

Pilot scale investigation of an advanced photo-electro-chemical oxidation process for treatment of effluents from pesticides manufacturing plants

SARASIDIS V.C. *, PETSIS P.N., PLAKAS K.V., KARABELAS A.J.

Natural Resources & Renewable Energies Laboratory, Chemical Process and Energy Resources Institute, Centre for Research and Technology-Hellas, 6th km Charilaou-Thermi Road, Thermi-Thessaloniki, GR 57001 GREECE

*corresponding author:

e-mail: sarasidis@certh.gr

Abstract This paper reports on the effectiveness of an innovative hybrid advanced oxidation process-scheme aiming to degrade recalcitrant organic compounds in industrial effluents for further sustainable final treatment. Following bench-scale experimental work, a pilot unit was developed combining two advanced oxidation processes, based on in-situ production of powerful hydroxyl radicals ($\cdot\text{OH}$); i.e., *electrochemical anodic oxidation (AO)* employing boron-doped diamond (BDD) electrodes and *photochemical oxidation via H_2O_2 photolysis under UV-C irradiation ($\text{H}_2\text{O}_2/\text{UV-C}$)*. The pilot-unit was operated, in a pesticides manufacturing plant, treating colored effluents characterized by high, recalcitrant organic load. The effect was examined of key process parameters, including current density, H_2O_2 concentration, recirculation flow rate and processing time, on system performance, mainly regarding organic-matter mineralization and discoloration rate. For the aforementioned effluent organic load, applying a near-optimal set of process-parameter values (i.e. 40 mA/cm² current density, 0.6 W/L UV-C dose, 'on-line' dosing of approx. 1140 mg·L⁻¹·h⁻¹ H_2O_2 and 8.4 L/min recirculation flow rate), TOC and color removal reached 71% and 93%, respectively. The effectiveness of the combined AO/ H_2O_2 /UV-C process, mainly due to high utilization of injected H_2O_2 (approx. 80-90%), is judged as very satisfactory, considering that the treated effluents meet the standards for safe disposal to local biological effluent-treatment plants.

Keywords: Industrial wastewater treatment, recalcitrant organic pollutants, hybrid advanced oxidation processes, anodic oxidation, UVC/ H_2O_2

1. Introduction

Pesticides are organic compounds that are necessary and extensively used on crops to control pest and related disease. However, many of these compounds have been identified as non-biodegradable, persistent in the environment and toxic, that can be detrimental to human health even at low concentration. Furthermore, the drastically increasing food demand due to rapid growth

of world population in the recent several decades, has led to excessive pesticides use and a serious pollution issue.

Conventional treatment methods of such pesticides-polluted streams are widely regarded as ineffective due to their recalcitrant character. However, Advanced Oxidation Processes (AOPs), are promising alternatives capable of degrading and mineralizing such organic pollutants. AOPs, including UV/ H_2O_2 , UV photolysis, photocatalysis, Fenton reagents, anodic oxidation (AO) etc., or combinations thereof, are based on the generation of highly reactive oxidants; i.e. hydroxyl radicals ($\cdot\text{OH}$) and are already widely used in water purification and wastewater treatment. The main advantage of AOPs over conventional processes is the non-selective organic species degradation, leading to an effluent stream either appropriate for local reuse or amenable to a final conventional treatment step for safe disposal.

Among various AOPs, UV/ H_2O_2 and AO appear to have interesting attributes for the removal of pesticides, including simplicity of application, rather low cost and process effectiveness; thus, they have been implemented/investigated in several laboratory (Vucic et al., 2021; Samet et al., 2010; Millan et al., 2019) and few pilot-scale (Yu et al., 2020; Miklos et al., 2018) studies. Furthermore, the literature on combination of UV/ H_2O_2 and AO for treating industrial effluents (particularly at pilot scale) is quite limited. However, results from a bench-scale study in this Laboratory, where integration of these two AOPs was implemented, provided very promising results, when treating 'difficult' effluents of interest from pesticides industry.

In view of this state of technology, this study aims to evaluate the advanced AO/ H_2O_2 /UV-C process at pilot scale, regarding organics mineralization and discoloration of effluents (with high recalcitrant organics load) from a Greek pesticides manufacturing plant. Moreover, to investigate the effect of several operating parameters on system performance, targeting to the selection of near-optimal process conditions towards implementation of this technology at full scale.

