Pak. J. Sci. Ind. Res. 2010 **53** (5) 252-257

Study of Colour Measurements of Leather Dyed with Walnut Bark Natural Dye

Bushra Khalid*, Azra Yaqub, Muhammad Farooq Arif, Lubna Liaquat and Benish Iqbal
Applied Chemistry Research Centre, PCSIR Laboratories Complex,
Ferozepur Road, Lahore-54600, Pakistan

(received October 13, 2009; revised April 13, 2010; accepted April 19, 2010)

Abstract. Natural dye was extracted from walnut bark and applied on grey split leather for colour measurement study. Premordanting method of dyeing was used with different concentrations of dye at different temperatures for an interval of 45 minutes. Dyed leathers were subjected to colour measuring system and the tristimulus values (XYZ), ANLAB values (LAB) and Munsell renotations (hue, lightness and chroma) were noted. Acetic acid, formic acid, citric acid and tartaric acid were used as mordants before dyeing. Tartaric acid showed best results relating to colour measurements.

Keywords: mordant, colour measurement, natural dye, walnut dye, leather dye

Introduction

Protection of environment has become a global issue during recent years. All over the world environmental regulations are becoming more strict and are forcing the shift of technology towards less polluting or particularly non polluting technological development (Thanikaivelan *et al.*, 2004; Shenghua, 2002). Water pollution and air pollution caused by the synthetic dyes and particularly the control of industrial effluent has become a big problem. Research has shown that synthetic dyes are suspected of releasing harmful chemicals that are allergenic and carcinogenic and detrimental to human health. Ironically Germany that discovered azo dyes, became the first country to ban certain azo dyes in 1966. At present many countries specially European and American stopped using fabrics dyed with these banned synthetic dyes. Investigators sponsored by ETAD (Ecological and Toxicological Association of the Dyestuff Manufacturing Industry) identified and assessed the risk to health caused by colourants based on benzidine (Waheed *et al.*, 1996). In this background an effort to promote the use of natural dyes deserves encouragement (Waheed and Alam, 2004).

Natural dyes are colourants derived from animals, vegetables, minerals and insects (Ali *et al.,* 2007; Junzo and Katsushi, 1994). More than 500 dye-yielding plant species are so far known. These colours have several applications in textiles, inks, cosmetics etc., but so far the work on leather is still limited. Natural dyes are ecofriendly and harmless. The extraction, refining and application of these dyes create least environmental problems (Junzo and Katsushi, 1994).

These dyes have tremendous commercial potential and are generally more compatible with the environment. Considerable research work is being undertaken around the world on the application of natural dyes with the use of different mordants as well as enzymatic pretreatment for richness of colour (Kanth *et al.*, 2009; Vankar *et al.*, 2007, Zaman *et al.*, 1993).

Leather industry is already using synthetic as well as vegetable tannins. However, the use is confined to cottage and small scale units. With some effort, the vegetable dyes may be used in leather sector on large scale (Koralia and Dilliwar, 2004).

Annual global trade of leather is 70,000,000,000 US$. Currently the leather processing industry is going through a phase change due to global environmental regulations. Pretanning and tanning processes with synthetic dyes contributed 80-90 % of total pollution load (BOD COD, TS, TDS, Cr, S^{-2}, sludge etc.). Further toxic gases like, ammonia and hydrogen sulphide are also emitted and solid waste like, lime, sludge is also a big problem. There is the need to improve leather processing and dyeing methods for the sustainability of leather industry (Thanikaivelan *et al.*, 2004).

Natural dyes are classified as monogenetic and polygenetic. Monogenetic dye material produce only one colour on textiles irrespective of mordants, while polygenetic dyes develop different colours according to the mordant applied before dyeing.

Extraction of dye can be carried out in aqueous, acidic or alkaline medium (Ali *et al.*, 2009). The present study concerns with the extraction of natural dye from the *Juglan regia*

*Author for correspondence; E-mail: pcsir@brain.net.pk

(walnut) bark, its application on split leather (with and without mordants) and colour measurements of the dyed leathers. Mordants used were of mild nature in consideration of the adverse effects of heavy metal mordants on human health and environment (Kongkachuichay *et al.*, 2002).

Juglan regia (walnut) belongs to family Juglandaceae. It is a slow growing tree in northern parts of Pakistan and is planted mainly for timber and nuts. All parts of the tree specially walnut bark contains brown dye while unripe walnut rinds give black dye (Khatchatrian and Khatchatrian 2002). The dye can be used to give various shades. The colours are fast and permanent. Mordants may be used to produce a range of shades, particularly with metals. The most important dye pigment in walnut is juglone, which is a derivative of naphthoquinone (Khalid *et al.*, 2008).

