

Acid Red 1 and Acid Red 114 decolorization in H₂O₂-modified subcritical water: process optimization and application on a textile wastewater

Berkant Kayan^{a,*}, Sema Akay^a, Esra Kulaksız^a, Belgin Gözmen^b, Dimitrios Kalderis^c

^aDepartment of Chemistry, Arts and Science Faculty, Aksaray University, Aksaray, Turkey, Tel. +903822882693; emails: berkantkayan@gmail.com (B. Kayan), sema.akay7@gmail.com (S. Akay), esra_kulaksiz@hotmail.com (E. Kulaksız)

^bDepartment of Chemistry, Arts and Science Faculty, Mersin University, Mersin, Turkey, email: bgozmen@yahoo.com

^cDepartment of Environmental and Natural Resources Engineering, School of Applied Sciences, Technological and Educational Institute of Crete, Chania, Crete, Greece, email: dkalderis@yahoo.com

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ABSTRACT

Solutions of Acid Red 1 and Acid Red 114 were treated in H₂O₂-modified subcritical water in the temperature range of 100°C–200°C for up to 60 min. Response surface methodology based on the Box-Behnken design was used to optimize the process. For Acid Red 1, optimum decolorization of 97% can be achieved at 192°C, 181 mM H₂O₂, 51.3 min treatment time, and 121 mg/L dye concentration. For Acid Red 114, the optimum conditions were 195°C, 157 mM H₂O₂, 38 min treatment time and 110 mg/L dye concentration, where 91% decolorization could be obtained from the proposed model. It was determined that temperature is the most important factor, followed by the oxidant concentration. Degradation was less efficient for AR114 due to the double azo bonds, compared to the single azo bond of AR1. Application of the optimum treatment conditions on real reactive dye wastewater resulted in 92.7, 79.1 and 20.4% removal of BOD₅, COD and TSS, respectively.

Keywords: Azo dyes; Textile wastewater; Subcritical water

1. Introduction

Modernization of the textile industry worldwide has resulted in more advanced chemical substances being used in the dyeing and finishing processes. A significant number of these substances are either hazardous or can be transformed to hazardous by-products. Additionally, the dyeing and finishing processes require large amounts of water and are difficult to optimize, thus leading to excess wastewaters that are potentially toxic and may require further treatment. Only part of the wastewater generated by the textile industries is biodegradable; therefore, it poses a serious environmental threat when discharged untreated into adjacent lakes and rivers. To date, approximately 10%–15% of the manufactured dyes are discharged as untreated wastewater into the environment [1].

Acid dyes – part of the larger azo dye family – are highly water soluble, and have better light fastness than basic dyes. They are commonly used for protein fibers such as silk, wool, nylon and acrylics. They contain sulphonic acid groups, which are usually present as sodium sulphonate salts. These increase solubility in water, and give the dye molecules a negative charge. In an acidic solution, the -NH₂ functionalities of the fiber are protonated to give a positive charge: -NH₃⁺. This charge interacts with the negative dye charge, allowing the formation of ionic interactions. Additionally, Van-der-Waals forces, dipolar bonds and hydrogen bonds are formed between the dye and fiber.

Several different processes have been proven successful in treating acid dye effluents. Scientists have mainly focused on advanced oxidation methods such as Fenton oxidation [2,3], photocatalysis [4–7], ultrasonic treatment [8,9], electrochemical oxidation [10–14] or a combination of these [15,16]. In many cases, oxidation of the dye is achieved

*Corresponding author.

through the production of the highly reactive $\text{OH}\cdot$ or other radical. Other methods include dye decolorization through microbial transformations [17,18], enzymatic degradation [19] and membrane treatment [20].

At temperatures between 100°C and 374°C (the critical temperature of water), water is at the subcritical (or superheated) phase. As the temperature is raised, significant changes in several of water's properties occur. In the subcritical phase, water is an efficient solvent for many moderately polar or non-polar pollutants; therefore, it can be used for extraction and degradation of several classes of contaminants from wastewaters, soils and sediments. In cases of not readily degradable pollutants, subcritical water can be modified with an environmentally friendly oxidizing substance, such as hydrogen peroxide. At elevated temperatures and pressures, hydrogen peroxide produces the highly reactive hydroxyl radical which reacts with the pollutant molecules and decomposes them. At the end of the process, hydrogen peroxide leaves no residues. The simplicity and effectiveness of using subcritical water to degrade organic contaminants has been well established [21]. However, the works that study the degradation of textile dyes in subcritical water are only a few.

This set up was successfully used in Daskalaki et al. [22], where Reactive Red 120 was completely degraded after 70 min treatment with 0.5% w/v hydrogen peroxide at 150°C, in subcritical water. It was determined that the experimental temperature – closely connected to the rate of H_2O_2 conversion to hydroxyl radicals – played the most important role in the degradation of Reactive Red 120. Comparable results were obtained recently by Daneshvar et al. [23] who studied the degradation of Acid Orange 7 under subcritical water conditions in the presence of hydrogen peroxide using practically the same experimental set-up. Their results showed that at the optimum conditions of 135°C, 0.4% w/v H_2O_2 and 6 min residence time, Acid Orange 7 as well as other basic or reactive dyes, can be degraded to >99%. Another azo dye – Congo Red – was also degraded successfully in subcritical water modified with H_2O_2 [24]. The author reported that degradation could reach 99.0% with a solution of 100 ppm of Congo Red and 50 mM H_2O_2 at 150°C and 60 min of treatment. Maximum conversion of the total organic carbon was recorded as 62.2%. Both degradation and TOC results are comparable to the studies mentioned earlier. The same authors went a step further and attempted to degrade Orange G by electrolysis in subcritical water [25]. They achieved 99% dye degradation and 98% TOC removal at temperatures of 180°C–250°C in 30 min. As in the previous studies, the temperature and concentration of the hydroxyl radical were the determining factors in the process.

Donlagić et al. [26] studied the decolorization of azo dye Orange II. They showed that at temperatures below 240°C, Orange II oxidation in subcritical water follows a parallel-consecutive reaction pattern in which oxidation proceeds through aromatic by-products and aliphatic acids to complete mineralization. More recently, Hosseini et al. [27,28] used a continuous flow of subcritical water to decompose Acid Orange 7. The experiments were performed in the temperature ranging from 180°C to 374°C, at a pressure range of 10–25 MPa and 60-s residence time. They concluded that the dye and all intermediates

produced can be effectively mineralized towards the high end of the temperature scale, that is, above 350°C.

