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ORIGINAL CONTRIBUTION

Dyeing Properties of Natural Dye *Syzygium cuminii* on Silk

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Abstract Dyeing behavior of natural dye extracted from the bark of *Syzygium cuminii* L has been studied on silk fabric. Colour values and colour co-ordinates were examined in terms of K/S and L* a* b* C and h. A range of shades were obtained by using various mordants and mordanting techniques. Dye was tested for some of the eco-parameters using atomic absorption spectrophotometry and GC/MS. The test results were compared with the set standards to determine the eco-friendliness of natural dye. Their concentrations were much below the stipulated limits. Dyed samples were tested for antimicrobial activity against Gram-positive and Gram-negative bacteria and were found to possess antibacterial activity.

Keywords Antimicrobial activity · Heavy metal · Mordant · Silk · *Syzygium cuminii*

Introduction

World-wide growing consciousness for use of ecofriendly products in daily life has generated renewed interest of consumers towards use of textiles dyed with ecofriendly natural dyes. Today natural colorants are emerging globally due to the fact that they are safer and more environment-friendly and thus the application of natural dyes is considered as a better alternative to synthetic dyes. Using natural dyes contributes to value addition of textiles and also responses to the increasing demand of compatibility with the environment. Recently there has been growing interest in the use of natural dyes in textile applications [1, 2]. This is a result of the stringent environmental standards imposed by many countries in response to the toxic and allergic reactions associated with synthetic dyes. Natural dyes exhibit better biodegradability and are generally more compatible with the environment.

Syzygium cuminii is a multipurpose, large and evergreen tree. It belongs to Myrtaceae family native to the tropics, distributed throughout the world, cultivated for its edible fruits and timber. The tree grows in widely differing localities, but is generally found along streams and in damp places and swamps where it is often gregarious; it is also found in sal and evergreen forests. Timber is used for constructional purpose and agricultural implements. The bark hitherto considered a waste material is used for the present study. Bark is rich in quercetin (Fig. 1), myricetin (Fig. 2), gallic acid (Fig. 3), ellagic acid (Fig. 4), flavonoids and tannins [3–5]. Bark is astringent, antimicrobial and antifungal. Its anti-inflammatory activity [6–8] and antidiarhoeal effect show good wound healing property [9–12]. The present work aims at studying the extraction and application of new source of natural dye for silk fabrics.

Experimental

Raw Material

Dried bark of *S. cuminii* L (1 kg) was collected from an Institute in Bangalore. The bark was washed in tap water

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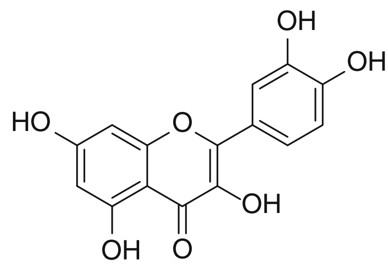


Fig. 1 Quercetin

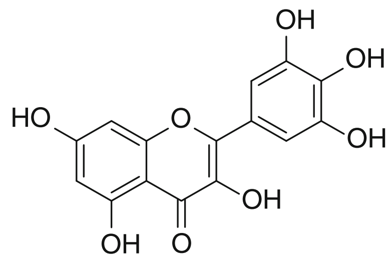
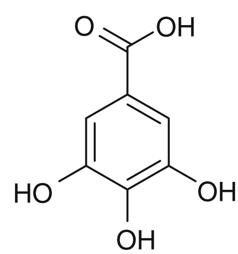


Fig. 2 Myricetin

Fig. 3 Gallic acid



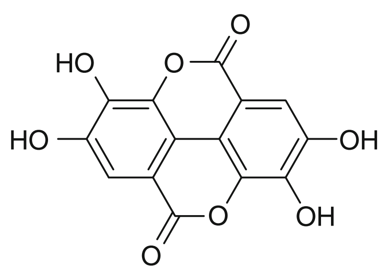


Fig. 4 Ellagic acid

and dried at room temperature. The dried bark was macerated to fine powder [13, 14].