The CIE system enables every possible light stimulus values XY and Z. The tristimulus values, XY and Z can be regarded as the axes of a three dimensional Euclidean space in which every perceivable colour can be located, not only the colour of the objects such as dyed textiles, leather etc. but also the colour produced by monochromatic light (McLaren, 1972).

In ANLAB and CIELAB colour space each colour can be defined by two coordinates A and B which give the position of colour in the hue plan; the depth of the colour of light is indicated by the third coordinate (L). The distance between any two colours is a measure of their colour difference. There are five principal hues, red (R), yellow (Y), green (G) blue (B) and purple (P) and five intermediate hues, YR, GY, BG, PB and RP (Waheed *et al.*, 1996). The system of colour notation was developed by A.H. Munsell in 1905. The Munsell system defines the position of any colour in such a spherical space by three cylindrical coordinates which are termed as hue, lightness and chroma (McDonald, 1987).

Materials and Methods

Walnut bark, acetic acid, formic acid, citric acid, tartaric acid, distilled water, grey split leather, micro drum assembly, water bath, and Z-E 80 II colour measuring system were used in the study.

Colour measurements. Colour measurement readings of dyed leather were taken on Z-E80 II colour measuring system. Tristimulus values (XYZ), ANLAB values and Munsell renotations (hue, lightness and chroma) were determined by putting first leathers dyed without mordants on the lense of the instrument and then the premordanted dyed leather pieces.

Extraction of dye from walnut bark. A commercial sample of walnut bark was purchased from Akbari Mandi, Lahore. It was thoroughly washed with water, dried then chopped into small pieces and weighed. Chopped bark, 1 kg, was soaked overnight in 10 L distilled water. It was heated upto boiling for 2 to 3 h then filtered walnut dye solution was kept cold for further use (Oenal *et al.*, 2004; Kongkachuichay *et al.*, 2002; Oparah *et al.*, 2001).

Preparation of solutions. Dye solutions 5% and 10%, and four mordants (acetic acid, formic acid, citric acid and tartaric acid) of 0.1 M concentrations were prepared (Waheed and Alam, 2004).

Dyeing without mordant. Leather pieces were first dyed with 5% and 10% solutions of dye extracts at 50 °C, 60 °C and 70 °C for 45 min without the use of any mordant (Haroun, 2005).

Dyeing with mordants. Premordant dyeing was completed at 50 °C, 60 °C and 70 °C with 5% and 10% dye solutions using 0.1 molar solutions of the four mordants (acetic acid, formic acid, citric acid and tartaric acid). In this method leather pieces were first immersed in aqueous solutions of acetic acid, formic acid, citric acid and tartaric acid for 30 min, one by one, and then dyed with natural walnut bark dye (Deo and Desai, 1999). Dyed leather pieces were then washed with cold water, dried and labelled. Tristimulus values (XYZ), ANLAB values (LAB) and Munsell renotations (hue, lightness and chroma) were noted for all the leather pieces on colour measuring instrument (Shams-Nateri, 2008; Kim *et al.*, 2003; Waheed and Ashraf, 2003).

Results and Discussion

Tristimulus values (XYZ), ANLAB values (LAB) and Munsell renotation values (hue, lightness and chroma) of all the leather pieces were recorded. Results of colour measurements of the leather samples dyed without mordant is given in Table 1 and with mordants are given in Tables 2-5.

Tristimulus values, ANLAB values and Munsell renotations (without mordant). Colour coordinates XYZ, LAB and Munsell renotation values were recorded for 5% and 10% dye solutions at different temperatures: 50 °C, 60 °C and 70 °C without any mordant; time of dyeing was 45 min (Table 1).

The value was 17.38 at 50 °C for X coordinate. At 60 °C it decreased to 14.41 while at 70 °C the value was 14.24 for 5% dyed leather.

For Y coordinate, its value was 16.03, 13.33 and 13.15 at 50 °C, 60 °C and 70 °C, respectively. Similary, value of Z

Table 1. Results of leather pieces dyed with walnut bark dye extract without mordant on colour measuring system

Concen-tration of dye (%)	Time of dyeing (min)	Temp. (°C)	Tristimulus values			ANLAB values			Munsell (renotations)		
			X	Y	Z	L	A	B	Hue (YR)	Lightness	Chroma
5	45	50	17.38	16.06	12.13	40.07	7.55	10.22	5.16	4.55	2.63
		60	14.41	13.33	9.64	36.51	7.63	10.10	5.14	4.50	2.15
		70	14.24	13.15	9.27	36.26	7.75	9.90	4.16	4.19	2.87
10	45	50	15.38	15.02	11.13	38.01	7.52	10.15	5.91	4.16	2.95
		60	14.11	12.21	8.60	35.06	7.49	9.58	5.76	4.12	2.97
		70	13.98	12.18	8.32	34.98	7.49	9.45	4.67	4.10	3.02

coordinate decreased with the increase of temperature. The values were 12.13, 9.64 and 9.27 at 50 °C, 60 °C and 70 °C, respectively. The observation showed that most of the values for XYZ coordinates decreased with the increase of temperature for 5% dye.

