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Dyeing of Cotton and Silk Fabric with Purified Natural Curcumin Dye

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Abstract-- The use of natural dyes is increasing day by day due to the eco-friendly approach of the people, though there are some limitations with the use of the dyes. The extraction process of natural dyes and technique of dyeing should be developed, so that they can replace the synthetic dyes, which are problematic for environment and human health. This work concerns with the extraction and purification of natural dyestuff from a plant Curcuma Longla L. and dyeing of cotton and silk fabric in exhaust dyeing method. The main coloring component of turmeric is curcumin, which produces yellow color in the textile material. The purified curcumin produces various shade on cotton and silk fabric with different dyeing parameters and use of mordants. The color fastness properties of the dyed fabrics are also good.

Keywords-- Column chromatography, Curcumin dye, Solvent extraction method, Thin layer chromatography

Introduction

Dyeing is one of the oldest techniques of human civilization. People have dyed the textile materials since thousands of years and most of the times the dyes have come from nature [1]. People used these dyes in cosmetics, food [2,3], leather and also in medicine [4]. The use of natural dyes has increased after the development of weaving technique for dyeing textile materials [5].

The use of synthetic dyes has become faster acceptability in the field of food [7], cosmetic [8] and more importantly in the field of textile industries [9] after the invention of synthetic dyes by William Henry Perkin in 1856 [6]. The manufacturers preferred the dyes because of easy dyeing process, variation of shades, color fastness properties as compared to natural dyes. But, the dyes cause some serious health hazards like allergic, carcinogenicity, and skin diseases [10], though they are widely and commercially popular. They pose also threat towards its eco-friendliness, as most of the dyes contain azo groups of aromatic amines that may be harmful to human health and environment [11]. As a result, recently a ban has been imposed all over the world including European Economic Community (EEC), Germany, USA and India on the use of some synthetic dyes [12]. Due to environmental awareness and harmful effects of either toxicity or non-biodegradable nature of synthetic dyes, the use of the dyes is gradually decreasing during the last few decades. On the other hand, the use of natural dyes is increasing in the field of food, pharmaceutical, cosmetic as well as the textile coloration process.

The present study focuses on the development of the optimum extraction conditions of coloring component from the natural material turmeric i.e. Curcuma Longla L. and then the major component of the dye i.e. curcumin is purified. The chemical structure of curcumin is shown in figure 1. Finally the purified dye is applied on cotton and silk fabric in exhaust dyeing method. The color strength value, dye exhaustion% and color fastness properties of the dyed fabrics are evaluated and compared with each other.

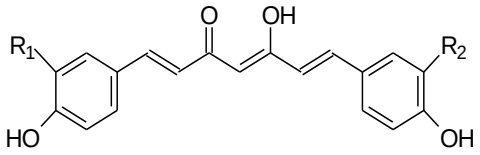

Fig. 1- Chemical structure of soluble curcumin[13]

Materials and experimental methods

Dyestuff used

Turmeric i.e. Curcuma Longla L. is used to obtain the dyestuff of curcumin, which is yellow in color. Turmeric is collected from the local market of Bangladesh.

Fabric used

Cotton and silk fabrics are selected for the present study, which are collected from WFK- GmbH, Germany. Cotton fabric is scoured-bleached and degumming is done for silk fabric before dyeing.

Chemicals used

Ethanol (C_2H_5OH), chloroform ($CHCl_3$), acetone (C_3H_50H) and n-hexane (C_6H_{14}) are used as solvent to extract the dye from Curcuma Longla L.

Mordants used

The following mordants are used: potassium aluminium sulphate ($AlK(SO_4)_2.12H_2O$), copper sulphate ($CuSO_4$) , and tartaric acid ($C_4H_6O_6$). They were pure grade chemicals.

Extraction of curcuminoid from turmeric

Fresh rhizomes of turmeric are washed and cleaned with distilled water. They are then sliced and dried in the sunlight for one week and again dried at 80^0c for one hour in a hot air oven. Dried rhizomes are made in powder form for getting proper extraction result. 10 gm of turmeric powder are taken into a thimble and placed in a soxhlet apparatus. 200 ml of solvent is added in soxhlet for 10 gm of sample and the extraction is carried out according to the boiling point (B.P.) of solvent for 8 hours. After extraction the dark brown extract is cooled, filtered, concentrated by evaporation. Finally, a crude dried extract is obtained, which is black orange in color. The dye is extracted from turmeric using different solvent according to their boiling point by the same method and yield is calculated. The extracts are dissolved in the same amount of water to compare the concentration of the color by using UV/VIS spectroscopy for getting the best extraction result.

