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Application of Eugenol-Derived Azo Dyes on Natural Textile Fabrics †

Filipa D. P. Mendes [1], Ana M. Fernandes [2], Carla J. Silva [2] and M. Sameiro T. Gonçalves [1,*]

[1] Centre of Chemistry of the University of Minho (CQ-UM), University of Minho, Campus of Gualtar, 4710-057 Braga, Portugal; pg52289@uminho.pt
[2] CITEVE—Technological Centre for Textile & Clothing of Portugal, Rua Fernando Mesquita, 2785, 4760-034 Vila Nova de Famalicão, Portugal; mfernandes@citeve.pt (A.M.F.); cjsilva@citeve.pt (C.J.S.)
* Correspondence: msameiro@quimica.uminho.pt

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Abstract

Eugenol, a natural product abundant in clove oil, represents a promising precursor for the synthesis of azo dyes, proving potential for textile coloration. The eugenol azo dyes were synthesized and characterized, showing stable absorption profiles across a wide pH range. Their application to cotton and wool knitted fabrics by exhaustion dyeing demonstrated good affinity, particularly for wool, while chitosan pretreatment improved washing fastness in cotton. These eugenol-derived azo dyes emerge as promising candidates for sustainable textile coloration.

Keywords: eugenol derivatives; azo dyes; textile dyeing; chitosan

1. Introduction

The textile industry has played a key role in developing technologies and products to meet the aesthetic and functional properties of textiles. The traditional dyeing process based on the use of synthetic dyes has a serious environmental impact. The intensive use of chemicals, water and energy contributes to the production of toxic effluents and the emission of greenhouse gases [1]. Among these environmental impacts, the discharge of dye-containing wastewater represents one of the most persistent challenges [2,3].

Textile effluents are considered highly toxic due to the presence of complex synthetic dyes, particularly azo dyes (-N=N--), which account for approximately 60% of all dyes used in the textile industry [4,5]. These compounds exhibit strong chemical stability and resistance to biodegradation and are often complemented by hazardous substances such as heavy metals, aromatic amines, chlorinated compounds, and various organic solvents [4]. Their release poses significant risks to aquatic ecosystems, soil quality, and human health, thereby constituting a critical environmental challenge requiring mitigation [4,6].

As a result, the industry is increasingly looking for more sustainable alternatives. The exploitation of natural dyes, which offer an ecological solution with less environmental impact, has appeared as a promising possibility, representing an environmentally friendly alternative to synthetic dyes due to their biodegradability and lower toxicity [7–9]. In addition, many of these dyes are bioactive compounds that exhibit properties such as antimicrobial, antioxidant, and aromatic activity, making them ideal candidates for functional textile applications. Compounds such as eugenol derived from essential oils

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have shown great potential for use in the textile industry. Eugenol (4-allyl-2-methoxyphenol) is a metabolite of the phenylpropanoid class that is produced in large quantities by various plants and is especially abundant in the essential oil of cloves (*Syzigium aromaticum*, *Myrtaceae*) [10].

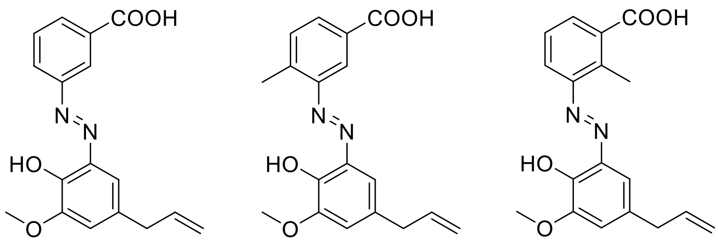
Dyeing is a crucial process in the coloring of textile materials to obtain a uniform and durable colour. The process is influenced by several factors, including the type of pretreatment, the pH of the dyeing solution, the nature of the fiber, the type of dye, the liquor ratio (L:R) and the process parameters such as temperature, time and agitation [11].

This study aims to synthesize azo dyes using the natural bioactive compound eugenol in combination with substituted amines, offering a sustainable and functional alternative to conventional synthetic dyes. Their light absorption properties were evaluated by ultraviolet/visible (UV/Vis) spectroscopy at different pH values, and their applicability in textile finishing processes, specifically exhaust dyeing, was validated while ensuring essential performance criteria such as washing and light fastness.

