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A B S T R A C T

This work aimed at comparing different UV and H_2O_2 based advanced oxidation processes (AOPs) −photolysis, UV/H_2O_2, and photo-Fenton reaction- for the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D), a common ingredient of phytosanitary products. The influence of oxidant dose (H_2O_2), catalyst type and concentration, pollutant concentration, water matrix and irradiation spectrum was also analyzed. Under reference conditions (25 mg/L of 2,4-D in osmosed water), photo-Fenton oxidation using Fe^{2+} salt, initial pH value of 2.6 and a low-pressure mercury vapor lamp (10 W, λ = 254 nm) yielded more than 85% of pollutant mineralization in one hour, as compared to 60% and less than 10% for UV/H_2O_2 and photolysis, respectively. Such a performance could be achieved in 10 min only when applying optimal concentration range for Fenton's reagent (2 to 5 times the stoichiometric amount of H_2O_2 and oxidant-to-catalyst molar ratio from 25 to 40). Conversely, addition of a ZSM-5 zeolite bearing iron active sites albeit catalyzing Fenton oxidation at natural pH – did not bring additional benefit to UV/H_2O_2 process. Use of wastewater treatment plant effluent as aqueous matrix or irradiation in the UVA-visible range somewhat lowered the fficiency of the homogeneous photo-Fenton process. Nonetheless, bench scale experiments under sunlight gave promising results for 2,4 D remediation in wastewater, leading to over 80% conversion of the pollutant within ten minutes.

1. Introduction

Phenoxyalkanoic herbicides are considered as serious contaminants of superficial and ground waters due to their high solubility in water and slow degradation by biological processes [1]. 2,4-Dichlorophenoxyacetic acid (2,4-D) is one of the most widely used herbicides in the world [2,3], and over 1500 commercial phytosanitary products contain 2,4-D as the main active substance [4]. This molecule has frequently been detected in surface and ground waters in Europe and North America [5], and it has been classified as refractory pollutant by the Environmental Protection Agency (EPA) [6]. 2,4-D may adversely affect the aquatic life in water bodies and can cause chromosomal aberrations in human lymphocytes [7]; the World Health Organization (WHO) referred it as moderately toxic (Class II) and hence set its maximum allowable concentration in drinking water to 100 ppb [8].

Therefore, development of efficient degradation processes for this compound and its derivatives is of great importance. Advanced Oxidation Processes (AOPs) have proved to degrade many different families of organic compounds, including pesticides. They are based on the generation of highly reactive species, principally the non-selective hydroxyl radicals (OH·). The hydroxyl radical has the ability to oxidize most of the organic molecules, ultimately converting them into water, carbon dioxide, and inorganic acids or salts.

Several publications have studied the degradation of 2,4-D in water by different AOPs, mainly: heterogeneous photocatalysis over TiO_2, Ca–Ce–W–TiO_2, Au/TiO_2–CeO_2 [9–12], electrochemical-based treatment [13–15], ozonation [16–20] − alone, or combined with UV [16], heterogeneous catalysts [17–19] or hydrogen peroxide [20]. Most of these works, reported total degradation of the pollutant and above 40% mineralization yield in 15 min of reaction time. The most successful process combined ozonation with UV and Fe(II) catalyst, resulting in full conversion of 2,4-D in 15 min and of total organic carbon in 90 min [18].

On the other hand, remediation of this pollutant using UV irradiation can be of interest, as it is known to be a simple, clean and rather efficient treatment. Moreover, UV light can ctivate the decomposition

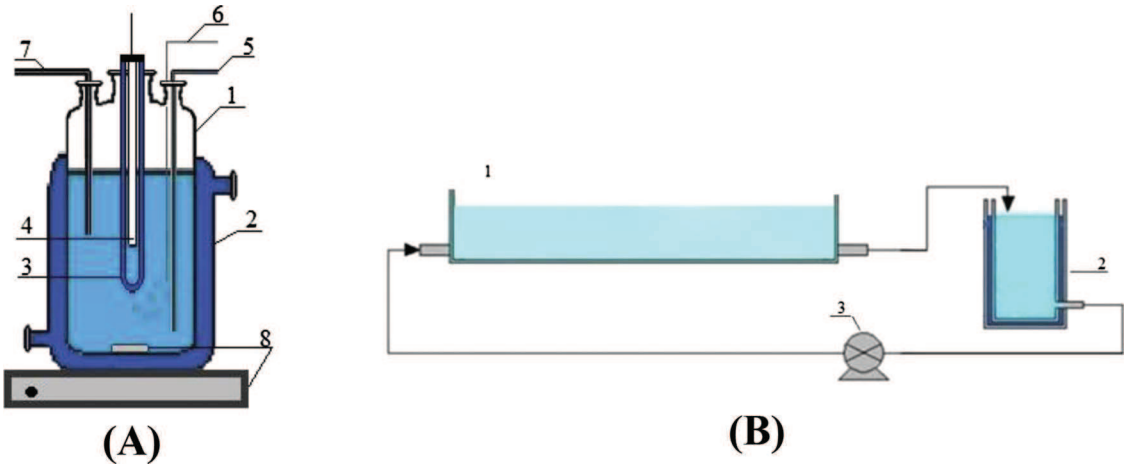

Fig. 1. Set-ups used for: (A) parametric study on photolysis and photo-Fenton oxidation (1- glass reactor, 2, 3- thermostated jacket, 4- UV/Vis lamp, 5- sampling tube, 6- bubbling of air, 7- thermometer, 8-magnetic stirrer bar and motor); (B) solar photo-Fenton treatment (1- open channel reactor, 2- stirred tank, 3- peristaltic pump).

of H_2O_2 into OH· or contribute to the regeneration of ferrous ion catalyst in the Fenton reaction [21].

Homogeneous Fenton mechanism can be briefly described by the following reactions:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \quad (2)$$

Regeneration of ferrous iron (Eq. (2)) is recognized as the limiting step of this catalytic process, which usually hinders mineralization of the pollutants. However, its rate can be significantly increased using photons, providing additional radicals s per to Eqs. (3) (photo-reduction of Fe^{3+}) and (4) (photolysis of H_2O_2) [21].

