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A New Approach to Eco-friendly Dyeing of Cotton Fabric with Vat Dyes Using Plant Extract as Natural Reducing Agents

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ABSTRACT

Vat dyes are one of the most popular dye classes producing brilliant hues on cellulose, viscose, and linen fabrics. Conventional vat dyes, to be converted into water-soluble leuco form, involve reduction with sodium dithionite which produces lots of harmful and non-renewable bi-products that causes environmental pollution. In this research work, apple, henna root, cabbage stem and amaranthus root have been used as organic reducing agents and compared with sodium dithionite in vat dyeing on cotton fabrics. Fruit extract (apple) and three plant extracts can pave a new way in the reduction process of vat dyes. Here reduction potential of reducing agents has been measured using a potentiometer coupled with photometric study and FTIR analysis has also been determined prior dyeing. The concentrations of reducing agents were noted to reach the required reduction potential which needs to be more negative than the range of -700 to -850 mV (vs. Ag/AgCl, 3M KCl) for reducing vat dye. The color strength of the dyed samples was analyzed by a Reflective Spectrophotometer and several colorfastness tests were also performed. The results show that using natural reducing agents in the reduction of vat dye can be appreciated because test results are closer to reduction with sodium dithionite. Furthermore, with introducing these substances, the production of hazardous chemicals is minimized and vat dyeing can be environmentally friendly. Prog. Color Colorants Coat. 16 (2023), 83-96© Institute for Color Science and Technology.

1. Introduction

Vat dyes have been a renowned dyestuff for producing brilliant hues in various shade ranges. Textile coloration with synthetic vat dyes was initiated in the market in 1901 following the invention of the first synthetic vat dye, namely indanthrene. In addition, vat dyes are very resistant to washing, sunlight, and chlorine bleaching applied on cotton, linen, rayon, and cellulose acetate [1]. But sodium dithionite used to reduce vat dye threatens the environment and eventually increases the cost of wastewater treatment. In recent years, low-environmental impact biotechnology inaugurates new types of treatment in reduction process of vat dyes with natural reducers. From the commercial point of view, the annual consumption of vat dyes is around 33,000 metric tons since 1992 that holds 24 % of cellulosic fabric dye

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market in value terms [2]. The water-insoluble vat dyes are first converted into water-soluble form (leuco dye) by reduction with a strong reducing agent usually by sodium dithionate. In its reduced form, the vat dye show it's substantivity towards cellulosic fabrics and, after absorption, is re-oxidized to the original water-insoluble form (in situ) in the fabric [3, 4]. Whereas sodium dithionate mostly used to reduce vat dyes forms hazardous chemicals such as sulphite, sulphate, thiosulphate, and toxic sulphur as byproducts in vat dyeing process [5, 6]. In many research works, researchers worked for replacing the sodium dithionite by ecologically more attractive alternatives [7]. From this continuation, some works conducted with *a*-hydroxyketone which meets requirements of vat dye reduction process in terms of reductive efficiency and biodegradability. But this compound is expensive and its use is restricted to closed systems due to the formation of strong smelling condensation products in an alkaline solution [8, 9]. Other sulphur containing compounds such as hydroxyalkyl sulphinate, thiourea, etc., are also been used to reduce vat dye [10, 11]. In addition, these compounds have relatively low amount of sulphur content and lower equivalent mass which eventually leads to lower sulphur-based salt in wastewater. However, $Fe(OH)_2$ being a strong reducing agent in alkaline medium, the possibility of using it has also been explored for reducing organic dyestuffs. The reducing effect of $Fe(OH)_2$ is accelerating with an increase in pH. But $Fe(OH)_2$ is fairly soluble in an alkaline solution while vat dyeing occurs in alkaline medium and also has tendency to be precipitated. Thus, it has to be complexed in order to hold it in solution [12]. Electrochemical reduction of vat dyes is also experienced by many researchers as an alternative route for ecological reasons. Electrochemical reduction can be achieved through either direct or indirect reduction process [13]. In direct electrochemical reduction reducing agents are replaced by electrons from electric current, and effluent contaminating substances can be dispensed with altogether [14, 15]. Although this technique is ideal, the stability of reduced dye species is poor and thus affects the color yield on dyed fabric. On the contrary, the rate limiting step of electrochemical reduction in electron transfer from the cathode surface to the surface of the microcrystal of the dispersed dye pigment makes the dyeing slower [15-19]. A natural reducing agent is also introduced in an experiment that comes from a plant source named sheghar but the results of colorfastness to light, rubbing, wash of dyed fabric didn't show satisfactory results to replace sodium dithionite in reducing vat dyes [20]. In a research work, three fruit extracts named date palm, banana, and apple were used to reduce natural indigo dyes and further studied the feasibility of natural reducing agents on indigo dye reduction. The extraction of these fruit extracts were carried out through boiling in diluted condition and further preserving at room temperature [21]. Another experiment was conducted on cotton dyeing with tea leaves by Adeel et al., Fazal-ur-Rehman et al. and others in 2021, the extraction process of natural leaf powder followed drying, grinding and further sieving [22]. Actually natural products have always been appreciated for environmental safety by using green technologies in their isolation and extraction process. In this research, microwave radiation was used as a green extraction tool to explore the natural coloring potency of tea leaves for the dyeing of cotton fabrics [22]. It was found that microwave radiation for 1-6 minutes in both aqueous and basic media had an excellent ability for isolation of colorant from tea leaves for that dyeing. In other research work of natural dye extraction from Acacia bark, Turmeric, Henna, and Pomegranate by Waseem arifeen et al in 2021, the extraction of natural colorants was done by drying, grinding and further filtration process [23]. In a research work with Arjun bark as natural colorant, the extraction process explored grinding and subsequent filtration process [24]. More specifically, the isolation of colorant from Arjun bark in that work was carried out in an acidified methanolic medium which was created using bio-mordants like zeera, ilaichi, neem etc after exposure to ultrasonic rays up to 60 min. There, the ultrasonic treatment as an environment-friendly tool also enhanced the color strength of natural colorant isolated from Arjun bark onto the cotton fabric under mild conditions. In another one research, colorants of varying shades from Brassicaceae plants using different extraction media such as acidic, alkaline, aqueous and organic [25]. Extraction was carried out by boiling 4.0 g of dyes from plants in above extraction media separately for 40 minutes at hot plate and after boiling, extracts was filtered and tested for dyeing of fabric. The stability of these vegetable residues based colorants in terms of fastness properties was found good to excellent in that research. Moreover, to reduce indigo dyes some researchers used some mono saccharides and disaccharides instead of sodium dithionite [19]. In another research work, researcher used ecofriendly α-hydroxyaldehyde (glucose) and α-hydroxycetone (acetol & acetoin) as reducing agents to replace sodium dithionite in indigo dyeing processes [26]. But for these α-hydroxycarbonyls, at higher temperature and in strongly alkaline solution, it gave color yield which was even higher than that obtained with the conventional hydrose. In one more research work focused on the use of alkaline iron (II) salt as the reducing agent for vat dyeing on cotton fabrics through a complete replacement of hydrosulphite [27]. But these iron (II) salt needed higher concentration of alkali and high temperature to obtain required reduction potential. Moreover, the removal of precipitated iron from dyed cotton was tiresome process after dyeing. Most researchers give alternatives of sodium dithionite by fruit extract or glucose, but plant extracts can also be a better alternative in this aspect. Other than that initially FTIR analysis and reduction potential measurement pave a way to get an approximate amount of reducing agents rather than conducting dyeing with different concentrations.