Separation of curcumin from curcuminoid by TLC

Solvent extracts are tested in TLC for presence of three different color components of turmeric. The process used a thin plastic plate (Merck-60 F254, KGaA, Deutschland). Using a capillary tube, a row of spots of the appropriate extract along a line about 1 cm from the bottom of TLC strip is applied. The spot have to dry completely and this took 30 seconds or more. The plate is placed vertically in a jar, which is pre-saturated with the mobile phase. As the solvent runs upward, it passes the sample and starts to carry the compounds upward with it. The different components in the mixture move up the plate at different rates due to differences in their partitioning behavior between the mobile liquid phase and the stationary phase. The more polar a molecule, the more strongly it is adsorbed. As a result, the compounds, the relatively more polar ones, remain near the bottom of the plate while others, less polar ones are carried by the solvent nearer the top. When the solvent front reaches the other edge of the stationary phase, the plate is removed, dried and spots are visualized in UV light. Finally, the R_f values of the components of different mobile phase mixture are calculated from the TLC plate as shown in figure 2.

The R_f values are determined by the equation no (1). The R_f value can be used to identify compounds due to their uniqueness to each compound.

$$R_f = \frac{\text{Distance from baseline traveled by solute}}{\text{Distance from baseline traveled by solvent}} \quad (1)$$

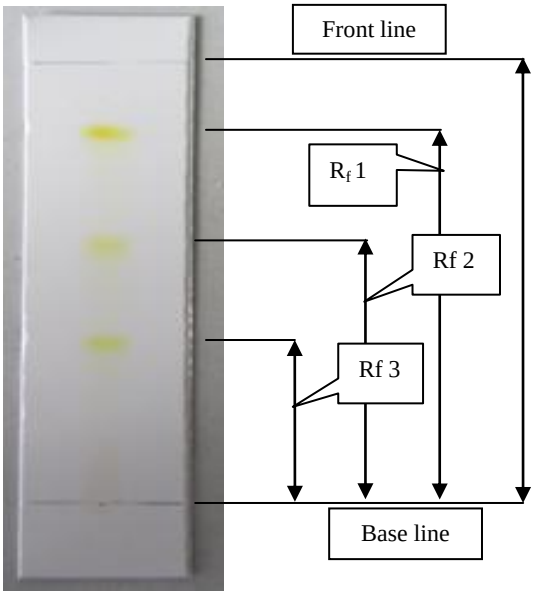

Fig.2 - Calculation of R_f from developed TLC plate

Purification of curcumin by column chromatography

The column chromatography consists of a glass tube with a diameter of 30mm and a height of 70cm with a tap at the bottom. The column is clamped vertically. The stopcock of the column is closed and it is fitted with fritted disk. The silica gel is weighed out in a flask and enough solvent (eluent) is added with stirring to form a slurry. Then, slurry is slowly transferred into the column using a glass funnel until the silica gel level is about 30-40cm. When the solvent reached the silica gel surface, slowly added the mixture solution of curcuminoid into the column using a dropper. After the sample is loaded, a small layer of sand is added to the top of the column. This helped to keep the top of the column level when added solvent eluent. Once the mixture is added and the protective layer of sand is in placed, continuously added the solvent eluent while collecting small fractions at the bottom of the column. The individual components are retained by the stationary phase differently and separated from each other while they are running at different speeds through the column with the eluent. Analyze is done for each of the collected fractions by TLC.

Identification of curcumin by IR spectroscopy

5mg dry sample purified by column chromatography is placed directly into the infrared beam of IR spectroscopy. As the IR radiation is passed through the sample, the transmitted energy is measured and a spectrum is generated. The resulting spectrum represents the molecular absorption and transmission creates a molecular fingerprint of the sample. As there is a unique combination of atoms in every material, so it is not possible to produce the same infrared spectrum of two compounds. Therefore, the instrument gives a positive identification of the purified material.

