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Talanta 66 (2005) 86–91

Talanta

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Simple and fast spectrophotometric determination of H_2O_2 in photo-Fenton reactions using metavanadate

Raquel F. Pupo Nogueira*, Mirela C. Oliveira, Willian C. Paterlini

UNESP – São Paulo State University, Institute of Chemistry of Araraquara, P.O. Box 355, 14801-970 Araraquara, SP, Brazil

Received 20 May 2004; received in revised form 29 September 2004; accepted 5 October 2004
Available online 23 November 2004

Abstract

This work proposes a spectrophotometric method for the determination of hydrogen peroxide during photodegradation reactions. The method is based on the reaction of H_2O_2 with amonium metavanadate in acidic medium, which results in the formation of a red-orange color peroxovanadium cation, with maximum absorbance at 450 nm. The method was optimized using the multivariate analysis providing the minimum concentration of vanadate (6.2 mmol L^{-1}) for the maximum absorbance signal. Under these conditions, the detection limit is 143 μmol L^{-1}. The reaction product showed to be very stable for samples of peroxide concentrations up to 3 mmol L^{-1} at room temperature during 180 h. For higher concentrations however, samples must be kept refrigerated (4 °C) or diluted. The method showed no interference of Cl^- (0.2–1.3 mmol L^{-1}), NO_3^- (0.3–1.0 mmol L^{-1}), Fe^{3+} (0.2–1.2 mmol L^{-1}) and 2,4-dichlorophenol (DCP) (0.2–1.0 mmol L^{-1}). When compared to iodometric titration, the vanadate method showed a good agreement. The method was applied for the evaluation of peroxide consumption during photo-Fenton degradation of 2,4-dichlorophenol using blacklight irradiation.

Keywords: Hydrogen peroxide; Vanadate; Photo-Fenton; 2,4-Dichlorophenol; Spectrophotometry; Degradation

1. Introduction

Hydrogen peroxide is a versatile chemical and strong oxidant, with a standard electrode potential of 1.763 V at pH 0 (Eq. 1) [1].

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O, \qquad E^\circ = 1.763\,V \qquad (1)$$

While main industrial applications of H_2O_2 are bleaching of textiles and paper, important environmental applications are the removal of inorganic and organic pollutants from wastewater. The use of H_2O_2 as $^\bullet OH$ generating agent in advanced oxidation processes (AOPs) such as ozonation (O_3/H_2O_2/UV) [2], hydrogen peroxide photolysis (UV/H_2O_2) [3] and Fenton processes (Fe^{2+}/H_2O_2) [4] improves its effectiveness, due to the higher oxidizing power of $^\bullet OH$ species ($E^\circ = 2.730$ V for $^\bullet OH$, H^+/H_2O) [5].

In the last decades, the AOPs have been intensively studied for the application in the treatment of water and wastewaters, and remediation of contaminated soils. They are considered good alternatives to conventional treatment processes due to its ability to degrade a great variety of organic pollutants [6–8].

Among AOPs, the Fenton and photo enhanced Fenton reaction (photo-Fenton process), have attracted great interest in the last years. Based on the decomposition of H_2O_2 catalyzed by Fe^{2+} (Eq. 2), they are attractive for industrial application due to its high oxidation power, simplicity of operation and low costs especially when solar light is applied for regeneration of Fe^{2+}. In the established cycle additional hydroxyl radicals are generated (Eq. 3) [9,10]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \qquad (2)$$

$$FeOH^{2+} + h\nu \rightarrow Fe^{2+} + {}^\bullet OH \qquad (3)$$

The destruction of organic contaminants using ferrioxalate as source of iron in photo-Fenton processes has been success-

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* Corresponding author. Tel.: +55 16 3301 6606; fax: +55 16 3322 7932.
E-mail address: nogueira@iq.unesp.br (R.F.P. Nogueira).

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doi:10.1016/j.talanta.2004.10.001

fully applied also under solar irradiation since it can absorb radiation up to 550 nm, employing considerable portion of the solar spectrum [11–14].