In this research, four natural reducing agents named apple (Malus domestic), henna root (Lawsonia inermis), cabbage stem (Brassica oleracea), amaranthus root (Amaranthus lividus)have been introduced to replace sodium dithionite in vat dyeing. These plant extracts being ever green shrubs are cultivated in natal to subtropical and tropical regions of world including South Asia, Africa and oases of Sahara Dessert and even in northern regions of Australia. Among these natural reducing agents, apples contain a variety of phytochemicals, including quercetin, catechin, phloridzin and chlorogenic acid, all of which are strong antioxidants. Main phyto-chemical constituents of henna are Lawsone (2-hydroxynaphthoquinone), mucilage, mannite, gallic acid and tannic acid. The main phyto-chemical components of cabbage are phenol, flavonoid and metnanolic extracts.Phytochemical analyses of Amaranthus also shows the presence of polyphenols, tannins, flavonoids, steroids, terpenoids, saponins and betalains. Here it is evident of the presence of hydroxyl group in these natural extracts which act as reducing agents in ultimate solubilization of vat dyes. The isolation of extracts from plants is done through dilution, squeezing and filtration steps in this work. The performance of the aforementioned natural ingredients as reducing agents was evaluated in terms of color strength, shade %, and fastness properties and compared with sample using sodium dithionite as the reducing agent. The reduction potential measurement and FTIR analysis before dyeing give an approximate quantity of reducing agents to use in the dyeing process. This work offers environmental benefits as well as prospects for improved process stability, especially for anthraquinone vat dyes.

2. Experimental

2.1. Materials

The Single Jersey cotton fabrics (150GSM) were collected from Metro Knitting & Dyeing Mills Ltd. in Bangladesh. The whiteness index of this bleached cotton fabric was 71.82 before dyeing, the yarn count of the cotton fabric was 30 Ne and bursting strength of it was 280 kPa. The absorbency of the fabric was tested by drop test which required 0.7 sec and by spot test with 1 % direct dye, the absorption area was nearly circular in shape. In addition, there was no finish applied before dyeing of this cotton fabric.

Sodium dithionite which was used as reducing agent in dyeing process was collected from Orient Chem. Tex Ltd. Natural reducing agents such as apple, henna plant root, cabbage plant stem, and amaranthus plant root were collected from local market of Dhaka.

Indanthren Dark Blue 5508, Indanthren Brown G, Indanthren Rubine R; vat dyes were supplied from Dyestar Bangladesh Ltd. Other auxiliary chemicals such as caustic soda, sequestering agent, wetting agent and dispersing agent were used from Orient Chem. Tex Ltd.