In our previous studies, the degradation of Acid Red 274 was investigated under subcritical water conditions using H_2O_2 [29,30]. Response surface methodology (RSM) was used to design the experiments and study the effects of temperature, oxidant concentration and residence time. The optimum values of experimental temperature, H_2O_2 concentration, and reaction time were 217°C, 111 mM, and 60 min, respectively, where 67% TOC removal could be obtained from the proposed model. From these and other studies, it has been proved that analysis of variance (ANOVA) based on central composite design is an effective method to optimize the degradation of dyes [31,32]. The scope of this investigation was to further deepen our understanding on the decolorization of azo dyes by studying Acid Red 1 (AR1) or Acid Red 114 (AR114) degradation in subcritical water. RSM was used to optimize the color removal efficiency and to determine the influence of temperature, initial dye concentration, time and initial H_2O_2 concentration. The optimum conditions derived from the model substances were tested against a real textile wastewater containing azo dyes. Through this work, we aim to establish the use of H_2O_2 -modified subcritical water as a simple, quick and efficient way for the treatment of textile industry wastewater, which potentially can be reused in textile processing.

2. Experimental

2.1. Materials

Acid Red 1 and Acid Red 114 dyes (Fig. 1) were purchased from Sigma-Aldrich (Steinheim, Germany). Stock solutions of the dyes were prepared at a concentration of 1,000 mg/L each, with ultra-pure water. Dye solutions of the appropriate concentrations were prepared with dilutions from the initial stock solution. Hydrogen peroxide 35% w/v (Merck-Turkey) was used as the oxidant in the subcritical water process. The textile wastewater was received from Epilektos Textile Industry S.A. (<http://www.stiafilco.com/gr/index.asp>) and contained various azo dyes and other additives (salts, auxiliaries) from cotton fabric processing. The exact specification and concentrations were unknown. It was stored at 4°C and used in the experiments without further treatment.

2.2. Subcritical water apparatus and method

Subcritical water experiments were carried out using a stainless steel high pressure reactor (Berghof BR-100, 75 ml capacity). The experimental process is described in detail in Kayan and Gözmen [29]. Briefly, the reactor was loaded with 50 ml dye solution then H_2O_2 was added and closed, allowing sufficient headspace for safety reasons. At the end of the treatment time, the reactor was cooled to room temperature in an ice bath. The range of values for the experimental variables used during treatment is shown in Table 1. The application of RSM resulted in a total of 29 experiments (Table 2). For reproducibility reasons, selected experiments were performed in triplicate.

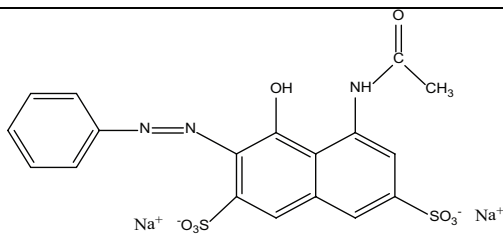
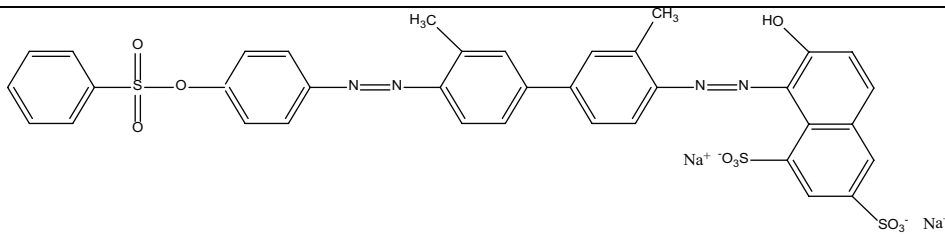
Structure	
	Acid Red 1 AR1 $C_{18}H_{13}N_3Na_2O_8S_2$ 509.44 g/mol $\lambda_{max} = 506 \text{ nm}$
	Acid Red 114 AR114 $C_{36}H_{26}N_4Na_2O_{10}S_3$ 816.58 g/mol $\lambda_{max} = 514 \text{ nm}$

Fig. 1. Chemical structure of the dyes used in this study.

Table 1
The level and range of independent variables

Independent variables	Factor	Range and levels		
		-1	0	1
Temperature (°C)	X_1	100	150	200
H_2O_2 concentration (mM)	X_2	50	150	250
Time (min)	X_3	15	37.5	60
Initial dye concentration (mg/L)	X_4	100	300	500

2.3. Analyses

The decolorization of AR 1 and AR 114 was monitored on a UV-vis spectrometer (Thermo Genesys 10-S) at 506 and 514 nm, respectively. The percentage decolorization (DE %) of AR1 and AR 114 was obtained through the following formula:

$$DE\% = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 and C_t correspond to the initial and remaining dye concentration at a specific time t , respectively.

In order to identify potential degradation products, GC-MS analyses were performed (Agilent 5975C series GC/MSD with a RESTEK Rtx-5MS crossbond 5% diphenyl-95% dimethyl polysiloxane 0.25 m, 30 m \times 0.25 mm column). Helium was employed as the carrier gas and the voltage of electron impact ionization was 70 eV. The temperature program was set as follows: 40 to 80°C, rate = 5°C/min and hold time 1 min, from 80 to 280°C, rate = 4°C/min and hold time 10 min.

The textile industry wastewater was characterized (before and after treatment, in triplicate) in terms of pH, conductivity, BOD₅, COD and total suspended solids (TSS) using standard laboratory protocols. Its color was

determined using the American Dye Manufacture Index (ADMI) color method as described in De Jager et al. [33]. This is the method of choice for textile wastewaters that contain several dyes of different colors and concentrations which often produce largely overlapping UV peaks. For real textile wastewaters there is no direct relationship between ADMI, absorbance and the dye concentrations [34].

The acute eco-toxicity of the wastewater was measured using the Microtox bioassay. The details of the method are described in Gottlieb et al. [35]. This test employs the *Vibrio fischeri* microorganisms, which are non-pathogenic, marine bacteria that luminesce as a natural part of their metabolism. When exposed to a toxic substance, the respiratory process of the bacteria is disrupted, reducing light output. Response to toxicity is observed as a change in luminescence – which is a by-product of cellular respiration – and expressed as the EC₅₀ value. The value has no absolute meaning and is only useful for comparison purposes, before and after treatment, to indicate the any reduction in toxicity. In cases of real wastewaters, where more than one toxic substances are present, the EC₅₀ value is expressed in percent dilution of the original sample [35].

