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Assessment of the Total Organic Carbon and Conductivity in Consecutive Dyeings with Reactive Dyestuffs Using Treated Effluent by UV/H_2O_2 Photocatalysis

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Abstract: The paper was monitored the conductivity ($g \cdot L^{-1}$ of NaCl), the absorbances values (Abs) and the amount of TOC (total organic carbon), before and after five consecutive dyeings made with reuse water, obtained from treated effluent by UV/H_2O_2 photocatalysis. All rates of decolorization were above 92%, the removal of total organic carbon was above 89% in all treatments and the economy of NaCl was from 3.10 in the first recipe, 3.17 in the second, 3.49 in the third, 3.79 in the fourth and 4.05 in the fifth recipe. The five dyeings compared with same dyeings made with deionized water presented a color deviation (ΔE^*) below 1. The conventional dyeings would consume 80 L/kg against 40 L/kg used in the dyeing process proposed in this study, representing a great economy of water, with no discharge of effluents.

Key words: Conductivity, reactive dyestuffs, reuse of water, photocatalysis, textile effluent.

1. Introduction

Dyestuff are used to colour the final products of different industries, such as textiles, papers and pulp mills, cosmetics, food, leather, rubber, etc.. The generation of these products leads to the formation of effluents contaminated with all classes of dyestuff and saving water in productive processes has gained special attention due to the aggregated value attributed to this commodity, through principles like “paying consumer” and “paying polluter”, recently incorporated into the authors’ legislation [1-3].

In the textile industry, they are still necessary techniques that prioritize the proper use of water resources, avoiding the inadequate discharges of pollutants with high toxic potential. Environmental problems are associated mainly with wastewater. With regard to globalization and scarcity of water, the possibilities for treatment and recycling of effluent in the textile industry are of the highest importance; therefore, the continuous search for improvement of its production process is essential [4-6].

Of all dyed textile fibres, cotton occupies the number one position, and more than 50% of its production is dyed with reactive dyes. It is estimated that about 10%-60% of reactive dyes are lost during textile dyeing, producing large amounts of coloured effluents. The dye-containing effluent discharged from these

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industries can adversely affect the aquatic environment by impeding light penetration and, as a consequence, precluding the photosynthesis of aqueous flora [7-10].

In recent years, the AOPs (advanced oxidation processes) have been applied as an alternative for treatment of textile effluents. The AOPs are processes in which the main oxidizing agent corresponds to the hydroxyl radical (-OH), generated by the combination of UV irradiation with substances such as H_2O_2 [11-13] or semiconductors such as TiO_2 [14-17]. Other types of treatments have been investigated such as, photocatalysis with nanoparticles of selenium-doped ZnO [18] and catalysis by mononuclear manganese complex II [19], both of them obtaining rates of decolorization above 90%. With high potential of decolorization and great possibilities for reuse of treated effluent, the AOPs present themselves as viable and competitive when compared to conventional processes for effluents treatment. Besides, sludge formation and large number of aromatic rings present in organic dye compounds may cause conventional biological treatments to be ineffective for their mineralization [20-23].

2. Experiments

2.1 Dyeings

Five dyeings of five different colors were done using Mathis Alt-1 dyeing machine. The bleaching of the samples was made according the process described by Rosa et al. [2] and the recipes of dyeings, with the necessary amounts of dyestuff and auxiliaries, are shown in Table 1. The chemicals and commercial synthetic dyes, bifunctional vinylsulphone monochlorotriazine C.I. Reactive Yellow 145 (mozoazo, 1.026 g·mol^{-1}), C.I. Reactive Red 239 (monoazo, 1.136 g·mol^{-1}), C.I. Reactive Blue 222 (diazo, 1.357 g·mol^{-1}) and vinylsulphone C.I. Reactive Blue 21 (phthalocyanine, 1.092 g·mol^{-1}), were supplied by local manufacturer, Golden Química, with a purity higher than 85%.

The dyeings were performed strictly according to instructions of the dyestuffs manufacturer, on liquor ratio equal to 10:1. The stages of dyeing and washing are shown graphically in Fig. 1.

All baths of all steps were collected and stored to photochemical treatment and posterior reutilization.

2.2 Effluent Treatment

2.2.1 Photochemical Step

After the storage, the effluent was diluted with water, in the ratio of 1:4. Then, the pH was adjusted to 7 and was added 2.27×10^{-2} mol of H_2O_2 in aliquots of 1 L [24]. Afterwards, the sample was exposed to UV-C radiation (provided by two Philips TL 6W lamps) and 298 K until complete decolorization. During photochemical reactions, 10 mL of liquid sample was taken out at fifteen minutes time interval in order to assess the absorbance decrease (Konica Minolta CM-3600d). To calculate the decolorization efficiency was used the Eq. (1).

$$D_E = [1 - (Abs_o \times Abs_f^{-1})] \times 100 \quad (1)$$

where, D_E = decolorization efficiency (%); Abs_o = initial absorbance; Abs_f = final absorbance.