The residual peroxide concentration during degradation of organic compounds in AOPs is a very important parameter to evaluate. In Fenton and photo-Fenton processes, when H_2O_2 is completely consumed, which can happen in a very short time depending on the organic matter concentration, the degradation reaction practically stops making new additions of the oxidant necessary [12]. On the other hand, it can also act as $^{\bullet}OH$ scavenger when high concentrations are present, hindering the photodegradation reaction due to the lower oxidation power of the formed radical $HO_2^{\bullet}$:

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad (4)$$

Different methods have been used to measure H_2O_2 in AOPs during degradation of organic compounds. Among them, the most commonly used in photo-Fenton processes is the iodometric titration [15–17]. Spectrophotometric methods employing titanium sulfate or oxalate and *N*,*N*-diethyl-*p*-phenylenediamine (DPD) are also often reported in recent studies dealing with photo-Fenton degradation of organic contaminants [18,19]. While some methods such as DPD use high cost reagents, the iodometric titration is subjected to errors due to volatilization and hydrolysis of I_2, and air oxidation of I^-, besides of demanding longer time than a spectrophotometric determination. The permanganate titration is considered a reliable method for determination of H_2O_2. However, it is not possible to use the method in photo-Fenton reactions because Fe^{2+} reacts with permanganate interfering in the peroxide determination. The spectrophotometric determination of I_3^- generated in the reaction of I^- and H_2O_2 has been also reported [20]. However, the absorption maximum of I_3^- at $\lambda = 351$ nm limits its application in samples showing high absorbance in this region, frequently observed in the case of wastewaters.

Kosaka and co-workers [21] have compared different methods of H_2O_2 determination for the evaluation of AOP and found that the fluorimetric method is the most sensitive. Although various methods can reach very low detection limits, in the range of 0.77 μmol L^{-1} (DPD method) to 29 μmol L^{-1} (titanium colorimetric method), what is important for determination of peroxide in natural waters, the detection limit should not be decisive for the choice of a method for H_2O_2 measurement in AOP, since the concentrations used in these processes are usually in the range of milimol per liter. A fast, simple and low cost method can be very advantageous for the rapid determination of H_2O_2 during photodegradation reactions, allowing the evaluation and optimization of AOPs.

The formation of a red-orange color peroxovanadium cation in the reaction of H_2O_2 with metavanadate has been previously described in the application for the vanadium determination [22]:

$$VO_3^- + 4H^+ + H_2O_2 \rightarrow VO_2^{3+} + 3H_2O \quad (5)$$

However, the use of this reaction for the determination of peroxide in photo-Fenton degradation process was first reported by Oliveira and co-workers [23], using a flow injection spectrophotometric system.

In the present work, the spectrophotometric determination of hydrogen peroxide by the reaction with metavanadate in acidic medium (vanadate method) was studied. The optimum concentrations of vanadate and sulfuric acid for the application in determination of H_2O_2 in photo-Fenton processes were determined using the surface response multivariate analysis. The multivariate analysis has been extensively applied for determination of the best conditions of analytical methods using mostly the central composite design, generally a quadratic model in which the synergistic and antagonist effects between the variables are taken into account [24–26]. The interference of species such as chloride, nitrate, iron and a chlorophenol on the absorbance signal was evaluated. After optimization, the method was applied for H_2O_2 determination during the photodegradation of 2,4-dichlorophenol (DCP).