2.4. Box-Behnken design and optimization of color removal of azo dyes

Design Expert 9.0.4 was used to design selection, mathematical modeling and optimization [36]. The RSM was used to determine the optimal experimental conditions for maximum decolorization. This methodology is a collection of statistical tools used to study the effect of several variables influencing the responses by varying them simultaneously [37]. RSM using Box-Behnken design (BBD) was applied. Temperature, initial H_2O_2 concentration, time and initial dye concentration were considered to be the independent variables (factors) and were labeled as X_1 , X_2 , X_3 and X_4 , respectively. In BBD, each factor was coded at three levels

(−1, 0, 1). Table 1 presents the independent variables and their experimental range and levels. The dependent variable Y was the color removal percent. The decolorization results of AR1 and AR114 were observed to be highly correlated with the quadratic model according to the ANOVA. A quadratic model which also includes the linear model is given according to Eq. (2).

$$Y\% = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j + \varepsilon \quad (2)$$

where Y is the response, X_i and X_j are the coded variables, β_0 is the constant coefficient, β_i , β_{ii} and β_{ij} the first-order, quadratic and interaction effects, respectively, i and j are the index numbers for factor, and ε is the residual error [38,39]. ANOVA and coefficient of correlation (R^2) were used to evaluate the suitability of the model.

3. Results and discussion

3.1. Optimization of decolorization conditions

The decolorization of the dye solutions was performed in subcritical water using H_2O_2 as an oxidant (ScW- H_2O_2). To assess the effectiveness of ScW- H_2O_2 to degrade AR1 and AR114, a total of 29 experiments were performed for each dye, as indicated by the Box-Behnken design (Table 2). The numbers of experiments were calculated as follows:

$$N = k^2 + k + cp \quad (3)$$

where k is the factor number and cp is the replicate number of the central point [40].

The obtained experimental data shown in Table 2 were used to fit the polynomial model representing the color

Table 2
The design and results of Box-Bhenken experiments

Run No.	Experimental design				Response Y: Color removal %			
	T (°C)	[H ₂ O ₂] ₀ (mM)	t (min)	[Dye] ₀ (mg/L)	AR1		AR114	
					Obs. Y	Pred. Y	Obs. Y	Pred. Y
1	100	50	37.5	300	10	12	7	8
2	200	50	37.5	300	64	66	52	56
3	100	250	37.5	300	18	20	12	14
4	200	250	37.5	300	91	94	83	87
5	150	150	15.0	100	56	59	48	51
6	150	150	60.0	100	65	68	54	58
7	150	150	15.0	500	32	33	21	22
8	150	150	60.0	500	36	37	24	27
9	100	150	37.5	100	34	34	27	27
10	200	150	37.5	100	97	100	91	93
11	100	150	37.5	500	9	7	5	3
12	200	150	37.5	500	68	69	57	58
13	150	50	15.0	300	31	35	22	25
14	150	250	15.0	300	49	49	41	40
15	150	50	60.0	300	36	37	26	27
16	150	250	60.0	300	63	59	51	49
17	100	150	15.0	300	14	12	8	8
18	200	150	15.0	300	84	78	71	66
19	100	150	60.0	300	19	20	11	11
20	200	150	60.0	300	85	82	79	74
21	150	50	37.5	100	64	58	54	48
22	150	250	37.5	100	72	70	67	64
23	150	50	37.5	500	26	23	19	16
24	150	250	37.5	500	45	47	36	36
25	150	150	37.5	300	62	62	51	51
26	150	150	37.5	300	64	62	51	51
27	150	150	37.5	300	60	62	53	51
28	150	150	37.5	300	61	62	49	51
29	150	150	37.5	300	62	62	50	51

removal % (response Y) as a function of temperature, initial H_2O_2 concentration, time and initial dye concentration. The decolorization results for both AR1 and AR114 were observed to be highly correlated to the quadratic model and the optimum fit model equation was obtained according to Eq. (2) as follows:

For AR1:

$$Y = 61.80 + 32.08X_1 + 8.92X_2 + 3.17X_3 - 14.33X_4 + 4.75X_1X_2 - 1.00X_1X_3 - 1.00X_1X_4 + 2.25X_2X_3 + 2.75X_2X_4 - 1.25X_3X_4 - 5.44X_1^2 - 8.44X_2^2 - 8.32X_3^2 - 4.07X_4^2 \quad (4)$$

For AR114:

$$Y = 50.80 + 30.25X_1 + 9.17X_2 + 2.83X_3 - 14.92X_4 + 6.50X_1X_2 + 1.25X_1X_3 - 3.00X_1X_4 + 1.50X_2X_3 + 1.00X_2X_4 - 0.75X_3X_4 - 2.77X_1^2 - 6.90X_2^2 - 8.65X_3^2 - 2.77X_4^2 \quad (5)$$

Coefficient of correlation (R^2) values for AR1 and AR114 oxidation with H_2O_2 in subcritical water were obtained as 0.9880 and 0.9867, respectively. The regular R^2 can be artificially inflated by simply continuing to add terms to the model, even if the terms are not statistically significant. The adjusted R^2 plateaus when insignificant terms are added to the model, and the predicted R^2 will decrease when there are too many insignificant terms. A rule of thumb is that the adjusted and predicted R^2 values should be within 0.2 of each other [36]. The high adjusted R^2 (0.9760 and 0.9734) and predicted R^2 (0.9332 and 0.9257) values for AR1 and AR114 also illustrate that the model is suitable for the experimental data [41]. The adequate precision value was the signal to noise ratio. The ratio of 33.77 and 32.35 for AR1 and AR114, respectively, indicates an adequate signal.

Fig. 2 provides Pareto graphic analysis which introduces a single or synergistic positive or negative effect of the variables on the color removal efficiency [42]. This analysis gives the percentage effect of each factor on the response according to following formula:

$$P_i = \left(\frac{\beta_i^2}{\sum \beta_i^2} \right) \times 100 \quad (i \neq 0) \quad (6)$$

It is demonstrated that the temperature (β_1), initial dye (β_4) and hydrogen peroxide (β_2) concentration are the crucial factors for the decolorization of AR1 and AR114.

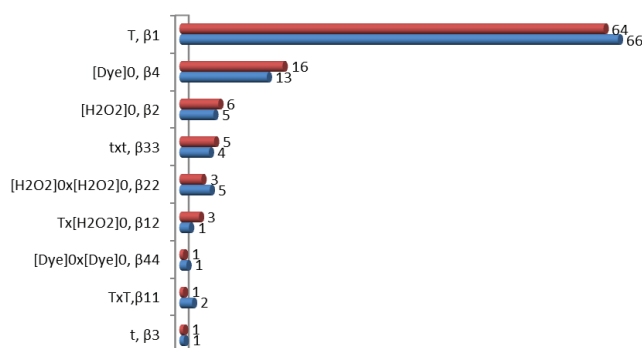


Fig. 2. Pareto graphic analysis.

