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Rare earth salts mediated improved rubbing fastness for Indigo dye

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Abstract

Indigo dye though rich in blue colour has poor affinity for cellulose cannot penetrate too well and thus it mostly remains at the surface of the fabric after dyeing. This phenomenon is called ring dyeing. Such ring-dyed materials have poor rubbing fastness towards dry and wet test methods. Our objective in this paper has been to use rare earth (RE) salts to overcome the rubbing fastness problem. The RE metals used in this research work is Cerous sulphate, Lanthanum chloride and Yttrium chloride.

Keywords: Indigo dyeing • Rare earth salts • Cerous sulphate • Lanthanum chloride • Yttrium chloride• Post mordanting

Introduction

Indigo is a vat dye and has the following properties: It is water-insoluble; before application it is made soluble by reduction with caustic soda and sodium hydrosulphite and oxidised after application on yarn or fabric. It has poor affinity for cellulose fibres. Its colour fastness to light and washing is moderate. The colour index of Indigo dye is C.I. Vat Blue 1 and its chemical formula is $C_{16}H_{10}O_2$. The Indigo dye is a small molecule which can exist in trans form mostly, however cis form also is present.

As indigo dye has poor affinity for cotton it is important to understand the morphology of the indigo dyed fabric. It is very well documented through microscopy studies that in indigo dyeing, the penetration of the dye into the cross-section of the cotton yarn solely depends on the pH of the bath. The best colour yield is obtained in the pH range of 10.5–11.5.

Monitoring the dyebath pH carefully can be an effective means of consistent and reproducible dyeing results. Depending on dyebath pH, reduced indigo can exist in three forms: i) nonionic enolic acid leuco compound, ii) monoenolate anion which is more soluble, and iii) doubly charged bisenolate anion which is less substantive. At the pH range 10.5-11.5, maximum colour is obtained in the dye bath. This colour yield correlates closely with the fractional amounts of these three species.

Cis–trans isomerization around double bonds in conjugated compounds can be triggered by heat, light, or catalysts such as the addition of protons, transition metal ions, Lewis acids and others [1]. The presence of several heteroatoms with free electron pairs, often in optimum position for chelate coordination, provided another dimension for several classes of dye molecules, allowing for the modification of absorption and redox properties via metal coordination. Chelate complexes are distinguished by a metal acyclic structure, with five- and six-membered rings as the most common configurations. Dye molecules can also offer more than one coordination site for metals within extended p systems, thereby allowing dye ligand mediated metal-metal interaction such as in mixed-valent systems [2].

The indigo molecule exists in a Tran's configuration regarding the central CC bond (Figure. 1), however, the cis configuration is a high-energy alternative. - The acidic N-H protons may be removed stepwise and replaced by one or two metals (Figure 2). Indigo forms as depicted in Figure 2 can bridge two metals, allowing for metal-metal interaction, including mixed valency. - The metal coordination for the trans conformer of indigo derivative results in six-membered chelate rings (N, O or N, O: N coordination) while the cis conformer may lead to five- and seven-membered ring chelates. Thus the proposed structures for metal chelated products with cerous (Ce), lanthanum (La) and yttrium (Y) are shown in Figure 2. Metal chelates are readily formed by these rare earth metals [3]. The stabilization of rare earth metal chelates can be rationalized on the basis of the interplay of crystal-lattice, acid-base, charge, size and redox factors.

Several researchers have attempted to improve the rub fastness of indigo dyed fabrics. The fastness to crocking improvement of Indigo and CI Sulphur Black 1 dyed cellulosic fabric, whilst retain its other desirable properties [4].

Since rubbing fastness is a major issue faced by indigo dyers. We tried to experiment with rare earth salts -Cerous sulphate, Lanthanum chloride and Yttrium chloride through post mordanting. It is known that rare earth metals

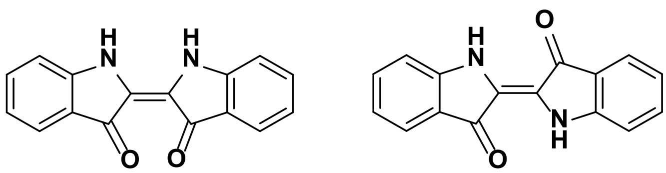

Figure 1; Cis and Trans conformers of Indigo.

