

Dyeing of Modified Acrylic Fibers with Curcumin and Madder Natural Dyes

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Abstract: Hydrophobic fibers are highly crystalline and non-polar polymers hence pose a big problem for dyes. Modified acrylic fiber containing different amounts of amidoxime groups as a function of the nitrogen content was obtained and dyed with curcumin and madder natural dyes. The dyeing parameters, such as dye concentration, dye bath pH, salt concentration, temperature, and time and the effect of alum and ferrous sulfate used as mordants were investigated. Compared with the dyeings obtained from modified acrylics, those of blank samples appeared less in color strength values. The color strength was proportional to the nitrogen content of the sample and the maximum value was obtained at pH 2 and pH 5 using madder and curcumin, respectively. The fixation of the dye molecules to the modified acrylic fibers was investigated to show mainly ionic and physical bonds. The washing, perspiration, and rubbing fastness properties for the dyed samples were enhanced by application of alum. The light fastness ratings were also improved using ferrous sulfate especially for the case of the samples dyed with madder.

Keywords: Modified acrylic fiber, Amidoxime, Curcumin, Madder, Mordant, Fastness

Introduction

The growing demand for more natural products and the toxicity problem in relation to synthetic dyes [1] are the principal factors in encouraging a revival in the use of natural dyes. Natural dyes can exhibit better biodegradability and generally have a higher compatibility with the environment. Recently, the potentiality of using natural dyes in textile coloration as anti-UV and anti-microbial has been investigated [2-4]. Several studies on the application of natural dyes have been reported [5-10]. A review on the use of natural dyes in textile coloration has been published [11].

Curcumin and madder are the most popular yellow and red natural dyes, respectively. Curcumin is an active ingredient in turmeric (*Curcuma longa L*) which is widely used as a food colorant. It is called C.I. Natural Yellow 3; WHO (World Health Organization) and FAO (Food and Agriculture Organization) committees have approved it as a food additive [12]. Curcumin exists in a keto-enol tautomerism with equilibrium strongly favoring an enol form (Figure 1). The enol structure enables curcumin to form additional inter- and intramolecular hydrogen bonds [13-15].

Madder, the root of *Rubia tinctorum L.*, has a long tradition as a dyestuff because of its bright red color. It has been cultivated as a source of dyestuff since antiquity in central

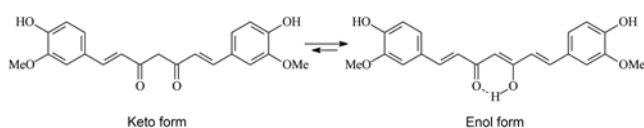


Figure 1. Chemical structure of curcumin.

Asia and Egypt, where it was grown as early as 1500 BC. The ancient Egyptians used rose madder to create pinkish rose-colored textile dyes. Cloth dyed with madder root pigment was found in the tomb of the Pharaoh Tutankhamun [16]. The Color Index name used by paint and textile chemists for Rose Madder is Natural Red 9. Madder, *Rubia tinctorum L.*, (Figure 2) contains mainly, alizarin (I, 1,2-dihydroxyanthraquinone), purpurin (II, 1,2,4-trihydroxyanthraquinone), pseudopurpurin (III, 1,2,4-trihydroxyanthraquinone-3-carboxylic acid), and munjistin (IV, 1,3-dihydroxyanthraquinone-2-carboxylic acid) [17].

Conventionally, acrylic fibers, which are spun from a copolymer of acrylonitrile containing 1-15 wt. % of several vinyl comonomers containing carboxylate or sulfonate groups, are dyed with cationic dyes [18,19]. The only known cationic dye of natural origin, berberine (a yellow dye