Optimization of dyeing conditions for cotton and silk fabrics

Cotton and silk fabrics are dyed with the curcumin dye at a liquor ratio of 1:40. For optimizing the dyeing conditions, at first, experiments are carried out to optimize the dyeing pH. Dyeing processes are carried out with 2% (o.w.f) concentration of purified dye at pH 3, 4.5, 7 and 9. To get the effect of dyeing temperature and dyeing time on the color strength, another set of experiment is carried out in optimized dyeing pH at 60, 75, 90 and 100°C for different time periods i.e. 30, 45, 60 and 90 minutes. Another set of experiment is also carried out at different dye concentration such as; 2%, 4%, 6%, and 8% in optimum dyeing conditions. Based on the K/S values of the dyed samples, optimum dyeing pH, temperature and time are selected and taken for further study. To study the effect of different mordants and their varying concentrations on color strength, mordanting is carried out with three metallic salts such as; aluminium potassium sulphate, copper sulphate and tartaric acid. Mordanting is carried out through two ways: 1) pre-mordanting, 2) post-mordating. The sample is taken 1gm for every experiment.

After dyeing, the dyed samples are rinsed with cold water, washed in a bath with a liquor ratio of 1:50 using 1 gm/liter of the soaping agent at 60^0C for 10 minutes and then they are rinsed and finally dried in a dryer.

Evaluation of color strength

Estimation of color strength of the dyed fabrics are carried out by determining the K/S values using a computer color matching system (CS-5, Applied color system, USA). The reflectance value (R) in the visible wavelength region is measured by means of the ACS spectrophotometer. The value of reflectance (R) of the dyed fabric is measured at the wavelength of 420 nm and also the K/S value of the sample is found directly from the instrument. Every dyed sample is

measured in the same way and the K/S values are obtained directly from the instrument, which followed the Kubelka-Munk theory as in equation (2).

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

Where, K refers to the constant of color, S is the constant of material and R is the degree of reflection. The value of K/S is directly proportional to the concentration of dye in the dyed fabric.

Measurement of exhaustion of dyes by UV/VIS spectroscopy

Degree of exhaustion is the amount of dyestuff, which is diffused in the fiber from the dye bath at the time of dyeing. UV/Vis spectrophotometer is used to measure the exhaustion and fixation of the dyestuff. By measuring the concentration of dye bath before and after the dyeing process, the percentage of exhaustion can be estimated with the equation (3) considering the color of metal salts.

$$E\% = \frac{C_1 - C_2}{C_1} x10 \quad (3)$$

Where, C_1 and C_2 are the concentrations of the dye bath before and after dyeing process respectively.

The concentrations of the dye solution before and after dyeing were measured using UV/VIS spectrometer at the wavelength of 420. Before measuring the absorbency, the wavelength of maximum absorbency is determined for the dye by using the calibration standard solutions. For the calibration standard solutions, a dye stock solution of 20 mg in 20 ml water is prepared. By pipetting 1 ml to 5 ml of this stock solution are taken and diluting to 100ml, 5 different calibration standard solutions are prepared. The concentrations of the calibration standard solutions ranged from 0.01 g/l to 0.05 g/l. The dye solution is taken into a cuvette with a width of 1cm and subsequently the absorption spectrum is recorded, which were presented in figure 3.

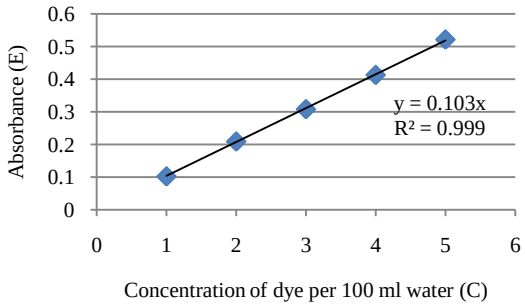

Fig.3 - Calibration curve of curcumin dye

The value of extinction coefficient is obtained from the linear regression line (y = mx), where the value of 'm' corresponds the extinction coefficient of the dyes.

