

Use of Microwave-Assisted Oxidation for Removal of the Pesticide Chlorpyrifos from Aqueous Media

Francisco Claudio F. Barros¹, Allen L. Barros¹, Marcos Antônio A. Silva¹, Ronaldo F. do Nascimento*¹.

¹ Federal University of Ceará, Fortaleza, Brazil

*Corresponding author at: Rua do Contorno S/N, Campus do Pici, Departamento de Química Analítica e Físico-Química, Universidade Federal do Ceará, Fortaleza, Brazil.

(Corresponding author, phone: +55 85 33669042; e-mail: ronaldo@ufc.br).

Abstract--The use of pesticides in agriculture has contributed to a massive increase in global food production. But the adverse impact of pesticides on living organisms has led to a growing concern about residues in soils and in aqueous media. Advanced oxidation processes (AOPs) have proven particularly useful in degrading toxic organic compounds found in wastewater to less toxic reaction products or ultimately to carbon dioxide and water. In this study, we investigated the efficiency of removal of the pesticide chlorpyrifos by AOP system that combines microwave radiation, ultraviolet radiation, titanium dioxide tablets and hydrogen peroxide solutions. The results showed that the MO/UV/TiO₂/H₂O₂ process was the most efficient to remove chlorpyrifos, with 100% removal reached within 6 minutes reaction time.

Index Term--Advanced oxidation processes, Microwave radiation, chlorpyrifos, Wastewater treatment

I. INTRODUCTION

The application of pesticides for crop protection, associated with the use of mineral fertilizers (nitrogen, phosphorus, potassium), intensive irrigation and more efficient machinery have promoted a massive increase in food production on arable land on the surface of the earth [1].

Pesticides are compounds or mixtures of compounds that aim to prevent, destroy, repel or mitigate any pest that is infesting and destroying a plantation. Among the active ingredients are carbamates, phenylacetic acid derivatives, triazines, and sulfonylureas (herbicides), organophosphates, carbamates, organochlorines, pyrethroids, and pyrethrins (insecticides), dithiocarbamates, and mercury-containing compounds (fungicides) [2].

But, despite the beneficial effects, the impact of pesticides has caused serious problems on the environment and on human health. Pesticide residues contaminate soil and water, persist in cultures and enter the food chain of animals and humans, and also contribute to biodiversity loss and removal of natural habitats [3]. Moreover, cases of resurgence of pests developing resistance to pesticides and destruction of non-target species have been reported [3].

One of the most commonly used pesticides is chlorpyrifos, or *O,O*-diethyl *O*-3,5,6-trichloropyridin-2-yl phosphorothioate (Figure 1) which is moderately toxic to humans, but cumulative exposure can produce typical

symptoms of acute poisoning by organophosphates, affecting the central nervous, cardiovascular and respiratory systems [4]. This compound has been investigated by several authors who studied properties such as absorption, tissue distribution, assessment and metabolism of chlorpyrifos in various microecosystem [5, 6, 7, 8].

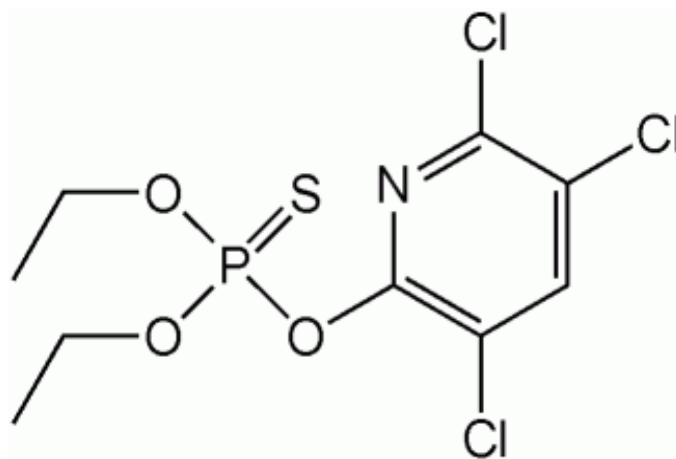


Fig. 1. Structural formula of chlorpyrifos.

Incineration, biological treatment, and adsorption process are common procedures to remove or destroy toxic organic compounds. However, incineration, besides being costly and possible formation of traces of dioxins and furans as byproducts of incomplete oxidation, is impracticable when dealing with a large volume of residues. Biological treatments, even though efficient compared with other processes, have the disadvantage of requiring long periods before the effluent reaches the required low levels. Alternative procedures such as adsorption using activated carbon or natural fibers such as coconut shell and cane sugar bagasse do not promote destruction of the target compounds [9].

Advanced Oxidation Processes (AOPs) are a set of procedures that prove particularly useful in removing organic materials from wastewater. The contaminants are oxidized by reagents such as ozone, hydrogen peroxide, oxygen and air combined with radiation sources and specific catalysts and are converted to water, carbon dioxide, and nontoxic or less toxic reaction products that can be reintroduced to nature or at least

pass through a conventional water treatment. AOPs are more sustainable for environmental decontamination [9]. They can be divided into homogeneous processes, which occur in only one phase (H_2O_2 , O_3 , and Fenton reagents combined or not with ultrasound or UV radiation) and heterogeneous processes that use solids that act as catalysts, such as TiO_2 , ZnO , and MnO_2 [10].

