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ORGANOPHOSPHATE ESTERS REMOVAL BY UV/H₂O₂ PROCESS MONITORED BY ³¹P NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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Abstract - The present work aims to study the photocatalytic degradation of three organophosphate esters considered environmental emerging contaminants by the UV/H₂O₂ system with the use of ³¹P NMR spectroscopy to investigative their removal after the treatment. Results demonstrated the efficiency of the oxidation system in removing the esters tris(2-butoxyethyl) phosphate (TBEP), tris(2-chloroethyl) phosphate (TCEP) and tri-butyl phosphate (TBP) from aqueous solutions when they were individually present and mixed. High levels of degradation of these chemicals were achieved, in addition to the good performance of the analytical technique applied in the study, which represents some advantages in comparison with other techniques reported in the literature. An increase in the ³¹P NMR signal removal could also be observed when the oxidizing agent concentration increases. Decreases in solution acute toxicity were also verified for both TBP and TBEP treated samples when compared with the samples before the treatment.

Keywords: ³¹P-NMR; Advanced oxidation processes; Flame retardants; Organophosphate esters; Photocatalysis; Ecotoxicity assessment.

INTRODUCTION

In recent years, the improvement of analytical methods has led to the discovery of emerging contaminants in the environment. This subject has become a top research focus of major organizations (e.g., the World Health Organization, Agencies of Environmental Protection and European Commission) (Estévez et al., 2012). Emerging contaminants (ECs) are defined as chemicals whose presence in the environment has recently been detected, and their ecological and health effects are causing growing concern. These include pharmaceuticals, personal care products, pesticides and disinfectants, among others (Estévez et al., 2012; Montes et al., 2015). A contaminant may also be "emerging" if discoveries of new sources, new pathways to humans or new detection methods or technologies are made (Murnyak et al., 2015; Kupper et al., 2008; Yougui et al., 2009).

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An important class of ECs are flame retardants (FRs), which are chemicals added to materials to prevent combustion and to delay the spread of fire after ignition. They have been used in polymers since the 1960s and incorporated in different materials to reduce the risk of fire either by providing an increased resistance to ignition or acting to slow down combustion and thereby delay the spread of flames (Veen et al., 2012; EFRA, 2007). Unlike other additives, some flame retardants are physically mixed with plastics and are not covalently bonded to the plastic polymers, which facilitates their desorption and release into the environment. Hence, they have been found worldwide, including in indoor environments, in precipitation, river waters, ocean waters, aerosols, mountain lakes and even in humans (Andresen et al., 2004; Martínez-Carballo et al., 2007; Cheng et al., 2013).

Phosphorus flame retardants (PFRs), which have been used for over 150 years, can be divided into three main groups (Veen et al., 2012). Three general structures of these PFRs may be recognized: organophosphate esters (OPEs), phosphonates, and phosphinates (EFRA, 2007). OPEs are compounds that are employed on a global scale, in large quantities and in many different ways (Fries and Püttmann, 2003; Flaskos, 2012). They are a re-emerging environmental issue considering the recent ban of polybrominated diphenyl ethers (PBDEs) in Europe (Cristale et al., 2013) They are widely used as plasticisers and flame retardants in plastic and appear in everyday plastic products (Stapleton et al., 2011). They also constitute the largest group of insecticides (Flaskos, 2012). Additionally, tris(2-chloroethyl) phosphate (TCEP) is widely applied as a plasticiser, antifoaming agent and additive in hydraulic fluids and in PVC. Tris(2-butoxyethyl) phosphate (TBEP) is also widely applied as a plasticiser, antifoaming agent and additive in hydraulic fluids (Möler et al., 2015). Tri-butylphosphate (TBP) is predominantly used as a plasticiser and lubricant and helps regulate pore sizes (Veen et al., 2012). Figure 1 shows the chemical structure of the three compounds.
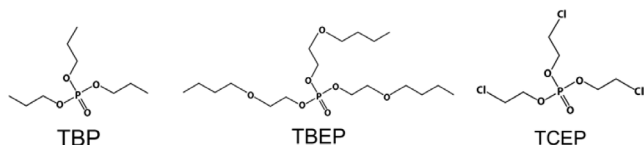
OPEs are not chemically bound in fire-proofed material and can easily leach into the environment via volatilisation, abrasion and dissolution. As a result, OPEs have been frequently detected in the environment, mainly in water systems, such as groundwater and seawater, and increasingly in indoor environments (Andresen et al., 2004; Möler et al., 2015). OPEs are known to cause direct toxic effects on a number of organs and systems in very low concentrations. However the primary target of OPE toxic action is the nervous system. OPEs are able to induce a number of distinct neurotoxicities (Flaskos, 2012), and elevated exposure has been shown to cause cancer, disturb nerve conduction, skin allergies, and affect reproduction. Their toxicity has also been shown to be present at relevant environmental concentrations. Furthermore, degradation experiments revealed that some of the OPEs may be persistent in the environment, especially chlorinated alkyl OPEs in ocean water (Cheng et al., 2013; Dyssig et al., 1991; Fries and Püttmann, 2001).

