Experimental Degradation of Nonylphenol (Endocrine Disruptor) by Using Ultraviolet Irradiation in the Presence of Hydrogen Peroxide

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ABSTRACT: The photodegradation of nonylphenol under UV irradiation was investigated in an aqueous solution containing hydrogen peroxide (H_2O_2) as the photochemically active substance was investigated. Influences of pH, the concentration of hydrogen peroxide, and the initial concentration of nonylphenol were studied. The following conditions were determined as optimal for nonylphenol removal: pH 1, H_2O_2 concentration of 40 mg/L, and an initial nonylphenol concentration of 15 of mg/L. Under these conditions, the removal of nonylphenol reached about 80% after 2 hours of irradiation. Identification of degradation products was done by gas chromatography-mass spectrometry, and analyses revealed Benzaldehyde, 4-methoxy and Diisobutyl phthalate as the main products of nonylphenol photodegradation. *Water Environ. Res.*, **86,** 759 (2014).

KEYWORDS: nonylphenol, UV irradiation, hydrogen peroxide, photodegradation, benzaldehyde, 4-methoxy.

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Introduction

Nonylphenols ($C_{15}H_{24}O$) are synthetic organic compounds that exist in a mixture of isomeric compounds with a phenolic ring and an attached lipophilic linear or branched nonyl group. Nonylphenols are subsets of alkylphenols and subjected to ethoxylation (the primary use of nonylphenols) to form nonylphenol ethoxylates, which are widely used as industrial surfactants (Ahel et al., 1994). Nonylphenols are supposed to react to form tris(4-nonyl-phenyl) phosphate, an antioxidant used to protect polymers such as rubber, vinyl, polyolefins, and polystyrenics (Siedel, 2004). The U.S. Food and Drug Administration has listed nonylphenols as indirect food contact substances (Vazquez et al., 2005), while Seidel et al. (2004) reported barium and calcium salts of nonylphenols as heat stabilizers for polyvinyl chloride. Nonylphenols are also used as catalytic diluents in epoxy resins (Siedel, 2004), paints and laquers, cleaning agents, pesticide formulations, and in limited amount as plastic softeners (Fauser et al., 2001).

Used in aqueous solutions, nonylphenols have been detected in different environmental media such as septic systems (Ying et al., 2002), wastewater and industrial wastewater treatment plants (Jobling et al., 1996; Komori et al., 2006), wastewater sludge and sediments, landfill leachates, and treated drinking water (Janssens et al., 1996). Several studies have reported nonylphenols and short-chain nonylphenol ethoxylates (NPEOs) to be the degradation products of long-chain nonylphenols ethoxylates (Lu et al., 2008; Wang et al., 2006; Wang et al., 2009). They have also been identified as endocrine disrupters (Rudel et al., 2003; Wenzel et al., 2004) and have been described as being more toxic than their parent substances (Hemmer et al., 2002; Jobling et al., 1996, Yadetie and Male, 2002).

Because of these hazards, the production and the use of nonylphenol and its ethoxylates were banned and/or further regulations were applied to protect the environment in many countries. However, significant concentrations are still found in effluents from water resource recovery facilities and in rivers. Therefore, other treatments should be considered before releasing effluents into receiving waters. Although many degradation processes, such as advanced oxydative processes (e.g., ozonation, photolytic degradation), have been applied to remove these compounds, some degradation products were also found to be toxic to the environment. For instance, in studies conducted by Sherrard et al. (1996) and Mizuno et al. (2002), NPEOs with a smaller number of Ethoxylate groups, acatate, oxalate, formate, formaldehyde, acetaldehyde, glyoxal, and methylglyoxal were degradation products of NPEOs and nonylphenol by using advanced oxidation process (AOP) treatment. Neamtu et al. (2006) identified phenol, 1,4-dihydroxybenzene, and 1,4-benzoquinone as products of nonylphenol photodegradation, while Lenz et al. (2000) concluded that chlorination by NaClO leads to the formation of more toxic byproducts. The objectives of this work were to investigate the best conditions of nonylphenol degradation under UV irradiation by studying influence factors, to identify degradation byproducts, and to discuss the possible pathways of photodecomposition so that the results could be used in degradation experiments of real wastewater samples concerning endocrine disrupts.