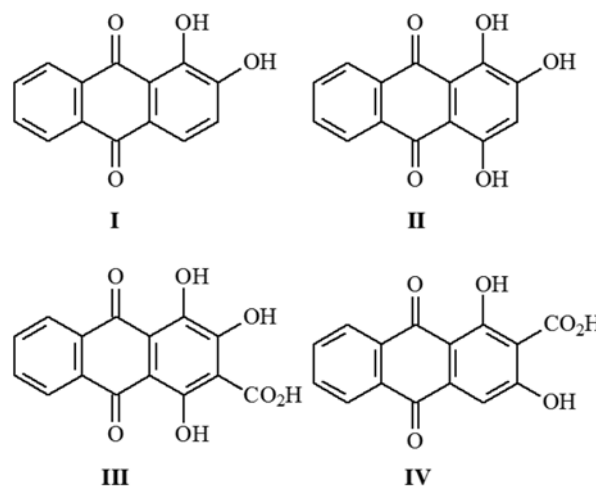


Figure 2. Main colorants present in aqueous extract of madder.

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extracted from the roots of *Berberis aristata*), has been applied to acrylic fibers [20,21]. Generally, natural dyes have similar structure to that of disperse dyes and therefore it was possible to dye nylon, polyester, and acrylic fibers at high temperature [22,23] and/or by using solvent and carrier [24].

In the interest of dyeing acrylic fiber with natural dyes without solvent or carrier and under atmospheric pressure, it was thought that the partial conversion of nitrile groups present in the fiber into amidoxime groups would render the fiber more hydrophilic by virtue of its content of active dye sites (amidoxime groups). These dye sites have proved effectiveness in increasing the affinity of acrylic fiber toward anionic dyes at acidic pH [25,26].

To the best of our knowledge, however, there is no report as yet has appeared on dyeing of modified acrylic fibers with natural dyes. As a part of our ongoing interest in exploring the dyeability of modified acrylic fibers, the dyeing of modified acrylic fibers with curcumin and madder natural dyes is reported in this study. The blank and two modified samples of acrylic fibers containing different nitrogen contents were thoroughly compared throughout the work. The dyeing conditions such as the concentration of the dye, the dye bath pH, the salt concentration, the dyeing temperature, the dyeing time, and the concentration of the mordants and the overall fastness properties were investigated.

Experimental

Materials

Acrylic Fiber

Plain 1/1 woven acrylic fiber was used (43-38 threads/inch, metric count 16, weft and warp and 562 den), which was kindly supplied by Misr El-Mehalla Co. (Egypt). The fabric was soaped with 2 g/l non-ionic detergent (Hostapal CV, from Clariant - Egypt) at 60 °C for 30 min, thoroughly rinsed and air dried.

Dyestuffs and Chemicals

The dyes used in this work were curcumin (*Curcuma longa*) and madder (*Rubia tinctorium* L.) roots. These commercial products were supplied by Hansen's Co. Egypt. Hydroxylamine hydrochloride, ammonium acetate, sodium sulfate, acetic acid, alum, and ferrous sulfate were laboratory reagent grade chemicals.

Pretreatment, Extraction, Dyeing, and Mordanting

Pretreatment

Following our previously described method [26], a known weight of acrylic fiber was pre-treated in a bath containing two concentrations of hydroxylamine hydrochloride (10 and 15 g/l) and two concentrations of ammonium acetate (20 and 30 g/l) at a liquor-to-goods ratio of 50:1 at 85 °C for 1 h. The pre-treated samples were thoroughly rinsed with water and

air dried.

Extraction

The extraction method was followed according to the optimum condition reported previously [27]. The plant materials (10 g) were soaked in water (100 ml) for 24 h and then the coloring matter was extracted at the boil for 30 min after which the solution was filtered off and kept in refrigerator.

Dyeing

In a dye bath containing different amounts of sodium sulfate (0-9 g/l) and different curcumin dye concentrations (1-5 % w/v) or different dilutions of madder extract (25-100 % v/v) with liquor ratio 50:1, acrylic fibers (blank and modified samples) were dyed at different pH values (2-6, adjusted with dilute hydrochloric acid) for different durations (30-90 min) and at different temperatures (60-100 °C). The dyed samples were rinsed with hot water, soaped in a bath of liquor ratio 50:1 using 3 g/l non-ionic detergent (Hostapal CV, Clariant) at 70 °C for 15 min, then rinsed and air dried.