2. Experimental

2.1. Reagents and solutions

All the solutions were prepared with ultra pure (Millipore Milli-Q) water. H_2O_2 30% (w/w) from Merck was diluted to the required concentration. The concentration of the purchased solution was determined by titration with $KMnO_4$ (Merck) after appropriate dilution [27]. Potassium iodide and thiosulfate used in iodometric titration were purchased from Merck. 2,4-Dichlorophenol from Merck was used as model compound in photo-Fenton process. For the preparation of vanadate solution, 9 mol L^{-1} sulfuric acid (Mallinckrodt) was added slowly to ammonium metavanadate (NH_4VO_3 from Vetec) under magnetic stirring and at 50 °C until complete dissolution. After complete dissolution, the red color solution was cooled down and then diluted with deionized water to the desired concentration, resulting in a yellow color. Potassium ferrioxalate ($K_3Fe(C_2O_4)_3 \cdot 3H_2O$) was prepared by mixing one volume of a 1.5 mol L^{-1} $Fe(NO_3)_3 \cdot 9H_2O$ solution (Mallinckrodt) with three volumes of a 1.5 mol L^{-1} potassium oxalate (Merck). The green complex was recristalized three times for purification. All other reagents used were analytical grade.

All the waste solutions containing vanadium were stored for precipitation of vanadium by the addition of caustic soda ($NaOH/Na_2CO_3$) and proper disposal of the solid.

2.2. Chemical analysis

The iodometric titration was applied in order to compare with the vanadate method for H_2O_2 determination [27]. Spectrophotometric determinations were performed using a UV Mini 1240 spectrophotometer from SHIMADZU and 1 cm cells. Appropriate volume of a 0.060 mol L^{-1} vanadate stock solution and of sample were diluted in a 10 mL volumetric flask. The blank solution was prepared in the same way but in absence of H_2O_2. Total organic carbon (TOC) concentration was determined using a TOC analyzer (TOC-5000A SHIMADZU) for the evaluation of the photodegradation process. The TOC concentration includes the carbon content of the target compound, and the intermediates generated during the experiment. All TOC determinations were performed immediately after samples withdrawal to avoid further reaction.

2.3. Experimental design

The central composite design was applied to investigate the effect of vanadate and sulfuric acid concentrations in the absorbance signal, aiming the highest sensitivity with lowest possible concentrations. For this design, it was necessary to realize twelve experiments, in which the two variables were codified in five levels including four central points for statistical validity within the range −1.41 to +1.41, which corresponds to the concentration range of vanadate between 1.6 and 9.6 mmol L^{-1} and sulfuric acid between 0.058 and 0.080 mol L^{-1} for the determination of a 6.0 mmol L^{-1} H_2O_2 sample. These ranges were chosen based on previous results obtained in flow system [23] and on other preliminary tests in batch system. The equation used to quantitatively describe the method and draw the response surface was built based on the absorbance data obtained using STATISTICA software (SW7127999218G51).

2.4. Photodegradation experiments

The experiments of DCP photodegradation were realized using a 15 W blacklight lamp and an up flow photoreactor as described previously [12]. The photoreactor was operated in a recirculation mode using a peristaltic pump (Masterflex L/S-7524-45) at a flow rate of 40 mL min^{-1}. The average irradiance of the lamp of 25 W m^{-2} was measured using a radiometer (Cole Parmer 9811-50, 365 nm). The pH of DCP solution (500 mL) was adjusted to 2.8 by addition of H_2SO_4 3 mol L^{-1} before starting the experiments, i.e. the optimum pH value according to previous work [12]. While DCP solution was magnetically stirred, the adequate volumes of $Fe(NO_3)_3$ and H_2O_2 stock solutions were added immediately before start of irradiation.

3. Results and discussion

In order to evidence the formation of the peroxovanadium cation in the reaction of vanadate with H_2O_2 and to determine the wavelength of maximum absorption, UV–vis absorption spectra in the range of 200–800 nm were obtained for the mixture of H_2O_2/vanadate and compared to H_2O_2 and vanadate solutions. The vanadate solution, of light yellow color, turns to red-orange in the presence of peroxide and a strong absorption band at 450 nm is observed, indicating the formation of the peroxovanadium cation (Fig. 1). All the subsequent absorption measurements were realized at 450 nm.

