http://dx.doi.org/10.5935/0103-5053.20140184

J. Braz. Chem. Soc., Vol. 25, No. 11, 2000-2006, 2014.
Printed in Brazil - ©2014 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Simultaneous Degradation of Hexazinone and Diuron Herbicides by H_2O_2/UV and Toxicity Assessment

Alysson S. Martins,[a] Tanare C. R. Ferreira,[a] Renato L. Carneiro[b] and Marcos R. V. Lanza[*,a]*

[a]*Departamento de Química e Física Molecular, Instituto de Química de São Carlos, Universidade de São Paulo, Av. Trabalhador São-carlense, 400, 13560-970 São Carlos-SP, Brazil*

[b]*Departamento de Química, Universidade Federal de São Carlos, 13565-905 São Carlos-SP, Brazil*

Diuron (DR) e hexazinona (HX) são agrotóxicos da classe dos herbicidas muito utilizados na agricultura, sendo que no Brasil, a sua formulação mista é utilizada principalmente na cultura de cana-de-açúcar. Esses compostos são tóxicos aos organismos aquáticos, sendo potencialmente cancerígenos. Os processos oxidativos avançados (AOP) são uma alternativa para o tratamento de DR/HX em ambientes aquosos. Neste estudo, avaliou-se a degradação simultânea de DR/HX via H_2O_2/UV e fotólise direta utilizando um planejamento experimental do tipo composto central. As concentrações iniciais de HX e DR foram 7 e 20 mg L^{-1}, respectivamente. No sistema, o planejamento indicou que a concentração de H_2O_2 tem maior influência do que o pH. As condições ótimas de degradação (7 mmol L^{-1} de H_2O_2 e pH 2,8) proporcionaram uma remoção de carbono orgânico total de 96,4%, enquanto que o processo de fotólise direta removeu apenas 17,2%. Análises cromatográficas indicaram a remoção completa dos dois agrotóxicos a partir de 2 min de reação, o que impossibilitou a diferenciação da cinética de degradação entre DR e HX. Após o tratamento, a toxicidade foi testada utilizando bactérias *Vibrio fischeri* bioluminescentes, com uma diminuição com a utilização de H_2O_2/UV. A degradação via H_2O_2/UV foi empregada com sucesso, mostrando excelente desempenho devido ao aumento da taxa de mineralização.

Diuron (DR) and hexazinone (HX) are potent herbicides worldwide consolidated in agricultural practices. In Brazil, their mixed formulation has been intensively applied to cultures of sugar cane crops. However, when detected in agricultural watersheds, these compounds are potentially toxic to aquatic organisms and may be potentially carcinogenic. Advanced oxidation processes (AOP) is an alternative treatment of DR/HX in aqueous environment. In this study, we evaluate the H_2O_2/UV simultaneous degradation and photolysis process of DR/HX using central composite design. The HX and DR initial concentrations were close to 7 and 20 mg L^{-1}, respectively. In the system, the planning showed that the H_2O_2 concentration has bigger influence than pH. The optimum degradation conditions (7 mmol L^{-1} of H_2O_2 and pH 2.8) provide a total organic carbon removing of 96.4% while the photolysis process only 17.2%. Since neither of the herbicides were detected after 2 min of reaction, it was not possible to differ kinetics degradation process of DR and HX during the process. After the treatment, the toxicity was tested using *Vibrio fischeri* bioluminescent bacteria and showed a decrease when H_2O_2/UV is applied. Degradation H_2O_2/UV was successfully employed, showing excellent performance due to increased mineralization.

Keywords: advanced oxidative processes, diuron, hexazinone, toxicity assessment

Introduction

Cultivation of sugarcane in Brazil, specifically in São Paulo state,[1] the bioethanol production has been related with the high demand for renewable fuels economically and environmentally sustainable in domestic and foreign markets. As a consequence of this intense agricultural activity, the groundwater and surface water are contaminated due to diffuse sources arising from the intense use of fertilizers and pesticides. Diuron (DR), (3-(3,4-dichlorophenyl)-1,1-dimethylurea), and hexazinone (HX), 3-cyclohexyl-6-dimethylamino-1-methyl-1,3,5-triazine-2,4-dione, are the most potent and known herbicides applied in various stages of the sugarcane production.[2]

