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Sustainable natural dyeing of cellulose with agricultural medicinal plant waste, new shades development with nontoxic sustainable elements

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ABSTRACT

The synthetic dyes used in textile industry cause severe health and environmental problems. Since production of these colors includes a noteworthy quantity of energy, water, and poisonous chemicals. Therefore, natural dyes from waste provide a significant source of study for the extraction of pigments. To use these natural dyes to its full extent, researchers used mordants to change the hue of the same natural dye and to get a range of shades from same source. Nonetheless, these mordants are toxic in nature. Therefore, to address this issue, in the present study, sustainable and environment friendly natural ingredients are studied to change the hue of the natural cutch dye. The results revealed that these natural ingredients can successfully developed new shades from the same natural dye without any negative effect on the fastness properties of the dyed cotton fabric.

1. Introduction

Use of synthetic dyes for coloration makes textile industries a major source of ecological pollution. These dyes are by-products of fuel industry and their production cause a substantial usage of energy, water, and noxious substances. On other side, Food and agricultural/forest left-over is a foremost problem worldwide. Foodstuff and cultivated surplus not only contributes to ecological contamination nevertheless also displays a damage of valued capitals. However, agricultural and foodstuff leftover also comprise of natural pigments that can be extracted and used as natural colorants. Therefore, to reduce the waste and valuable resources, researchers have turned to agricultural and food waste as a new source to extract natural pigments that can be used as colorants.

Waste from agriculture contains many bioactive substances which can be used as a raw material for production of different chemicals/colors or other products. This, in turn decrease the manufacturing price of colorants/chemicals and also helps in management and reduction of pollution from the surroundings [1]. These agricultural wastes can also use to manufacture natural colorants [2]. Cutch from *Acacia catechu* is one such source that has been used to make natural dye from centuries. It belongs to the Fabaceae *(subfamily Mimosoideae)* species and recognized as *Khair* or *Cutch* tree and is a by-product of Katha *manufacturing industry. It is* used in *tanning industry*, as an additive and preservative in many *industries* and also for textile dyeing [3]. Cutch is a medicinal plant [4] and possesses diverse pharmacological properties [5]. Cutch has been consumed in customary medications, due to its anti-inflammatory and anticancer properties [6].

Catechu comprises 40–55% tannins which are polyphenolic complexes and offer a biochemical protection against marauders and UV radiations to the plant life [7]. Hence cutch is also used as a functional finishing in textile for antimicrobial [8, 9], antioxidant [10] and Uv protection property [11]. Cutch has a long history to be used as a dye [12, 13], with other natural dyes [14], leather dyeing [15], as well as a bio mordant [16]. Recently, Cutch has been used for coloration of recycled paper from agro waste [17] and as a dye sensitized solar cells [18]. This cutch dye is listed in natural organic dye standard which shows that it is nontoxic and can be used as an environmental friendly alternative to synthetic dyes [19].

Use of agricultural waste enhanced the circular economy model and help in sustainable development goals globally. But unfortunately, the increase in the use of natural sources is more than the developments to improve the optimized usage of these sources [20]. For sustainable use of natural resources, the process must be optimized to its optimum extent it can provide for particular products. For instance, limited shades is a big problem of consuming natural colors in textile colorations [21]. However, Natural dyes can produce an extensive range of shades with same source of natural dye by changing only the mordants [22]. Researchers have been developed different shades with different mordants as a beauty of natural colors such as an author developed different shades with cutch dye by using alum and copper sulphate mordants [23]. Recently, cutch natural dye was combined with indigo dye and different mordants to provide range of attractive colors [24]. In another study, effect of mordants on color shades of cotton with acacia catechu was investigated [25]. Though, most of the mordants are metals and they are most likely harmful for natural surroundings such as humans and aquatic life [26]. This in turn reduced the sustainability and environment friendliness of natural dyes. Thus, there is a need to investigate alternative natural and environment friendly sources if any, to develop range of shades with one source of natural dye. Investigations on development of diverse shades using natural nontoxic elements without the use of metal mordants is still unexplored. Therefore, in this study, investigations was performed on the effect of different environment friendly alkaline and acidic natural ingredients on shades development of cutch natural dye to provide various shades with one source of natural dye. Results of this study reveals that cutch dye (dark brown) can change shades/colors from dark brown to red and to light peach shade in alkaline pH (with baking soda and soda ash) without changing the concentration of mordants. However change in acidic pH (lemon and vinegar) did not show any remarkable change in shades but shades change from dark brown to light brown in color. This study shows that various shades can be achieved with only one source of natural dye by changing the pH of the dye bath with natural nontoxic ingredients.

