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SCIENTIFIC PAPER

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A METHOD FOR DYEING POLYESTER FIBRES WITH QUINONE DERIVATIVES AND EVALUATION OF THEIR ANTIOXIDANT ACTIVITY

Article Highlights

- Ten *S*,*S*-disubstituted-1,4-naphthoquinone compounds were synthesized
- The compounds were applied to polyester fibers and their dyeing properties were investigated
- The staining and rubbing fastnesses of the dyeing were found to be "5"
- The dyes were screened for their antioxidant capacity using the CUPRAC method

Abstract

*In this study, a series of bis(thio)substituted-1,4-naphthoquinone compounds (**4a-j**) were synthesized via Michael addition reaction and their structures were determined by infrared spectrometry, ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy, mass spectrometry and elemental analysis. The synthesized substances were applied to polyester fibers and the dyeing properties were investigated. The rubbing fastness, wash fastness and optical properties of synthesized compounds were also studied. The color change and staining test results were found to be "4" to "4-5" for the most of the dyed samples. There is only a small number of previous studies interested with dyeing properties of synthetic derivatives of heteroatom-substituted-1,4-naphthoquinone compounds in existing literature. The synthesized dyes were screened for their antioxidant activity, using the CUPRAC method against trolox (TR) as the standard reference compound at room temperature. The aims of this study were the synthesis of the quinone compounds, the investigation of the capability of dyeing polyester fibers and the evaluation of their antioxidant capacity, using the CUPRAC method. The dyed polyester fibers are promising candidates for biologically active fabrics to be used in various ways. We were encouraged to do this study in order to determine the dying properties and antioxidant activities of the quinone compounds.*

Keywords: 1,4-naphthoquinone dyes, disperse dyestuffs, dyeing, CUPRAC antioxidant assay.

Some of the pigments related to 1,4-naphthoquinone are found naturally in plant structures such as henna, walnut shells, taiga or lapachol wood, red sanders wood and barwood, and were used as colorants in the past [1]. These dyes produce orange, red, or reddish-brown shades like anthraquinone dyes. The advantage of the naphthoquinone dyes is their strong and stable coloring ability [2,3], so they are extensively used in the cosmetics industry in the production of cosmetic dyes, especially hair dyes [4].

Synthetic naphthoquinone dyes are mainly derived from 2,3-dichloro-1,4-naphthoquinone, due to its availability, inexpensiveness and high chemical reactivity. Certain types of these dyes are used as colorants in many areas. For example, mono- and di-(thio) substituted naphthoquinone dyes, which con-

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tain a naphthoquinone group as a chromophore and sulphur atoms and carbonyl fragments as donor and acceptor groups, are all-purpose coloring dyes and they can provide a full range of colors [5]. Fluoro- and trifluoromethylphenylamino substituted naphthaquinones have been used for coloring wool and polyester. Heterocyclic naphthoquinone derivatives have been gaining importance in the manufacturing of dyes and pigments because of their substantivity to cellulosic and hydrophobic fibers [1].

In addition, heterocyclic compounds bearing 1,4--naphthoquinones have long been the focus of synthetic chemistry due to their broad spectrum of application in the field of biological, pharmaceutical, and material sciences [6]. The naphthoquinone scaffold was an important pharmacophore found in a large number of biologically active compounds [7]. N-, S-, O-substituted-1,4-naphthoquinones are also reported to have good biological properties [8].

Antioxidant activity/capacity is an important parameter used to analyze the free radical scavenging activity of several compounds. This activity is related to compounds which are effective in preserving a biological system against the possible destructive effects of oxidative processes. In addition, it is necessary that the range of novel biological active dyes is increased for the textile industry. In our previous study of new naphthoquinone derivatives, we have found that the synthesized S,S- and S,O-substituted 1,4-naphthoquinones exhibited good antioxidant activity [9] and strong color shades [10]. These encouraging results prompted us to extend the study on other *S*,*S*-substituted-1,4-naphthoquinones derivatives.

In this study, 2,3-substituted-1,4-naphthoquinone dyes synthesized from 2,3-dichloro-1,4-naphthoquinone and aliphatic thiols were used for dyeing polyester fibers and screened for their antioxidant capacity using the CUPRAC antioxidant assay. The synthesis and the spectral properties of these compounds were reported in our previous studies [11,12]. In this work, the properties of dyeing polyester fibers and the coloristic properties of the dyed materials were investigated. The synthesis of N,O-, N,S-substituted-1,4-naphthoquinone compounds and their application in dyeing polyester fabrics have been recently studied [10]. However, there is no published information regarding dyeing polyester fiber with S,S-disubstituted-1,4-naphthoquinone dyes. The synthesized compounds **4a-j** were screened for their antioxidant activity using the CUPRAC method [13] against trolox (TR) as the standard reference compound, at room temperature.