*e-mail: marcoslanza@iqsc.usp.br

DR exhibits moderate water solubility (42 mg L^{-1} at 20 °C), therefore, it is highly persistent (one month to one year) and can contaminate diverse environments such as soil, sediments and water. According to the Environmental Protection Agency of the United States (USA-EPA), DR is in the list of carcinogenic contaminants to humans.[3] HX is slightly soluble in water (33 mg L^{-1}) and highly mobile in soil.[4] Although it is not highly toxic to humans, it causes irritation to the eyes, nose and throat.[5] Recently, HX has been detected in cane sugar plantation areas in Australia, in concentrations up to 5 μg L^{-1}.[6] It presents an effective concentration (EC_{50}) of 3.0 to 3.6 μg L^{-1}.[7] In surface water, it is toxic to primary producers affecting the reducing food availability.[8] In this context, the detection and degradation of theses contaminants have been the subject of many studies. Magnusson *et al.*,[9] tested the toxicity of many herbicides using tropical microalgae (*Navicula sp. Cylindrotheca* and *closterium (Ochorophyta*) and *Nephroselms pyriformis (Chlorophyta*)) which DR and HX have been showed the most toxic. According to Chen *et al.*,[10] DR has been detected in the water in California, USA. The study suggests that DR may be a precursor for the formation of carcinogen compound, nitrosodimethylamine (NDMA).

The conventional wastewater treatment is not effective for the complete degradation of herbicides. In this context, the advanced oxidation processes (AOP's) have been developed to degrade these refractory contaminants in surface water and industrial effluents. The AOP's are constituted by a combination of oxidizing agents such as UV radiation and hydrogen peroxide (H_2O_2).[11] H_2O_2 is a strong oxidizing agent (oxidation potential of 1.8 V and 0.8 V, 14 and 0 pH's, respectively).[12] However, hydrogen peroxide alone is not strong enough to oxidize most of the herbicides. When combined with other physical and chemical agents, such as ozone, ferric ions and UV radiation, the formation of radicals is facilitated. Oxidizing ability may be attributed to the formation of $^{\bullet}OH$, $HO_2^{\bullet}$ and O_2^{-} in the H_2O_2/UV process (subsequent reactions). The formation of $^{\bullet}OH$ is facilitated by the photolysis of H_2O_2,[13] which degrades the structure of the contaminants by the homolytic splitting of the O–O bonds of oxidant.[14-16] In comparison to Cl_2 and O_3, the use of H_2O_2 as the oxidizing agent presents advantages, such as commercial feasibility, thermal stability, high water solubility, absence of problems related to mass transfer and no formation of halogenated hydrocarbons and bromide ions.[17,18] Regarding effectiveness, an important requirement of AOP's is evaluate the presence of coproducts and derivatives compounds from pollutants that have biological activity and toxicity. According to Fatta-Kassinos *et al.*,[19] only few studies have dealt with this topic.

Initiation[6,20]

$H_2O_2 + h\nu \rightarrow 2\ \bullet OH$	$K = 5.3 \times 10^9$ L mol^{-1} s^{-1}
$H_2O_2 \leftrightarrow HO_2^- + H^+$	$K = 1.25 \times 10^{-2}$ L mol^{-1} s^{-1}

Propagation[6,20]

$\bullet OH + H_2O_2 \rightarrow HO_2\bullet + H_2O$	$K = 2.7 \times 10^{-7}$ L mol^{-1} s^{-1}
$H_2O_2 + O_2^- \rightarrow O_2 + OH^- + OH$	$K = 0.5$ L mol^{-1} s^{-1}
$HO_2- + O_2 \rightarrow HO_2\bullet + O_2$-	

Termination[16,21]

$\bullet OH + HO_2\bullet \rightarrow H_2O_2 + O_2$	$K = 7.15 \times 10^9$ L mol^{-1} s^{-1}
$\bullet OH + \bullet OH \rightarrow H_2O_2$	$K = 5.2 \times 10^9$ L mol^{-1} s^{-1}

The present paper reports on a study of the simultaneous degradation of DR and HX herbicides by H_2O_2/UV process and photolysis. The efficiencies of these processes were evaluated by high-pressure liquid chromatography (HPLC), ion chromatography (IC) and total organic carbon (TOC) assay. The influence of pH and H_2O_2 concentration was studied using a central composite design. The toxicity was measured using a LUMIStox test using bioluminescent bacteria *Vibrio fischeri (V. fischeri).*

