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Removal of Azo Dye Acid Red 88 by Fenton-Based Processes Optimized by Response Surface Methodology Box-Behnken Design †

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Abstract: Acid Red 88 (AR88) is an azo dye highly used in the textile industry. This industry generates high volumes of wastewater with recalcitrant properties that can persist in nature for many years. This work intends to use a statistical model to better predict and understand the influence of different operational conditions. A Box-Behnken response surface methodology (RSM) was used, in which variables (H_2O_2, Fe^{2+}, and radiation intensity) were changed. At the same time, the RSM model allowed the assessment of several advanced oxidation processes (AOPs). The results exhibited the photo-Fenton process as the most efficient, and the best operational conditions ([AR88] = 0.125 mM, pH = 3.0, [H_2O_2] = 7.9 mM, [Fe^{2+}] = 0.22 mM, time = 30 min) were used in four different reactors (UV-C, UV-A, ultrasound, and solar). US reactors achieved high AR88 removal (98.2%, 50 min), similar to UV-C and UV-A (97.8 and 98.2%, respectively, 60 min). A solar reactor is concluded to be the most feasible choice, with 98.4% AR88 removal after 25 min.

Keywords: Box-Behnken model; solar radiation; ultrasound; UV-C radiation; UV-A radiation

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1. Introduction

Acid Red 88 (AR88) is a textile dye used in fabrication sectors like leather, cosmetics, textiles, food treatment, pharmaceuticals, printing, etc. [1]. Due to the washing of printed textile products, it generates extensive wastewater volumes filled with different types of dyes, causing waste (280,000 tons of dyes/year) [2]. When disposed of without proper treatment in water streams, dyes are stable to light. As oxidizing agents, the waste dyes discharged in wastewater disrupt light transmission in water bodies, inhibiting the photosynthetic activity of aquabiota [3].

Advanced oxidation processes (AOPs) were accepted as successful, feasible treatments for contaminant elimination [4,5]. They are based on hydroxyl radical ($HO^{\bullet}$) production, are non-selective, and are greatly reactive, with an E° of 2.80 V, degrading organic contaminants that are considered to be recalcitrant [6]. Among the AOPs, it can be highlighted ozonation, direct UV, UV/H_2O_2, UV/H_2O_2/O_3, Fenton (H_2O_2/Fe^{2+}), and photo-Fenton (UV/H_2O_2/Fe^{2+}) [7,8]. In photo-Fenton processes, different UV sources can be applied to treat wastewater, such as UV-C [9], UV-A [10,11], and solar [12]. In recent years, ultrasonic radiation has been shown to be an efficient alternative to conventional radiation sources. Thus, the aim and novelty of this work were to create a statistical model that could be applied to different reactors to treat textile wastewater.

2. Material and Methods

2.1. Reagents

Acid Red 88 ($C_{20}H_{13}N_2NaO_4S$), iron (II) sulfate heptahydrate, hydrogen peroxide (H_2O_2 30% *w/w*), sodium hydroxide, and sulfuric acid were supplied by José Manuel Gomes dos Santos, Portugal. Solutions were groomed with distilled water.

2.2. Fenton-Based Processes (FBPs) Setup

FBPs were performed in a reactor with a capacity of 250 mL, and all its internal surfaces were formed by mirrors. As radiation sources, it employed (a) UV-A LEDs (12 Indium Gallium Nitride lamps, λ_{max} = 365 nm, 32.7 W m^{-2} power); (b) a UV-C low-pressure mercury vapor lamp (λ_{max} = 253.7 nm, Heraeus, Hanau, Germany); (c) an ultrasonic processor with 500 W power (Vibracell, Church Hill Rd., Newtown, CT, USA); (d) solar radiation, employing a silver-coated panel to reflect the sun light. To optimize the Fenton-based processes, an RSM Box-Behnken design was employed in a solution with 0.125 mM AR88, pH 3.0, and a time of 30 min. Three autonomous variables were used in this study (Table 1): H_2O_2 concentration (X_1), Fe^{2+} concentration (X_2), and UV-A radiation intensity (X_3).

Table 1. Symbols and coded factor levels of variables.