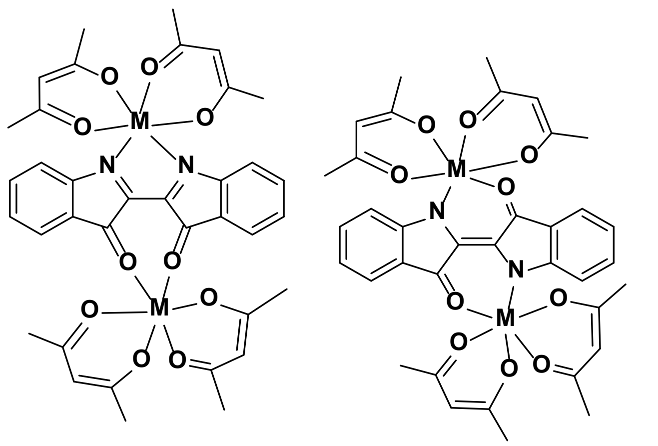

Figure 2: Metal chelation sites for cis and Trans conformers.

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form chelates with dye molecules particularly Yttrium [3]. We wanted to explore the use of rare earth salts in natural dyeing.

Materials and Methods:

Materials

Bio indigo dye was procured from AMA Herbal, Luck now, rare earth salts, Cerous sulphate, Lanthanum chloride and Yttrium chloride were procured from Indian rare earths limited (IREL), head office. Standard soap was procured from SDC Enterprises Limited; it was used for washing the dyed silk fabrics. Sodium hydroxide, sodium dithionite and citric acid were procured from Loba Chemical Pvt Ltd. Silk fabric was purchased from Sanjay Shah and Associate Company.

Methods

Indigo Dyeing and Post Mordanting

The insoluble indigo dye is converted to water-soluble leuco compound by reducing with sodium hydrosulphite in the presence of sodium hydroxide at 60–65°C. Leuco salts are converted into sodium salt with excess alkali. After dipping in this solution, the dyed fabric is run in air for a short duration when the soluble leuco salt is oxidised back into original insoluble indigo.

The indigo dyed swatches were prepared by using 0.25%, 0.50% and 1.00% of natural indigo dye powder and then the mordanting with RE salts was done in second step. The process of post-mordanting was carried at 50–55°C with gentle stirring and continued for 45 minutes, for the RE mordents- Cerous sulphate (Cerous Sul), Lanthanum chloride (LanCl) and Yttrium chloride (Yttr Cl). The process of post mordanting was carried out by using 1% of RE mordant solution and maintaining 1:30 material-to-liquor ratio. The material was then removed and washed with water 2–3 times followed by drip drying operations at room temperature. The dyeing scheme is shown in Figure 3.

Figure 3: Indigo Dyeing and Post mordanting scheme.

Measurement of reflectance (%) & colour strength (K/S)

Reflectance (%) of the dyed fabric samples were measured by using Premier Colour scan spectrophotometer. As the strength of any dye is related to its absorption property, so by using Kubelka–Munk formula [5] the following relation between reflectance and absorbance can be derived:

$K/S = [\{(1-R)^2 / 2R\}]$

Where R is the reflectance, K is absorbance and S is the scattering. By using the above equation colour strength of different indigo dyed samples were measured.

Evaluation of Fastness Properties

Launder-o-meter for testing washing fastness and fadometer with xenon arc lamp for testing light fastness were used. Crock master rubbing tester was used to test the rubbing fastness of dyed samples. The dyed samples were tested according to Indian standard methods. The specific tests were: colour fastness for light, IS-2454-85, colour fastness to rubbing, IS-766-88. The washing fastness of samples was evaluated by the standard test method, ISO: 105 C: 10.

Results and Discussion

Dyeing was done with 0.25 %, 0.50% and 1.0% of Indigo dye. The K/S Value and the CIE Lab values are shown in the table 1.

Figure 4 shows the shade deepening with increase in percentage of dye used. Although the K/S values of the indigo dyed silk samples show little differences in their intensities, but there is no bathochromic or hypochromic changes observed. In each of the percentage of indigo dyed samples Yttrium chloride post mordanting showed the best results as shown in Table 1.

However, grades of the mordanted samples recorded showed better results than that of the (unmordanted) control samples.

Among the three RE mordants Yttrium chloride showed the best dyeing effect, we assessed the wash, light and rubbing fastness's of Yttrium chloride post mordanted samples for the three dye percentages against the control sample. The wash and light fastness are shown in Table 2 while the rubbing fastness (dry) and (wet) are shown in table 3. With increase in dye % there is an apparent improvement in wash and light fastness's of the dyed samples. The best results are obtained with 1% indigo dye for Yttrium chloride post mordanted sample. This indicates that higher % of dye offers more chelation sites for the better dye adherence.