Mordanting

Pre-mordanting was chosen as the most suitable process for mordanting acrylic fibers. The mordant was dissolved in water to make the liquor ratio 50:1. The pH of the bath was adjusted to 4 with acetic acid. The pre-wetted sample was treated with the mordant solution (3 g/l) and then it was brought slowly to the boil for 1 h. The mordanting bath was then allowed to cool to room temperature and the samples were removed, squeezed, and air dried.

Color Measurements

The relative color strength of dyed fibers expressed as K/S , where K and S are the absorption and scattering coefficients, respectively, was measured by the light reflectance technique using the Kubelka-Munk equation (equation (1)) [28]. The reflectance (R) and CIELAB values of dyed samples were measured using a spectrophotometer (Datacolor International SF 600 plus, D65) interfaced with a personal computer. The color characteristics ($L^*a^*b^*$) of the dyed fabrics were assessed for all samples dyed in the presence and absence of mordants.

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

Nitrogen Percentage

The percentage of nitrogen of untreated and treated acrylic fibers was determined by the Kjeldahl method [29].

Color Fastness Properties

Fastness testing for the dyed samples was tested according to ISO standard methods. The specific tests were: ISO 105-X12 (1987), color fastness to rubbing; ISO 105-C02 (1989), color fastness to washing; and ISO 105-E04 (1989), color fastness to perspiration. The dyed samples were subjected to tests, for fastness to light by AATCC test method 16-1993.

Results and Discussion

The realization of anionic coloration of acrylic fibers [25,26] has prompted us to study the possible dyeability of modified acrylic fibers with natural dyes. Three samples of different nitrogen contents, namely blank (22.73 %) and two modified acrylic fibers A (22.83 %) and B (23.00 %) were dyed with madder and curcumin natural dyes. Therefore, comparative studies for the dyeability of these samples as well as the different factors that may affect these processes were investigated.

Dyeing

Effect of Dye Concentration

Figures 3 and 4 show the effect of dye concentration on the color strength obtained for the dyed fabrics. As shown, the K/S value increases as the concentration of the dye increased up to certain level (ca. 75 and 4 % of madder and curcumin, respectively), after which the fibers started to become saturated especially for samples A and B. It is clear that the dye uptake of modified samples A and B is better at all concentrations used than that of the blank sample and the dyeability is ranked as follows: $B > A > \text{blank}$. This result reflects the extent of fiber modification and in a good agreement with the nitrogen content of the dyed samples.

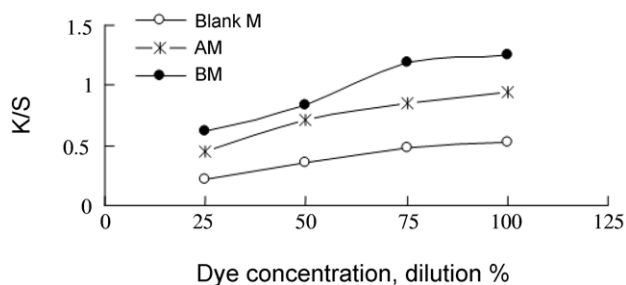


Figure 3. Effect of madder dye concentration on the color strength of dyed acrylic fabrics. Dyeing conditions pH 5, 1 g/l salt, 60 min, LR 50:1, and 100 °C.

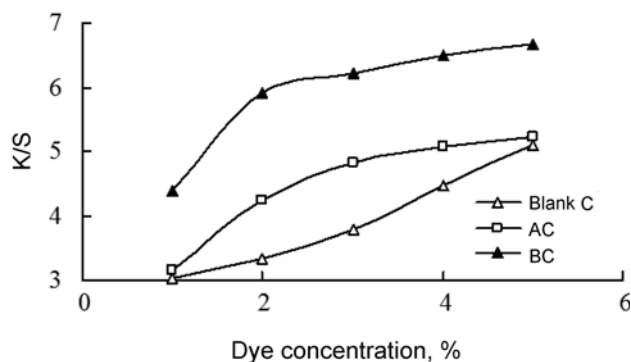


Figure 4. Effect of curcumin dye concentration on the color strength of dyed acrylic fabric. Dyeing conditions pH 5, 0 g/l salt, 60 min, LR 50:1, and 100 °C.

