic bath from Micronal S.A. The reactor was irradiated from the center by a medium-pressure 400W Hg lamp (8 cm long by 2 cm wide), which was purchased from Hangzhou Elc Corp. Factory. This lamp was placed in a quartz immersion well, with a diameter of 5 cm, located in the center of the reactor. The hydrogen peroxide was acquired from Degussa while ferric sulfate and sodium chloride, hydrochloric acid, sulfuric acid and sodium thiocyanide were purchased from Merck & Co. Inc. All chemicals used in the present work were of analytical grade and used without further purification.

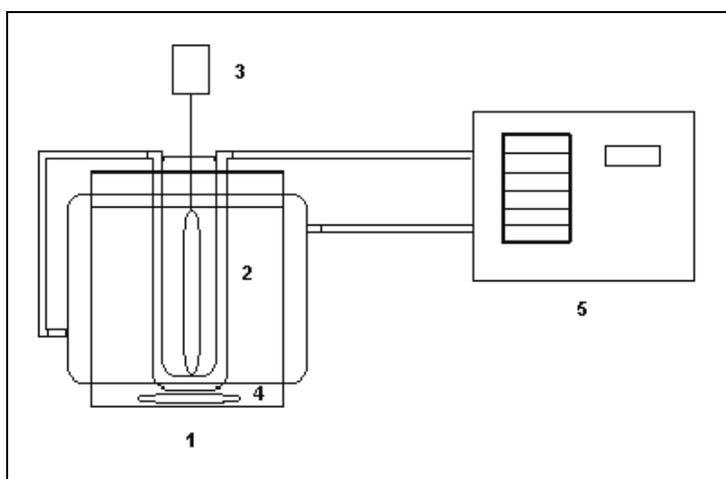


Figure 1: 1 reactor; 2 quartz immersion well; 3 Hg lamp and source; 4 magnetic bar; 5 thermostatic bath.

Analysis

The hydrogen peroxide concentration was followed by reaction with permanganate in acid medium. The ferric ion was determined by reaction with a large excess of thiocyanide (SCN^-) in acid medium, producing a red complex that may be quantified by spectrophotometry (Jeffery et al., 1991).

Experimental Procedure

Initially, the reactor was loaded with 600 mL of water, and then the initial pH was adjusted to 3.0 by adding some drops of sulfuric acid (H_2SO_4). The salinity was set to the desired value by addition of sodium chloride (NaCl). Before starting the addition of hydrogen peroxide, the solution was stirred in the system to promote the stabilization of the temperature at 30°C , and the light was turned on to

guarantee the maximum emission during the batch. Afterwards, 100 mL of a solution of Fe^{3+} was fed together with 100 mL of a solution of the hydrogen peroxide (H_2O_2). This moment was considered as the beginning of the reaction. All experiments of this work were carried out with ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) at $\text{pH} = 3$ and temperature of 30°C .

RESULTS AND DISCUSSION

Some experiments were first carried out to qualitatively evaluate the influence of UV light, NaCl and the total iron content on the photodecomposition of H_2O_2 . The experimental device described in Figure 1 was used to treat individually 800-mL batches comprising solutions of H_2O_2 (400 mM) containing NaCl (0 and 60 g.L^{-1}) and Fe^{3+} (0 and 2 mM) at a temperature of 30°C . Reactions with and without light were performed.

These reactions were conducted with initial pH of 3 because this is the optimal value for the photodegradation of several organic compounds and also to assure that the iron ions are soluble in the liquid medium. Moreover, in this pH value, the complex ions FeOH^{2+} and FeOH_2^+ , both photosensitive and involved in the photoreduction of Fe^{2+} , reached the highest concentrations in aqueous phase (Knight & Sylva, 1975; Faust & Hoigné,

1990). Thus, it is necessary to realize what happens to the hydrogen peroxide under these conditions. In Figure 2, the experiments 1a and 1b were performed in the absence of UV light, while all others (2a, 2b, 2c and 2d) were carried out in the presence of UV radiation. Table 1 describes the experimental parameters established in these assays, as far as the use of UV light and the contents of NaCl and/or Fe^{3+} are concerned.