EXPERIMENTAL

Materials

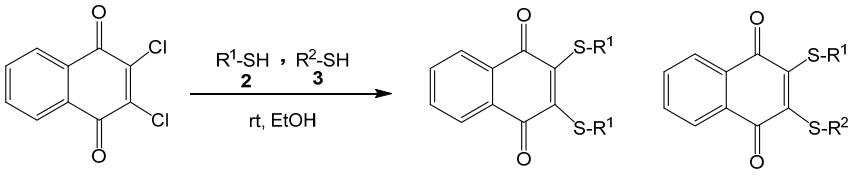
A series of thio-substituted naphthoquinone dyes were used in dyeing of 100% woven polyester fabric (82 g/m^2). The preparation method and the chemical structure of these dyes are given in this section. All chemicals and solvents were obtained commercially and used without purification. An ethoxylated dispersing agent (Setalan DFT) was added to each dyebath. The following chemicals, used for antioxidant capacity measurement, were supplied from their corresponding sources: copper(II) chloride ($CuCl_2$) and ammonium acetate (NH_4Ac) from Merck Chemicals (Darmstadt, Germany); neocuproine (Nc) from Sigma Aldrich Chemicals (Steinheim, Germany).

Preparation of thio-naphthoquinone dyes

Naphthoquinone dyes **4a-j** were synthesized from the reaction of 1,4-naphthoquinone (**1**) with alkyl thiols (**2** and **3**) following the previously reported procedures [11] and confirmed by melting point determination, elemental analysis and IR spectroscopy in comparison with published data [11,12]. Products were isolated by column chromatography on SiO_2 (Fluka Kieselgel 60, particle size 63–200 μm). TLC plates: silica $60F_{254}$ (Merck, Darmstadt), detection with ultraviolet light (254 nm). The melting point was measured on a Büchi B-540 melting point apparatus. Elemental analysis was performed with a Thermo Finnigan Flash EA 1112 elemental analyzer. Infrared (IR) spectra were recorded in KBr pellets in Nujol mulls on a Perkin Elmer Precisely Spectrum One FTIR spectrometer.

Equimolar amounts of 2,3-dichloro-1,4-naphthoquinone (**1**) and S-nucleophile compounds (**2** and **3**) in abs. ethanol (50 mL) were stirred at room temperature. The color of the solution quickly changed and the extent of the reaction was monitored by TLC and then chloroform (30 mL) was added to the reaction mixture. Subsequently, the organic layer was separated, washed with water (4×30 mL) and dried with sodium sulphate (Na_2SO_4). The resulting solution was concentrated in vacuo and the residue was subjected to column chromatography on silica gel using a suitable solvent. The structures of the synthesized (thio)--substituted naphthoquinone dyes **4a-j** are shown in Scheme 1.

4a: m.p. 85-86 °C. $C_{46}H_{78}O_2S_2$: Calculated (%): C, 75.97; H, 10.81; S 8.81; Found (%): C, 74.92; H, 10.67; S, 8.45. IR (KBr), ν / cm^{-1}: 2850, 2919 (C-H); 1656 (C=O); 1590 (C=C).



4a: $R^1 = R^2 = (CH_2)_{17}\text{-}CH_3$ (93%) (1:2 mole/mole)
4b: $R^1 = R^2 = (CH_2)_{15}\text{-}CH_3$ (90%) (1:2 mole/mole)
4c: $R^1 = (CH_2)_{17}\text{-}CH_3$, $R^2 = (CH_2)_{15}\text{-}CH_3$ (56%) (1:1 mole/mole)
4d: $R^1 = (CH_2)_{15}\text{-}CH_3$, $R^2 = CH_2\text{-}CH_3$ (24%) (1:1 mole/mole)
4e: $R^1 = (CH_2)_{17}\text{-}CH_3$, $R^2 = CH_2\text{-}CH_3$ (45%) (1:1 mole/mole)
4f: $R^1 = (CH_2)_{15}\text{-}CH_3$, R^2 = (*tert*-butyl) (50%) (1:1 mole/mole)
4g: $R^1 = (CH_2)_{17}\text{-}CH_3$, R^2 = (*tert*-butyl) (51%) (1:1 mole/mole)
4h: $R^1 = (CH_2)_{15}\text{-}CH_3$, $R^2 = (CH_2)_4\text{-}CH_3$ (50%) (1:1 mole/mole)
4i: $R^1 = (CH_2)_{15}\text{-}CH_3$, $R^2 = (CH_2)_3\text{-}CH_3$ (36%) (1:1 mole/mole)
4j: $R^1 = (CH_2)_{15}\text{-}CH_3$, $R^2 = (CH_2)_2\text{-}CH_3$ (45%) (1:1 mole/mole)