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + OH^{\bullet} + H^{+} \quad (3)$$

$$H_2O_2 + h\nu \rightarrow 2OH^{\bullet} \quad (4)$$

In addition, this so-called photo-Fenton process can benefit from a wider range of the irradiation spectrum than photolysis or UV/H_2O_2, as wavelengths up to 580 nm were found active for the photoreduction of dissolved ferric iron [22]. Therefore, the use of solar light has gained attention in photo-Fenton reaction due to the possibility of reducing the energy demand [23].

Even though it is well known that irradiation spectrum and intensity are key parameters of the photolytic degradation of organic compounds, the role of these parameters on 2,4-D degradation has not been systematically studied before. Neither has the optimization of hydrogen peroxide and ferrous salt concentrations been previously carried out. This work will pay attention to both aspects with the purpose of achieving the degradation of the pesticide and its mineralization in less time.

The aim of this work was thus to propose an efficient and economical alternative for 2,4-D degradation based on UV–vis irradiation, either as a single treatment or combined with chemicals (H_2O_2 or Fenton's reagent) and to optimize the operating conditions of the selected process. For that purpose, the influence of key parameters, such as irradiation spectrum (UV, UV/Vis or Vis range) and intensity, oxidant dose, catalyst type (Fe^{2+} or supported iron oxide) were carefully examined, as well as the effect of pollutant concentration and water matrix using influent or effluent from wastewater treatment plant (WWTP).

2. Materials and methods

2.1. Chemicals

2,4-D (purity ≥ 99.0%), H_2SO_4 (95–97%), hydrogen peroxide (Ph Eur, 30% w/w solution), and $Fe_2SO_4{\cdot}7H_2O$ (99.5%) were supplied by Sigma-Aldrich. In addition, a commercial iron containing zeolite of ZSM-5 structure (Fe-MFI-27, 3.5 wt% Fe provided by Süd-Chemie AG), was evaluated as catalyst for the Fenton oxidation.

KI (99.5%), Na_2SO_3 (99.0%), KH_2PO_4 (99.0%), $Na_2HPO_4.2H_2O$ (99.0%) from Sigma-Aldrich, HPLC grade acetonitrile (Scharlau-Chemie) and orthophosphoric acid (89%, Fluka) were used for the analysis of the liquid samples.

2.2. Experimental set-ups and procedures

Most of the experiments performed in the lab-scale photochemical reactor used synthetic solutions containing 25 mg L^{-1} (0.11 mmol L^{-1}) of pesticide in osmosed water. Initial pH of this solution was 3.5. Effects of aqueous matrix (using the effluent of a municipal WWTP) and pollutant concentration were also evaluated for the best process (cf. § 3.3.3). For bench-scale assays, pesticide solutions were prepared with tap water or inlet stream of WWTP.

A quenching solution containing KI (0.1 mol L^{-1}), Na_2SO_3 (0.1 mol L^{-1}) and a phosphate buffer (mixture of KH_2PO_4, 0.05 mol L^{-1} and $Na_2HPO_4.2H_2O$, 0.05 mol L^{-1}, pH 7.2) was prepared for the treatment of the withdrawn samples before analysis. KI and Na_2SO_3 reduced H_2O_2, while the phosphate buffer precipitated dissolved iron. For bench scale experiments, residual iron was eliminated by addition of $Ca(OH)_2$ solution (10 wt% aqueous solution).

2.2.1. Photochemical reactor

The experimental set-up used for parametric study on photolysis and photo-Fenton oxidation (Fig. 1A) consisted of a 1 L stirred Pyrex reactor, equipped with a jacket to maintain the temperature of the solution at 30 °C. It included a jacketed immersion well, made either of quartz or borosilicate glass, in which the artificial light source was placed. Three different types of lamp were used: a medium-pressure mercury vapor lamp (MP Hg, λ = 200–600 nm, 450 W Hanovia PC451.050 lamp, arc length 4.8 cm), a low-pressure mercury vapor lamp (LP Hg, λ = 254 nm, 10 W Heraeus GPH212T5L/4 lamp) and a xenon arc lamp (Xe-arc, λ = 360–700 nm, 150 W Peschl Ultraviolet TXE 150). For safety reasons, this photochemical reactor was installed inside a closed cabinet and equipped with an automatic shutdown system if the temperature of the solution exceeded 60 °C or the box door was opened. The solution (700 mL) was agitated by a magnetic stirrer rotating at 350 rpm and by gentle bubbling of air. For homogeneous (photo-)Fenton oxidation, the initial pH of the solution was adjusted to 2.6 with 10% H_2SO_4, after which the catalyst and H_2O_2 were added. Experiments using the Fe-zeolite included a preliminary adsorption step of 300 min before addition of the oxidant.

2.2.2. Bench scale solar reactor

The set-up used for solar photo-Fenton treatment (Fig. 1B) was composed of a tank of 15 L, a peristaltic pump (Easy-Load Masterflex) and an open channel reactor (250 mm width × 640 mm length × 110 mm height; useful volume: 15 L) made of stainless steel. It was operated in a closed-loop mode using a recirculation flow rate of 1 L min^{-1}.

The stoichiometric amount of H_2O_2 required for the mineralization of the pesticide was calculated based on the following equation:

$$C_8H_6Cl_2O_3 + 15H_2O_2 = 8CO_2 + 17H_2O + 2HCl \quad (5)$$

It corresponded to 1.7 mmol/L of H_2O_2 for an initial pollutant concentration of 25 mg L^{-1}.

2.3. Analytical methods

2.3.1. Sample preparation

During the 5 h of oxidation, 10 mL aliquots were withdrawn at selected time intervals (after 10, 20, 60, 180 and 300 min of oxidation process). (Photo)-Fenton oxidation samples were treated prior to analysis. For total organic carbon measurement, 7 mL of the reacting solution were mixed with 3 mL of the quenching solution to prevent any further oxidation. The sample was passed through 0.45 mm regenerated cellulose membrane syringe filter and diluted with ultrapure water to 15 mL. It was checked that retention of 2,4-D over the selected membrane was negligible. For chromatography analysis, 1.5 mL of sample was mixed with 0.5 mL of phosphate buffer (to prevent any interference from the reducing agents) and filtered, before being readily injected.

