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Electrical energy determination for an azo dye decolorization and mineralization by UV/H_2O_2 advanced oxidation process

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Abstract

This study examined the photolytic degradation of C.I. Acid Orange 7 azo dye, in aqueous solution by combined UV and hydrogen peroxide. A continuous circulated photoreactor equipped with a low-pressure mercury lamp was used. Different initial dosages of hydrogen peroxide and initial concentrations of dye were used for the synthetic wastewaters preparation. The rate of color removal and aromatic ring destruction were monitored spectrophotometrically at the visible maximum absorption wavelength and UV region. The decrease in total organic carbon (TOC) in dye solutions was measured to monitor the dye mineralization process. Decolorization and mineralization reactions after decolorization period follow apparent first order kinetics. The pseudo-first order rate constants values for each case were calculated from the experimental kinetic curves. It was found that mineralization of C.I. Acid Orange 7 undergoes about five times slower kinetics than decolorization reaction. By applying only 3.75 $\mathrm{W\,l^{-1}}$ of the UV dosage in the reaction mixture of 17.5 $\mathrm{mg\,l^{-1}}$ dye and 525 $\mathrm{mg\,l^{-1}}$ H_2O_2, nearly 90% total organic carbon can be removed in 100 min. Process electrical energy consumption for different synthetic wastewaters was determined.

Keywords: Dye removal; Mineralization; TOC; UV/H_2O_2; Figure-of-merit

1. Introduction

The textile industry consumes considerable amounts of water during the dyeing, printing and finishing operations. Dye pollutants from this industry are an important source of environmental contamination. Azo dyes are an important class of synthetic textile dyes used as coloring agents in the textile, paint, ink and plastics industries, accounting for 50% of all commercial dyes [1]. They are characterized by the presence of one or more azo group (–N=N–) bound to aromatic rings. However, large amounts of these dyes remain in the effluent after the completion of the dyeing process. Consequently, the textile wastewaters are strongly colored. Azo dyes are stable compounds, difficult to destroy or to be decomposed by common treatment in a biological treating station [2]. Seshadri et al. [3], reported that an anaerobic fluidized bed reactor accomplished the cleavage of the azo bond, leading to decolorization of AO7, AO8, AO10 and Acid Red 14 dyes under hydraulic retention time of 24 h. The results obtained by Ong et al. [4], have shown insignificant removal of C.I. Acid Orange 7 by aerobic process.

Advanced oxidation processes (AOPs) are widely used for the decolorization of dyes and wastewater treatment [5–9]. The mechanism of dye destruction in AOPs is based on the formation of a very reactive hydroxyl radical ($^{\bullet}$OH), that, with an oxidation potential of 2.80 V [10], can oxidize a broad range of organic compounds.

Homogeneous advanced oxidation process employing hydrogen peroxide with UV light has been found to be effective in the decolorization and mineralization of dye pollutants [11–15]. In comparison with other AOPs, such as Fenton, Ozone, UV/O_3, UV/TiO_2, etc., the photolysis of hydrogen peroxide shows some advantages such as the complete miscibility of H_2O_2 with water, the stability and commercial availability of hydrogen peroxide, no phase transfer problems and lower investment costs. It can be carried out under ambient conditions and may lead to complete mineralization of organic carbon into CO_2 [16,17]. Unfortunately, the molar absorptivity of H_2O_2 is low in the readily accessible UV region. The absorption spectrum exhibits a slow

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and steady rise from 400 and at 254 nm the molar absorptivity is about 19 l mol^{-1} cm^{-1} [18].

Azo dye decolorization by UV/H_2O_2 process has been studied by numerous authors [19,20]. However, since the UV/H_2O_2 process is an extensive electricity consumer process and electrical energy can represent an important fraction of the operating cost, therefore one can conclude that the optimum operational parameters still need investigating.

Concerning C.I. Acid Orange 7 dye mineralization by UV/H_2O_2 process in a pilot scale photoreactor, there are not to our knowledge many publications available, even if the decolorization of the dye has been studied by several authors.

The aim of the present work was the decolorization and mineralization study of C.I. Acid Orange 7 (AO7) under various conditions in the pilot scale photoreactor and the process electrical energy consumption determination. AO7 was chosen as a model of the hydrosoluble phenylazonaphtol dye due to its resistance to biological degradation and in fact that it is widely used in wool textile dyeing, food and cosmetics [1].

2. Experimental

2.1. Reagents

The 4-(2-hydroxy-1-naphthylazo) benzene sulfonic acid sodium salt, commonly named C.I. Acid Orange 7 (90%) was obtained from Aldrich chemicals. The dye solutions were prepared by dissolving a defined quantity of the dye in deionised water. The characteristics of the dye are as presented in Table 1.