*Scheme 1. The structures of the synthesized bis(thio)substituted quinone derivatives (**4a-j**).*

4b: m.p. 84-85 °C. $C_{42}H_{70}O_2S_2$: Calculated (%): C 75.16, H 10.51, S 9.55; Found C 75.02, H 10.51, S 9.08. IR (KBr), ν / cm^{-1}: 2918, 2851 (C-H), 1656 (C=O), 1590 (C=C).

4c: m.p. 59-60 °C. $C_{44}H_{74}O_2S_2$: Calculated (%): C, 75.58; H, 10.66; S, 9.17; Found (%): C, 75.62; H, 10.33; S, 8.62. IR (KBr), ν / cm^{-1}: 2848, 2915 (C-H); 1666 (C=O); 1589 (C=C).

4d: m.p. 82-83 °C. $C_{28}H_{42}O_2S_2$: Calculated (%): C 70.83, H 8.92, S 13.50; Found C 71.73, H 8.65, S 14.80. IR (KBr), ν / cm^{-1}: 2950, 2917, 2850 (C-H), 1654 (C=O), 1589 (C=C).

4e: m.p. 83-84 °C. $C_{30}H_{46}O_2S_2$: Calculated (%): C, 71.66; H, 9.22; S 12.75; Found (%): C, 71.79; H, 8.78; S, 12.83. IR (KBr), ν / cm^{-1}: 2850, 2917, 2950 (C-H); 1653 (C=O); 1589 (C=C).

4f: m.p. 48-49 °C. $C_{30}H_{46}O_2S_2$: Calculated (%): C 71.66, H 9.22; Found C 71.67, H 9.45. IR (KBr), ν / cm^{-1}: 2954, 2919, 2850 (C-H), 1662 (C=O), 1591 (C=C).

4g: m.p. 58-59 °C. $C_{32}H_{50}O_2S_2$: Calculated (%): C, 72.40; H, 9.49; Found (%): C, 72.02; H, 9.49. IR (KBr), ν / cm^{-1}: 2848, 2922, 2954 (C-H); 1666 (C=O); 1591 (C=C).

4h: m.p. 64-65 °C. $C_{31}H_{48}O_2S_2$: Calculated (%): C 72.04, H 9.36, S 12.40; Found (%): C 72.31, H 9.34, S 11.58. IR (KBr), ν / cm^{-1}: 2950, 2917, 2850 (C-H), 1656 (C=O), 1590 (C=C).

4i: m.p. 66-67 °C. $C_{30}H_{46}O_2S_2$: Calculated (%): C 71.66, H 9.22; Found (%): C 71.87, H 8.97. IR (KBr), ν / cm^{-1}: 2950, 2917, 2850 (C-H), 1655 (C=O), 1590 (C=C).

4j: m.p. 68-69 °C. $C_{29}H_{44}O_2S_2$: Calculated (%): C 71.26, H 9.07; Found (%): C 71.55, H 9.35. IR (KBr), ν / cm^{-1}: 2976, 2950 (C-H), 1655 (C=O), 1590 (C=C).

Dyeing

5 g fabric samples were dyed with 0.4% o.m.f. (% on mass of fibre) of each dye. The exhaust dyeing process was carried out in a laboratory scale HT dyeing machine (Roaches) using a liquor ratio of 40:1. 1 g/L dispersing agent was added to each dyebath. The dyeing was initiated at 30 °C with pH 4.0-4.5. Acetic acid was used to adjust the pH of the dyebath. After 10 minutes, the temperature was raised to 130 °C at a heating rate of 3 °C/min and the dyeing was carried out at 130 °C for 30 min. The dyebath was then cooled down at a cooling rate of 2 °C/min. The samples were taken out from the dyeing tubes and given a reduction washing with 2 g/L sodium dithionite, 2 g/L NaOH (38°Be) and 2 g/L dispersing agent at 75 °C for 25 min. Then, the samples were washed in hot water and rinsed with cold water.