3.2. Analysis of variance

The regression model was tested by ANOVA results to ensure the statistical significance of the quadratic model employed for explaining the experimental data at a 95% confidence level, as shown in Table 3. From Table 3, it was observed that the proposed model was highly significant due to a very low p-value ($p < 0.0001$) and a very high F value (82.49 for AR1, 74.18 for AR114). Fitting the experimental results to Eq. (4) and (5) leads to the optimum decolorization conditions for the two dyes. For Acid Red 1, optimum decolorization of 97% can be achieved at 192°C, 181 mM H_2O_2 , 51.3 min treatment time, and 121 mg/L dye concentration. For Acid Red 114, the optimum conditions were 195°C, 157 mM H_2O_2 , 38 min treatment time and 110 mg/L dye concentration, where 91% decolorization could be obtained from the proposed model.

3.3. Interactive effect of the process independent variables

In order to gain a better understanding of the influence of the independent variables and their interactions on the response (dependent variable), 3D response surface and 2D contour plots for the measured responses of AR1 and AR114 were formed based on the model Eqs. (4) and (5).

Fig. 3 shows the effects of initial H_2O_2 concentration and temperature on decolorization of 200 mg/L AR1 and AR114, after 35 min treatment. At subcritical water conditions, hydrogen peroxide decays to produce hydroxyl radicals which are non-selective and the second strongest oxidant known due to their high standard reduction potential ($E^\circ(OH\cdot/H_2O) = 2.80$ V/SHE) [21,22].

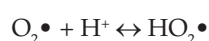


For both dyes, an increase in temperature from 100 to 200°C resulted in a sharp increase in color removal, from 22% to 75% for AR1 and 18% to 62% for AR114 (at 50 mg/L oxidant concentration). This critical effect of temperature is also obvious at all other H_2O_2 concentrations. At constant temperature, increasing H_2O_2 concentration has a much lesser effect on decolorization. Even at the highest temperature of 200°C, a 5-fold increase in oxidant concentration only increased color removal by 24% (75%–99%) for AR1 and 29% (63%–92%) for AR114. When H_2O_2 concentration was increased from 200 to 250 mM, the decolorization rate remained practically the same for both dyes. This may be due to the higher consumption rate of the hydroxyl radical from secondary reactions (Eq. (8–12)) [43,44]. These reactions involve $OH\cdot$ attacks on H_2O_2 giving hydroperoxyl radical ($HO_2\cdot$) and superoxide anion radical ($O_2\cdot^-$) by reaction (8) and (9), respectively. The superoxide anion radical is the conjugate base of $HO_2\cdot$ ($pK_a = 4.8$) (Eq.(9)). The reaction with the hydroperoxyl radical (Eq. (11)) and dimerization of hydroxyl radical (Eq.(12)) are also included in these reactions.

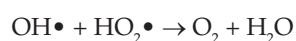


Table 3
ANOVA for response surface quadratic model for azo dyes decolorization by ScW/H₂O₂

Source	Degrees of freedom	Sum of squares	Mean squares	F-value	p-value
Model for AR1	14	16,873.31	1,205.24	82.49	<0.0001
X ₁	1	12,352.08	12,352.08	845.41	<0.0001
X ₂	1	954.08	954.08	65.30	<0.0001
X ₃	1	120.33	120.33	8.24	0.0124
X ₄	1	2,465.33	2,465.33	168.73	<0.0001
X ₁ ²	1	90.25	90.25	6.18	0.0262
X ₂ ²	1	4.00	4.00	0.27	0.6090
X ₃ ²	1	4.00	4.00	0.27	0.6090
X ₄ ²	1	20.25	20.25	1.39	0.2587
X ₁ X ₂	1	30.25	30.25	2.07	0.1722
X ₁ X ₃	1	6.25	6.25	0.43	0.5237
X ₁ X ₄	1	192.08	192.08	13.15	0.0028
X ₂ X ₃	1	462.24	462.24	31.64	<0.0001
X ₂ X ₄	1	448.65	448.65	30.71	<0.0001
X ₃ X ₄	1	107.27	107.27	7.34	0.0169
Residual	14	204.55	14.61		
Lack of fit	10	195.75	19.58	8.90	0.0247
Pure error	4	8.80	2.20		
Model for AR114	14	15,654.81	1,118.20	74.18	<0.0001
X ₁	1	10,980.75	10,980.75	728.41	<0.0001
X ₂	1	1,008.33	1,008.33	66.89	<0.0001
X ₃	1	96.33	96.33	6.39	0.0241
X ₄	1	2,670.08	2,670.08	177.12	<0.0001
X ₁ ²	1	169.00	169.00	11.21	0.0048
X ₂ ²	1	6.25	6.25	0.41	0.5301
X ₃ ²	1	36.00	36.00	2.39	0.1446
X ₄ ²	1	9.00	9.00	0.60	0.4526
X ₁ X ₂	1	4.00	4.00	0.27	0.6145
X ₁ X ₃	1	2.25	2.25	0.15	0.7051
X ₁ X ₄	1	49.95	49.95	3.31	0.0902
X ₂ X ₃	1	308.82	308.82	20.49	0.0005
X ₂ X ₄	1	485.34	485.34	32.19	<0.0001
X ₃ X ₄	1	49.95	49.95	3.31	0.0902
Residual	14	211.05	15.07		
Lack of fit	10	202.25	20.22	9.19	0.0233
Pure error	4	8.80	2.20		



(10) of destruction of the azo linkage (–N=N–) by the attack of oxidizing radicals. This linkage connects the two aromatic groups in the AR1 and AR114 structures.



(11) The dramatic effect of temperature can also be seen in Fig. 4, where the interactive effect of time and temperature (at constant dye and H₂O₂ concentration) is shown. At the minimum treatment time of 15 min, increasing the temperature from 100°C to 200°C resulted in a 65% and 68% increase in color removal for AR1 and AR114, respectively. Similar behavior was also observed up to the treatment time of 60 min. Time appeared to have very little effect in the process. At 200°C, increasing treatment time from 15 to 60 min, had only a minor effect in color removal, indicating that



(12)

During subcritical water treatment with H₂O₂, the hydroxyl radicals (OH•) and the weaker oxidant hydroperoxyl radical (HO₂•) are mainly responsible for the degradation of organic pollutants to the final products [45]. The decolorization of both AR1 and AR114 occurs as a result