Materials and Methods

Reagents and Chemicals. Technical Nonylphenol (Pestanal, analytical standard, ≥98% purity) was obtained from Fluka Chemicals (Sigma-Aldrich, St. Louis, Missouri). Envi-grade Dichloromethane (DCM) (≥99.5% purity) was provided by ROWE Scientific Pty. Ltd. (Victoria, Australia). Acetonitrile and methanol high-performance liquid chromatography/Spectrograde with a purity of 99.9% were purchased from Tedia

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Company Inc. (Fairfield, Ohio). The stock solution (1 g/L) was prepared by dissolving 100 mg of nonylphenol in 100 ml of DCM. Ferric chloride ($FeCl_3.6H_2O$), with a purity of ≥99%, was purchased from Tianjin Flourish Chemical Co., Ltd. (Tianjin, China). Sodium sulfate (Na_2SO_4), with a purity of 99% and a density of 2.68 g/mL at 25 °C, was provided by J&K Scientific Ltd. (Shanghai, China). Potassium nitrate (KNO_3, 1 g/mL at 20 °C) was obtained from Meryer Chemical Technology Co., Ltd. (Shanghai, China). All chemicals used for solutions (buffer, eluents, etc.) were used without further purification. Milli-Q water was used to prepare the stock solution of photochemical active substances (PAS) (10 g/L) and hydrogen peroxide, which was obtained from Sigma-Aldrich in Hong-Kong, China, with the following specifications: concentration, 30%, and vapor pressure, 23.3-mm Hg.

Photodegradation Experiment. Nonylphenol photodegradation experiments were carried out in 25-mL glass tubes containing 10 mL of aqueous solution. All the experiments under the catalyst/UV system were carried out in an annular glass reactor equipped with a low-pressure mercury lamp (30 W, peak emission at λ=254 nm, outer diameter of 2.5 cm, length of 35 cm) from Nanjing Electronic Vacuum Devices Co., Ltd. (Nanjing, China). A pump provided continuous oxygenation at a low flowrate (0.2 L/min) to minimize the formation of foam through a thin tube immersed in the solution. The aeration provides oxygen for the photo-oxidation process to improve the degradation efficiency. Experiments were carried out at room temperature (25 to 30°C). Photochemical active substances, which should be used to run the experiment, was chosen among several chemicals such as ferric chloride ($FeCl_3.6H_2O$), hydrogen peroxide (H_2O_2), potassium nitrate (KNO_3), and sodium sulfate (Na_2SO_4). The concentration effect (ranging from 10 to 100 mg/L) of the chemical that enhanced more of the photo-induced experiment was then studied, followed by the influence of the initial concentration of nonylphenol (5 mg/L to 100 mg/L). pH conditions (1, 3, 5, 7, 9, and 11, by either adding 0.1M of HCl or 0.1M of NaOH) were also investigated and the experimentation times were 30 minutes and 1, 2, 4, and 8 hours.

Method of Extraction. Solid-phase extraction was used to extract the chemicals. Waters Oasis HLB (Milford, Massachusetts) cartridges (3 mL, 5 cc, and 200 mg) were cleaned by successive washings with 6 ml of DCM and methanol, then with 12 ml of deionized water. Percolation of the samples was done at a flowrate of 15 ml/min by using a slight vacuum, followed by elution with 18 ml of acetonitrile. The collected extracts were successively evaporated to dryness by using a rotary evaporator (R-210; Swiss Buchi, Flawil, Switzerland), then transferred into a 2-ml glass vial and brought to dryness under a stream of nitrogen; finally, the extracts were redissolved in 1 mL of DCM for gas chromatography-mass spectrometry (GC-MS) analyses. Samples of standard solutions were also processed through the same extraction method and recoveries were between 88.11 and 95.59%.

Analysis. An Agilent gas chromatograph (6890N; Agilent Technologies, Inc., Santa Clara, California), coupled with an Agilent quadrupole mass spectrometer (5975) and equipped with a fused silica capillary column DB-5MS (coated with 5% phenyl methyl siloxane; film thickness of 0.25 μm, length of 30 m, and 0.25-mm i.d.), was used to analyze nonylphenol degradation. The temperature of the column oven was held at 70°C for the first minute, then programmed at 25°C/min incrementally to 130°C, followed by 2°C/min to 290°C, and held for 7 minutes (Zhang et al., 2012). Helium was used as the carrier gas at 15.00 psi and the ionization potential was 70eV. The temperatures of the ion source and the transfer line were respectively 250°C and 275°C.

Results and Discussion

Influencing Factors of Nonylphenol Degradation. *Choosing the Photochemically Active Substance.* The photochemically active substance, which should be used to run experiments, was chosen among different chemicals such as $FeCl_3$, H_2O_2, KNO_3, and Na_2SO_4. The following conditions were randomly chosen to start the experiment: PAS = 20 mg/L, initial concentration of nonylphenol = 25 mg/L, pH = 7, and UV irradiation = 1 hour. Figure 1 shows that all PAS enhanced the removal of nonylphenols with different levels of efficiency. Hydrogen peroxide was more efficient, achieving about 40% removal after 2 hours of irradiation. Hanci et al. (2011) and Wang et al. (2009) reported respectively high and low efficiency of H_2O_2 used for the degradation of organic compounds. The different results obtained in the studies cited above can be explained by the fact that the efficiency of AOPs depends greatly on the rate of free radicals generated. Thus, more the rate of free radicals generated is high, more the degradation of nonylphenols should be efficient. It can, therefore, be stated that the rate of $OH^{\bullet}$ generated by H_2O_2 was higher than the other photochemically active substances used. In addition, H_2O_2 is known as one of the most powerful oxidizers, with 1.8V as the oxidation potential. These results are important to subsequent experiments since H_2O_2 would be safe for the environment. Despite its oxidizing power, H_2O_2 is a natural metabolite for many organisms. These organisms decompose H_2O_2 into oxygen and water. On the other hand, H_2O_2 does not create problems of gaseous release or chemical residues that are associated with other chemical oxidants. By simply adjusting the conditions of the reaction (e.g., pH, temperature, dose, reaction time, and/or catalyst addition), the selectivity of H_2O_2 allows it to oxidize one pollutant over another or even to favor different oxidation products from the same pollutant.