Color measurement

The reflectance values of the undyed, dyed and reduction cleared samples were measured using a Datacolor SF 600+ spectrophotometer. The CIELab values were calculated using Illuminant D65 and 10° Standard Observer values by Datamatch 3.2 software. The specular component included (SCI) mode and a large area view (LAV) 30 mm diameter measurement plate were used in the measurements. The color strength values of the reduction cleared samples were calculated at the wavelengths of maximum absorption in accordance with Equation 1.

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (1)$$

where K and S are absorption and scattering coefficients at the wavelength of maximum absorbance of the dyed material, respectively, and R is reflectance value of the dyed material at the wavelength of maximum absorption in a decimal way (20%R = 0.20R)

Cupric reducing antioxidant capacity (CUPRAC) assay

The CUPRAC method, as described by Apak *et al.* [13] is based on the reduction of a cupric neocup-

roine complex (Cu(II)-Nc), using antioxidants, to the yellow-orange colored cuprous chelate (Cu(I)-Nc). 1 mL of 10 mM $CuCl_2{\cdot}2H_2O$, 1 mL of 7.5 mM Nc, 1 mL of 1.0 M pH 7 NH_4Ac buffer solution and *x* mL of the sample solution (1 mM) and (1.1-*x*) mL DMSO were added into a test tube, respectively. The mixture with a total volume of 4.1 mL was incubated for 30 min, and the absorbance at 450 nm was recorded against a reagent blank using a Perkin Elmer Lambda 35 UV--Vis spectrophotometer using a pair of matched quartz cuvettes of 1 cm thickness. The calibration curves (absorbance *vs*. concentration graphs) of each compound were constructed under the described conditions, and their trolox equivalent antioxidant capacities (TEAC coefficients) were calculated. All determinations were carried out at least three times and in triplicate at each separate concentration of the compounds in order to generate consistent data with statistical errors.

RESULTS AND DISCUSSIONS

A series of *S*,*S*-substituted-1,4-naphthoquinones **4a-j** were synthesized from the reactions of 2,3--dichloro-1,4-naphthoquinone **1** with different thiols (**2** and **3**) for the investigation of their dyeing capability of polyester fiber and the evaluation of their antioxidant capacity. The color analysis of the dyed samples gave information on the change in color attributed by each substituent attached to the compound, as shown in Scheme 1. The reflectance curves and the *K*/*S* graphs of the reduction cleared dyeing are given in Figures 1 and 2, respectively. The dye concentration used for each dyeing was low, so that the low *K*/*S* values and the pale shade dyeing were achieved. The CIELab and tristimulus values of the dyed and reduction cleared samples are summarized in Table 1.

K/*S* values at λ_{max} of the dyed and reduction cleared samples were given in Table 2. Among the dyed samples, three groups appear at three different

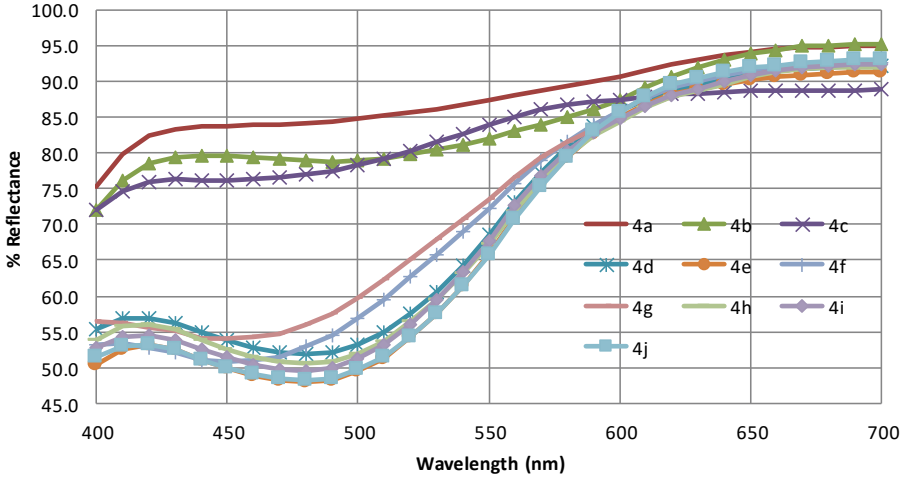


Figure 1. Spectral curves of the dyed and reduction cleared materials.