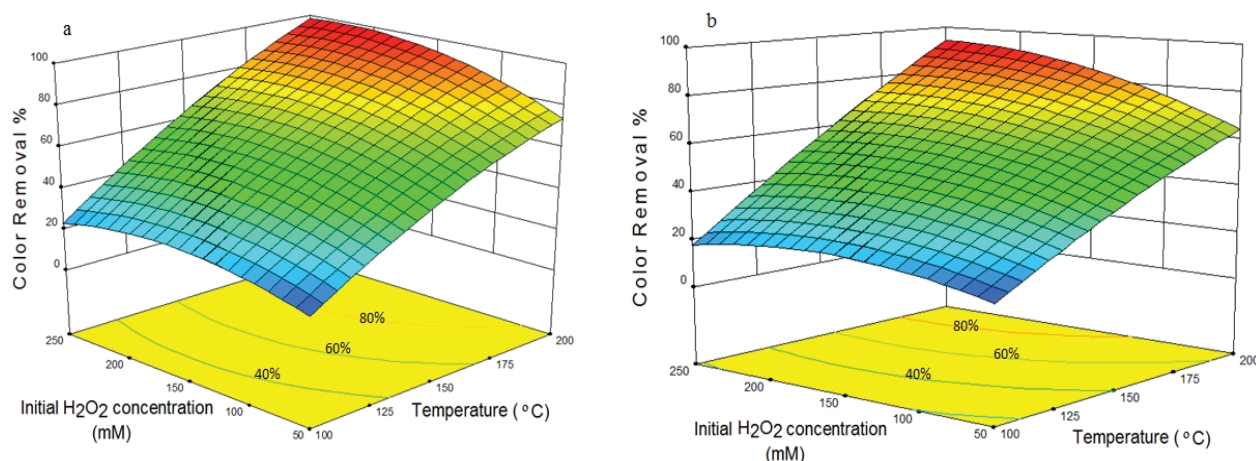


Fig. 3. 3D response surface and 2D contour plots for the effect of the initial H_2O_2 concentration and temperature for color removal % of (a) AR1 and (b) AR114 ($[\text{Dye}]_0 = 200 \text{ mg/L}$, $t = 35 \text{ min}$).

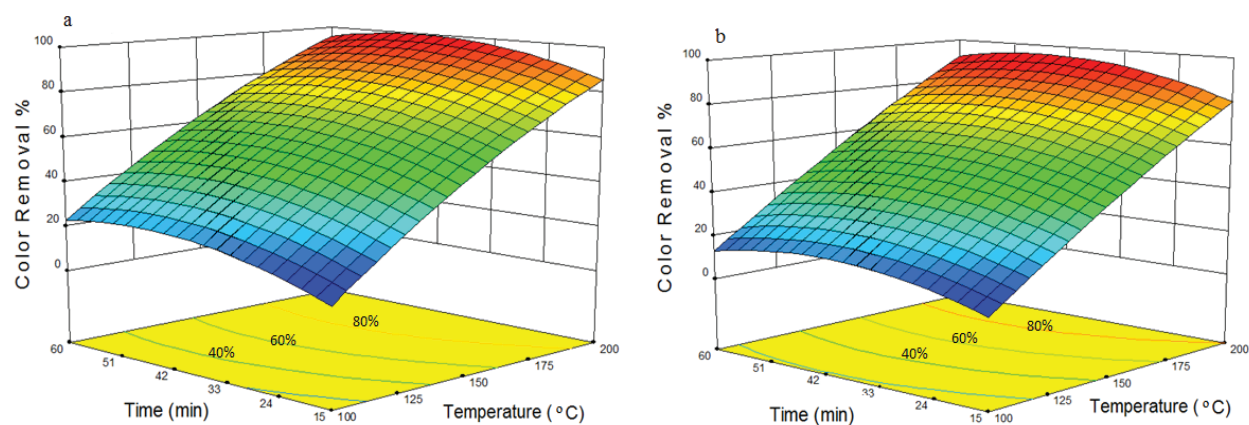


Fig. 4. 3D response surface and 2D contour plots for the effect of the time and temperature for color removal % of (a) AR1 and (b) AR114 ($[\text{Dye}]_0 = 200 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 250 \text{ mM}$).

the decolorization reactions were not kinetically hindered. Time could perhaps play a more important role at low oxidant concentrations and/or higher dye concentrations.

Fig. 5 shows dye decolorization with respect to temperature and initial dye concentration, at a H_2O_2 concentration of 150 mM. In the 175°C–200°C range, decolorization % for AR1 was increased as the dye concentration was decreased. At a concentration of 100 mg/L, nearly 100% decolorization was achieved, whereas at 500 mg/L color removal dropped to approximately 68%. (Fig. 5(a)). At temperatures below 175°C, color removal % dropped rather sharply, confirming that temperature is the determining factor of the process. A similar trend was observed for AR114 (Fig. 5(b)). At temperatures higher than 175°C, a color removal of approximately 90% was achieved at a dye concentration of 100 mg/L, whereas when the concentration was increased to 500 mg/L, the color removal % dropped to below 50%. In both cases, this indicates that regardless of temperature, the H_2O_2 concentration was not adequate to produce enough OH^\bullet radicals to fully oxidize the higher dye concentrations. Additionally, decolorization was not as successful

for AR114 as it was for AR1. This is probably due to the higher complexity of AR114 and the presence of two N=N linkages, compared to one in AR1.

Fig. 6(a) and (b) shows the predicted color removal % as a function of time and H_2O_2 concentration at constant temperature and dye concentration. For both dyes, the color removal % increased with increasing H_2O_2 concentration and decreased after 40 min treatment time. This is to be expected, as the concentration of H_2O_2 increased more OH^\bullet radicals were produced and attacked the dye molecules. Two possible explanations may account for the decrease observed after ~40 min. First, the production of OH^\bullet may have decreased, leading to a subsequent reduction in the decolorization rate. Second, it may be due to the participation of hydroxyl radicals to competitive secondary reactions with by-products not produced at an earlier time. Overall, it is shown that AR1 decolorization was more efficient compared to AR114 – the same trend observed in earlier figures.