In the aqueous phase, due to a very rapid intermolecular proton transfer, AO7 exists as an azo (AT)–hydrazone (HT) mixture, although the population of HT's is larger than that of AT's [21]. Factors such as solvent play a significant part in determining the tautomeric equilibrium. The hydrazone form is usually more stable [22]. Hydrogen peroxide (30%, w/w) was obtained from Prolabo.

2.2. Photoreactor and methods

The reactor used in this study is a continuous column circulation photo reactor fitted with a 15-W electric power low-pressure mercury lamp (Philips emission at 253.7 nm). The radiant flux of this lamp was determined by means of the chemical actinometer hydrogen peroxide [18]. The incident photon flux was 6.1×10^{-6} Einstein s^{-1}. The unit for the continuous circulation reactor was described in our previous paper [23]. The reservoir of the UV reactor was loaded with 4000 ml of the synthetic reaction mixture. The liquid level in the radiation column was kept constant at 1600 ml. The liquid inside the column was exposed to a UV lamp. The treated wastewater was returned to the reservoir and then left to circulate back to the reactor column at a constant flow rate of 3.5 l min^{-1}.

A Jasco V-530 spectrometer recording the spectra over the 200–1100 nm range was used for determination of AO7 concentration and decolorization kinetics study. Total organic carbon (TOC) of dye solutions was measured by catalytic oxidation followed by IR spectrometry for CO_2 quantification using a Shimadzu TOC-VCPN instrument, equipped with an automatic sample injector. TOC values represent the average of three measurements.

In our recent work [24], we have reported the effect of initial dye and H_2O_2 concentrations on the decolorization of the C.I. AO7 dye by using 7.5 W l^{-1} volumetric UV dosage. The decrease in decolorization rate with increasing initial dye concentration was observed. In addition, the rate of dye decolorization increases with increasing concentrations of H_2O_2 up to a threshold value, above which it declines, exhibiting typical inhibition. Mineralization of dye solution has not been studied. In this work we have investigated the dye decolorization followed with dye mineralization, by applying only 3.75 W l^{-1} UV dosage. The reactions were carried out with three different synthetic wastewaters presented in Table 2.

Table 1
Main characteristics of the C.I. Acid Orange 7 azo dye

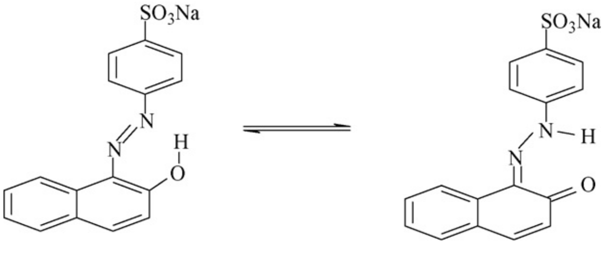
C.I. Acid Orange 7, Acid Orange ll	Name
$HOC_{10}H_6N{=}NC_6H_4SO_3Na$, ($C_{16}H_{11}N_2NaO_4S$)	Formula
350.32 g mol^{-1}	Mol. WT
Yellow powder	Physical state
Soluble (116 g l^{-1})	Solubility in water
483 nm	λ_{max}
19.43×10^3 l mol^{-1} cm^{-1}	$\varepsilon_{\lambda max}$
11.96×10^3 l mol^{-1} cm^{-1}	$\varepsilon_{253.7}$
 (AT) (HT)	Structure

Table 2
The different reaction mixtures studied, total treated volume = 4000 ml

Synthetic wastewater solution	Dye initial concentration $[AO7]_0$ ($mg\,l^{-1}$)	H_2O_2 initial concentration $[H_2O_2]_0$ ($mg\,l^{-1}$)	H_2O_2 relative mass concentration $[H_2O_2]_0/[AO7]_0$
A	30	285	9.5
B	17.5	166.25	9.5
C	17.5	525	30

Solution A has a higher initial dye and H_2O_2 concentrations than solution B, but the ratio of initial mass concentration of H_2O_2 to that of the dye is the same (initial H_2O_2 *relative mass concentration was kept constant*). Solution B and solution C contain the same initial dye concentrations and different initial H_2O_2 dosages. From these reaction mixtures we can verify if the initial dye and H_2O_2 relative mass concentrations have similar effects on the mineralization and on the decolorization reaction kinetics.