2.3.2. Physicochemical analysis

2,4-D concentration was measured by a High Performance Liquid phase Chromatograph with UV detection (UV2000 diode array detector, Thermo Finnigan). The separation was achieved on a C18 reverse phase column (ProntoSIL C18 AQ) using an isocratic mobile phase (40/60 mixture of acetonitrile and ultrapure water acidified at pH 1.6 with H_3PO_4) fed at 1 mL min^{-1}. The wavelength was set to 230 nm for 2,4-D detection. Quantification was made from a calibration curve periodically updated with fresh standard solutions (with 2,4-D concentration ranging from 1 to 25 mg L^{-1}). The relative uncertainty was less than 1.7% and the quantification limit was 1 mg L^{-1}.

The total organic carbon (TOC) concentration was calculated from the difference between total carbon (TC) and inorganic carbon (IC) concentrations measured with a Shimadzu TOC-VCSN analyzer. Quantification limit for TC was 0.05 mg L^{-1}. Reported values corresponded to the mean of three successive measurements showing a variation coefficient (CV) of less than 2%.

3. Results and discussion

3.1. Photolysis

Irradiation spectrum and intensity are key parameters of the photolytic degradation of organic molecules. To investigate their effect separately, the applied wavelength range was first varied by using the MP Hg lamp with either a quartz or glass immersion well. According to the supplier, the MP Hg lamp emits 40–48% of its energy in the ultraviolet part of the spectrum and 40–43% in the visible range. The glass holder should cut most of the radiation below 280 nm, about 50% of the emission at 310 nm, and shows full transmittance above 355 nm. In addition, the performance of a low intensity LP Hg lamp was examined, which mainly exhibits a monochromatic emission at 254 nm. Fig. 2 shows the evolution of 2,4-D and TOC concentrations during the corresponding photolysis experiments.

For both conversion and mineralization, the removal yield of 2,4-D ranged in the following order: MP Hg lamp + quartz lamp holder > > LP Hg lamp + quartz lamp holder > > MP Hg lamp + borosilicate lamp holder. This behavior could be explained by the absorbance spectrum of the molecule, which exhibited maxima at 201, 230 and 283 nm and by the differences in lamp irradiation intensity in this wavelength range. In the best conditions, 2,4-D was totally degraded by direct photolysis in 10 min and total mineralization was achieved in 1 h. The results obtained with the LP Hg lamp (using quartz immersion well) were consistent with those reported by other authors [16,24–27] in similar conditions.

3.2. UV/H_2O_2 photo-oxidation

Addition of H_2O_2 is expected to promote pollutant degradation since it is decomposed by UV light into highly reactive hydroxyl radicals [28,29]. On the other hand, a too high excess of H_2O_2 might not be beneficial as it also competes with the target compounds for $OH^\bullet$ radicals, according to:

$$OH^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \quad (6)$$

$$HO_2^\bullet + OH^\bullet \rightarrow H_2O + O_2 \quad (7)$$

Another set of experiments was thus carried out with LP Hg lamp in order to study the effect of initial H_2O_2 concentration in the combined process. Dosages between 2 and 7 times the stoichiometric amount for complete mineralization (cf. Eq. (5)) were applied.

Under dark conditions, addition of H_2O_2 in stoichiometric excess only converted up to 1% of 2,4-D after 5 h of reaction. However its effect was remarkable when combined with the lowest intensity lamp, allowing complete conversion of the pesticide in the first 10 min and much higher mineralization yields than the sole photolysis (Fig. 3).

On the other hand, the influence of H_2O_2 dosage was rather moderate in the investigated range. Increasing oxidant concentration was beneficial up to 8.5 mM, after which a slight decrease in TOC removal was observed, that could be ascribed to H_2O_2 scavenging effect. The oxidation of 2,4-D by $OH^\bullet$ exhibits a rate constant of $5.1 \cdot 10^9$ L mol^{-1} s^{-1} at ambient temperature [26], which is much higher than that reported for the reaction in between H_2O_2 and $OH^\bullet$ (Eq. (6)): $(1.7–4.5) \cdot 10^7$ L mol^{-1} s^{-1} [30]. However, at the highest excess of H_2O_2 (11.9 mM *vs.* 0.11 mM of 2,4-D), the rates of the two reactions became comparable, resulting in competition effect.

The influence of irradiation spectrum in the photo-H_2O_2 process was also investigated. Fig. 4 compares conversion and mineralization yields obtained with LP Hg lamp and quartz lamp holder to those of MP Hg lamp and glass lamp holder.

Despite higher power of the MP Hg lamp, a slower elimination of 2,4-D was observed for wavelengths above 280 nm, which is due to the low absorbance of H_2O_2 in the UVB-Vis range [31].

3.3. Photo-Fenton oxidation

Synergy effect between UV irradiation and Fenton's reagent has also been reported in numerous studies [23,32–35]. As one of the activation mechanisms,the photoreduction of ferric iron (Eq. (3)) may be initiated in the visible range [28], beneficial effect can be expected over a much larger zone of the irradiation spectrum than in the UV/H_2O_2 process.

Therefore the influence of light source was assessed first, using the optimal oxidant concentration previously found and a concentration of ferrous salt corresponding to a $[H_2O_2]/[Fe]$ molar ratio of 10.

