

Sonochemical degradation of 4-*tert*-octylphenol in aqueous solutions: ideal acoustic frequency, influencing parameters, and desert sand particles synergy

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Received 13 December 2019; Accepted 30 November 2020

ABSTRACT

Sonochemical degradation of the non-volatile anion surfactant 4-*tert*-octylphenol (4-OP) as an endocrine disruptor at different ultrasonic frequencies was investigated. The effect of different operating parameters such as the initial concentration of substrate, temperature, initial pH, power and frequency of ultrasound irradiations and saturating gases on sonochemical degradation of 4-OP in aqueous solution has been studied. The experimental results have shown that the degradation rate increases when substrate concentration, ultrasound power and temperature increase in the experimental domain studied. 278 kHz sonochemical degradation of 4-OP enabled the highest degradation yields (90% in 60 min) in comparison to 20, 600, 800 and 1,700 kHz ultrasound irradiation. Degradation in the presence of saturating gases follows the order: argon > air > nitrogen. The most suitable degradation pH was acidic media under optimal conditions. The rate of 4-OP degradation and hydrogen peroxide formation as a function of the initial concentration of substrate was evaluated. The extent of the degradation process is limited by the quantity of hydroxyl radicals diffused from the cavitation bubbles region, therefore, the effect of bromide ions, terephthalate, methanol and the *tert*-butanol on sonolytic degradation of 4-OP was investigated. Ultrasonic treatment, for the removal of 4-OP, was promoted in complex matrices, such as natural water, seawater and sewage water, and the results were compared with distilled water. The addition of desert sand particles in the ultrasonic reactor experiments had a positive effect on degradation. To obtain detailed information on the interfacial region of cavitation bubbles, sonolytic degradation data were analyzed by the kinetic models of Okitsu, developed on the basis of a Langmuir-Hinshelwood mechanism. Results obtained were in good agreement with the proposed kinetics model. Decreasing the chemical oxygen demand and total organic carbon of the 4-OP initial solution is an indication that ultrasonic irradiation may be effective for the mineralization of the solution.

Keywords: Sonochemical degradation; Endocrine disruptors; 4-*tert*-octylphenol; Hydroxyl radical; Wastewater

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1. Introduction

Endocrine disruptors (EDs) are substances that mimic natural hormones in the endocrine system thus cause adverse effects on humans and wildlife [1]. Numerous compounds have been reported to have these effects. Alkylphenol ethoxylates (APEs), which constitute one of the main families of ED compounds, are widely employed in domestic and industrial fields. APEs are a group of surfactants that have been used for many years as dispersing agents, emulsifiers, and detergents [2]. During the biodegradation of APE in sewage treatment plants, alkylphenols are produced [3]. The degradation of alkylphenols gives nonylphenol and, in particular, octylphenol (OP). Those compounds can be considered more toxic and have more tendency toward bioaccumulation than parent compounds [4]. According to the available information, OP and its ethoxylates are considered to be “toxic” as defined in Section 64 of the Canadian Environmental Protection Act, 1999 [5]. They were also included in the 11 substances list proposed as “priority substances under review” in the Decision of the European Parliament and of the Council (from 16.01.2001, Brussels) [6]. Considering the importance of this recalcitrant substance, a need for more intensified process, that can reduce its presence in the environment, has become evident. For this purpose, numerous techniques have been employed to treat octylphenol, such as adsorption, biological treatment, flocculation and coagulation, which were found to be poorly efficient. For example, in the adsorption process, the organic pollutants are transferred from water to another phase, consequently, causing secondary pollution (undesirable sludge) which needs further treatment. Biological treatments, on the other hand, are very economical compared to other methods; however, for refractory and non-biodegradable compounds, these techniques are ineffective and require significant processing time. For example, the degradation efficiency of 4-*tert*-octylphenol (4-OP) through aerobic approach reached 90%, whereas it took 15 d of treatment time, which is considered to be very long compared to advanced oxidation techniques, in order to have the same efficiency [7]. 4-OP could be biodegraded by *tolypothrix*, however, its degradation efficiency was only 54.64% after 5 d exposure [8]. Corvini et al. [9] also studied the microbial degradation of nonylphenol. In this case, a more efficient technique, such as advanced oxidation, is needed. Advanced oxidation processes (AOPs) have been developed to degrade biorefractory organics in water. Almost all of the AOPs are based on the generation of very reactive and non-selective species, such as hydroxyl radicals ($\cdot\text{OH}/2.80\text{ V}$). In recent years, numerous studies have shown that ultrasound-induced-cavitation of aqueous solutions, containing non-biodegradable pollutants, proved to be an effective technique for their degradation [10–13]. Additionally, the sonolysis process is not affected by toxicity and low biodegradability of toxic pollutants and does not generate additional waste streams. The chemical effects of ultrasound are due to the acoustic cavitation phenomenon, which involve the formation, growth and subsequent collapse of microbubbles from acoustical wave compression/rarefaction. The lifetime of these microbubbles are of the order of microseconds, and their sudden

collapse leads to localized, transient high temperatures and pressures, resulting in the generation of highly reactive species, including hydroxyl ($\cdot\text{OH}$), hydrogen (H^{\cdot}), hydroperoxyl (HO_2^{\cdot}) radicals and hydrogen peroxide (H_2O_2) [13–16]. Reaction mechanisms are dependent on the physicochemical properties of the sonicated medium and particular compounds [17]. A volatile compound is degraded preferentially by thermolysis in the vapor phase of the cavitation bubble [18,19]. Non-volatile hydrophobic and surface-active compounds are thought to accumulate and react at the interface of the cavitation bubble [17,20], a region that is characterized by moderate temperature (interfacial properties) [21], along with high hydroxyl radical concentrations. Non-volatile hydrophilic compounds do not partition into the vapor phase and do not significantly accumulate at the bubble interface. Therefore, they are slowly degraded in bulk solution by reaction with $\cdot\text{OH}$ radicals or H_2O_2 that have diffused from the cavitation bubbles interface [22].

The aim of this study was to investigate the degradation of 4-OP by different frequency ultrasonic irradiation and to optimize the operating parameters for enhancing process efficiency. The effect of these parameters (substrate initial concentration, initial pH, temperature, power and frequency of ultrasound and saturating gases) was investigated. Potential reaction sites were investigated by monitoring the degradation rate in the presence of various quantities of bromine ion (Br^-), terephthalate, methanol and *t*-butanol, which are strong scavengers of reactive species in the bulk solution and at the liquid/bubble interface. Additionally, sonochemical degradation of 4-OP in a complex matrix such as natural water (Mineral and Zamzam), seawater (Dead Sea-Jordan and Mediterranean Sea-Skikda-Algeria), sewage water was compared to degradation in distilled water and discussed. In order to improve the efficiency of the ultrasonic process, the effect of the presence of sand particles has been studied. The kinetics model of the sonochemical degradation of 4-OP, with optimized conditions, was proposed and discussed. And finally, the chemical oxygen demand (COD) abatement and mineralization percentage of the 4-OP solution represented by total organic carbon (TOC) was examined.

2. Experimental

2.1. Sonication experiments

Aqueous solutions of 4-OP ($\text{CH}_3(\text{CH}_2)_7\text{C}_6\text{H}_4\text{SO}_3\text{-Na}$) purchased from Aldrich, UK, (CAS: 140-66-9) with initial concentrations of 2, 5, 7 and 10 mg L^{-1} were prepared by dissolving the compound into distilled water under sonication (at low ultrasonic power and low frequency) for a very short irradiation time. Degradation experiments were conducted in a cylindrical water-jacketed glass reactor, in order to control the temperature (Fig. 1). Ultrasonic continuous wave modes (20, 278, 600, 800 and 1,700 kHz), with a power of 3.03 W cm^{-2} , as determined by calorimetry, were delivered from the bottom of the reactor, through a piezoelectric disc (diameter 41 mm) fixed on a Pyrex plate (diameter 50 mm) and a multifrequency ultrasonic generator (radiocoms systems). The temperature of the solution was monitored using a thermocouple immersed in the reacting