Similarly for 10% dyeing, values of X coordinate decreased from 15.38 to 13.98 as temperature increased from 50 °C to 70 °C. For Z coordinate values also decreased from 11.13 to 8.32 with increase of temperature.

As for LAB values, value of L coordinate, A coordinate and B coordinate decreased with the increase of temperature which was also in sequence of the above mentioned values (Table 1).

As the dye saturation on leather pieces increased either with the increase of temperature or with the increase of percent dyeing shade, values of XYZ and LAB coordinates decreased. So XYZ and LAB values were found to be inversely proportional to the concentration shade on leather pieces. Munsell values i.e., hue, lightness and chroma were also recorded for dyeing without mordant (Table 1).

Hue is the attribute of colour by means of which colour is perceived to be red, yellow, green, blue, purple etc, while pure white, black and grey do not possess any hue. Lightness is the brightness of the colour towards light and chroma is the colour saturation. With increase of shade on leather pieces by increasing temperature, hue and lightness values decreased, while chroma value i.e., colour saturation increased on the leather.

For 5% shade, at 50 °C, 60 °C and 70 °C, values of hue were 5.16 YR, 5.14 YR and 4.16, respectively. For 10% dyeing shade, values decreased from 5.91 YR to 4.67 YR for 50 °C dyeing and 70 °C dyeing which shows that with increase of temperature and with increase of percent dyeing, values of shade hue decreased. For 10% dyeing hue values decreased more as compared to 5% dyeing. The hue values, denoted by YR, show that walnut dye is a mixture of yellow and red colour.

Lightness shows behaviour of fabric towards brightness. So, as concentration of dye on leather increased, their lightness or brightness decreased. This decrease was both with the increase of temperature as well as with the increase of percent shade. The value at 50 °C for 5% shade was 4.55, at 60 °C it was 4.50 and at 70 °C it was 4.19. Similarly for 10% dyeing, shade values decreased from 4.16 to 4.10 when dyeing was performed at 50 °C and 70 °C, respectively.

Chroma is the colour saturation on the leather. As dye saturation increased on the leather with the increase of temperature, chroma values also increased. The values of chroma for 5% shade were less than the values for 10% shade. Values of chroma for 5% shade at 50 °C was 2.63, for 70 °C it was 2.87 but for 60 °C it was 2.15 which may be due to some dyeing factor. For 10% shade, the value increased from 2.95 to 3.02 i.e. at 50 °C it was 2.95, at 60 °C temperature it was 2.97 and at 70 °C, 3.02. So (XYZ) and (LAB) value decreased with the increase of temperature for different dyeing concentration. Hue and lightness value also decreased with increase of temperature while chroma values increased (Table 1).

Tristimulus values, ANLAB values and Munsell renotations (with mordants). Tables 2, 3, 4 and 5 show values of colour measurement in the presence of different mordants i.e. acetic acid, citric acid, formic acid and tartaric acid with molar concentrations of 0.1 M. Premordanting dyeing method was used. Values of colour coordinates XYZ and LAB coordinates gradually decreased with the increase of concentration shade and with the increase of temperature. These values were less than the values obtained by dyeing without mordant (Table 1).

Similarly, Munsell renotation values of hue and lightness were less than the values shown for dyeing without mordant, (Table 1); this was according to the trend i.e., these values

Table 2. Results of leather pieces dyed with walnut bark dye extract using acetic acid as mordant on colour measuring system

Concen-tration of dye (%)	Mordant concentration (M)	Time (mins.)	Temp. (°C)	Tristimulus values X	Y	Z	ANLAB values L	A	B	Munsell (renotations) Hue (YR)	Lightness	Chroma
5	0.1	45	50	14.51	13.18	10.16	36.90	7.37	10.05	5.12	4.27	2.72
			60	12.29	12.62	9.74	36.77	7.32	9.70	5.00	4.17	2.92
			70	11.05	12.09	9.04	34.30	7.30	9.43	4.37	4.01	2.93
10	0.1	45	50	13.73	12.11	10.05	36.79	7.08	9.89	5.08	4.08	3.06
			60	12.14	10.92	9.31	34.04	7.04	8.76	4.92	4.02	3.19
			70	11.57	10.49	9.05	33.38	7.04	8.56	4.76	3.80	3.21