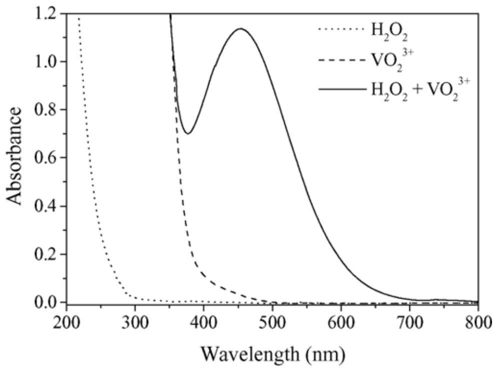

Fig. 1. Absorbance spectra of peroxide, vanadate and peroxide in the presence of vanadate solution.

3.1. Optimization of metavanadate and sulfuric acid concentration using multivariate analysis

Results obtained in previous work showed that the concentration of vanadate is an important parameter to consider for the best absorbance signal. The sulfuric acid is necessary once the reaction of vanadate and H_2O_2 occurs in acidic medium. However, it can influence the absorbance signal, besides of being advantageous to minimize its concentration. An optimum concentration in this context is considered to be the minimum concentration of the reagents that results in the highest response. For the optimization of vanadate and sulfuric acid concentration, the multivariate analysis, in the form of surface methodology response was used. It permits to determine the importance of each variable and the optimum concentration range of the involved reagents. The absorbance data were first analyzed in order to determine the second-order equation including term of interaction between the two variables. Eq. (6) was obtained based on the statistical analysis of the absorbance data (not shown).

$$Z = 98.76 + 6.61x_1 + 0.13x_2 + 0.49x_1x_2 - 5.92x_1^2 + 1.61x_2^2 \quad (6)$$

In Eq. (6), Z represents the response factor corresponding to the absorbance percentage, variation relative to the maximum absorbance measured. The variables x_1 and x_2 are the vanadate and sulfuric acid concentrations, respectively. The coefficients of the quadratic model were calculated by multiple regression analysis and indicate the importance of each variable, which depends on their signs and values. Positive coefficients indicate that the absorbance signal is increased in the presence of high concentrations of the respective variable within the range studied, while negative coefficients indicate that the absorbance signal is favored in the presence of low concentrations. Positive quadratic coefficients of x_1x_2 variables indicate a synergistic effect, while negative coefficients, an antagonistic effect between the variables.

An analysis of Eq. (6) shows that linear coefficient of x_1 has a high positive value (6.61) suggesting a strong absorbance signal for high vanadate concentrations. On the other hand, the negative coefficient of x_1^2 (−5.92), indicates that very high values of vanadate concentration result in a decrease of absorbance signal. The net effect can be observed in Fig. 2, which shows the surface response with a maximum relative absorbance percentage in positive codified range between 0.2 and 0.9. This corresponds to concentrations of vanadate between 6.2 and 8.3 mmol L^{-1}, decreasing above 8.3 mmol L^{-1}. Considering the low values of the coeffcents of x_2 and x_2^2, it can be concluded that the concentration of sulfuric acid plays a minor role on the absorbance signal. Based on these results, the concentrations chosen for the determination of H_2O_2 were 6.2 mmol L^{-1} vanadate, which is the lowest concentration within the optimum range determined, and 0.058 mol L^{-1} H_2SO_4, which is the lowest concentration of the tested range. The possibility to minimize reagents for maximum spectral response using multivariate analysis results in lower costs and reduced generation of sulfuric acid and vanadate residues.

In a next step, an analytical curve for peroxide in the range 0.0250–6.00 mmol L^{-1} (concentrations in 10 mL volumetric flask) was obtained using the optimized concentrations of vanadate and sulfuric acid (not shown). The obtained curve showed good linearity ($R = 0.9997$) up to the concentration of 5.00 mmol L^{-1} (absorbance = 1.46), with a slight deviation for 5.50 and 6.00 mmol L^{-1} concentration. The linear data fit ($n = 8$) resulted in the equation $\Delta A_{450} = 283\,[H_2O_2]$, where ΔA_{450} represents the difference of absorption between the sample and blank solution at 450 nm and $[H_2O_2]$, the H_2O_2 concentration (mol L^{-1}). The slope of the curve, giving the molar absorptiviy ε is 283 ± 2 mol L^{-1} cm^{-1}. The calculated detection limit (3× standard deviation of the curve/slope) is 143 μmol L^{-1}. The peroxide concentrations can be then calculated by the following relation:

$$\Delta A_{450} = 283[H_2O_2]\frac{V_1}{V_2} \tag{7}$$

where V_1 is the volume of aliquot taken for analysis (mL) and V_2 is the final volume to which the aliquot V_1 is diluted (mL) before absorbance measurement.

