ADDRESSING THE ENVIRONMENTAL PROBLEMS OF WASTEWATER: REDUCING THE POLLUTION WHILE PROVIDING MULTIFUNCTIONAL WOOL FABRICS

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Abstract

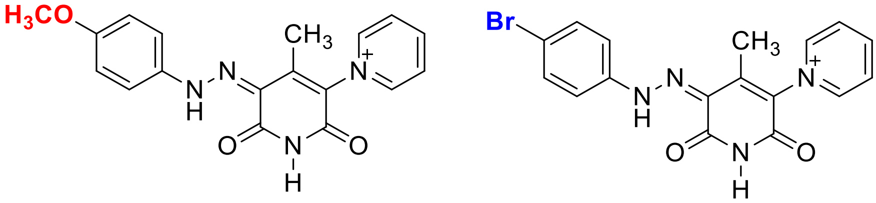
The reduction of water pollution represents one of the priority topics of the EU's goal to achieve climate neutrality by 2050. Considering this, the concept of reusing the same dyebath for multiple dyeing cycles is proposed. For this purpose, two pyridinium-based azo pyridone dyes with improved solubility and affinity towards different fibers, are used for dyeing wool fabric. It is demonstrated that the dye concentration in wastewater could be reduced up to four times by recirculation of the same dyebath 5 times. The dyed fabrics obtained in each cycle are further characterized regarding color strength (*K*/*S*) and ultraviolet protection factor (UPF), while their antioxidant potential is evaluated by ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid)) test. The results revealed that the proposed concept could be used for obtaining multifunctional wool fabrics by following the principles of sustainable development of reducing the effluent load in wastewater.

Introduction

The practices within the textile industry have given rise to numerous environmental and social issues, including high emissions, high water and/or energy consumption and heavy pollution [1]. Among them, the disposal of colored effluents from the textile industry into the natural ecosystem constitutes a major concern. It is estimated that textile production is responsible for about 20% of global clean water pollution from dyeing and finishing products. To tackle the adverse impact on the environment, the European Union aims to reduce textile waste and increase the life cycle and recycling of textiles as part of the plan to achieve a circular economy by 2050 [2]. The proposals encompass boosting sustainable products and empowering consumers to participate in the green transition.

Moreover, much effort has been made to develop eco-friendly dyes from natural sources, but synthetic dyes are still superior due to their excellent dyeing capabilities and color fastness properties. Among them, azo pyridone dyes have gained wide commercial application due to the simplicity of their preparation, good color fastness, high tinctorial strength, thermal and optical stability [3]. Generally, they are applied to textile as disperse dyes, colorants characterized by low water solubility which are, in their colloidal form, suitable for dyeing and printing of hydrophobic fibers. Recently, it has been shown that the introduction of the pyridinium ring into pyridone molecule resulted in enhanced water solubility of the dyes and improved affinity towards various natural and synthetic fibers, especially wool and cellulose diacetate fibers [4].

In order to address environmental issues caused by the textile industry, this work aims to reduce wastewater by using the same dyebath for multiple dyeing cycles while providing multifunctional wool fabrics at the same time. Two pyridinium-based pyridone dyes bearing different substituents in *para*-position of the phenyl ring (Figure 1) were used for dyeing wool fabrics. The results show that the same dyebath can be efficiently used up to 5 times. In addition, the obtained fabrics from different cycles are further characterized by *K*/*S* values and UPF factor, while antioxidant activity is evaluated by ABTS test.



1 **2**

Figure 1. Structure of the pyridinium-based azo dyes used for dyeing wool fabrics.

Experimental

Dyeing experiments

Wool fabric (7 cm × 7 cm) was used for dyeing experiments. The dyeing of the wool was performed at pH 8.5 and 80 °C for 60 min under constant shaking. The dyebath was prepared by dissolving the corresponding amount of dye (1% o.w.f., i.e. on the weight of fiber) in distilled water (C_0 = 0.2 mg/mL). After dyeing, the fabric was washed with warm distilled water and dried in the air at room temperature. The procedure was repeated four times for each dye using the previous dyebath. The dye exhaustion after each dyeing cycle was determined by UV-Vis absorption spectra on a Shimadzu 1700 spectrophotometer.

Characterization of the fabrics

Reflectance fabric spectra were recorded on the Shimadzu UV-Vis-Nir 3600 plus spectrophotometer using Datacolor ColorTools QC version 1.2.1 software. Thereafter, the color strength of dyed fabrics was calculated from the reflectance values (*R*) by using the Kubelka-Munk equation [5]. The fabric UPF was determined according to the standard test method EN 13758–1:2001 + A1:2006 using the Shimadzu UV-Vis 2600 spectrophotometer.

Determination of antioxidant activity

The antioxidant potential of the wool fabrics was determined using ABTS test according to the procedure described in the literature [6].

Results and discussion

The dyes used in this study were characterized previously, and it has been shown that they exist in the hydrazone form in an acidic medium, while in an alkaline medium dyes exist in the equilibrium between hydrazone form (cationic form) and deprotonated (zwitterionic) form [4]. The screening of the dyeing process (by using multifiber fabric) showed that the best dyeing performance was achieved for wool and cellulose diacetate fabrics at pH of 8.5. Thus, in this study, two dyes bearing different substituents (methoxy group (**1**) or bromine atom (**2**), Figure 1) are selected for the dyeing wool fabrics with the aim to reduce waterwaste by using the same dyebath multiple times.