As example of homogeneous processes, Yuan *et al* investigated the effects of humic acid and inorganic ions on photochemical degradation of acid pharmaceuticals in aqueous media using the UV/ H_2O_2 process [11]. In other study, the results of the photochemical decomposition of bezafibrate in surface water and effluent by UV/ H_2O_2 process showed that process was a promising method to remove the contaminant at low concentration, generally at mg.L^{-1} level [12]. Synthetic dye solutions containing disperse dyes were treated with Fenton's reagent (H_2O_2 and iron ions) under solar-light oxidation processes, with elevated removal efficiencies [13].

In heterogeneous processes, the incidence of photons of UV radiation on the surface of a photocatalyst leads to formation of positive holes (h^+) which may react with an oxidizing agent or even water, thereby producing hydroxyl radicals ($\cdot\text{OH}$). These highly reactive radicals degrade organic compounds very efficiently [14].

Microwave radiation has found applications in a wide variety of domains including oxidative degradation of organic pollutants in aqueous media.

In this context, Horikoshi *et al* [15] examined the characteristics of a device for UV-VIS irradiation activated by microwaves in the photo-degradation of the cationic dye (rhodamine-B). The results show a significant decomposition of the dye by simultaneous processes of photocatalysis and photosensitization. Sodr e *et al* [16] assessed the efficiency of digestion of natural unfiltered water using photochemical oxidants in combination with UV-radiation activated by microwaves. In a solution of 40 mg.L^{-1} of humic acid, a 99% reduction in the concentration of dissolved organic carbon was found after 15 minutes of digestion. In the presence of H_2O_2 , only 3 minutes were needed to accomplish an almost quantitative reduction. Zhang *et al* [17] promoted the photocatalytic decomposition of azo dye X-3B with an electrodeless discharge lamp as a source of UV-radiation, microwave radiation, and TiO_2 as a photocatalyst. The photodegradation was favored by a low initial pH, an elevated temperature, and a high light intensity.

In this study, we are proposing an AOP system assisted by microwave radiation for removal of the pesticide chlorpyrifos from aqueous media.

II. MATERIALS AND METHODS

A. Reagents

TiO_2 tablets were prepared from pure titanium dioxide P.A. grade (Carlo Erba). Solutions are prepared from hydrogen peroxide P.A. grade (Vetec) and methanol (Vetec). Chromatographic analyses were performed with methanol HPLC grade (Vetec). Deionized water ultrapure grade (Milli-Q) was used in all experiments and for the analyses.

B. Preparation of TiO_2 tablets

Several samples of 0.2 g TiO_2 powder were placed in cylindrical stainless steel molds (0.5 mm ID) and pressed in a hydraulic press at 1.0 ton.m^{-2} for 5 minutes. Then, the resulting TiO_2 tablets were sintered in a muffle furnace at $1,100 \text{ }^\circ\text{C}$ for 4 hours. The average mass of sintered TiO_2 tablets was 0.18 g.

C. AOPs set-up

The set-up used to perform the AOPs operated in a discontinuous flow (batch) without stirring, according to Figure 2. A commercial microwave oven (Panasonic) with ten power levels (80 to 800 W) was used.

A Teflon connection (32 mm I.D.) was adapted at the top of the oven to allow placement of a glass condenser, thus avoiding evaporation losses of solvent. The condenser was connected to a round-bottom flask of 25 mL inside the microwave oven. The electrodeless UV-lamp was placed adjacent to the round-bottom flask.

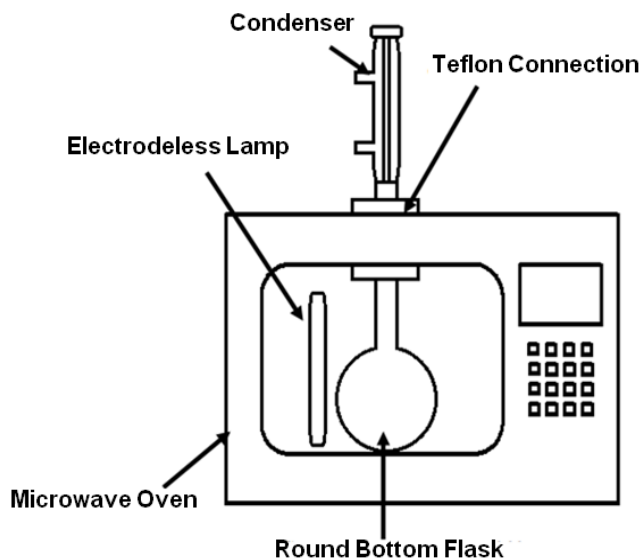


Fig. 2. Offset-up for AOPs assisted by a microwave oven.

D. Study of AOPs

Samples of aqueous dispersions of chlorpyrifos (75 mg.L^{-1} and 300 mg.L^{-1}) were prepared from 480 g.L^{-1} chlorpyrifos commercial solution (Nufarm).