3.3.1. Effect of lamp type

As previously, different artificial light sources were tested, including a xenon arc lamp that mimicked solar irradiation due to its emission spectrum in the UVA-Vis range (λ = 360–740 nm). For all three lamps, 2,4-D was eliminated in the first 10 min. TOC removal, Fig. 5, ranged in the following order: LP Hg lamp + quartz lamp holder > Xe-arc lamp + quartz lamp holder > MP Hg lamp + borosilicate lamp holder. However, much lower differences were observed between the

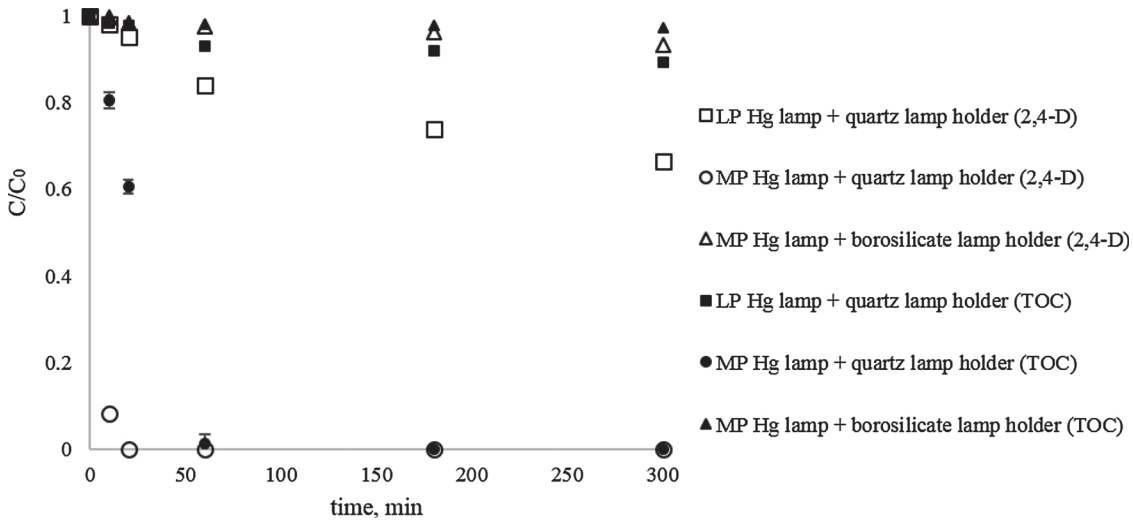

Fig. 2. Effect of irradiation spectrum and lamp power on the degradation of 2,4-D by photolysis. $[2,4\text{-D}]_0$ = 25 mgl.L^{-1}, pH_0 = 3.5, T = 30 °C.

two extremes with respect to photo-H_2O_2 process. Interestingly, Xe-arc lamp resulted in a similar activation of the Fenton reaction as LP Hg lamp, outlining perspectives in the use of solar light as substitute of UV lamps for a more economical process. It is also worth noting that despite its lower power and rather similar emission spectrum range, Xe-arc lamp was found to be more efficient than the filtered MP Hg lamp.

3.3.2. Effect of iron: source: heterogeneous vs. homogeneous photo-Fenton oxidation

The biggest drawback of the homogeneous photo-Fenton process comes from the necessity of a post-treatment, as iron concentrations usually applied (about tens of ppm) are much higher than the maximum allowable discharge concentration (2 mg L^{-1} in the EU [36]). Moreover Fenton oxidation operates within a narrow pH range, usually between 2 and 4, mostly to prevent iron precipitation during the reaction. Neutralization of the effluent thus follows the oxidation process both to remove iron and reach the release standards, producing hardly disposable sludge, besides chemical consumption and catalyst lost. To overcome these issues, heterogeneous iron-based catalysts have been used in the so-called Fenton-like process, allowing wider operated pH ranges and facilitating the reuse of catalyst [37,38]. Fe-containing zeolites are interesting candidates for heterogeneous Fenton reaction due to the combination of their adsorptive, acidic and catalytic properties.

A group of experiments was then carried out in order to evaluate the catalytic activity of a ZSM-5 zeolite bearing iron active sites in (photo-) Fenton oxidation. To limit light scattering/absorption by the particles, slurry concentration was set to 1 g L^{-1} which corresponded to 0.62 mM of total iron.

Preliminary contacting step between the Fe-zeolite and 25 mg L^{-1} 2,4-D solution revealed a marginal adsorption of the pesticide onto the catalyst (with less than 0.5% uptake from the aqueous phase for a catalyst concentration of 1 g L^{-1}). This can be explained by several factors. First, molecular size of 2,4-D (0.85 × 0.54 × 0.22 nm, calculated by MOPAC 2016) is close to that of ZSM-5 cages (with pore openings of 0.51 nm × 0.55 nm and 0.54 nm × 0.56 nm for sinusoidal and straight channels, respectively [39,40]), limiting the access of the molecule to the micropores. Moreover, the pH of the solution after contact was 3.5, which is higher than the point of zero charge (PZC) of the catalyst (2.9) and the pKa of 2,4-D (2.7). Therefore both the zeolite surface and the molecule exhibited negative charges, resulting into mutual electrostatic repulsion that thus impeded adsorption of 2,4-D.

Fig. 6 compares the performance of heterogeneous Fenton and photo-Fenton processes to that of the homogeneous counterparts (using $FeSO_4{\cdot}7H_2O$) at similar total iron concentration (0.84 mM) and H_2O_2 concentration of 8.5 mM. A difference was in the initial pH of the solution which was set to 2.6 for the homogeneous system, but not adjusted in the presence of the zeolite.

As under such conditions, UV/H_2O_2 already allowed the complete elimination of 2,4-D within 10 min, only mineralization results are plotted for the case of photo-Fenton oxidation in Fig. 6. TOC removal by UV/H2O2 is also recalled in this figure.