Table 1. CIE Lab and K/S values of RE post mordanted Indigo dyed silk swatches.

% of Indigo	K/S	L*	a*	b*	dE*	Remark
0.25%						
Control	**23.07**	**54.19**	**-6.16**	**-16.52**	**--**	
Cerous Sul	**23.70**	**53.55**	**-4.61**	**-17.36**	**1.86**	
Lan Cl	**24.54**	**53.10**	**-4.99**	**-17.23**	**1.74**	
Yttr Cl	**24.62**	**53.05**	**-5.09**	**-17.14**	**2.07**	**Best**
0.50%						
Control	**30.81**	**48.10**	**-5.64**	**-18.28**	**--**	
Cerous Sul	**32.75**	**48.61**	**-3.95**	**-17.24**	**2.05**	
Lan Cl	**33.57**	**48.41**	**-4.73**	**-17.37**	**1.32**	
Yttr Cl	**38.11**	**46.17**	**-3.29**	**-16.89**	**3.35**	**Best**
1.0%						
Control	**50.48**	**42.71**	**-5.72**	**-19.25**	**--**	
Cerous Sul	**56.87**	**40.07**	**-2.31**	**-16.44**	**5.15**	
Lan Cl	**57.95**	**40.15**	**-3.51**	**-18.25**	**3.53**	
Yttr Cl	**62.10**	**38.67**	**-1.59**	**-16.74**	**6.29**	**Best**

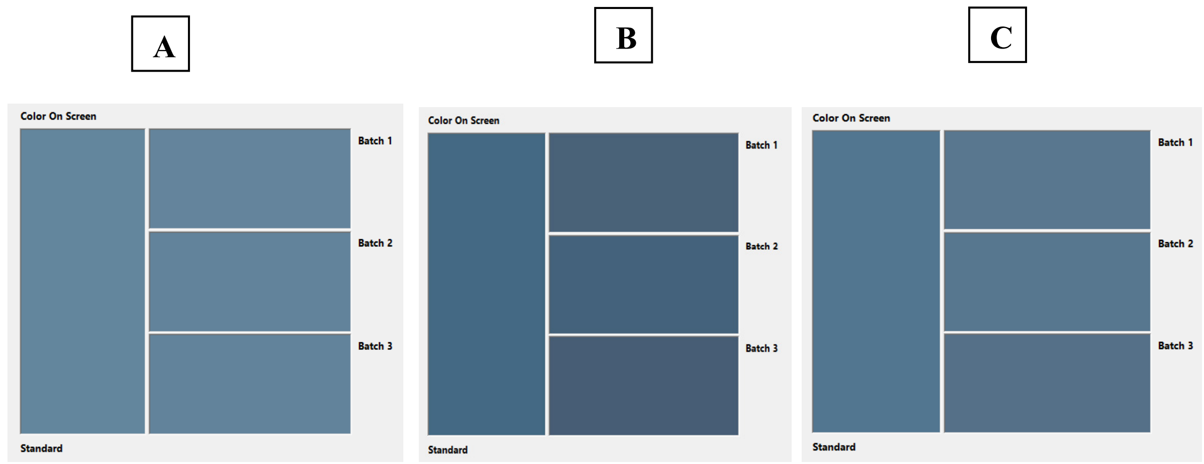

Figure 4: A. Dyed swatches 0.25%, B. Dyed swatches 0.50%, C. Dyed swatches 1.00% (Std-Control, Batch-1Cerous Sul; Batch-2Lan Cl; Batch-3 Yttr Cl).

Table 2. Washing and Light fastness of Indigo dyed silk swatches.

Indigo samples post mordanted	Washing fastness	Light fastness
0.25% Control	3-4	2
0.25% Yttr Cl	4	2-3
0.5% Control	3-4	2-3
0.5% Yttr Cl	4	3
1% Control	3	3
1% Yttr Cl	4	3-4

Table 3. Rubbing Fastness of Indigo dyed silk swatches.