Extraction of the Dye

The finely macerated bark was weighed and both cold and hot water extracts were prepared. In case of cold water extract, the powder was soaked in water 20 % (w/v) and kept for 48 h: in case of hot water extraction, two sets of experiments were performed. In the first set, the material was cooked in water in the MLR of 1:30 at boiling temperature with the variation of time from 60–180 min. In the second set, the cooking temperatures were ranged from 40–100 °C with extraction time of 3 h. The resultant liquid was then filtered. The extracted dye solutions were concentrated and oven dried at 60–70 °C till dry. The dry material was then removed and weighed to find out the yield [15, 16].

Dyeing of Silk Fabrics

Plain woven degummed mulberry silk fabric weighing 40 g/m^2 with a yarn density of 519 ends/dm and 456 picks/dm was selected for dyeing. The dyeing was carried out at 90 °C for silk in a dye bath containing 10 % dye (owf) at MLR 1:40 in a beaker dyeing machine for 60 min. The dyed samples were subsequently washed in 5 gpl non-ionic detergent at 60 °C for about 5 min and dried at room temperature [17, 18].

Method of Mordanting

The substrates were mordanted using 2 and 5 % (owf) solutions of each of potassium aluminum sulphate. Tannic acid and tartaric acid were employed with MLR ratio 1:20 for 30 min at 60 °C. The fabrics were subsequently rinsed and dried [19].

Measurement of Surface Colour Strength and Colour Value

Colour values were evaluated by means of K/S and CIELAB color co-ordinates with illuminant D_{65}/10° observer on Gretag Macbeth Color Eye 7000 A Spectrophotometer. Four measurements were made for each sample and the reflectance values over a range of 350–750 nm were recorded. The K/S values were assessed using the Kubelka–Munk equation.

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

where, R is the observed reflectance, K is the absorption co-efficient and S is the light scattering co-efficient [20, 21].

Dye exhaustion and fixation

The extent of dye exhaustion was determined spectrophotometrically, the absorbance of dye, the bath solution before and after the dyeing process, was recorded at the λ_{max} of the dye. The percentage dye of the bath exhaustion (%E) was calculated using Eq. (2) [22], where A_0 and A_1 are the absorbance of the dye bath before and after dyeing, respectively.

$$\%E = [(A_0 - A_1)/A_0] \times 100\% \tag{2}$$

The total fixation efficiency (T), which is the percentage of the fixed dye, was calculated using Eq. (3) [22]

$$\%T = [(A_0 - A_1 - A_2)/A_0] \times 100\% \quad (3)$$

where A_0, A_1, and A_2 are the respective absorbance values of the dye before dyeing (A_0), after dyeing (A_1), and in the wash-off solution after stripping with *DMF* (A_1) respectively. From the dye exhaustion and the total fixation efficiency values, the fixation values of the dye absorbed (F), sometimes termed the fixation ratio, were calculated using Eq. (4) [22].

$$\%F = \%T/\%E \quad (4)$$

Measurement of Fastness Properties

Colour fastness to light, washing and crocking was carried out in a Fad-O-meter, Launder-O-meter and Crock-O-meter respectively as per ISO standard methods, light fastness: IS 2454: 1985, washing fastness: ISO 105 C02 method and rubbing: ISO: 105-X12.

Elemental Analysis of Dye

Heavy metal concentrations in the digested samples were determined with A6300 Shimadzu flame atomic absorption spectrophotometer with Shimadzu auto sampler (Asc-600). The calibration curves were prepared separately for all the metals by running different concentrations of standard solutions. Samples in quadruplicate and blanks were used as a part of the quality assurance–quality control [23–25].

Antimicrobial Activity

Escherichia coli (E. coli) a Gram-negative bacterium, was selected due to its popularity of being a chosen test organism and its resistance to common antimicrobial agents, *Staphylococcus aureus (S. aureus)*, a pathogenic Gram-positive bacterium was used because it was the major cause of cross-infection in hospitals and it is the most frequently evaluated species [26–28].

Antimicrobial Screening Test

1 g silk fabric (dyed and undyed) was introduced into 100 ml nutrient broth inoculated with the desired microbe and incubated at 37 °C overnight for 16 h. The reduction of bacterial growth by dye was expressed as follows:

$$R = 100(A - B)/A$$

where R = % reduction in bacterial population; A = absorbance (660 nm) of the media inoculated with bacteria and undyed fabric; B = absorbance (660 nm) of the media with bacteria and dyed fabric [29–31].