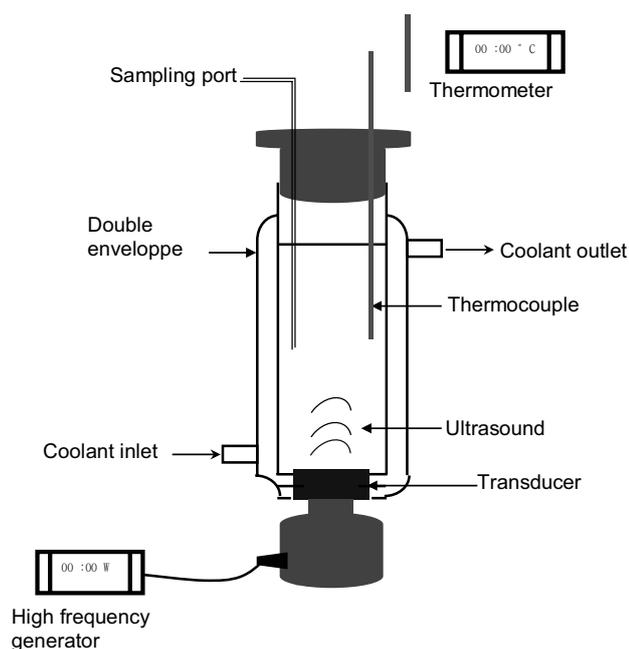


Fig. 1. Experimental setup.

medium. The temperature inside the reactor was maintained at $20^{\circ}\text{C} \pm 1^{\circ}\text{C}$ by circulating cooling water through a jacket surrounding the cell. The pH of the aqueous solution was determined by WTW pH-meter from Xylem Company (pH-730 equipped with a SenTix 41 electrode). The volume of the solutions sonicated was 300 mL. During irradiation, 3 mL aliquots were withdrawn at appropriate time intervals and the concentration of 4-OP at various time intervals was analyzed. Acoustic power dissipated in the reactor was determined using the standard colorimetric method [23].

2.2. Analysis

Aliquot samples (4-OP) were withdrawn at appropriate times, filtrated and analyzed by a high-performance chromatography HPLC equipped with a Supercosil LC-18 column (ID = 4.6 mm, length = 250 mm) and a UV detector (Waters model 486). Sample injections were achieved with a Rheodyne injection system equipped with a 200 μL loop for the lowest concentration. The used eluent was a mixture of methanol and pure water (60:40 v/v) at a flow rate of 1 mL min^{-1} .

2.3. Determination of hydrogen peroxide concentration

The hydrogen peroxide generated during sonication experiments, for different applied frequencies, was determined by the KI colorimetric method; it involves, the oxidation of iodide ion by H_2O_2 in the presence of ammonium heptamolybdate under slightly acidic conditions (pH 5.85). The produced I_3^- was spectrophotometrically determined at 355 nm ($\epsilon = 2.6 \times 10^4\text{ M}^{-1}\text{ cm}^{-1}$) [24].

2.4. Total organic carbon

TOC was measured with a Shimadzu 5050 TOC Analyser which functionality is based on combustion/non-dispersive

infrared (NDIR) gas analysis. Total carbon was determined first, followed by inorganic carbon, and TOC was determined by subtracting inorganic from total carbon. The uncertainty in this assay, quoted as the standard deviation of three separate measurements, was never larger than 1% for the range of TOC concentrations under consideration. As suggested by the manufacturer, the instrument was calibrated before each use with standard solutions.

2.5. Chemical oxygen demand

COD was measured according to the method presented by Thomas and Mazas [25], using a dichromate solution (Aldrich) as the oxidizing agent in a strong acidic medium. 2 mL of test samples (or distilled water for the control) were transferred into the dichromate reagent (in hermetically sealed tubes and after homogenization) and reacted at 150°C for 120 min. The concentration was determined by measuring the optical density using a UV-vis spectrophotometer (Ocean Optics HR2000 series). In order to avoid the interference of the residual hydrogen peroxide, samples were neutralized with sodium hydroxide and treated with catalase (supplied by Merck) prior to performing the COD analysis. COD was determined by the dichromate micro-digester method [25]. Each reported value is the average of three measurements per vial was taken, and the maximum deviation between three different sample vials did not exceed 1.5%.

3. Results and discussion

3.1. Effect of initial 4-OP concentration

Fig. 2 shows 4-OP concentration-time profiles during sonochemical degradation at 278 kHz, $20^{\circ}\text{C} \pm 1^{\circ}\text{C}$, 3.92 W cm^{-2} and an initial solute concentration of 2, 5, 7 and 10 mg L^{-1} (this substrate concentration range is chosen just to better understand the degradation phenomena under ultrasound, and for a future application to real matrices (concentration of the order of ng L^{-1})). It was observed that the concentration of pollutants decreased exponentially with time. The extent of degradation is found to be inversely proportional to the initial concentration of solute. The removal of 4-OP has almost achieved after just 1 h of treatment with an initial substrate concentration of 2 mg L^{-1} , however, the degradation percentage decreased to 79% for 5 mg L^{-1} 4-OP, 70% for 7 mg L^{-1} and 44% for 10 mg L^{-1} . The notable feature of this plot is that the degradation of the 4-OP exponentially varies with the sonication time instead of the expected linear behavior. Fig. 3 shows the effect of the initial substrate concentration on the rate of 4-OP degradation. The rate of 4-OP degradation increases with an increase in the initial substrate concentration from 2 mg L^{-1} up to 10 mg L^{-1} . Similar results have been obtained for the sonolytic of bisphenol A (BPA) [26], and of 4-cumylphenol (CyP) [10], and of ibuprofen (IBP) [27].

As shown in Fig. 4, the sonochemical rate of 4-OP decreased as a function of the irradiation time. In this figure, the significant correlation coefficient ($R = 0.986$) indicates that direct sonolysis of 4-OP follows first-order reaction kinetics, with about 90% of the substrate was degraded

after only 45 min of irradiation time. The apparent reaction rate equation can be written as:

$$\ln\left(\frac{C}{C_0}\right) = -kt \tag{1}$$

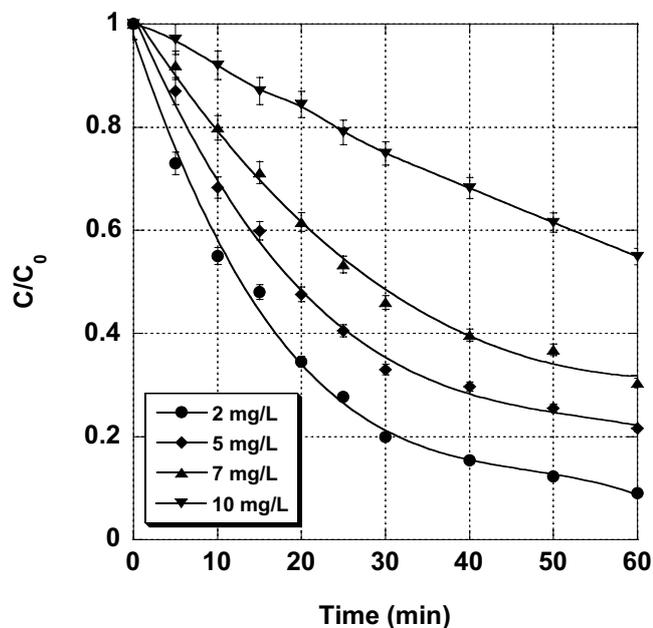


Fig. 2. Sonochemical degradation of 4-OP for various initial solute concentrations (ultrasonic frequency: 278 kHz; acoustic power: 3.92 W cm⁻²; volume: 300 mL; pH: 6.55; temperature: 20°C ± 1°C).

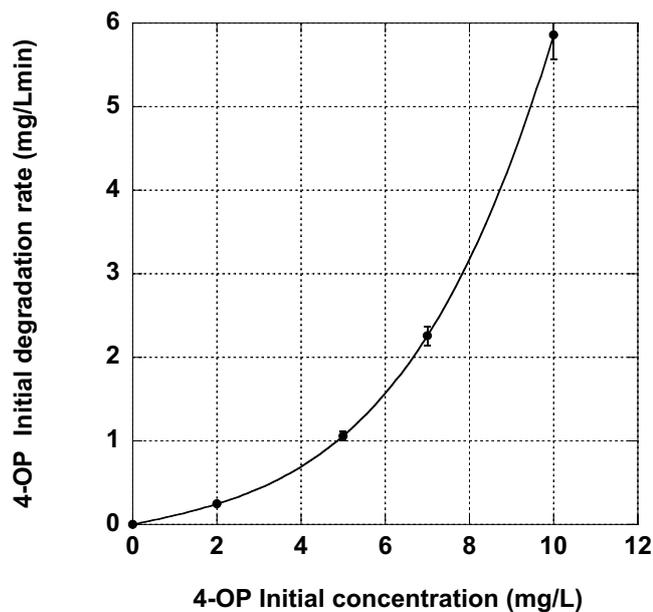


Fig. 3. Evolution of initial degradation rate of 4-OP as a function of initial substrate concentration (ultrasonic frequency: 278 kHz; acoustic power: 3.92 W cm⁻²; volume: 300 mL; pH: natural (6.55); temperature: 20°C ± 1°C).