2. Materials and Methods

2.1. Materials and chemical reagents

The industrial wastewater employed in the experiments originated from a pesticides and plant protection products manufacturing plant (K&N Efthymiadis S.A., Thessaloniki, Greece), just after a preliminary coagulation/separation to remove suspended matter. From characterization of this wastewater the following physicochemical properties were obtained: pH 6.2-6.8, eC 12.2-14.7 mS/cm, Color 92-150 CU, COD 2860-3710 mg/L, TOC 891-1100 mg/L, TN 201-375 mg/L, TP 3.4-7.6 mg/L, TSS 23-112 mg/L. The electrochemical cell (EC) used in this work equipped with two 10 x 10 cm electrodes, i.e. the anode and the cathode, made of Boron Doped Diamond (BDD, Electro Cell A/S) and Stainless Steel (SS304, TEMAK SA) respectively. The UV-C disinfection system equipped with two single-ended, 4 pined germicidal lamps (GPH810T5L/4C, Puro Water Technology) with nominal power 40W, emitting at 253.7 nm. A cartridge filter with nominal pore size 5-25 μm was used for the rejection of TSS. Hydrogen peroxide (H_2O_2) solution 50% w/w, supplied by Feri-Tri was used as the oxidizing agent, whereas titanium (IV) oxysulfate (TiOSO_4) supplied by Sigma-Aldrich was used for the determination of H_2O_2 concentration. All H_2O_2 solutions were prepared with tap water (TW).

2.2 Analytical methods

A TOC/TN analyzer was employed for the direct measurements of Total Organic Carbon (TOC) and Total Nitrogen (TN) concentrations of the samples. Color and H_2O_2 concentration were determined colorimetrically at 510 nm and 410 nm respectively using a UV-visible spectrophotometer. For the color measurements, the samples were first treated with 0.45 μm syringe filters of Nylon fiber. Electrical conductivity (eC) was measured by a conductivity meter. A portable radiometer and a suitable sensor were used for light intensity measurements of the UV-C lamps. Finally, concentration of the various drastic organic compounds detected in the wastewater was measured by Liquid Chromatography Mass Spectrometry (LC-MS).

2.3 Experimental set-ups and procedures

The pilot unit was constructed by TEMAK SA, a Greek company with expertise in the water treatment, in close collaboration with NRRE/CPERI/CERTH. The experimental set-up (Fig. 1) consisted mainly of an electrochemical cell and a UV photoreactor. The commercial electrochemical cell (Electro MP Cell, Electro Cell A/S) is of plate-and-frame type, made of stainless steel, in which different electrodes of specific active surface area (0.01 m^2) can be adapted. Three PVDF spacers were placed within the cell to improve fluid distribution and flow conditions. The UV photoreactor is a commercial disinfection system (Puro 2S, Puro Water Technology) equipped with two lamps and an embedded control panel. Essentially, the

photoreactor is a 10 L cylindrical closed chamber, vertically positioned, made of stainless steel. Two more vessels are employed in the pilot unit, i.e. a 160 L feed tank where the wastewater is collected and a 50 L H_2O_2 vessel where the preparation of the H_2O_2 solution takes place. A cartridge filter is used for the retention of TSS to minimize fouling phenomena on electrodes active surface. A centrifugal pump provides recirculation of the wastewater between the EC and the photoreactor, whereas a dosing pump assists for addition of H_2O_2 solution into the system under constant flow rate. Moreover, two 3-way electromagnetic valves, changing their state depending on the implemented process, control the wastewater flow direction. In addition, a power supply (connected with the two electrodes) supplies the electrical current within the cell, while various measuring devices and sensors, located in specific points of the unit, serve to measure key operating variables such as pH, temperature, oxidation reduction potential (ORP), pressure and flow rate. Finally, a programmable logic controller (PLC) and a Human-Machine Interface (HMI) are installed in the unit to record data, monitor and control various functions during the experiments, regardless of the applied process, thereby offering many advantages (e.g. remote control, ease of use etc.).