2.2. Methods

2.2.1. Extraction of reducing agents

Apple, henna plant root, cabbage plant stem, and amaranthus plant root were first cut from the plants and were cleaned with water to remove any foreign material in them. Then these natural ingredients were dried under sunlight. After that these dry natural ingredients were blended in blender and collected in grinded state. Then these natural extracts were used in weight basis according to the recipe-9 g/L reducing agents which satisfy the requirement of reduction potential in between -700 to -800 mV.

2.2.2. Dyeing of fabrics

At first three vat dyes were reduced by five different reducing agents at 30 °C for 60 minutes. After 60 minutes the cotton fabric were added to the dye solution and temperature of dye bath was raised to 50 °C. After that the dyeing takes place at 50 °C for 30 minutes and dyed fabrics were oxidized in open air for 10 minutes. Then again the dyeing was conducted at 50 °C for 30 minutes and dyed fabrics were re-oxidized in open air for 10 minutes. After dyeing the fabrics were rinsed with water and dried in an eco-dryer for 30 minutes. Here, the auxiliary chemicals named sequestering agent was added in the dye bath to reduce water hardness, wetting agent was added to lower surface tension of the dye liquor for easy penetration into the fabric and dispersing agent was added to prevent coagulation of dye particles during solubilization of vat dyes.

2.3. Characterization

2.3.1. Reduction potential measurement

At first two redox electrodes-(A) platinum-redox electrode and (B) Ag/AgCl, 3M KCl reference electrode were calibrated by redox buffer. The reduction potential (E_{oR}) was measured by primary electrode (A) and reference electrode (B) which were connected to a potentiometer (654 pH-meter, Metrohm) [28]. The redox measurement was performed every 2 min and recorded in millivolt (mV). In the meantime, the leuco solution was also circulated through a cuvette (d ¼ 1.00 mm) by means of a peristaltic pump with a flow rate of 0.38 mL/min. The photometry of the leuco solution was performed by a UV-Vis photometer in the range of 400-700 nm. The solution of reducing agents (40 %w/v, 5 mL) i.e. sodium dithionite (hydrose), apple extract, henna root extract, cabbage stem extract and amaranthus root extract were injected for each experiment by a syringe (D) into the thermostated dye bath at 50 ºC. The dye bathcontained 0.04 g vat dye and 0.6 g NaOH in 100mL deionized water. The redox reaction was monitored at 50 ºC under argon protective gas atmosphere.For reduction potential measurement of this experiment, the liquor was prepared with dyes, reducing agents, caustic soda, sequestering agent, wetting agent and dispersing agent according to the amount of above dyeing recipe.

Table 1: Sample Description.

Sample ID	Reducing Agent	Dyeing Recipe
SD1	Sodium dithionite	Vat Dye (Indanthren Dark Blue 5508): 2 % owf Reducing Agent: 9 g/L Caustic Soda(38 °Be): 75 g/L Sequestering Agent: 2 g/L Wetting Agent: 2 g/L Dispersing Agent: 2 g/L
SD2	Apple	
SD3	Henna root	
SD4	Cabbage stem	
SD5	Amaranthus root	
SB1	Sodium dithionite	Vat Dye (Indanthren Brown G) : 2 % owf Reducing Agent:9 g/L Caustic Soda(38 °Be): 75 g/L Sequestering Agent: 2 g/L Wetting Agent: 2 g/L Dispersing Agent: 2 g/L
SB2	Apple	
SB3	Henna root	
SB4	Cabbage stem	
SB5	Amaranthus root	
SR1	Sodium dithionite	Vat Dye (Indanthren Rubine R): 2 % owf Reducing Agent: 9 g/L Caustic Soda(38 °Be): 75 g/L Sequestering Agent: 2 g/L Wetting Agent: 2 g/L Dispersing Agent: 2 g/L
SR2	Apple	
SR3	Henna root	
SR4	Cabbage stem	
SR5	Amaranthus root	

2.3.2. FTIR

In this experimental work, ATR analysis of apple juice, henna root extract, amaranthus root extract and cabbage stem extract were measured [29] from CARS (Centre for Advanced Research in Sciences), Dhaka University, Bangladesh. An FTIR spectrometer (Brand Name: SHIMADZU, Origin: Japan) simultaneously collects high-resolution spectral data over a wide spectral range and measures intensity over a narrow range of wavelengths at a time.

2.3.3. Color strength (K/S) measurement

Reflectance of the dyed fabric samples were measured by using Data Color 650 Spectrophotometer [30]. For strength of the dyestuffs related to absorption property, Kubelka-Munk (Eq. 1) gives the following relation between reflectance and absorbance.

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

Where, R is the reflectance, K is the absorbance and S is the scattering.

In this experiment color measurement was performed at maximum wavelength for the specific color. For the combination of Indanthren Dark Blue 5508, it was considered that the wavelength range is 450-495 nm, in case of the combination of Indanthren Brown G dye 570-600 nm wavelength range were considered and for the combination of Indanthren Rubine R dye, the wavelength in between 620-670 nm were considered. In addition to it, for the combination of Vat Indigo light-yellow dye, in between the wavelength of 550-580 nm in visible spectrum, the maximum peak values were found.