2. Experimental

2.1. Materials

In this study, 100 % cotton cellulosic fabric was used with density of 70 ends/inch and 90 picks/inch. The GSM of fabric used was 154. The bark of Cutch *(Acacia catechu Willd.)* from Pakistan was used as raw materials for the extraction of natural dye. The Sodium bicarbonate (baking soda) and Sodium carbonate (Soda ash) of analytical grade were purchased from Dae-Jung Korea. Lemon and vinegar were purchased from local market, Hyderabad. Sirrix Antox, Sifa stabilizer, Levelling agent: drimagen E2R were purchased from Archroma Pakistan LTD. Natural alum was used as a bio mordant in natural dyeing of cellulosic fibres. Natural tannins from pomegranate peels were used to enhance the mordant bond with cellulose.

2.2. Methods

2.2.1. Dye and tannins extraction

The tannins were extracted from the pomegranate peels. The peels of pomegranate was dried in shade for 1 week and then in oven for 24 hours at 100 °C. The peels were then grinded in powder form and this powder was mixed in water to form a stock solution to treat the cotton fabric. For the extraction of dye, the wood bark of *catechu* tree was grinded in powder form after washing and drying. The powdered cutch was mixed in de-ionized water for dyeing of cotton fabric.

2.2.2. Tannins, mordanting and dyeing of cotton fabric

Natural tannins were applied onto cotton fabric before mordanting as shown in Fig. 1. After tannin application, mordanting and dyeing was performed by Exhaust method on Rapid Labortex CO. LTD H-12c 5423. For all the samples, concentration of tannins and mordanting was kept same. The mordant was applied at 15 % o.w.f (of weight of fabric) and the dyeing was performed at 30 % o.w.f (control). To observe the effect of different environment friendly ingredients on shades development with cutch dye, concentration from 10-50 % o.w.f of all ingredients was varied with constant 30 % cutch natural dyeing (control). These all elements are added in the dye bath with cutch dye separately to see

their effects on pH of the dye bath and hence shades variations. The schematic diagram for the recipe follow for premordanting and dyeing by exhaust method is given in Fig. 1 and Table 1.

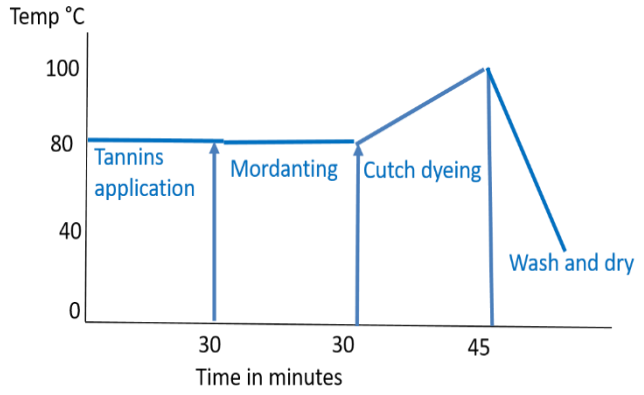

Fig. 1. Schematic diagram for Tannins, mordanting and dyeing of cotton

Table 1

Recipe for different ingredients used in dyeing of weight of fabric.

a

	Concentration
Tannins	Stock solution
Alum mordanting	15 % *o.w.f
Cutch dye	30 % o.w.f
Baking Soda	0, 10, 20, 30,40 50 % o.w.f.