Advanced oxidation processes (AOPs) have been proposed as valuable methods for degrading persistent organic compounds because unselective hydroxyl radicals are able to promote their oxidation at high reaction rates (Tiburtius et al., 2004; Prieto-Rodriquez et al., 2012; Burrows et al., 2002). Although these processes use different reaction systems, they can promote the degradation of several organic compounds in short reaction times. Additionally, they can degrade refractory compounds which normally resist conventional biological treatment such as activated sludge (Higarashi et al., 2000; Oller et al., 2011; Molina et al., 2013). Recently, different AOPs have been studied for the removal of pollutants in urban effluents (Klamerth et al., 2010; Naddeo et al., 2009; Baumgarten et al., 2007), industrial wastes (da Rocha et al. 2010), urban river contaminated sediment (Dickson et al., 2015) and drinking water (Dantas et al., 2010; Sanches et al., 2010). UV/H_2O_2 process is able to produce hydroxyl radicals (HO•) by the photo cleavage of hydrogen peroxide with UV irradiation (Equation 1). Once the radicals are formed, they are able to react with organic molecules non-selectively and achieve the complete degradation and mineralization (Eq. 2) (Litter, 1999). In some cases, the partial oxidation of organic pollutants may result in the formation of intermediates with higher toxicity than the parent compounds (Torun et al., 2015).

Figure 1: Molecular structure of organophosphorus esters TBP, TBEP and TCEP.

$$H_2O_2 + h\nu \rightarrow 2\ HO\bullet \qquad (1)$$

$$HO\bullet + R_1 \rightarrow R_2 \qquad (2)$$

where R_1 is the substrate and R_2 is the oxidized substrate.

In recent studies, organophosphate esters were analysed using comprehensive two-dimensional gas chromatography with flame photometric detection in P mode, liquid chromatography coupled to mass spectrometry and gas chromatography coupled to tandem mass spectrometry (GC-EI-MS/MS) (Cheng et al., 2013; Fries and Püttmann, 2003; Fries and Püttmann, 2001; Liu et al., 2013; Mihajlovic et al., 2011; Cristale and Lacorte, 2013). Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for structural elucidation, being extensively used in organic chemistry (Silva et al., 2010) as well as in the monitoring of biodegradation processes (Silva et al., 2014). Phosphorus-31 (³¹P) is an excellent nucleus for NMR studies due its natural abundance (100%), nuclear spin equal to 1/2 and large spectral window. There are reports of its application in various studies, i.e., to investigate the distribution of organic P fractions and compounds in soils of China (Li et al., 2013). Since AOPs promote the conversion from OPEs to inorganic phosphates and phosphorus nuclei from OPEs are more shielded than PO_4^{3-}, ³¹P NMR spectroscopy can be a powerful tool to monitor the OPEs lower ³¹P chemical shift (δ_P) than that observed in inorganic phosphates. Three advantages are observed in the use of ³¹P NMR spectroscopy when compared with chromatographic techniques: (i) the possibility to use samples without pre-treatment (*in natura*); (ii) generally the analyses rate is faster than a chromatographic analysis; (iii) It reduces the cost with chemicals.

Apart from the removal of OPEs, the assessment of by-product toxicity is essential to guarantee the security of the treatment. This is especially important when advanced oxidation treatment processes are used, considering that more toxic intermediates may be produced (Fels et al., 2016). For that purpose, the toxicity of the target OPEs (TBEP, TCEP and TBP, individually) were studied before and after the AOP treatment, determining the LC_{50} for each sample using *Artemia salina* larvae. *A. salina* is a branchiopod crustacean highly sensitive to many contaminants and its short generation time makes it useful to investigate the level of environmental pollution in aquatic bodies. A standardized and reliable ecotoxicological test model was

available to evaluate the sample toxicity. Thus, the intermediates and final degradation products effects could be assessed (Karci et al., 2013).