2.3.4. Color coordinate and MI values

Different color coordinate value such as L, a^*, b^*, C and H and had been determined by following CIELAB method under light source D65 at 10° observer. Along with that Metamerism Index (MI) values has been measured under four different light sources at 10° observer to determine the color consistency of dyed fabric.

2.3.5. Color fastness

Various colorfastness properties of vat dyed fabrics were measured here. Color fastness to wash was measured according to ISO-105-C06 (C2S) test method. Color fastness to rubbing was measured according to BS EN ISO 105X12 test method using Crock meter. Color fastness to perspiration and color fastness to light for dyed samples were measured according to ISO 105 E04 using Perspirometer and ISO-B01-B08 using Xenon Arc light source, respectively.

2.3.6. Ecological performance measurement of effluent

Detailed investigation of ecological parameters of effluents was done and comparative analysis was performed in between conventional and extracts-based processes. The effluent load had been measured in the comparison of BOD (Bio-chemical Oxygen Demand), COD (Chemical Oxygen Demand), TDS (Total Dissolved Solids) and DO (Dissolved Oxygen) load values from five experiments using five reducing agents.

3. Results and Discussion

3.1. Reduction potential measurement

The value of Reduction potential of dye liquors with different reducing agents are shown in following Table 2 which is essential to identify the quantity of introducing natural reducing agents in dyeing. The Table 2 shows that 9 g/L henna root extract with three vat dyes such as Indanthren Dark Blue (SD3), Indanthren Brown (SB3) and Indanthren Rubine (SR3) gives reduction potential values -680, -810 and -790 mV, respectively. Again 9 g/L cabbage stem and 9 g/L amaranthus root with the above three dyes give reduction potential values (-503.4, -620 and -580 mV) and (-520, -608 and -530 mV,) respectively. From fruit extract- apple gives reduction potential values -627.3, -700 and -740 mV with Indanthren Dark Blue (SD2), Indanthren Brown (SB2) and Indanthren Rubine (SR2) vat dyes. Here, it is clear that, henna root extract gives the lowest reduction potential among four natural reducing agents and the values were most closer to reduction potential values -820, -875 mV and -860 mV using conventional sodium dithionite with above three vat dyes.

In addition to it, we have reduced Vat Indigo Light Yellow dyes (2 %) with five reducing agents (5 g/L) in presence of above auxiliary chemicals, whose reduction potentials have been added in the below table. Here it is seen that SV_I1, SV_I2, SV_I3, SV_I4 and

SV$_{I}$5 indicates the liquors having reducing agents Hydrose, Apple extract, Henna root extract, Cabbage extract and Amaranthus root extract, respectively. The dye liquors for conventional hydrose give us reduction potential -820 mV while the natural reducing agents give us -760 mV for Apple extract, -800 mV for Henna, -610 mV for Cabbage and -600 mV for Amaranthus extract. This reduction potential measurement with Vat Indigo dyes evident that the results are near to the range of -700 to -800 mV which was the required values for reducing vat dyes. Moreover, reduction potential measurement for vat indigo dyes can strengthen the previous measurement of reduction potential for conventional Hydrose as well as natural reducing agents with Vat Anthraquinone (Indanthren) dyes.

3.2. FTIR analysis

To determine the functional groups in the natural reducing agents, Fourier Transform Infrared Radiation has been done. Figure 1 depicts the FTIR spectrum of all natural reducing agents, here mostly the peak values are in the range of wavenumber 1050 to 3500 cm^{-1} against transmittance T %. All the natural reducing agents show the broad spectrum in 3300-3350 cm^{-1} which probably exhibit that hydroxyl group is present as a functional group in all these plant extracts and fruit extract. In addition to it, the depth of transmittance % in between the wavenumber 1000 to 1800 cm^{-1} indicates methyl ($-CH_3$), methylene ($=CH_2$), methyne ($=CH-$) and carboxyl ($C=O$) functional groups in them. The average spectra of conventional Sodium dithionite are found at the wavenumbers of 3800, 1880 and 1300 cm^{-1} [31]. As a result, these natural reducing agents bear the reduction capacity.

Table 2: Reduction potential (mV).

Sample ID	Reduction Potential (mV)	Sample ID	Reduction Potential (mV)	Sample ID	Reduction Potential (mV)	Sample ID	Reduction Potential (mV)
SD1	-820	SB1	-875	SR1	-860	SV$_{I}$1	-820
SD2	-627.3	SB2	-700	SR2	-740	SV$_{I}$2	-760
SD3	-680	SB3	-810	SR3	-790	SV$_{I}$3	-800
SD4	-503.4	SB4	-620	SR4	-580	SV$_{I}$4	-610
SD5	-520	SB5	-608	SR5	-530	SV$_{I}$5	-600