b

	Concentration
Tannins	Stock solution
Alum mordanting	15 % *o.w.f
Cutch dye	30 % o.w.f
Soda Ash	0, 10, 20, 30,40 50 % o.w.f.

c

	Concentration
Tannins	Stock solution
Alum mordanting	15 % *o.w.f
Cutch dye	30 % o.w.f
Vinegar	0, 10, 20, 30,40 50 % o.w.f.

d

	Concentration
Tannins	Stock solution
Alum mordanting	15 % *o.w.f
Cutch dye	30 % o.w.f
Lemon	0, 10, 20, 30,40 50 % o.w.f.

2.3. Characterization

For the color strength readings of the colored cotton fabric, Reflectance values of each dyed sample were measured on a Data color SF600 spectrophotometer with illuminate D65 and UV and specular component included. Each sample was measured at three different locations and the average value was calculated. Using the reflectance value at maximum absorption, the color yield (K/S) was calculated with the Kubelka–Munk equation Eq. 1 [27]

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

In the above equation, R is the reflectance %; K is the absorbance; and S is the scattering of dyes. This is the result of the reduction percentage of light owing of absorbance and sprinkling and is created on reflectance. CIE Lab system was used to obtain the color characteristics of the fabric. The lighter/darker hue of color (where 100 shows white and 0 shows black) denotes by L*. The greater lightness designates that less color is achieved by dyed material and vice versa. Similarly, a* and b* describe the tendency of the color, positive values of a* and b* shows redder and yellower tendencies whereas negative value indicates greener and bluer shades respectively. Furthermore, C* standards shows the chroma or concentration of color and h° resembles to hue angle. Washing fastness of the colored cellulose were measured by ASTM-105:C03.

3. Results and Discussion

3.1. Effect Of Baking Soda On Color Strength And Color Attributes

Fig. 2. And Fig. 6 (b), Shows the effect of baking soda on the hue of 30 % cutch natural dye on cotton fabric. The color of cotton fabric was shifted from the dark brown to the dark red color by adding baking soda which is entirely a new shade. This might be due to the change in pH of the dyeing bath with addition of baking soda. The baking soda has a pH of lowest alkalinity i-e 8.5. The change in pH from neutral to alkaline changed the protonation state of the cutch dye and hence intensity of absorption light changed and hence a different hue is observed [28]. The functional groups of the cutch natural dye are *catechol and catechins* [29], which change their molecular structure as the pH of the solution changes. Upon addition of alkaline solution as baking soda, the protonation state of these functional groups changes, altering the electronic properties and hence color of the pigment molecule. This effect is similar to the results shown on wool fabric with cutch dye at alkaline pH [30]. The color strength was not much affected by the concentration of the baking soda, as shown in Table 2, however the hue is changed and is also shown by color attributes. Positive value of a* shows that hue is changed from brown to more red shade and red tone is increased with concentration of baking soda.

Table 2

CIE L*a*b*C*h* and K/S Values of Cutch Dyed fabric

Ingredient	Ingredient Concentrations (%)	K/S	L*	a*	b*	C*	h*
Baking Soda	0	7.4	49.29	17.10	26.71	31.71	57.36
	10	6.0	51.70	24.02	25.00	34.70	46.23
	20	7.0	48.28	21.60	25.86	33.76	50.06
	30	7.0	48.59	24.35	27.96	37.08	48.95
	40	8.4	49.39	23.00	26.40	35.00	48.00
	50	8.0	45.78	23.89	23.89	31.90	48.47