The present study aims to assess the UV/H₂O₂ system performance as an alternative removal method to be applied to water solutions containing TBEP, TCEP and TBP as a single contaminant, as well as to remove a mixture of them. This study also aims to verify the use of ³¹P NMR spectra to monitor OPEs during their degradation. The ecotoxicity assessment before and after the treatment was also performed in order to measure the safety of the treated samples.

MATERIALS AND METHODS

Photochemical Treatment

The experiments were carried out in a photocatalytic reactor with a germicidal lamp (UVC radiation, Philips 20 W) with capacity to irradiate, from the top, 7 open glass vessels of 300 mL of capacity in volume each and dimensions of 9.0 cm in diameter and 5.5 cm in height. . Four different samples were treated, one of each of the three individual compounds and one for the mixture of them. In all the cases, the seven vessels were filled with 150 mL of 0.5 mg L⁻¹ of an OPE solution and seven different concentrations of H₂O₂ (0.25, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 mg L⁻¹). The solutions were prepared with distilled water and the mixture of chemicals contained 0.5 mg L⁻¹ of each OPE studied. The inside of the reactor was coated with reflective material and the lamp was aligned up along the vessels in a row at a distance of 12 cm. They were exposed to UV radiation for 6 hours. The reactor with germicidal lamps emitted 2,500 lux with an irradiance of 53 µW.cm⁻² for wavelengths and the lamps were preheated for 10 minutes to stabilize the photoemissions. Each treatment consisted of 6 hours of exposition to UVC radiation in order to verify the efficiency of the process and resistance of the chemicals. The temperature of the reaction was maintained at room temperature by controlling the temperature of the room. Temperature and pH of the solutions were measured before and after the treatment.

The chemicals used in the experiments were tris(2--butoxyethyl) phosphate (TBEP, 94%), tris(2-chloroethyl) phosphate (TCEP, 97%) and tri-butyl phosphate (TBP, 99%) purchased from Sigma-Aldrich, Brazil. All samples were stored in amber bottles at 6°C. Hydrogen peroxide (30.0%) was purchased from Quimica Moderna, Brazil.

Analytical Methods – ^{31}P NMR spectroscopy

All studied compounds are mono-phosphates and have chemical shifts (δ) between 0 and 5 ppm. The spectra were obtained using a VNMRS400 spectrometer, operating at 161.8 MHz, 5 mm PFG probe, 25 kHz spectral window, 1.60 s acquisition time, 1.00 s relaxation delay, 45º pulse of RF and 256 repetitions. All spectra were processed using line broadening at 1.0 Hz. Phosphoric acid 85% was used as external reference of chemical shift (δ_p 0 ppm).

Bioassay using *Artemia salina* larvae

To assess the risks caused by potentially toxic oxidation products of the target compound degradation, a toxicity assessment was performed. To perform this evaluation the tests were carried out in solutions of TBEP, TCEP and TBP, all at 0.5 mg L^{-1}. The analyses were carried out before and after the treatment. In all the cases, the residual H$_2$O$_2$ concentrations were below the detection limit of the potassium permanganate volumetric analysis, which avoided interference in the measurement.

Artemia salina (brine shrimp) eggs were incubated in seawater, which was collected until 48 h before the assay. After 24 h, eggs were hatched in the absence of light, at 25 °C and pH 7-8 (Rocha-Filho et al., 2015; Freitas et al., 2011). After they hatched they were moved to Falcon tubes, which had 2.5 mL of seawater. Each tube had ten crustaceans. In the next step, 2.5 mL of raw or treated solution of TCEP, TBEP and TBP were added to the tube. The crustaceans were put in contact with four different concentrations (12.5%, 25%, 50% and 100% v/v). The bioassays were conducted in a chemical incubator with temperature and aeration control.

The repeatability of the bioassay was evaluated with at least five replicates for each concentration as recommended in the literature (Freitas et al., 2011). In the negative control, larvae were only incubated in seawater, without the effluent, and ten *A. salina* were placed in 5 mL of seawater (Meyer et al., 1982). After

inoculation for 24 h, the survival rate (%) was reported and the concentration required to kill 50% (LC$_{50}$) of the larvae was determined with a 95% confidence interval. The acute toxicity related to the LC$_{50}$ was calculated by *Statistica 8.0.*

RESULTS AND DISCUSSION

Acute Toxicity

The first set of experiments was devoted to verify if the UV/H$_2$O$_2$ treatment of water containing the target compounds would form intermediates with higher toxicity. That information is essential to determine if the treatment produces more dangerous intermediates than the parent compounds, especially in water treatment methods based on oxidation (Dantas et al., 2007; Dantas et al., 2008). From the samples collected before and along the treatment, the LC$_{50}$ (lethal concentration for 50% of the population) was calculated. It is important to remark that the LC$_{50}$ is inversely proportional to toxicity.