Influence of Hydrogen Peroxide Concentration on Nonyphenol Removal. The difference between the aforementioned results and those from Wang et al. (2009) were elucidated by alternating different concentrations of H_2O_2 (10 to 100 mg/L) while stabilizing other conditions. As shown in Figure 2, removal of nonylphenol increases by increasing the dose of H_2O_2 up to 40 mg/L, and then decreases with concentrations superior to 40 mg/L. The removal efficiency reached about 65% (with a H_2O_2 concentration of 40 mg/L) after 2 hours of irradiation, while, using the same irradiation time, the degradation rate was less than 35% when the applied concentration was 100 mg/L.

This phenomenon is explained by the mechanisms of the reaction of H_2O_2 under UV irradiation. In fact, the degradation of nonylphenols is caused by the generation of hydroxyl radicals upon the photolysis of hydrogen peroxide (Arslan and Balcioglu, 1999). Many studies have proposed different reaction mechanisms for this photolysis, and it is widely accepted that the main interaction (under UV irradiation) between H_2O_2 and free hydroxyl radicals is well represented by the following reactions (Alfano et al., 2001):

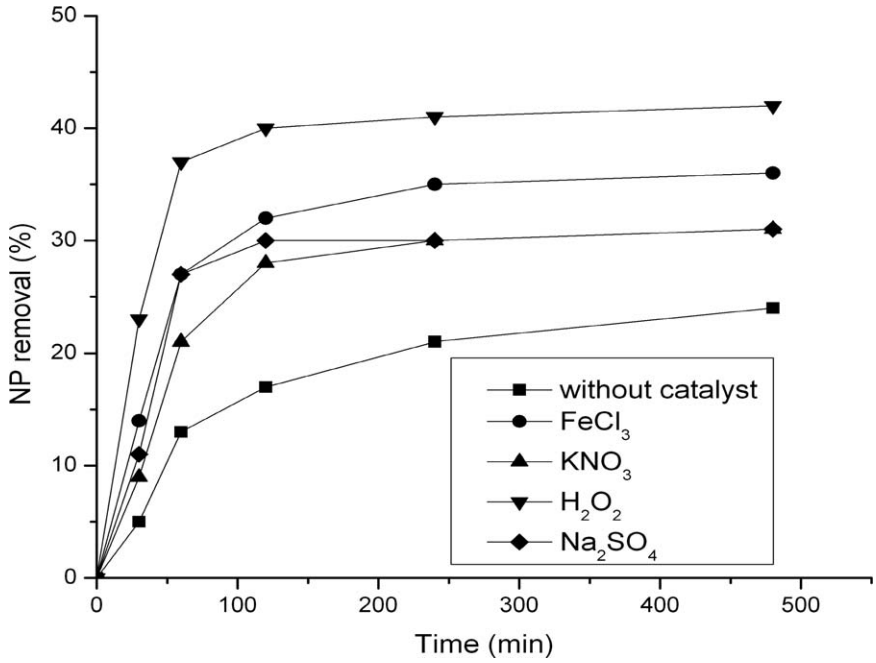

Figure 1—Efficiency of different PAS on nonylphenol photodegradation (PAS = 20 ng/μL, nonylphenol = 25 ng/μL, and pH = 7).

Initiation

$$H_2O_2 + h\nu \rightarrow 2OH^{\bullet} \quad (1)$$

Propagation

$$H_2O_2 + OH^{\bullet} \rightarrow O_2H^{\bullet} + H_2O_2 \quad (2)$$

$$H_2O_2 + O_2H^{\bullet} \rightarrow OH^{\bullet} + H_2O \quad (3)$$

Termination

$$OH^{\bullet} + O_2H^{\bullet} \rightarrow H_2O_2 + O_2 \quad (4)$$

$$O_2H^{\bullet} + O_2H^{\bullet} \rightarrow H_2O_2 + O_2 \quad (5)$$

$$OH^{\bullet} + O_2H^{\bullet} \rightarrow H_2O + O_2 \quad (6)$$

The hydroxyl radicals react with organic molecules (nonylphenols), as follows, resulting in their destruction:

Decomposition

$$RX + OH^{\bullet} \rightarrow \text{products} \quad (7)$$

$$RX + O_2H^{\bullet} \rightarrow \text{products} \quad (8)$$

The $OH^{\bullet}$ radicals, as follows, are capable of oxidizing organic compounds mostly by hydrogen:

Abstraction

$$RH + OH^{\bullet} \rightarrow R^{\bullet} + H_2O \quad (9)$$

When enough hydrogen peroxide is present in the solution, it starts to compete with nonylphenols to react with hydroxyl radicals. Aleboyeh et al. (2005) noticed that high concentrations of hydrogen peroxide have a diminishing effect on the reaction rate. Indeed, in this condition, $OH^{\bullet}$ radicals produce hydroperoxyl radicals, which are much less reactive and do not appear to contribute to oxidative degradation. Furthermore, $OH^{\bullet}$ radicals generated at a high local concentration readily dimerize to H_2O_2. In other words, high concentrations of hydrogen peroxide act as a fixing agent for hydroxyl radicals according to the reactions in the following equations (Buxton et al., 1988; Mao et al., 2012):

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (10)$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2^{\bullet} \quad (11)$$

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2 \quad (12)$$

On the other hand, low concentrations of H_2O_2 do not generate enough hydroxyl radicals ($OH^{\bullet}$); this leads to the oxidation rate slowing down (Aleboyeh et al., 2005). Therefore, it is important to optimize the concentration of hydrogen peroxide to maximize the performance of UV/H_2O_2 oxidative degradation. Thus, a concentration of H_2O_2, which could induce an optimum efficiency, should be a trade-off between low and high concentrations (40 mg/L for this study).

Effect of pH on Nonylphenol Photodegradation. pH has been shown to be an important parameter in photodegradation studies of numerous organic pollutants. In this study, the influence of pH on nonylphenol degradation was investigated by simply changing the pH values; results are shown in Figure 3. The increase in pH from pH 1 to pH 11 induced a decrease in nonylphenol removal efficiency from about 83% to less than 40% after 2 hours of irradiation. Therefore, it was concluded that the degradation of nonylphenols was more efficient at lower pH, as reported by Galindo and Kalt (1998). Indeed, hydrogen peroxide undergoes decomposition at alkaline pH, leading to the formation of O_2 and H_2O, rather than producing $OH^{\bullet}$ (Adel et al., 2004). In addition, H_2O_2 reacts with NaOH to form sodium peroxide (Na_2O_2) under alkaline conditions, and, as result, less

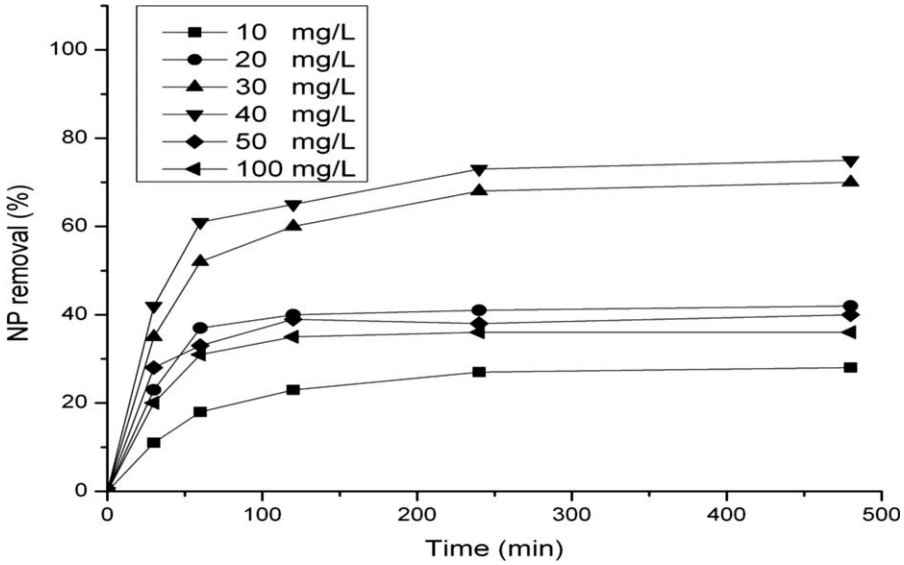

Figure 2—Influence of H_2O_2 concentrations on nonylphenol photodegradation (nonylphenol = 25 ng/μL and pH = 7).

hydrogen peroxide is available for the formation of hydroxyl radicals; which decreases the efficiency of nonylphenol degradation. This is particularly noticeable at higher concentrations of NaOH, according to the reaction given in the following equation (Adel et al., 2004):

$$2NaOH + H_2O_2 + 6H_2O \rightarrow Na_2O_2 + 8H_2O \qquad (13)$$

Impact of the Initial Concentration of Nonylphenol on the Degradation Process. The last factor studied in the present work was the effect of the initial concentration of nonylphenol on photodegradation efficiency. Results (Figure 4) show that by increasing the initial concentration of nonylphenol from 5 to 100 mg/L, the removal efficiency decreased from 100% to about 45% after 2 hours. Apparently, no significant change was observed concerning nonylphenol removal when initial concentrations were 15 and 25 mg/L. This suggests that the removal of nonyphenols reached a threshold at 15 mg/L. As stated previously, hydroxyl radicals are mainly responsible for nonylphenol degradation and their concentration remains constant for all nonylphenol concentrations. The increase of the nonylphenol concentration and not the hydroxyl radical concentration induces a decrease in the removal rate, as stated by Amin et al. (2008) for dye decolorization. The aforementioned reasons may be partially or fully responsible for the