Fig. 7(a) and (b) shows the predicted color removal as a function of initial H_2O_2 and dye concentration,

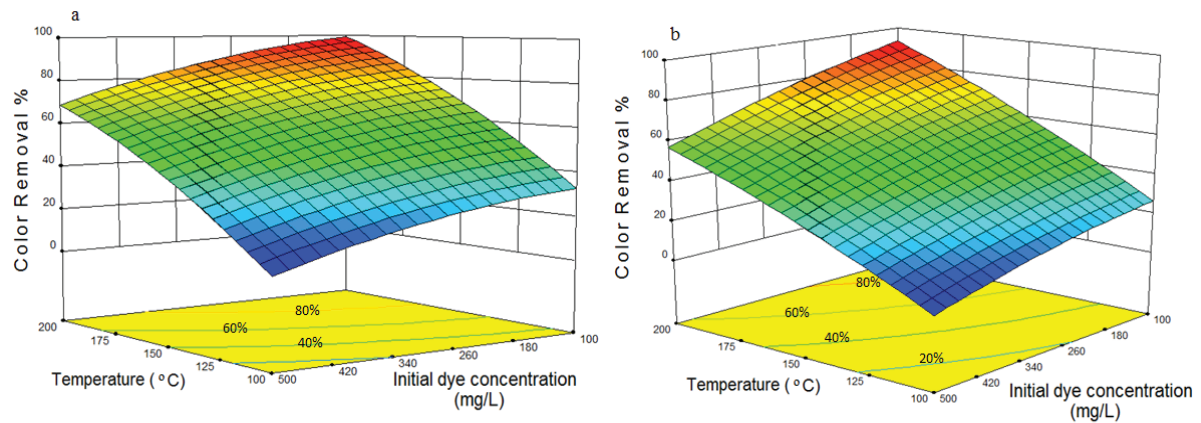


Fig. 5. 3D response surface and 2D contour plots for the effect of the initial dye concentration and temperature for color removal % of (a) AR1 and (b) AR114 ($[H_2O_2]_0 = 150 \text{ mM}$, $t = 35 \text{ min}$).

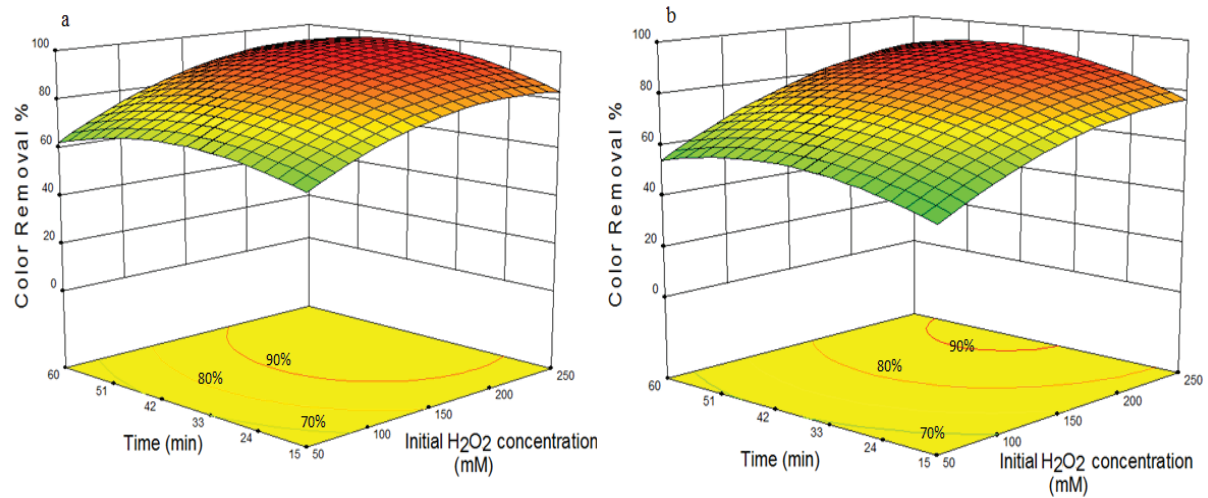


Fig. 6. 3D response surface and 2D contour plots for the effect of the initial H_2O_2 concentration and time for color removal % of (a) AR1 and (b) AR114 ($[Dye]_0 = 250 \text{ mg/L}$, $T = 200^\circ\text{C}$).

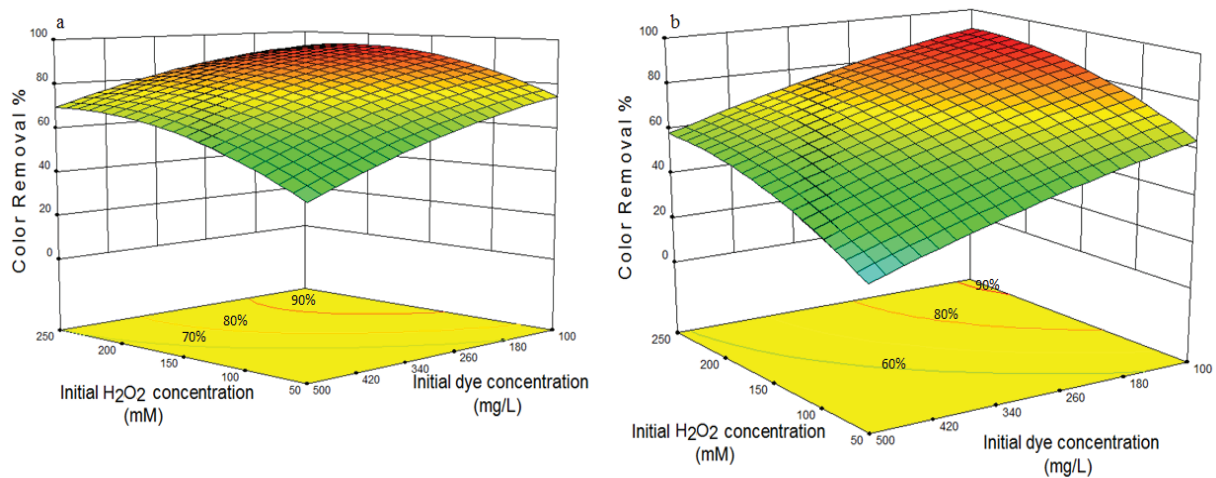


Fig. 7. 3D response surface and 2D contour plots for the effect of the initial H_2O_2 concentration and initial dye concentration for color removal % of (a) AR1 and (b) AR114 ($T = 200^\circ\text{C}$, $t = 20 \text{ min}$).

at a constant temperature (200°C) and treatment time (20 min). For a high AR1 concentration (500 mg/L) the color removal increased from 40%–70% as the H_2O_2 concentration increased from 50 to 250 mM (Fig. 7(a)). It is interesting to note, however, that the rate of decolorization is gradually reduced as the H_2O_2 concentration increased. This means that dye decolorization does not necessarily respond to the increased OH^\bullet concentration. Therefore, it appears that secondary OH^\bullet reactions play an important role at higher H_2O_2 concentrations. The same trend can be observed for AR114 (Fig. 7(b)), where color removal % was lower at the same conditions, compared to AR1. At the lowest concentration of 100 mg/L, increasing the oxidant concentration from 50 to 250 mg/L leads to a color removal % of 75%–93% and 65%–90%, for AR1 and AR114, respectively.