For the AOPs assisted by microwave, were evaluated in the following systems:

- System 1: only microwave radiation (MO);
- System 2: microwave radiation and UV-radiation (MO/UV);
- System 3: microwave radiation and hydrogen peroxide(MO/ H_2O_2);
- System 4: microwave radiation, UV-radiation, hydrogen peroxide, and titanium dioxide (MO/UV/ TiO_2 / H_2O_2).

For all systems, were tested the following parameters: microwave power (320, 480, and 640 W), removal time (4, 6, and 8 minutes), concentration of hydrogen peroxide (55.495 mg.L⁻¹ and 110.990 mg.L⁻¹) concentration of chlorpyrifos (75 mg.L⁻¹ and 300 mg.L⁻¹), with or without TiO₂ tablet (mass of 0.18 g), and incidence or not of UV-radiation (with or without an electrodeless lamp). The UV light emitted by the electrodeless lamp had an emission maximum at 365 nm.

E. Chromatographic analyses

The initial and final concentrations of chlorpyrifos in the samples investigated were analyzed by high-performance liquid chromatography with UV-Vis detection (HPLC-UV). The equipment (Smartliner, Knauer) was operated under the following conditions:

- Mobile phase: methanol HPLC grade (85%) and deionized water (15%);
- Flow rate: 1.0 mL.min⁻¹;

- Column: LiChroCART® 250-4 (C18);
- Column temperature: 35 °C;
- Injection volume of the sample: 20 µL;
- Detector: UV/Vis detector, at a wavelength of 205 nm;
- Running time: 6 minutes.

III. RESULTS AND DISCUSSION

All solutions had pH values around 3.4. All AOP experiments were performed at least twice. The relative standard deviations (%RSD) were below 10%, indicating an adequate precision.

The first AOP evaluated only the thermal effect of the microwave on the variation in the concentration of chlorpyrifos as a function of the sample treatment time. The data are shown in table I.

Table I
Removal (%) of chlorpyrifos according to system 1 (only microwave radiation, MO).

| Concentration of chlorpyrifos (mg.L ⁻¹) | Power (W) | Time (min) | Removal (%) |
|---|-----------|------------|-------------|
| 75 | 320 | 4 | 88.1 |
| | | 6 | 100.0 |
| | | 8 | 100.0 |
| | 480 | 4 | 99.1 |
| | | 6 | 100.0 |
| | | 8 | 100.0 |
| | 640 | 4 | 100.0 |
| | | 6 | 100.0 |
| | | 8 | 100.0 |
| 300 | 320 | 4 | 16.6 |
| | | 6 | 18.1 |
| | | 8 | 52.0 |
| | 480 | 4 | 16.2 |
| | | 6 | 61.5 |
| | | 8 | 99.8 |
| | 640 | 4 | 39.3 |
| | | 6 | 99.8 |
| | | 8 | 100.0 |

A 640-W power was sufficient to fully decompose a sample of 75 mg.L⁻¹ solution of chlorpyrifos in 6 minutes. This efficiency could be achieved with a 320-W power in 8 minutes. However, when the concentration of pesticide was 300 mg.L⁻¹, the system efficiency decreased considerably. In general applications, microwave radiation is used to produce thermal energy. There are three types of heating by microwaves: (i) dielectric heating, (ii) conduction loss heating,

and (iii) magnetic loss heating [19]. The thermal energy P produced per unit volume originating from microwave radiation is given by Eq. (1):

$$P = \pi f \epsilon' \epsilon'' |E|^2 + \frac{1}{2} \sigma |E|^2 + \pi f \mu' \mu'' |H|^2 \quad (1)$$

Where: |E| and |H| denote the strength of the electric field and the magnetic field of the microwaves, respectively; σ

is the electrical conductivity; f is the frequency of the microwaves; ϵ' is the permittivity in vacuum; ϵ'' is the dielectric loss factor; μ_0 is the magnetic permeability in vacuum; μ'' is the magnetic loss.

The first term in Eq. (1) expresses the dielectric loss heating; the second term denotes the conduction loss heating, whereas the magnetic loss heating is given by the third term. Thus, for this AOP, the effect of microwave heating of the samples can be attributed almost exclusively by dielectric loss heating.

For better visualization of the kinetic phenomena of pesticide removal by system 1, figure 3 illustrates the trend of

the relation between the final and the initial concentrations of the pesticide (C and C_0 , respectively) as a function of reaction time. In figure 3, it can be observed that the tendency to decompose 80% of the pesticide (75 mg.L^{-1}) within 4 minutes reaction time. For a high concentration of the pesticide (300 mg.L^{-1}), the time for obtaining 50% decomposition occurs with increasing microwave power (4 minutes with a 640-W power, almost 5.5 minutes with a 480-W power, and 8 minutes with a 160-W power).