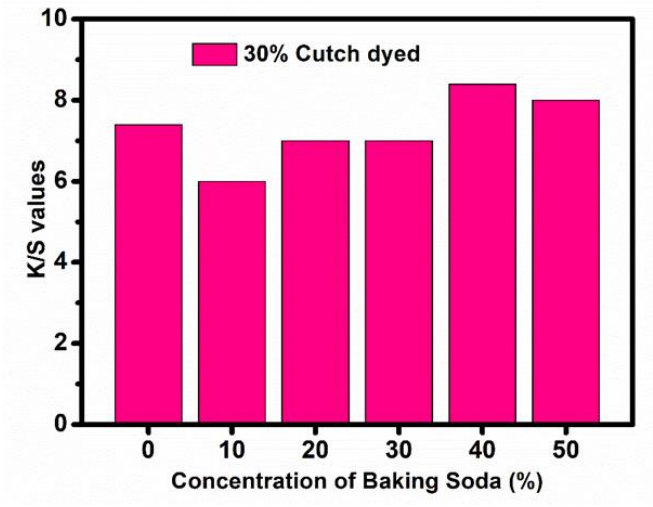

Fig. 2. Effect of baking soda on color strength

3.2. Effect Of Soda Ash On Color Strength And Color Attributes

Fig.3. and Fig. 6 c shows the effect of soda ash on color strength and color attributes. The soda ash has more alkaline pH i-e 11, then baking soda. Addition of soda ash in dyeing bath provides OH ions and cause the dye to come into protonated form. This in turn change the way in which dye bond configure with cotton, therefore it causes the dye to absorb and reflect light differently results in the entirely different hue of the cotton fabric, i-e peach colored fabric. The color strength of the cotton fabric dyed without soda ash is higher than the color strength of the cotton fabric dyed with soda ash. This is due to the change in molecular structure of dye which results in light absorption and reflection which results in light hue. Moreover, the color attributes L* also confirms the light hue of the colored cotton with soda ash which shows increased lightness value with increase in concentration of soda ash. The a* also decreased gradually with increased in concentration of soda ash which shows the lighter hue of red color achieved and this also confirms with c* value which indicates pureness of color shade and is decreased.

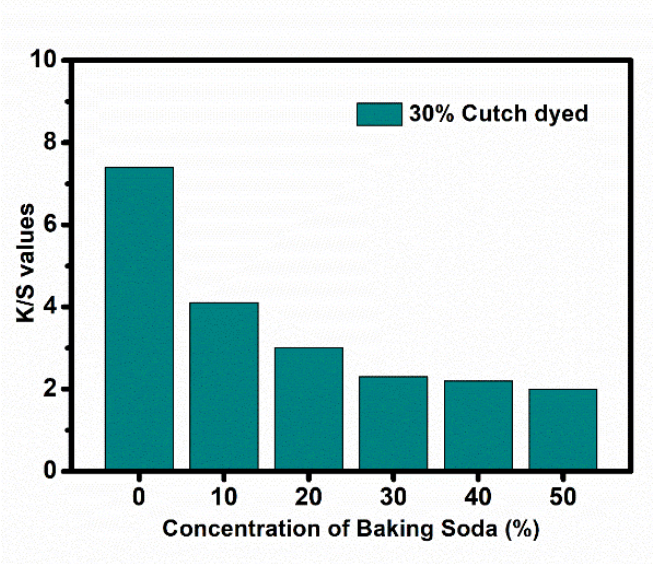

Fig. 3. Effect of soda ash on color strength

Table 3

CIE L*a*b*C*h* and K/S Values of Cutch Dyed Cotton Fabric

Ingredient	Ingredient Concentrations (%)	K/S	L*	a*	b*	C*	h*
Soda Ash	0	7.4	49.29	17.10	26.71	31.71	57.36
	10	4.1	58.29	15.30	24.56	31.63	50.94
	20	3.0	59.90	13.40	14.75	17.49	60.71
	30	2.3	67.63	11.59	20.20	23.31	60.16
	40	2.2	64.43	11.42	20.43	24.40	56.70
	50	2.0	63.00	10.60	18.70	23.70	51.98

3.3. Effect Of Vinegar On Color Strength And Color Attributes

Fig. 4. and Fig. 6 (e) shows the effect of vinegar on the color strength of 30 % cutch dyed cotton fabric. It is clear from the figure that there is not considerable change in hue is seen when cotton fabric dyed in presence of vinegar. This is because, in acidic form, hydrogen bonds protonated, more hydrogen bonds changed the structure of the dye to some extent and the way of light absorption, and therefore no change in hue is observed, but color of same dark brown changed to light brown in color. This is due to high concentration of hydrogen bonds, light absorption and intensity of light results in lighter shade of brown color. This also confirms by the k/s value of the fabric that is decreased from 7.4 (control) to 5.2 and lightness L* value as shown in Table 4.

