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Dyeing of wool with natural anthraquinone dyes from *Fusarium oxysporum*

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Abstract

Two anthraquinone compounds are described which were produced by liquid cultures of *Fusarium oxysporum* (isolate no. 4), isolated from the roots of citrus trees affected with root rot disease. These anthraquinone compounds are 2-acetyl-3,8-dihydroxy-6-methoxy anthraquinone or 3-acetyl-2,8-dihydroxy-6-methoxy anthraquinone. Dyeing of wool fabrics with these new anthraquinone compounds as natural dyes has been studied. The values of dyeing rate constant, half-time of dyeing and standard affinity have been calculated and discussed. The effect of dye bath pH, salt concentration, dyeing time and temperature were studied. Colour strength values and the dye uptake were high. The results of fastness properties of the dyed fabric were good.

Keywords: Natural dyes; Anthraquinone; Dyeing; Wool; Kinetic; Fungi; *Fusarium oxysporum*

1. Introduction

Recently a revival interest in the use of natural dyes in textile coloration has been growing. This is a result of the stringent environmental standards imposed by many countries in response to the toxic and allergic reactions associated with synthetic dyes [1]. Natural dyes are friender to the environment than synthetic dyes and can exhibit better biodegradability and generally have a higher compatibility with the environment [2–4].

The production and evaluation of microbial pigments as textile colorants is currently being investigated [5]. Fungi are more ecological interesting source of pigments, since some fungal species are rich in stable colorants such as anthraquinone [6–9]. Anthraquinone derivatives were previously isolated from the fungus *Dermocybe sanguinea* [10]. A number of anthraquinone derivatives, Fig. 1, have been identified from various species of fungi and Lichens [11]. These metabolites are of interest because many of them possess significant antibiotic activity, primarily against Gram-positive bacteria and *Pseudomonas aeruginosa*. Anthraquinones are also reported to have antiprotozoal and cytotoxic activities [12,13].

The purpose of this research is to evaluate the anthraquinone dyes isolated from the fungus *Fusarium oxysporum* in dyeing wool and their effectiveness on different factors affecting dyeability and fastness properties.

2. Experimental

2.1. Materials

Anthraquinone compounds extracted from the culture of *F. oxysporum* are used as natural dyes.

Scoured and bleached wool fabric with the following characteristics was purchased from Misr for Spinning and Weaving Company, Mahalla El-Kobra, Egypt; weight 205 g m^{-2}, 72 ends per inch, 64 picks per inch. Before using, the fabric

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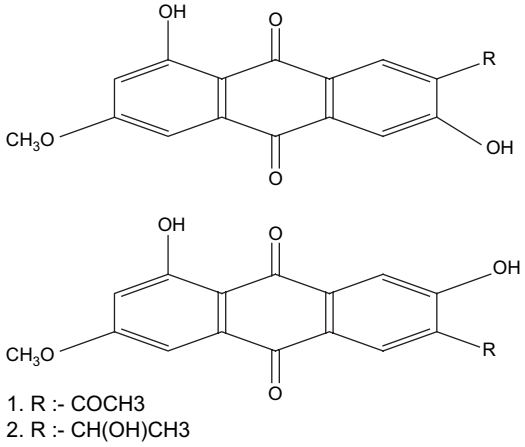

Fig. 1. Structure of *F. oxysporum* anthraquinone.

was treated with a solution containing 5 g L^{-1} nonionic detergent (Hostapal CV, Clariant), at 50 °C for 30 min.

Then, the fabric was thoroughly washed with water and air dried at room temperature.

2.2. Methods

2.2.1. Fungal isolates

Five isolates of *F. oxysporum* were isolated from naturally infected feed roots of citrus trees affected by wilt and root rot disease [14,15]. *F. oxysporum* (isolate no. 4) with highly pinkish purple pigment on PDA medium was used in this study to evaluate their ability in producing anthraquinone dyes.