Table 1: Parameters related to curves shown in Figure 1.

Experiments	UV light	NaCl (g.L^{-1})	$[\text{Fe}^{3+}]$ (mM)
1a (\diamond)	without	0	0
1b (\square)	without	60	0
2a (\square)	with	0	0
2b (\blacktriangle)	with	0	2
2c (\diamond)	with	60	0
2d (\bullet)	with	60	2

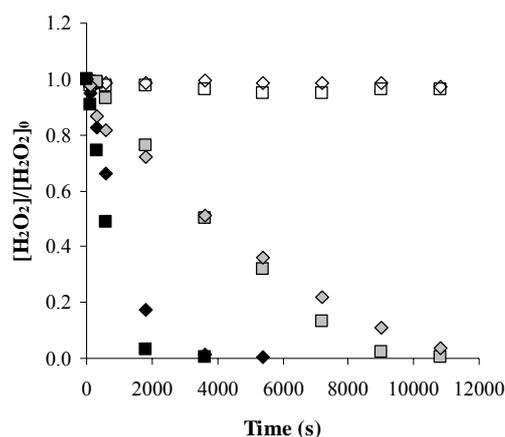


Figure 2: Dimensionless hydrogen peroxide profiles of batches carried out at 30 °C. Experimental conditions (system illumination, concentration of salt and Fe^{3+} , respectively): 1a (\diamond) without light, 0.0 g.L^{-1} , 0.0 mM; 1b (\square) without light, 60.0 g.L^{-1} , 0.0 mM; 2a (\square) with light, 0.0 g.L^{-1} , 0.0 mM; 2b (\blacktriangle) with light, 0.0 g.L^{-1} , 2.0 mM; 2c (\diamond) with light, 60.0 g.L^{-1} , 0.0 mM; 2d (\bullet) with light, 60.0 g.L^{-1} , 2.0 mM.

The curves presented in Figure 2 reflect the strong influence of the UV radiation upon the reaction of H_2O_2 photodecomposition. The four photo-irradiated runs may be evaluated in pairs. Comparing curves 2a and 2c with curves 2b and 2d, it can be observed that the presence of iron does increase the rate of photodecomposition of H_2O_2 . Moreover, each pair of curves can be individually compared with regards to the effect of NaCl. In that respect, three sets of data, namely 1a-1b, 2a-2c and 2b-2d, are analyzed in terms of the absence (first component in each set) and presence (second component in each set) of salt. These curves show a negligible effect of salt upon the peroxide

photodecomposition, especially for the reactions in the dark (set 1a-1b).

The weak effect of chloride observed on the H_2O_2 photodecomposition is opposite to the one found on the photo-oxidation of organic composites. As stated by several researchers (Pignatello, 1992; Moraes et al., 2004), chloride ions inhibit the photo-oxidation of organic compounds in aqueous phase, despite having only a slight influence on the reactivity of the Fe^{3+} ions. For this reason, the inhibition of the consumption of 2,4-D occurs mainly due to the undesirable pathways of consumption of the hydroxyl radical.

In order to describe better the photodecomposition of hydrogen peroxide, a series of experiments was performed, evaluating the concentration dependence of Fe^{3+} , H_2O_2 and temperature in a saline aqueous solution. A volume of 800 mL of a peroxide solution was irradiated from the center by means of the mercury vapor lamp according to the system described in Figure 1. A 2^3 experimental planning was employed, with 8 points corresponding to the extremities of the domain and 3 central points corresponding to the average values of each interval of concentration and temperature studied. The variables considered in the present

study were $[\text{Fe}^{3+}]$ (1.0 and 2.5 mM), $[\text{H}_2\text{O}_2]$ (230 and 630 mM) and temperature (20 and 50 °C). All runs were started with an initial pH of 3 and a concentration of NaCl of 60 g.L⁻¹. The parameters utilized in the kinetic study are shown in Table 2.

The experiments were developed in this particular domain of concentration and temperature because these parameters are very common in several oxidative processes.

The curves presented in Figures 3, 4 and 5 show the experiments carried out at the plus level (630 mM), minus level (230 mM) and central points of the peroxide concentration, respectively.