Parameters	Code	Levels		
		−1	**0**	**1**
$[H_2O_2]$ mM	X_1	0	4	8
$[Fe^{2+}]$ mM	X_2	0	0.15	0.30
I_{UV} W m^{-2}	X_3	0	18.3	32.7

To determine the concentration of AR88 removed, a calibration curve was obtained by varying different AR88 concentrations (0, 10, 50, 100, 150, 200, 250, and 300 mg/L). AR88 concentration was determined by a calibration curve (λ_{max} = 505 nm). The removal percentage of AR88 was determined by Equation (1), where $[AR88]_0$ and $[AR88]_t$ are concentrations of AR88 at time 0 and t, respectively:

$$\text{Removal } (\%) = \frac{[AR88]_0 - [AR88]_t}{[AR88]_0} \times 100 \quad (1)$$

Furthermore, 2 mL of dye solution was retreated at regular intervals and analyzed in the UV-vis scanning spectrum at 200–800 nm (Genesis, Tokyo, Japan). All the experiments were performed in triplicate, and statistical analysis was performed using Minitab Statistical Software version 21.1.0 (State College, PA, USA).

3. Results and Discussion

3.1. Response Surface Methodology—Box-Behnken Design

The AR88 degradation was optimized by the performance of a Box-Behnken design with three independent variables. Table 2 shows the observed and predicted values of AR88 concentration after each experiment.

Table 2. Box-Behnken design: operational variables consequence on AR88 removal.

Experiment	Coded Level			AR88 Removal (%)	
	X_1	X_2	X_3	**Observed**	**Predicted**
F1	0	0.30	18.3	61.2	56.8
F2	4	0.15	18.3	96.3	96.3
F3	8	0.15	0.0	84.1	81.6
F4	4	0.15	18.3	96.3	96.3
F5	0	0.15	32.7	57.3	59.8

Table 2. *Cont.*

Experiment	Coded Level			AR88 Removal (%)	
	X_1	X_2	X_3	Observed	Predicted
F6	4	0.15	18.3	96.3	96.3
F7	0	0.00	18.3	0.0	0.0
F8	4	0.00	32.7	0.0	8.1
F9	4	0.00	0.0	0.0	0.0
F10	4	0.30	32.7	91.7	93.6
F11	8	0.00	18.3	0.0	4.4
F12	0	0.15	0.0	28.2	40.7
F13	8	0.15	32.7	96.3	83.8
F14	4	0.30	0.0	90.5	82.4
F15	8	0.30	18.3	96.0	100.0

Intercept, linear, quadratic, and interaction regression coefficients were determined (least squares method) by analysis of variance (ANOVA) (Table 3). The models did not display a significant lack of fit ($p > 0.05$); thus, these statistical parameters designated well-fitting models for the described variables.

Table 3. Analogous F-values and *p*-values for tabbed responses for each coefficient. n.s.: Non-significant. Significant at * $p < 0.05$ and *** $p < 0.001$.

Variable	X_1	X_2	X_3	X_1X_1	X_1X_2	X_1X_3	X_2X_2	X_2X_3	X_3X_3
F-value	14.39	98.54	1.55	8.22	2.07	0.49	38.36	0.00	3.51
p-value	*	***	n.s.	n.s.	n.s.	n.s.	*	n.s.	n.s.

The regression coefficient (R^2) was 0.970, meaning that the model meets AR88 removal appropriately. The response surface plots gathered supported the contribution to the optimal AR88 removal condition for each variable evaluated and were confirmed by the value of the coefficient of each factor obtained in the polynomial equation (Equation (2)).

$$Y = -31.7 + 11.95\,X_1 + 742\,X_2 + 65.6\,X_3 - 1.127\,X_1 \times X_1 - 1732\,X_2 \times X_2 - 47.1\,X_3 \times X_3 + 14.5\,X_1 \times X_2 - 2.11\,X_1 \times X_3 + 4.0\,X_2 \times X_3 \quad (2)$$

Based on the RSM, different AOPs were studied under the operational conditions [AR88] = 0.125 mM, pH = 3.0, $[H_2O_2]$ = 4 mM, $[Fe^{2+}]$ = 0.30 mM, radiation UV-A 32.7 W m^{-2}, time = 30 min. Results obtained showed an AR88 removal of <0.5% with enforcement of H_2O_2, UV-A, and H_2O_2 + UV-A (Figure 1a). These AOPs were not able to generate hydroxyl radicals ($HO^{\bullet}$) to degrade the AR88, which agrees with Do et al. [13], who showed only 4% removal of methylene blue with H_2O_2 and visible light. With the application of UV-A + Fe^{2+}, the action of the UV wavelength improved, and AR88 removal achieved 61.2%. The highest removals achieved with the Fenton and photo-Fenton processes reached an AR88 removal of 90.5 and 91.7%, respectively. This removal is due to the $HO^{\bullet}$ production of H_2O_2 with the Fe^{2+} reaction. The higher AR88 color removal observed in the photo-Fenton process suggests that a certain regeneration of Fe^{2+} took place, increasing the removal rate [14,15]. Throughout the use of the statistical program, the best operational conditions were obtained: pH = 3.0, $[H_2O_2]$ = 7.9 mM, $[Fe^{2+}]$ = 0.22 mM, radiation UV-A = 32.7 W m^{-2}, and time = 30 min.