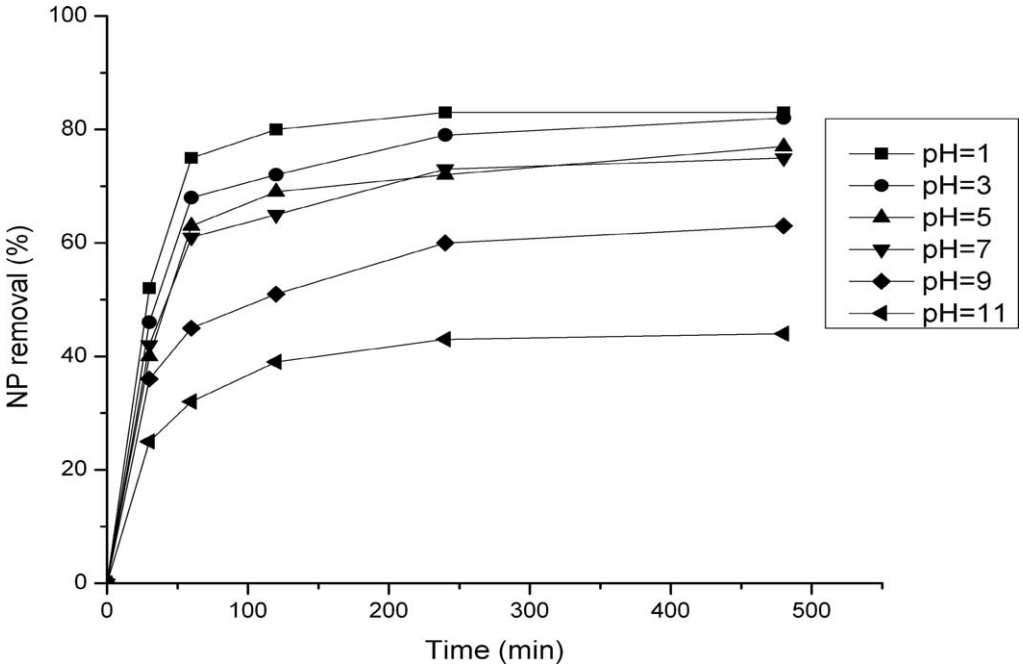

Figure 3—Effect of pH on nonylphenol photodegradation (nonylphenol = 25 ng/μL and H_2O_2 = 40 ng/μL).

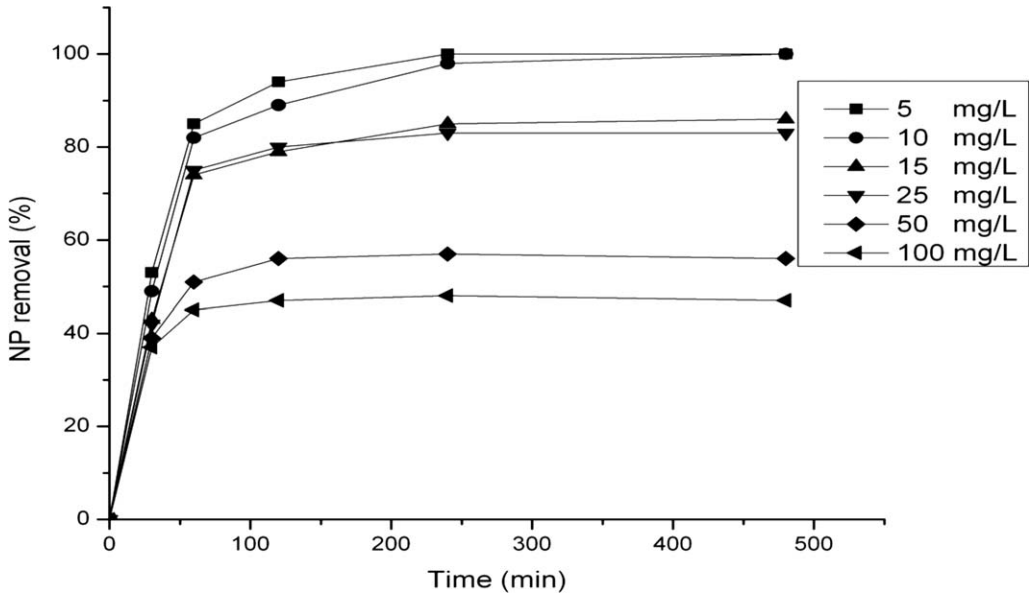

Figure 4—Effect of initial concentrations of nonylphenol on the photodegradation experiment ($H_2O_2 = 40$ ng/μL and pH = 7).

difficulty of effective removal at high concentrations of nonylphenols in wastewater.