Table 3. Results of leather pieces dyed with walnut bark dye extract using formic acid as mordant on colour measuring system

Concen-tration of dye (%)	Mordant concentration (M)	Time (mins.)	Temp. (°C)	Tristimulus values X	Y	Z	ANLAB values L	A	B	Munsell (renotations) Hue (YR)	Lightness	Chroma
5	0.1 M	45	50	12.70	11.60	8.15	34.05	7.25	9.65	4.52	3.93	2.80
			60	12.02	11.45	8.12	34.01	7.20	9.60	4.45	3.89	2.93
			70	12.02	11.30	8.09	33.11	7.15	9.26	4.37	3.18	3.05
10	0.1 M	45	50	12.10	11.25	8.10	33.41	7.09	9.24	4.49	3.84	3.16
			60	12.08	11.04	8.05	33.20	7.01	9.30	4.35	3.75	3.53
			70	12.07	11.06	8.02	33.09	6.9	9.25	4.00	3.68	3.75

Table 4. Results of leather pieces dyed with walnut bark dye extract using citric acid as mordant on colour measuring system

Concen-tration of dye (%)	Mordant concentration (M)	Time (mins.)	Temp. (°C)	Tristimulus values X	Y	Z	ANLAB values L	A	B	Munsell (renotations) Hue (YR)	Lightness	Chroma
5	0.1	45	50	12.47	11.34	8.12	33.67	6.95	9.06	4.04	3.50	2.84
			60	11.81	10.69	7.67	33.30	6.75	8.87	3.84	3.30	2.99
			70	9.90	9.07	6.80	32.26	6.14	8.78	3.17	3.12	3.17
10	0.1	45	50	11.58	10.22	8.08	30.49	6.54	9.06	4.83	3.82	3.18
			60	11.06	10.08	7.44	30.28	6.44	8.53	4.93	3.55	3.55
			70	9.39	9.30	6.20	30.14	6.14	8.29	5.10	3.17	3.85

Table 5. Results of leather pieces dyed with walnut bark dye extract using tartaric acid as mordant on colour measuring system

Concen-tration of dye (%)	Mordant concentration (M)	Time (mins.)	Temp. (°C)	Tristimulus values X	Y	Z	ANLAB values L	A	B	Munsell (renotations) Hue (YR)	Lightness	Chroma
5	0.1	45	50	11.13	10.99	8.05	32.62	6.66	9.02	4.22	3.06	2.78
			60	10.49	10.41	7.16	32.77	6.48	8.16	4.00	3.07	2.99
			70	9.14	9.01	7.00	32.25	6.18	7.29	3.66	3.46	3.05
10	0.1	45	50	11.83	10.67	7.86	32.66	6.48	8.59	4.18	3.48	3.28
			60	10.29	9.27	7.09	30.44	6.29	7.59	3.72	3.04	3.30
			70	8.45	7.72	5.92	27.78	6.04	6.81	3.45	2.92	3.90

were inversely proportional to the colour saturation values. Chroma values increased with increase of percent dye shade when mordants were used.

The value for increase in shade mainly depends on two factors: dye concentration and the temperature. Mordants also increased the dye shade by fixing the dye on leather pieces. In the actual dyeing process, a mordant combines chemically with a soluble dye to form a very complex aggregated, insoluble lake of high molecular weight within the fibre. The 'lake' makes the fiber resistant to the external influences in washing and finishing processes. Fastness depends on the formation of the 'lake' inside the fiber (Waheed and Alam, 2004). Leather also showed the same behaviour during dyeing in the presence of mordants. Colour coordinates XYZ and LAB decreased more in the presence of mordants.

Mansell renotations recorded during the study in the presence of mordants were mostly lower for hue and lightness and higher for chroma when mordants were used in comparison to those without mordant (Table I) because colour saturation on leather increased. When comparison was made between different mordants, it was found that leather pieces premordanted with tartaric acid when dyed showed less values of XYZ and LAB colour coordinates than with other mordants i.e. acetic, formic and citric acids. Chroma 'C' showed higher values and hue and lightness values decreased when dyed with tartaric acid as mordant. The results of colour fixing were in the sequence of tartaric acid > citric acid > formic acid > acetic acid (Table 2-5). Trend of increasing and decreasing values was smooth but exceptions were also present.

Conclusion

Though walnut bark dye is substansive (direct) dye but when applied on leather in the presence of mordants gave better results. Tartaric acid as mordant gave best result at 70 °C at 10% concentration of dye. Walnut bark dye has the potential to replace some of the carcinogenic dyes. Heavy metal mordants can also be replaced by mild or natural mordants to control effluent problems.

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