Experimental

Materials

DR and HX (analytical standard; 99.5% and 99.9% purity, respectively) were used for calibration curves and were obtained from Sigma-Aldrich (St. Louis, MO, USA; product number 330-54-1 and 51235-04-2). The mixed formulation (JUMP; Milenia Agrociências SA, Londrina, PR, Brazil) containing 53.3% w/w of DR and 6.7% w/w of HX was obtained from an agricultural store and was used for experiments degradation. The mixed formulation was used in the experiments due to representation of applications in agricultural cultures and the influence of inert compounds in the degradation. Methanol, acetonitrile and sulphuric acid were commercially obtained from Mallinckrodt (Xalostoc, Edomex., Mexico). Sodium sulphite and ammonium metavanadate were acquired from Sigma Aldrich (St. Louis, MO, USA) and the 30% (w/w) solution of hydrogen peroxide (reagent grade) was from Ecibra (São Paulo, SP, Brazil). Sodium carbonate and sodium bicarbonate were acquired from JT Baker (Phillipsburg, NJ). Purified water (18.2 MΩ cm resistivity; 0.039 mg C L^{-1}) was prepared using a Millipore (Eschborn, Germany) Milli-Q water purification system.

The photodegradation experiments were carried out on a laboratory scale using a UV photoreactor (Figure 1) thermostatically controlled (25 °C) and irradiated by a

Philips (Amsterdam, The Netherlands) 125 W UVC lamp (254 nm emission peak, 22,874.83 mW m^{-2}). In each experiment, the reactor was filled with 0.2 L of the test solution and operated with a constant magnetic stirring.

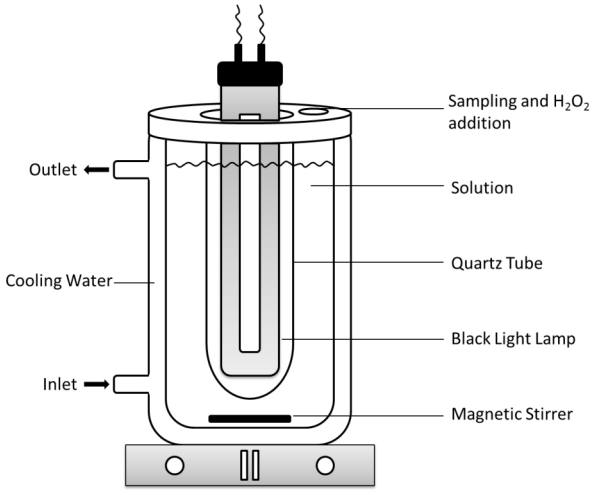

Figure 1. Schematic of the photo-reactor.

Evaluation of pH and H_2O_2 concentration in the degradation process

The levels of hydrogen peroxide and pH required for the most efficient H_2O_2/UV degradation of DR and HX herbicides were determined using a central composite design (CCD). Experimental calculations design were performed using Matlab 2011a software (Mathworks, Natick, MA, USA). The central point concentrations for CCD, represented by the coded values 0, were established as 7 for pH and 7 mmol L^{-1} for hydrogen peroxide. The coded values (*Cv*) for further levels of the two independent variables tested (Table 1) were obtained by the equation:

$$Cv = (2 \times Rv - (Rv_{+1} + Rv_{-1})) / (Rv_{+1} - Rv_{-1}) \quad (1)$$

where *Rv* is the real value, Rv_{+1} is the real value for +1 level and Rv_{-1} is the real value for –1 level. The equation that relates the content of total organic carbon removed with the process parameters (pH and H_2O_2 concentration) was obtained by a linear regression between the parameters of the experiments and the experimental responses. The response surfaces were constructed in order to achieve the best degradation performance. The statistical model was evaluated by analysis of variance (ANOVA) at 95% confidence level.

Analytical procedures

The DR and HX concentrations were determined by HPLC using a Shimadzu (Kyoto, Japan) Prominence LC 20 AT modular system comprising two CBM-20 A pumps, a CTO-10AS oven, an SIL 20A autosampler, an SPD-20A variable wavelength detector and an LC-10 Workstation Class data processor. Separations were carried out on a Supelco (Bellefonte, PA, USA) Supelcosil C-18 column (250 mm × 4.6 mm i.d.; 5 μm), protected by a Supelcosil C-18 column guard column (20 mm × 4.6 mm i.d.; 5 μm) and eluted with mixtures of water:methanol (70:30). The chromatographic conditions were oven temperature of 35 °C, flow rate of 0.8 mL min^{-1}; injection volume of 20 μL (Rheodyne loop); and UV detection at 254 nm (retention time 5.7 and 7.4 min for HX and DR, respectively).