The effects of all the independent variables simultaneously on the color removal efficiency of AR1 and AR114 in the design space were compared in the perturbation plots (Fig. 8(a)–(b)). Examination of the perturbation plots showed that for effective color removal, temperature (A), initial H_2O_2 concentration (B), time (C) and initial dye concentration (D) are the controlling parameters. Sharp curvatures for temperature and initial dye concentration show that the response of color removal efficiency was very sensitive to these parameters.

Several works has been published in literature for decolorization of AR1 and AR114 by using different methods (Table 4). The comparison of the present study with those obtained by other authors clearly indicates the favorable color removal efficiency of ScW- H_2O_2 process. The most efficient AOPs between these studies for the removal of color seem to be anodic oxidation (AO) with H_2O_2 and electro-Fenton processes. Subcritical water using H_2O_2 is also an attractive option for treatment of textile effluents which have a wide range of pH values. The pH of the solution is not an important parameter for ScW- H_2O_2 method in contrast to AO and E-Fenton processes.

3.4. Identification of products

Based on the degradation products identified by the GC-MS, a possible pathway for AR1 and AR114 degradation was proposed (Fig. 9). For AR1, hydroxylation and cleavage of the azo group bonds may lead to 8-aminonaphthalene-1,3-diol (1), aniline (2) and then nitrobenzene (3). In the first stages of degradation, desulfonation and separation of the propanone group may occur. Compound (1) could be further oxidized to 3,5-dihydroxyphthalic acid (4) before further hydroxylation, denitration and oxidative opening of the aromatic ring occurred. Similarly, compounds (2) and (3) underwent attack by the hydroxyl radical to form the hydroquinone (6) and benzoquinone (7) intermediates. AR114 has a larger structure compared to AR1 with two azo groups. Assuming that the hydroxyl radical attacked both azo groups at the same time, six different by-products may be formed (8–13). The cleavage of the first azo bond – followed by desulfonation – may lead to the formation of phenol (8) and aniline (9). The cleavage of the second azo bond may lead to the formation of 3,3-dimethyl-[1,1'-biphenyl]-4,4'-diamine (10) and naphthalene derivatives (11–13).

3.5. Treatment of a textile industry wastewater at the optimum conditions

For the subcritical water treatment of the real wastewater, the optimum conditions determined for AR1 were selected (192°C, 181 mM H_2O_2 , 51.3 min residence time). Given the complexity of real wastewater, the higher oxidant concentration and the longer treatment time of the two were chosen. The before and after treatment values as well as the Environmental Protection Agency limits of discharge for this type of wastewater are shown in Table 5. Comparing these values with those reported in the literature is not feasible due to the different compositions of textile wastewater and treatment methods used.

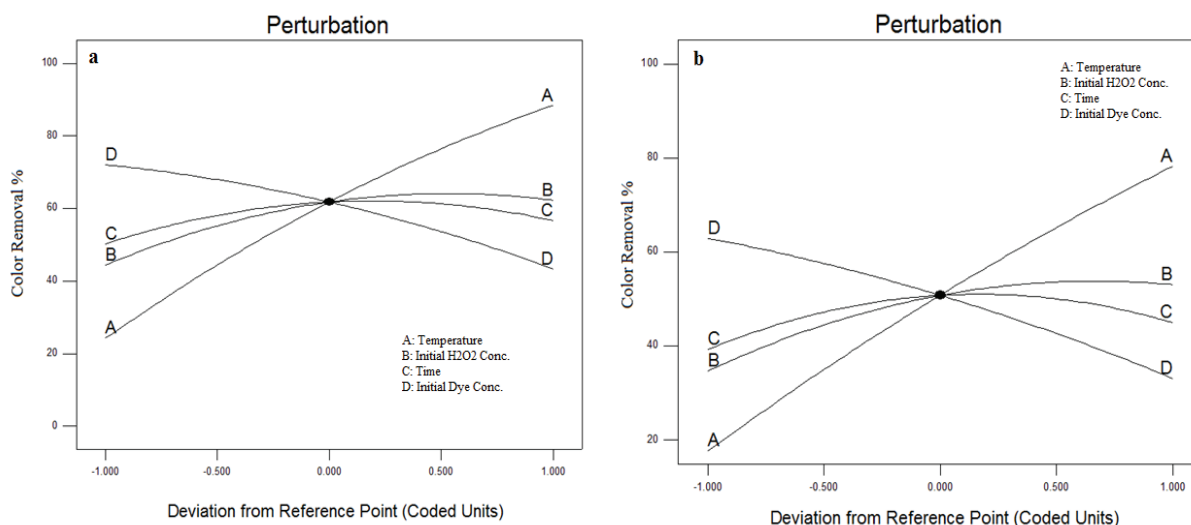


Fig. 8. Overlay plot of perturbation of all the variables for (a) AR1 and (b) AR114.

Table 4
Comparison of color removal efficiency for AR1 and AR114 when other advanced oxidation methods were used

Method	Experimental conditions	Color removal %
Fenton-like	[AR1] ₀ = 50 mg/L, [H ₂ O ₂] ₀ = 8.0 mM, 4.0 g/L of 0.080 wt.% Fe-kaolin, T = 30°C, pH 3.0, t = 240 min, V = 200 mL	98.5 [50]
Fenton-like	[AR1] ₀ = 50 mg/L, [H ₂ O ₂] ₀ = 16.0 mM, 5.0 g/L of 0.14 wt.% Fe(III) oxide immobilized on Montmorillonite K10 (Fe–MK10), T = 30°C, pH 2.5, t = 150 min, V = 200 mL	99.0 [51]
Photo-Fenton	[AR1] ₀ = 1 × 10 ⁻⁴ mol/L, [Fe(II)] ₀ = 5 × 10 ⁻⁵ mol /L [H ₂ O ₂] ₀ = 1 × 10 ⁻³ mol/L, pH = 2.9, t = 10 min	99.7 [16]
UV/H ₂ O ₂	[AR1] ₀ = 1 × 10 ⁻⁴ mol/L, [H ₂ O ₂] ₀ = 1 × 10 ⁻³ mol/L, pH = 3.45, t = 15 min	99.3 [16]
Photolysis of ferric perchlorate (FPC)	[AR1] ₀ = 1 × 10 ⁻⁴ mol/L, [FPC] ₀ = 1.45 × 10 ⁻³ mol/L, pH = 2.5, t = 10 min	86.6 [16]
Solar photodegradation	[AR1] ₀ = 40 mg/L, 0.20 g catalyst (Degussa P25 or Ca–Ce–W–TiO ₂ composite) t = 150 min, V = 300 mL	99.9 [52]
Fenton-like	[AR1] ₀ = 50 mg/L, [H ₂ O ₂] ₀ = 16.0 mM, 2.5 g/L of 0.80 wt.% of Fe–zeolite Y type (Fe–ZYT) catalyst, T = 30°C, pH 2.5, t = 60 min, V = 200 mL	99.0 [53]
Anodic oxidation with electrogenerated H ₂ O ₂	[AR1] ₀ = 236 mg/L, pH = 3.0, T = 35°C, I = 100 mA/cm ² , V = 100 mL, BDD anode, t = 240 min	100 [13]
Electro-Fenton with BDD anode	[AR1] ₀ = 236 mg/L, [Fe ²⁺] ₀ = 236 mg/L, pH = 3.0, T = 35°C, I = 100 mA/cm ² , V = 100 mL, t = 10 min	100 [13]
Photodegradation	[AR114] ₀ = 50 mg/L, 40 mg/L of 10 wt% TiO ₂ / clinoptilolite (CP), T = 25°C, pH = 7, t = 140 min.	99.9 [54]
ScW-H ₂ O ₂	[H ₂ O ₂] ₀ = 150 mM, T = 200°C, T = 35 min, [AR1] ₀ = 100 mg/L, [AR1] ₀ = 300 mg/L, [AR1] ₀ = 500 mg/L,	99.2 88.1 68.8 (This study)
ScW-H ₂ O ₂	[H ₂ O ₂] ₀ = 150 mM, T = 200°C, T = 35 min., for; [AR114] ₀ = 100 mg/L, [AR114] ₀ = 300 mg/L, [AR114] ₀ = 500 mg/L	92.8 77.7 57.1 (This study)