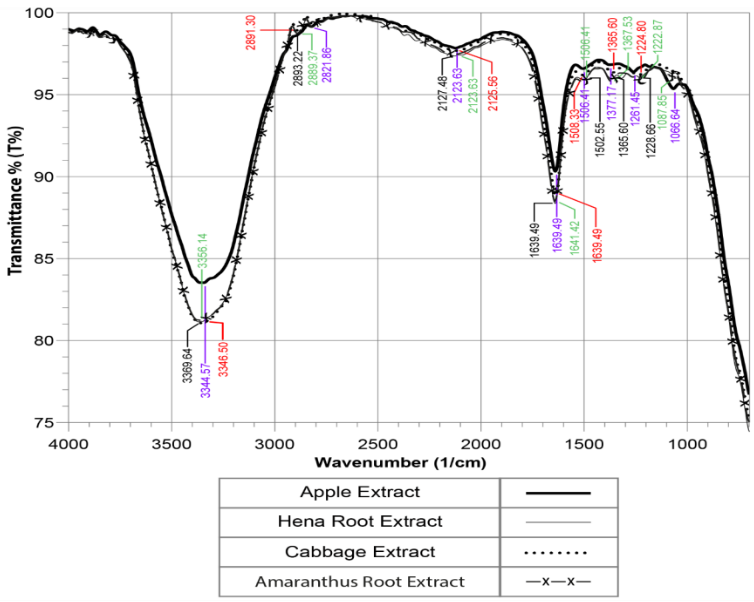

Figure 1: FTIR analysis of natural reducing agents.

3.3. Color co-ordinate value

From Figure 2, it is seen that the lightness values for three vat dyes such as Indanthren Dark Blue, Indanthren Brown and Indanthren Rubine dyes with every reducing agent give dissimilar values. For Indanthren Dark Blue vat dye, using apple extract and henna root extract, 30.13 and 29.93 lightness values were obtained, while using cabbage extract and amaranthus root extract, yields 20.08 and 21.13 lightness values. Here, it is clear that apple and henna root both provide closer lightness values to 29.33 which is found using sodium dithionite in dyeing with Dark blue dyes. Again, for Indanthren Brown dyes using sodium dithionite, apple, henna, cabbage and amaranthus extracts give lightness values of 13.15, 13.33, 13.38, 13.31, and 13.11 respectively. For Indanthren Rubine dyes using above five reducing agents give lightness values 4.78, 4.81, 4.68, 4.05 and 4.05, respectively. Thus it is clear that, for brown and rubine dyes, dyed fabrics are almost similar in color depth using natural reducing agents and conventional reducing agent (hydrose).

On the other hand, Table 4 shows difference between the a, b, C and H values of dyed fabrics with three categories of dyes using four natural reducing agents against sodium dithionite reducing agent. The value of a* is higher for fabrics dyed with Dark Blue and Rubine dyes and a* is slightly lower for fabrics dyed with Brown dyes, and as a result, they fall on the H (hue) of-1.77, 1.21 and -1.11 for Dark Blue, Brown and Rubine dyes reduced by henna root extract; -1.33, 1.25 and -1.00 for above three dyes using apple extract; -1.28, 0.86 and -0.56 using cabbage extract and -1.03, 1.15 and -0.68 using amaranthus extract against using sodium dithionite (Table 3). Whereas the chromaticity values (C) of dyed fabric with natural reducing agent has been increased using four natural reducing agents than sodium dithionite and overall it is better for apple extract and henna root extract.

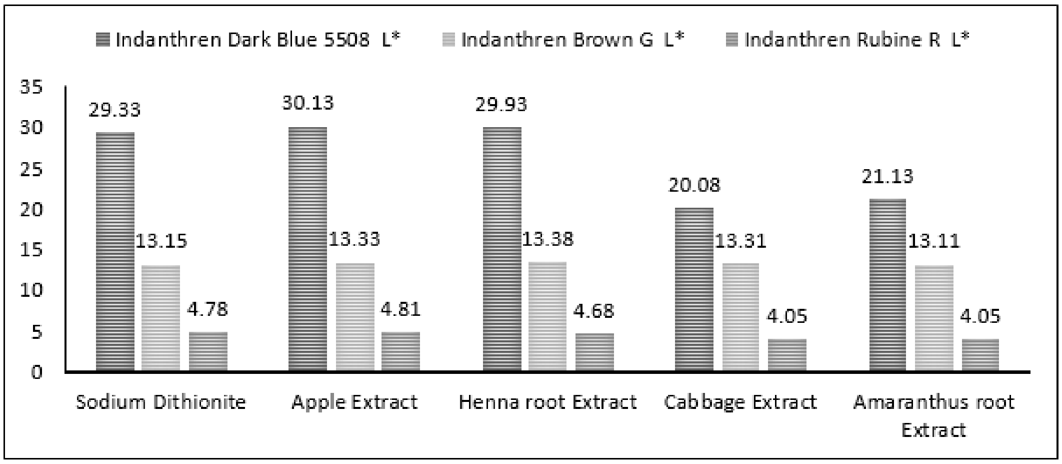

Figure 2: Lightness values of dyed fabrics.