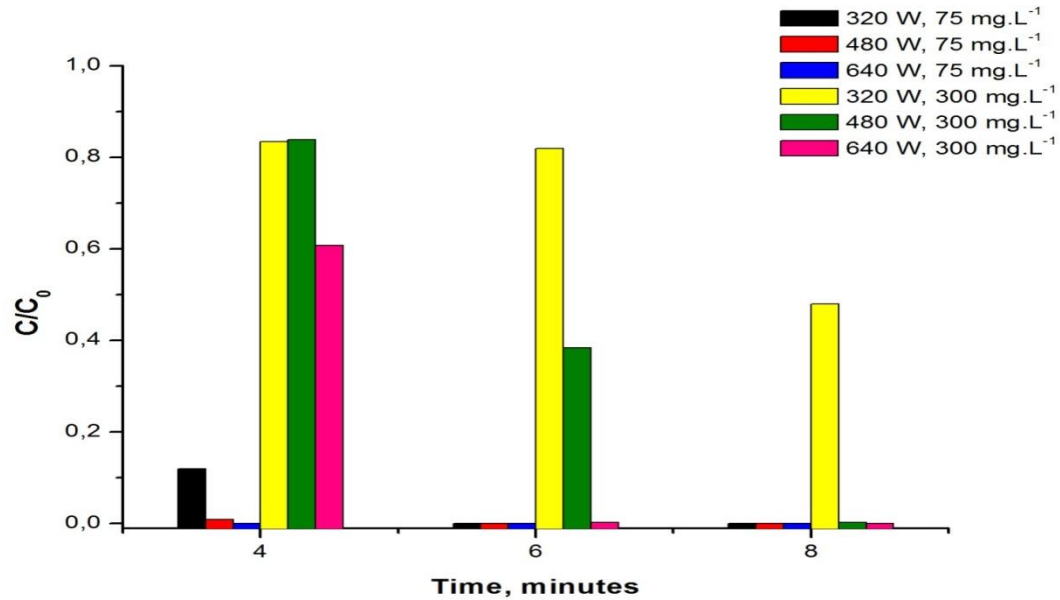


Fig. 3. Relation between the initial and the final concentrations of the pesticide chlorpyrifos as a function of time (system 1).

The data obtained for the second system (AOP with UV-radiation and microwave radiation) are shown in Table II.

Table II
Removal (%) of chlorpyrifos according to system 2 (microwave radiation and UV-radiation, MO/UV).

| Concentration of chlorpyrifos (mg.L ⁻¹) | Power (W) | Time (min) | Removal (%) |
|---|-----------|------------|-------------|
| 75 | 320 | 4 | 35.9 |
| | | 6 | 52.8 |
| | | 8 | 31.5 |
| | 480 | 4 | 81.9 |
| | | 6 | 68.0 |
| | | 8 | 89.5 |
| | 640 | 4 | 88.4 |
| | | 6 | 89.9 |
| | | 8 | 93.5 |
| 300 | 320 | 4 | 26.5 |
| | | 6 | 93.1 |
| | | 8 | 95.1 |
| | 480 | 4 | 55.8 |
| | | 6 | 97.9 |
| | | 8 | 98.4 |
| | 640 | 4 | 98.8 |
| | | 6 | 99.6 |
| | | 8 | 100.0 |

Comparing these results with system 1 shows a decrease in the efficiency for decomposition of samples of 75 mg.L⁻¹ pesticide. This observation can be explained due to the absorption of part of the energy of the microwave radiation by the electrodeless lamp which was used to generate UV-radiation. However, the results for samples of 300 mg.L⁻¹ chlorpyrifos proved to be better than the results presented in system 1. Optimum results achieved in system 2 were obtained after 8 minutes treatment of samples of 300 mg.L⁻¹ of chlorpyrifos.

Figure 4 shows a tendency to increase the pesticide removal with increased time of exposure to UV-radiation, which in turn is related to the increased power of the microwave radiation. This was observed for both 75 mg.L⁻¹

and 300 mg.L⁻¹ solutions of chlorpyrifos, but the treatment was more efficient for 300 mg.L⁻¹ solutions. This shows the importance of applying greater microwave powers when using electrodeless lamps. The intensity of UV-radiation emitted by electrodeless lamps increases with increasing microwave power [20].

In system 3, AOPs were evaluated with microwave radiation and an oxidizing agent, in this case, solutions of hydrogen peroxide. The results (Table 3) show that the pesticide removal was equivalent or even less effective when compared to the results produced in system 1.

Table III
Removal (%) of chlorpyrifos according to system 3 (microwave radiation and hydrogen peroxide, MO/H₂O₂).