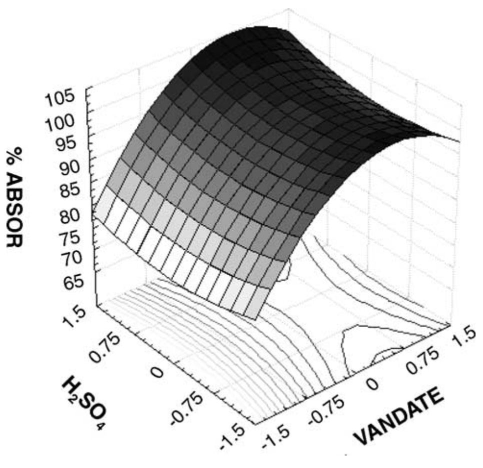

Fig. 2. Response surface of quadratic model for vandate absorption as a function of sulfuric acid and vanadate concentration.

It is important to note that although the linear range of the calibration curve was up to 5.00 mmol L^{-1}, higher peroxide concentrations can be determined after appropriate dilution of the sample, avoiding absorbance values above 1.5.

3.2. *Comparison between vanadate and iodometric method*

Considering that the iodometric titration is one of the most used methods for the determination of H_2O_2 in AOP [16,17], it was used for the comparison with the proposed method. Both methods were applied for the determination of H_2O_2 in samples taken from DCP photo-Fenton degradation. A solution containing initially 1.0 mmol L^{-1} DCP, 1.5 mmol L^{-1} ferrioxalate and 15 mmol L^{-1} H_2O_2 was irradiated and 20.0 mL samples were taken at 0, 5, 10 and 20 min reaction, and used for H_2O_2 determination by iodometric titration and by spectrophotometric vanadate method. The average result ($n = 3$) obtained for each sample by both mehtods is shown in Table 1. Although the results obtained by the vanadate method are something lower than that obtained by iodometric titration, there is a good agreement between the two methods. This fact shows clearly the applicability of the vanadate method in photo-Fenton reactions.

3.3. *Optical stability of the reaction products and possible interferences*

The optical stability of the VO_2^{3+} formed in the reaction of peroxide and vanadate was evaluated using 4.00 mL peroxide samples of concentrations between 1.00 and 12.0 mmol L^{-1}, which were diluted to 10.0 mL after addition of 1.6 mL of 60 mmol L^{-1} vanadate solution. It can be

Table 1

Concentration of hydrogen peroxide determined by iodometric titration and vanadate method in samples taken from 1.0 mmol L^{-1} DCP photodegradation in the presence of 1.5 mmol L^{-1} FeOx and 15 mmol L^{-1} H_2O_2 (initial concentrations)

Sample	Reaction time (min)	Iodometric[a] (mmol L^{-1})	Vanadate[a] (mmol L^{-1})
1	0	15.3 ± 0.02	14.4 ± 0.05
2	5	10.1 ± 0.02	9.63 ± 0.06
3	15	3.63 ± 0.01	3.78 ± 0.04
4	25	0.500 ± 0.01	<0.143

[a] $n = 3$.