Table 3: Color coordinate values of dyed fabric

Reducing Agent Used	Indanthren Dark Blue 5508				Indanthren Brwon G				Indanthren Rubine R			
	Δa*	Δb*	ΔC	ΔH	Δa*	Δb*	ΔC	ΔH	Δa*	Δb*	ΔC	ΔH
Apple Extract	10.55	-13.87	17.38	-1.33	0.03	-2.38	2.03	1.25	4.75	-1.49	4.88	-1.00
Henna root Extract	9.03	-13.60	16.15	-1.77	-0.10	-2.29	1.94	1.21	4.38	-1.25	4.42	-1.11
Cabbage Extract	6.67	-10.32	13.81	-1.28	-0.33	-2.43	2.29	0.86	6.07	0.40	6.06	-0.56
Amaranthus root Extract	6.64	-21.13	-10.92	-1.03	-0.30	-2.29	2.10	1.15	5.48	0.54	5.99	-0.68

Table 4: Wash fastness grading for degree of staining (Indanthren Dark Blue 5508 dye).

Reducing Agent Used	Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
Sodium Dithionite	3	4-5	4-5	4-5	3-4	4-5
Apple Extract	4	4-5	4	4-5	4	4-5
Henna root Extract	3-4	4-5	4-5	4-5	4	4-5
Cabbage Extract	3	4	4	4-5	3-4	4-5
Amaranthus root Extract	3-4	4-5	4	4-5	3-4	4

3.4. Color strength (K/S)

The following Figure 3 represents the color strength (K/S) values of all dyed samples. It is seen that, K/S values for Indanthren Dark Blue dyes are 28.5, 26.67, 21.78, 16.45 and 15.5 using sodium dithionite, apple, henna, cabbage and amaranthus extract as reducing agents. Again K/S values for Indanthren Brown dyes are 22.67, 18.86, 17, 13.8 and 15.35 using above reducing agents, respectively. Furthermore, K/S values for Indanthren Rubine dyes are 27.79, 27.2, 26.35, 21.78 and 25.89 using above five reducing agents. Here, for three vat dyes reduced by apple extract among natural reducing agents gives mostly closer color strength values to dyed fabrics using sodium dithionite as reducing agent. Here also noteworthy that among three plant extracts, for three dyes reduced by henna root gives the nearest values to both apple extract and hydrose. In addition to the above analysis, several samples have been dyed without any dyestuff as blank experiments for which negotiable K/S values have been found as shown in the below figure. More specifically, from visual assessment the apple and henna extract gives slight colors on the white fabrics while cabbage and amaranthus extract gives no color after dyeing. Moreover, K/S values from Vat Indigo light yellow (2 %) dyed samples have been added with five reducing agents in the below figure. These added values to the figure shows that the color strength values for natural reducing agents are closer to the K/S value of dyed sample reduced by conventional dithionite reducing agent. From the above analysis, it is evident that for three anthraquinone vat dyes, K/S values are significantly lower while using natural reducing agents. But simultaneously, it has been seen that for vat indigo dye, K/S values of dyed samples using natural reducers are not so far from K/S value using conventional sodium dithionite.

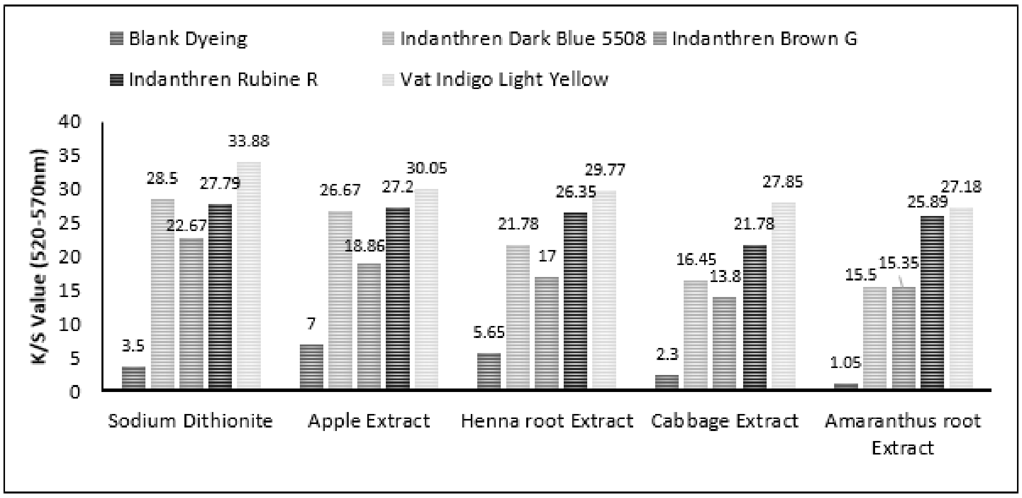

Figure 3: Color strength measurement.

3.5. Metamerism index

The following Figure 4 shows the metamerism index values of all dyed samples under four light sources such as D65, TL83, F11 and A10. Here, it is clearly seen that, metamerism values are within 4-5 in observation under three light sources with D65 at 10^0 observer for dyed fabrics by Indanthren Dark blue dyes. In addition, it is also seen that, metamerism values are within 1.5-2.5 at same light condition for dyed fabrics by Indanthren Rubine dyes and metamerism values are less than 1 for dyed fabrics with Indanthren Brown dyes.