The extinction coefficient of the dye is determined as per Beer-Lambert Law, based on the equation no (4):

$$\log \frac{I_0}{I} = E = \varepsilon cd \quad (4)$$

Where,

I_o - is intensity of the initial light
I - is intensity of the light after passing through the dye liquor
E - is Extinction at a specific wavelength of λ
ε - is extinction coefficient
c - is concentration of the dye liquor
d - is cuvette width

Evaluation of color fastness properties

Wash fastness of the samples dyed under the optimized conditions is tested according to ISO 105-CO3 method. Washing solution containing 5 gm/l soap and 2 gm/l sodium carbonate is taken with a liquor ratio of 1:50. The specimen is treated for 30 minutes at 60^0c. ISO 105-X12 test method is followed to measure the rubbing fastness. Color fastness of textile material to day light is of considerable importance to the consumer. The specimen should be tested according to ISO test method. The light fastness of the dyed test samples (1x 3 cm) are exposed to UV light of a Xeno tester for 30 hours. The temperature of the machine was 30^0c, R.H. 65% and irradiation dose 980 KJ/m^2. The fastness is assessed by comparing the fading of the specimen with that of blue wool patterns.

Results and discussion

Result of solvent extraction

Soxhlet extracts are weighted after drying and weight percentage of curcuminoid dye are calculated, those are shown in table 1. Maximum amount of curcuminoid dye is obtained in the form of dark black orange color by using methanol and ethanol. So the ethanol or methanol extracted curcuminoid dye is used to separate the curcumin dye.

Table 1 - Amount of extracted curcuminoid dye in percentage

Solvent	Extraction % of curcuminoid
Ethanol	5.15
Methanol	5.25
Acetone	4.10
Water	2.60

The absorbance of the extracted curcuminoid dye is also analyzed by UV-visible spectroscopy at 420nm. The extracted dyes are dissolved in a definite amount of water to compare the concentration of different solvent extract. It is found that ethanol and methanol extracted dye has more concentrations than the other, as the absorbance of solution is directly related to the concentration by Lambert-Beer's Law. The concentration of ethanol extract is also found more than methanol extract, so ethanol extracted dye is used in column chromatography to get pure curcumin dye.

Result of column chromatography

The better R_f values are found 0.28, 0.19, 0.12 for curcumin (C), dimethoxy-curcumin (DMC), bisdimethoxy-curcumin (BDMC) respectively, when chloroform and hexane are used as the mobile phase.

Different compositions of mobile phase are also tested in TLC for the separation of curcumin dye. The R_f values of the components are calculated, which are shown in table 2. If the

other solvent mixtures are used for separating curcumin dye components by column chromatography, which have high or low R_f values, then the separation will take very short time or very long time. This can affect on the result of purification of curcumin dye. That's why; the other results are not used in column chromatography. Hence the mixture of chloroform and n-hexane in the ratio of 4:1 is suitable solvent for the separation of curcumin in column chromatography.

Table 2 - R_f values using different mobile phase

TLC mobile Phase	Ratio	R_f values		
		C	DMC	BDMC
$CHCl_3$:CH_3OH	19:1	0.49	0.33	0.21
$CHCl_3$:Hexane	4:1	0.28	0.19	0.12
$CHCl_3$:Hexane	3:1	0.33	0.13	0.04

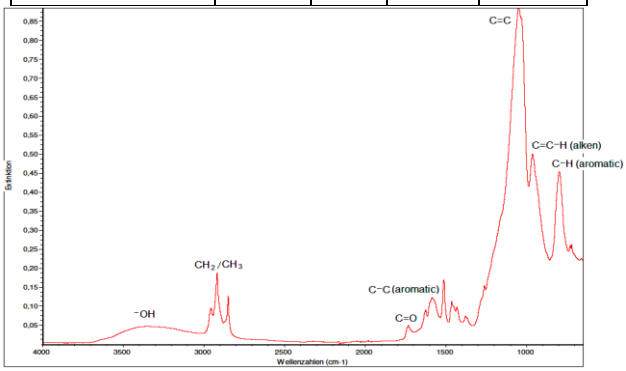

Fig.5 - Effect of concentration of curcumin dye on color strength of cotton and silk fabrics

The ethanol extracted curcumin dye is subjected to column chromatography by using the mobile phase of chloroform and n-hexane and the fractions are collected and tested with TLC. The test showed that the curcumin dye is separated. From the collected fractions of the component, the percentage of curcumin is calculated and it is found 3.15%.

Result of IR spectroscopy

The infrared spectrum of curcumin is shown in figure 4, which is determined by IR spectroscopy. The purified curcumin spectrum is almost same as the spectrum of Ferrari and Lazzari [14].