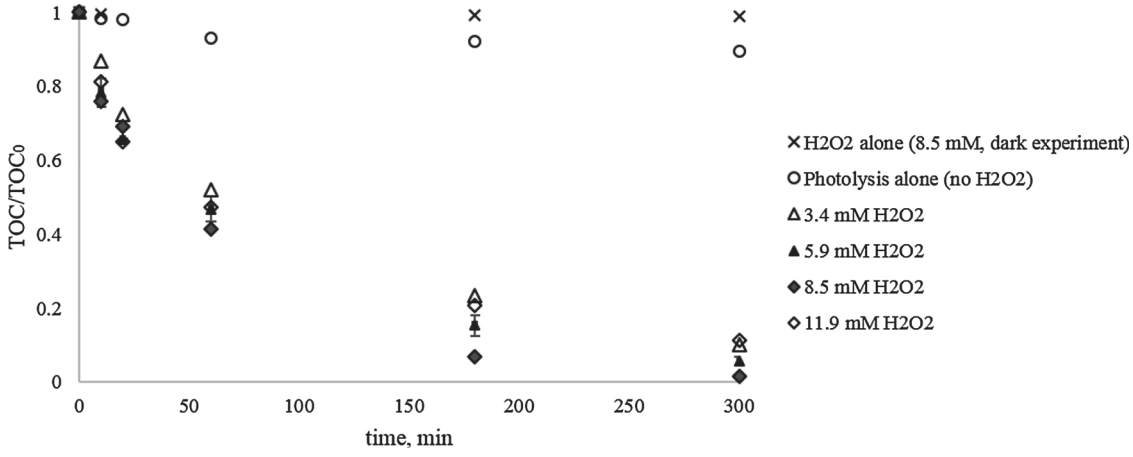

Fig. 3. Effect of H_2O_2 dosage on the mineralization of 2,4-D by photo-H_2O_2 process. $[2,4\text{-D}]_0$ = 25 mgl.L^{-1}, pH_0 = 3.5, T = 30 °C, 10 W LP Hg lamp and quartz lamp holder.

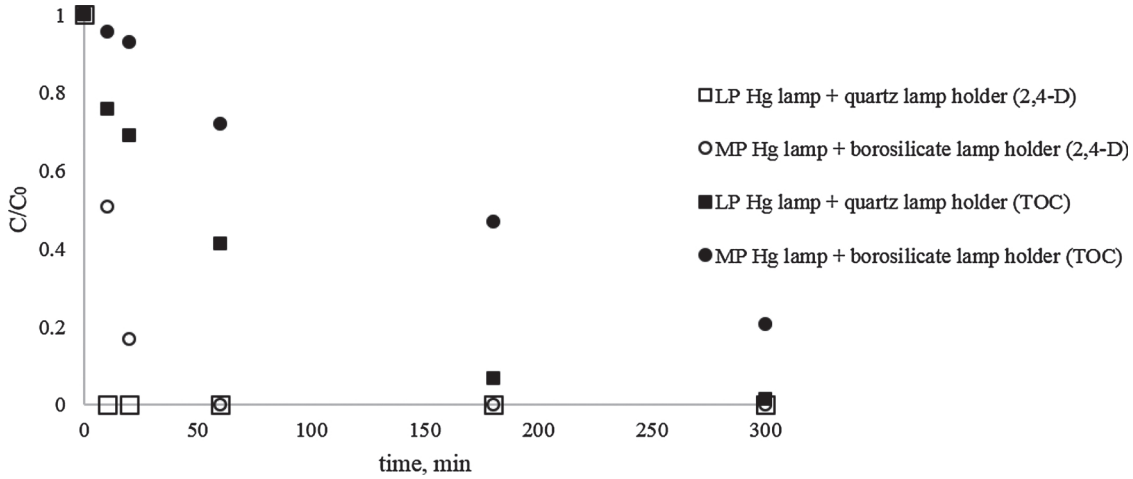

Fig. 4. Effect of irradiation spectrum and lamp power on the degradation of 2,4-D by UV/H_2O_2 photo-oxidation. $[2,4\text{-D}]_0 = 25$ mgl L^{-1}, T = 30 °C, $[H_2O_2]_0 = 8.5$ mM, $pH_0 = 3.5$.

Under dark conditions, the Fe-zeolite yielded 94% conversion of the pesticide after 5 h *vs.* complete conversion in 10 min with the ferrous salt. Initial mineralization rate was also significantly lower with Fe-zeolite, but, contrarily to the homogeneous system, TOC concentration did not seem to plateau.

Under UV irradiation, the effect of this catalyst was in fact marginal as the heterogeneous photo-Fenton process resulted in essentially the same TOC evolution as with UV/H2O2. Therefore it was not considered in the further work.

3.3.3. *Matrix effect*

In order to investigate the efficiency of homogeneous photo-Fenton oxidation in real application, a set of lab-scale experiments was performed using wastewater matrix and varying the initial concentration of 2,4-D. The effluent from of a municipal wastewater treatment plant located in Nailloux village (France) was used (effluent A), whose physicochemical properties are given in Table S1 (Supporting information). In particular, its contribution to TOC was lower than that of 2,4-D at the reference concentration (25 mg L^{-1}) and it also contained a significant amount of carbonate and bicarbonate ions as shown by its IC value (29.4 mg L^{-1}). However, the latter were probably removed by the preliminary acidification at pH 2.6.

Fig. 7 compares the normalized TOC concentration–time profiles during the homogeneous photo-Fenton oxidation, for two initial concentrations of 2,4-D: 5 and 25 mg L^{-1}. The results corresponding to the solution prepared with osmosed water matrix (at same pesticide concentration) are shown for comparison purpose. It should be first noted that complete degradation of 2,4-D was still achieved within 10 min for all the conditions. At the reference pesticide concentration, similar initial mineralization rates were observed in the two aqueous matrixes; however residual TOC (about 10%) remained after 5 h for the wastewater effluent while full abatement was obtained in osmosed water. A possible explanation for this behavior could be the presence of more refractory compounds in effluent A. Reduction of 2,4-D concentration by a factor 5 indeed lowered final mineralization yield in wastewater effluent, while it led to a faster TOC removal in osmosed water. Note that this concentration effect in osmosed water was consistent to that reported in different UV-based processes [9,24].

3.3.4. *Optimization of Fenton's reagent concentration*

Table 1 indicates the results of photo-Fenton oxidation of 2,4-D after 10 min, using LP Hg lamp and quartz lamp holder. Concentrations of Fe^{2+} and H_2O_2 were varied, following a factorial 3^2 experimental design (rows 5–13).