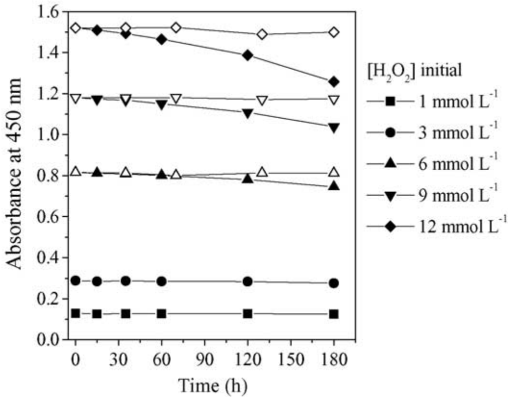

Fig. 3. Optical stability of vanadate/peroxide solution as a function of storage time at ambient temperature (solid symbols) and at 4 °C (open symbols).

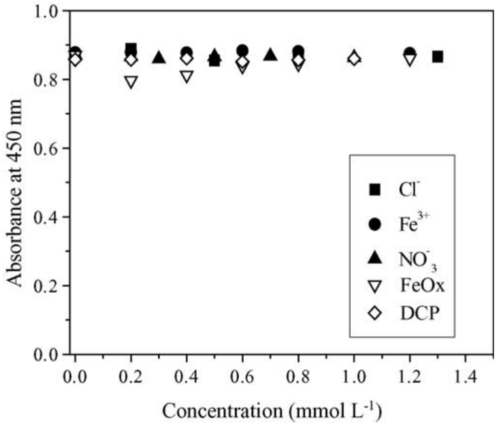

Fig. 4. Influence of different species on the absorbance signal of vanadate/peroxide solution.

observed in Fig. 3 that the reaction product is very stable since the measured absorbance of peroxide samples of 1 and 3 mmol L^{-1} remained unchanged during a period of 180 h at room temperature. However, as the peroxide concentration increases, the absorbance decreases gradually with storage time. While the absorbance of the reaction product of 6 and 9 mmol L^{-1} peroxide samples was stable up to 35 h, a decrease of 17% after 180 h was observed for the sample containing 12 mmol L^{-1} peroxide kept in the dark at room temperature. The appearance of yellow colour when excess peroxide is added was observed previously and attributed to the formation diperoxoorthovanadate (V) ions [28], what could explain the decrease of absorbance at 450 nm. On the other hand, all the solutions were very stable when kept at 4 °C. This stability permits to delay the peroxide determination in favor of other analysis which, due to the difficulty in stopping the Fenton reaction, are more sensitive to reaction time such as TOC and determination of the target compound concentration.

Some ions such as chloride and nitrate are usually present in wastewater samples, either from the acid used for pH adjustment or as a product of photodegradation of organochlorine and nitro compounds. Fe^{3+} added in the Fenton reaction is also present after photodegradation, due to the fast conversion of Fe^{2+} to Fe^{3+}. Therefore, the possible interference of these ions, including ferrioxalate, which is often used as source of iron, and DCP, was examined in order to evaluate the vanadate method. The following concentration ranges were tested: Cl$^-$ (0–1.3 mmol L^{-1}), NO$_3{}^-$ (0–1.0 mmol L^{-1}), Fe^{3+} (0–1.2 mmol L^{-1}), DCP (0–1.0 mmol L^{-1}) and ferrioxalate (0–1.2 mmol L^{-1}) in the presence of 6.0 mmol L^{-1} H_2O_2. The results shown in Fig. 4 indicate that no significant differences were observed in the absorbance signal obtained by the vanadate method in the presence of these species in the concentration ranges tested. The only exception is ferrioxalate at low concentrations of 0.2 and 0.4 mmol L^{-1}, where a decrease of about 9 and 7% in the absorbance values were observed, respectively. This decrease of the absorbance can be a consequence of the reduction of vanadium (V) to vanadium (IV) [29]. This small difference, however, causes only a small interference in the determination of H_2O_2 in the present application, since the ferrioxalate concentration used in photo-Fenton treatment is usually much higher, above 1 mmol L^{-1} [12,14].