2.3. Analysis

Each selected amount of dye was dissolved in deionised water. During the photolysis, sample aliquots were taken from the reactor at regular time intervals. The decolorization of AO7 was monitored by measuring the absorbance at $\lambda = 483$ nm. Total carbon organic was determined by TOC analyzer. Absorption spectra of the dye solutions irradiated by UV light were recorded. It was found that the maximum absorption band intensity varied, depending on the solution concentration. In addition, no new absorption peaks occurred near the original maximum. As a result, we can conclude that intermediate oxidation products do not disturb the absorption bands. The concentration of the residual dye in solution was calculated by Beer Lambert law using the optical density and molar extinction observed at the characteristic wavelength ($\lambda = 483$ nm). The efficiency of color removal and dye mineralization were defined by the following expressions:

$$\text{Decolorization}\,(\%) = \left(1 - \frac{[AO7]}{[AO7]_0}\right) \times 100 \qquad (1)$$

$$\text{Mineralization}\,(\%) = \left(1 - \frac{[TOC]}{[TOC]_0}\right) \times 100 \qquad (2)$$

where [AO7] and [TOC] are dye and TOC concentrations at time *t*, respectively. $[AO7]_0$ and $[TOC]_0$ are dye and TOC initial concentrations, respectively.

3. Results and discussion

3.1. Dye decolorization

Our results show very slow direct photolysis of the dye. When hydrogen peroxide is applied simultaneously with UV irradiation there is a drastic increase in the decolorization reaction rate. Fig. 1 shows the spectral evolution upon photo irradiation for dye solution B at various irradiation times. The spectrum obtained prior to UV irradiation is characterized by two bands in the visible region, corresponding to the (HT) form (483 nm) and (AT) form (430 nm) of dye, which correspond to the n–π* transition of the two forms of the dye. The bands in the ultraviolet region, located at 224 and 310 nm, correspond to π–π* transitions in the benzoic and naphthalene rings of AO7, respectively. We have presented the normalized absorbance at 483 and 224 nm as a function of the irradiation time in Figs. 2 and 3. It was observed that UV irradiation of the aqueous AO7/H_2O_2 mixture causes a decrease in the intensity of the absorption bands of the dye in the visible region with time. These bands disappear after 30–40 min of UV irradiation time, resulting in complete decolorization of the solutions. This is accompanied by a parallel and slower decrease in the intensity of the bands in the UV region

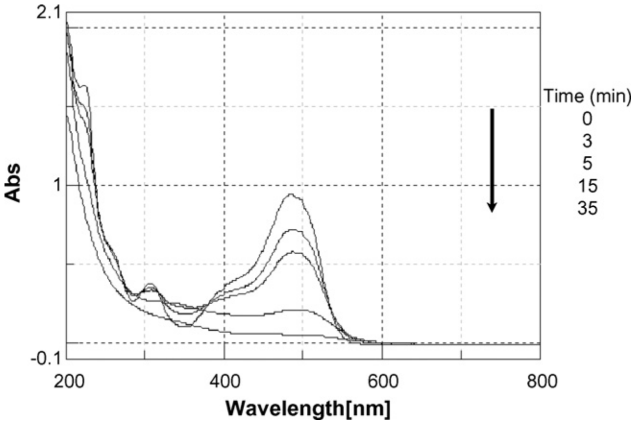


Fig. 1. Spectral evolution upon photo irradiation for different times of radiation in AO7 reaction mixture; $[AO_7]_0 = 17.5\,mg\,l^{-1}$; $[H_2O_2]_0 = 166.25\,mg\,l^{-1}$; $[H_2O_2]_0/[AO_7]_0 = 9.5$.

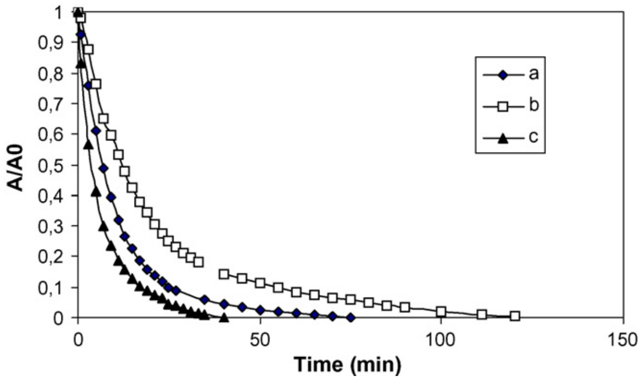


Fig. 2. Normalized absorbance of AO7 solutions at $\lambda = 483$ nm as a function of UV irradiation time. (a) $[AO_7]_0 = 30\,mg\,l^{-1}$; $[H_2O_2]_0 = 285\,mg\,l^{-1}$; $[H_2O_2]_0/[AO_7]_0 = 9.5$. (b) $[AO_7]_0 = 17.5\,mg\,l^{-1}$; $[H_2O_2]_0 = 166.25\,mg\,l^{-1}$; $[H_2O_2]_0/[AO_7]_0 = 9.5$. (c) $[AO_7]_0 = 17.5\,mg\,l^{-1}$; $[H_2O_2]_0 = 525\,mg\,l^{-1}$; $[H_2O_2]_0/[AO_7]_0 = 30$.

