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Color removal of Remazol® dyebaths wastewater by UV/H_2O_2 does not decrease TOC, BOD/COD, and toxicity of the effluent

Maraíssa Silva Franco, Eduardo Bessa Azevedo*

Chemistry and Molecular Physics Department, Institute of Chemistry of São Carlos, Universidade de São Paulo (USP), Trabalhador São-Carlense Avenue, 400 – Centro, São Carlos, SP 13560-970, Brazil
Tel. +55 16 3373 9962; Fax: +55 16 3373 9975; email: bessa@iqsc.usp.br

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ABSTRACT

The present paper aimed at treating the dyebath wastewater of a textile industry by the UV/H_2O_2 process, mainly to remove color due to reactive Remazol® dyes (Chemical Oxygen Demand [COD] 600 mg O_2 L^{-1}; Biochemical Oxygen Demand [BOD] 220 mg O_2 L^{-1}; Total Organic Carbon (TOC) 310 mg C L^{-1}). Experimental designs were performed to assess the effects of variables (initial pH, temperature, and initial [H_2O_2]) and optimize treatment conditions. Those were: initial pH = 11, temperature (T) = 50°C, and initial [H_2O_2] = 3.1×10^{-4} mol L^{-1}. The response variables were color removal and residual [H_2O_2]. After two hours of irradiation, color removals of approximately 80 and 75% for UV/H_2O_2 and direct photolysis were respectively achieved. BOD/COD ratios, TOC, and COD analyses showed no significant changes. Acute ecotoxicity tests, using lettuce (*Lactuca sativa*) seeds, showed a slight increase in the ecotoxicity of the treated wastewater, for both processes. So, they are not recommended for treating this kind of wastewater.

Keywords: AOP; UV/H_2O_2; RSM; Dye; Reactive dye; Dyebath

1. Introduction

Wastewaters generated by textile industries are known for their high organic loads, high concentrations of non-biodegradable compounds, and strong color, as approximately 12% of the dyes may be lost during production.

When discarded without proper treatment, the intense color causes disturbances in the aquatic life, besides being a source of aesthetic pollution and eutrophication [1]. According to Banat et al. [2], for some dyes, concentrations less than 1 mgL^{-1} are enough to cause the abovementioned problems.

Dyes also present the problem of being resistant to conventional biological treatment methods, due to their structural complexity. The Biochemical Oxygen Demand to Chemical Oxygen Demand ratio (BOD/COD), which can show the biodegradability of organic compounds, is typically less than 0.1 for dyes [3].

Physical-chemical treatments such as coagulation, flocculation, adsorption on activated carbon, ozonation and others [4], showed better results when compared to biological process. However, many problems occur when using those types of treatments: sludge production, excessive use of chemical reagents, and high costs for the system implementation and maintenance [5]. Moreover, technologies like coagulation,

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*Corresponding author.

flocculation, and adsorption do not destroy the contaminants; they just change them from the aqueous phase to a solid one [6].

Advanced Oxidation Processes (AOPs) are promising alternatives for treating toxic, refractory, and non-biodegradable pollutants. Organic compounds destruction occurs due to transient species, especially the hydroxyl radical ($^{\bullet}OH$). It is known that the oxidation potential of this radical is 2.80 V, lower only than fluorine's (3.03 V) [7].

Besides the possible mineralization of pollutants, AOPs have also fast reaction kinetics and are used as *in situ* pre- or post-treatments (regarding biological treatments).

Another characteristic is the non-selectivity of those processes, which can degrade many kinds of pollutants in the aqueous phase, gas phase, or adsorbed on a solid matrix. However, AOPs are less efficient when hydroxyl radicals scavenging species, such as CH_3COO^-, HCO_3^-, CO_3^{2-}, and Cl^-, are present [8].

One of the most used AOPs for treating textile effluents is UV/H_2O_2. H_2O_2 photolysis generates two hydroxyl radicals per molecule Eq. (1) [9].

$$H_2O_2 \xrightarrow{hv} 2^{\bullet}OH \tag{1}$$

The advantage of the UV/H_2O_2 process when compared to other AOPs is that it generates no sludge, making it more feasible.