3.4. Application: evaluation of peroxide consumption during photo-Fenton degradation of 2,4-dichlorophenol

The influence of DCP initial concentration (0.25 and 2.50 mmol L^{-1}) on the peroxide consumption during photodegradation was evaluated using the proposed method for peroxide determination using optmized concentrations of vanadate (6 mmol L^{-1}) and H_2SO_4 (0.058 mol L^{-1}). The initial concentrations of H_2O_2 and Fe^{3+} used were 11 and

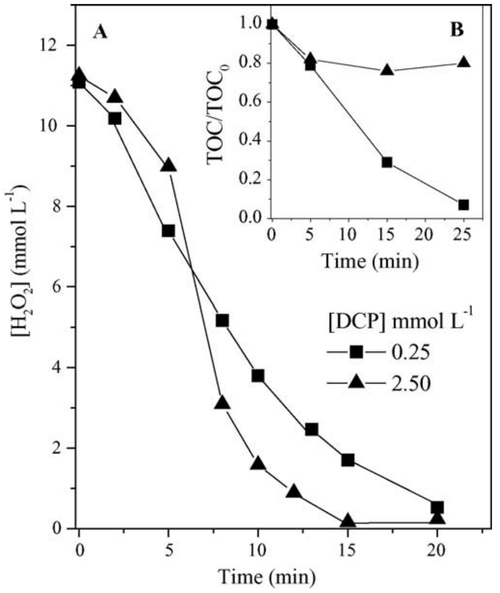

Fig. 5. Photodegradation of DCP. (A) Consumption of H_2O_2; (B) TOC removal. Initial concentrations: [H_2O_2] = 11 mmol L^{-1} and [Fe^{3+}] = 0.88 mmol L^{-1}.

0.88 mmol L^{-1}, respectively. Comparing the consumption rates of peroxide for the two different DCP concentrations, similar rates were observed at the begining of the reaction. However, as the reaction proceeds, sharper decrease of peroxide concentration is observed in the presence of the higher DCP concentration (Fig. 5A), a consequence of the higher content of organic matter. In this case, after total consumption of peroxide in 15 min, a lower mineralization percentage and stagnation of TOC removal reaction are observed (Fig. 5B). Similar behaviour was reported by Fallmann and co-workers (1999) [15] in the treatment of a mixture of herbicides, where higher consumption of H_2O_2 occured when TOC started to decrease. On the other hand, multiple additions of H_2O_2 during photodegradation reaction are reported to increase the processes efficiency [12].

4. Conclusions

A simple, fast and reliable determination of hydrogen peroxide using a cheap reagent, amonium metavanadate, is proposed. The multivariate analysis provided the definition of the minimum concentration of vanadate for the maximum absorbance signal, found to be 6.2 mmol L^{-1}. Furthermore, it was also found that sulphuric acid concentration plays minor role on the absorbance signal, therefore the lowest concentration tested was used (0.058 mol L^{-1}). Under these conditions, the ε is 283 M^{-1} cm^{-1} and the detection limit is 143 μmol L^{-1}. The reaction showed to be very stable for samples of peroxide concentrations up to 3 mmol L^{-1} once no significant change in the absorbance at 450 nm was observed at room temperature until 180 h. However, for higher concentrations, absorbance starts to decrease after 15 min, what can be avoided keeping the solutions refrigerated at 4 °C, or by dilution of the sample. The method showed no significant interference of Cl^- (0.2–1.3 mmol L^{-1}), NO_3^- (0.3–1.0 mmol L^{-1}), Fe^{3+} (0.2–1.2 mmol L^{-1}), FeOx 0.2–1.2 mmol L^{-1}) and DCP (0.2–1.0 mmol L^{-1}). When compared to iodometric titration, the values determined by the vanadate method in a shorter time are in good agreement and opens the possibility of sample storage for further analysis. The method was applied for the evaluation of peroxide consumption during photodegradation of DCP. The decrease of H_2O_2 concentration until total consumption after 15 min irradiation limited the degradation reaction for 2.50 mmol L^{-1} DCP. The demand for H_2O_2 depends on the concentration and structure of the contaminants present on the wastewater and therefore will determine a considerable part of the treatment costs. In this regard, the proposed method can be very useful due to the fast and simple determination of H_2O_2.