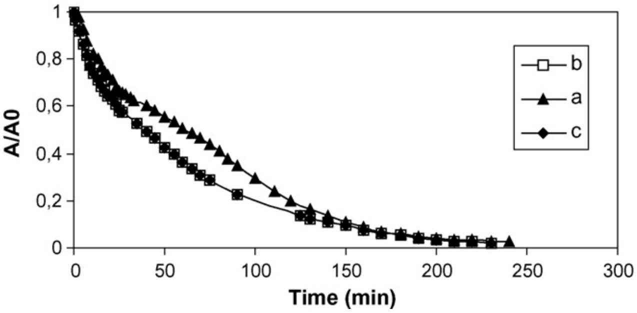


Fig. 3. Normalized absorbance of AO7 solutions at $\lambda = 224$ nm as a function of UV irradiation time. (a) $[AO_7]_0 = 30$ mg l^{-1}; $[H_2O_2]_0 = 285$ mg l^{-1}; $[H_2O_2]_0/[AO_7]_0 = 9.5$. (b) $[AO_7]_0 = 17.5$ mg l^{-1}; $[H_2O_2]_0 = 166.25$ mg l^{-1}; $[H_2O_2]_0/[AO_7]_0 = 9.5$. (c) $[AO_7]_0 = 17.5$ mg l^{-1}; $[H_2O_2]_0 = 525$ mg l^{-1}; $[H_2O_2]_0/[AO_7]_0 = 30$.

located at 224 and 310 nm, indicating total destruction of the benzoic and naphthalene rings after 200 min for three synthetic wastewaters.

Fig. 4 shows the effect of the dye and hydrogen peroxide initial concentrations on the decolorization reaction kinetics. Indeed in the solutions A and B, initial relative concentration of H_2O_2 is the same (=9.5), but solution A contains a higher quantity of dye than solution B. As we can see from this figure, color removal efficiency in the solution B is higher than solution A. We can conclude that the increase of the dye initial concentration cannot be counterbalanced by keeping constant H_2O_2 initial relative concentration. Increasing the dye concentration should logically enhance the probability of collision between AO7 molecules and oxidizing species ($^{\bullet}$OH), leading to an increase in the decolorization rate. However, the molar extinction of AO7 at 253.7 nm is very high (11.96×10^3 l mol^{-1} cm^{-1}), so that a rise in its concentration induces an inert filter effect [24], the solution becomes more and more impermeable to UV irradiation. Hydrogen peroxide can then only be irradiated by smaller portions of UV light. As the rate of photolysis of H_2O_2 directly depends on the fraction of incident light absorbed by H_2O_2 molecules, the $^{\bullet}$OH formation rate slows down and the rate of decolorization of dye decreases. So decolorization rate was more influenced by AO7 initial concentration than hydrogen peroxide. This hypothesis can be verified by comparative study of color removal efficiency of solution B and C containing the same quantity of dye. In the solution C, H_2O_2 initial concentration is nearly three times higher than the solution B, but the decolorization rate was not influenced in the same proportion. In Fig. 5 the logarithmic variations of the dye concentration as a function of the UV irradiation time is illustrated. The dye destruction is a pseudo-first order reaction with respect to dye concentration. For each dye solution, color removal apparent rate constants (k_1) were evaluated using a linear regression of the plot of color degradation with time and presented in Table 3. The values of the correlation coefficients (R^2) confirm the goodness of the assumed kinetics for the UV/H_2O_2 photolytic decolorization reaction of AO7 dye.

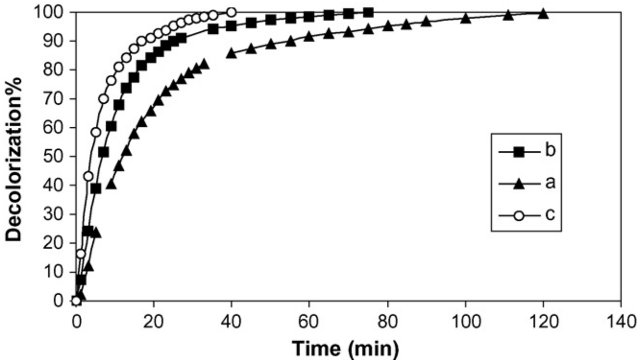


Fig. 4. Decolorization percent of AO7 solutions as a function of UV irradiation time. (a) $[AO_7]_0 = 30$ mg l^{-1}; $[H_2O_2]_0 = 285$ mg l^{-1}; $[H_2O_2]_0/[AO_7]_0 = 9.5$. (b) $[AO_7]_0 = 17.5$ mg l^{-1}; $[H_2O_2]_0 = 166.25$ mg l^{-1}; $[H_2O_2]_0/[AO_7]_0 = 9.5$. (c) $[AO_7]_0 = 17.5$ mg l^{-1}; $[H_2O_2]_0 = 525$ mg l^{-1}; $[H_2O_2]_0/[AO_7]_0 = 30$.