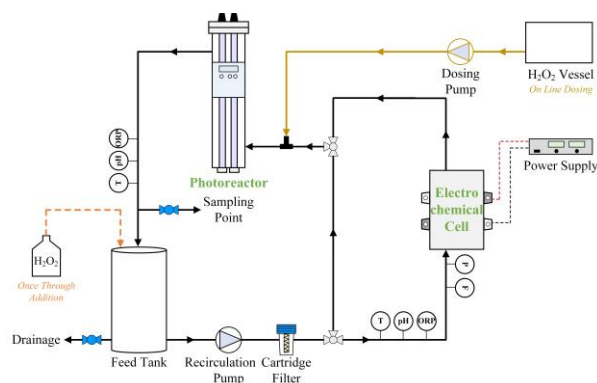


Figure 1. Schematic diagram of the AO/ H_2O_2 /UV-C pilot

First, 40L of wastewater are placed in the feed tank and recirculated into the system for about 10 min to achieve homogeneity. In parallel, a H_2O_2 solution of known concentration is prepared, diluting a specific volume of stock solution with TW. Next, the diluted H_2O_2 solution is either added directly into the feed tank ('once through addition'-OT mode), or placed in the H_2O_2 vessel and then injected to the system with a constant rate during the experiment ('on-line dosing'-OLD mode). At the same time, UV-C lamps and power supply are switched on, denoting the beginning of the experiment. Treated wastewater samples are collected at specific time intervals for color, TOC and H_2O_2 concentration measurements. At the end of each experiment, the cell is disassembled and its individual parts (electrodes, spacers) are cleaned meticulously to remove deposits, thus mitigating flow channel clogging during testing. The pilot unit is also operated with fresh water for a certain time period (~1h), effectively rinsing all others parts (photoreactor, vessels, pipes, etc.). For a test, the cartridge filter is always replaced by a new one.

3. Experimental Results

Twelve tests with the industrial wastewater (Table 1), were conducted in the premises of K&N Efthymiadis S.A. plant, where the pilot unit was operated in batch mode. The effect of operating parameters, such as recirculation flow rate (Q), current density (CD), H_2O_2 concentration (C), mode of H_2O_2 addition and experimental time (t) on system performance was examined. The latter mainly concerned TOC and color percentage removal, as depicted in aggregate in Fig. 2. The treated volume was 45L and the UV-C dose was constant 0.60 W/L.

Table 1. Summary of main experimental conditions during all pilot tests with industrial wastewater.

Exp. No	Process	Q L/min	CD mA/cm ²	C g/L	$R_{H_2O_2}$ mg/L/h	t h
1	AO	8.8	11	-	-	27
2	H_2O_2 /UV-C	8.4	-	16.0	OT	27
3	AO/ H_2O_2 /UV-C	8.3	25	16.6	612	27
4	AO/ H_2O_2 /UV-C	9.0	36	23.8	1830	13
5	AO/ H_2O_2 /UV-C	8.4	40	30.7	1140	27
6	AO/ H_2O_2 /UV-C	8.4	24	30.0	2310	13
7	AO/ H_2O_2 /UV-C	8.7	20	7.0	OT	27
8	AO/ H_2O_2 /UV-C	9.0	35	13.2	OT	27
9	AO/ H_2O_2 /UV-C	8.8	20	14.1	OT	27
10	AO/ H_2O_2 /UV-C	8.5	22	15.3	OT	27
11	AO/ H_2O_2 /UV-C	8.5	40	30.0	OT	27
12	AO/ H_2O_2 /UV-C	5.2	8	16.6	OT	27

3.1 Effect of operating parameters

At first, the wastewater was treated separately with the AO (Exp. No 1) and H_2O_2 /UV-C (Exp. No 2) process. Results show (Fig. 2a) that AO alone leads to rather low discoloration performance (39% color removal), while the mineralization rate of wastewater is even lower (12% TOC removal) after 27h of treatment. This is probably due to the very low current density applied in the specific experiment; i.e. 11 mA/cm². However, with H_2O_2 /UV-C clearly better performance is attained compared to AO; i.e. 32 and 23 percentage units increase of color and TOC removal respectively; this indicates that the former represents the main process in the combination with AO. Afterwards, a series of tests with the combined AO/ H_2O_2 /UV-C process (Exp. No 3-12) was carried out. The efficiency of the combined process compared to either AO or H_2O_2 /UV-C alone, is significantly improved as expected, regardless of the mode of H_2O_2 addition into the system; i.e. OLD (Fig. 2a) or OT (Fig. 2b). Among experiments with AO/ H_2O_2 /UV-C, in Exp. No 5 improvement is shown of the discoloration performance by another 31% and doubling of the mineralization, which reach the level of 93 and 71% respectively, due to the synergistic effects of combined photochemical and electrolysis reactions taking place in the pilot unit.

A clearly negative effect on the overall system performance is noted, when the recirculation flow rate is adjusted at a lower value. For instance, the decrease of flow rate from 8.8 (Exp. No 9) to 5.2 L/min (Exp. No 12) leads to a considerable reduction of TOC and color removal, by approx. 22% and 17% respectively, after 27h treatment with AO/ H_2O_2 /UV-C (Fig. 2b). This trend is attributed to the inadequacy of convection at low flow rates to disperse the generated gases in the AO process.