2.2.2. Cultures grown

Cultures of *F. oxysporum* (isolate no. 4) were grown on a defined mineral salts–glucose medium [16]. This medium contains the following, in ppm; $NaNO_3$, 848; KCl, 300; $MgSO_4 \cdot 7H_2O$, 165; NaH_2PO_4, 100; $CaCl_2 \cdot 2H_2O$, 40; H_3BO_4, 5.7; $FeSO_4 \cdot 7H_2O$, 5.0; $ZnSO_4 \cdot 7H_2O$, 4.4; $MnSO_4 \cdot H_2O$, 3.1; $Na_2MoO_4 \cdot 2H_2O$, 25; $CuSO_4 \cdot 5H_2O$, 0.4; and glucose, 20,000. Mineral salts and glucose solutions were autoclaved separately and combined after cooling in culture flasks in a sterile laminar-flow hood. All flasks were inoculated by a mycelial disk (5 mm diam.) from PDA culture of *F. oxysporum* which were grown at 27 °C in the dark as stationary cultures for 4–6 weeks.

2.2.3. Extraction

Cultures were filtered after 4–6 weeks, and the filtrate was adjusted to pH 3 with HCl. The acidified filtrate was then passed through a column of Amberlite XAD-7 for absorption of the pigments.

Compounds were removed from the column by elution with acetone, the acetone being removed using a Buchi rotary evaporator and the aqueous phase extractions were combined and reduced using the rotary evaporator for chromatographic analysis.

2.2.4. Chromatography

Column chromatography was performed on a 5 × 20 cm column packed with Kieselgel 60 reinst (70–230 mesh ASTM) that had been deactivated with acetic acid and H_2O, washed with acetone and then chloroform. The sample was loaded in chloroform, then eluted with chloroform, followed by consecutive elutions with chloroform containing acetone at 3, 8 and 20%; fractions eluted from the column were purified by TLC on 250 μm silica gel GF plates, using (A) benzene–nitro methane–acetic acid (75:25:2) or (B) chloroform–methanol–acetic acid (195:5:1). The R_f values (15 cm) for compound **1** in solvent system A and B were 0.65 and 0.55; for compound **2**, 0.30 and 0.08.

2.2.5. Toxicity assay

Filtrate extract (10 mL) and 100 mL of different concentrations of eluated anthraquinone pigment were prepared for testing by diluting with 0.2 mL of ethanol, applied to sterile 9 cm diam. Whatman No. 1 filter paper disks in Petri dishes, and drying a sterile laminar-flow hood. After all solvent was removed, 5 mL of sterile water was added. Then 10 surface disinfected seeds of sour orange, Rangpur lime and Volkamer lime were placed on the wetted paper. Ten Petri dishes were used as replicates for each treatment. After 21 days of incubation at 27 ± 1 °C, total root growth (germination) was measured and compared to control (untreated), and expressed as root growth inhibition %.

2.2.6. NMR and mass spectra

^{1}H NMR spectra at 270 MHz with tetramethyl silane as an internal standard in deuterated chloroform and mass spectra (MS) were obtained through Central Lab of Service in National Research Center.

2.2.7. Dyeing procedure

Dye bath containing different amounts of sodium chloride (0–20 g L^{-1}) and the calculated amount of the dye with liquor ratio 40:1 was heated at different durations (12–120 min) and at different temperatures (30–100 °C).

The dyed samples were rinsed with cold water, washed in a bath of liquor ratio 40:1 using 3 g L^{-1} nonionic detergent (Hostapal CV, Clariant) at 50 °C for 30 min, then rinsed and finally dried at ambient temperature.

The pH values were recorded with Hanna pH meter and adjusted with dilute solutions of sodium carbonate.

2.2.8. Dyeing rate

The wool fabric samples were cut into pieces approximately 1 cm^2 and dyed at pH 2.5 in a beaker with 160 mL aqueous solution containing 1 g nonionic wetting agent (Hostapal CV, Clariant) and the calculated amount of the dye at liquor ratio 40:1 and at 100 °C with frequent shaking.