This enhancement in the fiber dyeability would be attributed to the presence of amidoxime groups present in the modified samples that render the fiber more hydrophilic and less crystalline [26].

Effect of Dye Bath pH

Figures 5 and 6 show that the pH values of the dye bath have a considerable effect on the dyeability of acrylic fabrics with natural dyes. For madder dye, the effect of pH (Figure 5) reveals that increasing the pH decreases the dyeability of the fabric.

The effect of dye bath pH can be attributed to the correlation between dye structure and the fibers used. Acidic pH is expected to reduce the negative charge of the surface of all acrylic samples in the dye bath and as a consequence the dyeability increases. This effect is further manifested for samples A and B due to their content of amidoxime groups which become protonated at acidic pH and the extent of dye adsorption mirrored the extent of protonation of the terminal amino groups in these fibers. It is an equilibrium process of protonation and deprotonation as depicted in Scheme 1 and therefore, the protonation of the amino groups will increase with decreasing the pH of the dye bath.

On the other hand, curcumin dye reveals (Figure 6) different results in which decreasing the pH less than 4 leads to lower dyeability. This result is mainly related to the effect of pH on the keto-enol tautomersim of curcumin (Figure 1).

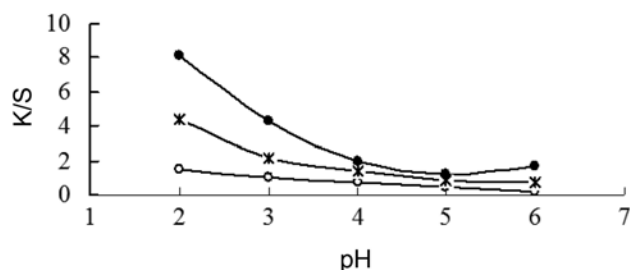
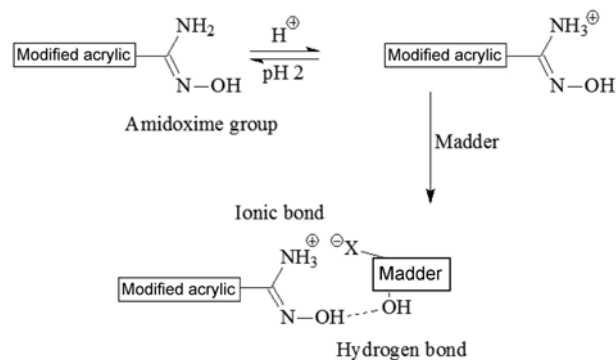


Figure 5. Effect of dye bath pH on the color strength of dyed acrylic fabrics. Dyeing conditions: 75 % dye, 1 g/l salt, 60 min, LR 50:1, and 100 °C. For legend, see Figure 3.



Scheme 1. Madder bonds with modified acrylic fibers. $X = \text{O}$ or CO_2 .

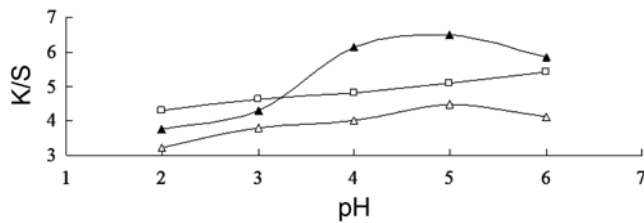


Figure 6. Effect of dye bath pH on the color strength of dyed acrylic fabrics. Dyeing conditions: 4 % dye, 0 g/l salt, 60 min, LR 50:1, and 100 °C. For legend, see Figure 4.

Curcumin exists in a keto-enol tautomerism with equilibrium strongly favoring the enol form. The enol structure enables curcumin to form additional inter- and intramolecular hydrogen bonds [3]. As the pH decreases, the equilibrium shifts to keto form which is not in favor for good dyeability. Additionally, the phenolic groups of curcumin are weakly acidic when compared with those of madder dye. Therefore, the course of dyeing with curcumin at pH 5 would mainly follow physical effects in a similar manner with disperse dyes toward synthetic fibers unlike the case of madder, which mainly follow ionic effects at pH 2 in a similar manner with acid dyes toward proteinic fibers.