Table 2: Experimental planning applied to the foto-Fenton decomposition of H_2O_2 with the parameters $[\text{Fe}^{3+}]$, $[\text{H}_2\text{O}_2]$ and temperature

Level	$[\text{Fe}^{3+}]$ (mM)	$[\text{H}_2\text{O}_2]$ (mM)	T (°C)
(-)	1.0	230	20
(+)	2.5	630	50
central	1.75	430	35

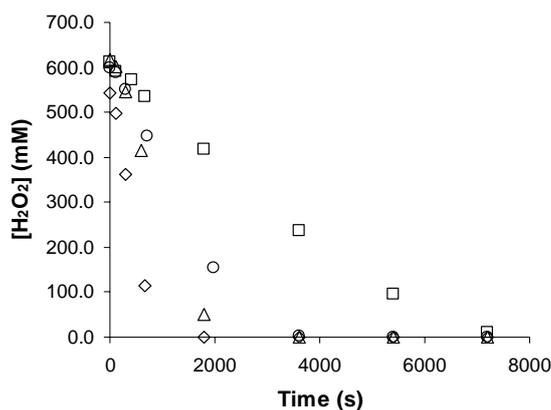


Figure 3: Curves of the photodecomposition of H_2O_2 carried out at 630mM of H_2O_2 . Levels: \square (-+-), \diamond (++)+, \triangle (-++), \circ (++-). These experiments show the influence of Fe(III) and temperature on the photo degradation profiles of two pairs of reactions.

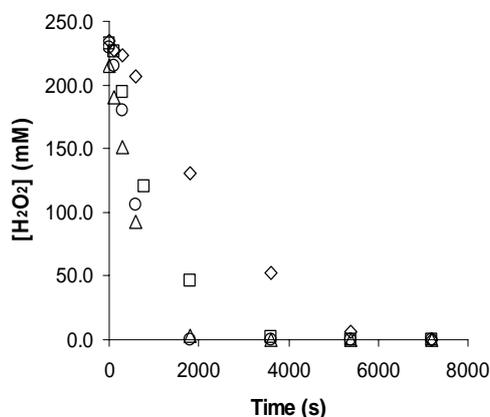


Figure 4: Curves of the photodecomposition of H_2O_2 carried out at 230mM of H_2O_2 . Levels: \square (+--), \diamond (---), \triangle (---+), \circ (+-+). These experiments show the influence of Fe(III) and temperature on the photo degradation profiles of two pairs of reactions.

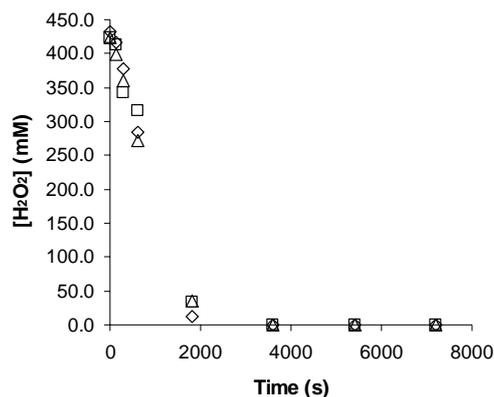


Figure 5: Curves of the photodecomposition of H₂O₂ carried out at central point.

An overview of Figures 3 and 4 enables the positive influences of the Fe(III) concentration and temperature on the H₂O₂ degradation process to be revealed. The central points represented in Figure 5 give an estimation of the data accuracy.

In almost all experiments a constant ratio between [Fe²⁺] and [Fe³⁺] was obtained, confirming

a steady-state (SS) behavior. In fact, the concentration of Fe³⁺ changes strongly at the beginning of the reaction but rapidly reaches a value which remains constant during most of the reaction. The molar ratio [Fe³⁺]_{ss}/[Fe³⁺]₀ has been calculated as an average value for all experiments and is presented in Table 3.