Before the photochemical treatment, the test revealed that the LC$_{50}$ values of solutions containing TBP and TCEP were 13.5 ± 0.4 mg mL^{-1} and 9.4 ± 0.5 mg mL^{-1}, respectively. The LC$_{50}$ value of the solution containing TBEP was not possible to calculate due to the low toxicity of the sample. After the treatment with 1.0 mg.L^{-1} of H$_2$O$_2$ and 6 hour of UV-C exposition the solution containing TBP had a LC$_{50}$ value of 17.5 ± 0.1 mg.mL^{-1}. The TCEP solution treated with 1.5 mg.L^{-1} of H$_2$O$_2$ and 6 hours of UV-C exposition had a LC$_{50}$ equal to 26.7 ± 1.7 mg.mL^{-1}. As cited before, the TBEP solution treated with 1.0 mg.L^{-1} of H$_2$O$_2$ and 6 hours of UVC exposition had a LC$_{50}$ below the detection limit of the method. At the end of the treatment, the LC$_{50}$ of TBP and TCEP were higher than before, indicating that there was toxicity reduction after the photochemical treatment. Even when all the compounds were put together and treated, the overall toxicity decreased. Table 1 summarizes the results of the toxicity tests.

Table 1: Ecotoxicity tests – Summary of LC$_{50}$ values observed for each sample (DL* ≈ 0.05).

Sample	Status	LC$_{50}$ value (Median ± SD) mg mL^{-1}
TBP – 0.5 mg L^{-1}	Before AOP	13.5 ± 0.4
	After AOP – 1.0 mg.L^{-1} of H$_2$O$_2$	17.5 ± 0.1
TBEP – 0.5 mg L^{-1}	Before AOP	< DL
	After AOP – 1.0 mg.L^{-1} of H$_2$O$_2$	< DL

Table 1: Continuation.

| TCEP – 0.5 mg L⁻¹	Before AOP	9.4 ± 0.5
	After AOP – 1.5 mg.L⁻¹ of H₂O₂	26.7 ± 1.7
TBEP + TBP + TCEP 0.5 mg L⁻¹ each	Before AOP	4.2 ± 0.7
	After of AOP – 1.0 mg.L⁻¹ of H₂O₂	9.8 ± 0.4
	After of AOP – 3.0 mg.L⁻¹ of H₂O₂	9.0 ± 0.3

*DL = Detection Limit

³¹P NMR results

Initially, each compound was individually studied. ³¹P NMR spectra from 0.5 mg.L⁻¹ solutions of TCEP, TBEP and TBP were obtained. Spectra of these solutions, which were treated with different concentrations of H₂O₂ (0.25 to 3.0 mg.L⁻¹) were obtained. Figure 2 presents the spectra of a solutions containing TBEP (0.5 mg.L⁻¹) before and after UV/H₂O₂ treatment with 0.25 mg.L⁻¹ of H₂O₂.

Before treatment, there was a signal from TBEP at δ_P –4.05 ppm. After treatment, new signals in the ³¹P NMR spectrum at δ_P –2.14, –2.27 and –2.39 ppm, which are attributed to the degradation products of TBEP, were observed. When a H₂O₂ concentration higher or equal to 1.0 mg.L⁻¹ was used, the signal at δ_P –4.05 ppm was not observed at the end of the experiment, suggesting that TBEP was completely degraded (Figure 3). Apart from TBEP removal, the disappearance of the signals at δ_P –2.14, –2.27 and –2.39 ppm indicated a continuous degradation of TBEP intermediates along the reaction time. In this case, the new products have signals at δ_P –4.61, –4.74 and –4.84 ppm, which are supposed to be new phosphate compounds.

The ³¹P NMR spectra of solutions containing TBP and TCEP indicated that they were completely destroyed when H₂O₂ concentrations of 1.00 and 1.50 mg.L⁻¹ were used. These experiments were carried out in a photoreactor during 6 hours of UV-C radiation (Figure 4).