Results and Discussion

Effect of Extraction Conditions on Dye Yield

It was observed that with the increase in extraction time at boiling temperature, there was increase in the yield of dye. But the rate of increase gradually decreased after 120 min of extraction. The temperature of extraction was varied from room temperature (30 °C) to 100 °C and the yields were found maximum at 100 °C (Fig. 5). Therefore, the optimum time for dye extraction was considered as 120 min (Fig. 6) at boiling (100 °C). The dye yield was found to be 24.5 %.

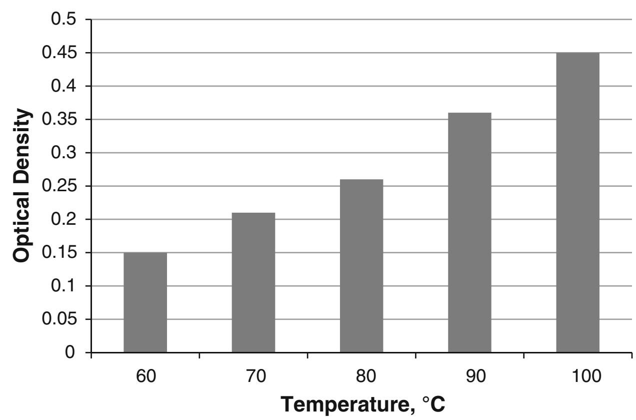


Fig. 5 Effect of temperature on dye yield

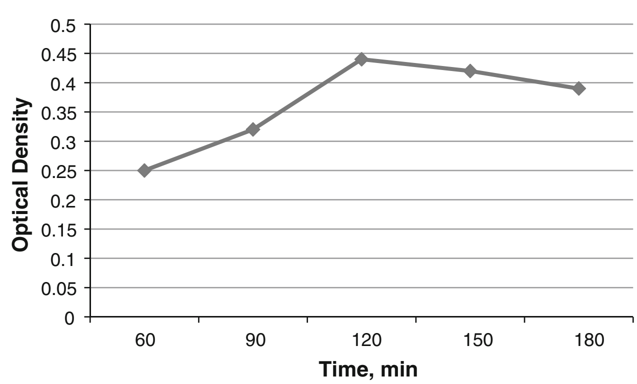


Fig. 6 Effect of duration on dye yield

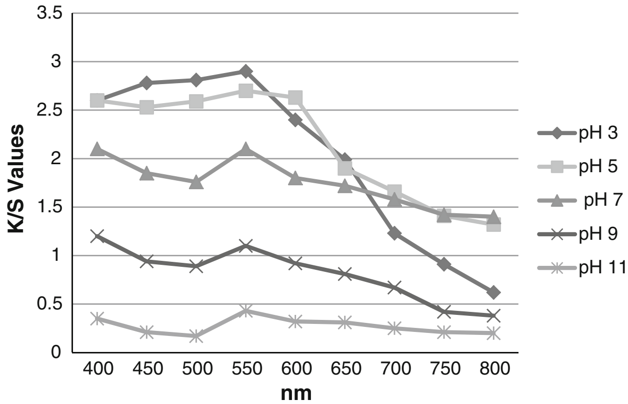


Fig. 7 Effect of dyeing pH on the spectra and reflectance

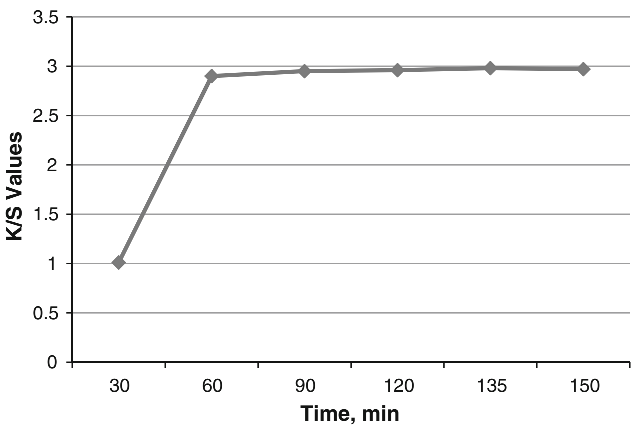