A concentration of inorganic ions formed during degradation was detected by IC using a Metrohm model 850 Pro-IC unit combined with a conductivity detector and fitted with a Metrosep A Supp 5 column. The chromatographic conditions were mobile phase-aqueous solution of sodium carbonate 3.2×10^{-3} mol L^{-1} and sodium bicarbonate 1.0×10^{-3} mol L^{-1} and elution-isocratic at a flow rate of 0.7 mL min^{-1}.

The decrease in the organic material during chemical degradation was monitored by a Shimadzu PC-Controlled TOC Analyzer model TOC-VCPN. The hydrogen peroxide consumed was estimated by absorption at 450 nm (Cary-50 Scan UV-VIS spectrophotometer; Varian Inc, Lake Forest, USA) following the addition of ammonium metavanadate to the reaction mixture.[22]

The remaining H_2O_2 was removed by the addition of sodium bisulfite (0.1 g) immediately after collection sample. For monitoring, samples were filtered on 0.45 μm cartridges and immediately analysed the DR, HX concentrations, total organic carbon and inorganic ions. A toxicity bioassay on bacteria luminescence was carried out with a LUMIStox 300 (Dr. Lange, Duesseldorf, Germany). Tests were performed using gram negative marine bioluminescent bacteria of the *V. fischeri* (GLX8400 lyo 5) species. The samples were treated with a NaCl solution of 20 g L^{-1} and brought to 50 mS cm^{-1} conductivity before analysis. Starting from the concentration of the sample, eight consecutive dilutions were tested (dilution factor 1:2); the inhibition of bioluminescence was measured at a wavelength of 490 nm, with readings after 5 and 15 min of incubation at 15 °C.

Results and Discussion

Direct UV photolysis

The UV radiation promotes the degradation of photolabile organic compounds by direct incidence.[23,24] However, few photolysis studies have results obtained with mixtures of xenobiotics wherein the competition effects can

alter the rate of degradation.[25] The assay performed in the photoreactor (Figure 1) by incidence UV radiation through a Hg-vapor lamp demonstrated that DR was rapidly degraded while the HX proved to be more resistant to photolysis. Figure 2 shows concentration of mixed formulation containing the DR and HX during the photodegradation process. The first one shows falling detection at limit of the HPLC/UV after 8 min and the HX curve has the same aspect with less pronounced delay compromising a considerable degradation. As long the herbicides are photodegraded, it is observed in the chromatograms (Figure 3) the formation of intermediates. In addition, the intermediates formation is also observed by the low total organic carbon removal, only 17.2%. This information may be related with the chemical composition of mixed, which suggests the presence of inert and recalcitrant compounds at the end of the process. Considering the high efficiency degradation during 30 min, comprised by the total removal of DR and HX (Figure 3), it is expected a low kinetic after this time, due to low concentration of remaining degradable compounds. Thus, at the end of the experiment, intermediates still are detected but in reduced concentration. Similar results for DR photodegradation are also described by Sanchez *et al.*.[26] With respect to hydrolisys, the DR and HX, do not suffer degradation during the 30-minute experiment.

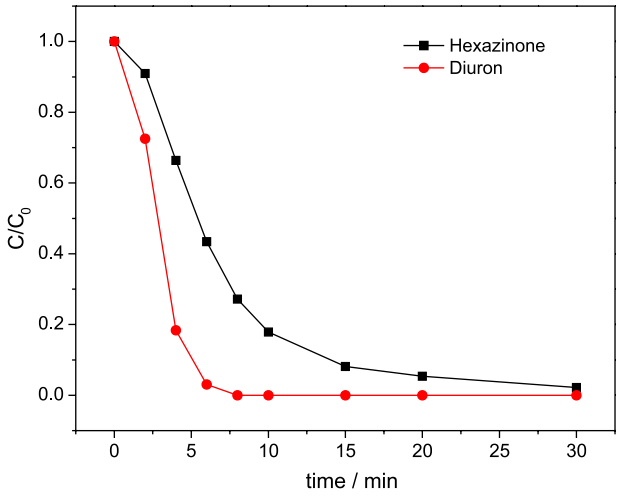

Figure 2. Monitoring of herbicides HX and DR during photolysis using the mixed formulation.

