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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: The 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 photo-Fenton process as 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 4 different reactors (UV-C, UV-A, ultrasound and solar). US reactors achieved high AR88 removal (98.2%, 50 min) similar to UV-C, UV-A (97.8 and 98.2% respectively, 60 min). 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 by fabrication sector like leather, cosmetic, textile, food treatment, pharmaceutical, printing, etc [1]. Due to printed textile products washing, it is generated extensive wastewater volumes filled with types of dyes, causing waste (280 000 tons of dyes/ year) [2]. When disposed without proper treatment in water streams, dyes are stable to light, oxidizing agents, the waste dyes discharged in wastewater disrupt with light transmission in water bodies, inhibiting the photosynthetic activity of aqua biota [3].

Advanced oxidation processes (AOPs) were accepted as successful, feasible treatments for contaminant elimination [4,5]. They are based in hydroxyl radicals ($HO^{\bullet}$) production, are non-selective and greatly reactive, with E° = 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+}), photo-Fenton (UV/H_2O_2/Fe^{2+}) [7,8]. In photo-Fenton processes, different UV sources can be applied to treat wastewaters, such as UV-C [9], UV-A [10,11] and solar [12]. In recent years, ultrasonic radiation has been shown as an efficient alternative to replace conventional radiation sources, thus aim and novelty of this work was created 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 sulphuric 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 reactor with capacity for 250 mL and all its internal surfaces are formed by mirrors. As radiation sources, it were 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) a ultrasonic processor with 500 W power (Vibracell, USA); (d) solar radiation, employing a silver coated panel to reflect the sun light. To optimize the Fenton-based processes, a RSM Box-Behnken design was employed to a solution with 0.125 mM AR88, pH 3.0, time = 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 variation of different AR88 concentrations (0, 10, 50, 100, 150, 200, 250 and 300 mg/L). AR88 concentration was determined by 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:

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

2 mL of dye solution was retreated at regular intervals and analyzed in UV–Vis scanning spectrum 200–800 nm (Tokyo, Japan). All the experiments were performed in triplicate, and statistical analysis was performed using Minitab Statistical Software 2018 (State College, PA, USA).

3. Results and discussion

3.1. Response Surface Methodology – Box-Behnken design

The AR88 degradation was optimized by performance of a Box-Behnken design with three independent variables. In Table 2, is shown 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
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 square method), by analysis of variance (ANOVA) (Table 3). The models did not display significant lack of fit ($P > 0.05$), thus, these statistical parameters designated well-fitting models for 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 model meets AR88 removal appropriately. The response surface plots gathered supported the contribution to AR88 removal optimal condition for of each variable evaluated and were confirmed by value of coefficient of each factor obtained in polynomial equation (Equation (2).

$$Y = -31{,}7 + 11{,}95\,X_1 + 742\,X_2 + 65{,}6\,X_3 - 1{,}127\,X_1{*}X_1 - 1732\,X_2{*}X_2 - 47{,}1\,X_3{*}X_3 + 14{,}5\,X_1{*}X_2 - 2{,}11\,X_1{*}X_3 + 4{,}0\,X_2{*}X_3 \quad (2)$$

Based in 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, H_2O_2 + UV-A (Figure 1(a)). 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 application of UV-A + Fe^{2+}, it was improved the action of the UV wavelength and the AR88 removal achieved 61.2%. The highest removals achieved with Fenton and photo-Fenton processes, reached an AR88 removal of 90.5 and 91.7%, respectively. This removal is reached due $HO^{\bullet}$ production by H_2O_2 with Fe^{2+} reaction. The higher AR88 color removal observed in photo-Fenton process suggests that a certain regeneration of Fe^{2+} took place, increasing the removal rate [14]. Throughout the use of the statistical program, 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.

3.2. Variation of radiation sources

In order to increase the AR88 removal rate, several radiation sources (UV-C, UV-A, ultrasound (US), 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 1(b). 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, solar-Fenton. They agree with Teixeira et al., et al., [15], who recognized elevated removal of acid red 88 with application of UV-A radiation.

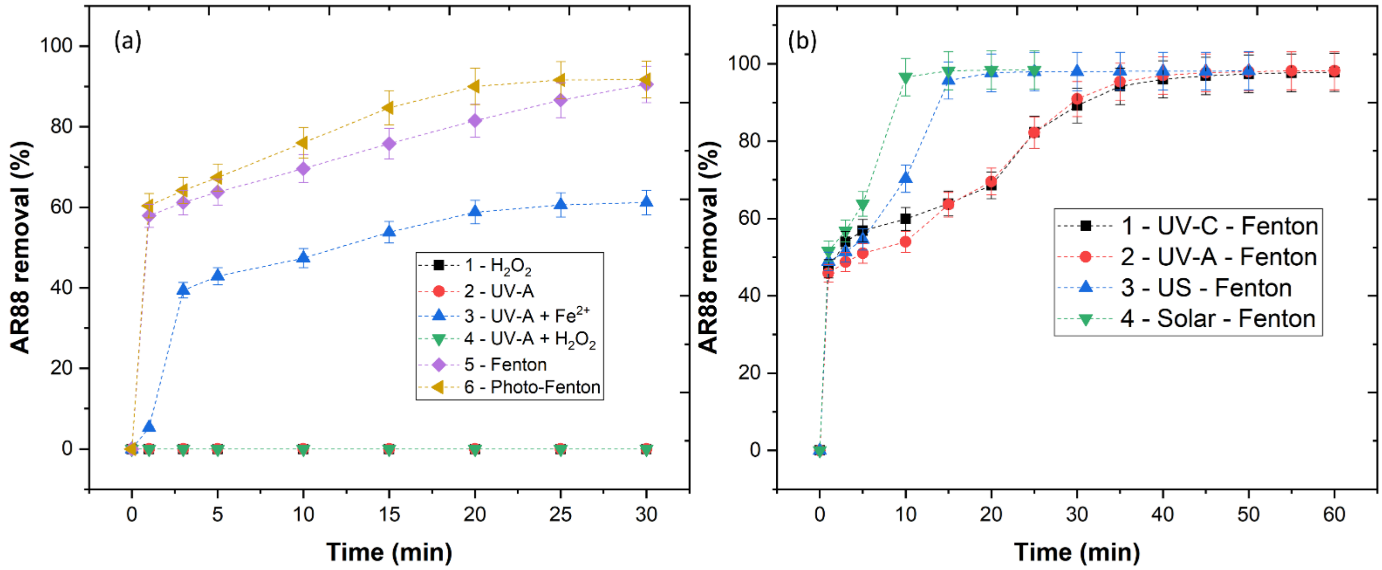

Figure 1. (**a**) AOPs variation in AR88 color removal ([AR88] = 0.125 mM, pH = 3.0, [H_2O_2] = 4 mM, [Fe^{2+}] = 0.30 mM, radiation UV-A 32.7 W m^{-2}, time = 30 min); (**b**) variation of radiation sources ([AR88] = 0.125 mM, pH = 3.0, [H_2O_2] = 7.9 mM, [Fe^{2+}] = 0.224 mM, time = 30 min).

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 solution. Finally, it is concluded that solar-Fenton is the most efficient, environmentally friendly and economic process to remove the AR88.

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