Effect of Salt Concentration

Figures 7 and 8 show the effect of salt concentration on the color strength obtained for the dyed fabrics. Both figures indicate that the color strength was slightly affected as the salt concentration increases up to 1 g/l after which further increase in the salt concentration has led to almost unchanged dyeability for all samples dyed with madder.

In the case of curcumin, however, increasing the salt concentration more than 1 g/l revealed almost unchanged

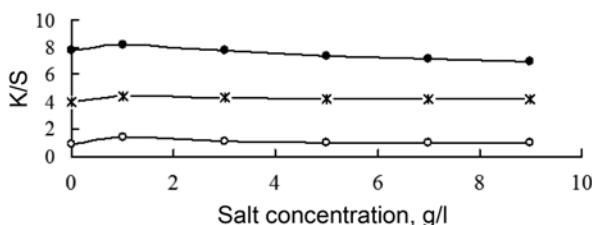


Figure 7. Effect of salt addition to the dye bath on the color strength of dyed acrylic fabrics. Dyeing conditions: pH 2, 75 % dye, 60 min, LR 50:1, and 100 °C. For legend, see Figure 3.

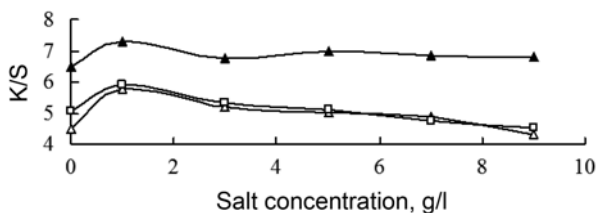


Figure 8. Effect of salt addition to the dye bath on the color strength of dyed acrylic fabrics. Dyeing conditions: pH 5, 4 % dye, 60 min, LR 50:1, and 100 °C. For legend, see Figure 4.

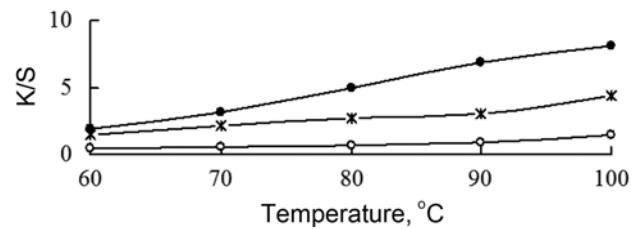


Figure 9. Effect of dyeing temperature on the color strength of dyed acrylic fabrics. Dyeing conditions: pH 2, 1 g/l salt, 75 % dye, 60 min, LR 50:1, and 100 °C. For legend, see Figure 3.

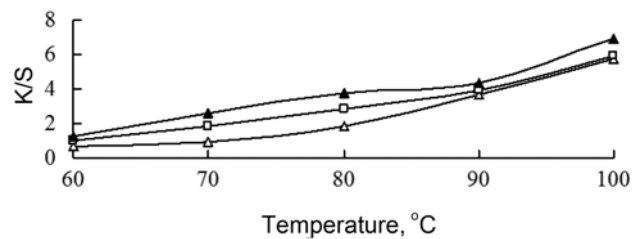


Figure 10. Effect of dyeing temperature on the color strength of dyed acrylic fabrics. Dyeing conditions: pH 5, 1 g/l salt, 4 % dye, 60 min, LR 50:1, and 100 °C. For legend, see Figure 4.

dyeability for sample B but a decline for A and blank samples. The decline behavior may be attributed to the adsorption nature of curcumin dye onto acrylic samples as mentioned above.