2. Results and Discussion

*2.1. Sythesis and pH-Dependent Absorption Spectra of Dyes **1–3***

The dyes 3-((5-allyl-2-hydroxy-3-methoxyphenyl)diazenyl)benzoic acid **1**, 3-((5-allyl-2-hydroxy-3-methoxyphenyl)diazenyl)-4-methylbenzoic acid **2** and 3-((5-allyl-2-hydroxy-3-methoxyphenyl)diazenyl)-2-methylbenzoic acid **3** (Figure 1) were successfully synthesized via diazotization of the corresponding amines–3-aminobenzoic acid, 3-amino-4-methylbenzoic acid, and 3-amino-2-methylbenzoic acid–with sodium nitrite in acidic medium, followed by coupling with eugenol in the presence of sodium hydroxide [12].



1 2 3

Figure 1. Structures of the eugenol derived azo dyes **1–3**.

Considering the importance of the different factors in dyeing and subsequent treatments, particularly pH, as mentioned previously, the light absorption properties of the dyes **1–3** were evaluated by UV/Vis spectroscopy across different pH values to assess the effect of acidity and alkalinity on their optical behavior.

Table 1 provides a summary of the corresponding absorption data, while Figure 2 shows the absorption spectra of all compounds at various pH, specifically pH 3, 5, 7, and 8, obtained at dye concentrations ranging from 2.4×10^{-5} to 3.2×10^{-5} M under these conditions.

Table 1. The absorption data of dyes **1–3** at different pH values.

Dye	pH 3		pH 5		pH 7		pH 8	
	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε
1	339	3.92	339	3.93	340	3.96	341	4.25
2	357	4.07	348	3.86	345	3.98	346	4.29
3	347	3.35	346	3.97	345	4.00	347	4.29