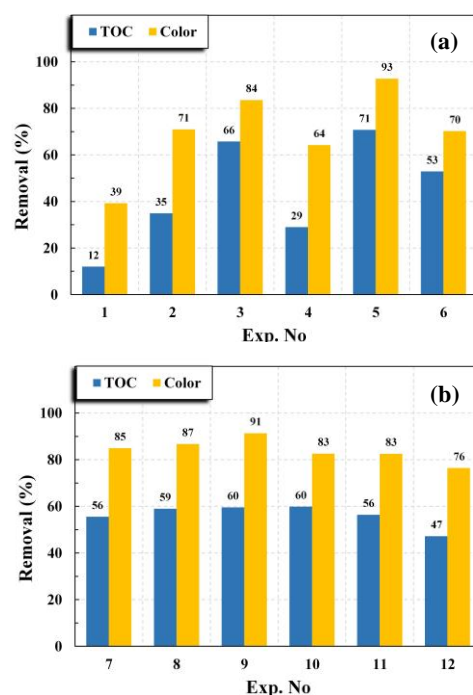


Figure 2. Mineralization and discoloration percentages after treatment with (a) AO, H_2O_2 /UV-C, AO/ H_2O_2 /UV-C OLD and (b) AO/ H_2O_2 /UV-C OT.

Therefore, an increase of ohmic resistance within the EC and a reduction of the applied CD takes place resulting in reduced efficiency. On the contrary, an increase of CD from 20 to 35 mA/cm² (Exp. No 9 and 8) does not lead to notable effect on AO/ H_2O_2 /UV-C process efficiency during pilot tests. However, CD below 20 mA/cm² (Exp. No 12), does not favor mineralization/discoloration due to inefficient AO.

Comparison between experiments with different mode of H_2O_2 addition, but otherwise identical conditions, shows that OLD (Exp. No 5) is preferable over OT (Exp. No 11). Specifically, an increase by approx. 27% TOC and 12% color removal is observed, after 27h of treatment with CD 40 mA/cm² and 30 g/L H_2O_2 addition. This enhanced efficiency is correlated with the higher % H_2O_2 consumption achieved in Exp. No 5, due to the specific point where H_2O_2 enters the system; i.e. closer to the photoreactor in case of OLD instead of inside the feed tank in case of OT addition. By increasing H_2O_2 concentration during experiments with OT addition, slight variations (<10%) of TOC and color removal are noted (Exp. No 7, 9 and 11). In general, TOC removal seems to reach a plateau (~60%), while sufficient mineralization and discoloration of the wastewater is achieved even when only 7 g/L H_2O_2 are added. In the case of OLD, the doubling of total H_2O_2 concentration, from 16 to 30 g/L (Exp. No 3 and 5), enhances the overall performance. Furthermore, the expected positive effect of treatment time is depicted in Fig. 2a (Exp. No 5 and 6). Prolonging the time up to 27h rises the performance by approx. 34%. Thus, for higher efficiencies, longer times are required due to the apparently slow mineralization kinetics of wastewater in the first 8h. Additionally, a larger H_2O_2 dosing rate does not lead to improved performance of the combined process, unless

it is matched by the system H_2O_2 consumption rate (Exp. No 3-5). Under the investigated conditions, a near optimum H_2O_2 dosing rate of approx. $1140\text{-}1200\text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ may be considered subject to further testing.

3.2 H_2O_2 consumption, Organics elimination & Kinetics

The percentage of H_2O_2 consumption is increased with treatment time (Fig.3), intensively after the first 8h, in all tests, indicating the rather slow reactions kinetics of the wastewater in shorter times. A higher H_2O_2 consumption means that larger quantity of H_2O_2 is photolyzed from UV-C irradiation generating more radicals $\cdot\text{OH}$, which are responsible for the mineralization of the wastewater. Therefore, a higher H_2O_2 consumption implies better efficiency in terms of TOC removal. Indeed, in Exp. No 5 the higher H_2O_2 consumption (87%) and the greater TOC removal (71%) of all tests is simultaneously noted. Similarly, in Exp. No 9, 12, 4 with H_2O_2 consumptions 79%, 55%, 51% respectively, TOC removal that follows the same trend is attained; i.e. 60%, 47%, 29% respectively, confirming the above correlation.