Therefore, the present work aimed at treating the dyebath wastewater of a textile industry by the UV/H_2O_2 process, mainly to remove color due to Remazol® dyes present, as the existing biological treatment is quite efficient in removing carbon, but not color. Remazol® dyes are a brand of vinyl sulfone fiber-reactive dyes used on animal fibers (silk and wool) and on cellulose/plant fibers (cotton and hemp) [10]. Experimental design and Response Surface Methodology (RSM) were used to assess the effects of the independent variables: initial pH, temperature, and initial hydrogen peroxide concentration, as well as optimizing treatment conditions.

2. Experimental

2.1. Industrial wastewater

This wastewater is highly variable and complex. Its color changes several times throughout the day, depending on the dyebath being used. Nevertheless, all dyes used are from the Remazol® family. Remazol® dyes contain a sulphatoethyl group ($R–SO_2CH_2CH_2–OSO_3H$), which generates the vinyl sulfone reactive group ($R–SO_2CH=CH_2$) when hydrolyzed in alkaline medium [11]. Those dyes are resistant to acid hydrolysis and hydrogen peroxide bleaching [12]. The wastewater complexity increases due to the large number of auxiliary substances used throughout the dyeing process (several salts, sizing and wetting agents, etc.).

The wastewater was collected at the outlet of the dyebaths, prior to pH adjustment and biological treatment. As the wastewater pH is neutralized by bubbling CO_2, hydrogencarbonate ions are generated, impairing the use of AOPs after pH correction. To obtain a representative sample of this wastewater, ten samples were collected in different days. They were mixed together, thus generating a composite and uniform wastewater. This composite wastewater was acidified with H_2SO_4 ($pH < 2$) and maintained refrigerated to avoid microbial degradation.

Typical parameters of the wastewater are: $pH \cong 11$, $T \cong 50^{\circ}C$, $COD \cong 600\ mg\ O_2\ L^{-1}$, $BOD \cong 220\ mg\ O_2\ L^{-1}$, and Total Organic Carbon $(TOC) \cong 310\ mg\ C\ L^{-1}$.

2.2. Statistical analysis

2.2.1. Experimental design

A major goal in performing a multivariate experiment is evaluating the effect of each variable and potential interactions among them. Experimental designs are chemometric tools for addressing this issue, maximizing information about the system, with a minimum number of experiments.

2.2.2. Full factorial design 2^3

Initially, a 2^3 factorial design generated by Statistica® 11 software was applied to investigate the effects of three independent variables (factors) studied at two different levels (initial pH: 5.0 and 9.0; initial concentration of H_2O_2: 1.2×10^{-4} and 4.9×10^{-4} mol L^{-1}; and temperature: 30 and 50°C), as well as the interactions between them. Those factors were coded according to Eqs. (2–4). Eight different tests were performed in a random way. The dependent variables used to assess the UV/H_2O_2 process efficiency were color removal and residual concentration of hydrogen peroxide.

$$x_1 = \frac{pH - 7.0}{2} \tag{2}$$

$$x_2 = \frac{[H_2O_2] - 3.05 \times 10^{-4}}{1.85 \times 10^{-4}} \quad (3)$$

$$x_2 = \frac{T - 40}{10} \quad (4)$$

2.2.3. Composite central design (CCD)

Next, according to the factorial design results, a CCD was performed around the optimal region. The CCD was chosen because it can account for nonlinearities of the system. New levels were used for the factors: initial pH (9.0 and 11.0) and initial $[H_2O_2]$ (3.1×10^{-4} and 6.7×10^{-4} mol L^{-1}). Temperature levels remained unchanged (30 and 50°C). Those factors were coded according to Eqs. (5) and (6). All variables were statistically significant for the optimization process, according to Statistica® 11 software.

$$x_4 = \frac{\text{pH} - 10.0}{1} \quad (5)$$

$$x_5 = \frac{[H_2O_2] - 4.9 \times 10^{-4}}{1.8 \times 10^{-4}} \quad (6)$$

Twenty experiments were performed for three variables at two levels. The following equation determines the total number of experiments: $2^n(2^3 = 8\,\text{factorial points}) + 2n(2 \times 3 = 6\ \text{axial points}) +$ 6 (replicates of the central point) [13].

According to the methodology described by Neto et al. [14], an empirical model was obtained describing the effects of the reaction parameters. Based on the determination coefficient (R^2) and the analysis of variance (ANOVA), the best treatment conditions were estimated.