Fig. 8 Effect of dyeing time on the color strength

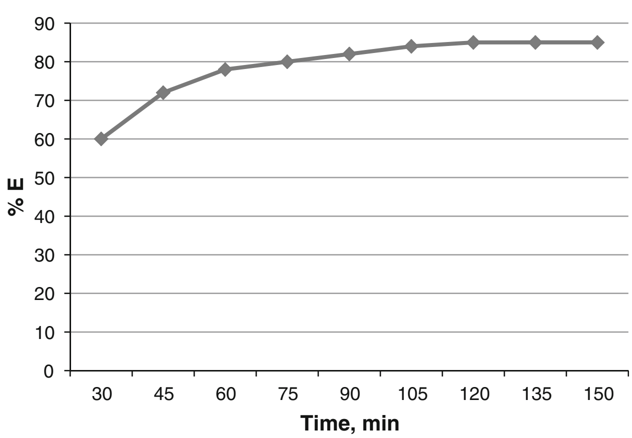


Fig. 9 Effect of dyeing time on the percentage dye bath exhaustion (%E)

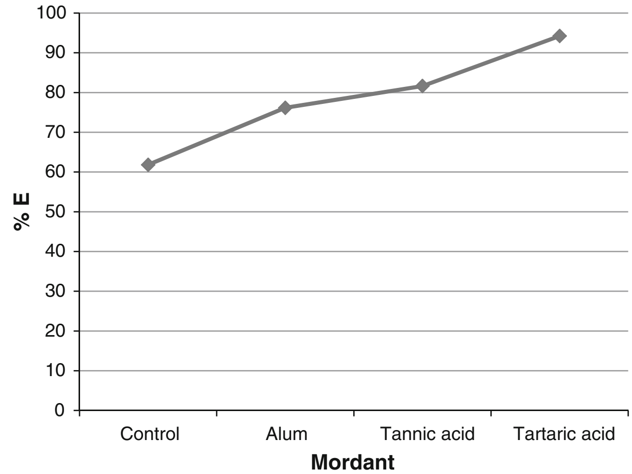


Fig. 10 Effect of mordants on the percentage of dye exhaustion (%E)

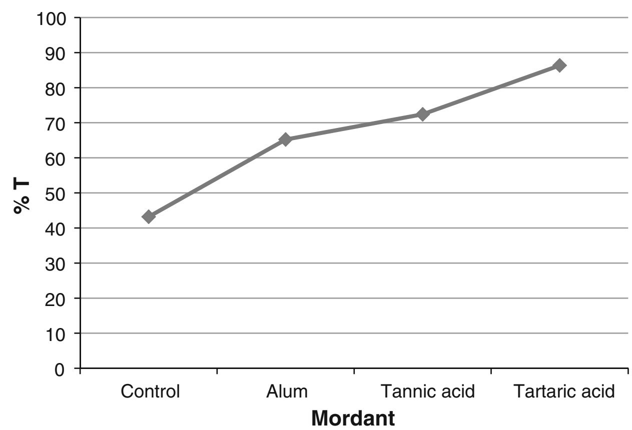


Fig. 11 Effect of mordants on the total fixation efficiency (%T)

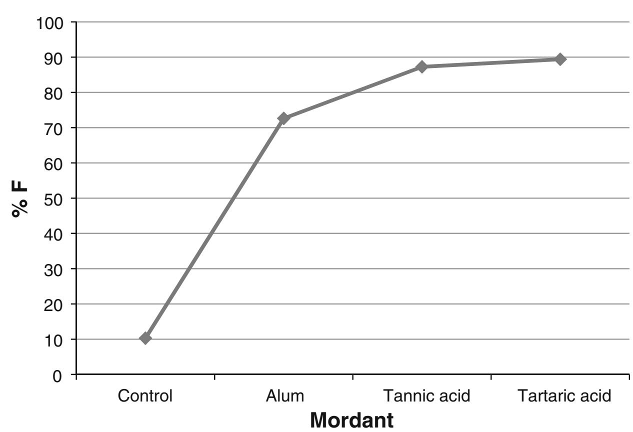


Fig. 12 Effect of mordants on the fixation ratio (%F)

Effect of Dyeing Conditions

Syzygium cuminii L dye has enough potential to be a good environmental-friendly natural dye, producing shades of brown, tan, almond, wheat, bisque, peach, puff etc. The behavior of its extract on silk can be considered in terms of columbic forces of interaction between mordants and dye molecules and the cationic sites in silk fibers [32].