Spectral data suggested that the process using UV/H₂O₂ achieved complete degradation of TBEP and TBP, using peroxide concentration equal to 1.0 mg.L⁻¹. However, for the complete degradation of TCEP (0.5 mg.L⁻¹), the concentration of H₂O₂ in the UV/ H₂O₂ treatment was increased to 1.5 mg.L⁻¹. This is an indication that TCEP is more resistant to HO• attack than TBEP and TBP. Some studies in the literature have also obtained similar results in the degradation of organic compounds using the UV/H₂O₂ reaction and analysing by chromatographic analysis (Torun et al., 2015; Mohapatra et al., 2014). ³¹P NMR signals of OPEs had chemical shifts less than those observed for inorganic phosphates due the C–O covalent bonds, which are not observed in inorganic phosphates. When these bonds are broken, the electron density at phosphorus decreases, resulting in new signals downfield. This is observed for the solutions containing
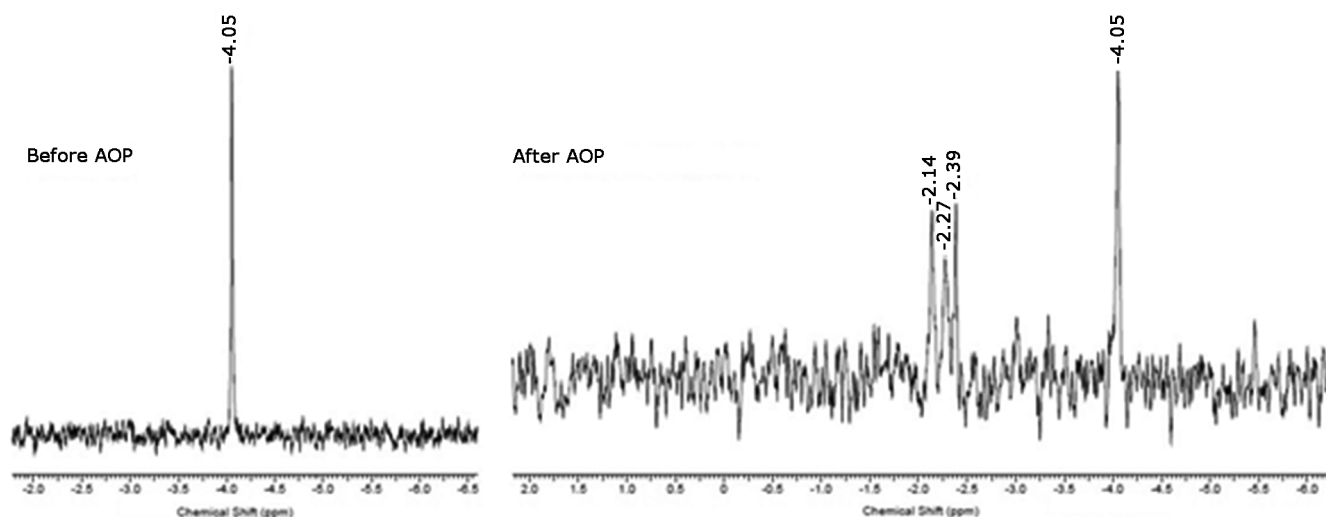
Figure 2: ³¹P NMR spectra (161.8 MHz) of solution containing TBEP 0.5 mg.L⁻¹ before (left) and after (right) UV/H₂O₂ (0.25 mg.L⁻¹) treatment.
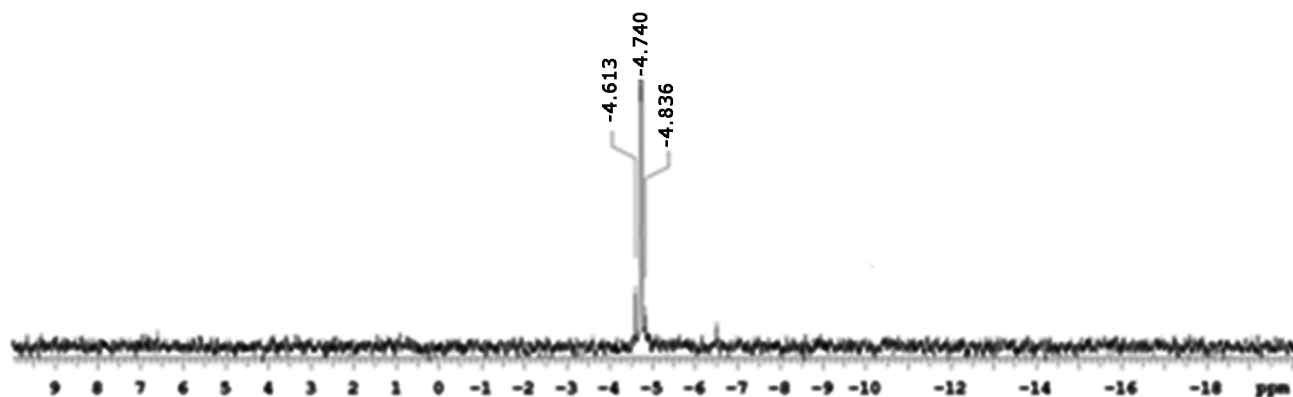
Figure 3: ^{31}P NMR spectrum (161.8 MHz) of solution containing TBEP 0.5 mg L^{-1} after UV/H$_2$O$_2$ (1.0 mg L^{-1}) treatment.
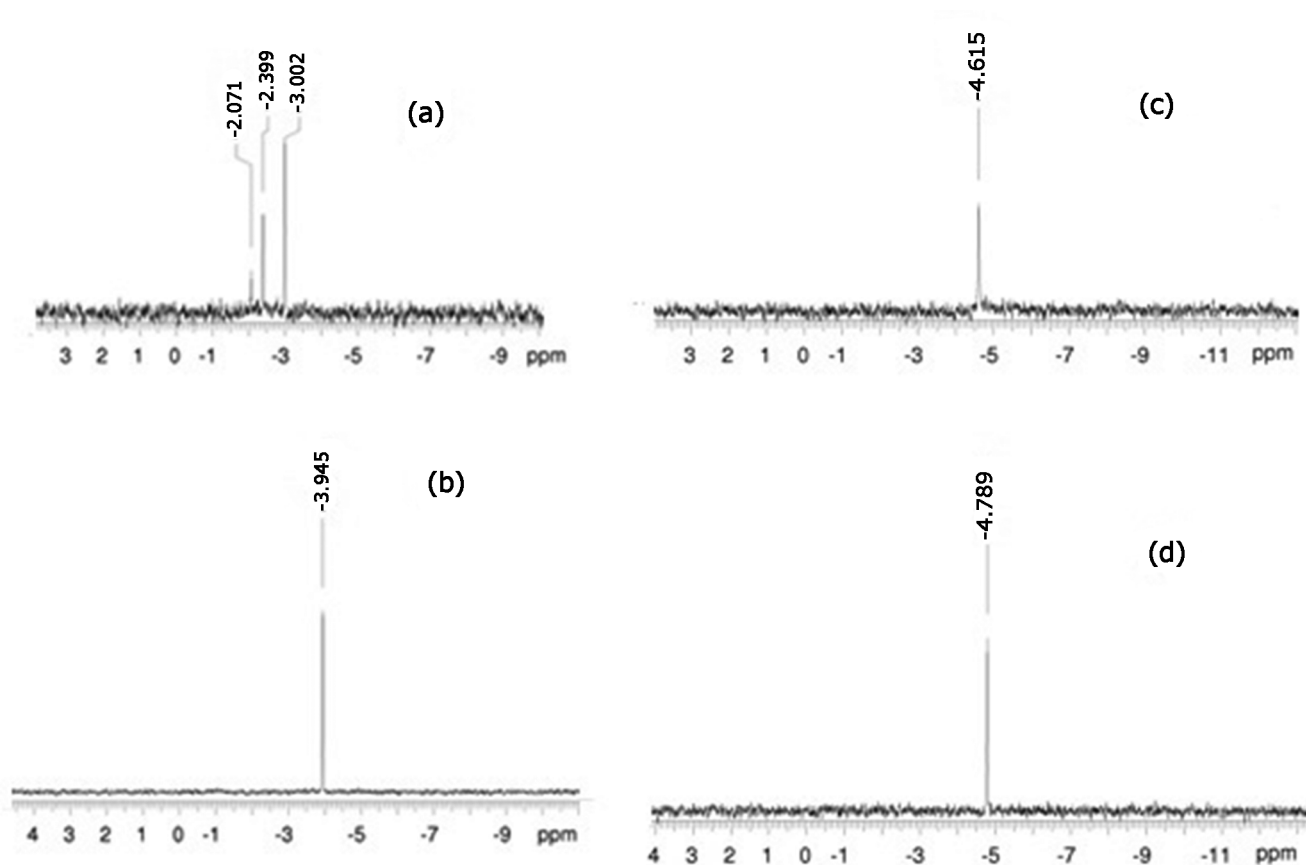