For all the studied conditions, photo-Fenton reaction yielded a complete conversion of 2,4-D and mineralization yield was higher than

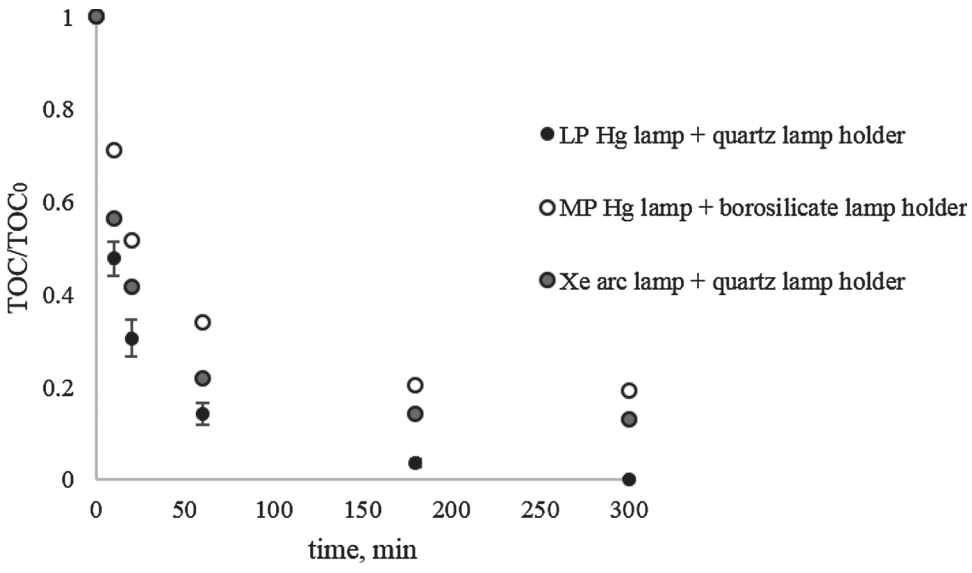

Fig. 5. Effect of irradiation spectrum and lamp power on the mineralization of 2,4-D by photo-Fenton oxidation. $[2,4\text{-D}]_0 = 25$ mgl.L^{-1}, $[H_2O_2]_0 = 8.5$ mM, $[Fe^{2+}]_0 = 0.84$ mM; T = 30 °C; $pH_0 = 2.6$.

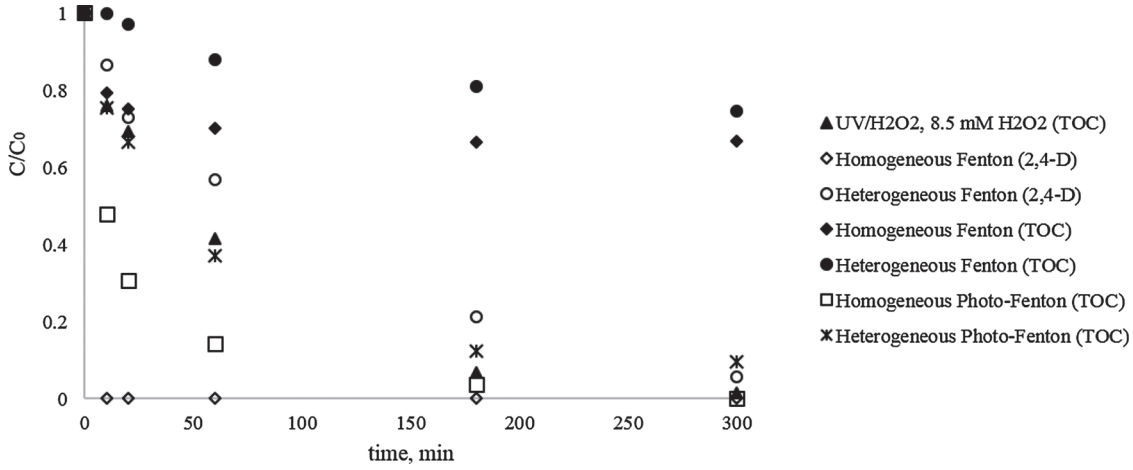

Fig. 6. Degradation of 2,4-D by homogeneous* ($Fe_2SO_4{\cdot}7H_2O$) and heterogeneous** (Fe-ZSM-5) (photo)-Fenton processes. $[2,4\text{-D}]_0 = 25$ mgl.L^{-1}, T = 30 °C; $[H_2O_2]_0 = 8.5$ mM, $[Fe^{2+}]_0 = 0.84$ mM, [zeolite] = 1 g L^{-1}. *pH_0: 2.6, **pH_0: 3.5, LP Hg lamp and quartz lamp holder for photo-assisted processes. TOC degradation by UV/H_2O_2 (8.5 mM) is recalled for comparison purpose.

50%, thus outperforming that of photolysis alone (first row in Table 1) and dark Fenton process (fourth row). In the initial investigated range, best TOC removal (84.1%) was obtained for 3.4 mM of H_2O_2 and 0.21 mM of Fe^{2+}, the latter value matching to the lowest bound of the experimental design. Therefore, two more experiments were carried out, by reducing the iron concentration with H_2O_2 concentration set at the optimal value. Corresponding results are given in rows 14–15 of Table 1, and showed that a lower amount of Fe^{2+} down to 0.08 mM was still beneficial. Moreover, it should be noticed that the use of iron catalyst reduced the optimal H_2O_2 concentration by a factor 2.5 with respect to UV/H_2O_2 process.