Kinetics of Nonylphenol Photodegradation. The temporal variation C/C_0 of the nonylphenol concentration was studied based on data about degradation influencing factors from the aforementioned experiments. The kinetic parameters are presented in Table 1. Mono-exponential curves were fitted with the correlation coefficients R^2, comprised between 0.96 and 0.999, according to the following expression:

$$C/C_0 = a + b\exp(k.t) \tag{14}$$

Where

a, b, and k = adjustable constants,

C_0 and C = measured concentrations of nonylphenols at initial and t time,

$k < 0$ and $a + b \approx 1$.

As Fuente et al. (2010) reported, this kinetic suggests the operation of two parallel mechanisms, one faster than the other, with the parameters *a* and *b* indicating the relative importance of each pathway.

Table 2, which is based on data from Table 1, clearly shows that "*b*" appears to be responsible for the high rate of nonylphenol removal and probably the faster parameter, while

Table 1—Kinetic parameters for the mono-exponential model.

		Exponential model parameters			
Process parameter	**Value**	***a***	***b***	***c***	**R^2**
H_2O_2 dosage	10	0.724	0.274	−0.017	0.996
	20	0.583	0.42	−0.03	0.989
	30	0.32	0.675	−0.023	0.99
	40	0.277	0.721	−0.029	0.985
	50	0.612	0.386	−0.039	0.988
	100	0.638	0.364	−0.029	0.996
pH	1	0.171	0.831	−0.035	0.996
	3	0.21	0.79	−0.03	0.987
	5	0.259	0.744	−0.027	0.988
	7	0.277	0.721	−0.029	0.985
	9	0.407	0.581	−0.025	0.96
	11	0.573	0.422	−0.025	0.986
Initial nonylphenol dosage	5	0.001	1.005	−0.028	0.993
	10	0.018	0.987	−0.025	0.986
	15	0.147	0.861	−0.027	0.983
	25	0.162	0.849	−0.028	0.977
	50	0.435	0.565	−0.039	0.999
	100	0.526	0.473	−0.05	0.999

Table 2—Relationship between factors influencing nonylphenol degradation, rate of removal, and parameters *a* and *b*.

Factors influencing nonylphenol degradation	Rate of nonylphenol removal	Kinetic parameters
H_2O_2 dosage	low	a>b
	high	b>a
pH	low	a>b
	high	b>a
Initial concentration of nonylphenol	low	a>b
	high	b>a

"*a*" appears to be responsible for the low rate of nonylphenol removal and probably the slower parameter.

Pathway of Nonylphenol Photodegradation. An initial concentration equal to 15 mg/L (pH 1 and H_2O_2 of 40 mg/L) was used to discuss the pathway of photo-induced degradation. The products of photocatalytic decomposition were identified based on their molecular ion and mass spectrometric fragmentation peaks (main fragments: m/z). Each peak was identified by structural elucidation and interpretation of the mass spectra obtained; byproduct similarities, compared with the NIST library (National Institute of Standards and Technology), ranged from 69.7 to 89.7%. Information obtained from GC-MS chromatograms show the appearance and disappearance of several peaks (Figure 5); only two peaks (peak 1 and 5) remained after 8 hours of irradiation. These two peaks were considered as end products of nonylphenol photodegradation.

The pathways of nonylphenol photodecomposition were discussed based on the resultant byproducts. Chemical structures of six kinds of compounds were identified and are listed in Table 3. The analysis of degradation products suggests two ways of nonylphenol disappearance, as shown in Figure 6. The first way leads to the formation of Benzaldehyde, 4-methoxy, starting with hydroxylation of the carbon atom that is bonded to the aromatic ring as proposed by Gabriel et al. (2005). This is followed by the formation of an ester function through a mechanism similar to Baeyer-Villiger oxidation (an organic reaction in which a ketone is oxidized to an ester by treatment with peroxy acids or hydrogen peroxide). This ester function is easily cleaved by a mechanism of hydrolysis to yield an alcohol and an aldehyde (Kim et al., 2005; Viggor et al., 2002), which is further reduced in Benzaldehyde, 4-methoxy.