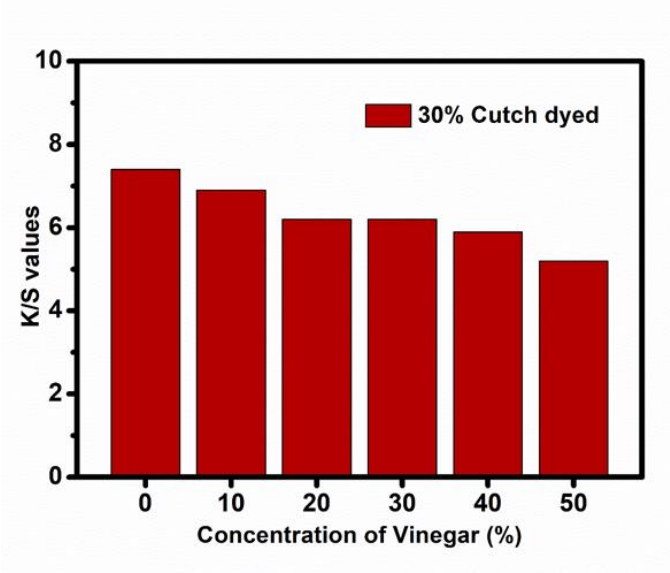

Fig. 4. Effect of vinegar on color strength

Table 4

CIE L*a*b*C*h* and K/S Values of Cutch Dyed Cotton Fabric

	Vinegar Concentrations (%)	K/S	L*	a*	b*	C*	h*
Vinegar	0	7.4	49.29	17.10	26.71	31.71	57.36
	10	6.9	54.60	11.90	24.90	27.60	64.44
	20	6.2	50.30	11.40	24.30	26.90	64.70
	30	6.2	50.13	12.89	24.81	26.20	64.75
	40	5.9	54.50	12.79	26.40	29.30	64.19
	50	5.2	52.10	12.20	24.80	27.60	63.69

3.4. Effect Of Lemon On Color Strength And Color Attributes

Fig. 5. and Fig. 6 (d), Shows the effect of Lemon on the color strength of 30 % cutch dyed cotton fabric. It is clear from the figure that there is not considerable change in hue is seen when cotton fabric dyed in presence of Lemon. This is because, Lemon also has the acidic pH and in acidic form, hydrogen bonds protonated, more hydrogen bonds did not change the structure and the way of light absorption, and therefore no change in hue is observed. Only due to high concentration of hydrogen bonds, light absorption and intensity of light results in minor change give a minor change in the same brown color. This also confirms by the k/s value of the fabric that is decreased from 7.4 (control) to 3.2 and lightness L* value as shown in Table 5.