H_2O_2/UV

The central composite design was performed for the evaluation of the influence of H_2O_2 concentration and pH during the mixed formulation degradation. In most experiments, the DR and HX concentrations were below the detection limit of the HPLC/UV at the end of the 30 min of reaction. From these results, only TOC percentage removal

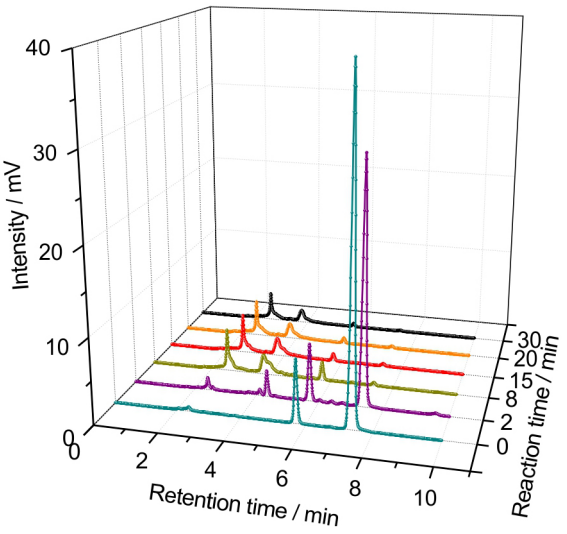

Figure 3. Chromatograms obtained from the analysis of HPLC/UV during the simultaneous photolysis of DR and HX using mixed formulation.

could be modeled. The experimental conditions for all experiments and the corresponding results are showed in Table 1. The experimental data were analyzed for the determination of the predictive quadratic model which describes the response TOC (y) as a function of process parameters H_2O_2 (x_1) and pH (x_2). The quadratic model is shown in equation 2 and the standard deviations of the coefficients are given in brackets.

$$COT = \underset{(\pm 1.684)}{87.67} + \underset{(\pm 1.033)}{9.12}\, x_1 - \underset{(\pm 1.033)}{2.88}\, x_2 - \underset{(\pm 1.227)}{9.90}\, x_1^2 + \underset{(\pm 1.227)}{3.07}\, x_2^2 + \underset{(\pm 1.458)}{1.968}\, x_1 x_2 \quad (R^2 = 0.61) \qquad (2)$$

Due to the lack of fit of the quadratic model, two more cubic terms were added to the model. Equation 3 describes this model.

$$COT = \underset{(\pm 4.799)}{87.67} - \underset{(\pm 9.294)}{18.83}\, x_1 - \underset{(\pm 9.294)}{4.834}\, x_2 - \underset{(\pm 3.498)}{9.90}\, x_1^2 + \underset{(\pm 3.498)}{3.07}\, x_2^2 + \underset{(\pm 5.879)}{18.636}\, x_1 x_2 - \underset{(\pm 5.879)}{5.14}\, x_1^3 + \underset{(\pm 4.157)}{1.97}\, x_2^3 \quad (R^2 = 0.72) \qquad (3)$$

As a result of the lack of fit, the quadratic and cubic models failed to predict the complex surface of empirical answers. The complexity of the empirical response surface is related to a simultaneous degradation of two herbicides, which each herbicide respond differently to experimental condition of degradation. They have different degradation kinetics, making this reaction difficult to model. Extra experiments planning (Table 1, experiments 10-13) were performed to improve the fit of the models, but no satisfactory results were obtained.

Within the experimental domain, it is possible to observe an irregular influence of the concentration of hydrogen peroxide only at −1.41 and −0.4 (0.66 and 5.2 mmol L^{-1} H_2O_2) presented TOC percentage removal below 81% (experiments 6 and 12 of Table 1, respectively). Concerning the pH, the experiments indicate that under high alkalinity, the process loses efficiency. This fact was confirmed by extra experiments planning (experiments 10 and 12), which was observed a 30% drop in efficiency degradation when the concentration of H_2O_2 remained constant and the pH was changed from 2.8 to 11.2. These results are in agreement with that provided by Catalkaya *et al.*,[27] who obtained an increase of 87% to 97% removal of DR when the pH was reduced from 11 to 3 units.