The second way of nonylphenol disappearance leads to the formation of Diisobutyl phthalate ester. The ipso-hydroxylation of the nonylphenol molecule, then a shift of the radical to the nearest electrophilic carbon, as reported by Giger et al. (2009), induces the formation of intermediate compounds such as 3-tert-Butyl-4-hydroxyanisole and Butylated Hydroxytoluene. A reduction reaction of 3-tert-Butyl-4-hydroxyanisole resulted in the formation of hydroquinone. The aforementioned alcohol that was produced is further oxidized into carboxylic acid (Giger et al., 2009), which reacts with chloride ions (Cl^-) to give acyl chloride. A reaction between acyl chloride (high reactivity) and the hydroquinone molecule (a combination of Friedel-Crafts C-acylation and the Baeyer-Villiger mechanism) occurred to form Phthalic acid and its esters, especially Diisobutyl phthalate ester. The appearance of Dibutyl phthalate is attributable to the presence of different isomers in the nonylphenol solution, precisely linear isomers. According to the kinetics discussed previously, the first way (short and probably fast) of nonylphenol degradation could be attributed to parameter "*b*" and the second way (long and probably slow) to parameter "*a*".

In summary, the nonylphenol degradation process resulted in the formation of Benzaldehyde, 4-methoxy (the main byproduct) and Phthalic acid, Diisobutyl ester. The significance of the present study is that no previous work has reported on these two

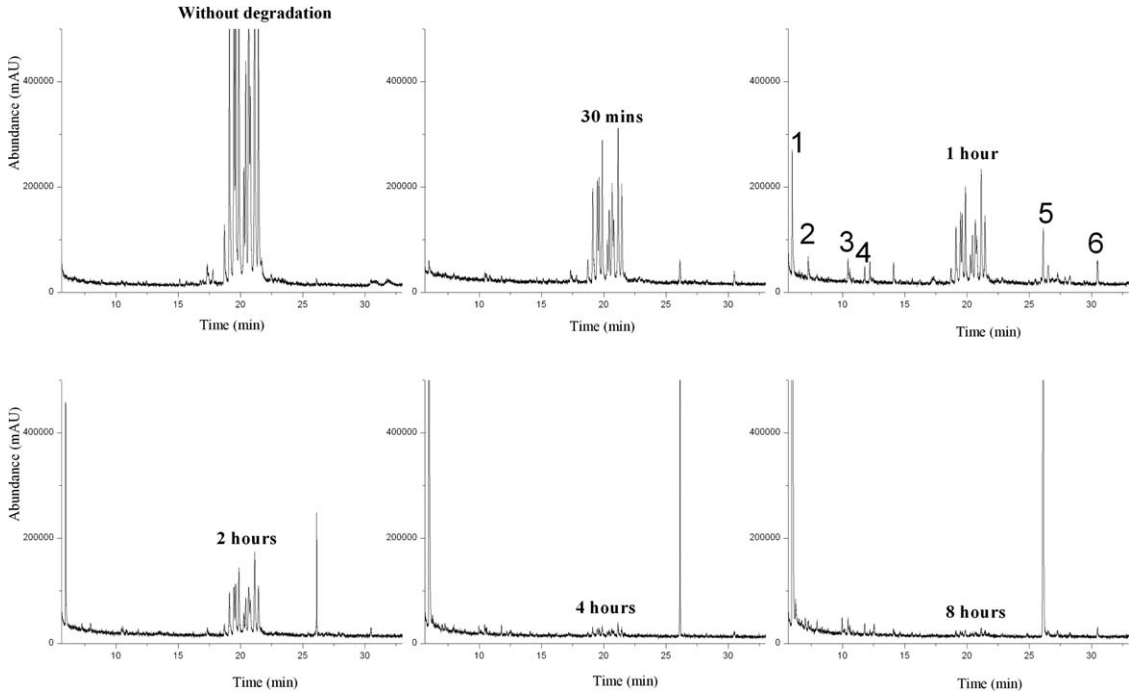

Figure 5—The GC-MS chromatogram of nonylphenol photodegradation products.

Table 3—Mass fragment ion and relative abundance of probable byproducts obtained from the spectra.

No	Retention time (min)	Compound	Largest peaks	mz/MW
1	5.958	Benzaldehyde, 4-methoxy-	135 (999), 136 (665), 77 (352), 92 (176), 107 (173), 39 (140), 63 (138), 65 (115), 64 (114), 50 (111)	135/136
2	7.24	Phthalic acid	104 (999), 76 (774), 50 (380), 148 (217), 74 (187), 75 (110), 105 (84), 77 (78), 38 (63), 37 (55)	104/166
3	10.439	3-tert-Butyl-4-hydroxyanisole	165 (999), 137 (485), 180 (475), 166 (108), 91 (86), 41 (83), 77 (78), 124 (75), 39 (62), 181 (61)	165/180
4	11.738	Butylated Hydroxytoluene	205 (999), 57 (284), 220 (242), 206 (169), 145 (138), 177 (120), 41 (103), 105 (82), 91 (74), 81 (62)	205/220
5	26.123	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	149 (999), 57 (261), 150 (94), 41 (91), 29 (72), 56 (65), 223 (64), 104 (51), 76 (35), 167 (34)	149/278
6	30.488	Dibutyl phthalate	149 (999), 150 (88), 41 (67), 76 (64), 104 (58), 223 (47), 205 (40), 29 (39), 65 (38), 93 (36)	149/278

compounds as results of nonylphenol degradation; there are also few available data and information on the ecotoxicity and environmental toxicity of Benzaldehyde, 4-methoxy. In addition, it is know that phthalates are subject to biodegradation in the environment. However, it is important to note that not all the peaks detected could be interpreted as results of nonylphenol degradation and that not all intermediates were detectable at the chosen times. In fact, certain species might be hardly detectable, which suggests that aromatic intermediates would have been rapidly oxidized (Jia et al., 2012). Further research should be done to fully elucidate the degradation pathways of nonylphenols.