Table 1 Amount of dyestuffs and auxiliaries.

Step	Dyestuff/auxiliary	Colour				
		2205	2286	2201	2237	2269
A	NaCl (g·L^{-1})	20	25	30	30	30
B	C.I. reactive yellow 145 (%)	0.30	0.10	0.10	0.24	0.60
	C.I. reactive red 239 (%)	-	-	0.20	0.04	-
	C.I. reactive blue 222 (%)	-	0.20	0.20	0.26	0.05
	C.I. reactive blue 21 (%)	0.14	-	-	-	0.09
C	Na_2CO_3 (g·L^{-1})	8.0	8.0	10.0	10.0	10.0
D	CH_3COOH (mL·L^{-1})	0.50	0.50	0.50	0.50	0.50
E	Levelling agent (g·L^{-1})	1.0	1.0	1.0	1.0	1.0

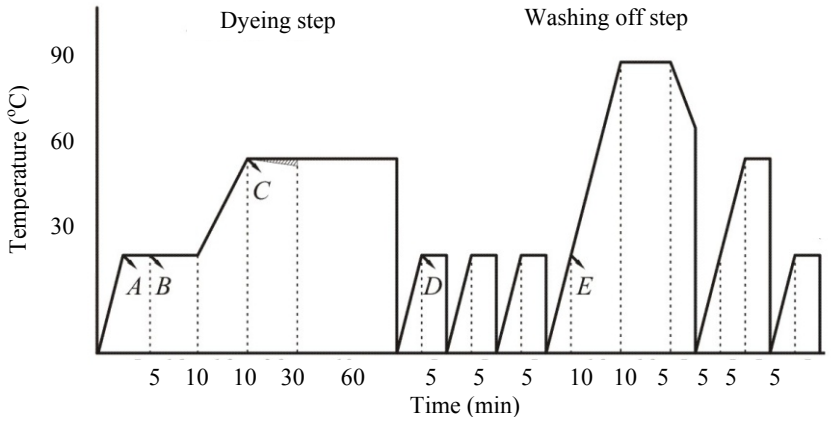

Fig. 1 Entire process of all dyeing.

2.2.2 Concentration of Electrolytes

After the photochemical treatment, the concentration of electrolytes was detected by conductivity (Quimis Q975A Conductivimeter). The conductivity was used to determinate the concentration of sodium chloride (Eq. (2)) in order to discount it from the next dyeing.

$$[NaCl] = (0.0004 \times \mu S \cdot cm^{-1}) + 0.027 \quad (2)$$

where, [NaCl] = NaCl concentration in $g \cdot L^{-1}$; $\mu S \cdot cm^{-1}$ = treated effluent conductivity.

2.2.3 TOC (Total Organic Carbon)

The TOC was determinated by 5310-D/14878 method [25], before and after the photochemical treatment. To calculate the percentage of removal, the Eq. (3) shown as follow.

$$R_{TOC} = [1 - (TOC_o \times TOC_f^{-1})] \times 100 \quad (3)$$

where, R_{TOC} = TOC removal (%); TOC_o = TOC value of effluent before treatment; TOC_f = TOC value after treatment.

2.2.4 Effluent Reutilization

The dyeings made with treated effluent were compared with dyes made with deionized water by visible spectrophotometry, CIELab system, analyzing the deviations of lightness (ΔL^*) and chromaticity (Δb^* and Δa^*). To calculate the total deviation (ΔE^*) was used the Kubelka-Munk equation (Eq. (4)).

$$\Delta L^* = [(\Delta L^* + \Delta a^* + \Delta b^*)]^{1/2} \quad (4)$$

where, ΔE^* = total deviation; ΔL^* = lightness axis deviation; Δa^* = green-red axis deviation; Δb^* = yellow-blue axis deviation.

3. Results and Discussion

3.1 Absorbance

All treatments obtained decolorization efficiency above 92%. The kinetics from all treatments indicated first-order reactions, equation equal to $C = C_o + e^{-kt}$. The data are shown in Table 2 and graphs for the treatment are shown in Fig. 2. The absorbance values admissible for the process of dyeing should be less than 0.05 [26]. The values obtained in all treatments were below than 0.015.

3.2 TOC

The TOC removal of all treatments was above 89%. The values for the rates of TOC before and after treatment are shown in Table 3.

3.3 Conductivity

The amount of NaCl present after each photochemical treatment was determinated by the equation obtained from the calibration curve of the conductivity. For dyeings made with treated effluent and with deionized water, the calculated amounts of NaCl were slaughtered from the original recipe. The data about the concentration of NaCl present in treated effluents are shown in Table 4.

