

DOI: 10.34658/9788366741751.128

BATH EXHAUSTION ON HALOCROMIC DYES

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ABSTRACT

Halochromic dyes change their colour with pH. There is a problem focused on the determination of the concentration for halochromic dyes attached to a fibre. This article studies the influence of halochromism on the absorbance measurement protocol of polyamide dyeing wastewater with Rose Bengal. For this purpose, two dyes are prepared at neutral and acid pH, and their concentrations are to be determined by absorbances of exhaustion and washing wastewaters. In addition, in order to check their fastness, a washing test is carried out on dyed fabrics and on fabrics post treated with a fixer.

KEYWORDS

Halochromism, Acid Red 94, absorbance, wavelength, dye, polyamide.

INTRODUCTION

In exhaustion dyeing, the aim is both, for the dye to enter the fibre and to remain fixed to it, so it is important to know when the fibre is saturated and to determine an optimum concentration for its application. In order to know the precise amount of dye that stays attached, the absorbance measurement method can be used to measure the absorbance of the dyeing wastewater by means of absorption spectrophotometry. For this, it is necessary to comply with Lambert Beer's Law, which relates the absorbance of a substance and its concentration proportionally if a certain saturation is not exceeded, therefore it is necessary that the samples are well diluted [1].

However, halochromism, despite being a quality that can be of interest for many purposes, such as obtaining sensors for healthcare [2], is a property that can be detrimental to the measurement procedure. By altering the colour, the wavelength at which the compound absorbs may be modified, which could lead to inconsistencies in the assessment of concentrations.

In previous investigations, it has been shown that this problem is generated in polyamide dyeing with Rose Bengal, since the halochromism of this dye produces a considerable decrease in colour intensity at highly acid pHs, and its wavelength of maximum absorbance shifts considerably when they are lower than 3.6. (Figure 1).

Rose Bengal dye has antibacterial properties and has been widely used in many chemical-health fields [3]. As a dye applicable to textiles, it is interesting to check at what concentration these antibacterial properties can be obtained by dyeing the fabric. Therefore, in this study, the dyeing of polyamide with Rose Bengal at neutral pH and acid pH is carried out, measuring the absorbances of the wastewater from the processes. In addition, a fixation treatment shall be applied to check by washing whether the fastness is improved.



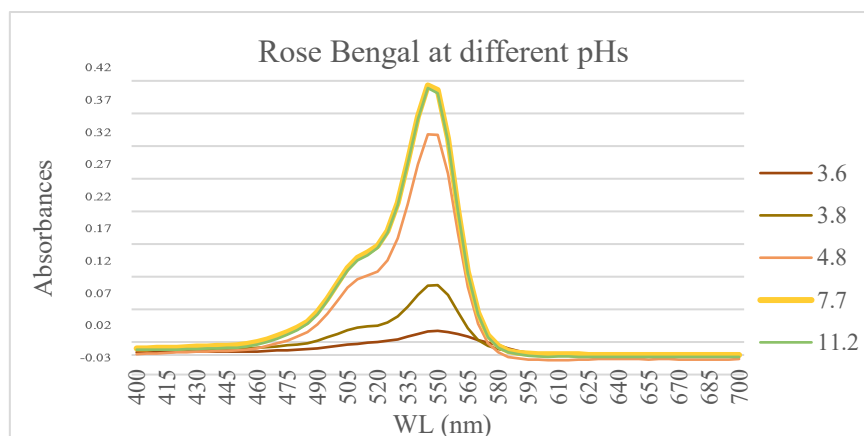


Figure 1. Absorbances of Rose Bengal at different pHs.

MATERIALS AND METHODS

To begin with, two 10 g samples of polyamide fabric were cut and placed in non-ionic wetting agent at 1 g/L at pH 7.7 for about 10 minutes, with this pre-treatment in an attempt to ensure that when dyeing takes place, the fabric is impregnated equally.

The parameters followed to prepare both solutions were: Bath ratio 1/40 and Acid Red 94 (Rose Bengal) dye at 1% over fibre weight (o.f.w). The difference between both preparations will be the application of 1 ml/L acetic acid in one of them.

A pHmeter model Crison pHMETER GLP22 was used to determine the pHs. The pHs obtained were 7.3 in the case of the solution with only distilled water and 3.7 in the case of the solution with acetic acid.

These adjustments were made because Rose Bengal is an acid dye, dyeing is conducted generally at acid pHs. At pH7 it has two negative charges [4] and polyamide has a positive charge. The aim of these tests is to check which provides the best depletion result.

Once the baths were obtained, and it was checked that there were no significant visual differences in colour intensity (Figure 2), the dyeing process was started, which in this case was carried out in Tint control Renigal Multi-mat. The dyeing temperature was 90° C for 60 minutes, adding 10 g/L of Na₂SO₄ at 20 and 40 minutes.



Figure 2. Dye baths pH 3.7 y 7.3.

At the end of the exhaustion process, the intensity and colour of the exhaustion wastewater was observed, and it can be seen (Figure 3) that at first sight it seems that exhaustion at pH 3.7 is higher, as almost no pink can be observed in solution. However, knowing the characteristics of this dye, both baths were brought to pH 11 in order to be able to compare correctly without the influence of halochromism.

Absorbance measurements of all test wastewaters were carried out at wavelength 550 nm using quartz cuvettes inserted in a Zuzi 4251/50 absorbance spectrophotometer.



Figure 3. Dye exhaustion wastewater pH 3.7 (A) to 11 (B) and pH 7.7 (C) to 11 (D).