Effect of dye concentration on color strength of cotton and silk fabric The color strengths (K/S) of the dyed cotton and silk fabrics are dependent on the concentration of the extracted curcumin dye as shown in figure 5. The color of the dyed cotton and silk fabrics are yellowish, when the percentage of dye (o.w.f) is less than 2. When the percentage of dye is more than 2, then the fabrics showed yellowish brown color. From the results, it is seen that the color strength, expressed as K/S, increased with increasing concentration of curcumin dye up to a certain limit. It is also observed from the result that there is a significant difference in the depth of shade between cotton and silk fabrics, though the dyeing condition and concentration of dye are same. It is found that the color strength of the silk fabric is higher than the cotton fabric at the same concentration. The color strength of silk is more because it has two different functional groups in its structure.

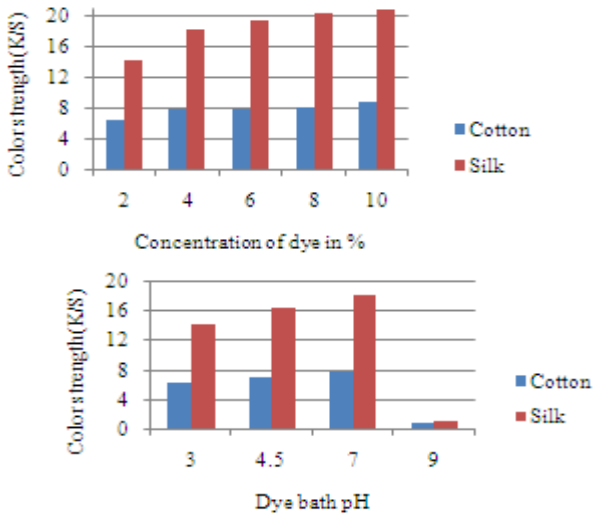

Fig.6 - Effect of pH on color strength of cotton and silk fabrics dyed with curcumin (4% shade)

Effect of pH on color strength

Figure 6 showed that the color strength (K/S) is increased with increases in the pH value of the dyeing bath from pH 3 to 7 for both the fabrics. The maximum dye uptake is obtained at pH 7 for both. In the alkaline solution, curcumin reacts with alkali, that's why it is not possible to dye the fabrics in the alkaline medium.

Effect of temperature

The effect of dyeing temperature on color strength of cotton and silk fabric is demonstrated in figure 7. As evident**,** the maximum color strength is obtained at 75^0C for both cotton and silk fabrics. The shade is also very uniform. If the temperature is increased more than 75^0c, then the depth of shade is decreased. The result is not good, if the fabrics are dyed less than 75^0c. The depth of shade is more in case of silk fabric than cotton fabric at the same concentration and temperature because of the structure of the fiber.

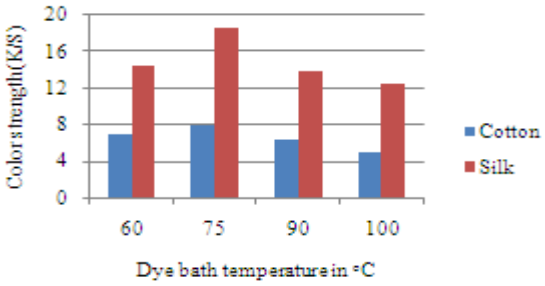

Fig.7 - Effect of temperature on color strength of fabrics dyed with curcumin dye (4% shade)

Effect of time

The effect of dyeing time on color strength is shown in figure 8. The best results with respect to time for dyeing cotton and silk fabrics are obtained at 45 minutes. The color strength is decreased, when the fabrics are dyed more than 1 hour. The decrease in color strength may be attributed to

desorption of the dye molecules as a consequence of over dyeing, if the process is carried out more than 45 minutes.