The first-order reaction rate constant k is estimated to be $1.77 \times 10^{-1} \text{ min}^{-1} (\pm 0.03)$, found from the slope of the plots of $\ln(C/C_0)$ vs. irradiation time.

In parallel to the sonochemical degradation process of 4-OP, hydrogen peroxide is formed in the solution. Fig. 5 illustrates the formation rate of H₂O₂, for four initial concentrations of 4-OP, and its respective value without substrate. It was found that the rate of H₂O₂ accumulation was largest

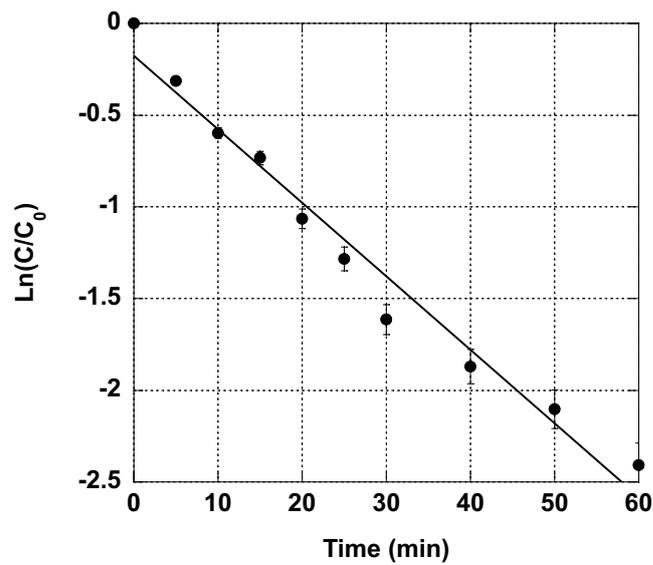


Fig. 4. Sonochemical degradation kinetics of 4-OP in aqueous solution (ultrasonic frequency: 278 kHz; acoustic power: 3.92 W cm⁻²; 4-OP initial concentration: 2 mg L⁻¹; volume: 300 mL; pH: 6.55; temperature: 20°C ± 1°C).

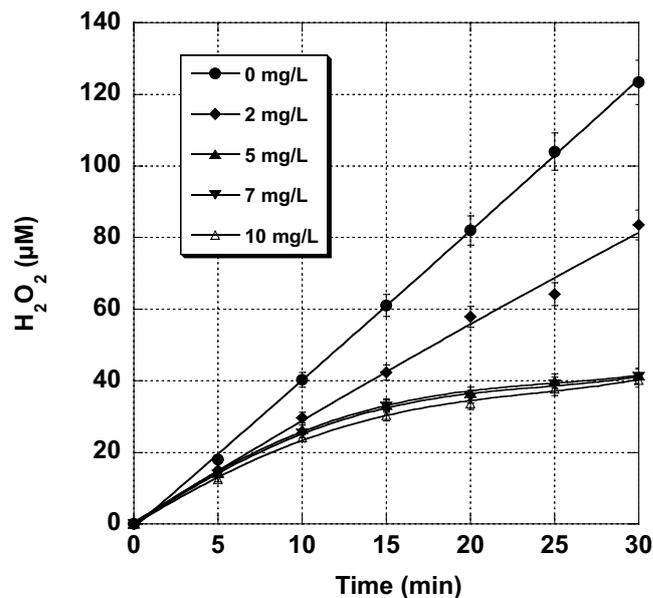


Fig. 5. Accumulation of hydrogen peroxide during sonication of distilled water with and without 4-OP (ultrasonic frequency: 278 kHz; acoustic power: 3.92 W cm⁻²; volume: 300 mL; pH: 6.55; temperature: 20°C ± 1°C).

Table 1
Selected physicochemical proprieties of 4-OP

Molecular	4- <i>tert</i> -octylphenol
CAS registry number	140-66-9
Synonyms	4- <i>tert</i> -octylphenol, <i>p</i> -octylphenol
EC number	205-426-2
Molecular formula	$\text{CH}_3(\text{CH}_2)_7\text{C}_6\text{H}_4\text{SO}_3\text{-Na}$
Chemical structure	
Melting point (°C)	79–82
Boiling point (°C)	150 at 4 mmHg
Molecular weight (g mol ⁻¹)	206.32
Water solubility (g L ⁻¹)	0.01
Vapour pressure (mmHg)	0.0005
Octanol-water distribution constant	5.28
pKa	10.1
Henry's law constant (atm m ³ mol ⁻¹)	6.89×10^{-6}

in the control reaction (without substrate) and decreased with increasing the concentrations of 4-OP, by scavenging reaction (screen effect) [10]. This tendency is in good agreement with the results shown in Fig. 2. An increase in substrate concentration would increase the probability of hydroxyl radicals attack on pollutant compounds. Because at the interface of the bubbles the $\cdot\text{OH}$ radical quantity is very important and the hydroxyl radical recombination would be the process, an increase of the solute concentration at this region would increase the hydroxyl radical quantities that react with the solute, and the degradation rate would be increased accordingly. Because of the low value of Henry's law constant (6.89×10^{-6} atm m³ mol⁻¹) Table 1, 4-OP cannot be degraded inside the cavitation bubble by pyrolysis. And due to its moderate solubility in water (5–10 mg L⁻¹) and relative high octanol/water partition coefficient ($\log K_{ow} = 5.28$ at 25°C), 4-OP may be removed through reaction with $\cdot\text{OH}$ radical at the second region (interface of cavitation bubble/solution). This observation is a clear indication of $\cdot\text{OH}$ -mediated oxidation as one of the degradation pathways of 4-OP. In the absence of solute in solution in the sonochemical reactor, the formation of hydrogen peroxide via the recombination reaction of hydroxyl radicals produced under the effect of ultrasonic irradiation reaches a peak. This result can be explained by the absence of competing species consuming hydroxyl radicals.

3.2. Effect of solution temperature

Sonochemical degradation of 4-OP conducted under different temperatures ranging from 20°C to 50°C for an initial substrate concentration of 2 mg L⁻¹ at 278 kHz and 3.92 W cm⁻² was studied. Evidently, increasing the temperature results in a moderate increase in the degradation

rate (Fig. 6). Generally speaking, increasing the temperature is likely to facilitate bubble formation due to an increase in the equilibrium vapor pressure. We have observed that the rate of production of radical species ($\cdot\text{OH}$ and $\text{HOO}\cdot$) increased with the temperature of the bulk phase, leading to higher solute degradation rates. Theoretically, the temperature solution affects the viscosity, surface tension, gas solubility and vapor pressure. As a result of increasing the temperature of the liquid, the surface tension and viscosity of the liquid decrease, and consequently, the cavitation threshold limit decreases. Following the results of subsequent studies on the influence of temperature in sonochemical processes, we think that the effect of temperature on sonochemical degradation rate rests a complicated phenomenon. In order to better simulate the natural conditions, and to optimize the relative kinetics of the reaction between the compound and hydroxyl radicals, the oxidation process temperature was maintained at 20°C for the rest experiment.