| Concentration of chlorpyrifos (mg.L ⁻¹) | H ₂ O ₂ Concentration (mg.L ⁻¹) | Power (W) | Time (min) | Removal (%) |
|---|---|-----------|------------|-------------|
| 75 | 55.495 | 320 | 4 | 95.2 |
| | | | 6 | 100.0 |
| | | | 8 | 100.0 |
| | | 480 | 4 | 100.0 |
| | | | 6 | 100.0 |
| | | | 8 | 100.0 |
| | 110.990 | 640 | 4 | 100.0 |
| | | | 6 | 100.0 |
| | | | 8 | 100.0 |
| | | 320 | 4 | 56.3 |
| | | | 6 | 92.5 |
| | | | 8 | 90.7 |
| 300 | 55.495 | 480 | 4 | 98.1 |
| | | | 6 | 99.3 |
| | | | 8 | 100.0 |
| | | 640 | 4 | 100.0 |
| | | | 6 | 100.0 |
| | | | 8 | 100.0 |
| | 110.990 | 320 | 4 | 38.9 |
| | | | 6 | 78.9 |
| | | | 8 | 56.5 |
| | | 480 | 4 | 68.9 |
| | | | 6 | 98.8 |
| | | | 8 | 89.6 |
| 300 | 55.495 | 640 | 4 | 98.1 |
| | | | 6 | 99.6 |
| | | | 8 | 99.7 |
| | | 320 | 4 | 30.7 |
| | | | 6 | 39.0 |
| | | | 8 | 58.3 |
| | 110.990 | 480 | 4 | 66.9 |
| | | | 6 | 88.4 |
| | | | 8 | 69.3 |
| | | 640 | 4 | 94.9 |
| | | | 6 | 98.3 |
| | | | 8 | 99.3 |

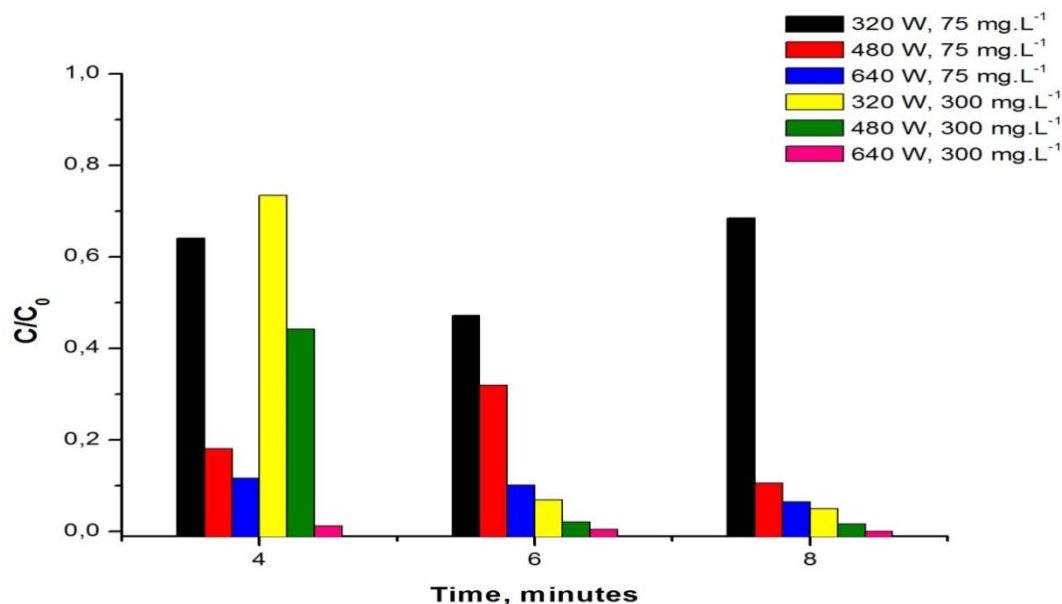


Fig. 4. Relation between the initial and final concentrations of the pesticide chlorpyrifos as a function of time (system 2).

This can be explained by the fact that excessive amounts of H_2O_2 interfere with thermal decomposition of the pesticide and inhibit the production of $\bullet OH$ radicals, as shown in reactions (1) - (4), thus, decreasing the removal rate [18].