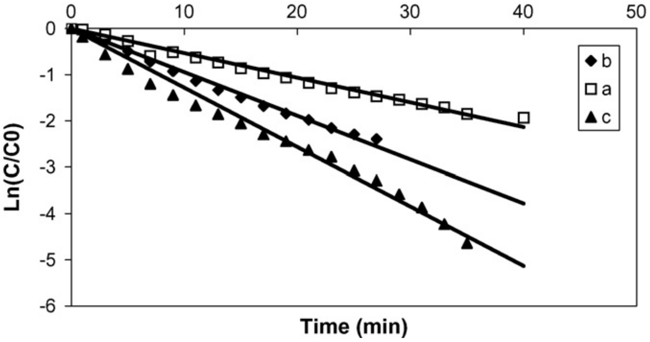


Fig. 5. First order plot of color degradation of AO7 solutions as a function of UV irradiation time. (a) $[AO_7]_0 = 30$ mg l^{-1}; $[H_2O_2]_0 = 285$ mg l^{-1}; $[H_2O_2]_0/[AO_7]_0 = 9.5$. (b) $[AO_7]_0 = 17.5$ mg l^{-1}; $[H_2O_2]_0 = 166.25$ mg l^{-1}; $[H_2O_2]_0/[AO_7]_0 = 9.5$. (c) $[AO_7]_0 = 17.5$ mg l^{-1}; $[H_2O_2]_0 = 525$ mg l^{-1}; $[H_2O_2]_0/[AO_7]_0 = 30$.

3.2. *Total organic carbon disappearance*

It is known that complete decolorization of AO7 does not mean that the dye is completely mineralized in to CO_2 and H_2O. The longer lived reaction intermediates formed may be more toxic than the original dye. Hence, it is necessary to simultaneously investigate the mineralization process. To achieve this goal, TOC removal ratio of the reaction mixture as a function of time under different conditions was measured. The kinetics of total organic carbon disappearance was examined for dye solutions under UV irradiation. As shown in Fig. 6 all three colored solutions followed the same pattern. We observed that, after

Table 3
Characteristics of the three synthetic AO7 solutions, R^2 and k values for decolorization and mineralization reactions

	Solution		
	A	B	C
AO_7 concentration (mg l^{-1})	30	17.5	17.5
$[H_2O_2]_0/[AO_7]_0$ (mass ratio)	9.5	9.5	30
R^2	0.995	0.994	0.977
k_1 (min^{-1})	0.0537	0.0961	0.127
R^2	0.983	0.994	0.984
k_2 (min^{-1})	0.0157	0.0119	0.0253

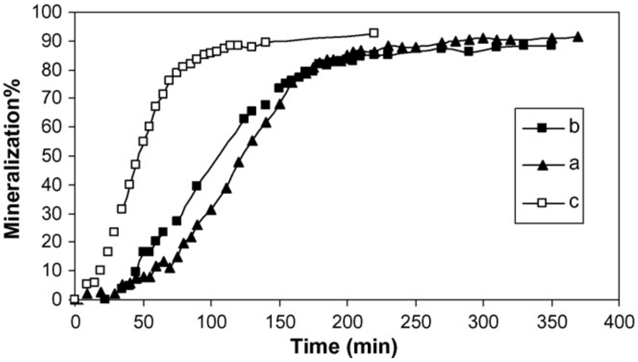


Fig. 6. TOC percent removal of AO7 solutions as a function of UV irradiation time. (a) $[AO7]_0 = 30\ \mathrm{mg\ l^{-1}}$; $[H_2O_2]_0 = 285\ \mathrm{mg\ l^{-1}}$; $[H_2O_2]_0/[AO7]_0 = 9.5$. (b) $[AO7]_0 = 17.5\ \mathrm{mg\ l^{-1}}$; $[H_2O_2]_0 = 166.25\ \mathrm{mg\ l^{-1}}$; $[H_2O_2]_0/[AO7]_0 = 9.5$. (c) $[AO7]_0 = 17.5\ \mathrm{mg\ l^{-1}}$; $[H_2O_2]_0 = 525\ \mathrm{mg\ l^{-1}}$; $[H_2O_2]_0/[AO7]_0 = 30$.

an initial period (decolorization period) of constant or slowly decreasing values, a relatively rapid decrease occurs. During the first 20, 45 and 55 min, about 10% of TOC degradation occurred in solutions C, B and A, respectively, indicating that TOC removal is very limited in the colored solutions. Generally, the final step toward complete mineralization starts only when decolorization is almost complete [11]. Our results clearly reveal that after the decolorization period, for synthetic wastewaters A and B, containing the different initial dye concentrations, TOC complete removal time is nearly similar (about 200 min).