2.3. Colour strength

The reflectance of the soaped samples was measured on a Perkin–Elmer Lambda 3B UV/vis spectrophotometer.

Relative colour strengths (*K/S* values) were determined using the Kubelka–Munk equation [17].

$$K/S = \frac{(1-R)^2}{2R} - \frac{(1-R)^2}{2R_0} \quad (1)$$

where R is the decimal fraction of the reflectance of dyed fabric, R_0 is the decimal fraction of the reflectance of undyed fabric, K is the absorption coefficient, and S is the scattering coefficient.

2.4. UV/vis absorption spectra

The UV/vis absorption spectra in water were recorded using a Shimadzu UV/vis spectrophotometer. The quantity of dye uptake was estimated using the following equation:

$$Q = (C_0 - C_f)V/W \quad (2)$$

where Q is the quantity of dye uptake (mg/g), C_0 and C_f are the initial and final concentrations of dye in solution ($mg\,L^{-1}$), respectively, V is the volume of dye bath (L) and W is the weight of fabric (g). The concentration of dye solutions was determined after reference to the respective calibration curve of the dye using Lambert–Beer's law.

2.5. Fastness testing

The dyed samples were tested according to ISO standard methods. The specific tests were as follows: ISO 105-X12 (1987), colour fastness to rubbing; ISO 105-C02 (1989), colour fastness to washing; ISO 105-E04 (1989), colour fastness to perspiration; and ISO 105-B02 (1988), colour fastness to light (carbon arc).

3. Results and discussion

Our experiments showed that cultures of *F. oxysporum* developed heavy floating mycelial mats, and began elaborating dark red pigments which leaked into the medium after one month from incubation at 27 ± 2 °C in the dark.

3.1. Dye extraction

Extraction of culture filtrate of *F. oxysporum* and spectrophotometric measurements show that there are two compounds.

3.1.1. Compound **1** (2-acetyl-3,8-dihydroxy-6-methoxy anthraquinone or 3-acetyl-2,8 dihydroxy-6-methoxy anthraquinone)

MS *m/z*: 312 (74%), 297 ($M^+ - CH_3$) 100%, 312 ($C1_7H_{12}O_6$) requires 312.0632, found 312.0638; yellow needles, MeOH; mp: 256–270 °C; IR^{KBr} (cm^{-1}): 1672, 1655, 1630, 1575, 1480, 1450, 1410^{max}, 1380, 1300, 1300, 1250, 1205, 1170, 1125, 1025, 970, 935w, 905, 890w, 865w, 830, 805, 755, 745, 715, 695; UV^{MeOH} (nm): 233, 280, 307sh, 348, 420^{max}, ($\log E$ 4.25, 4.43, 4.05, 3.68, 3.54); ^{1}H NMR: 2.81(3H, s, CH_3C), 3094 (3H, s, MeO-6), 6.74 (1H, d, $J = 2.5$, H-7), 7.39 (1H, d, $J = 2.5$, H-5), 7.81 (1H, s, H-4), 8.76 (1H, s, H-1), 12.90 (1H, s, OH 2 or 3), 12.90 (1H, s, OH-8), addition of D_2O removes both OH signals.

This yellow compound (Fig. 1) has an M^+ at *m/z* 312 consistent with the formula $C_{17}H_{12}O_6$. The aromatic protons between 6.74 and 8.76 indicate the anthraquinone structure. The ^{1}H NMR spectrum shows a three-proton singlet at 2.81, a methyl group adjacent to a carbonyl; a three-proton singlet at 3.94, a methoxy group; two one-proton doublets at 6.74 and 7.39, with coupling constants characteristic of a disubstituted A ring; two one-proton singlets at 7.81 and 8.76 indicating another disubstituted aromatic ring (the proton at 8.76 is adjacent to a deshielding nucleus); there are also chelated hydroxyls at 12.72 and 12.91. The IR spectrum shows no hydroxyl absorption and shows three bands in the region between 1600 and 1700 cm^{-1} at 1672, 1655 and 1630 cm^{-1}; the band at 1672 represents a chelated carbonyl, that at 1630 an unchelated carbonyl and that at 1655 a carbonyl which could be chelated [18]. An acetyl group in the 2-position is the deshielding nucleus next to the proton at 8.76, while a hydroxyl in the 3-position is chelated to the acetyl carbonyl and accounts for the hydroxyl resonance at 12.72 [19]. A hydroxyl group in the 8-position is chelated to the quinone carbonyl (1672 cm^{-1}), and a methoxy group in the 6-position completes the structure.