From multiple polynomial regression of the data using Statgraphics PLUS version 5.0 software, a mathematical model was derived that predicts 2,4-D mineralization yield after 10 min of photo-Fenton oxidation as a function of hydrogen peroxide and Fe^{2+} concentrations:

$$X_{TOC,10min} = 66.5 + 4[H_2O_2] + 62.8[Fe^{2+}] - 6[H_2O_2]\times[Fe^{2+}] - 0.2[H_2O_2]^2 - 64.2[Fe^{2+}]^2$$

The above equation adequately describes the experimental data as shown by the analysis of variance in Table S2 (Supporting information). For this model the correlation coefficient (R^2) was 98.06%, therefore showing a good fit of the model. Setting the level of significance to 0.1 (P-value < 0.1), only Fe^{2+}, $H_2O_2 \times Fe^{2+}$ and $Fe^{2+} \times Fe^{2+}$ are actually relevant parameters in the model, $H_2O_2 \times Fe^{2+}$ interaction showing the most important effect on TOC removal efficiency. Then, the final form of the statistic model is:

$$X_{TOC,10min} = 81.0 + 51.2[Fe^{2+}] - 4.2[H_2O_2]\times[Fe^{2+}] - 63.7[Fe^{2+}]^2$$

Fig. 8 exhibits the response surface and contour plots corresponding to the second-order polynomial fit. It can be observed that mineralization yield of the pesticide was more than 85% in a range lasting from 3.4 to 8.5 mM of H_2O_2 and from 0.2 to 0.3 mmol/L of iron, beyond which it decreased with an increase of either H_2O_2 or Fe^{2+} concentration.

3.3.5. Bench scale experiments in solar photo-reactor

Finally, taking in account the promising results obtained with the xenon-arc lamp, experiments were carried out using solar light. In these experiments, two different aqueous matrixes were used: (A) tap water and (B) inlet stream from wastewater treatment plan of Almendares river (Habana, Cuba) (effluent B, without any prior treatment contrarily to effluent A). Table 2 indicates the physicochemical properties of the 2,4-D solution (25 mg L^{-1}) prepared in effluent B, before treatment and after photo-Fenton oxidation (5 h of reaction time). The optimal concentration of Fenton's reagent deduced from the experimental design were first used (labelled as "low [FR]"), without accounting for the chemical composition of the matrix. Then, theis concentration was

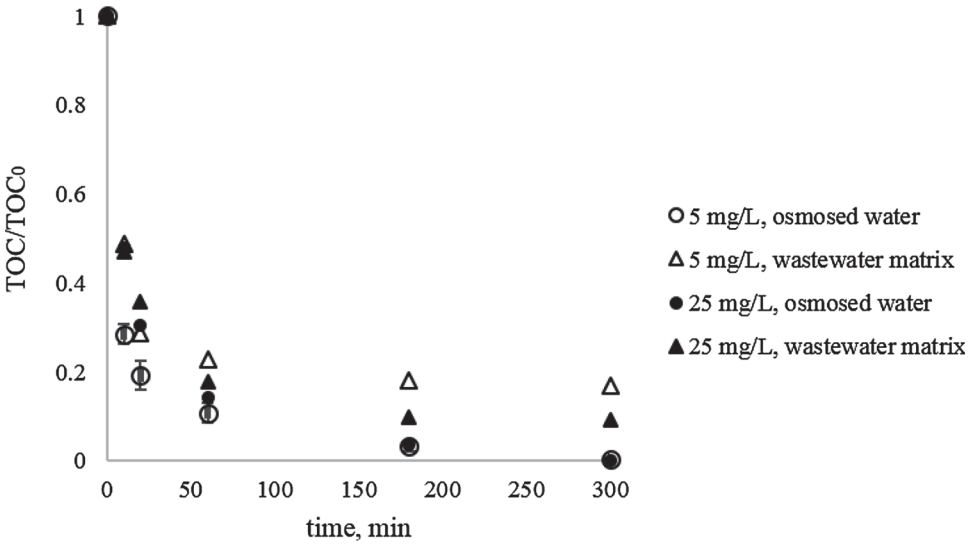

Fig. 7. Effect of 2,4-D initial concentration and matrix composition on the degradation of 2,4-D by photo-Fenton process. T = 30 °C; 10 W LP Hg lamp and quartz lamp holder; $[H_2O_2]_0 = 8.5$ mM, $[Fe^{2+}]_0 = 0.84$ mM; $pH_0 = 2.6$.

Table 1
Effect of Fenton's reagent (Fe(II)/H_2O_2) concentration on the degradation of 2,4-D by photo-Fenton process. $[2,4\text{-D}]_0 = 25\ mg\ L^{-1}$, T = 30 °C; 10 W LP Hg lamp and quartz lamp holder for photo-assisted processes and $pH_0 = 2.6$ for Fenton-based oxidation; t = 10 min.

Row Number	Concentration of H_2O_2, mM	Concentration of Fe^{2+} ($FeSO_4{\cdot}7H_2O$), mM	H_2O_2/Fe^{2+}	Conversion, %	Mineralization, %
1	0	0	0	2	1.5
2	8.5	0	0	100	24
3	8.5	0	0	1.1*	0*
4	8.5	0.84	10	100*	21*
5	3.4	0.21	16	100	84.1
6	5.9		28	100	83.5
7	8.5		40	100	83.6
8	3.4	0.48	7	100	80.8
9	5.9		12	100	82.3 ± 0.2
10	8.5		17	100	71.7
11	3.4	0.84	4	100	71.1
12	5.9		7	100	60.8
13	8.5		10	100	52.1
14	3.4	0.14	24	100	90.9
15	3.4	0.08	40	100	90.2

* Dark experiments.

adjusted according to the chemical oxygen demand of the wastewater matrix ("high [FR]", corresponding to 25.6 mM of H_2O_2 and 0.6 mM of Fe^{2+} to keep the same $[H_2O_2]/[Fe]$ molar ratio).

Concentration-time profiles of 2,4-D and TOC are also depicted in Fig. S1 for the two water matrixes and the two applied concentrations of Fenton's reagent (see Supporting information). For all the investigated conditions, more than 95% conversion of 2,4-D was reached in one hour. Mineralization efficiency followed the order: tap water (low [FR]) > wastewater (high [FR]) > wastewater (low [FR]), where 5 h of reaction resulted in TOC removal of 80.1, 76.0 and 70.7%, respectively. Thus adjusting the Fenton's reagent concentrations to the matrix composition increased TOC removal close to the value achieved in tap water. These mineralization yields are better than those reported in previous studies about 2,4-D degradation by heterogeneous photocatalytic process using simulated solar light [12] and solar photo-Fenton oxidation [24]. In addition to TOC abatement, proposed treatment of the solution (including neutralization by $Ca(OH)_2$ and filtration) allowed to eliminate more than 50% of initial BOD, COD, sedimented solids and iron content. Moreover, Table 2 shows that he pollution indicators were then below the values fixed by Cuban norm (NC-27-2012) [40] for wastewater discharge, and removal efficiency of BOD, COD, TOC, sedimented solids and iron was above 50%.