3.6. Color fastness

Wash fastness of all dyed samples are measured by color staining parameter using grey scale. Tables 3, 4 and 5 show the wash colorfastness grading in regards to three categories of dyes in presence of five reducing agents. Form Tables 4 and 5 it is readily apparent that color fastness to wash of dyed fabric for reducing agents apple extract and henna root extract provide wash fastness grading (4/4.5) and for reducing agents cabbage extract and amaranthus root extract provide grading (3/4) while dyed fabrics with reducing agent sodium dithionite provide fastness grading (3.5/4.5) in respect of Indanthren Dark Blue 5508 and Indanthren Brown G dyes. Again from Table 6 it is witnessed that wash fastness grading for dyed fabrics with Indanthren Rubine R dye reduced by apple, cabbage and amaranthus extract are within 3 to 4.5 which is similar to dyed fabrics using sodium dithionite. But for henna root extract the color fastness to wash grading is slightly lower for Indanthren Rubine dyes. Overall, among four natural reducing agents, apple extract and henna root provide better fastness grading and the nearest grades on grey scale to sodium dithionite reduced dyed fabrics.

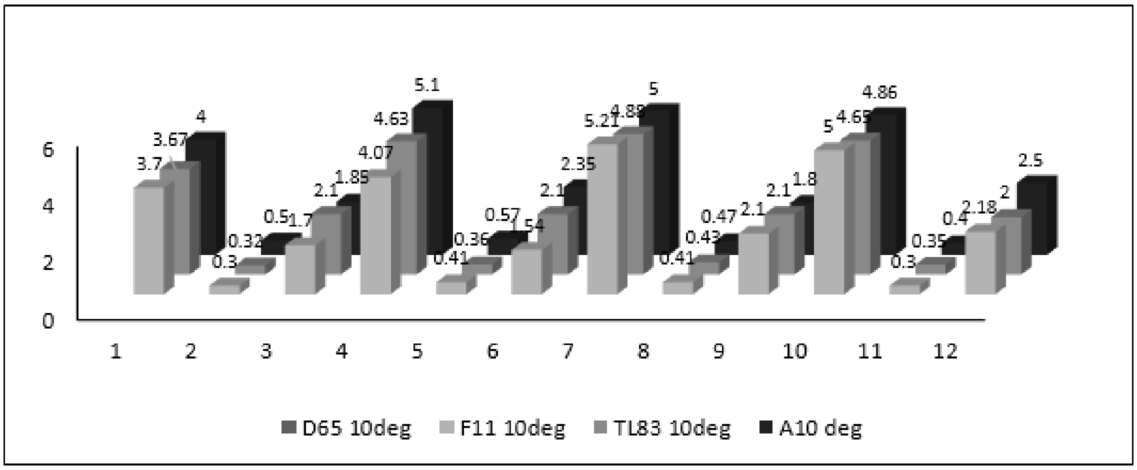

Figure 4: Metamerism values for dyed samples.

Table 5: Wash fastness grading for degree of staining (Indanthren Brown G dye).

Reducing Agent Used	Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
Sodium Dithionite	4-5	4-5	3-4	4	4	4-5
Apple Extract	4-5	4-5	4	4-5	4-5	4-5
Henna root Extract	4-5	4-5	4	4-5	4	4-5
Cabbage Extract	4	4-5	3-4	4	4-5	4
Amaranthus root Extract	4	4-5	4	4-5	4-5	4-5

Table 6: Wash fastness grading for degree of staining (Indanthren Rubine R dye).

Reducing Agent Used	Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
Sodium Dithionite	3	4-5	3-4	4-5	4	4-5
Apple Extract	3	4-5	4	4-5	3-4	4
Henna root Extract	2-3	4	3-4	4-5	4	4-5
Cabbage Extract	3	3-4	4	4	4	4
Amaranthus root Extract	3	4	4	4-5	4-5	4-5

A slight change of rubbing fastness grading has been observed in Figure 5 among three categories of dyes as well as five reducing agents. Dry and wet rubbing fastness of dyed fabric with conventional reducing agent (sodium dithionite) exhibit fastness grading (4.5/4) for three vat dyes- Indanthren Dark Blue, Indanthren Brown and Indanthren Rubine dyes. On the other hand, fabrics dyed with above three dyes using henna root extract, apple extract and cabbage extract give fastness grading in between 3.5 to 4.5 while using amaranthus extract, color fatness to rub grade is 4. Thus it is apparent that both henna root extract and apple extract show better results in color fastness to rubbing test among natural reducing agents. In addition, dyed fabrics using these two natural reducing agents give mostly closer values to dyed fabrics using sodium dithionite.

In perspiration fastness test, the color change grading is determined in both in acid solution and alkaline media. It is observed from the Figure 6 that perspiration fastness has been varied in both media. In acid solution, perspiration fastness grading of dyed fabric using henna root extract provide better result (grading 4.5) among all natural reducing agents except for Indanthren Rubine R dye where sodium dithionite gives 4.5 fastness rating. On the other hand, in case of alkali perspiration only apple extract shows very good fastness grading (4.5) in respect of all dyes applied in this experiment using various natural reducing agents which is also better than synthetic reducing agent sodium dithionite.