2.3. Reactor

The experiments were performed in an irradiation chamber in which a medium-pressure mercury-vapor lamp (Philips HPL-N, 250 W, without the outer bulb, was placed 15 cm above the wastewater surface, contained by a Pyrex® cylindrical reactor, open at the top (Fig. 1). The emission spectrum of the lamp, measured with a StellarNet EPP2000C spectroradiometer at a distance of 15 cm, is shown in Fig. 2. The effective volume used was 50 mL (reactor total volume: 250 mL), with magnetic stirring of 450 rpm. The wastewater temperature was controlled by a thermostatic bath and the chamber one by coolers. The chamber also had an air pump with a maximum flow rate of 100 L h^{-1}, bubbling the reactor volume.

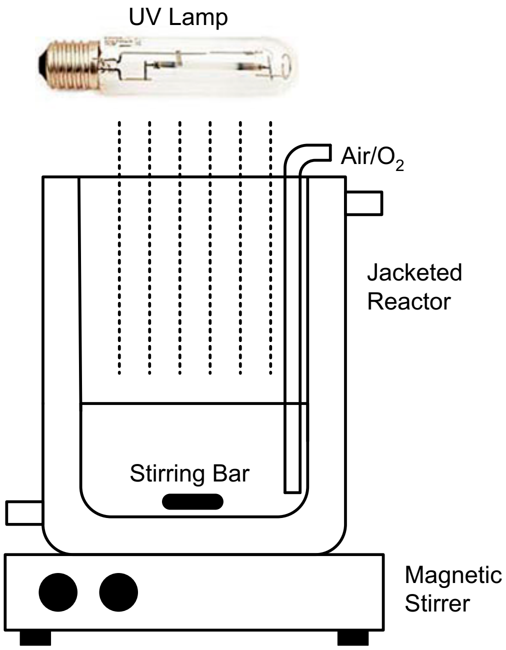

Fig. 1. Reactor scheme.

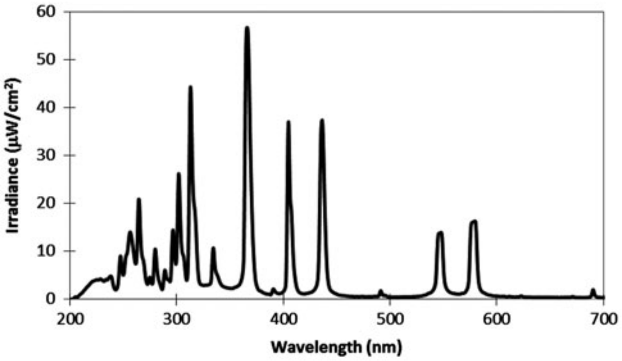

Fig. 2. Emission spectrum of the medium-pressure mercury-vapor lamp used.

2.4. Analyses

Color removal was spectrophotometrically monitored in the visible region (400–700 nm), using a Varian Cary Win UV Scan spectrophotometer. The obtained spectra were numerically integrated and the respective areas used as an indirect measurement of color. All spectra were obtained at pH 10, using H_2SO_4 and NaOH to adjust pH.

Residual hydrogen peroxide concentration was determined using the ammonium vanadate spectrophotometric method [15]. It is based on the red-orange peroxovanadium cation formation when H_2O_2 reacts with the metavanadate ion. That cation was monitored at 457 nm, in the same spectrophotometer abovementioned.

The degradation kinetic constant was estimated by adjusting a pseudo-first-order model to the experimental data using the least squares method.

COD, BOD, and TOC were determined according to standard protocols [16]. TOC analyses were performed in a Shimadzu Vcph TOC Analyzer.

To determine the ecotoxicity of the wastewater after treatment, ecotoxicological tests using lettuce (*Lactuca sativa*) seeds as the test-organism were performed. The Germination Index (GI), calculated by Eq. (7), was the response variable, in which G is the number of germinated seeds, L is their hypocotyl length; G_0 and L_0 are respectively, the number of germinated seeds and their hypocotyl length in the control experiment. The hypocotyl is the stem of a germinating seedling, found below the cotyledons (seed leaves) and above the radicle (root).

$$\mathrm{GI}\ (\%) = \frac{G \times L}{G_0 \times L_0} \times 100 \tag{7}$$

Those tests were performed in quintuplicate according to the protocols proposed by Ortega et al. [17] and Rossi and Beltrami [18]; the EC_{50} after 120 h, was calculated using the adjusted Spearman-Karber method [19].