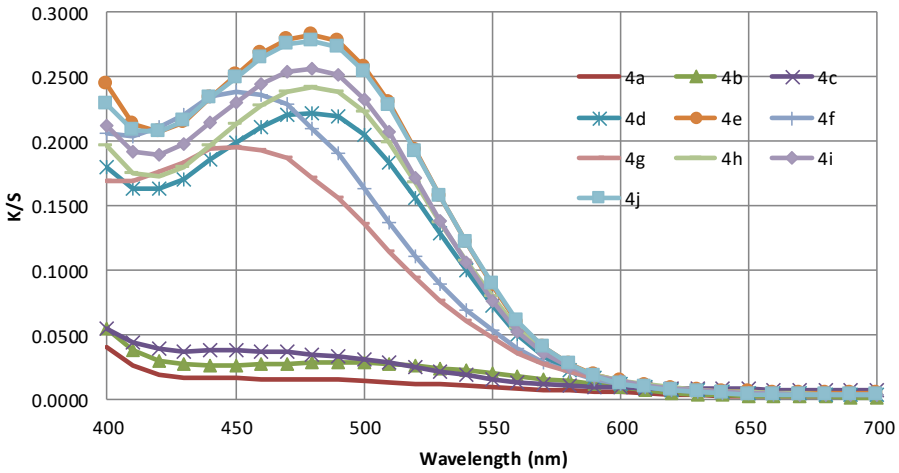


Figure 2. Wavelengths vs. K/S values of the dyed and reduction cleared materials.

Table 1. CIELab and tristimulus values of the dyed and reduction cleared samples

Dye ID	Sample	CIELab Values					Tristimulus values		
		*L**	*a**	*b**	*C**	*h°*	*X*	*Y*	*Z*
-	Blank Dyeing	95.27	1.42	0.65	1.56	24.47	84.43	88.26	93.75
4a	Dyed	94.12	2.13	2.42	3.22	48.59	82.20	85.54	88.33
	Reduction cleared	95.03	1.94	3.05	3.62	57.51	84.16	87.70	89.68
4b	Dyed	92.95	3.41	2.70	4.35	38.35	80.28	82.86	85.13
	Reduction cleared	93.04	3.97	2.98	4.96	36.93	80.77	83.07	84.96
4c	Dyed	92.14	1.99	6.85	7.13	73.77	77.81	81.03	77.71
	Reduction cleared	93.18	2.11	5.46	5.86	68.86	80.13	83.39	81.91
4d	Dyed	87.75	12.07	13.59	18.18	48.38	73.48	71.55	60.57
	Reduction cleared	86.90	12.68	14.50	19.26	48.82	72.02	69.80	58.0
4e	Dyed	85.83	13.16	15.87	20.62	50.33	70.09	67.65	54.63
	Reduction cleared	85.71	14.05	16.44	21.63	49.48	70.26	67.41	53.84
4f	Dyed	87.63	8.09	17.77	19.52	65.52	71.35	71.31	55.88
	Reduction cleared	88.07	8.68	18.70	20.62	65.10	72.51	72.20	55.69
4g	Dyed	89.14	7.14	16.11	17.62	66.09	73.98	74.46	60.43
	Reduction cleared	88.59	7.29	16.43	17.97	66.07	72.92	73.29	59.05
4h	Dyed	86.61	12.95	14.83	19.69	48.88	71.55	69.21	57.10
	Reduction cleared	86.32	12.96	14.66	19.57	48.52	70.98	68.63	56.77
4i	Dyed	86.40	12.09	15.28	19.48	51.65	70.73	68.79	56.27
	Reduction cleared	86.36	12.92	15.98	20.55	51.04	71.03	68.70	55.45
4j	Dyed	84.97	15.27	18.67	24.12	50.72	69.34	65.95	50.35
	Reduction cleared	85.84	14.49	16.52	21.97	48.75	70.71	67.66	53.98