Conclusions

To obtain the optimum efficiency of nonylphenol photodegradation, influences of initial concentrations of nonylphenols, pH, and H_2O_2 concentrations were investigated using GC-MS analyses. Optimal conditions were as follows: pH 1, 40-mg/L

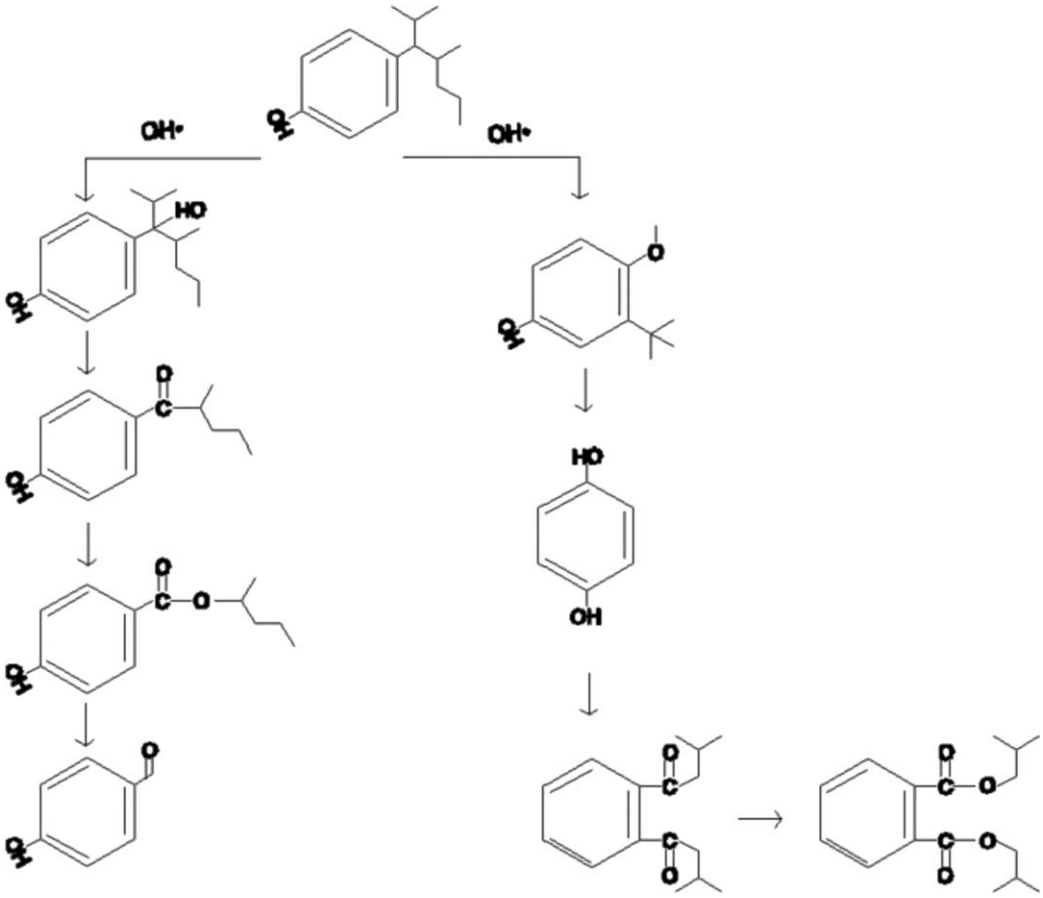

Figure 6—Pathway flowchart of nonylphenol degradation.

concentration of H_2O_2, and an initial nonylphenol concentration of 15 mg/L. These conditions allowed an efficient removal of nonylphenols. Benzaldehyde, 4-methoxyand Diisobutyl phthalate ester were the final products. Based on the byproducts that were identified, the degradation of nonylphenol occurred by several pathways, implying reactions between not only the hydroxyl radical and nonylphenol or intermediates, but also between many unstable compounds. The degradation process under UV irradiation in this study proved to be an efficient method for the removal of nonylphenol (an endocrine disrupting compound) from aqueous media. However, although pH 1 might be an optimum condition of nonylphenol removal, further studies should be conducted to determine if the conditions of the present study are applicable to real environmental samples. This will contribute significantly to not only designing a practical photocatalyzed oxidation system, but also in selecting an effective wastewater treatment technique.

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