Table 1 K/S values and colorimetric data of the silk samples dyed with *Syzygium cuminii* L extract

Mordant	Method	%	K/S	L*	a*	b*	C	h
Control	–	–	1.10	55.36	12.08	10.62	46.08	48.43
	Pre	2	6.00	48.65	12.00	11.95	46.14	62.88
A		5	6.22	47.68	11.80	10.46	45.78	69.56
	Post	2	6.23	47.62	11.64	11.74	41.14	67.80
		5	6.42	46.92	11.52	11.27	46.12	69.86
	Pre	2	6.52	46.85	11.15	10.47	45.30	65.19
B		5	6.70	46.75	10.54	09.40	44.13	67.79
	Post	2	6.10	48.65	12.63	08.41	45.18	73.65
		5	6.75	46.43	11.52	07.05	43.51	69.48
	Pre	2	5.92	48.88	11.54	10.81	45.81	63.11
C		5	6.95	45.36	05.86	10.56	42.05	61.19
	Post	2	6.82	46.11	04.12	12.54	43.17	71.75
		5	7.12	45.12	09.07	03.82	39.84	68.85

a aluminium potassium sulphate, *b* tannic acid, *c* tartaric acid, *pre* pre-mordanting, *meta* simultaneous mordanting and *post* post-mordanting

Table 2 Fastness properties of silk samples dyed with *Syzygium cuminii* L extract

Mordant	Method	%	Light fastness	Wash fastness		Perspiration fastness				Rubbing fastness	
						Acidic		Alkali			
				CC	CS	CC	CS	CC	CS	Dry	Wet
Control	–	–	2	3	5	3	5	3	5	5	4
	Pre	2	2	3	5	4	5	4	5	5	4
A		5	3	4	5	4	5	4	5	5	4–5
	Post	2	3	3	5	4	5	4–5	5	5	4–5
		5	2	3–4	5	4	5	4	5	5	4–5
	Pre	2	2–3	2–3	5	3	5	4	5	5	4
B		5	2	3	5	3–4	5	4	5	5	4
	Post	2	3	4	5	4	5	4–5	5	5	4
		5	2	4	5	4	5	4	5	5	4–5
	Pre	2	2–3	3	5	4	5	4	5	5	3
C		5	3	4	5	4	5	4	5	5	3–4
	Post	2	2	4	5	4	5	4–5	5	5	4–5
		5	3	4	5	4	5	4	5	5	4–5

cc color change, *cs* color staining

Figure 7 shows that the pH values of the dye bath have a considerable effect on the dye-ability of silk fabric. As the pH increases, the dye-ability decreases, the effect of the dye bath pH can be attributed to the correlation between dye and silk fibers. Since the dye used is a water soluble dye containing anionic groups it would interact ionically with the protonated terminal amino groups of silk fibers at acidic pH via ion exchange reaction [32]. This ionic attraction would increase the dye ability of the fiber as clearly observed. The effect of dyeing time on color strength is shown in Fig. 8. Longer dyeing time means higher color strength until dye exhaustion attains equilibrium and there is no significant increase after further increase in dyeing time. The decrease in color strength for 120 min of dyeing may be attributed to desorption of the dye molecules as a consequence of over dyeing [33].

It is clear that the type of mordants have an influence on the color strength, fixation ratio, hue as well as the fastness to wash and light by forming additional linkage with dye molecules compared to the silk samples dyed without any mordant [34]. This can be determined by the increase in the dye exhaustion and fixation in Figs. 9, 10, 11 and 12 as well as the colorimetric analysis in Table 1 and fastness to wash and light in Table 2. It is evident that the highest values of color strength and fixation, as well as fastness to wash and light were achieved when using mordants.

Evaluation of Colour Co-ordinates of Dyed Samples

The K/S values and CIELAB co-ordinates of silk fabric dyed with *S. cuminii* L is shown in Table 1. It is observed that the K/S values of the dyed material using different mordants (alum, tannic acid and tartaric acid) increased as compared to the control sample. The K/S values seems to be the highest in the case of dyed samples mordanted with alum and tannic acid (pre mordanting technique) and tartaric acid (post mordanting technique).