3.3. Effect of ultrasonic power

The sonochemical degradation of aqueous 4-OP solution (2 mg L⁻¹) was investigated at different acoustic power (0.98–4.89 W cm⁻²) at 278 kHz and 20°C ± 1°C. As shown in Fig. 7, it is clear that the higher the power, the higher is the degradation of 4-OP and hence the degradation rate. These results may be explained via the increase in the number of collapsing cavities leading to an increase in the quantities of $\cdot\text{OH}$ radical produced [27]. Additionally, an increase in ultrasonic power means an increase in the acoustic amplitude. This acoustic amplitude affects several parameters such as bubble collapse time, internal pressure in the cavitations bubble and the transient temperature

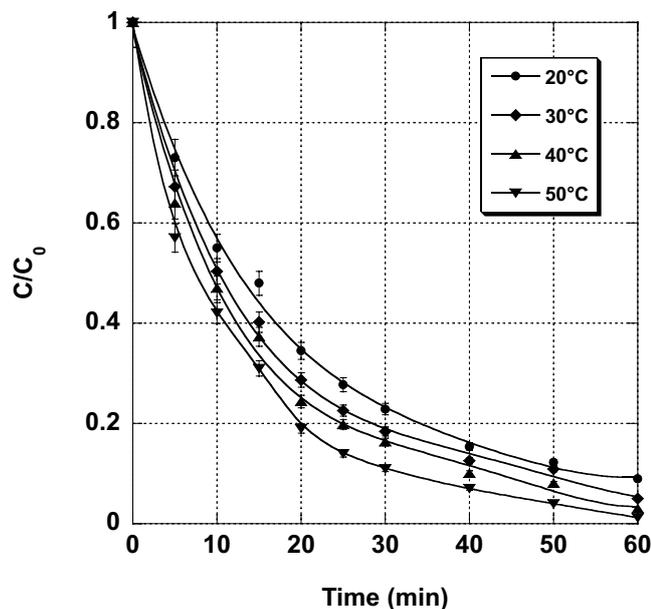


Fig. 6. Effect of temperature on the sonochemical degradation of 4-OP (ultrasonic frequency: 278 kHz; acoustic power: 3.92 W cm⁻²; 4-OP initial concentration: 2 mg L⁻¹; volume: 300 mL; pH: 6.55).

(the activity of bubbles). At higher acoustic amplitudes, the cavitations bubble collapse will be more violent [28]. The obtained results showed that the highest degradation was obtained at an ultrasonic power of 3.92 W cm⁻², which was used in all subsequent experiments, as seen in the below figures (noted though that the acoustic power of 100 W reduces the life of the piezoelectric ceramic).

The rapport of electrical energy per mass (EE/M); defined as the kWh of electrical energy required to remove 1 kg of the contaminant such as 4-OP as a model molecule (Table 2):

$$\frac{EE}{M} = \frac{p \times t}{v \times (c_i - c_f)} \quad (2)$$

where EE/M = electrical energy per mass (kWh kg⁻¹); p = power input of the US emetteur (kW); t = treatment time (h); v = volume of treated aqueous pollutant (m³); $(c_i - c_f)$ = initial and final pollutant concentrations or collective environmental parameter respectively.

This relationship is mostly used as an efficiency indicator in laboratory-scale studies, particularly for the total elimination of organic matter. Comparing the energy consumption of the sonochemical process for pollutant degradation (4-OP), it has been observed from Table 2, that at this operating conditions of the experiment, such as the reactor configuration, the type and power of the ultrasound transmitter, the actual oxidation process appears economically very satisfactory.

3.4. Effect of ultrasonic frequency

It is well known that the sonochemical degradation process of organic species is ultrasonic frequency-dependent.

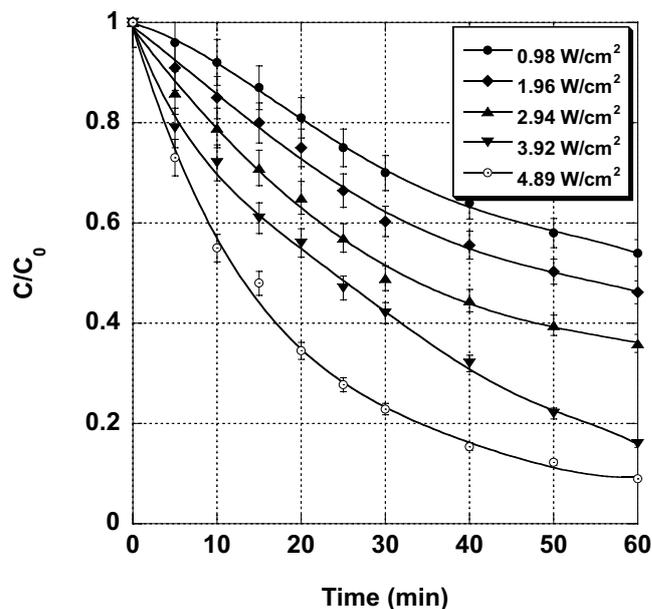


Fig. 7. Effect of acoustic power on the degradation of 4-OP (ultrasonic frequency: 278 kHz; volume 300 mL; 4-OP initial concentration: 2 mg L⁻¹; pH: 6.55; temperature: 20°C ± 1°C).

Table 2

Ultrasonics process performances for the treatment of 4-OP solutions at different power

Acoustic power (W cm ⁻²)	EE/M ⁽⁰⁾ (kWh kg ⁻¹)
0.98	15.50
1.96	25.16
2.94	31.74
3.92	32.52
4.89	37.03

In order to study the effect of ultrasonic frequency on the degradation of 4-OP, five ultrasound frequencies (20, 278, 600, 800 and 1,700 kHz) were investigated with the same acoustic power and the optimum results were obtained at an ultrasonic frequency of 278 kHz (Figs. 8 and 9). The obtained results showed that the degradation rate increase with the ultrasonic frequency up to 278 kHz. However, a further increase in the ultrasonic frequency resulted in a sharp decrease in 4-OP degradation efficiency. The decomposition rate is dependent on the rate of •OH radical formation, hydroxyl mass transfer and other reactive species, in other words, the rate of cavitation occurrence which is a function of the cavitation period and the number of the transient cavitations bubble (a number of micro-reactors). The collapse of the cavity is rapid and more violent at higher frequencies, resulting in an increase in the efficiency of •OH radical production. However, at either very high or low frequency, the cavitation effect is reduced and the •OH radical quantities decreases and consequently will result in a decrease of the 4-OP degradation. It's well known and based on the results obtained, the frequency has a profound effect on the

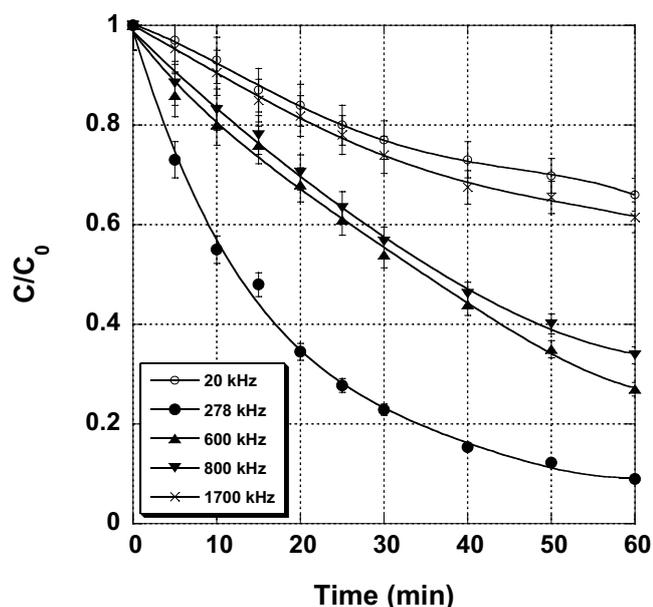


Fig. 8. Effect of ultrasonic frequency on the sonochemical degradation of 4-OP (acoustic power: 3.92 W cm^{-2} ; volume: 300 mL; 4-OP initial concentration: 2 mg L^{-1} ; pH: 6.55; temperature: $20^\circ\text{C} \pm 1^\circ\text{C}$).

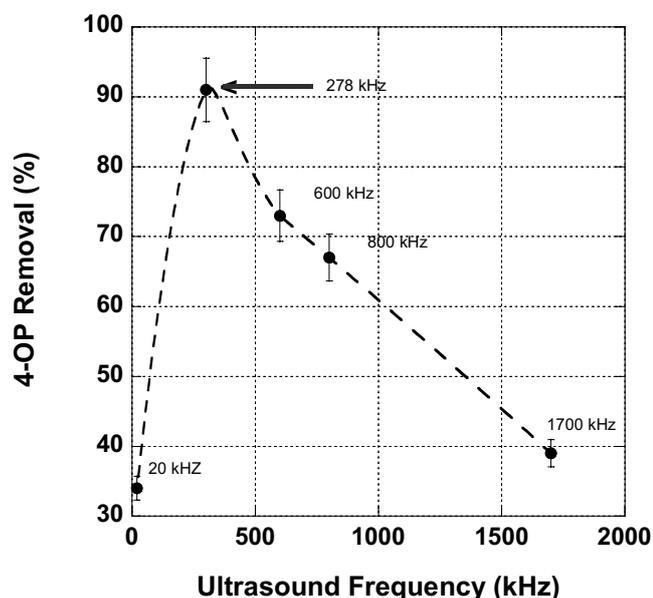


Fig. 9. Sonochemical degradation of 4-OP as function of ultrasonic frequency (acoustic power: 3.92 W cm^{-2} ; 4-OP initial concentration: 2 mg L^{-1} ; volume: 300 mL; pH: 6.55; temperature: $\pm 20^\circ\text{C}$).

degradation rate, therefore, an optimum frequency value should be utilized. 278 kHz frequency was selected as the optimum value, which was applied in all subsequent experiments. Dalodière et al. [29] followed the kinetics of hydrogen peroxide formation under ultrasonic irradiation, where they found that this speed is dependent on the ultrasonic frequency and the atmosphere.