Acknowledgements

The authors thank FAPESP for the financial support of this work (02/00737-9) and scholarship of W.C. Paterlini (proc. no. 00/08870-4), and to CNPq for the scholarship of M.C. Oliveira. The authors thank also Dr. P. Hammer for the revision of the manuscript.

References

[1] S.G. Bratsch, J. Phys. Chem. Ref. Data 18 (1989) 1.
[2] D. Vogna, R. Marotta, A. Napolitano, R. Andreozzi, M. d'Ischia, Water Res. 38 (2004) 414.
[3] S.R. Cater, M.I. Stefan, J.R. Bolton, A. Safarzadeh-Amiri, Environ. Sci. Technol. 34 (2000) 659.
[4] S. Meric, D. Kaptan, T. Olmez, Chemosphere 54 (2004) 435.
[5] P. Wardmann, J. Phys. Chem. Ref. Data 18 (1989) 1637.
[6] R.J. Watts, P.C. Stanton, Water Res. 33 (1999) 1405.
[7] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Catal. Today 53 (1999) 51.
[8] M. Pera-Titus, V. Garcia-Molina, M.A. Banos, J. Gimenez, S. Esplugas, Appl. Catal. B47 (2004) 219.
[9] J.J. Pignatello, Environ. Sci. Technol. 26 (1992) 944.
[10] E. Neyens, J. Baeyens, J. Hazard. Mater. B98 (2003) 33.
[11] A. Safarzadeh-Amiri, J.R. Bolton, S.R. Cater, J. Adv. Oxidation Technol. 1 (1996) 18.
[12] R.F.P. Nogueira, J.R. Guimarães, Water Res. 34 (2000) 895.
[13] R.F.P. Nogueira, A.G. Trovó, D.F. Modé, Chemosphere 48 (2002) 385.
[14] C.A. Emilio, W.F. Jardim, M.L. Litter, H.D. Mansilla, J. Photochem. Photobiol. A151 (2002) 121.
[15] H. Fallmann, T. Krutzler, R. Bauer, S. Malato, J. Blanco, Catal. Today 54 (1999) 309.
[16] Y.W. Kang, K. Hwang, Water Res. 34 (2000) 2786.
[17] I. Arslan, I.A. Baocioglu, D. Bahnemann, Dyes Pigm. 47 (2000) 207.
[18] J. De Laat, G.T. Le, B. Legube, Chemosphere 55 (2004) 715.
[19] P. Mazellier, B. Sulzberger, Environ. Sci. Technol. 35 (2001) 3314.
[20] N.V. Klassen, D. Marchington, C.E. McGowan, Anal. Chem. 66 (1994) 2921.
[21] K. Kosaka, H. Yamada, S. Matsui, S. Echigo, K. Shishida, Environ. Sci. Technol. 32 (1998) 3821.
[22] E.B. Sandel, Colorimetric Determination of Traces of Metals, third ed., Interscience Publishers, New York, 1959, 929.
[23] M.C. Oliveira, R.F.P. Nogueira, J.A.G. Neto, W.F. Jardim, J.J.R. Rohwedder, Quim. Nova 24 (2001) 188.
[24] C.E. Miller, Chemom. Intell. Lab. Syst. 30 (1995) 11.
[25] B. Barros-Neto, I.S. Scarminio, R.E. Bruns, Como fazer experimentos: pesquisa e desenvolvimento na ciência e na indústria, UNICAMP, Campinas, 2001.
[26] R.F.P. Nogueira, A.G. Trovó, W.C. Patterlini, Water Sci. Technol. 49 (2004) 195.
[27] D.C. Harris, Quantitative Chemical Analysis, fifth ed., W.H. Freeman and Company, New York, 1999, 429.
[28] G. Svehla, Vogel's Qualitative Inorganic Chemistry, seventh ed., Longan, Singapore, 1996, 294.
[29] V.I.E. Bruyére, L.A.G. Rodenas, P.J. Morando, M.A. Blesa, J. Chem. Soc., Dalton Trans. 24 (2001) 3595.