3. Results and discussion

3.1. Determination of variables effects and best treatment conditions

According to the initial 2^3 factorial design (Table 1), one can observe that the highest color removal obtained corresponds to the lower temperature (30°C), higher initial $[H_2O_2]$ (4.9×10^{-4} mol L^{-1}), and higher initial pH (9.0)—run 4. In those experiments, the highest residual $[H_2O_2]$ was 6.5 mg L^{-1}.

There is a trend of increasing color removal when the temperature decreases, the initial concentration of H_2O_2 increases and the pH increases also.

Following this pattern, the factorial design was extended around the point with the highest color removal, resulting in new levels for the three variables (Table 1).

The new point with the highest color removal (%)—run 14—was made the central point of a CCD. Although temperature at this point was 30°C, a temperature of 40°C was chosen at the center point, otherwise some experiments would be performed at temperatures below the ambient one, which is not feasible for industrial applications.

Table 2 shows the CCD experiments and results for the response variables color removal and residual concentration of hydrogen peroxide.

From Table 2, it was possible to develop a mathematical model describing the behavior of the studied process. The polynomial equation, presented in Eq. (8), was estimated by Statistica® 11 software. $\hat{Y}$ refers to the percentage of color removal and the variables x_1, x_2, and x_3 to the codified independent variables: initial pH, temperature, and initial $[H_2O_2]$, respectively. It can be observed that the polynomial comprises five statistically significant parameters (95% confidence limits).

Table 1
Initial 2^3 factorial design

	Runs	Uncoded (coded) factors			Color removal (%)
		pH (x_1)	$[H_2O_2]$ (x_2)	T (x_3)	
Initial	1	5.0 (–1)	1.2 (–1)	30 (–1)	19
	2	9.0 (+1)	1.2 (–1)	30 (–1)	28
	3	5.0 (–1)	4.9 (+1)	30 (–1)	30
	4	9.0 (+1)	4.9 (+1)	30 (–1)	40
	5	5.0 (–1)	1.2 (–1)	50 (+1)	8
	6	9.0 (+1)	1.2 (–1)	50 (+1)	0
	7	5.0 (–1)	4.9 (+1)	50 (+1)	1
	8	9.0 (+1)	4.9 (+1)	50 (+1)	0
Extended	9	9.0 (+1)	3.1 (0)	30 (–1)	36
	10	7.0 (0)	4.9 (+1)	30 (–1)	33
	11	9.0 (+1)	4.9 (+1)	40 (0)	35
	12	9.0 (+1)	6.8 (+2)	30 (–1)	43
	13	9.0 (+1)	4.9 (+1)	20 (–2)	42
	14	11.0 (+2)	4.9 (+1)	30 (–1)	60

Note: $[H_2O_2]$ = hydrogen peroxide concentration ($\times 10^{-4}$ mol L^{-1}); T = temperature (°C).

Table 2
Central composite design with the results obtained for the response variables color removal and residual [H_2O_2]

Runs	Uncoded (coded) factors			Color removal (%)	Residual [H_2O_2] (mg L^{-1})
	pH (x_4)	[H_2O_2] (x_5)	T (x_3)		
1	9.0 (–1)	3.1 (–1)	30 (–1)	29	1.2
2	9.0 (–1)	3.1 (–1)	50 (+1)	58	7.1
3	9.0 (–1)	6.7 (+1)	30 (–1)	49	nd
4	9.0 (–1)	6.7 (+1)	50 (+1)	46	5.8
5	11.0 (+1)	3.1 (–1)	30 (–1)	72	nd
6	11.0 (+1)	3.1 (–1)	50 (+1)	75	nd
7	11.0 (+1)	6.7 (+1)	30 (–1)	55	11.3
8	11.0 (+1)	6.7 (+1)	50 (+1)	78	0.5
9	8.3 (–1.682)	4.9 (0)	40 (0)	39	nd
10	11.7 (+1.682)	4.9 (0)	40 (0)	77	1.8
11	10.0 (0)	1.9 (–1.682)	40 (0)	55	nd
12	10.0 (0)	7.9 (+1.682)	40 (0)	62	4.8
13	10.0 (0)	4.9 (0)	23 (–1.682)	44	5.3
14	10.0 (0)	4.9 (0)	57 (+1.682)	66	nd
15	10.0 (0)	4.9 (0)	40 (0)	43	6.1
16	10.0 (0)	4.9 (0)	40 (0)	49	4.4
17	10.0 (0)	4.9 (0)	40 (0)	45	4.3
18	10.0 (0)	4.9 (0)	40 (0)	51	4.7
19	10.0 (0)	4.9 (0)	40 (0)	44	7.2
20	10.0 (0)	4.9 (0)	40 (0)	44	6.9