In some cases of textile wastewater, it may be preferable to recycle and re-use it in the fabric processing cycle. This option would usually require lower treatment standards, which may in turn reduce the overall cost of textile processing. Therefore, both options have to be examined – technically and economically – when assessing the fate of textile wastewater.

The pH and conductivity values were slightly decreased, to 8.8 and 5.1 mS/cm, respectively. Since the real wastewater contains inorganic salts, they would play a dominant

role in the pH and conductivity values. It is well known that subcritical water conditions do not affect inorganic species in anyway, therefore this explains the similar values before and after treatment. The value of pH falls within the EPA guidelines limits. Additionally, it is not a critical factor when it comes to wastewater re-use, since pH can be controlled at any stage of textile processing. With respect to conductivity, the presence of inorganic salts affects some dyeing processes more than others. For example, anionic salts cannot be tolerated in process waters used to apply

cationic fixing agents to direct dyes. A high salt concentration may cause direct dyes to exhaust too rapidly, resulting in uneven dyeing.

A small reduction (20.4%) was observed in the total suspended solids. This may be due to the high temperature which solubilized a fraction of the solid components which they remained in solution even after cool-down. Total solids can interact with the dye molecules and hinder the dyeing process; therefore, it is an important factor to consider when recycling the wastewater.

As expected at such strongly oxidizing conditions, BOD₅ showed a high percent removal (92.7%). The COD removal was not as high (79.1%), indicating only partial oxidation of one or more of the wastewater organic substances. The problem associated with partial oxidation lies in the unknown nature of the secondary products formed and the risk that some of these may be more toxic in comparison to the initial substances. In a multi-component wastewater, it is practically impossible to determine all the reactions and mechanisms – especially at high temperatures and pressures. It is interesting to note that Punzi et al. [46] drew a similar conclusion when they studied a combined biological-ozonation process for the treatment of real textile wastewater. They observed a reduced degree of mineralization which they attributed to the non-selective reactivity nature of the hydroxyl radical towards other organic and inorganic molecules – such as detergents and salts – and not only the dye substances themselves [24,47].

In our case, since the most important parameters are temperature and H₂O₂ concentration, complete mineralization of all organic substances in a textile wastewater may be achieved if temperature is kept at the optimum value and excess H₂O₂ is used. This would result in high OH• concentrations and given enough time, complete oxidation could be achieved. Additionally, the process would maintain its environmentally friendly profile, whereas the cost would also remain the almost the same, since temperature and residence time would not change (only the increased cost of the excess H₂O₂ used).

The effluent color was deep brown as received and it was measured at 1,881 ADMI units. After treatment, 77.5% of the color was removed and the effluent was measured at 423 ADMI units (light to a transparent medium brown color). This indicates that there were still non-oxidized dye molecules present and/or secondary colored degradation products. Colored effluents have a negative aesthetic result but more importantly, they cannot be recycled and re-used within the textile industry. Joshi et al. [48] reviewed the environmental issues associated with residual color in textile effluents and the various decolorization methods [48]. With respect to H₂O₂, they concluded that it is the main oxidant used in chemical treatment methods; however, its decolorization efficiency depends on method of activation (H₂O₂/Fe²⁺ salts, H₂O₂/ozone, H₂O₂/UV radiation) and types of dyes.

The EC₅₀ toxicity value showed a 20-fold reduction after treatment. This is a low reduction factor, comparable with those reported in the literature for various other types of real textile wastewater. Given the sensitivity of *V. Fischeri*, this low value may be partially attributed to the salts present in the effluent [49].

4. Conclusions

This paper presented the decolorization of Acid Red 1 and Acid Red 114 using hydrogen peroxide in subcritical water. Optimization of the process was achieved through the RSM, in particular the Box-Behnken design. Of all the parameters examined, temperature was the most important factor as it controlled the production of the OH• radical. For Acid Red 1, optimum decolorization of 97% can be achieved at 192°C, 181 mM H₂O₂, 51.3 min treatment time, and 121 mg/L dye concentration. For Acid Red 114, the optimum conditions were 195°C, 157 mM H₂O₂, 38 min treatment time and 110 mg/L dye concentration, where 91% decolorization could be obtained from the proposed model. AR1 was more effectively degraded, probably due to the single azo group compared to the double azo group of AR114. Tested on a real textile wastewater, the method was not as successful probably due to the complex composition of the real effluent (several dyes, salts and other auxiliaries present). However, a significant decrease in COD, BOD and toxicity was still achieved. Total suspended solids and conductivity remained practically the same, indicating that subcritical water oxidation does not affect inorganic species. Overall, the simplicity and efficiency of H₂O₂-modified subcritical water method was demonstrated in treating textile processing wastewaters. It is an environmentally friendly method, since near-complete mineralization of the target contaminants can be achieved in less than 60 min and hydrogen peroxide leaves no residues after treatment. The method would be a reliable candidate to combine with another process, perhaps with a membrane technology that would increase color and suspended solids removal. More work is under way to establish the method at larger scale and determine its economic feasibility.

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