Figure 4 shows the empirical results as function of pH and H_2O_2 concentration. It also shows the existence of several maxima and minima within the experimental domain (indicated by the double arrows), justifying the lack of fit of the models. The planning indicates an optimum condition for degradation at 7 mmol L^{-1} H_2O_2 and pH 2.8, corresponding to 96.4% removal of total organic carbon (Figure 5a), and this value is obtained within 30 min of degradation, comprising the high efficiency of process. Hydrogen peroxide was completely consumed within 50% of the total reaction time (Figure 5b). After 8 min of treatment, DR and HX were not detected by HPLC/UV (Figure 6). The inorganic ions formation comprises the degradation of herbicides. In this respect, at the end of the process, it was observed 8.1 mg L^{-1} of chloride, 2.1 mg L^{-1} of nitrate and 0.49 mg L^{-1} of nitrite, which approximate to the theoretical values (5.21 mg L^{-1} of nitrogen and 9.89 mg L^{-1} of chloride). These agreements show the high mineralization of herbicides and no formation

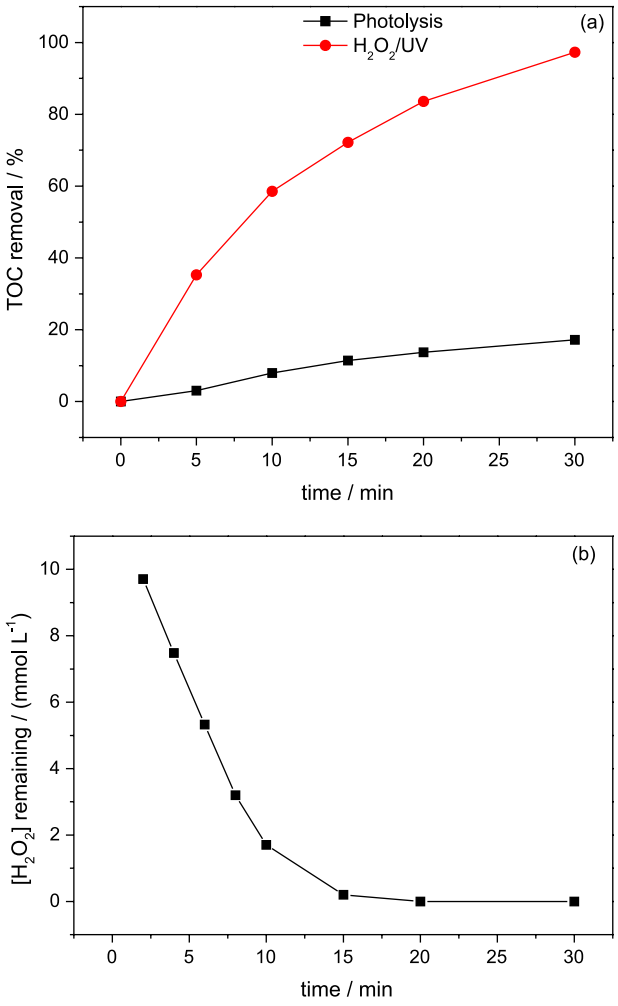

Figure 5. Percentage of TOC removal (experiment 8-Table 1) (a) and concentration of remaining H_2O_2 in the H_2O_2/UV process (experiment 8, Table 1) (b).

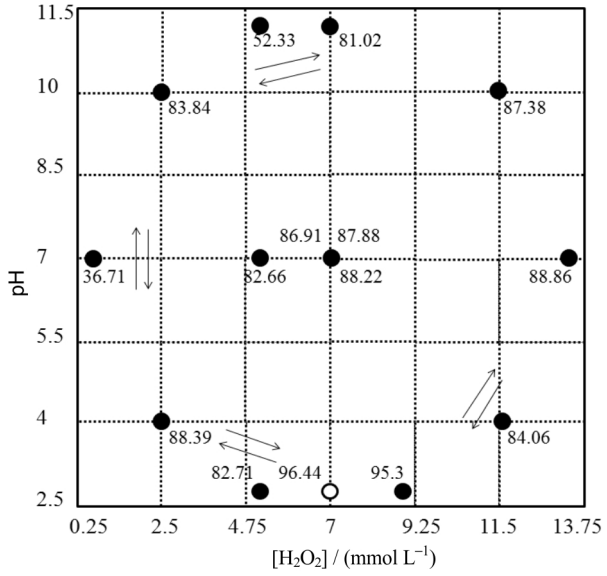

Figure 4: Empirical results from the central composite design, whose independent variables were H_2O_2 (mmol L^{-1}) and pH.