Table 3: Values of molar ratio of Fe³⁺ for all experiments

Levels of Fe ³⁺ , H ₂ O ₂ and temperature	*[Fe ³⁺] _{ss} /[Fe ³⁺] ₀	Levels of Fe ³⁺ , H ₂ O ₂ and temperature	*[Fe ³⁺] _{ss} /[Fe ³⁺] ₀
(+--)	0.628	(---)	1.06
(++-)	0.784	(-+-)	0.947
(+++)	0.956	Central	0.811
(+-+)	1.036	Central	0.862
(-++)	1.09	Central	0.834
(--+)	0.904	-	-

*The term [Fe³⁺]_{ss} represents the concentration of the iron (III) ion in the steady state.

THE KINETIC MODEL

Simplified models are useful when comparing different reactions in similar reactors and for calculations in process design purposes. This work is especially interested in obtaining a model to describe the photodecomposition of H₂O₂ as a function of the following properties: reactor volume, concentration of Fe³⁺, concentration of H₂O₂ and temperature.

According to Calvert and Pitts (1966), for homogeneous photochemical reactions under monochromatic light, the overall quantum yield (ϕ_λ) may be used:

$$\phi_\lambda = \frac{\left[\begin{array}{c} \text{Volumetric rate of appearance} \\ \text{or disappearance of a given} \\ \text{molecule with monochromatic light} \end{array} \right]}{\left[\begin{array}{c} \text{Local volumetric rate of} \\ \text{monochromatic photon absorption} \end{array} \right]} = \frac{R_\lambda}{e_\lambda^a} \left[= \right] \frac{\text{mol.m}^{-3}.\text{s}^{-1}}{\text{Einstein.m}^{-3}.\text{s}^{-1}} \quad (1)$$

In Eq. 1, the local volumetric rate of photon absorption (e_λ^a) may be represented by the simplest model applied to an annular reactor with monochromatic irradiation, which is *The Linear Source with Emission in Parallel Planes* (Cassano and Alfano, 1989):

$$e_\lambda^a = \mu_\lambda \frac{E_{0,\lambda}}{2\pi L_L} \frac{1}{r} \exp \left[- \int_{r_0^*}^{r^*} \mu_\lambda dr' \right] \quad (2)$$

Here, the energy rate emitted by the lamp is the term $E_{0,\lambda}$ (Einstein. s⁻¹), L_L is the length of the lamp (m), μ_λ is the attenuation coefficient (m⁻¹) and r is the distance of a generic point P(r,ϕ,z) from the lamp.

In practical applications, when the source is polychromatic, the *quantum efficiency* concept is very useful (Braun et al., 1986):

$$\eta = \frac{\left[\text{Volumetric rate of appearance or disappearance of a given molecule} \right]}{\left[\text{Volumetric rate of photo absorption} \right]} = \frac{R_{\sum\lambda}}{\int_{\lambda} e_{\lambda}^a d\lambda} \left[= \right] \frac{\text{mol.m}^{-3} \cdot \text{s}^{-1}}{\text{Einstein.m}^{-3} \cdot \text{s}^{-1}} \quad (3)$$

In Eq. 3, $\int_{\lambda} e_{\lambda}^a d\lambda$ is obtained by integrating Eq. 2 over all interval of wavelength that promotes photochemical reaction. The numerator in Eq. 3, $R_{\sum\lambda}$, was chosen to represent the observed volumetric rate due to the action of all absorbed photons in the band which effectively yields reaction. The wavelength range used to promote the photochemical reaction goes from the lower limit of emission of the lamp up to the highest wavelength absorbed by the complex ion FeOH^{2+} , i.e., 220 to 420 nm (Knight & Sylva, 1975; Faust & Hoigné, 1990; Luna, 2005).

The mass conservation equation may be obtained considering that the reactor is closed to the gas and liquid phase (a batch reactor). Moreover, some hypotheses must be assumed: (i) the fluid is Newtonian with constant physical properties (μ , ρ , D_i , etc.) during most part of the reaction time; (ii) the symmetry is angular; (iii) the axial and radial diffusions are negligible; (iv) the reactor is well stirred, i.e., the hydrogen peroxide concentration is only time-dependent. Using these assumptions the mass conservation equation may be written as follows:

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = R_{\text{H}_2\text{O}_2} \quad (4)$$

In Eq.4, the term $R_{\text{H}_2\text{O}_2}$ groups thermal and photochemical steps of reaction. It was observed experimentally that the photodecomposition rate is half-order dependent with respect to the peroxide concentration and of first order in relation to the iron concentration in the steady state.