Figure 4: ^{31}P NMR spectra (161.8 MHz) of solutions containing TBP 0.5 mg.L^{-1} before (a) and after (b) UV/ H$_2$O$_2$ (1.00 mg.L^{-1}) treatment and TCEP 0.5 mg.L^{-1} before (c) and after (d) UV/ H$_2$O$_2$ (1.50 mg.L^{-1}) treatment.

TBP and TBEP, since signals around –2 ppm are observed, which are attributed to Q^0 inorganic phosphates nuclei. This result is compatible with the increase of LC$_{50}$ observed in the toxicity test. On the other hand, for the solution containing TCEP, signals around –2 ppm were not observed, only a small chemical shift change. Nevertheless, the toxicity test for this sample indicates a significant increase of LC$_{50}$. Therefore, the

signals observed (δ_P –4.79 ppm and –4.62 ppm, before and after treatment, respectively) are attributed to different species. However, inorganic orthophosphates with signals around δ_P –5 ppm are not common. Normally, in this spectral region signals of Q^1 from inorganic phosphates nuclei are observed, which are named pyrophosphates. Probably, pyrophosphates are being produced.

After the study of individual compounds, a situation where the three organophosphates esters are simultaneously present in solution was simulated. Figure 5 shows the ^{31}P NMR spectra of an aqueous solution containing the three compounds (TBP, TCEP and TBEP) before and after UV/H_2O_2 with 0.25 mg.L^{-1} of H_2O_2. The δ_p observed in the mixture are different from those observed in the individual solutions. These changes occur because the ^{31}P chemical shift is sensitive to changes in composition of the mixture, or even changes in the pH of the solution.

In Figure 5a, there are three signals attributed to TBP (δ–3.20 ppm), TBEP (δ–4.05 ppm) and TCEP (δ–4.91 ppm). After the UV/H_2O_2 (0.25 mg L^{-1}) treatment (5b), there was a decrease in the ratio of integrated signal areas, as follows: TBP *versus* TCEP and TBEP *versus* TCEP. Therefore, the relative concentration of TBP and TBEP are lower after treatment. New signals were also observed, suggesting the formation of new species. It indicates that TBEP and TBP are preferentially degraded and TCEP is more resistant to degradation.
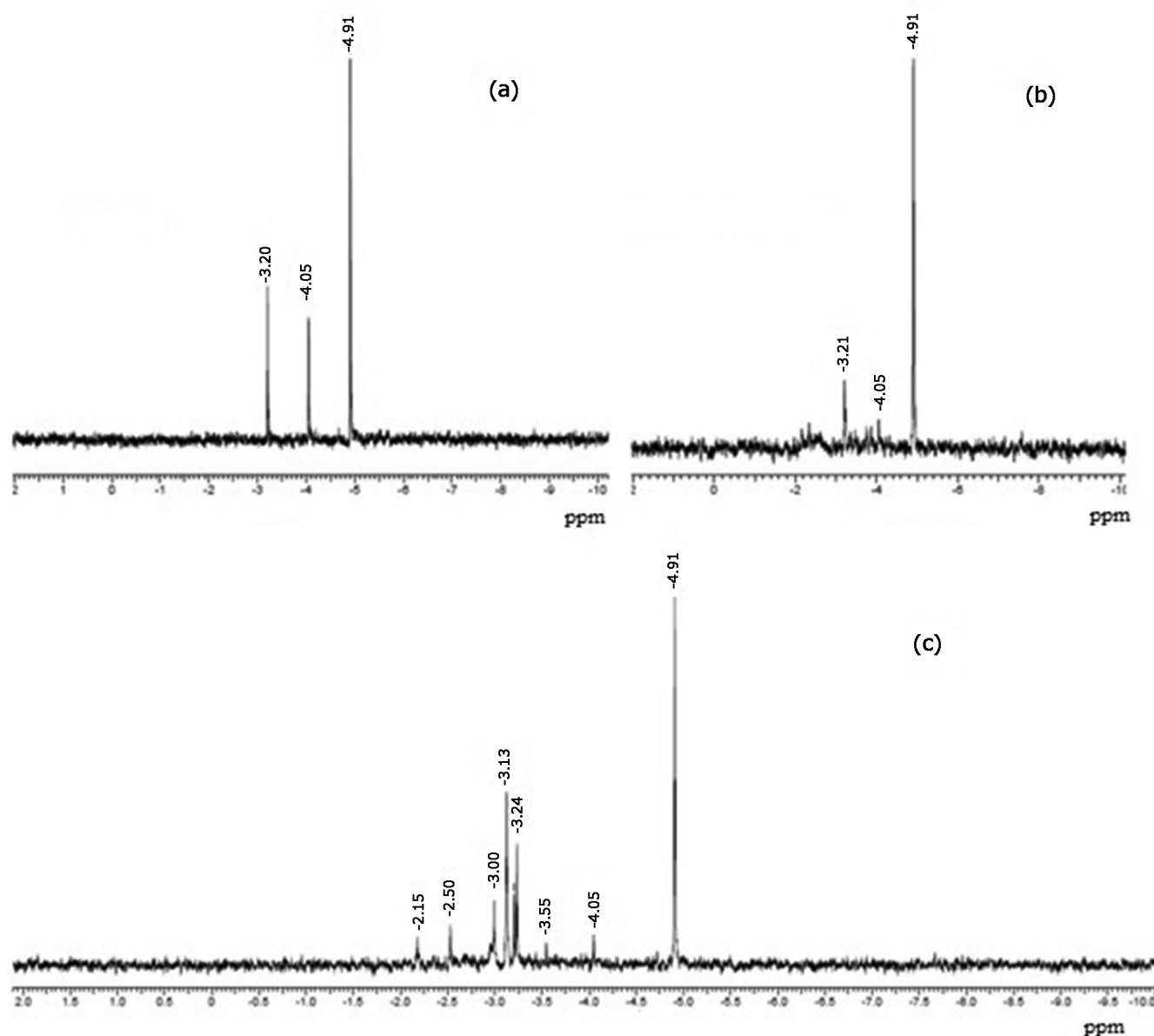
Figure 5: ^{31}P NMR spectra (161.8 MHz) of a mixture containing TCEP (δ_p 4.91 ppm), TBEP (δ_p 4.05 ppm) and TBP (δ_p 3.20 ppm) before (a) and after UV/H_2O_2 (0.25 mg.L^{-1}) (b) and ent. TBP, TCEP and TBEP after UV/H_2O_2 (1.50 mg.L^{-1}) treatment.