Indigo samples post mordanted	Rubbing fastness (dry)	Rubbing fastness (wet)
0.25% Control	3-4	3
0.25% Cerrous Sulphate	3-4	3-4
0.25% Lanthanum Chloride	3-4	3-4
0.25% Yttrium Chloride	4	4
0.5% Control	3	3
0.5% Yttrium chloride	3-4	3-4
1% Control	3	3
1% Yttrium chloride	3-4	3-4

For rubbing fastness's dry and wet we evaluated for all the three mordants-Cerous sulphate, Lanthanum chloride and Yttrium chloride for 0.25% indigo dyed samples. Since the values for Cerous sulphate and Lanthanum chloride postmordanted samples were found to be lower, we carried out only the rubbing fastness's for 0.50% and 1.00% dyed samples of Yttrium chloride mordanted samples only as shown in table 3.

Conclusion

Several researchers have used different types of fixing agent which are not usually safe chemicals. We have shown that rare earth salts which are eco-friendly can be a safe alternative to enhance the dye adherence. Thus it can be concluded that post mordanting with RE salt –Yttrium chloride has made a significant improvement in the fastness properties of Indigo dyed silk sample utilizing its unique chelation property.

References

1. Chandra S, James B, Macauley B and Magee R. "Studies on the fungicidal properties of some organo-tin compounds". *J Chem Tech Biotec* 39(2007):65-73.
2. Benns B, Gingras B and Bayley C. "Antifungal Activity of Some Thiosemicarbazones and Their Copper Complexes". *J Applied Microbiology* 8(1960): 353-356.
3. Bellí N, Marín S, Sanchis V and Ramos A. "Impact of fungicides on Aspergillus carbonarius growth and ochratoxin a production on synthetic grape-like medium and on grapes". Food Additives Contaminants 23(2006):1021-1029.
4. Zhang D, Chen L, Zang C and Chen Y, et al. "Antibacterial cotton fabric grafted with silver nanoparticles and its excellent laundering durability." *Carbohydrate Polymers* 92(2013):2088–2094.
5. Abdel-Mohsen AM, Abdel-Rahman RM and Hrdina R. "Green synthesis of hyaluronan fibers with silver nanoparticles". *Carbohydrate Polymers* 83(2012):411-422.
6. Imramovsk´y A, Burgert L, Aly AS. "Antibacterial cotton fabrics treated with core-shell nanoparticles." *Int J Biol Macromolecules* 50(2012): 1245-1253.
7. Zhang F, Wu XL, Chen YY and Lin H. "Application of silver nanoparticles to cotton fabric as an antibacterial textile finish." *Fibers Polymers* 10(2009):496-501.
8. Jain A, Duvvuri SL, Farah S and Beyth N, et al. "Antimicrobial polymers." *Adv Healthcare Materials* 3(2014): 1969-1985.
9. Perelshtein I, Applerot G, Perkas N and Guibert G, et al. "Sonochemical coating of silver nanoparticles on textile fabrics (nylon, polyester and cotton) and their antibacterial activity." *Nanotechnology* 19(2008): 245705.
10. Ravindra S, Murali Mohan Y, Narayana Reddy N and Mohana Raju K. "Fabrication of antibacterial cotton fibres loaded with silver nanoparticles via 'Green Approach." *Physicochemical and Engineering Aspects* 367(2010):31-40.
11. Jiang T, Liu L, Yao J. "In situ deposition of silver nanoparticles on the cotton fabrics." *Fibers and Polymers* 12(2011):620-625.
12. Du BD, Phu DV, Quoc LA and Hien NQ."Synthesis and Investigation of Antimicrobial Activity of Cu." *J Nanoparticles* 2007(2017): 1-6.
13. Jia B, Mei Y, Cheng L and Zhou J, et al. "Preparation of copper nanoparticles coated cellulose films with antibacterial properties through one-step reduction." *ACS Applied Materials & Interfaces* 4(2012):2897-2902.
14. Kalhapure RS, Akamanchi KG, Mocktar C and Govender T. "Synthesis and antibacterial activity of silver nanoparticles capped with a carboxylic acid-terminated generation 1 oleodendrimer." *Chemistry Letters* 43(2014):1110-1112.

15. Laskowski L, Laskowska M, Fijalkowski K. “New Class of Antimicrobial Agents: SBA-15 Silica Containing Anchored Copper Ions.” *J Nanomaterial’s* 2017(2017):1-2.

16. Sun C, Li Y, Li Z and Su Q, et al. “Durable and Washable Antibacterial Copper Nanoparticles Bridged by Surface Grafting Polymer Brushes on Cotton and Polymeric Materials.” *J Nanomaterial’s* 2018(2018):1-7.

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