Under the conditions applied in this work, the

presence or absence of chloride does not affect significantly the reaction (Figure 2). Thus, this variable was not considered in the kinetic model. The photochemical and thermal effects were incorporated in the apparent kinetic constant. The mass conservation equation, Eq. 4, can now be rewritten taking into account the observed reaction orders with respect to Fe (III) and H_2O_2 concentrations.

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = k [\text{Fe(III)}]_{\text{SS}} [\text{H}_2\text{O}_2]^{1/2} \quad (5)$$

where $[\text{Fe(III)}]_{\text{SS}}$ is the mean value of the Fe^{3+} concentration. Eq. 5 may be solved considering that, for $t=0$, $[\text{H}_2\text{O}_2] = [\text{H}_2\text{O}_2]_0$. Thus,

$$[\text{H}_2\text{O}_2] = \left(\frac{\sqrt{[\text{H}_2\text{O}_2]_0} - k}{[\text{Fe(III)}]_{\text{SS}} t} \right)^2 \quad (\text{mol} \cdot \text{m}^{-3}) \quad (6)$$

The kinetic rate constants were calculated to each experiment and plotted against the inverse of the temperature to determine the apparent activation energy and the frequency factor. The frequency factor and activation energy observed were calculated as $277093 \text{ m}^{3/2} \cdot \text{mol}^{-1/2} \cdot \text{s}^{-1}$ and $27.6 \text{ kJ} \cdot \text{mol}^{-1}$, respectively. The apparent activation energy is coherent in order of magnitude with experimental results published in literature (Lee et al., 2003).

Finally, the resulting model expressed by Eq. 6 was used to correlate all experimental data depicted in figures 2, 3 and 4. Figure 6 shows the calculated concentrations of H_2O_2 against experimental values.

Figure 6 shows that the performance of the kinetic model proposed herein is satisfactory for the photodecomposition of hydrogen peroxide in saline medium throughout the whole range of concentration and temperature studied. A correlation coefficient of 98% for the whole experimental data set, with an explicit model, was obtained. The absolute deviations for the data set are symmetrically distributed around zero.

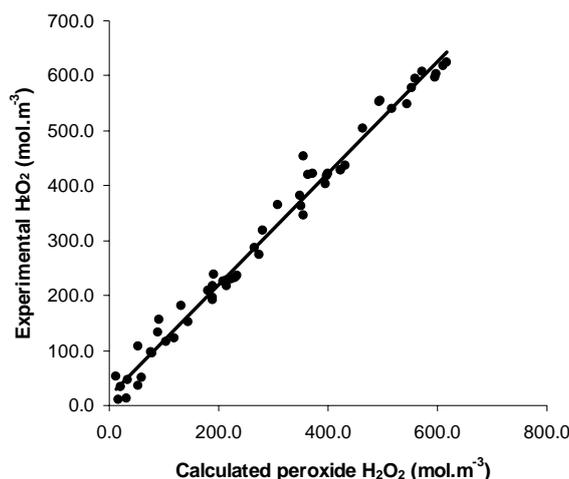


Figure 6: Experimental versus calculated photodecomposition data of H_2O_2 .

CONCLUSION

Under the conditions employed, it has been observed that the influence of chloride ions upon the photodecomposition of hydrogen peroxide can be neglected. The behavior of the hydrogen peroxide photodecomposition has been determined experimentally. The measurements have been satisfactorily correlated through the kinetic model, which incorporates both temperature and photon dependences in the estimated constant. In practical systems of photodegradation of organic compounds, the photochemical component of the peroxide decomposition rate cannot be avoided. However, the thermal component may be minimized through a more rigid control of temperature.

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REFERENCES

- Alfano, O.M. and Cassano, A.E., Photoreactor Design. In: Handbook of Heat and Mass Transfer, v 3, Gulf Publishing Company (Book Division), 583 (1989).
- Barb, W.G., Baxendale, J.H. and Hargrave, K.R., Reactions of Ferrous and Ferric Ions with

Hydrogen Peroxide, *Trans. Faraday Soc.*, 47, 462 (1951).