The dye exhaustion after each dyeing cycle was determined by UV-Vis absorption spectra (Figure 2). The results show that the dye exhaustion after the first cycle was relatively low (17 and 20% for dyes **1** and **2**, respectively). Thus, the remaining solution was further used for the next dyeing cycles. The dyeing experiments showed that the same dyebath could be efficiently used for dyeing wool up to 5 times for each dye. After the fifth cycle, the total exhaustion of the dyes was 79 and 82%, for **1** and **2** respectively, indicating that the dye load in the wastewater could be reduced up to four times by recirculation of the same dyebath.

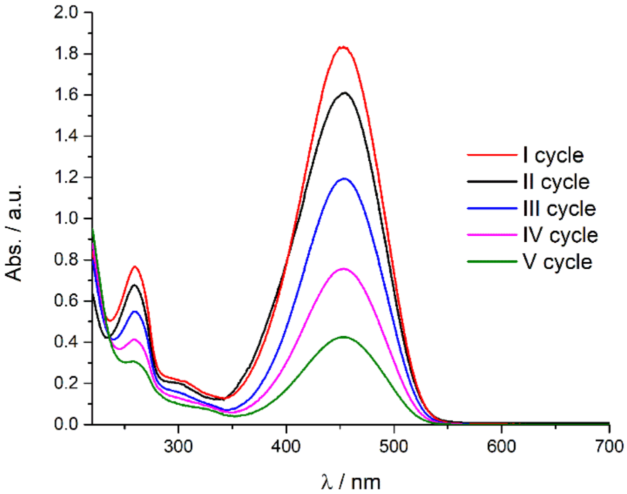


Figure 2. UV-Vis spectra of the dye solutions after each dyeing cycle with dye **1**.

Dyed fabrics were further characterized by reflectance spectra that were further used for the calculation of the color strength (*K*/*S*), Table 1. The results listed in Table 1 show, as expected, that *K*/*S* values decrease with a higher number of dyeing cycles being the highest for the first cycle and the lowest for the fifth cycle. It should be emphasized that even though the decline is substantial, wool fabric *K*/*S* value after the fifth dyeing cycle is still satisfactory (> 1). Considering dyes, it should be pointed out that higher color strength is obtained for bromine-substituted dye **2** for each cycle indicating better adhesion of this dye to wool fabric.

Table 1. *K*/*S* values and the visual appearance of the dyed fabrics for different dyeing cycles

	Dye **1**		Dye **2**	
I cycle	12.74		23.65	
II cycle	5.43		12.44	
III cycle	4.32		6.46	
IV cycle	2.95		3.91	
V cycle	1.62		1.99	

Further, the fabrics are characterized by UPF factor. Obtained results revealed that wool fabrics dyed with dye **2** irrespectively on the dyeing cycle and fabrics dyed with dye **1** for the first three cycles have excellent UV protection (UPF values are 50+). Fabrics obtained after the fourth and fifth dyeing cycles with dye **1** show unsatisfactory UV protection.

Figure 3 depicts the antioxidant activity of the dyed wool fabrics over the different dyeing cycles. The results show moderate radical scavenging ability of the fabrics dyed with **1** for the first three cycles, while fabrics dyed with **2** have low antioxidant potential. It can be also observed that increasing the number of dyeing cycles significantly reduces the antioxidant capability of the wool fabrics dyed with **1**, while for fabrics dyed with **2**, no significant changes in their activity could be observed.

It can be summarized that most of the investigated dyed fabrics, besides good color strength have remarkable UV protection properties and moderate antioxidant activity (in the case of samples dyed with **1** for the first three cycles) and therefore provide additional value to the textile, making them suitable for application as protective fabrics.

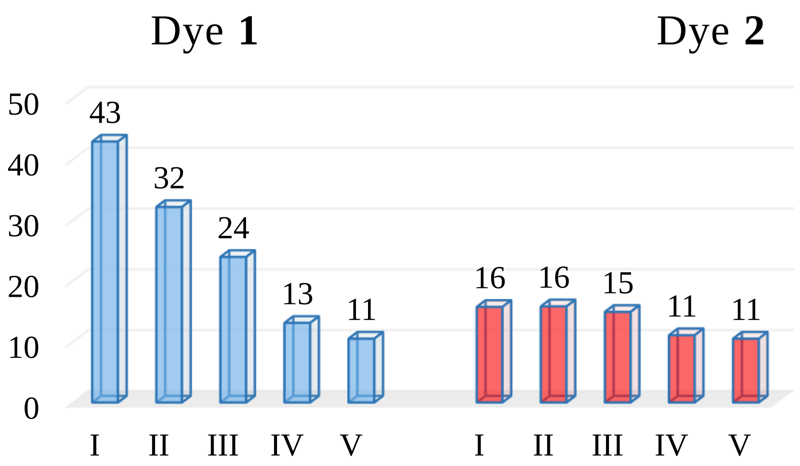


Figure 3. Antioxidant potential of the dyed fabrics for different dyeing cycles.

Conclusion

In this study, two pyridinium-based pyridone azo dyes are used for dyeing wool fabrics. The same dyebath was used 5 times in order to reduce the concentration of the dye in the wastewater (up to 4 times) while providing multifunctional fabrics having different color shades. The obtained wool fabrics are characterized by excellent color strength and remarkable UPF factors (except fabrics dyed with **1**, fourth and fifth cycles). Wool dyed with **1** for the first three cycles shows moderate antioxidant activity. All these properties provide additional value to the textile, making them suitable for protective fabrics. Reusability of the same dyebath for five dyeing cycles will ensure better source usage and recycling that will provide environmental benefits and cost effectiveness of the dyeing process and wastewater treatment.

Acknowledgments

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