Table 2. K/S values at λ_{max} of the dyed and reduction cleared samples

Dye	R^1	R^2	Molecular mass of dye, g/mol	*K/S*	λ_{max} / nm
4c	$-(CH_2)_{17}-CH_3$	$-(CH_2)_{15}-CH_3$	699.21	0.0545	400
4b	$-(CH_2)_{15}-CH_3$	$-(CH2)_{15}-CH_3$	671.15	0.0544	
4a	$-(CH_2)_{17}-CH_3$	$-(CH_2)_{17}-CH_3$	727.20	0.0405	
4f	$-(CH_2)_{15}-CH_3$	$-C(CH_3)_3$	502.80	0.2382	450
4g	$-(CH_2)_{17}-CH_3$	$-C(CH_3)_3$	530.88	0.1959	
4e	$-(CH_2)_{17}-CH_3$	$-CH_2-CH_3$	502.82	0.2853	480
4j	$-(CH_2)_{15}-CH_3$	$-(CH_2)_2-CH_3$	488.30	0.2777	
4i	$-(CH_2)_{15}-CH_3$	$-(CH_2)_3-CH_3$	502.82	0.2558	
4h	$-(CH_2)_{15}-CH_3$	$-(CH_2)_4-CH_3$	516.85	0.2416	
4d	$-(CH_2)_{15}-CH_3$	$-CH_2-CH_3$	474.7	0.2217	

λ_{max}, namely 400, 450 and 480 nm. The samples **4a-c** had a maximum absorbance wavelength of 400 nm and they have two substituents with long linear chains and high molecular weights. As expected, they gave dyeing with low chroma *C** values (5.86, 4.96 and 3.62). The samples **4f** and **g** had a maximum absorbance wavelength at 450 nm. The chroma *C** values of these samples were 20.62 and 17.97, respectively. These dyes have two substituents with a linear long chain and a branched short chain. In terms of the chroma *C** and *K/S* values, better dyeing was obtained in the following order: **4e** (21.63) > **4j** (21.97) > **4i** (20.55) > **4h** (19.57) > **4d** (19.26).

The colour coordinates of the samples are given in Table 1 and in Figure 3. An increase in (+*a**) means the colour is getting reddish and an increase in (-*a**) means the colour is getting greenish. Also, an increase in (+*b**) means the colour is getting yellowish, and an increase in (-*b**) the colour is getting blueish. As shown in Figure 3, the colors of the dyeing were divided into three groups. The actual shades obtained with these dyes were pale pink in color. The first group is the substituted dyes with two long linear

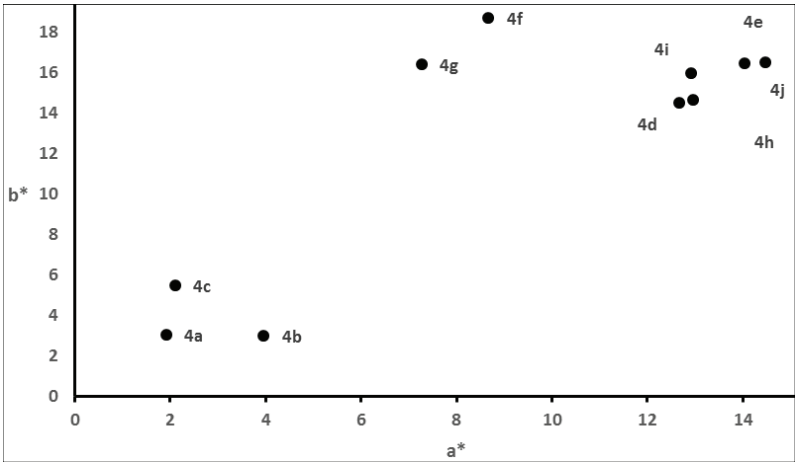


Figure 3. CIELab a b* diagram of bis(thio)naphthoquinone dyes and reduction cleared samples.*

chains. These gave less reddish and less yellowish shades than the other dyes. The dyes in the second group have substituents with one long chain and one short branched chain. These gave less reddish shades than the third group but more reddish-yellowish shades than the first group. The third and the largest group among these dyes are those substituted with one long and one short linear chain. These are the most reddish and yellowish in shade.

The total color differences and the hue differences between the dyeings, were calculated in accordance with CIELab 1976 formulas given in Eqs. (2) and (3):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2)$$

$$\Delta H^* = \sqrt{(\Delta E^*)^2 - (\Delta L^*)^2 - (\Delta C^*)^2} \quad (3)$$

where ΔL^*, Δa^*, Δb^* and ΔC^* are differences between the color coordinates of the batch, and the standard. ΔE^* and ΔH^* are the total color difference and the hue difference between the batch and the standard, respectively.