3.5. Effects of pH

In wastewater treatment, pH is a crucial parameter influencing the efficiency of the sonochemical degradation of organic pollutants. In order to study the sonochemical action on the ionic and neutral forms of the substrate, effects of pH on the removal of 4-OP were investigated by using different initial pH values changing from 2.5 to 11, under fixed process parameters. Dilute sodium hydroxide and sulfuric acid solutions were used for the pH adjustments. Fig. 10 shows the effect of pH on the sonochemical degradation of 4-OP. The results indicated that the ultrasonic degradation rates, in strongly acidic solution; pH equal 2.5 and natural pH equal to 6.5, are higher than those obtained at alkaline conditions (pH range 8 to 11). The lower degradation is observed at pH 11. The degradation rate decreases with increasing solution pH. This can be attributed to the dependency of 4-OP ionization on the pH value. The pK_a values of 4-OP are approximately 10 [30,31]. It doesn't dissociate in an acidic medium; stays in the molecular form. These observations can be confirmed by the evaluation of the ionic fraction. The ionic fraction of 4-OP ion (ϕ_{ions}) can be calculated from:

$$\phi_{\text{ions}} = \frac{1}{1 + 10^{(pK_a - \text{pH})}} \quad (3)$$

Obviously, ϕ_{ions} increases as the pH value increased. Hence, at pH 2.5 to 6.5, the substrate exists mainly in molecular form ($\phi_{\text{ions}} = 3.16 \times 10^{-9}$ to 3.16×10^{-5}), while at pH 8 it is partly in ionic form. And at pH = 11, the compound is mostly in its ionic form ($\phi_{\text{ions}} = 0.90$) due to deprotonation of the phenolic group. At pH 11, the decomposition is completely carried out in the bulk of the solution far to cavitation bubbles where there are a few quantities of hydroxyl radicals ($\cdot\text{OH}$). The important degradation of 4-OP in acidic condition must be due to the enriched hydrophobicity of the molecule. This behavior promotes the phenomenon of diffusion of substrate molecules through the bubble-solution interface at acidic pH, where in the amount produced hydroxyl radicals is higher. Theoretically, the ionic form of 4-OP has much more hydrophilicity and soluble character compared to its neutral state and therefore less likely to approach the bubble-solution interface.

3.6. Effects of diverse scavengers

3.6.1. Effect of *tert*-butyl alcohol and KBr addition

In order to obtain information on the different zones of sonochemical reactions, the formation of oxidative intermediate species under sonolysis conditions and their role in the 4-OP degradation has been studied by using the appropriate scavengers. In cases where the degradation kinetics of the model organic molecules are considerably reduced in the presence of these radical inhibitors (or scavengers), then it is possible to confirm the involvement of a radical reaction. Fig. 11 shows the normalized concentration-time profiles of 4-OP during degradation at 2 mg L^{-1} of the substrate, 278 kHz, 3.92 W cm^{-2} , $20^\circ\text{C} \pm 1^\circ\text{C}$ and in the presence of *tert*-butyl alcohol or KBr as radical

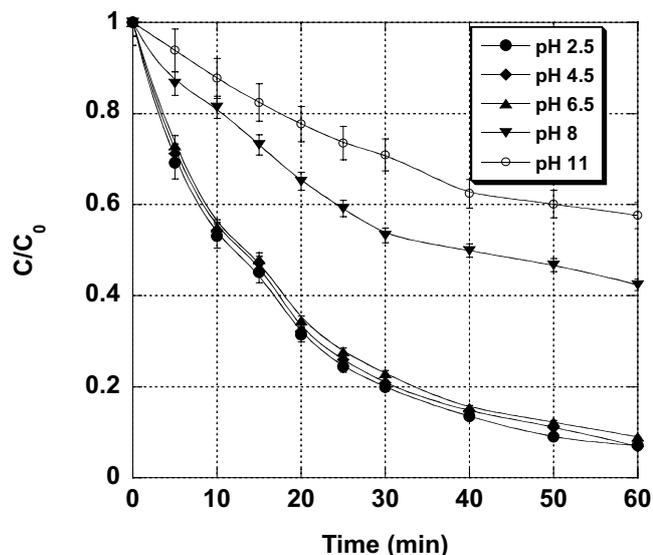


Fig. 10. Effect of initial pH on the sonochemical degradation of 4-OP (ultrasonic frequency: 278 kHz; acoustic power: 3.92 W cm^{-2} ; 4-OP initial concentration: 2 mg L^{-1} ; volume: 300 mL; temperature: $20^\circ\text{C} \pm 1^\circ\text{C}$).

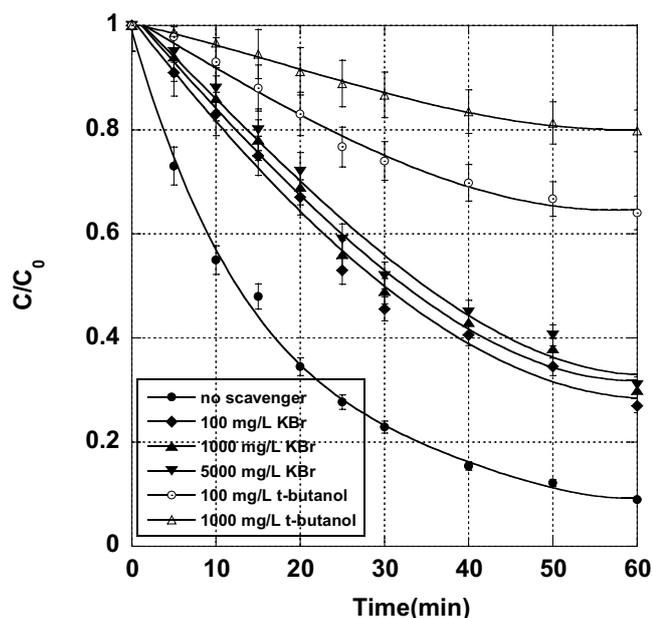


Fig. 11. Effect of bromide and *tert*-butanol concentration on the sonochemical degradation of 4-OP (ultrasonic frequency: 278 kHz; acoustic power: 3.92 W cm^{-2} ; 4-OP initial concentration: 2 mg L^{-1} ; volume: 300 mL; pH: 6.55; temperature: $20^\circ\text{C} \pm 1^\circ\text{C}$).

scavengers. *Tert*-butyl alcohol is a known scavenger for the interior region of the bubble and/or interfacial region of the cavitation bubbles. As clearly seen, the degradation efficiency of 4-OP was considerably reduced upon the addition of *tert*-butyl alcohol in the applied range ($100\text{--}1,000 \text{ mg L}^{-1}$) considerably reduced. In addition, potassium bromide, which is a known scavenger for the bulk solution region and possibly for the interfacial region of the collapsing

bubbles, is a non-volatile strong electrolyte that can be readily degraded by free radicals. The figure also demonstrates that the addition of $100, 1,000$ and $5,000 \text{ mg L}^{-1}$ of KBr resulted in a small decrease of 4-OP decomposition. This suggests that the main mechanism of 4-OP decomposition is chemical oxidation by the hydroxyl radicals. This observation also suggests that the degradation takes place mainly at the interfacial region of cavitation bubbles-solution where the substrate is oxidized by hydroxyl radicals produced within the cavitation bubbles as a result of the water sonolysis. The formation of volatile products from the *tert*-butyl alcohol degradation that accumulates inside the bubble can affect the degradation rate of 4-OP. Such volatile products decrease the temperature inside the bubbles, which, in return, slow the sonolytic reactions. For similar cases, several subsequent studies find that the presence of alcohols such as *tert*-butanol, methanol or isopropyl alcohol [32–37] scavenge the formation of hydroxyl radicals in the surface of the bubbles and in the bulk solution.