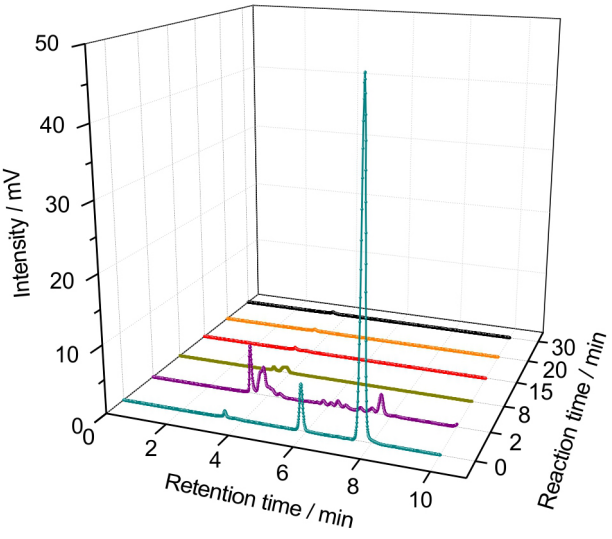

Figure 6. Chromatogram obtained by the analysis of HPLC/UV during the H_2O_2/UV process (experiment 8, Table 1).

Table 1. Degradation of diuron and hexazinone and the removal of total organic carbon by H_2O_2/UV reaction in central composite design experiments in which hydrogen peroxide (x_1) and pH (x_2) were independent variable

Experimental run	Coded level		Actual level		Observed response
	x_1	x_2	H_2O_2 x_1 / (mmol L^{-1})	pH x_2	Total organic carbon y / (% removal)
1	−1	−1	2.50	4.00	88.39
2	1	−1	11.5	4.00	84.06
3	−1	1	2.50	10.0	83.84
4	1	1	11.5	10.0	87.38
5	0	0	7.00	7.00	82.71
5	0	0	7.00	7.00	87.88
5	0	0	7.00	7.00	88.22
6	−1.41	0	0.66	7.00	36.71
7	1.41	0	13.5	7.00	88.86
8	0	−1.41	7.00	2.80	96.44
9	0	1.41	7.00	11.23	81.02
10[a]	–0.4	−1.41	5.2	2.80	82.71
11[a]	–0.4	0	5.2	7.00	82.66
12[a]	–0.4	1.41	5.2	11.23	52.33
13[a]	0.3	−1.41	8.35	2.80	95.30

[a]Experiments extra planning.

of organochlorine and nitrogen intermediates. Thus, these results suggests that after 30 min, the degradation reaction will follow a low kinetic that will results in the small variation of overall TOC.

In order to evaluate the biological potency and toxicity of coproducts formed during the H_2O_2/UV process, the *V. fischeri* test was performed. The assays were conducted at the initial and finished stages of the optimum condition for degradation. The initial sample presented effective concentration to 20% of test organisms (EC_{20}) of 33% and the sample collected after treatment presented EC_{20} 41%. The increase in EC_{20} after treatment points indicated the reduction of toxicity. The H_2O_2/UV process promotes a decrease in toxicity according to the mineralization of DR and HX. Noteworthy, the present work shows more promising than related studies of area involving degradation of herbicides HX and DR.

Conclusions

The DR and HX are potent and toxic herbicides applied to diverse cropping, mainly sugar cane cultivation. Concerning effluents treating methods, we have demonstrated the important applicability of APO's to DR/HX simultaneous degradation. The H_2O_2/UV method has proved more efficient than DR/HX photolysis degradation. For the H_2O_2/UV, the removal of organic carbon rate for 30 min of degradation was 96.4% while for the photolysis had less efficacy and accuracy (17.2%). This fact is related to the formation of more polar byproducts than DR/HX herbicides during the photolysis degradation. The planning to H_2O_2/UV shows that the quadratic and cubic models failed to predict the complex response surface in the empirical process. This feature is explained by overlapping degradation mechanisms of herbicides, as consequence a highly complex surface can not be requested. However, an optimum condition could be found for the simultaneous degradation (7 mmol L^{-1} H_2O_2 and pH 2.8). In addition, the ion chromatography showed the formation of nitrate, chloride and nitrite after the process, comprising the molecules breaking. The acute toxicity assay using a microbe *V. fischeri* showed a toxicity decrease in both methods. All these results indicate that H_2O_2/UV methods can be utilized for an efficient decontamination of wastewaters containing DR/HX. Furthermore, H_2O_2/UV process was more effective than only the photolysis process. Considering the radiation use and the experimental acid condition, the process may be an economic and viable method of herbicide removal, since it does not generate subproducts with the effective degradation of HX and DR without phase transference of contaminants. Therefore, it appears to be a promising technology for the removal of aqueous herbicides.

