SOME STUDIES ON NATURAL DYES

by

DEEPTI BAHL

A thesis submitted in
fulfilment of the requirements
for the award of the degree of

DOCTOR OF PHILOSOPHY

Department of Textile Technology
INDIAN INSTITUTE OF TECHNOLOGY, DELHI

December, 1994

TO MY HUSBAND
... WITH LOVE

CERTIFICATE

This is to certify that the thesis entitled **Some Studies on Natural Dyes** being submitted by Ms. Deepti Bahl to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy is a record of bonafide research work carried out by her under my guidance and supervision.

To the best of my knowledge this thesis has reached the required standard. The material presented in this thesis, in part or full has not been submitted to any other University or any other Institute for the award of degree or diploma.

M.L.Gulrajani
Professor
Department of Textile Technology
Indian Institute of Technology
New Delhi - 110016

ACKNOWLEDGEMENTS

It is with a deep sense of gratitude that I thank my project supervisor Prof. M.L.Gulrajani, without whose foresight and continued guidance, this work could not have been undertaken or completed successfully.

Sincere thanks are due to Prof R.C.D Kaushik, Director TIT&S, Bhiwani for granting me leave and providing other facilities to continue with the experimental and writing work while at the Institute.

I thank Dr. Khanna, Vice President, Ranbaxy R&D Centre for allowing me full use of all facilities at their centre and Dr. J.Singh and other scientists for helping out so enthusiastically with the chromatographic and characterization studies.

I express my thanks to Dr. Raghavan of Physics department and Dr. G.S.Kapoor, Ms Anju Khanna and all other friends, colleagues and technical staff of Chemistry Department, who helped me with small and big things all through this work.

I am grateful to Dr. Sushil Kumar, Director CIMAP and Dr. K.C Gupta of GBPUA&T, for helping out with literature survey.

Thanks are due to the faculty members of Textile Department for providing valuable guidance, whenever required. To my colleagues Sheetal, Deepali, Shailja and Kannanji for the memorable lunch and tea sessions. Also to Mr. V.A. Passi, Mr. Rajender Prasad, Mr. Prakash Chand, Mr. Shiv Charan, Jagdish, Suresh and Ashok of Textile Chemistry Lab; to Mr. Didarmal, Mr. Padam and Mr. Prabhu for rendering timely assistance.

Special thanks to Mr. Rajesh Arora for typing this manuscript always in time with my schedule.

I thank my parents and my mother and brother-in-law for their unwavering support and co-operation throughout. Finally, I thank my husband for believing in me, for being so patient and for everything else that helped make all these years of work so enjoyable. Last, but not the least, I thank my little daughter for sparing me the time, which was rightfully hers, to complete this manuscript.

DEEPTI

ABSTRACT

In recent years, the world has become increasingly aware of the environmental issues. Synthetic dyestuffs, in particular, have come under severe criticism for they are highly polluting in their stage of manufacturing as well as application. At the same time there has been a renewal of interest in the use of natural colouring matters for dyeing of textiles.

Many empirical studies have been conducted on colour characteristics, fastness properties and dyeing methods used for dyeing with indigenously available natural dye materials. Studies are also being conducted for identification, preservation and restoration of the natural dyes present on ancient museum textiles. Systematic scientific studies in this field are few.

This thesis is an attempt to study in detail, the mechanism of dyeing various textile fibres with natural dyes; to standardise a method for separation and purification of colouring compounds present in a selected plant material and to characterize and identify them; to comprehensively review natural dyes and their fastness properties to test and document the fastness properties of some prominent Indian dyes and to study the kinetics of light fading of a particular dye.