3.1.2. Compound **2** (2-(1-hydroxyethyl)-3,8-dihydroxy-6-methoxy anthraquinone or 3-(1-hydroxyethyl)-2,8-dihydroxy-6-methoxy anthraquinone)

MS *m/z*: 314 (29%), 296 ($M - H_2O$) 100%, 314 ($C_{17}H_{14}O_6$) requires 314.0788, found 314.0771; orange needles, $CHCl_3$; mp: 208–212 °C; IR^{KBr} (cm^{-1}): 3420, 1667, 1630, 1580, $1480w^{max}$, 440, 1390, 1360, 1305s, 1270, 1240sh, 1215, 1160, 1080, 1030, 1005, 970, 930, 900, 875, 835, 800; UV^{MeOH} (nm): 219, 285, 305sh, 341, 466 ($\log E$ 4.31^{max}, 0.49, 4.01, 3.63); ^{1}H NMR: 1.68 (3H, d, $J = 6$, CH_3-CHOH), 3.93 (3H, s, MeO-6), 5.20 (1H, q, $J = 6$, CH_3-OH), 6.70 (1H, d, $J = 2.5$, H-7), 7.35 (1H, d, $J = 2.5$, H-5), 7.76 (1H, s, H-4), 7.94 (1H, s, H-1), 12.96 (1H, s, OH-8), addition of D_2O removes signal at 12.96.

This orange compound (Fig. 1) has an M^+ at *m/z* 314. The ^{1}H NMR spectrum shows a three-proton doublet at 1.68, a methyl group split by a single hydrogen; a three-proton singlet at 3.93, a methoxy group; a proton quartet at 5.20 split by a methyl group; two one-proton doublets at 6.70 and 7.35 characteristic of a disubstituted A ring; two one-proton singlet at 7.67 and 7.94 indicating another disubstituted aromatic ring and there is one chelated hydroxyl group at 12.96. The IR spectrum shows an absorption band which is sharp at 3420 cm^{-1} (characteristic of a free hydroxyl group) and broad at the base, and two absorption bands in the region between 1600 and 1700 cm^{-1} at 1660 and 1630 cm^{-1} characteristic of chelated and nonchelated quinone carbonyls. This compound was obviously related to compound **1**. The above data are consistent with a 1-hydroxyl group which increases the

molecular weight of this compound by 2 compared to that of compound **1** with the carbonyl at this site.

Reduction of compound **1** with sodium borohydride gave compound **2**, identical by NMR and MS to the naturally produced compound **2**. Oxidation of compound **2** gave compound **1**, identical to the naturally produced compound **1** in all respects. Compounds **1** and **2** fluoresce orange under ultra violet (UV light 354 nm). Similar fungal anthraquinones have been reported from *Dermocybe cinaborina* [20].

The chemical and spectral evidences show that the two metabolites identified are either of the structures shown in Fig. 1, example 1, or an isomer of this structure with the groups at the 2- or 3-reversed.