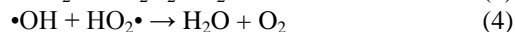
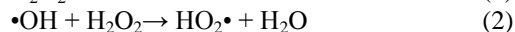
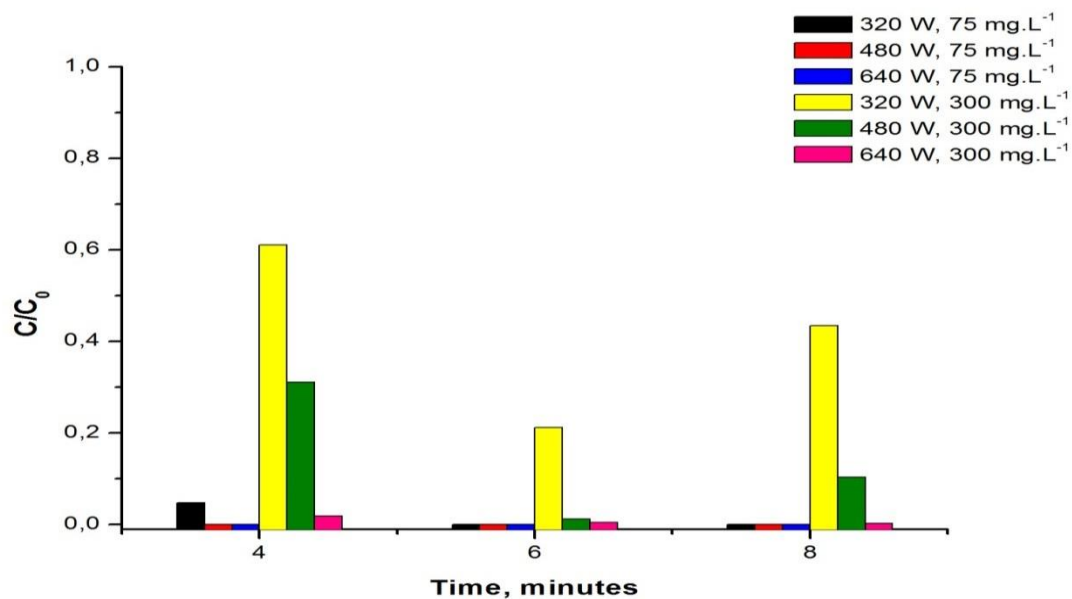
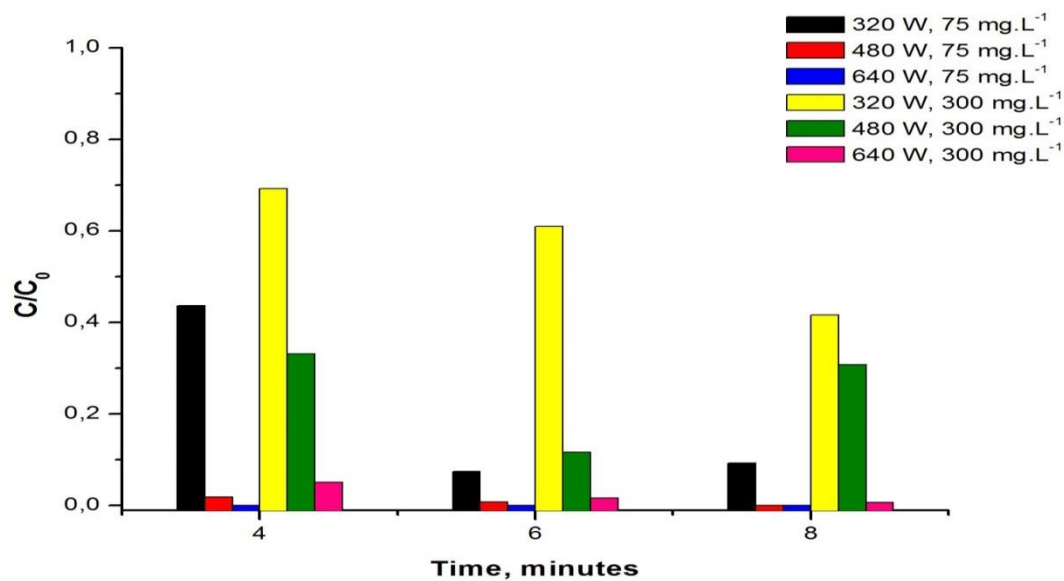


Figure 5a and 5b show the relations between the final and initial concentrations of the pesticide as a function of time for system 3 with different H_2O_2 concentrations. In figure 7a, it is noted that the pesticide removal varies slightly with microwave powers for the samples of 75 mg.L^{-1} chlorpyrifos. For the high concentration of chlorpyrifos (300 mg.L^{-1}), an increase of the power enhanced pesticide removal. Figure 7b shows how increasing the concentration of hydrogen peroxide interferes in AOPs of samples of 300 mg.L^{-1} chlorpyrifos.



(a)



(b)

Fig. 5. Relation between the initial and the final concentrations of the pesticide chlorpyrifos as a function of time (system 3) using (a) 55.495 mg.L⁻¹ H₂O₂ solution, and (b) 110.990 mg.L⁻¹ H₂O₂ solution.

Table IV shows the results of the treatment of samples of chlorpyrifos using system 4, in which microwave radiation was used in combination with UV-radiation, titanium dioxide, and hydrogen peroxide. Comparing these results with those of other systems, system 4 clearly gave the most efficient removal of the pesticide and even quantitative

removal was observed for samples of 75 mg.L⁻¹ at any microwave power and reaction time. For samples of 300 mg.L⁻¹, total removal occurred only from 480-W microwave power.

Table IV
Removal of chlorpyrifos (%) according to system 4 (microwave radiation, UV-radiation, TiO₂, and H₂O₂, MO/UV/TiO₂/H₂O₂).

| Concentration of chlorpyrifos (mg.L ⁻¹) | H ₂ O ₂ Concentration (mg.L ⁻¹) | Power (W) | Time (min) | Removal (%) |
|---|---|-----------|------------|-------------|
| 75 | 55.495 | 320 | 4 | 72.0 |
| | | | 6 | 94.7 |
| | | | 8 | 100.0 |
| | | 480 | 4 | 96.8 |
| | | | 6 | 93.6 |
| | | | 8 | 100.0 |
| | 110.990 | 640 | 4 | 100.0 |
| | | | 6 | 100.0 |
| | | | 8 | 100.0 |
| | | 320 | 4 | 99.6 |
| | | | 6 | 100.0 |
| | | | 8 | 100.0 |
| 300 | 55.495 | 480 | 4 | 100.0 |
| | | | 6 | 100.0 |
| | | | 8 | 100.0 |
| | | 640 | 4 | 100.0 |
| | | | 6 | 100.0 |
| | | | 8 | 100.0 |
| | 110.990 | 320 | 4 | 47.5 |
| | | | 6 | 31.1 |
| | | | 8 | 19.3 |
| | | 480 | 4 | 89.3 |
| | | | 6 | 91.4 |
| | | | 8 | 80.9 |
| 640 | 480 | 4 | 99.5 | |
| | | 6 | 98.9 | |
| | | 8 | 100.0 | |
| | 320 | 4 | 74.3 | |
| | | 6 | 87.1 | |
| | | 8 | 88.1 | |
| 110.990 | 480 | 4 | 97.5 | |
| | | 6 | 99.2 | |
| | | 8 | 100.0 | |
| | 640 | 4 | 100.0 | |
| | | 6 | 100.0 | |
| | | 8 | 100.0 | |