3.6.2. Effect of terephthalic acid and methanol

In order to better understand the degradation mechanism of 4-OP under ultrasound, as well as their degradation byproducts, two other scavenger molecules, namely terephthalic acid or terephthalate (TA) and methanol (Me-OH), were added to the initial irradiated solution. Terephthalic acid (TA) is used to scavenge $\cdot\text{OH}$ in the bulk solution formed from sonication. It can be considered as a good competitor in order to trap all the formed hydroxyl radicals during the implosion of the cavitation bubble (i.e., limits the diffusion of the hydroxyl radicals produced). It is capable of insuring complete inhibition of the reactions with the hydroxyl radicals. In this study, TA was used to estimate the theoretical quantities of hydroxyl radicals produced by ultrasound and consumed by 4-OP. To examine and to confirm whether the reaction occurred in the bulk solution and/or in the interfacial region, TA (different concentrations such as 2, 5 and 10 mM) were added to 4-OP initial solution at 2 mg L^{-1} of initial concentration systems to scavenge $\cdot\text{OH}$. As shown in Fig. 12, the $\cdot\text{OH}$ production rate in presence of the substrate was very close to that in its absence, indicating that TA effectively trapped $\cdot\text{OH}$ in 4-OP systems. The presence of TA decreased the $\cdot\text{OH}$ production rates compared to those in the absence of TA. However, TA was not able to completely remove all of $\cdot\text{OH}$ produced in the medium, indicating that the dissolution reaction mostly occurred in both the bulk solution and probably in the interfacial areas of cavitation bubbles.

The presence of methanol (with a concentration of 2, 5 and 10 mM), slowed down sonolysis of 4-OP processes but incomplete removal of hydroxyl radical was observed. This observation suggested the important role of $\cdot\text{OH}$ as a reactive transient (Fig. 12).

3.7. Effects of saturating gas

Dissolved gas saturation is one of the common methods that have been applied to enhance the degradation reactions of aqueous pollutants in sonochemical processes, by improving the cavitation phenomena. The sonochemical

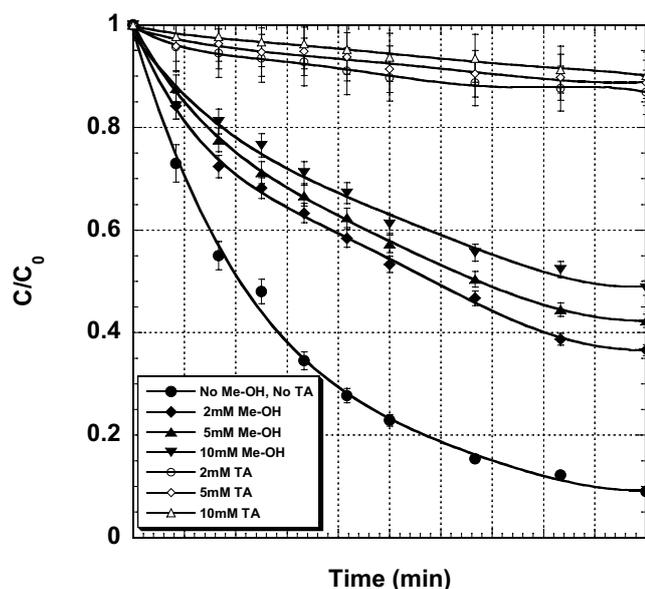


Fig. 12. Effect of terephthalic acid (TA) and methanol (Me-OH) concentration on the sonochemical degradation of 4-OP (ultrasonic frequency: 278 kHz; acoustic power: 3.92 W cm⁻²; 4-OP initial concentration: 2 mg L⁻¹; volume: 300 mL; pH: 6.55; temperature: 20°C ± 1°C).

degradation of 4-OP for the gas sparging of argon, air or nitrogen was reported (Fig. 13). Compared with the value at constant flow rates, high sonochemical degradation of 4-OP was observed for most sparging cases. It can be clearly seen that the order of degradation ratio is as follows: argon > air > nitrogen. It is well known that low thermal conductivity (λ) and high polytropic gas ratio (γ) favor higher collapse temperature [10]. Additionally, the thermal conductivities can determine the heat transfer t rate to the surrounding liquid [33]. The values of λ and γ for the different used gas such as for Ar ($\lambda = 179 \times 10^{-4} \text{ Wm}^{-1} \text{ K}^{-1}$, $\gamma = 1.67$), air ($\lambda = 259 \times 10^{-4} \text{ Wm}^{-1} \text{ K}^{-1}$, $\gamma = 1.4$) and nitrogen ($\lambda = 240 \times 10^{-4} \text{ Wm}^{-1} \text{ K}^{-1}$, $\gamma = 1.4$). Since it has the maximum polytropic ratio and the lowest thermal conductivity, argon produces the highest potential energy during bubble collapse. In addition, it has been shown that small amounts of oxygen, which could be present in argon as the saturating gas under laboratory operating conditions, can increase radical hydroxy production. The above factors possibly explain the higher 4-OP degradation when using argon as the saturating gas. The existence of nitrogen, on the other hand, results in the lowest implosive energy since it has the highest thermal conductivity. As a result, nitrogen transfers the heat comparatively quicker from the hot spots to the surrounding liquid, and the presence of nitrogen in the reactor can inhibit the formation of hydroxyl radicals and the accumulation of hydrogen peroxide, which reduces the degradation of pollutants. Ultrasonic activity causes oxygen dissociation when air is used, which creates extra hydroxyl radicals that can promote the degradation of contaminants. While Ar presented the best performance, the use of air as the saturating gas is preferred from a practical point of view.

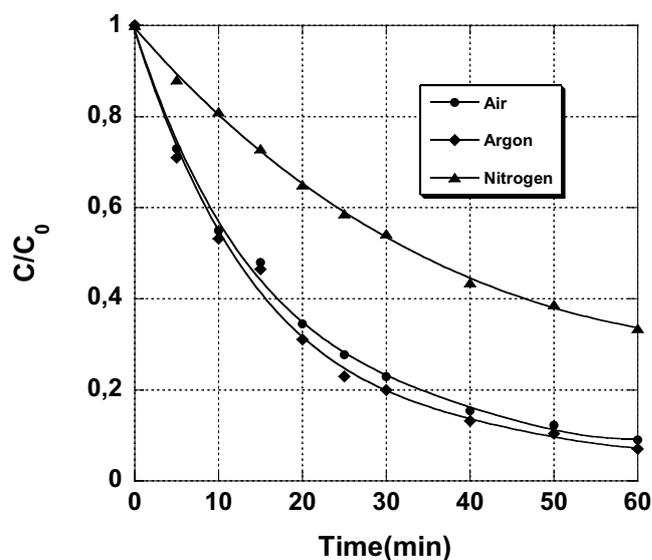


Fig. 13. Effect of saturating gas on the sonochemical degradation of 4-OP (ultrasonic frequency: 278 kHz; acoustic power: 3.92 W cm⁻²; 4-OP initial concentration: 2 mg L⁻¹; volume: 300 mL; pH: 6.55; temperature: 20°C ± 1°C).