Fig. 6 shows that the TOC removal ratio increases significantly by increasing the initial H_2O_2 dosage (solution C, $[H_2O_2]_0/[AO7]_0 = 30$). After 100 min of UV irradiation time, we can observe about 35, 45 and 90% TOC removal, respectively, in solutions A, B and C. Fig. 7 shows logarithmic variation of TOC in AO7 solutions as a function of UV irradiation time. As we can see from Fig. 8, TOC decay after the decolorization period, follows the apparent first order kinetics verified by linear regression of the $-\ln(\mathrm{TOC})/(\mathrm{TOC})_0 = k_2 \times t$. The similar results have been reported by Colonna et al. [11]. We have presented k_2 values in Table 3. From these values, we can observe that mineralization reaction rate was highly affected by increasing initial H_2O_2 concentration. So initial dye and H_2O_2 relative mass concentrations do not have similar effects on the degradation and on the decolorization reaction kinetics. These reaction rate constants are much lower than those for the decolorization, suggesting that the breakage of the azo bond is the first step of photo catalytic AO7 degradation. Initial $^\bullet$OH attack leads to intermediates which maintain an aromatic structure. Further reactions with $^\bullet$OH lead to smaller organic molecules. The presence of a constant level of TOC in the solution after extended irradiation time suggests that the end products that cannot be completely mineralized to water and CO_2 during that time.

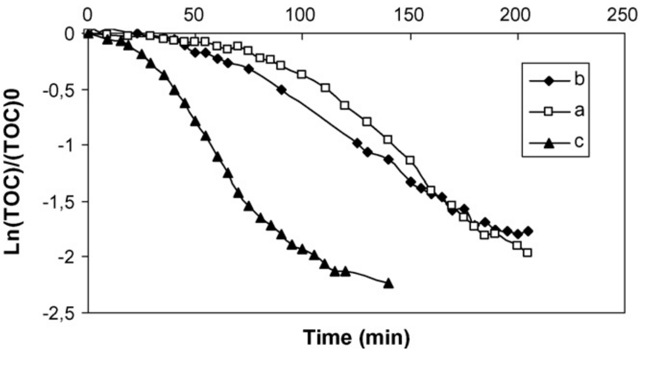


Fig. 7. Logarithmic variation of TOC in AO7 solutions as a function of UV irradiation time. (a) $[AO7]_0 = 30\ \mathrm{mg\ l^{-1}}$; $[H_2O_2]_0 = 285\ \mathrm{mg\ l^{-1}}$; $H_2O_2]_0/[AO7]_0 = 9.5$. (b) $[AO7]_0 = 17.5\ \mathrm{mg\ l^{-1}}$; $[H_2O_2]_0 = 166.25\ \mathrm{m.l^{-1}}$; $[H_2O_2]_0/[AO7]_0 = 9.5$. (c) $[AO7]_0 = 17.5\ \mathrm{mg\ l^{-1}}$; $[H_2O_2]_0 = 525\ \mathrm{mg\ l^{-1}}$; $[H_2O_2]_0/[AO7]_0 = 30$.

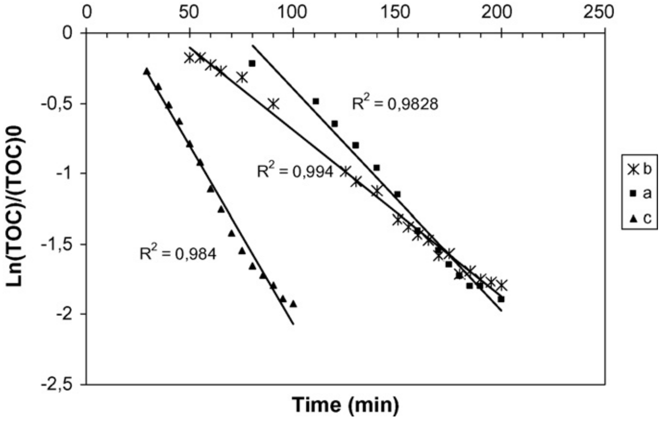
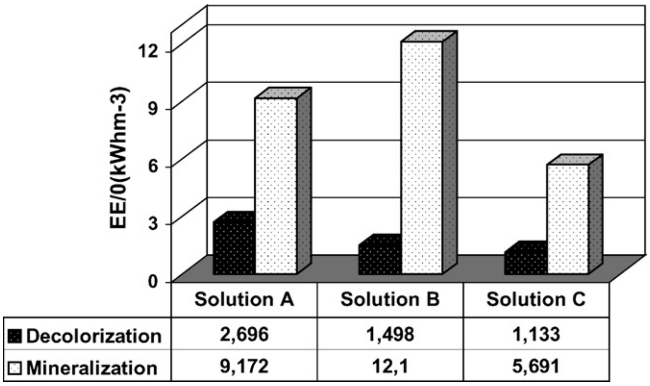