Lawsone (2-hydroxy-1,4-naphthoquinone) is the colouring compound found in henna leaves. The dye, possessing the characteristics of a disperse dye was used to conduct thermodynamic and kinetic studies on six different textile fibres

and at three different temperatures. Results showed that rate of dyeing is directly related to the denier and diffusion coefficient of fibres. The mechanism of dyeing on all fibres resembled the partition mechanism corresponding to the Nernst isotherm at 70 and 100^{o}C. However, at 50^{o}C isotherms were curved, indicating the attainment of a pseudo equilibrium - caused most probably by the aggregation of dye in solution at that temperature. Excessive uptake of dye was observed for all fibres. Experimental evidence showed that this was due to the aggregation of dye molecules inside the fibre. Standard affinity was seen to increase with increase in temperature and heat of dyeing ΔH was positive indicating an exothermic reaction in all cases except wool. On wool, affinity was found to be independent of temperature change. Mordanting with Al^{3+} ions did not appear to affect the equilibrium dye uptake by wool and silk fibres.

Identical studies, as for lawsone, were conducted with juglone - the 5-hydroxy isomer of lawsone. It is the pigment extracted from the rind of green walnuts. Results of the study were quite similar to those for lawsone. Diffusion coefficient was directly related to the diameter of fibres. Adsorption isotherms were linear at both 50^{o}C and 100^{o}C for all fibres and the standard affinity increased with temperature. Juglone, in general, showed higher affinity for hydrophobic fibres, as compared to hydophilic fibres but there is little difference in the affinity of individual fibres in each class.

Dye extracted from the roots of dolu or Himalayan rhubarb gives a variety of deep and bright shades on wool and silk. A literature survey showed that the roots contain several derivatives of hydroxy anthraquinones which are responsible for the colouring power. Thus it was decided to develop a procedure to separate the pigments, purify and identify them, and study their dyeing mechanism. TLC analysis of the extract established the presence of five coloured species and some colourless impurities in the extract. Two solvent systems were standardised as mobile phases for preparative column chromatography. Flash chromatographic technique was employed to elute the columns.

Compounds collected from columns were recrystallized for further purification. HPLC analysis of crude extract and the purified fractions (A,B,C,D and E) estimated the purity of the five compounds as 100%, 97.5%, 98%, 99.44% and 91% respectively.

The melting point, Ultra violet and visible spectrum, Infrared spectrum, mass spectrum and Proton NMR spectrum of the fractions were recorded, interpreted and compared with reported data to arrive at their structure. First three compounds were identified as - chrysophanic acid (3-methyl, 1,8-dihydroxy anthraquinone), physcion (1,8-dihydroxy, 3-methyl, 6-methoxyl, anthraquinone) and emodin (1,3,8-trihydroxy, 6-methyl anthraquinone).

Dyeing studies, similar to those conducted with lawsone and juglone were conducted on polyester with the purified dye chrysophanic acid separated from rhubarb extract. The dye exhibited no affinity for silk fibres. Linear isotherm was obtained at 130^{o}C but at 100^{o}C the isotherm was curved - indicating the establishment of a pseudo-equilibrium.

Extensive light and wash fastness tests were conducted on wool and silk fabrics dyed with some prominent yellow, red and brown dyes of India and their fastness ratings recorded as per ISO standards. No natural yellow dye was found to have a fastness grade more than 4 as most yellow dyes are based on the flavonoid molecule which is sensitive to light. Also, several yellow shades turn brown instead of bleaching on exposure to light. Red dyes, in comparison exhibit better fastness, as they are mostly anthraquinone based mordant dyes. Brown and black dyes mostly obtained from combining tannins with ferrous salt also exhibit moderate to good light fastness. Wash fastness of most dyes was good, ranging between 3-4 grade. But good fastness to light was not always found in dyes having good fastness to washing.

Kinetics of light fading tests showed interesting results. On silk samples the rate of fading curve showed an initial darkening of shades followed by no fading. On wool samples, the curves were near horizontal, indicating little or no fading. The rate, or nature of fading was neither influenced by humidity nor mordanting. The rate of change in colour (DE) was retarded by ferrous mordanting on silk. Unmordanted and

alum mordanted wool samples showed a much higher rate of change in colour than the other mordanted samples.

Spectral curves of silk samples showed increased absorbance in the entire visible region after exposure. On wool samples there were very little change in the spectral curve after exposure. All samples in general turned redder on exposure to light. From these results it could be concluded that the dye is present in a highly associated form in the fibre, due to which it is highly resistant to colour change when exposed to light.

CONTENTS