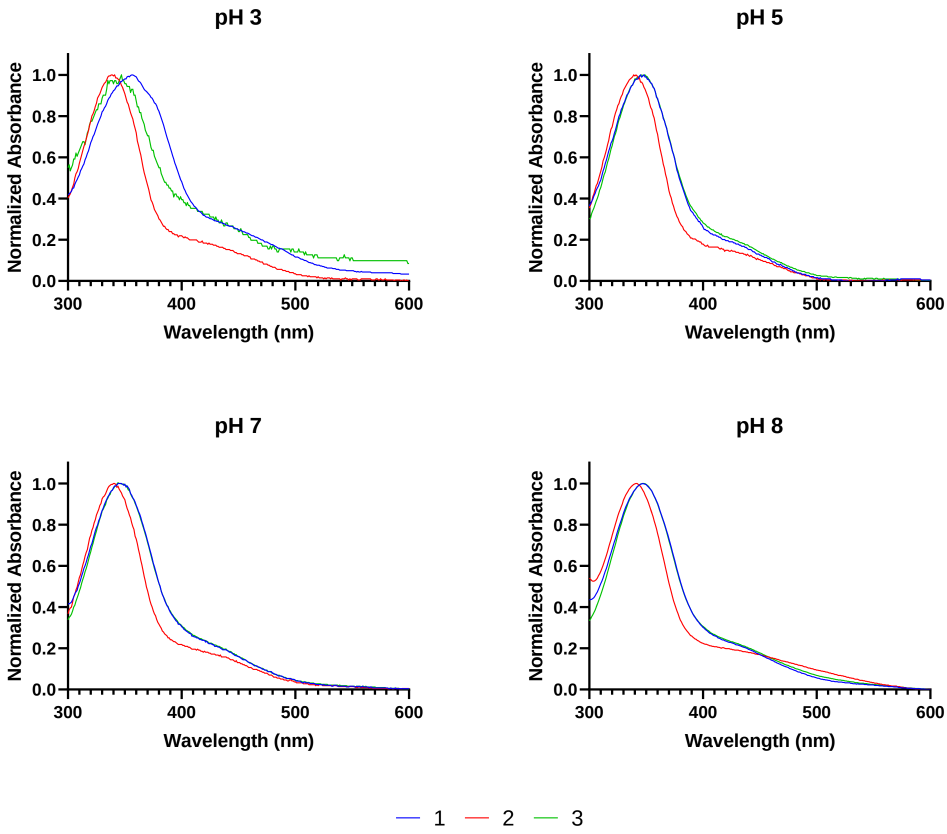


Figure 2. Absorption spectra of dyes **1–3** at different pH values**.**

The eugenol azo dyes **1–3** demonstrate greater spectral stability across the pH range, with relatively constant maximum absorption wavelength (λ_{max}) values. The molar absorption coefficient (ε), expressed as log ε, generally increases as the pH increases from 3 to 8, indicating enhanced absorption efficiency. Notably, the presence and position of the methyl substituent appear to influence this behavior. The compound **3**, which has a methyl group at position 2, exhibits a smaller shift in λ_{max} compared to compound **2**, where the methyl substituent is located at position 4 of the benzoic acid.

2.2. Textile Application by Exhaustion Dyeing

Following previous preliminary studies on the potential of azo dyes **1–3** for reactive dyeing of polyamide [12], their applicability to natural fibers, namely cotton and wool knitted fabrics was assessed. It was also evaluated the effect of substrate modifications (pretreatments), namely with chitosan (CS) (Table 2). Chitosan, a natural polymer, exhibits cationic character due to its protonated amino groups in acidic media, enabling the introduction of positive charges onto fibers and representing an eco-friendly alternative for improving dye affinity [13–15].

The K/S values obtained by exhaust dyeing with the eugenol azo dyes **1–3** revealed differences between cotton and wool substrates, as well as between untreated and pretreatment with chitosan. The wool fibers exhibited higher K/S values than cotton fibers. The chitosan pretreatment enhanced dye uptake in wool fibers, as reflected in the increase in K/S values (excepted in compound **2**). This improvement results from the introduction of amino groups by chitosan, which enhances the dye-fiber interaction through electrostatic and hydrogen bonding. By contrast, the effect of chitosan treatment on cotton was less pronounced, and the K/S values were even lower with the pretreatment.

Table 2. Color shades and color strength (K/S) values obtained by exhaust dyeing of CO, WO, CO-CS and WO-CS with eugenol azo dyes **1–3** at concentrations of 2%. Values are expressed as mean ± standard deviation from n = 3.

Dye	**Untreated**		**Chitosan**	
	CO	**WO**	**CO-CS**	**WO-CS**
1				
K/S ± SD	0.78 ± 0.01	2.64 ± 0.58	0.31 ± 0.01	2.65 ± 0.35
2				
K/S ± SD	0.55 ± 0.01	5.91 ± 0.21	0.50 ± 0.01	4.95 ± 0.21
3				
K/S ± SD	0.98 ± 0.01	3.14 ± 0.06	0.50 ± 0.01	5.36 ± 0.22

Given the significance increase in K/S values observed for chitosan pretreatment on wool knitted fabrics, Table 3 provides the corresponding CIEL*a*b* colorimetric coordinates to complement these findings.

Table 3. CIEL*a*b* coordinates (L*, a*, b*) for dyed WO and WO-CS with eugenol azo dyes **1–3** at concentrations of 2%. Values are expressed as mean ± standard deviation from n = 3.

Dye	**L* ± SD**		**a* ± SD**		**b* ± SD**	
	WO	**WO-CS**	**WO**	**WO-CS**	**WO**	**WO-CS**
1	71.83 ± 0.50	71.49 ± 0.04	13.11 ± 0.93	14.72 ± 0.37	31.33 ± 0.64	33.16 ± 0.53
2	57.60 ± 0.08	63.81 ± 0.71	27.24 ± 0.08	19.15 ± 0.04	37.74 ± 0.57	38.03 ± 0.26
3	68.63 ± 0.66	60.34 ± 0.44	14.44 ± 0.10	20.70 ± 0.44	33.03 ± 0.35	35.61 ± 0.08

The positive a* values for all eugenol azo dyes **1–3** confirm the predominance of red tones. The b* values highlight the yellow component of coloration. Accordingly, the dyes derived from eugenol presented predominantly orange to red shades. The WO-CS samples showed lower L* values (excepted in compound **2**), in agreement with the observed K/S values (highest values), especially for compound **3**.