Fig. 8. First order plot of mineralization of AO7 solutions as a function of UV irradiation time after decolorization period. (a) $[AO7]_0 = 30\ \mathrm{mg\ l^{-1}}$; $[H_2O_2]_0 = 285\ \mathrm{mg\ l^{-1}}$; $[H_2O_2]_0/[AO7]_0 = 9.5$. (b) $[AO7]_0 = 17.5\ \mathrm{mg\ l^{-1}}$; $[H_2O_2]_0 = 166.25\ \mathrm{mg\ l^{-1}}$; $[H_2O_2]_0/[AO7]_0 = 9.5$. (c) $[AO7]_0 = 17.5\ \mathrm{mg\ l^{-1}}$; $[H_2O_2]_0 = 525\ \mathrm{mg\ l^{-1}}$; $[H_2O_2]_0/[AO7]_0 = 30$.

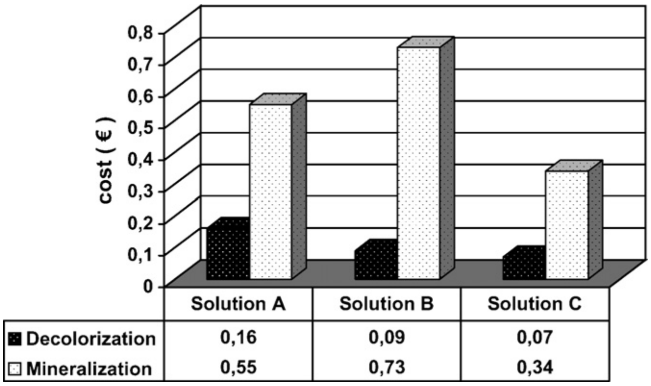
3.3. Evaluation of electrical energy per order

There are a number of important factors in selecting a waste-treatment technology, inducing economics, economy of scale, regulations, effluent quality goals, operation (maintenance, control, safety) and robustness (flexibility to change/upsets). Although these factors are important, economics is often paramount. Since photodegradation of aqueous organic pollutant is an electric-energy-intensive process, and electric energy can represent a major fraction of the operating costs, simple figures-of-merit based on electric energy consumption can be very useful and informative. These figures-of-merit are based on electrical energy consumption within two phenomenological kinetic order regimes: one for high contaminant concentration (electrical energy per mass, EE/M) and one low concentration (electrical energy per order of magnitude per $\mathrm{m^3}$, EE/O). Simple understanding of the overall kinetic behaviour of organic degradation in wastewater (i.e., whether zero or first order reaction) is necessary for describing meaningful electrical efficiencies [25]. In the case of low pollutant concentrations (pseudo-first order reactions), which applies here, the appropriate figure-of-merit is the electrical energy per order (EE/O), defined as the number of kWh of electrical energy required to reduce the concentration of a pollutant by 1 order of magnitude (90%) in $1\ \mathrm{m^3}$ of contaminated water. The EE/O ($\mathrm{kWh\ m^{-3}\ order^{-1}}$) can be calculated



	Solution A	Solution B	Solution C
■ Decolorization	2,696	1,498	1,133
☐ Mineralization	9,172	12,1	5,691

Fig. 9. Number of kWh electrical energy needed to reduce the dye and TOC concentrations by 1 order magnitude (90%) in 1 m^3 of dye solutions. Solution A: $[AO_7]_0 = 30\,mg\,l^{-1}$; $[H_2O_2]_0 = 285\,mg\,l^{-1}$; $[H_2O_2]_0/[AO_7]_0 = 9.5$. Solution B: $[AO_7]_0 = 17.5\,mg\,l^{-1}$; $[H_2O_2]_0 = 166.25\,mg\,l^{-1}$; $[H_2O_2]_0/[AO_7]_0 = 9.5$. Solution C: $[AO_7]_0 = 17.5\,mg\,l^{-1}$; $[H_2O_2]_0 = 525\,mg\,l^{-1}$; $[H_2O_2]_0/[AO_7]_0 = 30$.



