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

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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 (·OH); i.e., electrochemical anodic oxidation (AO) employing boron-doped diamond (BDD) electrodes and photochemical oxidation via H₂O₂ photolysis under UV-C irradiation (H₂O₂/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, H₂O₂ 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 H₂O₂ and 8.4 L/min recirculation flow rate), TOC and color removal reached 71% and 93%, respectively. The effectiveness of the combined AO/H₂O₂/UV-C process, mainly due to high utilization of injected H₂O₂ (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/H₂O₂

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/H₂O₂, 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 (·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/H₂O₂ 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/H₂O₂ 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/H₂O₂/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 (GPHB10T5L/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 (H₂O₂) solution 50% w/w, supplied by Ferri-Tri was used as the oxidizing agent, whereas titanium (IV) oxysulfate (TiOSO₄) supplied by Sigma-Aldrich was used for the determination of H₂O₂ concentration. All H₂O₂ solutions were prepared with tap water (TW).

2.2 Analytical methods

A TOC/TN analyzer was employing for the direct measurements of Total Organic Carbon (TOC) and Total Nitrogen (TN) concentrations of the samples. Color and H₂O₂ 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 m²) 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 H₂O₂ vessel where the preparation of the H₂O₂ 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 H₂O₂ 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/H₂O₂/UV-C pilot](image-url)
3. Experimental Results

Twelve tests with the industrial wastewater (Table 1), were conducted in the premises of K&N Ethymiadias 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), H₂O₂ concentration (C), mode of H₂O₂ 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.

<table>
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<th>Exp No</th>
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<th>CD mA/cm²</th>
<th>C  g/L</th>
<th>R_{H2O2} mg/L/h</th>
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3.1 Effect of operating parameters

At first, the wastewater was treated separately with the AO (Exp. No 1) and H₂O₂/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 H₂O₂/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/H₂O₂/UV-C process (Exp. No 3-12) was carried out. The efficiency of the combined process compared to either AO or H₂O₂/UV-C alone, is significantly improved as expected, regardless of the mode of H₂O₂ addition into the system; i.e. OLD (Fig. 2a) or OT (Fig. 2b). Among experiments with AO/H₂O₂/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/H₂O₂/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, H₂O₂/UV-C, AO/H₂O₂/UV-C OLD and (b) AO/H₂O₂/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/H₂O₂/UV-C process efficiency during pilot tests. However, CD below 20 mA/cm² (Exp. No 12), does not favor mineralization/discholoration due to inefficient AO.

Comparison between experiments with different mode of H₂O₂ 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 H₂O₂; addition. This enhanced efficiency is correlated with the higher H₂O₂ consumption achieved in Exp. No 5, due to the specific point where H₂O₂ 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 H₂O₂ 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 H₂O₂ are added. In the case of OLD, the doubling of total H₂O₂ 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 H₂O₂ dosing rate does not lead to improved performance of the combined process, unless
it is matched by the system H$_2$O$_2$ consumption rate (Exp. No 3-5). Under the investigated conditions, a near optimum H$_2$O$_2$ dosing rate of approx. 1140-1200 mg L$^{-1}$ h$^{-1}$ may be considered subject to further testing.

3.2 H$_2$O$_2$ consumption, Organics elimination & Kinetics

The percentage of H$_2$O$_2$ 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$_2$O$_2$ consumption means that larger quantity of H$_2$O$_2$ is photolyzoned from UV-C irradiation generating more radicals -OH, which are responsible for the mineralization of the wastewater. Therefore, a higher H$_2$O$_2$ consumption implies better efficiency in terms of TOC removal. Indeed, in Exp. No 5 the higher H$_2$O$_2$ consumption (87%) and the greater TOC removal (71%) of all tests is simultaneously noted. Similarly, in Exp. No 9, 12, 4 with H$_2$O$_2$ 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$_2$O$_2$ consumption versus time during treatment with AO/H$_2$O$_2$/UV-C process.

The concentration of 54 different organic substances identified in the wastewater was measured before and after 27th treatment with AO/H$_2$O$_2$/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$_2$O$_2$/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$_2$O$_2$/UV-C process employing waste- water from a pesticides production plant. The dominant role of H$_2$O$_2$/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$_2$O$_2$ 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$_2$O$_2$ dosing rate 1140 mg L$^{-1}$ h$^{-1}$, mostly due to the high utilization of injected H$_2$O$_2$ (~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$_2$O$_2$/UV-C technology, for treatment of similar heavily polluted industrial effluents.

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References