4. Conclusions

Degradation of 2,4-D by AOPs using differentUV sources and chemicals (H_2O_2 and iron-based catalysts) was studied. With a medium-pressure mercury vapor lamp the sole photolysis achieved total mineralization of the pollutant in one hour. On the other hand, homogeneous photo-Fenton oxidation outperformed the other investigated processes at 254 nm: after optimization of reagent concentration by response surface methodology, this process led to complete conversion of the molecule and mineralization yield over 85% within 10 min. Optimal concentration of Fenton's reagent corresponded to 2 times the stoichiometric amount of H_2O_2 (3.4 mM) and oxidant-to-catalyst molar ratio of 40. Use of wastewater effluent as aqueous matrix lowered the mineralization yield of the homogeneous process, most likely due to the presence of other refractory compounds as indicated from results at different initial 2,4-D concentration. Interestingly, xenon lamp mimicking solar irradiation exhibited similar activation effect on the Fenton reaction as low pressure mercury vapor lamp. The potential of solar photo-Fenton oxidation was further investigated in bench scale experiments under sunlight, using wastewater effluent as aqueous matrix. After proper setting of the operating conditions, the treatment was found efficient for both elimination of the pesticide (still achieved

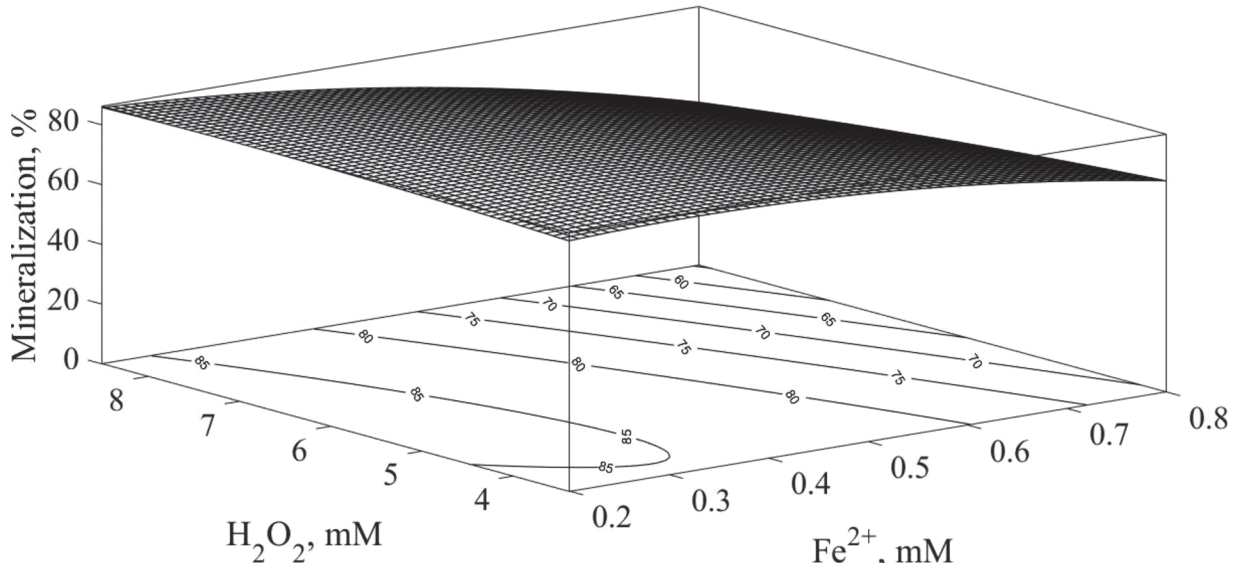

Fig. 8. Response surface and contour plots for mineralization of 2,4-D achieved by photo-Fenton oxidation after 10 min. $[2,4\text{-D}]_0 = 25\ mg\ L^{-1}$, T = 30 °C; 10 W LP Hg lamp and quartz lamp holder and $pH_0 = 2.6$.

Table 2
Characterization of 2,4-D/wastewater mixture (25 mg L^{-1} of 2,4-D in effluent B), before treatment and after 5 h of photo-Fenton oxidation (the solution being acidified to pH_0 = 2.6 prior to the reaction).

Parameter	Initial solution	Treated solution[1]	Cuban norm (NC-27–2012) [41]	Removal efficiency (%)
Temperature (°C)	27	27	< 40	–
pH	6.5	7 ± 0.5	6–9	–
BOD-5 (mg L^{-1} of O_2)	67.6	25.3*	< 40	62.6*
		24.1**		64.3**
COD (mg L^{-1} of O_2)	218	< 90*	< 90	> 58*
		< 90**		> 58**
Sedimented solids (mL L^{-1})	2,5 ± 0,1	0*	< 2	100*
		0**		100**
Iron (mg L^{-1})	0.5	0.07*	–	86.7*
		0.1**		72.1**
Floating matter	present	absent	absent	–
Conductivity (μS cm^{-1})	1310	65*	< 2000	–
		60**		
TOC (mg L^{-1} of C)	83.1	23.1*	–	70.6*
		19.4**		76.7**

[1] These values were determined after precipitation of Fe^{2+} and neutralization with Ca $(OH)_2$.
* "low [FR]": H_2O_2 3.4 mM and Fe^{2+} 0.08 mM.
** "high [FR]": H_2O_2 25.6 mM and Fe^{2+} 0.6 mM.

in 10 min) and TOC removal (> 75% after 5 h).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jece.2017.12.049.

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