Note: [H_2O_2]—hydrogen peroxide concentration (× 10^{-4} mol L^{-1}); T—temperature (℃); nd—not detected.

$$\hat{Y} = 48.5 \pm 4.82 + 11.9x_1 \pm 3.76 + 6.62x_2 \pm 3.76 + 3.9 \pm 3.654x_1^2 + 4.19x_3^2 \pm 3.65 \quad (8)$$

The plot of residuals against experimental data showed no perceivable structure. This polynomial was responsible for explaining 82% (R^2) of the variance.

The same procedure could have been adopted for the development of a model for the response variable: residual concentration of hydrogen peroxide. However, increasing that variable was not a choice.

Ledakowicz and Gonera state that H_2O_2 is the most detrimental oxidant to activated sludge bacteria and should be used in very low concentrations [20]. Although those bacteria could be adapted to hydrogen peroxide, as the existing biological reactor is effective for removing carbon, [H_2O_2] was kept low so that no adaptation was needed.

Prior results (not shown here) indicated that if [H_2O_2] was below 10 mg L^{-1}, no significant inhibition occurred. By observing Table 2, one can see that the response surface would lie below that limit, except for the region around run seven, which is slightly greater. Therefore, there was no need for developing another model.

The factorial design and the CCD performed have shown a tendency towards increasing color removal when x_1 and x_2 are high and x_3 is small. Then, the typical pH and temperature of the wastewater ($x_1 = x_2 = +1$) and a somewhat small concentration of hydrogen peroxide ($x_3 = –1$) were chosen. Those would decrease treatment costs and give a theoretical color removal of approximately 75%.

3.2. Kinetic study

From Fig. 3, one can observe an interesting finding: the degradation performance of the UV/H_2O_2 process was statistically equal to that of direct photolysis (experiments performed without the addition of H_2O_2). Probably, better results could have been achieved with higher hydrogen peroxide concentrations. However, increased hydrogen peroxide concentrations would impair the biological treatment that follows.

A pseudo-first-order kinetic model was adjusted to the obtained data. A rate constant (k) equals to $(1.4 \pm 0.18) \times 10^{-2}$ min^{-1} and $R^2 = 0.982$ was estimated.

3.3. Wastewater biodegradability

No statistically significant changes were observed in COD and BOD during treatment time, both for the

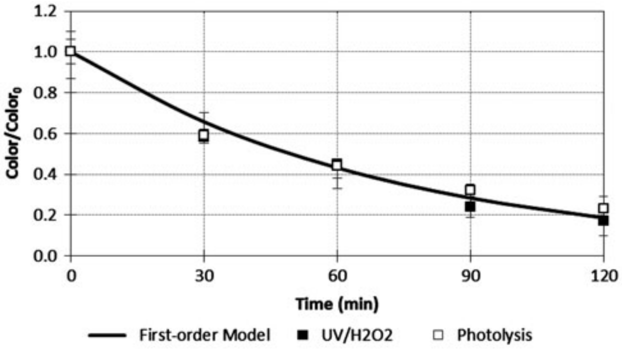

Fig. 3. Color removal by UV/H_2O_2 and photolysis over 120 min at pH 11 and 50°C. Line represents the first-order model fitted to kinetic data.

AOP and for direct photolysis. The BOD/COD ratios were 0.33 and 0.36 for UV/H_2O_2 and photolysis, respectively, in 120 min.

Both values did not significantly differ from the corresponding BOD/COD ratio for the initial wastewater (0.37), indicating that there was little improvement in the biodegradability of the treated wastewater.

According to Talinli and Anderson [21], 1.0 mg of H_2O_2 corresponds to 1.02 mg O_2 L^{-1}. Due to the low concentration of hydrogen peroxide remaining after 120 min of treatment, when compared to the high values for COD (approximately 600 mg O_2 L^{-1} for the initial effluent and 550 mg O_2 L^{-1} after 120 min of treatment), the interference caused by H_2O_2 in the COD analysis was negligible.