3.8. Effects of water matrix

During the last few years, studies in the literature have applied ultrasonic waves in wastewater and water treatment, but many of them studied the effect of the water real matrix on the process efficiency. The ultrasonic process has gained considerable interest due to their effective decontamination efficiencies compared to other advanced oxidation processes. Thus, evaluation of the potential of the ultrasonic process for the destruction of the inorganic and organic compounds present in a real water matrix has emerged as a promising technique due to the fact that the kinetics of destruction of organic matter is not affected [34,36]. In order to evaluate this effect, 4-OP was dissolved in several water matrices of namely: distilled water (DW), natural mineral water (NMW), Zamzam natural water (ZNW), Mediterranean seawater (MSW), Dead seawater (DSW), and sewage water (SW). These latter water matrixes have different properties and the main characteristics are presented in Table 3. Fig. 14 shows the comparative degradation of 4-OP in (DW), (NMW), (ZNW), (MSW), (DSW), and (SW) at the same initial substrate concentration (2 mg L⁻¹). As noticed in Fig. 14, a negative effect on the sonochemical degradation process of 4-OP was reported for 4-OP dissolved in either DSW or SW. In this type of matrix, the phenomenon of interference where the existence of several chemical species, which competes with the target substrate, react with the hydroxyl radicals produced under irradiation. In other words, the inhibiting effect of these species can be explained by its ability to disturb the cavitations phenomenon (such as number of bubbles, bubble life and bubble activity, etc.), and/or by the screen effect (by the material transfer limitation). However, as seen in Fig. 14, in natural mineral water, Mediterranean seawater and Zamzam natural water matrix, the enhancement rate of 4-OP degradation was found to be more effective compared to a distilled water matrix. It can

Table 3
Characteristics of the different matrix water

	Distilled water (DW)	Natural mineral water (NMW)	Mediterranean seawater (MSW) ($\times 10^{-3}$)	Dead seawater (DSW)	Zamzam natural water (ZNW)	Sewage water (SW)
Ca ²⁺ (mg L ⁻¹)	/	468	0.4	14.4	114	4.3
Mg ²⁺ (mg L ⁻¹)	/	74.5	1.27	35.2	27.97	3.1
Na ²⁺ (mg L ⁻¹)	/	9.4	10.56	34.9	/	2.9
K ⁺ (mg L ⁻¹)	/	2.8	0.38	7.56	/	0.6
SO ₄ ²⁻ (mg L ⁻¹)	/	1,121	2.65	0.54	610.53	/
HCO ₃ ⁻ (mg L ⁻¹)	/	372	0.14	240	285	8.8
Cl ⁻ (mg L ⁻¹)	/	20	20	208	147.50	2
NO ₃ ⁻ (mg L ⁻¹)	/	2.9	/	/	7.96	28
F (mg L ⁻¹)	/	0.36	0.001	/	0.72	/
pH	6.5	7.4	/	/	7.6	7.4
Salinity (g L ⁻¹)	/	2.078	35	270	0.5	/

be concluded that the chemical composition of these three types of water matrix has a positive effect on the cavitation phenomenon, which promotes the production of hydroxyl radicals and other selective radical species that react with 4-OP with an acceptable rate constant. Therefore, at high frequency, the sonochemical degradation of 4-OP in the complex matrix represents a very interesting advanced oxidation process.

3.9. Degradation of 4-OP in aqueous suspensions of desert sand (Sahara of Algeria)

The degradation of 4-OP by ultrasonic irradiation in the presence of aqueous suspensions of desert sand has been investigated. The idea of using sand particles is to regulate the boiling phenomenon (which is soft and regular) by adding pumice grains in the distillation process in the laboratory. That is, bubbles are formed without sudden changes in pressure. In the same way, the presence of sand grains in the sonochemical oxidation reactor will regulate the successive steps of the formation of cavitation bubbles such as birth, growth and implosion. And secondly, the main effect observed when a biphasic solid-liquid medium is sonicated by ultrasound is the production of excess cavitation nuclei for a larger number of collapse events, that will result in the formation of hydroxyl radicals and other radical. The desert sands are primarily derivatives of titanium and zinc. Technically, the following constituents are most prevalent: Ti from 4,000–16,000 ppm; and of Zn \approx 200 ppm [38]. The effect of the presence of sand particles on the sonochemical degradation of 4-OP at 278 kHz and 3.92 W cm⁻² are shown in Fig. 15. The degradation of 4-OP was higher in the presence of sand particles, compared to those without sand particles. The effect of sand particles may be partially explained by considering two effects during the degradation process, the first effect is the activity of hydroxyl radicals formed from cavitations phenomenon during the sonolysis of water, and the second effect is probably the synergy between sonolysis and the photocatalytic process. From this competition between the two effects, one may therefore expect substrate concentration

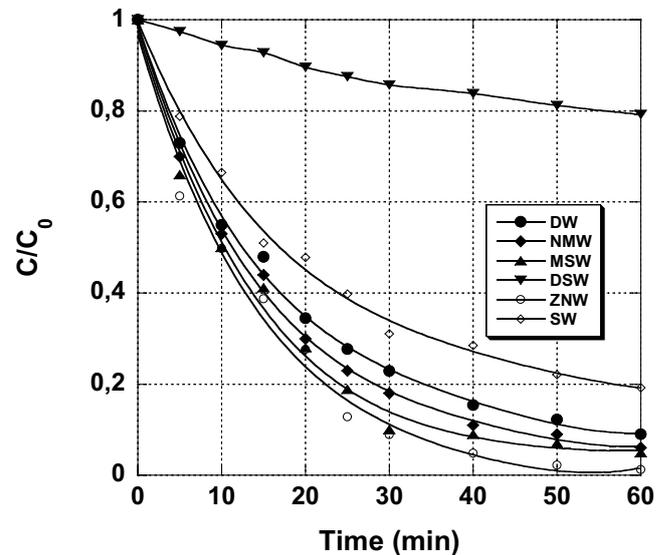


Fig. 14. Sonochemical degradation of 4-OP in different water matrices such as distilled water (DW), natural mineral water (NMW), Zamzam natural water (ZNW), Mediterranean seawater (MSW), Dead seawater (DSW) and sewage water (SW) (ultrasonic frequency: 278 kHz; acoustic power: 3.92 W cm⁻²; 4-OP initial concentration: 2 mg L⁻¹; volume: 300 mL; pH: natural; temperature: 20°C \pm 1°C).

should be decreased for both effects. When the sonocatalytic is coupled with sonolysis a higher efficiency of the ultrasonic system is expected due to the additional generation of hydroxyl radicals and sonolytic splitting of water molecules. This is attributed to the interaction of ultrasound with solid particles, which is able to produce highly oxidative species that are capable to oxidize 4-OP effectively. Several studies have found that the sonochemical reactivity increases in the presence of inert glass beads since the presence of a heterogeneous catalyst seems to increase the formation rate of cavitation bubbles by providing additional nuclei [39,40]. It can be concluded that in wastewater

treatment applications, the sonocatalytic technique can be integrated as a hybrid process at treatment stations.

3.10. Development of sonochemical degradation mechanisms

In order to determine the exact region of sonochemical degradation of 4-OP in solution (the effective reaction site), it is necessary to find a nonlinear kinetic model that accurately describes the evolution of the kinetics of the substrate degradation process. The rate of degradation is a function of the initial concentration of the organic molecule model. Since 4-OP is a hydrophilic and non-volatile compound, the degradation rate of 4-OP could be described by the Langmuir–Henshelwood type kinetic model proposed by the study of Okitsu. Furthermore, as the heterogeneous reaction system is similar to that of Michaelis–Menten which is applied to enzymatic reactions, this kinetic model can be applied to the sonochemical degradation of organics substrate [41–46]. The Langmuir-type kinetic model described by Eq. (4) was applied to predict the 4-OP degradation rate.

$$r = \frac{k_0 K_0 C_0}{1 + K_0 C_0} \quad (4)$$

where r is the initial degradation rate ($\text{mg L}^{-1} \text{min}^{-1}$), k_0 is the pseudo-rate constant ($\text{mg L}^{-1} \text{min}^{-1}$), K_0 is the equilibrium constant (L mg^{-1}), and C_0 (mg L^{-1}) is the initial substrate concentration.

The kinetics of sonochemical degradation of 4-OP was investigated for large initial substrate concentrations in the range of 0–10 mg L^{-1} . The linearized form of Eq. (17) was determined by non-linear regression method using Kaleida-Graph® software and the curve was reconstituted using the determined values are shown in Fig. 16. Based

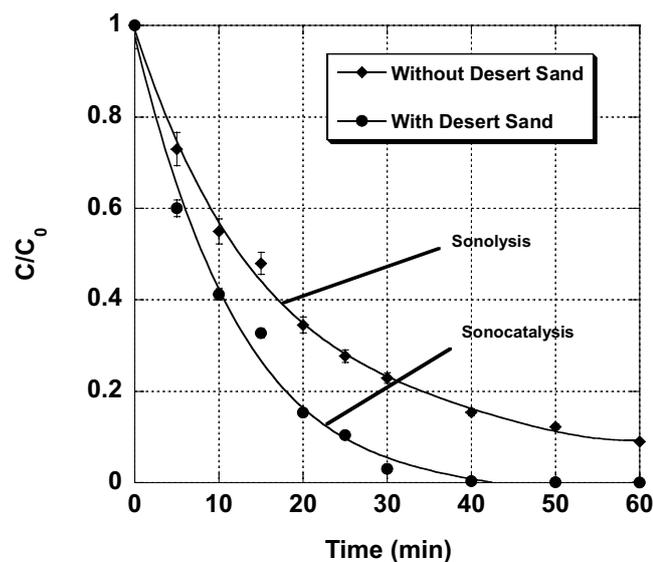


Fig. 15. Sonochemical degradation of 4-OP in the absence and presence of desert sand (from Sahara of Algeria) (ultrasonic frequency: 278 kHz; acoustic power: 3.92 W cm^{-2} ; 4-OP initial concentration: 2 mg L^{-1} ; volume: 300 mL; pH: 6.55; desert sand mass: 30 g L^{-1} ; temperature: $20^\circ\text{C} \pm 1^\circ\text{C}$).

on the determination coefficients and APE value (<5%), it was found that the sonochemical degradation of 4-OP can be the best fit by the Okitsu kinetic model. This model has shown (R^2) values higher than 0.9989% at all different initial substrate concentrations. These results indicate 4-OP degradation predominantly undergoes in the bulk solution and mostly at the bubble/solution interface.