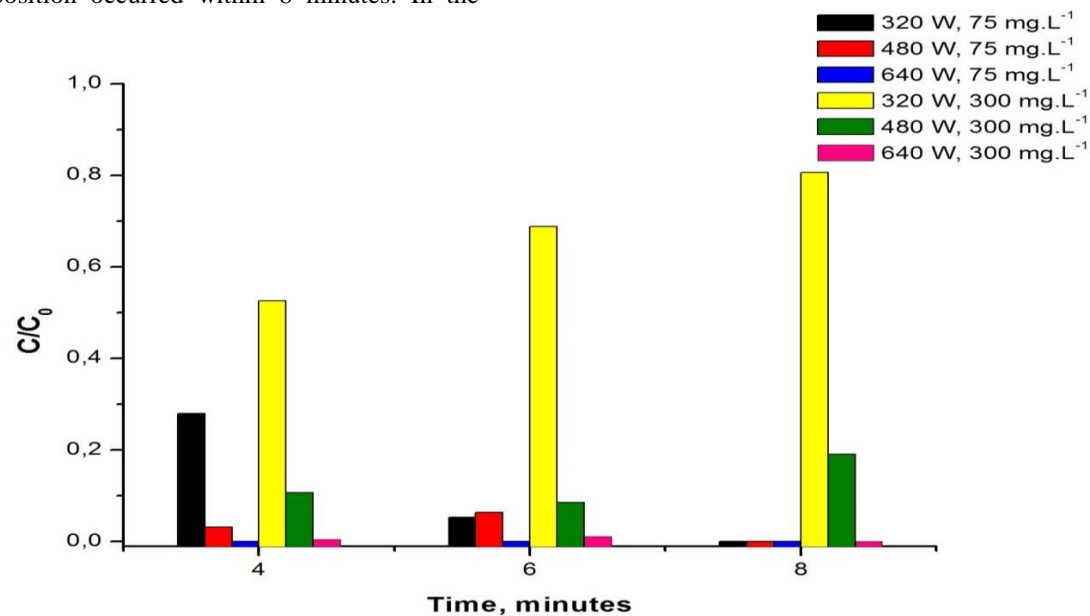
Other studies had investigated the degradation of organic pollutants by AOPs combining microwave radiation, UV-radiation, oxidizing agents and TiO₂ [21]. Removal of pollutants was achieved due to the formation of hydroxyl radicals and the polarization effect of TiO₂ [22]. The presence of Ti⁴⁺ sites at the surface of TiO₂ leads to a hydrophobic

character. In the presence of UV-radiation Ti⁴⁺ sites are photoreduced to Ti³⁺ the surface of the photocatalyst turns hydrophilic as covered by water [23]. This event inhibits binding of the organic compounds to oxidation sites at the surface of TiO₂. Under the action of microwaves, TiO₂ regains

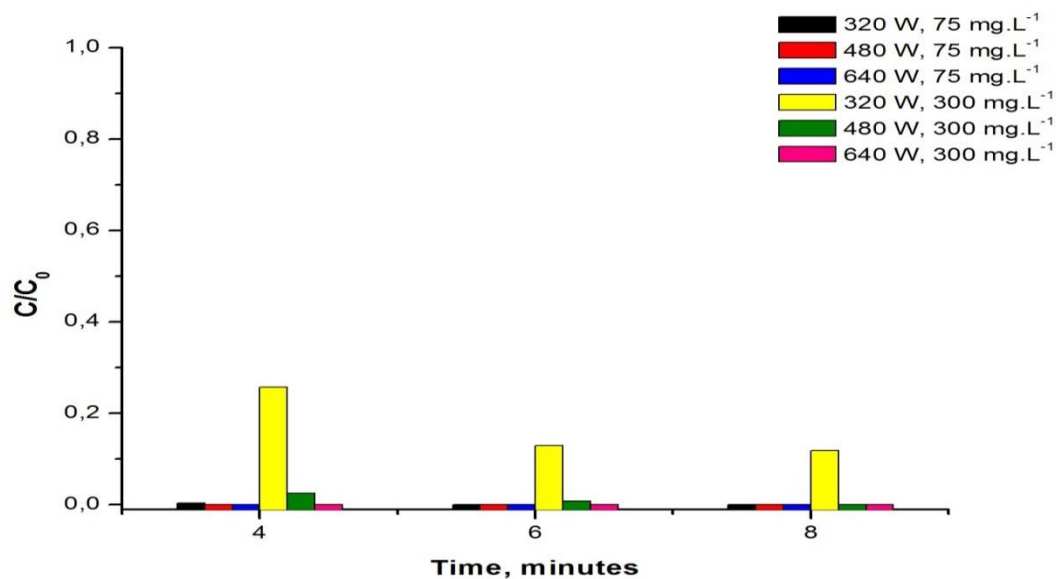
its hydrophobic character, which increases the contacts between the pollutants and the surface of catalyst [24, 25].