Acknowledgements

The authors would like to acknowledge the Brazilian funding institutions FAPESP and CAPES for the financial support and the provision of fellowships to this research.

References

1. http://www.conab.gov.br/OlalaCMS/uploads/arquivos/13_08_08_09_39_29_boletim_cana_portugues_-_abril_2013_1o_lev.pdf, accessed in January 2014.
2. Cerdeira, A. L.; Dornelas-De, S. M.; Bolonhezi, D.; Queiroz, S. C. N.; Ferracini, V. L.; Ligo, M. A. V.; Pessoa, M. C. P. Y.; Smith, S.; *Bull. Environ. Contam. Toxicol.* **2005**, *75*, 805.
3. http://www.epa.gov/oppsrrd1/reregistration/REDs/diuron_tred.pdf, accessed in December 2013.
4. Jensen, K. I. N.; Kimball, E. R.; *Bull. Environ. Contam. Toxicol.* **1987**, *38*, 232.
5. http://www.epa.gov/oppsrrd1/REDs/factsheets/0266fact.pdf, accessed in January 2014.
6. Lewis, S. E.; Brodie, J. E.; Baindridge, Z. T.; Rohde, K. W.; Davis, R. M.; Masters, B. L.; Maughan, M.; Devlin, M. J.; Mueller, J. F.; Schaffelke, B.; *Environ. Pollut. (Oxford, U. K.)* **2009**, *157*, 2470.
7. Thompson, D. G.; Holmes, S. B.; Thomas, D.; MacDonald, L.; Solomon, K. R.; *Environ. Toxicol. Chem.* **1993**, *12*, 1695.
8. http://extoxnet.orst.edu/pips/hexazin.htm, accessed in January 2014.
9. Magnusson, M.; Heimann, K.; Quayle, P.; Negri, A. P.; *Mar. Pollut. Bull*. **2010**, *60*, 1978.
10. Chen, W.; Young, T. M.; *Environ. Sci. Technol*. **2008**, *42*, 1072.
11. Ikehata, K.; Gamal El-Din, M.; *J. Environ. Eng. Sci.* **2006**, *5*, 81.
12. Neyens, E.; Baeyens, J.; *J. Hazard. Mater.* **2003**, *98*, 33.
13. Venkatadri, R.; Peters, R. W.; *Hazard. Waste Hazard. Mater.* **1993**, *10*, 107.
14. Langford, C. H.; Wingham, M.; Sastri, V. S.; *Environ. Sci. Technol.* **1973**, *7*, 820.
15. Westerhoff, P.; Song, R.; Amy, G.; Minear, R.; *Ozone-Sci. Eng.* **1997**, *19*, 55.
16. Tang, W. Z.; *Physico-Chemical Treatment of Hazardous Wastes,* 1st ed.; CRC Press: London, 2004.
17. Legrini, O.; Oliveros, E.; Braun, A. M.; *Chem. Rev.* **1993**, *93*, 671.
18. Symons, J. M.; Zheng, M. C. H.; *J. Am. Water Works Assoc.* **1997**, *89*, 106.
19. Fatta-Kassinos, D.; Vasquez, M. I.; Kümmerer, K.; *Chemosphere* **2011**, *85(5)*, 693-709.
20. Bielski, B. H. J.; Cabelli, D. E.; Arudi, R. L.; Ross, A.; *J. Phys. Chem.* **1985**, 1041-1100.
21. Christensen, H.; Sehested, K.; Corfitzen, H.; *J. Phys. Chem.* **1982**, *86*, 1588-1590.
22. Nogueira, R. F. P.; Oliveira, M. C.; Paterlini, W. C.; *Talanta* **2005**, *66*, 86.
23. Linden, K.; Shin, G.; Faubert, G.; Cairns, W.; Sobsey, M.; *Environ. Sci. Technol.* **2002**, *36*, 2519.
24. Sharpless, C.; Linden, K.; *Environ. Sci. Technol.* **2003**, *37*, 1933.
25. Pereira, V. J.; Linden, K. G.; Weinberg, H. S.; *Water Res.* **2007**, *41*, 4413.
26. Sanches, S.; Barreto-Crespo, M. T.; Pereira, V. J.; *Water Res.* **2010**, *44*, 1809.
27. Catalkaya, E. C.; Kargi, F.; *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* **2009**, *44*, 630.

Submitted on: June 15, 2014
Published online: August 8, 2014

FAPESP has sponsored the publication of this article.