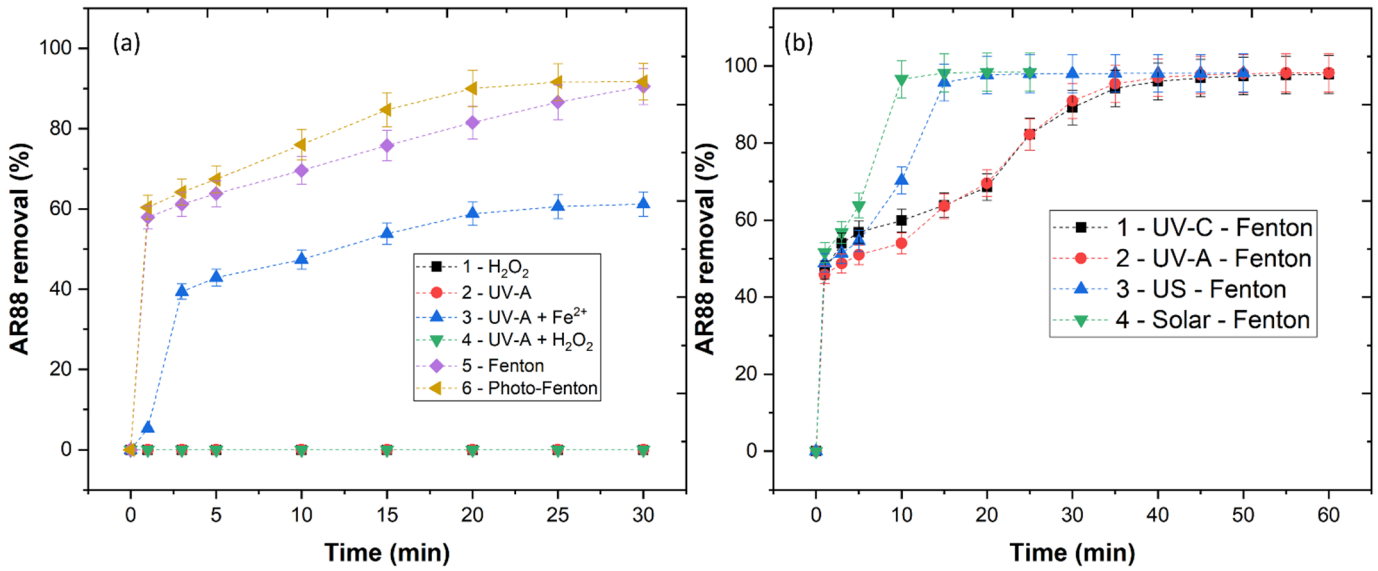

Figure 1. (**a**) AOPs variation in AR88 color removal ([AR88] = 0.125 mM, pH = 3.0, [H_2O_2] = 4 mM, [Fe^{2+}] = 0.30 mM, radiation UV-A 32.7 W m^{-2}, time = 30 min); (**b**) variation of radiation sources ([AR88] = 0.125 mM, pH = 3.0, [H_2O_2] = 7.9 mM, [Fe^{2+}] = 0.224 mM, time = 30 min).

3.2. Variation of Radiation Sources

In order to increase the AR88 removal rate, several radiation sources (UV-C, UV-A, ultrasound and solar) were applied in combination with the best operational conditions obtained in Section 3.1 to a solution with an AR88 concentration of 0.250 mM (Figure 1b). Results showed color removal of 97.8% (60 min), 98.2% (60 min), 98.2% (50 min), and 98.4% (25 min), respectively, for UV-C-Fenton, UV-A-Fenton, US-Fenton, and solar-Fenton. They agree with Teixeira et al. [16], who recognized elevated removal of acid red 88 with the application of UV-A radiation.

4. Conclusions

An RSM statistical model can be useful to optimize the conditions of AR88 color removal by Fenton-based processes. The employment of UV radiation enhances AR88 removal from aqueous solutions. Finally, it is concluded that solar-Fenton is the most efficient, environmentally friendly, and economic process to remove the AR88.

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