Figure 6a highlights the tendency to remove 80% of chlorpyrifos in almost all samples using 55.495 mg.L⁻¹ H₂O₂ solutions within 5 minutes reaction time. In some cases, complete decomposition occurred within 8 minutes. In the

same system, using 110.990 mg.L⁻¹ H₂O₂ solutions, 90% removal of the pesticide was achieved within 4 minutes for most samples, and quantitative removal was reached within 6 minutes for almost all samples (Figure 6b).



(a)



(b)

Fig. 6. Relation between the initial and the final concentrations of the pesticide chlorpyrifos as a function of time (system 4) using (a) 55.495 mg/L H₂O₂ solution, and (b) 110.990 mg/L H₂O₂ solution.

In order to compare the results obtained in this work, some studies involving microwave-AOP systems are discussed. Bae & Jung studied the Propylene degradation in a

microwave/UV/TiO₂ system [26]. The UV radiation was generated using a discharge electrodeless lamp. The maximum degradation efficiency was 30.40%. Bae *et al* used a

microwave/UV/ozone/TiO₂ photocatalyst system to degradation propylene gas [27]. With this set-up, the degradation efficiency increase to 86.80%. The Propylene photodegradation was monitored by FT-IR Gas Analyzer. The identified intermediate products were CH₄ and C₂H₆, whose were mineralized into CO₂, H₂O, and CO. The experiments of Han *et al* [28] showed that the microwave irradiation combined with UV radiation and H₂O₂ can raise both the phenol mineralization up to 50.00%. Also, microwave irradiation accelerate the degradation rate of intermediates, hydroquinone and catechol, produced in the course of phenol oxidative decomposition. Ju *et al* [29] investigated the photodegradation of malachite green using a microwave/UV/H₂O₂ with two electrodeless discharge lamps.

The results showed that 99.70% of dye was removed within 5 min treatment. The pH variation of aqueous dyes solution played minor role. The Photocatalytic degradation of three different single-component organic dyes, bromothymol blue, rhodamine B, methylene blue, and their mixture was investigated using a microwave/UV/O₃/H₂O₂/TiO₂ process system [30]. The decomposition rates of all organic dyes occurred with 1.78 g.h⁻¹ ozone injection rate and 39.457 mg.L⁻¹ H₂O₂ solutions. The decomposition of all organic dyes was higher in single-component experiments (up 99.92%) than in mixed solution (between 98.18% and 99.94%). Table V shows results of degradation efficiency of these investigations reported in the literature.

Table V
Effect of microwave-assisted AOP systems on the degradation of organic

| Contaminant | AOP System | Findings | Reference |
|--|--|--|-----------|
| Propylene | Microwave/UV/TiO ₂ | 30.40 % degradation efficiency | [26] |
| | Microwave/UV/O ₃ /TiO ₂ | 86.80 % degradation efficiency | [27] |
| Phenol | Microwave/UV/H ₂ O ₂ | Up to 50 % mineralization | [28] |
| Malachite green | | 99.70 % Removal | [29] |
| Bromothymol blue (single-component) | Microwave/UV/O ₃ /H ₂ O ₂ /TiO ₂ | 99.92 % degradation efficiency | [30] |
| Rhodamine B (single-component) | | ~ 100 % degradation efficiency | |
| Methylene blue (single-component) | | 100 % degradation efficiency | |
| Bromothymol blue (mixture) | | 98.18 % degradation efficiency | |
| Rhodamine B (mixture) | | 98.18 % degradation efficiency | |
| Methylene blue (mixture) | | 99.94 % degradation efficiency | |
| Chlorpyrifos | | Microwave/UV/H ₂ O ₂ /TiO ₂ | |

The microwave-assisted AOP systems show a high efficiency on the degradation of organic pollutants in aqueous medium. They reduce the energy consumption, chemical use and reaction time when compared to individual/combined chemical and conventional heating methods [31]. However, more research is necessary for microwave-assisted AOP systems application in large-scale wastewater treatment.

IV. CONCLUSION

A microwave oven set-up was found to be adequate for removal of chlorpyrifos, as a model for pesticides, in aqueous solution. A combination of microwave radiation, UV-radiation, TiO₂ and H₂O₂ proved to be the most efficient system to remove chlorpyrifos for short reaction times and diluted concentrations of the oxidizing agents. Identification

of the oxidative reaction products and the prevalent mechanisms will be examined in a forth coming study.

V. ACKNOWLEDGMENT

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