If the total color differences (ΔE^*) between the colors of these groups are calculated, the color difference, $\Delta E^*_{(\mathbf{4a,4f})}$, between **4a** (batch) and **4f** (standard) is 18.4, which is above the tolerance level. This is due to the high chroma differences between the two colors. However, the hue difference, $\Delta H^*_{(\mathbf{4a,4f})}$ is 1.05, which indicates that there is a slight hue difference between these colors. Between **4j** (batch) and **4a** (standard) colors, $\Delta E^*_{(\mathbf{4j,4a})}$ is 20.57, and it is a very big color difference. However, there is only a slight increase in the hue difference, $\Delta H^*_{(\mathbf{4j,4a})}$, which is 1.39. An extreme hue difference was found between **4g** (batch) and **4j** (standard) colors, where $\Delta E^*_{(\mathbf{4g,4j})}$ is 7.71, but the hue difference, $\Delta H^*_{(\mathbf{4g,4j})}$ is 5.99. This is a significant hue difference, and the sign of $\Delta H^*_{(\mathbf{4g,4j})}$ is positive, which indicates that the shade becomes yellowish.

The wash fastness test of the dyed fabrics was determined using James Heal GyroWash equipment in accordance with BS EN ISO 105-C06 standard (Table 3) [14]. The "dry" and "wet" rubbing fastness test was carried out using a James Heal crockmeter in accordance with BS EN ISO 105-X12 standard and the results were very good [15]. The light fastness test was carried out in a James H. Heal Microsol light fastness tester by exposing the dyed samples and the blue scale fabrics to 250 W UV light bulb at 40 °C for 40 h. The washing and rubbing color fastness test results for the reduction cleared samples are given in Table 4. The samples did not stain the multifibre at all and the results for all of the samples were found to be "5", in accordance with the gray scale for staining. However, the color changes were found to be "4" to "4-5" for most of the dyed samples, except for the sample **4j,** which was "3-4". The light fastnesses of these dyes were not good and were found to be "1" in the blue scale rating.

The synthesized compounds **4a-j** were assessed for their antioxidant capacity using the CUPRAC methods [13] against trolox as the standard reference compound at room temperature. The linear calibration equations of these compounds (as absorbance in a 1 cm cell *vs.* molar concentration) gave the molar absorption coefficient as the slope. The molar absorptivity of the tested antioxidant compound divided by that of trolox, under the same conditions, gave the TEAC or TEAC coefficient (unitless) of that compound tested for antioxidant power (Table 4). Actually, this corresponds to the number of trolox equivalents given by a compound in reducing antioxidant capacity assays. Among the synthesized dyes, **4g** showed the maximum antioxidant capacity,

Table 3. Washing and rubbing fastness test results of the reduction cleared samples; Ac: cellulose acetate; Co: cotton; PA: polyamide; PES: polyester; PAN: acrylic; Wo: wool

Dye ID	Washing fastness							Rubbing fastness	
	Colour change	Staining							
		Ac	Co	PA	PES	PAN	Wo	Dry	Wet
4a	4-5	5	5	5	5	5	5	5	5
4b	4-5	5	5	5	5	5	5	5	5
4c	4	5	5	5	5	5	5	5	5
4d	4	5	5	5	5	5	5	5	5
4e	4	5	5	5	5	5	5	5	5
4f	4	5	5	5	5	5	5	5	5
4g	4	5	5	5	5	5	5	5	5
4h	4	5	5	5	5	5	5	5	5
4i	4-5	5	5	5	5	5	5	5	5
4j	3-4	5	5	5	5	5	5	5	5

Table 4. Calibration equations of synthesized compounds, linear ranges and TEAC coefficients; $TEAC_{compound} = \varepsilon_{compound} / \varepsilon_{TR}$ (TR: trolox); $\varepsilon_{TR} = 1.59\times10^{4}$ L mol^{-1}cm^{-1} (in DMSO)