- Braun, A.M., Maurette, M.T. and Oliveros, E., *Technologie Photochimique*. Presses Polytechniques Romandes, Paris (1986).
- Buxton, G.V., Greenstock, C.L., Helman, W.P. and Ross, A.B., Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms and Hydroxyl Radicals ($\cdot\text{OH}/\text{O}^-$) in Aqueous Solution, *J. Phys. Chem. Ref. Data*, 17, 513 (1988).
- Calvert, J.G., Pitts Jr., J.N., *Photochemistry*. Wiley, New York (1966).
- Faust, B. C., Hoigné, J. Photolysis of Fe(III)-Hydroxy Complexes as Sources of OH Radicals in Clouds, Fog and Rain. *Atmospheric Environment*, 24A(1), 79, 1990.
- Jayson, G. G., Parsons, B. J. Some Simple, Highly Reactive, Inorganic Chlorine Derivatives in Aqueous Solutions, *J. Chem. Soc. Faraday Trans.*, 69, 1597 (1973).
- Jeffery, G. H., Bassett, J., Mendham, J., Denney, R. C. *Vogel's Textbook of Quantitative Chem. Anal.*, 5^a Edition, Longman Scientific & Technical, Burnt Mill, England, 690 (1991).
- Knight, R. J., Sylva, R. N. Spectrophotometric investigation of iron(III) hydrolysis in light and heavy water at 25°C. *J. Inorg. Nucl. Chem.*, 37, 779 (1975).
- Luna, A. J. Degradação Fotoquímica do Fenol, 2,4-Diclorofenol e Ácido 2,4-Diclorofenoxiacético em Meio de Alta Salinidade. Thesis of doctorate from University of Sao Paulo, (2005).
- Lee, Y., Lee, C., Yoon, J., High Temperature

- Dependence of 2,4-Dichlorophenoxyacetic Acid Degradation by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ System, *Chemosphere*, 51, 963 (2003).
- Machulek Jr., A., Vautier-Giongo, C., Moraes, J. E. F., Nascimento, C. A. O., Quina, F. H. Laser Flash Photolysis Study of the Photocatalytic Step of the Photo-Fenton Reaction in Saline Solution, *Photochemistry and Photobiology*, 82, 208 (2006).
- Moraes, J.E.F., Quina, F.H., Nascimento, C.A.O., Silva, D.N. and Chiavone-Filho, O. Treatment of Saline Wastewater Contaminated with Hydrocarbons by the Photo-Fenton Process, *Env. Sci. Technol.*, 38, 1183 (2004).
- Nadtochenko, V., Kiwi, J. Photolysis of $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{Cl})^{2+}$ in aqueous solution. Photodissociation kinetics and quantum yields. *Inorg. Chem.* 37, 5233 (1998a).
- Nadtochenko, V., Kiwi, J. Primary Photochemical Reactions in the Photo-Fenton System with Ferric Chloride. 1. A Case Study of Xylidine Oxidation as a Model Compound, *Environ. Sci. Technol.*, 32, 3273 (1998b).
- Pignatello, J.J. Dark and Photoassisted Fe^{3+} -Catalyzed Degradation of Chlorophenoxy Herbicides by Hydrogen Peroxide, *Environ. Sci. Technol.*, 26, 944 (1992).
- Vione, D., Maurino, V., Minero, C., Calza, P., Pelizzetti, E. Phenol Chlorination and Photochlorination in the Presence of Chloride Ions in Homogeneous Aqueous Solution, *Environ. Sci. Technol.*, 39, 5066 (2005).
- Walling, C., Weil, T. The ferric ion catalyzed decomposition of hydrogen peroxide in perchloric acid solution, *Int. J. Chem. Kinet.*, 6, 507 (1974).
- Wang, Q., Lemley, A. T. Kinetic Model and Optimization of 2,4-D Degradation by Anodic Fenton Treatment, *Environ. Sci. Technol.*, 35, 4509 (2001).