3.2. Toxicity assay

The results in Table 1 clearly show that *F. oxysporum* yielded culture extract causes inhibition of citrus seeds' germination by more than 55%. Meanwhile, anthraquinone pigment of this isolate reduced germination of all tested seeds by 70–82%, 76–100% and 82–100% at 25, 50 and 100 ppm concentrations, respectively. Seeds of sour orange were more affected by cultural filtrate or anthraquinone concentration followed by Rangpur lime. But Volkamer lime seeds were less affected. These data show that *F. oxysporum* (isolate no. 4) from root rotted citrus trees has the potential to produce phytotoxins and high amount of pigments [6,15,21]. These toxins disrupt plant metabolism, cause growth reduction and chlorosis [15]. As they interfere with respiration by inhibiting the anaerobic decarboxylation of α-ketoglutarate [22]. Many investigators reported that anthraquinone compounds are derivatives of these phytotoxins or pigments [11,16,19,20].

3.3. Dyeing

3.3.1. Effect of dye bath pH

Fig. 2 shows that the pH values of the dye bath have a considerable effect on the dyeability of wool fabrics while using the *Fusarium* anthraquinone dye (FA dye). The effect of the dye bath pH can be attributed to the correlation between dye structure and wool fabric. Since the dye used is sparingly soluble in water, containing OH groups, it would interact ionically with the protonated terminal amino groups of wool fibres at acidic pH via ion exchange reaction due to the acidic character of the OH groups. The anion of the dye has complex characters, and when it is bound on the fibre, with ionic forces, this ionic attraction would increase the dyeability of the fibre as is clearly observed from Fig. 2. It was noticed from the figure that dyeability was higher at pH 3, then the dyeability decreases due to the decreasing number of protonated terminal amino groups of wool fibres, and therefore the ionic interaction decreases.

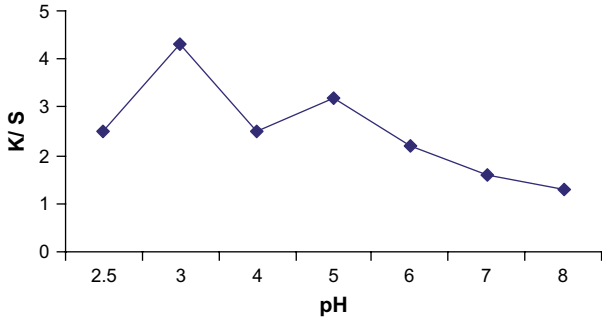

Fig. 2. Effect of dye bath pH on the colour strength on wool fabrics. Dyeing conditions: 2% shade, LR 40:1, at 100 °C, 40 min for 1 h.

3.3.2. Effect of salt addition

Fig. 3 shows the effect of salt concentration on the colour strength obtained for the dyed fabrics. It is clearly indicated that as the salt concentration increases the colour strength decreases, it is also noticed that at 0 °C the value of the colour strength was maximum, i.e., dyeing without salt addition is the best condition, this is similar to those reported by Kamel et al. [23].

3.3.3. Effect of temperature

The effect of temperature on the dyeability of wool fabrics with *F. oxysporum* dye was conducted at different temperatures (30–100 °C). As shown in Fig. 4, it is clear that the colour strength increases with the increase of dyeing temperature and reaches a maximum value at 100 °C.

Table 1
Root growth inhibition of some citrus root stock seeds by cultural filtrate and anthraquinone pigment of *F. oxysporum*

Treatment	Concentration (ppm)	Root growth inhibition (%)[a]		
		Sour orange	Rangpur lime	Volkamer lime
Cultural filtrate	–	68	62	55
Anthraquinone pigment	25	82	76	70
	50	100	82	76
	100	100	90	82
Control (untreated)[b]	–	6	4	3

[a] The percentages of nongerminated seeds.
[b] Filter papers were wetted by 5 mL of sterile water only.

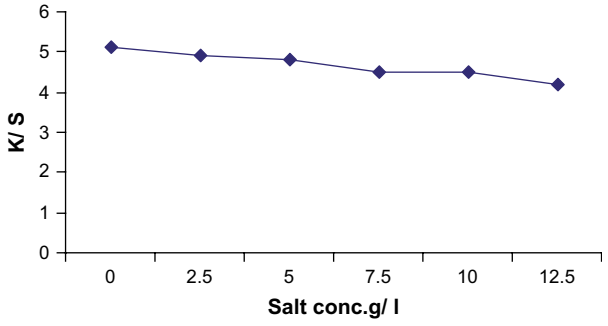

Fig. 3. Effect of salt addition to the dye bath on the colour strength of dyed wool. Dyeing conditions: 2% shade, LR 40:1, 10 gm L^{-1} sodium chloride, 1 h, at 100 °C.