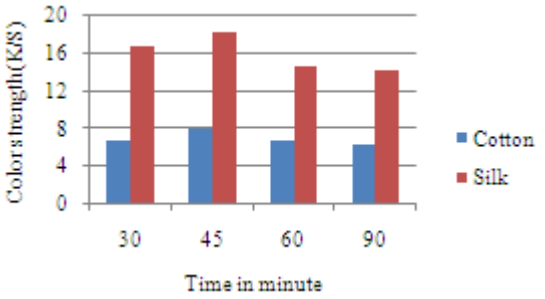

Fig.8 - Effect of time on color strength of fabrics dyed with curcumin dye (4% shade)

Effect of mordanting on color strength of cotton and silk fabrics dyed with curcumin

The effects of mordant on relative color strength for the pre-mordanting method are shown in figure 9. It is observed that relative color strength values are higher for samples dyed with premordanted fabric at 100°C in comparison with samples dyed without mordant. Since the mordant has affinity for curcumin, so it attracts more coloring component from dye bath to fabric. It is also observed in the figure 10 and figure 11 that the relative color strength is increased with increasing the mordant concentration and reached a maximum at 10 gram per liter. It is also seen that the effect of different mordants are not same. The results of alum and copper sulphate are very good in terms of color strength value. But the deviations in shade tone and brilliancy among the above mentioned dyed sample cannot be measured in terms of color strength value. It is seen that different brilliant shade can be produced on cotton and silk fabrics with curcumin dye by using same amount of different mordants.

Cotton and silk fabrics produced yellowish color, when dyed without mordants. If alum is used, then yellowish-brown color is produced. The samples mordanted with copper sulphate and tartaric acid produced a medium to dark yellowish-greenish and yellowish brown color respectively.

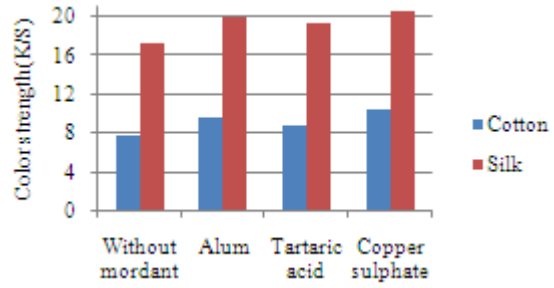

Fig.9 - Effect of pre-mordanting (2 gm/l) on color strength of fabrics (4% shade)

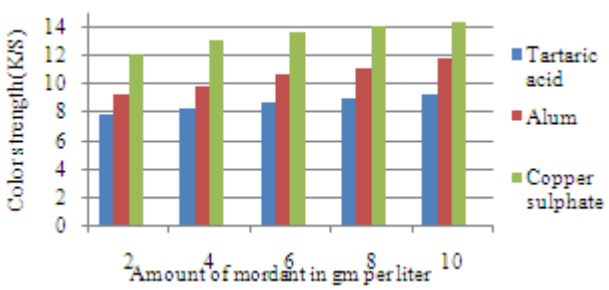

Fig.10 - Effect of pre-mordanting on color strength of cotton fabric (2% shade)

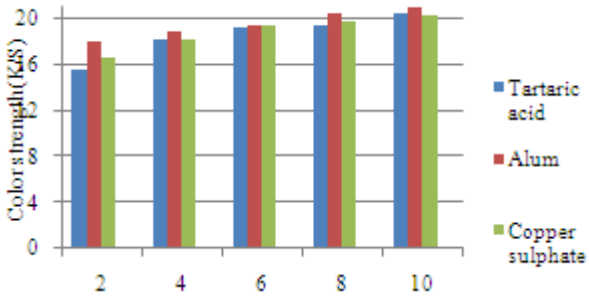

Fig.11 - Effect of pre-mordanting on color strength of silk fabric (2% shade)

It is clearly seen in figure 12 that the relative color strength decreased by the application of mordant. Thus, the pre-mordanting method showed a higher depth of shade in comparison with the post-mordanting method.

Copper sulphate, alum, tartaric acid are well known for their ability to form coordination complexes and to readily chelate with the dye. As a result, these mordants helped to increase the color strength of the dyed fabric. It is also seen that tartaric acid ions form weak coordination complexes with dye than copper sulphate and alum; so the color strength of the dyed fabrics mordanted with tartaric acid is less than the dyed fabrics mordanted with copper sulphate and alum.

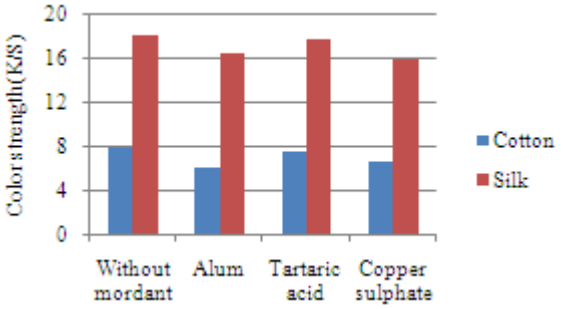

Fig.12 - Effect of post-mordanting (2 gm/l) on color strength of cotton and silk fabrics (4% shade)

Result of dye exhaustion

The highest degree of exhaustion of cotton and silk fabrics, which were dyed with different methods, are determined by UV-Visible spectroscopy and the results were shown in table 3.