	Solution A	Solution B	Solution C
■ Decolorization	0,16	0,09	0,07
☐ Mineralization	0,55	0,73	0,34

Fig. 10. The cost of electrical energy needed to reduce the dye and TOC concentrations by 1 order magnitude (90%) in 1 m^3 of dye solutions. Solution A: $[AO_7]_0 = 30\,mg\,l^{-1}$; $[H_2O_2]_0 = 285\,mg\,l^{-1}$; $[H_2O_2]_0/[AO_7]_0 = 9.5$. Solution B: $[AO_7]_0 = 17.5\,mg\,l^{-1}$; $[H_2O_2]_0 = 166.25\,mg\,l^{-1}$; $[H_2O_2]_0/[AO_7]_0 = 9.5$. Solution C: $[AO_7]_0 = 17.5\,mg\,l^{-1}$; $[H_2O_2]_0 = 525\,mg\,l^{-1}$; $[H_2O_2]_0/[AO_7]_0 = 30$.

from the following equations:

$$\mathrm{EE/O} = \frac{P \times t \times 1000}{V \times 60 \times \log(C_\mathrm{i}/C_\mathrm{f})} \tag{3}$$

$$\ln\left(\frac{C_\mathrm{i}}{C_\mathrm{f}}\right) = k \times t \tag{4}$$

where *P* is the rated power (kW) of the AOP system, *t* the irradiation time (min), *V* the treated wastewater volume (l), C_i and C_f the initial and final pollutant concentrations and *k* is the pseudo-first order rate constant (min^{-1}) for the decay of the pollutant concentration [25,26].From Eqs. (3) and (4), EE/O can be written as follows:

$$\mathrm{EE/O} = \frac{38.4 \times P}{V \times k} \tag{5}$$

Fig. 9 shows the calculated EE/O values for AO7 color removal and mineralization.

This standard figure-of-merit provides a direct link to the electrical efficiency (lower values mean higher efficiency) of an advanced oxidation process. As we can observe, the electrical energy required for solution C ($[AO7] = 17.5\,mg\,l^{-1}$, $[H_2O_2] = 525\,mg\,l^{-1}$) mineralization is less than is needed for the treatment of solution B ($[AO7] = 17.5\,mg\,l^{-1}$, $[H_2O_2] = 166.25\,mg\,l^{-1}$) and solution A ($[AO7] = 30\,mg\,l^{-1}$ $[H_2O_2] = 285\,mg\,l^{-1}$). These results are reasonable because the amount of electrical energy required to bring about a reduction by one order of magnitude in TOC concentration is independent of initial [TOC]. However, EE/O parameters are inversely proportional to fundamental efficiency factors, such as the lamp efficiency, the fraction of the emitted light flux that is absorbed in the wastewater and the quantum yield of generation of active OH radicals. The higher electrical energy requirement in the case of solution A decolorization, can be explained by filter effect of the dye solution ($[AO7] = 30\,mg\,l^{-1}$, the most colored solution).

Finally, it is useful to relate the EE/O values found in this study to treatment costs. For instance, if the treatment objective for C.I. Acid Orange 7 ($[AO7]_0 = 30\,mg\,l^{-1}$) is $3\,mg\,l^{-1}$, this means the total electrical energy required is $2.696\,kWh\,m^{-3}$. If the cost of electricity, in France is $0.06\,€\,(kWh)^{-1}$, the contribution to the decolorization treatment cost from electrical energy will be $0.161\,€\,m^{-3}$ of the wastewater. In addition, there will be the cost factors for the hydrogen peroxide used and for lamp replacement. Fig. 10 shows the color removal and TOC destruction electrical costs for the three synthetic wastewaters studied in this work.

4. Conclusion

It can be concluded that the UV/H_2O_2 process using an annular continuous circulated batch photoreactor using $3.75\,W\,l^{-1}$ volumetric UV dosage, provides good performance in the decolorization and mineralization treatment of C.I. Acid Orange 7 dye in water. The obtained results show the economic benefit of our researches. We observed that after decolorization periods, the degradation of the dye is a pseudo-first order reaction with respect to the dye concentration. The mineralization reaction rate is much slower than the corresponding decolorization reaction rate. Under optimal operational conditions ($[H_2O_2]_0/[AO7]_0 = 30$), nearly 100% decolorization and 95% TOC removal of $17.5\,mg\,l^{-1}$ AO7 dye can be achieved in 25 and 120 min of UV irradiation times, respectively. In the other studied cases in this work, 90% mineralization was obtained in no more than 4 h. The analysis of our results shows that the initial dye and H_2O_2 relative mass concentrations do not have similar effects on the mineralization and on the decolorization process. The electrical energy needed for mineralization process can be notably reduced by using optimal H_2O_2 dosage.

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