The washing and light fastness of the dyed fabrics was evaluated (Table 4).

Table 4. Grey-scale classification of CO, WO, CO-CS and WO-CS knits dyed with eugenol-based azo dyes **1–3** at 2% concentration, following washing and light fastness tests.

Dye	**Washing Fastness**				**Light Fastness**			
	CO	**WO**	**CO-CS**	**WO-CS**	**CO**	**WO**	**CO-CS**	**WO-CS**
1	1	1	2	1	4	4	3–4	4
2	1	1	1	1	4	4	3–4	4
3	1	1	2	1	4	4	4	3

The washing fastness results were generally low for all dyes, with grey scale values of 1 for untreated cotton and wool. The chitosan pretreatment slightly improved washing fastness in cotton, reaching grey scale values of 2 for compounds **1** and **3**, while no significant effect was observed in wool.

In contrast, the light fastness results were more favorable, demonstrating higher grey scale values. All samples showed values between 3 and 4, indicating moderate to good stability under light exposure. Chitosan treatment did not markedly enhance light fastness. These results underscore the potential of eugenol azo dyes, although further optimization is still required.

3. Experimental Procedure

3.1. UV/Vis Absorption of the Azo Dyes **1–3**

The absorption properties of dyes **1–3** were determined in aqueous solutions at different pH values (3, 5, 7, and 8), prepared using buffer solutions of boric acid, citric acid, and sodium phosphate. The pH variation assay was carried out according to the protocol described by [16]. The concentrations of the solutions in the different media ranged from 2.4×10^{-5} to 3.2×10^{-5} M.

3.2. Pretreatment

The pretreatment using chitosan was applied by using a solution of 0.5% (*w*/*v*) chitosan containing 2% (*v*/*v*) acetic acid, that was left to stir for 1.5 h at 40 °C.

Each 4 g of knitted fabric was cationized with 80 mL of the solution and then placed in the exhaust dyeing machine Labomat BFA Mathis (Mathis AG, Germany) at 60 °C for 20 min with a heating gradient of 1 °C/min and 25 rpm.

3.3. Exhaustion Dyeing

The dyeing bath (80 mL) was prepared with 5 g/L sodium carbonate, 15 g/L sodium chloride, using a L:R of 1:20, and containing 2% of the dye. The dyeing was performed at 60 °C for 60 min with a heating gradient of 1 °C/min and 25 rpm in the exhaustion machine. At the end of the dyeing process, the dyed cotton or wool sample was washed with warm water and dried in the open air.

For the cotton samples with the pretreatments (CO-CS and WO-CS), the dyeing conditions were maintained, but without the addition of salt (sodium chloride).

3.4. Colorimetric Characterization of the Textiles and Validation Tests

The colour fastness to washing of the dyed textiles was performed in the exhaust dyeing machine at 40 °C with 4 g/L of standard detergent (ECE—Phosphate Reference Detergent) for 30 min with a heating gradient of 2 °C/min and 25 rpm. To assess the colour fastness to light, an internal method was used. The textile samples dyed were exposed to sunlight for 3 consecutive days.

Washing and light fastness was evaluated based on the color differences in the colorimetric coordinates before and after washing/light exposure. The colorimetric characterization of the textile samples was performed in Datacolor SF450 UV Colorimetric System by accessing the colour coordinates from CIEL*a*b* colour space. All measurements were performed on the Datacolor equipment.

4. Conclusions

The eugenol azo dyes **1–3** synthesized exhibited stable absorption profiles across different pH values. Their potential application to dye natural fibers was confirmed by the K/S values and colour coordinates, with enhanced performance on wool compared to cotton knitted. Chitosan pretreatment improved the light fastness in cotton but had limited effect on wool. Despite favorable light fastness, washing fastness remained low, highlighting the need for further optimization of dyeing conditions and pretreatment strategies.

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