Similarly the L values of the dyed samples decreased with the increase of mordanting percentage, which indicates that the shade gets darker as compared to control sample.

In all mordanting techniques change in a* and b* values were noticed. The values were positive for all mordanted samples. Color hues (tone) were redder or yellower.

Fastness Properties

The fastness ratings of silk fabric dyed with or without mordants are presented in Table 2. The results show that the control sample exhibited poor fastness properties and mordanted samples showed improved fastness properties with reference to light. This is attributed to the fact that the presence of 3-hydroxy groups in Quercetin reduces the light fastness due to lower photostability [35] washing, rubbing and perspiration fastness. The probable reason attributed is the tannin component of the dye, which may help in bonding with the fiber, thereby assisting in proper fixation on the fibrous material. Hence, after mordanting alter the light sorption characteristic of tannin as well as make them insoluble in water and ultimately improves washing fastness properties.

Toxic Heavy Metals

The heavy metal content in the extracted dye was determined by using atomic absorption spectrophotometer. It was found that the concentrations were much below the stipulated limits (Table 3). This may be due to the avoidance of red listed heavy metal based mordants. Furthermore, since extraction was carried out in alkaline medium (pH 9), the natural metal contaminants are present only in trace amounts.

Table 3 Concentration of red listed chemicals in the extracted natural dye

Parameters	Permissible range, ppm	Dye, ppm
Heavy metals		
Arsenic	0.02	0.01
Cadmium	0.1	0.002
Chromium	1.0	Ab
Cobalt	1.0	0.08
Copper	10	Ab
Lead	0.08	Ab
Mercury	0.02	Ab
Nickel	1	0.07
Zinc	10	0.29
Pesticides	–	NT
Banned aryl amines	–	NT

nt not traceable

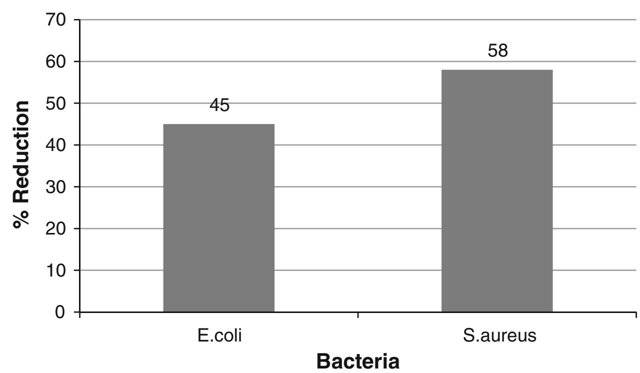


Fig. 13 Antimicrobial activity of silk fabrics on *E. coli* and *S. aureus*

Banned Aryl Amines

The extracted dye was further analyzed for the presence of banned aryl amines after reductive cleavage and isolation using GC/MS. The results indicated absence of red-listed aryl amines. This is because the dye is based on flavonoids and tannins and not on azo linkages. In view of the above findings, the extracted dye may be considered eco-friendly and safer for intimate contact with skin used as colouring component for clothing material. Although traces of red listed heavy metals and pesticides are present in the dye, it may be termed as non-hazardous to health as their concentrations are much below the stipulated limits.

Antimicrobial Activity

It was important to study the antimicrobial activity on dyed textile substrate (silk fabric) because the natural dyes showed inhibition effect against test bacteria in solution. The results are shown in Fig. 13. A reduction of 45 and 58 %

growth is seen both *E. coli* and *S. aureus* respectively. The results from these experiments indicated that the dye had antimicrobial activity both on solutions and substrate.

Conclusions

Dyeing of silk with *S. cuminii* bark extract is found to be effectively accomplished at acidic pH. The post mordanted dyed samples show better fastness properties and colour strength values. The colour co-ordinates of dyed samples lie in yellow–red quadrant of colour space diagram. The fastness properties ranged from good to excellent, while light fastness was fair to good. Fabrics showed antibacterial activity against Gram positive and Gram negative bacteria. Since *S. cuminii* bark is abundantly available in many of the countries, the colorant may be considered as a possible substitute to synthetic dye, sometimes toxic antimicrobial agents available in the market study and use this dye on commercial basis focusing on the environmental issues and user friendliness.

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