After dyeing the fabrics, a colour fixation procedure was carried out at pH 7 using 30g/L of PROESfix KN25 cationic fixative for polyamide, the fabrics were split in half to apply the fixative to one of their parts, dipped in the fixative solution at room temperature for 30 minutes, passed through the foulard, dried at 90° C and thermofixed at 150°C for 45 sec.

The washing test was conducted, for the 4 samples obtained, at pH 10, in lintiest Fong's based on the UNE-EN ISO 105-C06:2010 standard, with A1S test conditions: sample cut to 40x100 mm, 150 ml of washing bath, 40° C, 30 min and with 4 g/L of bleach-free detergent and 10 steel balls. In addition, a standardised multi-fibre test piece sewn to one end of the sample.

Once the fabrics were completely dry, the chromatic coordinates were determined with a MINOLTA SPECTROPHOTOMETER CM-3600d reflection spectrophotometer with D65 illuminant and 10° observer.

RESULTS AND DISCUSSION

The concentrations were determined according to the equation of a previously calculated calibration line as shown in Figure 4.

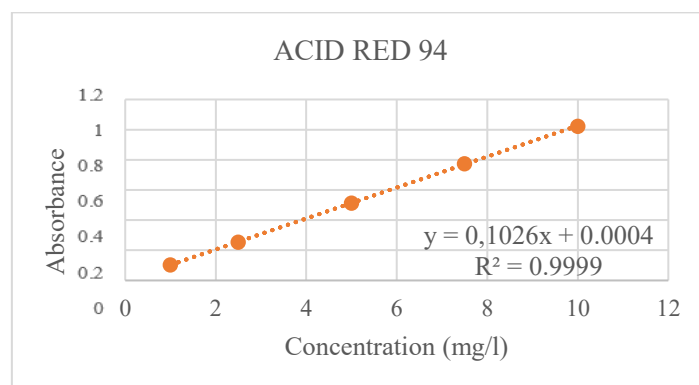


Figure 4. Calibration line Rose Bengal pH7.

The absorbances measured and their concentration calculation are shown in table 1. The percentage of exhaustion achieved is distinguished depending on the pH adjustment made. The value considered significant and appropriate for comparing the exhaustion efficiency of the different baths is that of both adjusted to pH 11, as it shows that, although at first sight it seems that the bath at pH 3.7 has achieved better exhaustion (fig.3), when the pH is adjusted to 11 along with the other bath, the absorbance measured is higher. Taking this into consideration, a % exhaustion of 91% is calculated in the case of the dyeing carried out at pH 3.7 and 98% in the case of the dyeing at pH 7.3. It can also be seen in the results of Table 1, where dilution with water or with a solution at the same pH as the starting pH, modifies the absorbance obtained and therefore, the calculated concentration.

Table 1. Absorbances and concentrations of water wastes.

		Absorbance	Concentration (mg/L)
pH 3.7	Initial solution (1/10 with water)	1.5361	149.678
	Initial solution (1/10 with water and acetic acid)	0.2089	20.322
	Exhaustion	0.0828	0.803
	Exhaustion pH11	1.5031	14.646
	Fixed	0.0806	0.782
	Washing without fixer	0.119	1.156
	Washing with fixer	0.0509	0.492
pH 7.3	Initial solution (1/10 with water)	1.7423	169.776
	Exhaustion	0.311	3.0273
	Exhaustion pH11	0.2923	2.845
	Fixed	0.0477	0.461
	Washing without fixer	0.1164	1.131
	Washing with fixer	0.027	0.259

**Figure 5. Colour fastness to laundry.**

The CIELAB chromatic coordinates obtained are shown in Table 2, from which it is determined that at pH7 the colour intensity is higher, since its L (lightness) is lower and its a (red) is higher. In addition, the coordinates of the fabrics fixed were measured, from which it is noted that the dyed fabric fixed at pH3.7 has an appreciable difference while that at pH7.3 does not.

Table 1. Colour coordinates dyed polyamide at different pHs.

	L	a	b	DE*ab
Acid Red 94 pH3.7	45.939	61.674	-17.963	1.719
Acid Red 94 pH7.3	44.807	62.658	-17.124	

The results of change in colour degradation from laundry, according to the indicated standard, by means of a normalised grey scale, are those indicated in Table 3.

Table 2. Washing degradation index.

	Degradation index
Washing AR94 pH3.7	4/5
Washing AR94 pH3.7 fixed	5
Washing AR94 pH7.3	4
Washing AR94 pH7.3 fixed	4/5

The staining values in the control are not indicated since it was observed that there were no significant differences in colour transfer by areas of the multifibre test piece. It is only noted that the control of the fabric dyed at pH7 without fixer shows higher stain.

CONCLUSION

Considering the variations that can be produced (Table 1), it is highlighted the importance of measuring absorbances at the same pH at which the calibration line was performed. Also, the benefits of fixation have been demonstrated, since in both cases a lower amount of dye was achieved in the waste water from laundry when fixative was applied (Table 1). In this study, the highest colour intensity was achieved at pH 7 (Table 2), which was also the one that left the lowest concentration of dye in the wastewater, although in the determination of degradation and discharge of the washing test it was the one that gave the worst result, therefore, the fact that the washing water has less dye may be due to the fact that the control absorbed higher quantity of dye (Table 3).

ACKNOWLEDGMENT

The authors would like to express appreciation for the support of the sponsors AVI on the Project ref INNEST/2021/28.

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