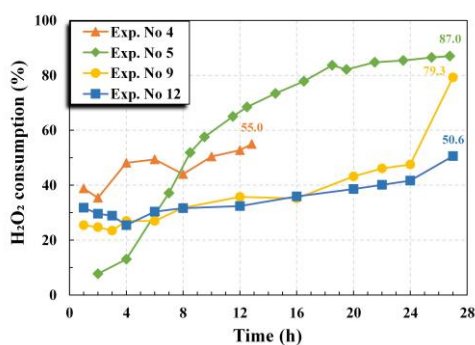


Figure 3. Percentage H_2O_2 consumption versus time during treatment with AO/ H_2O_2 /UV-C process.

The concentration of 54 different organic substances identified in the wastewater was measured before and after 27h treatment with AO/ H_2O_2 /UV-C in Exp. No 3. Ten of these organics (e.g. Imidacloprid, Clopyralid, Acetamiprid, etc.), were of concentration 1.5 to 10 ppm in the untreated wastewater, while the rest were at ppb levels (<10 ppb). Complete degradation (>99%) of 53 such micropollutants was achieved, denoting the great effectiveness of the process on decomposition and deconstruction of recalcitrant organic molecules.

Variations of normalized TOC concentration versus time exhibited the same behaviour in all experiments for the 3 process variants tested (Fig. 4). Mineralization rate of the wastewater during short times (0-8h) is rather low, however it increases thereafter until the end of experiment (8-27h), becoming more intense in case of AO/ H_2O_2 /UV-C, which is the most effective process. This trend is attributed to the heavy organic load of the wastewater. In reverse, discoloration kinetic reactions occur clearly faster even in the first 8 h of treatment, revealing the refractory nature of the chromophores that delays the mineralization of the wastewater.

4. Conclusions

Evaluation at pilot scale was performed of an advanced combined AO/ H_2O_2 /UV-C process employing waste-

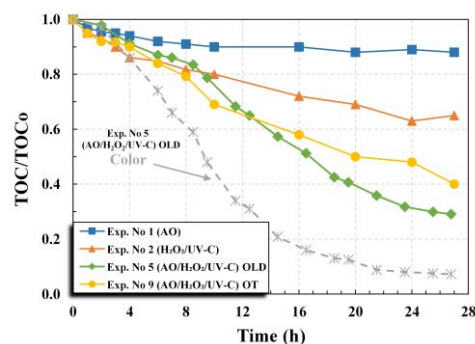


Figure 4. Temporal variation of normalized TOC concentration during treatment with AO, H_2O_2 /UV-C and AO/ H_2O_2 /UV-C process.

water from a pesticides production plant. The dominant role of H_2O_2 /UV-C process was evident, compared to AO. Current density in the applied range indicated no considerable effect on the overall system performance, thus confirming the secondary but synergistic role of AO during the combined oxidation process. Nevertheless, high efficiencies were observed when the addition of H_2O_2 was made either dosimetrically or all at once. Complete discoloration and up to 71% TOC removal was achieved after 27h of treatment with a H_2O_2 dosing rate $1140\text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$, mostly due to the high utilization of injected H_2O_2 (~90%). The system performance is judged as remarkable, considering that complete degradation was observed of the 53 out of the total 54 organic compounds identified in the wastewater tested. Therefore, the demonstrated technology is considered an attractive, potentially sustainable alternative to the currently employed special treatment, which involves chemical coagulation/granular activated carbon adsorption and necessitates further costly extra-treatment of the resulting secondary wastes. Based on the new results, steps are currently in progress towards implementation at full scale, of the hybrid AO/ H_2O_2 /UV-C technology, for treatment of similar heavily polluted industrial effluents.

5. Acknowledgements

This work has received financial support through the project: CERESiS – ContaminatEd land Remediation through Energy crops for Soil improvement to liquid biofuel Strategies, funded from the European Union's HORIZON 2020 Research and Innovation Programme under Grant Agreement (Project No. 101006717).

References

- Radovic Vucic, M., Baosic, R., Mitrovic, J., Petrovic, M., Velinov, N., Kostic, M., Bojic, A., (2021), *Process Safety and Environmental Protection*, **149**, 786-793.
- Yu, L., Iranmanesh, S., Keir, I., Achari, G., (2020), *Water*, **12**, 1200.
- Miklos, D.B., Hartl, R., Michel, P., Linden, K.G., Drewes, J.E., Hübner, U., (2018), *Water Research*, **136**, 169-179.
- Samet, Y., Agengui, L., Abdelhedi, R., (2010), *Chemical Engineering Journal*, **161**, 167-172.
- Millan, M., Rodrigo, M.A., Fernandez-Marchante, C.M., Canizares, P., Lobato, J., (2019), *ACS Sustainable Chem. Eng.*, **7**, 8303-8309.