Effect of Temperature

The effect of temperature on the dyeability of acrylic fabrics with natural dyes is shown in Figures 9 and 10. Both figures clearly indicate that the color strength values increase with the dyeing temperature for all samples and those of samples B and A revealed higher K/S values at all temperatures when compared with those of blank sample. Generally, the increase in dye uptake can be explained by fiber swelling and hence, enhanced dye diffusion. Also, the presence of amidoxime groups in the fiber acts as dye sites and thus facilitates further dye uptake. This effect is clearly observed for the case of madder dye where the difference in the dyeability between B, A, and the blank samples is increasing with the temperature. This result reflects the increased ionization of madder dye molecules as the temperature increased and thus facilitates dye-fiber ionic bond formation.

For curcumin (Figure 10), however, the difference in the dyeability between B, A, and the blank samples, although always in favor in the order: B>A>blank, remains almost the same at all temperature. This result indicates that the course of dyeing follow a rather physical effects.

Effect of Dyeing Time

Figures 11 and 12 show the effect of dyeing time on the color strength obtained for the dyed fabrics. For both dyes and at all dyeing times, the order of the dyeability always remains the same: B>A>blank. For madder, the difference in

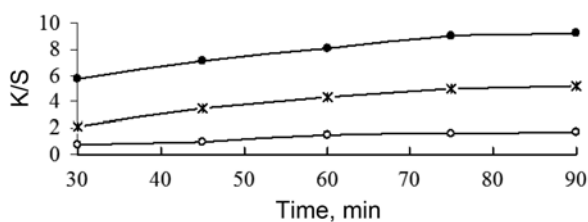


Figure 11. Effect of dyeing time on the color strength of dyed acrylic fabrics. Dyeing conditions: pH 2, 1 g/l salt, 75 % dye, LR 50:1, and 100 °C. For legend, see Figure 3.

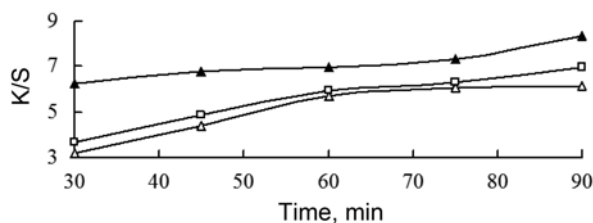


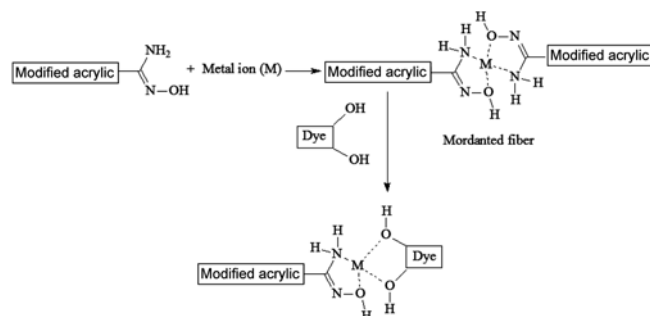
Figure 12. Effect of dyeing time on the color strength of dyed acrylic fabrics. Dyeing conditions: pH 5, 1 g/l salt, 4 % dye, LR 50:1, and 100 °C. For legend, see Figure 4.

the dyeability between B, A, and the blank samples is clearly emphasizing the difference in amidoxime contents between all samples, whereas for curcumin although the dyeability difference exists between all samples, it is rather clear for sample B when compared with A and the blank samples. This result further confirms the difference between madder and curcumin in their dyeing behavior toward all acrylic samples.

Mordanting

A mordant is usually a metal ion used to set dyes on fabrics by forming an insoluble compound with the dye. It was thought that the presence of amidoxime in the modified acrylic fibers would increase the reactivity of the fiber toward metal ion by virtue of its metal forming complex, which would help further dye-fiber bond fixation as depicted in Scheme 2.

Alum and ferrous sulfate mordants were used in 3 g/l for pre-mordanting acrylic fiber samples to produce different



Scheme 2. Mordanting and dye fixation on modified acrylic fibers.

hues of color. Tables 1 and 2 show L^* , a^* , and b^* values of acrylic samples (blank, A, and B) dyed with madder and curcumin, respectively.