Compound	Working range, mol L^{-1}	Calibration equation	Correlation coefficient (r)	CUPRAC-TEAC
4a	2.20×10^{-5}-1.17×10^{-4}	$y = 4836x + 0.014$	0.9932	0.304
4b	1.96×10^{-5}-1.21×10^{-4}	$y = 4221x + 0.027$	0.9960	0.266
4c	2.26×10^{-5}-1.20×10^{-4}	$y = 4426x + 0.020$	0.9841	0.278
4d	2.18×10^{-5}-1.18×10^{-4}	$y = 4672x + 0.008$	0.9890	0.294
4e	3.26×10^{-5}-1.53×10^{-4}	$y = 3648x - 0.001$	0.9789	0.230
4f	2.55×10^{-5}-1.19×10^{-4}	$y = 5246x - 0.014$	0.9918	0.330
4g	2.74×10^{-5}-1.28×10^{-4}	$y = 7377x - 0.082$	0.9816	0.464
4h	2.72×10^{-5}-1.25×10^{-4}	$y = 3566x - 0.017$	0.9944	0.224
4i	2.47×10^{-5}-1.23×10^{-4}	$y = 5697x - 0.031$	0.9994	0.328
4j	2.58×10^{-5}-1.27×10^{-4}	$y = 4426x + 0.006$	0.9868	0.278

and the CUPRAC-TEAC coefficients (in parentheses) decreased in the following order: **4g** (0.464) > **4f** (0.330) > **4i** (0.328) > **4a** (0.304) > **4d** (0.294) > **4c,4j** (0.278) > **4b** (0.266) > **4e** (0.230) > **4h** (0.224). Dyes **4g** and **4f** showed the highest antioxidant potential, possibly due to their structures with *tert*-butylthio groups (moiety). Seemingly, Prochaska et al. (1985) found that *tert*-butylhydroquinone was the most active chemoprotective (cancer protective) enzyme inducer [16]. Laguerre et al. (2009) have also reported that antioxidant activity increases as the alkyl chain is lengthened [17].

CONCLUSIONS

In this study, ten thio-substituted naphthaquinone dyes were synthesized **4a-j**, applied to polyester fabric and their antioxidant capacity using the CUPRAC method was evaluated. The dyeing, coloristic and fastness properties of the dyeings to washing, rubbing and light were investigated. The results obtained from washing and rubbing fastness processes of the dyeings were good. Due to their high molecular weight, the penetration of the substituted dyes with two long chain groups gave the worst dyeing. However, the thio-substituted dyes with a short and non-branched chains gave slightly better dyeing. According to the evaluation of antioxidant capacity results, dyes **4g** and **4f** showed the highest antioxidant potential, possibly due to their structures with *tert*-butylthio groups [17]. Antioxidant activity increases as the alkyl chain is lengthened. These dyes are believed to potentiate the development of some new multi-purpose antioxidants with enhanced antioxidant activity.

In conclusion, the synthesis of active derivatives which are produced through simple procedures should be of increasing interest, as these derivatives have a potential for future applications due to their dyeing properties and the colored polyester fibers could be applied as biologically active fabrics and used in various ways.

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NAUČNI RAD

BOJENJE POLIESTARSKIH VLAKNA POMOĆU HINONSKIH DERIVATA I ODREĐIVANJE NJIHOVE ANTIOKSIDATIVNE SPOSOBNOSTI

*U ovom radu je prikazana sinteza bis(tio)-supstituisanih 1,4-naftohinonskih jedinjenja (**4a-j**) Michael adicijom. Struktura sintetisanih jedinjenja je određena pomoću IR, ^{1}H- i ^{13}C-NMR spektroskopije, masene spektrometrijom i elementarne mikroanalize. Sintetisana jedinjenja su naneta na poliesterska vlakna pa su proučavane njihove karakteristike kao boja. Takođe, proučavana je njihova postojanost na trljanje, brzina ispiranja i optička svojstva. Promena boje i test bojenja pokazali su za većinu obojenih uzoraka vrednosti "4" i "4-5". Mali broj ranijih istraživanja se bavio bojenjem pomoću sintetičkih derivata heteroatom-supstituisanih-1,4-naftohinonskih jedinjenja. Antioksidativna aktivnost sintetisanih boja je, takođe, testirana pomoću CUPRAC metode, korišćenjem troloksa kao standarda na sobnoj temperaturi. Cilj ovog rada bila je sinteza hinonskih jedinjenja, njihovo testiranje kao boja za poliesterska vlakna i određivanje njihove antioksidativne aktivnosti korišćenjem CUPRAC metodom. Obojena poliesterska vlakna predstavljaju obećavajuća biološki aktivna vlakna raznovrsne primene.*

Ključne reči: 1,4-naftohinonske boje, disperzne boje, bojenje, antioksidativna metoda CUPRAS.