Figure 5c shows the ^{31}P NMR spectrum of an aqueous solution containing the three compounds (TBP, TCEP and TBEP) after UV/H_2O_2 with 1.50 mg.L^{-1} of H_2O_2. In this case, TBEP and TBP were fully consumed and new compounds were produced. Nevertheless, the signal attributed to TCEP is still present, even with the increment of the oxidant concentration, indicating again its high resistance to treatment.

From these spectral data, we concluded that TBEP (δ 4.05 ppm) is more susceptible to degradation than TBP and TCEP. This behaviour is in accordance with similar works that reported higher resistance of chlorinated organophosphates esters when they are subjected to advanced oxidation treatments (Yuan et al., 2015).

The solution containing only TCEP was fully degraded when 1.50 mg.L^{-1} of H_2O_2 was used. However, in the mixture containing the three OPEs, TCEP was not degraded even using 3.0 mg.L^{-1} of H_2O_2. In this case, the degradation process is continuous and by-products of TBEP and TBP might be more reactive to HO• than TCEP. Nevertheless, the advanced oxidation process used was efficient, since apart from the target compound degradation, it had reduced the toxicity of the sample, increasing the LC_{50} value.

The temperature variation of the samples in the reactor was not significant, remaining at 37 ±0.1 ºC after 6 hours of treatment. Despite the heat released by the lamp, the room was kept under refrigeration, which can explain the maintenance of temperature. The pH of all the samples decreased from 6 to a value around 4. This can be explained by the formation of short chain carboxylic acids usually formed during AOP oxidation of organic molecules, which may have caused an acidification of the medium.

Another fact to be taken into account is that the use of higher concentration of the oxidant to improve the removal of the target contaminants or even promote the degradation of TCEP could cause an inhibition of HO• oxidation. Moreover, in a real wastewater synergetic effects caused by inhibitors or other contaminants must be taken into account. Blank experiments also demonstrated that H_2O_2 alone was not able to promote the degradation of the compounds.

CONCLUSIONS

In this paper, a UV-C radiation and H_2O_2 based Advanced Oxidation Process was used to degrade three organophosphate esters (TCEP, TBP and TBEP). The efficiency of the process was evaluated using ^{31}P NMR spectroscopy and ecotoxicity assays. ^{31}P NMR spectroscopy was a reliable technique for the evaluation of OPE degradation. It was also useful for the evaluation of degradation of three OPE in the same solution, showing that TBEP and TBP were more sensitive to the process, being completely degraded when a H_2O_2 concentration of 1.5 ppm was used. ^{31}P NMR spectroscopy showed that TCEP is very resistant to the process. When the three OPEs were used in same solution, TCEP was not degraded, even upon increasing the concentration of oxidant. An ecotoxicity test indicated a toxicity reduction since all the treated samples presented LC_{50} values higher than the parent solution, which can be considered to be an important result due to the high damaging effects of those compounds even at low concentrations.

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