It is clear that different mordants not only cause difference in hue and changes in K/S values but also change color characteristics. Also, it can be seen that mordants which

Table 1. Color characteristics of acrylic samples dyed with madder in the absence and presence of mordant

Mordant	Blank				
	$K/S^{\#}$	Color	L^*	a^*	b^*
Without	1.45	Beige	73.12	12.74	20.47
Alum	1.82	Light orange	69.49	16.49	26.05
Ferrous sulfate	2.07	Grayish yellow	62.57	6.08	9.44

Mordant	A				
	K/S	Color	L^*	a^*	b^*
Without	4.38	Light brown	59.13	20.48	17.68
Alum	4.14	Light brown	62.51	21.10	22.50
Ferrous sulfate	5.51	Light brown	56.71	15.43	20.22

Mordant	B				
	K/S	Color	L^*	a^*	b^*
Without	8.12	Brownish red	73.12	12.74	20.47
Alum	8.01	Brownish red	69.49	16.49	26.05
Ferrous sulfate	10.29	Brownish	62.57	6.08	9.44

[#] K/S values of madder dyed samples were measured at the reflectance wavelength of 400 nm.

Table 2. Color characteristics of acrylic samples dyed with curcumin in the absence and presence of mordant

Mordant	Blank				
	$K/S^{\#}$	Color	L^*	a^*	b^*
Without	5.72	Lemon yellow	82.04	-14.96	55.43
Alum	5.94	Yellow	78.61	-5.53	51.53
Ferrous sulfate	5.84	Yellow	76.36	-2.42	58.42

Mordant	A				
	K/S	Color	L^*	a^*	b^*
Without	5.93	Yellow	82.12	-4.62	36.42
Alum	6.20	Yellow	77.22	-1.18	55.27
Ferrous sulfate	6.55	Pale brownish yellow	59.79	10.24	41.65

Mordant	B				
	K/S	Color	L^*	a^*	b^*
Without	6.95	Yellow	77.20	0.33	58.44
Alum	8.43	Dark yellow	77.41	1.84	67.5
Ferrous sulfate	8.75	Brownish yellow	57.63	12.15	44.27

[#] K/S values of curcumin dyed samples were measured at the reflectance wavelength of 440 nm.

Table 3. Ratings for color fastness of acrylic samples dyed with madder in the absence and presence of mordant

Mordant	Blank											
	Washing			Perspiration						Rubbing		Light fastness
	Alt.	St.*	St.**	Acidic			Alkaline			Dry	Wet	
				Alt.	St.*	St.**	Alt.	St.*	St.**			
Without	4	4-5	4-5	4	4	4	4	3-4	4	3-4	3	3-4
Alum	4	4-5	4-5	4	4	4-5	4	4-5	4-5	4	3-4	3-4
Ferrous sulfate	4	4	3-4	4	3-4	4	4	4	4	3-4	3	4

Mordant	A											
	Washing			Perspiration						Rubbing		Light fastness
	Alt.	St.*	St.**	Acidic			Alkaline			Dry	Wet	
				Alt.	St.*	St.**	Alt.	St.*	St.**			
Without	4	3-4	4-5	4	3-4	4	4	3-4	4	3-4	3	3-4
Alum	4	4-5	4-5	4	4	4-5	4	4-5	4-5	4	3-4	4
Ferrous sulfate	4	4	3-4	4	3-4	3-4	4	4	4	3-4	3	5-6

Mordant	B											
	Washing			Perspiration						Rubbing		Light fastness
	Alt.	St.*	St.**	Acidic			Alkaline			Dry	Wet	
				Alt.	St.*	St.**	Alt.	St.*	St.**			
Without	4	4-5	4-5	4	4-5	4	4	4-5	4-5	3-4	3	5
Alum	4	4-5	4-5	4	4-5	4-5	4	4-5	4-5	4	3-4	5
Ferrous sulfate	4	4	4	4	4	4-5	4	4-5	4	3-4	3	6

Alt.: change in color, St.*: staining on cotton, and St.**: staining on wool.