The degree of exhaustion of silk fabric dyed with curcumin dye is found higher than that of cotton fabric as shown in table 3. This is because of the molecular structure of the fiber. Silk fiber has more functional groups in its structure than cotton fiber. As a result, the dye exhaustion is more in case of silk fiber than the cotton. The results also showed higher dye exhaustion is occurred on mordanted cotton and silk fabrics than unmordanted samples.

Result of fastness properties

The wash fastness rating of cotton and silk fabrics dyed with or without mordants at the dye concentration of 2% and 6% (owf) are presented in table 4. The result showed that the color fastness ratings of the cotton and silk dyed fabrics without mordanting method are not good. The fastness properties have improved significantly, when different types of mordants are used before dyeing. The mordanting with copper sulphate demonstrated better result than the others. It is due to the formation of strong bond between the dye and fiber.

Conclusion

The main goal of the work is to extract and purify the curcumin dye from the plant Curcuma Longla L., which is used to dye the cotton and silk fabric to compare the properties of the dyed fabric. To fulfill the aim of the task, solvent extraction method is applied to extract the curcuminoid dye using soxhlet and then the curcumin dye is separated by column chromatography method. The purified dye is used to color the cotton and silk fabric in exhaust dyeing method. Then the properties of the dyed cotton fabric are compared with the properties of dyed silk fabric.

The result shows that the color strength value of dyed cotton fabric are higher than the dyed silk fabric, though they are dyed in same method. The dye exhaustion percentage of the silk fabric is also higher than cotton fabric. It is observed that mordant has a great effect to increase the color strength of the fabric and the effect of different mordants are not same. Copper sulphate shows the better result than the other two.

Depending on the dyeing procedure and the types of mordant used, a variety of colors also can be produced using the same percentage of curcumin dye. Pre-mordanting and post-mordanting also affect to change the shade for dyeing cotton and silk.

Most of the natural dyes are known as antioxidants, as the dyes are derived from nature. Clothes dyed with natural dyes also have the potential to be sold at a higher price.

So extraction & purification of natural dyes and their application can be a great significance in the future of the commercial and domestic dyeing industries. The dye processing cost and the cost for effluent treatment plant (ETP) are certainly lower than that of other synthetic dyes.

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Table 3 - Maximum exhaustion of curcumin dye by cotton and silk fabrics

Fabric dyed with curcumin	Dye exhaustion (%)
Cotton without mordant	48
Cotton pre-mordanted with tartaric acid	62
Cotton pre-mordanted with $CuSO_4$	75
Cotton pre-mordanted with alum	72
Silk without mordant	73
Silk pre-mordanted with tartaric acid	80
Silk pre-mordanted with $CuSO_4$	85
Silk pre-mordanted with alum	83

Table 4 - Fastness properties of cotton and silk fabrics dyed with curcumin dye

Dyeing Technique	Shade% (owf)	Fastness Rating									
		Wash fastness				Rubbing fastness					
		Color change		Staining (cotton)		Staining (wool/silk)		Dry rubbing		Wet rubbing	
		cotton	silk	cotton	silk	cotton	silk	cotton	silk	cotton	Sill

2 6	2 1-2	2 1-2	2-3 2	2-3 2-3	3 2-3	3 2-3	3 2-3	2-3 2	2-3 2	2-3 2	1-2 1-2	1-2 1-2
2 6	2-3 2-3	2-3 2-3	3 2-3	3-4 3	3 2-3	3-4 3	3-4 3	3 2-3	3-4 3	3 2-3	2 2	2 2
2 6	2-3 2-3	2-3 2	3 2-3	3 2-3	3-4 3	3-4 3	3 2-3	2-3 2-3	3-4 3	2-3 2-3	2-3 2	2-3 2-3
2 6	3 3	3 3	3-4 3-4	3 3	3-4 3	3-4 3	3 3	3 2-3	3 2-3	3 2-3	3 2-3	3 2-3