3.4. Mineralization

The same behavior also occurred with TOC analyses. In other words, no statistically significant differences between UV/H_2O_2 and photolytic treatments were observed.

These results, when compared to the somewhat high rate of decolorization, can be explained as follows: breaking the bonds of the chromophore groups is enough to remove color; the rest of the molecules probably remained intact, thus resulting in small changes in the values of COD and TOC.

Noteworthy also is the presence of the auxiliary agents, in higher concentrations than the dyes, certainly making the degradation process more difficult.

3.5. Wastewater ecotoxicity

The wastewater treated by the UV/H_2O_2 process presented an EC_{50} (%) of $39.92^{+3.77}_{-3.43}$, pretty much the same value found for the wastewater treated by direct photolysis only, EC_{50} (%) of $39.11^{+4.26}_{-4.19}$. Those values, when compared to the EC_{50} (%) of the raw wastewater of $49.52^{+5.46}_{-4.92}$, show that there was a slight increase in the wastewater ecotoxicity, probably due to the oxidation products formed during the degradation processes.

That information is extremely important. One should not just worry about how to degrade a particular pollutant, but also with the quality of the treated wastewater, mainly regarding ecotoxicity. This helps in deciding among treatment processes, both if a biological treatment should follow or environmental impacts on ecosystems are of concern.

3.6. Comparison with other studies

It is a particular difficult task to compare our results with others already published. This is so for many reasons: (a) experimental conditions are very different; (b) most studies published deal with individual dyes, not wastewaters [9,22,23]; (c) among the very few papers dealing with real wastewaters, none of them deals with dyebath wastewaters [6,24–28]; and (d) as a consequence of treating dyebath wastewaters, the concentration of dyes and auxiliary substances is quite high.

Probably due to those reasons, our findings differ from the existing literature: (a) optimal conditions were found in an alkaline pH range; (b) no statistically significant changes were detected in COD, BOD, and TOC analyses; and (c) direct photolysis and UV/H_2O_2 process presented similar results.

In fact, the initial hydrogen peroxide concentration showed to have the smallest effect on the color removal process. That effect also depends largely on the dye structure, as pointed out by the results of Chen et al. [29], who studied Remazol Black 5 and Remazol Brilliant Orange 3R.

Finally, none of those works showed results for residual [H_2O_2] and ecotoxicity of the solution/wastewater. Those are very important because many wastewaters like this one need an additional treatment, for example a biological one, for carbon removal purposes.

4. Conclusion

The UV/H_2O_2 process had a good performance in removing color from the textile wastewater tested, achieving approximately 80% of color removal in 120 min. Optimized conditions were: pH 11, temperature 50°C, and initial [H_2O_2] of 3.1×10^{-4} mol L^{-1}. It is worthwhile mentioning that those conditions of pH and temperature match the wastewater ones at the dyehouse outlet. Therefore, no corrections would be necessary prior to the tested treatment.

However, the wastewater direct photolysis (same conditions but without adding hydrogen peroxide), showed a very similar behavior to that found with the UV/H_2O_2 process, with approximately 75% of color removal in 120 min.

From these results, it could be concluded that only photolysis is enough for achieving good rates of color removal with this kind of wastewater. However, both treatments, UV/H_2O_2 and direct photolysis, caused a slight increase in the wastewater ecotoxicity, probably due to toxic products formation. This fact would have a negative impact in the biological treatment that follows.

Although the aim of this study was color removal, it must be also observed that both processes did not significantly removed BOD, COD, and TOC.

Therefore, it is not recommended the use of UV/H_2O_2 (at least with the employed hydrogen peroxide concentrations) or direct photolysis for treating Remazol® dyebaths wastewater for color removal purposes.

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List of symbols

ANOVA — analysis of variance
AOP — advanced oxidation processes
BOD — biochemical oxygen demand (mg O_2 L^{-1})
CCD — central composite design
COD — chemical oxygen demand (mg O_2 L^{-1})
EC_{50} — half maximal effective concentration (%)
G — number of germinated seeds
G_0 — number of germinated seeds in the control experiment
GI — germination index (%)
k — rate constant (min^{-1})
L — hypocotyls length (mm)
L_0 — hypocotyls length in the control experiment (mm)
R^2 — determination coefficient
RSM — response surface methodology
TOC — total organic carbon (mg C L^{-1})
UV — ultraviolet

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