The model kinetic parameters such as the coefficient of determination, the rate constant (k_0), the equilibrium constant (K_0) and the average percentage errors (APE% calculated from Eq. (5)) are shown in Table 4.

$$\text{APE}(\%) = \frac{\sum_{i=1}^N \left| \frac{r_{\text{experimental}} - r_{\text{predicted}}}{r_{\text{experimental}}} \right|}{N} \times 100 \quad (5)$$

where N is the number of experimental data.

3.11. Mineralization rate

Sonochemical oxidation of real organic compounds generally results in the formation of less complex organic compounds and more biodegradable intermediates

Table 4
Parameters of the model of Okitsu obtained using the non-linear regression method

Model equation type	Parameters	Distilled water (DW)
$r = \frac{k_0 K_0 C_0}{1 + K_0 C_0}$	k_0 ($\text{mg L}^{-1} \text{min}^{-1}$)	3.1001
	K_0 (L mg^{-1})	0.02496
	R	0.9988
	APE (%)	4.43

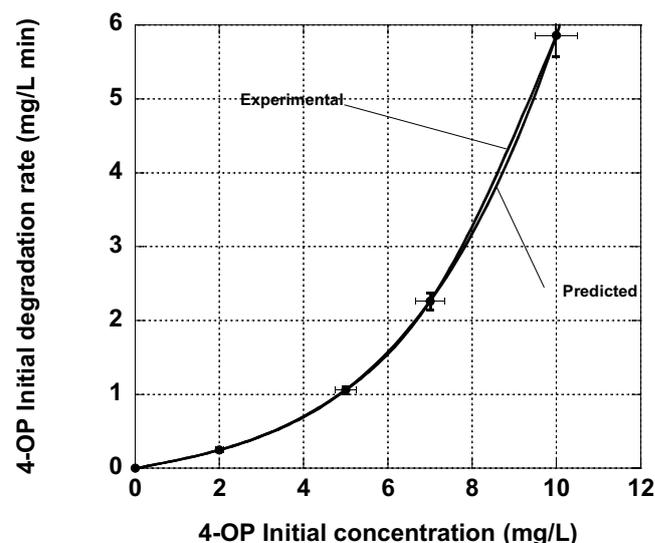


Fig. 16. Comparison of experimental and predicted initial degradation rates at different initial concentration of 4-OP (ultrasonic frequency: 278 kHz; acoustic power: 3.92 W cm^{-2} ; volume: 300 mL; pH: 6.55; temperature: $20^\circ\text{C} \pm 1^\circ\text{C}$).

(by-products), which still give a non-negligible value for COD and TOC, That is before the complete step of mineralization. However, monitoring of apparent degradation processes (relative to the initial compound conversion percentage) allows us to gather more meaningful information regarding compliance with environmental standards. The evolution of COD and TOC degradation rates under the optimum operating condition were determined. The obtained results prove the applicability of sonication energy as a treatment technique to decrease the concentration of 4-OP to an acceptable level as set by the environmental standards. Fig. 17 depicts the evolution of COD and TOC removal during sonication of 2 mg L⁻¹ of 4-OP at 278 kHz and 3.92 W cm⁻². It is clear from Fig. 17 that both COD and TOC removal is significant. For instance, in the first hour from startup the COD, and TOC decreases to 63% and 64% of the initial values, respectively. Phokhalekar et al. found a promising result for the degradation of 4-OP by ultrasound, the degradation percentage reached 100% calculated relative to dissolved oxygen demand during 2 h of ultrasound treatment [47].

4. Conclusions

Degradation of 4-OP in water by ultrasonic irradiation at high frequency was investigated. The sonochemical reactor was characterized; the different oxidizing species generated during sonication was evaluated. The kinetic study conducted in this work showed that sonodegradation of 4-OP follows the first-order model with a reaction constant rate of $1.77 \times 10^{-1} \text{ min}^{-1}$. Under optimum operating conditions 91% degradation of 4-OP was achieved after 1 h of sonication at 3.92 W cm⁻² and 278 kHz. The effect of various operating conditions (substrate initial concentration, temperature, pH, power and ultrasonic frequency, saturating gases, scavengers, promoters addition and

water matrices) was studied. The initial degradation rate increased as the initial substrate concentration. Reactions kinetics are strongly affected by the initial solution temperature, pH, ultrasonic power and frequency. The accumulation rate of hydrogen peroxide in 4-OP solutions is lower than that observed in distilled water (free of any substances). This suggests that 4-OP sonochemical degradation in water occurs mostly through reactions with hydroxyl radicals at the bubble/solution interface. The degradation efficiency was decreased upon the addition of scavengers, such as bromide ions, terephthalate, methanol and *tert*-butanol, indicating that hydroxyl radicals play an important role in 4-OP degradation. The sonodegradation of 4-OP was improved by the addition of dissolved argon via the formation of active species. However, the sonodegradation efficiency inhibited with the addition of nitrogen gas due to its free radical scavenging effect in vapor phase within the cavitation bubble. Thus, the presence of air (O₂/N₂) enhanced the degradation rate of 4-OP. The water matrix is also likely to affect process performance due to the presence of compounds that may act as radical inhibitors and/or promoters as well as change the physicochemical properties of the irradiated solution. The Okitsu model (based on the Langmuir–Hinshelwood type mechanism) appropriately described the degradation kinetics. In addition, The sonodegradation of 4-OP was maximized under optimum operating conditions. Finally, this study indicates that sonochemical treatment could be applied effectively as an alternative technology for the degradation of 4-OP and the mineralization of complex solution (i.e., initial substrate and by-products). And our perspectives will be focused on the identification of degradation by-products. This suggests that ultrasonic treatments can be easily incorporated with other advanced oxidation processes, such as heterogeneous photocatalytic processes in the presence of desert sand.

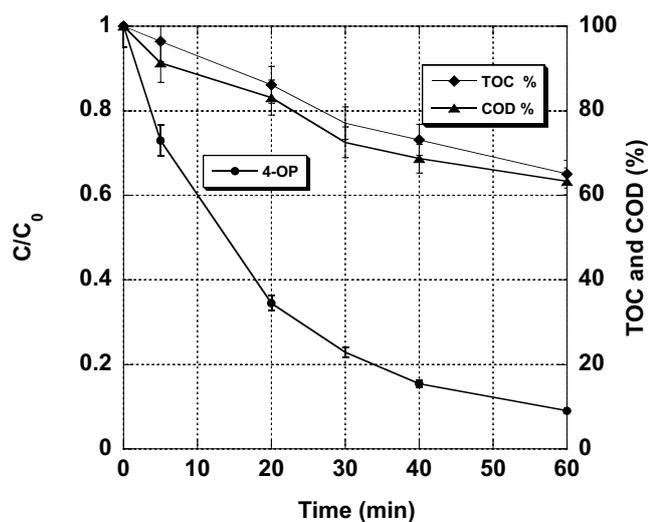


Fig. 17. Relative conversion, degradation and mineralization of 4-OP against irradiation time (ultrasonic frequency: 278 kHz; acoustic power: 3.92 W cm⁻²; 4-OP initial concentration: 2 mg L⁻¹; volume: 300 mL; pH: 6.55; temperature: 20°C ± 1°C).

Acknowledgments

The financial support by the Ministry of Higher Education and Scientific Research of Algeria (project No A16N01UN210120190003) is greatly acknowledged.

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