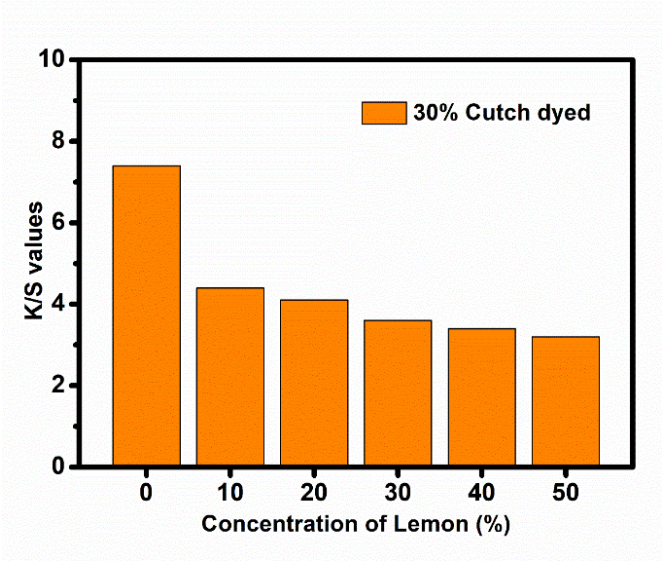

Fig. 5. Effect of lemon on color strength

Table 5

CIE L*a*b*C*h* and K/S Values of Cutch Dyed Cotton

Ingredient	Lemon Concentrations (%)	K/S	L*	a*	b*	C*	h*
Lemon	0	7.4	49.29	17.10	26.71	31.71	57.36
	10	4.4	58.30	13.30	20.72	24.62	57.31
	20	4.1	62.27	17.90	26.18	31.00	55.00
	30	3.6	58.70	12.30	21.70	25.00	60.00
	40	3.4	53.60	12.72	12.40	24.90	59.20
	50	3.2	52.5	12	12.2	23.5	59

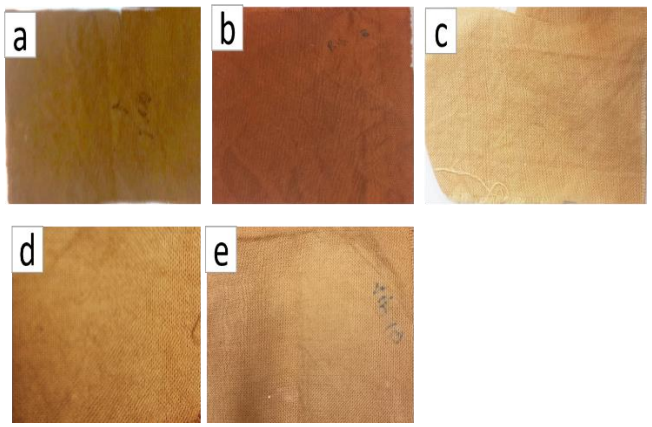

Fig. 6. Schematic representation of the shades developed with 30 % cutch dye by adding (a) cutch dye (control/actual), (b) Baking soda, (c) Soda Ash, (d) Lemon and (e) Vinegar

3.5. Fastness Properties

In Table 6, the fastness to washing, light and rubbing is shown for cotton fabric dyed with and without any addition of ingredients. As shown in Table 6, all the samples has satisfactory results of washing, light and

rubbing fastness which shows that hue of natural cutch dyed cotton fabric can be changed without the addition of toxic mordants and without any compromise on washing fastness properties.

Table 6

Fastness properties of cotton fabric dyed with cutch and different ingredients

	Cutch dye	Baking soda	Soda Ash	Lemon	Vinegar
Washing Fastness	4/5	3-4	4/5	4/5	4/5
Light fastness	5	4/5	4/5	4/5	4/5
Rubbing Fastness	4/5	4/5	4	4	4

4. Conclusion

The present study shows the effect of nontoxic ingredients used in our daily lives on the dyeing properties of the cotton fabric dyed with cutch natural dyeing. This study shows that various shades can be achieved with one natural dye with addition of environment friendly ingredients in the dyeing bath without any negative influence on the washing fastness and other fastness properties of the cotton fabric. Results of this study reveals that cutch dye (dark brown) can change shades/colors from dark brown to red and to light peach shade in alkaline pH (with baking soda and soda ash) without changing the concentration of mordants. However change in acidic pH (lemon and vinegar) did not show any remarkable change in shades but shades change from dark brown to light brown in color. This study shows that various shades can be achieved with only one source of natural dye by changing the pH of the dye bath with natural nontoxic ingredients. The dye used in this study is listed in organic dye standard and all the fastness testing used with same standards listed in NODS, and results also shows satisfactory according to NODS. For future studies, this research shows the possibility of achieving a range of shades with other natural dyes using this new sustainable approach in future.

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