Table 4. Ratings for color fastness of acrylic samples dyed with curcumin in the absence and presence of mordant

Mordant	Blank											
	Washing			Perspiration						Rubbing		Light fastness
	Alt.	St.*	St.**	Acidic			Alkaline			Dry	Wet	
				Alt.	St.*	St.**	Alt.	St.*	St.**			
Without	4	4	4	4	4	4-5	4	4	4-5	3-4	3	2
Alum	4	4-5	4-5	4	3-4	4-5	4	4	4-5	2-3	2-3	2
Ferrous sulfate	4	3	3	4	4	4-5	4	4	4-5	3-4	2-3	2-3

Mordant	A											
	Washing			Perspiration						Rubbing		Light fastness
	Alt.	St.*	St.**	Acidic			Alkaline			Dry	Wet	
				Alt.	St.*	St.**	Alt.	St.*	St.**			
Without	4	4	4-5	4	3-4	4-5	4	4	4-5	3-4	2-3	2
Alum	4	4	4	4	4	4-5	4	3-4	4-5	2-3	3	2
Ferrous sulfate	4	2-3	3	4	4	4-5	4	4	4-5	2-3	2-3	3

Mordant	B											
	Washing			Perspiration						Rubbing		Light fastness
	Alt.	St.*	St.**	Acidic			Alkaline			Dry	Wet	
				Alt.	St.*	St.**	Alt.	St.*	St.**			
Without	4	4-5	4-5	4	4	4-5	4	4-5	4-5	3-4	3-4	2-3
Alum	4	4-5	4-5	4	4	4-5	4	4-5	4-5	3-4	3-4	2-3
Ferrous sulfate	4	4	4	4	4	4-5	4	4	4-5	3-4	3	3

For footnote see Table 3.

show higher value of L^* show lighter shades while lower L^* values signify deeper shades. Similarly, negative a^* and negative b^* represent green and blue, respectively.

Fastness Properties

Tables 3 and 4 show the fastness ratings of washing, perspiration, rubbing, and light fastness of samples that had been dyed with madder and curcumin natural dyes, respectively. As shown in Table 3, the fastness ratings of madder indicate good to very good for washing and perspiration and fair to good for rubbing. This result indicates the existence of strong bonds between the dye molecules and the fabrics.

The ratings of light fastness (fair to very good) shown in Table 3 was improved from unmordanted to mordanted samples and was in the order B>A>blank.

This enhancement could be due to the complex formation between the dye molecule, fiber, and the mordant used. Therefore, it is expected that sample B that has more amidoxime groups would have more capacity than A and blank samples in making dye/fiber metal complex. Although ferrous sulfate as mordant was less effective than alum for improving the ratings of washing, perspiration, and rubbing, it was more effective for the improvement of light fastness.

For curcumin (Table 4), the fastness ratings for washing and perspiration were similar to the results obtained for madder. However, the rating for rubbing was poor to fair for samples A and blank and fair to good for sample B. Also, a little enhancement in the light fastness was observed using ferrous sulfate. This rating difference between madder and curcumin is mainly attributed to the difference in the dye structure.

Conclusion

Modified acrylic fibers could be dyed with curcumin and madder natural dyes. The acidity difference between the hydroxyl groups present in madder and those present in curcumin has changed the course of dyeing with these dyes. The optimum pH values for dyeing were 2 and 5 for madder and curcumin, respectively. These acidic pH values suggest that the bonds between madder and modified acrylic fiber is suggested to be mainly ionic bonds together with other physical bonds, whereas those of curcumin might be mainly physical bonds together with possible ionic bond formation. The dyeability of the acrylic fiber samples was clearly dependent on the amidoxime content (nitrogen content) especially in the case of using madder dye. The fastness rating was improved dependent on the type of the sample, the type of the dye, and the type of the mordant. Madder has shown the best overall fastness ratings especially the light fastness when compared with curcumin. Since acrylic fiber is a less expensive alternative to wool due to its similar feeling properties, we believe that this work would inspire

the production of anionic and natural dyeable wool/acrylic and/or cellulosic/acrylic fibers with better properties. Future work is under way to further explore the coloration of acrylic blends.

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