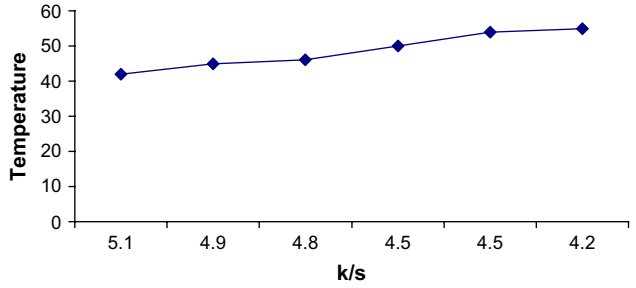

Fig. 4. Effect of dyeing temperature on the colour strength of dyed wool fabrics. Dyeing conditions: 2% shade, LR 40:1, pH 3, 1 h, 0 g salt concentration.

3.3.4. Effect of dyeing time

As shown in Fig. 5, the colour strength obtained was increased as the time increases up to 60 min, then it decreases, i.e., dyeing for 60 min gave high colour strength values.

3.3.5. Fastness properties

Fastness properties of the dyed fabrics are shown in Table 2. The results indicate good fastness properties of the dyed samples.

3.3.6. Kinetic of dyeing

It is known that the rate of any process means a change in one of the starting materials that takes place in the process or the product that obtained per unit time. Applying this definition in the dyeing process, it can be regarded as the change in the dye uptake per unit time.

Time–dye uptake isotherms of wool fabrics dyed with FA dye are shown in Fig. 6. The figure shows that the isotherms indicate high dye uptake for FA dye.

The data in Fig. 6 can be analyzed by using the derivable general form of the first order rate equation (Eq. (3)) [24];

$$\frac{A_f - A_f}{A_0 - A_f} = e^{-kt} \tag{3}$$

where A_t is the absorbance at time t, A_0 is the initial absorbance, A_f is the final absorbance, t is the reaction time and k is the reaction rate.

Since the absorbance of solution is directly related to the concentration by Lambert–Beer's Law, therefore Eq. (3) can be written in terms of dye uptake to give Eq. (4):

Table 2
Fastness properties of dyed wool fabrics

Washing			Rubbing		Perspiration		Light fastness
A	C	W	Rd	Rw	a	b	7–8
4–5	4	4	5	5	4–5	4–5	

A = change in colour, C = staining on cotton, W = staining on wool, Rd = dry rubbing, Rw = wet rubbing, a = acidic, and b = alkaline.

$$\frac{Q_t - Q_f}{Q_0 - Q_f} = e^{-kt} \tag{4}$$

where Q_t is the dye uptake at time t, Q_0 is the dye uptake at zero time, Q_f is the final dye uptake, t is the dyeing time and K is the dyeing rate. Taking the logarithm of Eq. (4) would lead to Eq. (5), and since Q_f is known, $Q_t - Q_f$ can be calculated as follows:

$$\ln |Q_t - Q_f| = \ln |Q_0 - Q_f| - K_t \tag{5}$$

A plot of $\ln |Q_t - Q_f|$ versus time is expected to be linear with a slope of $-K$ and an intercept of $\ln |Q_0 - Q_f|$, if the reaction is first order. Fig. 7 shows the plot of $\ln |Q_t - Q_f|$ as a function of time for dyeing wool cotton fabric with FA dye. As can be seen in this figure the linear fitting rate constants could be obtained.