Table 2 Data of photochemical treatments.

Color	Abs_o	Abs_f	D_E (%)	λ_{max} (nm)	t (min)	k (min^{-1})
2237	0.0239	0.0019	92.1	580	60	-1.610
2286	0.0264	0.0011	95.8	660	75	-1.838
2201	0.0464	0.0011	97.6	540	75	-2.225
2205	0.0514	0.0022	95.7	620	120	-1.503
2269	0.0956	0.0042	95.6	540	120	-1.498

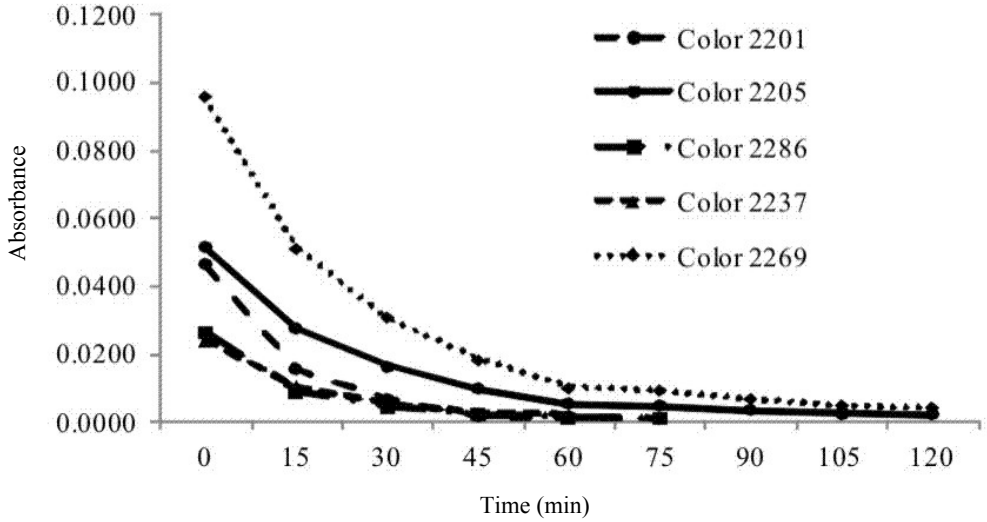

Fig. 2 Graphics of photochemical degradation.

Table 3 TOC removal rates.

Color	TOC_o (mg·L^{-1})	TOC_f (mg·L^{-1})	R_{TOC} (%)
2237	159.00	< 5	96.9
2286	132.00	< 5	96.2
2201	133.00	< 5	96.2
2205	525.00	31	94.1
2269	558.00	60	89.2

Table 4 Concentration of NaCl in treated effluents.

Color	Conductivity (μS·cm^{-1})	NaCl (g·L^{-1})
2237	7,820	3.10
2286	7,980	3.17
2201	8,800	3.49
2205	9,540	3.79
2269	10,180	4.05

3.4 Reuse of the Treated Effluent

In all dyeings, deionized water against treated effluent, the values of total deviation (DE*) did not exceed 1.0, acceptable values for the Brazilian industry of clothing. The colors were assessed by spectrophotometry and the values of partial and total deviations are shown in Table 5.

4. Conclusions

It was observed that with the increase in the number of reuses of the effluent, although the TOC removal rates above 89% in all treatments, there was a increase of 29 mg·L^{-1} from the fourth dyeing to the fifth dyeing, with a final concentration of TOC equal to 60 mg·L^{-1}. There was also an increase in the amount of NaCl from the first dyeing to the last dyeing. The increase in the

Table 5 Deviation between colors developed.

Color	Bath	ΔL^*	Δa^*	Δb^*	ΔE^*
2237	DW	55.27	-8.44	6.81	0.39
	TE	55.37	-8.45	7.19	
2286	DW	61.38	-10.37	-0.39	0.38
	TE	61.60	-10.12	-0.20	
2201	DW	67.97	6.30	4.42	0.45
	TE	68.24	6.51	4.13	
2205	DW	79.99	-18.26	7.19	0.94
	TE	79.26	-18.75	6.85	
2269	DW	65.23	-5.06	38.77	0.63
	TE	65.28	-4.98	38.14	

Legend: DW = deionized water; TE = treated effluent.

rate of NaCl was smaller than the increase in the rate of TOC because the concentration of the salt was detected by conductivity and slaughtered from the posterior recipe. Those facts, joined with the evaporation of the water, suggest a water replacement after a certain number of dyeings. The conventional dyeings would consume 80 L/kg against 40 L/kg used in the dyeing process proposed in this study, representing a great economy of water, with no discharge of effluents.

However, the study was restricted to only a five specific colors and made with four specific dyes. The progressive increase in the rate of TOC, for example, suggests that a water replacement will be necessary at certain time.

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