The time of half dyeing $t_{1/2}$ which is the time required for the fabric to take up half of the amount of dye taken at equilibrium, is estimated either from each isotherm directly (Fig. 7) and/or from the following equation:

$$t_{1/2} = \frac{\ln 2}{k} \tag{6}$$

The data for dyeing equilibria are reported as the standard affinity of dyeing, $-\Delta\mu$ [25]. It has been reported that the dyeing of wool fibres using natural dyes follows the same mechanism as that of disperse dyes, i.e., via partition mechanism [26]. Therefore, the standard affinity can be calculated using Eq. (7):

$$-\Delta\mu = RT \ln \frac{C_f}{C_s} \tag{7}$$

where R is the gas constant, T is the absolute temperature (K), C_f and C_s are dye concentrations in the fibre and the dye bath,

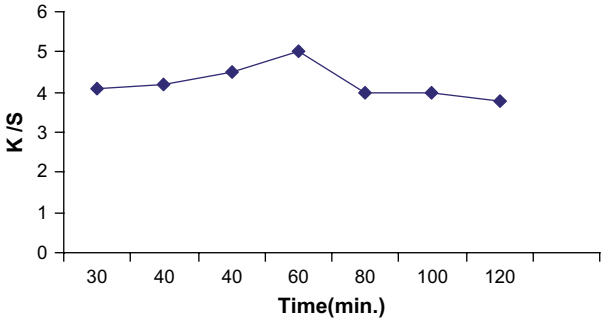

Fig. 5. Effect of dyeing time on the colour strength of dyed wool fabrics. Dyeing conditions: 2% shade, LR 40:1, pH 3 at 100 °C, 0 g salt concentration.

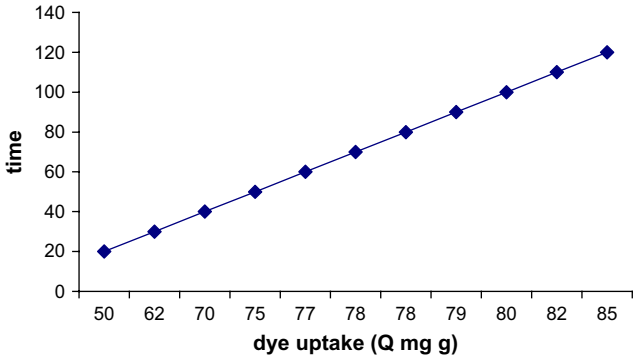

Fig. 6. Dyeing rate of wool fabric. Dye conditions, see Section 2.

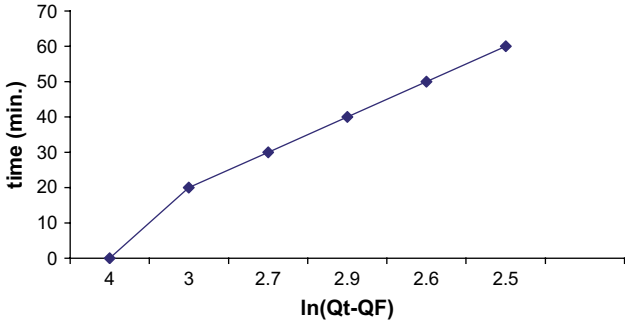

Fig. 7. Plot of $\ln(Q_t - Q_f)$ versus time of dyeing wool fabrics.

respectively. The values of dyeing rate constant K, times of half dyeing time $t_{1/2}$, standard affinity $\Delta\mu$ and amount of final dye uptake by wool fabric Q_f obtained were $K \times 100$ $(\text{min}^{-1}) = 5.2$, $-\Delta\mu$ (kJ/mol) $= 11.5$, $t_{1/2}$ (min) $= 13.1$, and Q_f (mg/g) $= 82.4$.

4. Conclusion

Anthraquinone compounds which were produced by stationary cultures of *F. oxysporum* could be used for dyeing wool with good fastness properties and high dye uptake.

Our study shows that natural anthraquinone dyes can provide bright hues and colour fastness properties. They can serve as a noteworthy source of raw material in the future. Chemical modification of natural compounds could be an interesting field of study as it could appreciably facilitate the synthesis of dye molecule.

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