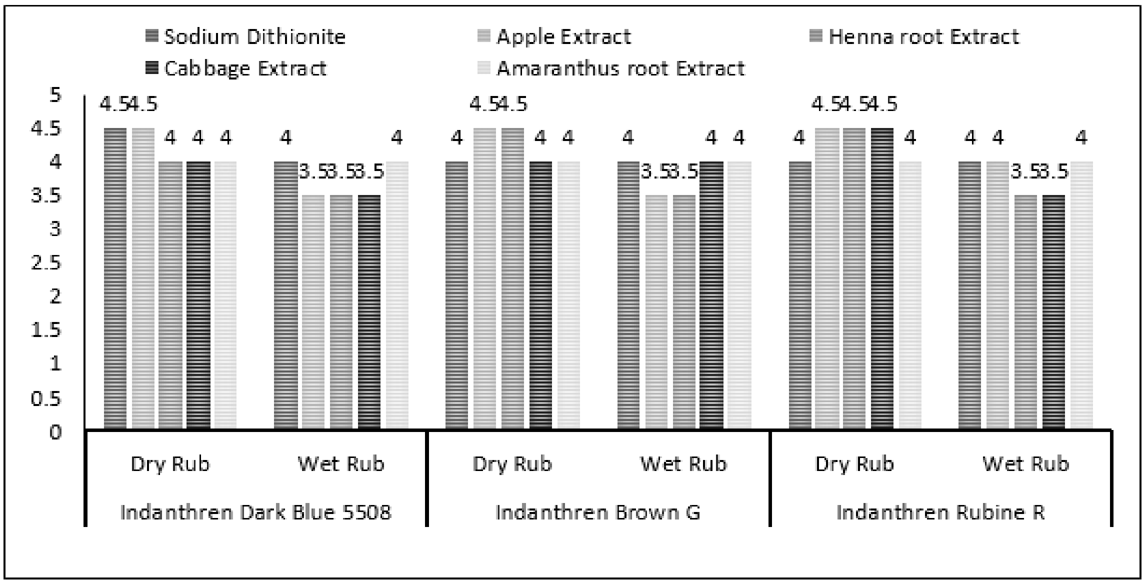

Figure 5: Rubbing fastness.

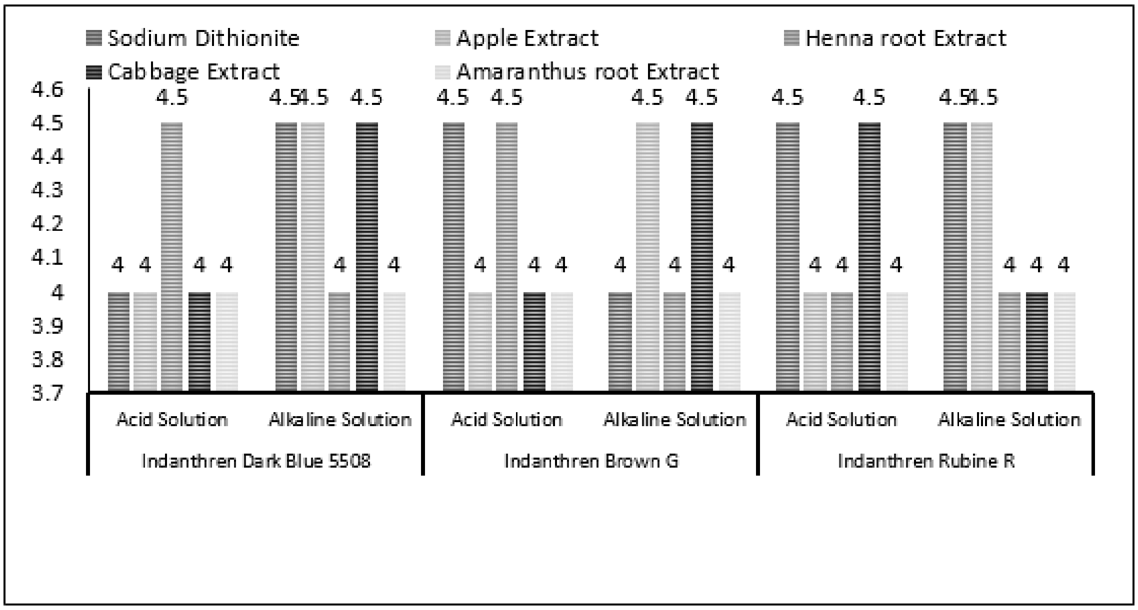

Figure 6: Perspiration fastness.

Vat dyes are mostly popular for high resistance in light fastness and it is clearly seen in the Figure 7 that synthetic reducing agent provides excellent light fastness (8). Besides that, for the all dye categories applied in this experiment, apple extract yields 8, 7-8 and 7-8 light fastness grading respectively while henna root extract yields 7-8, 7, 7; cabbage extract provide 7-8, 7-8, 7-8 and amaranthus root extract give 7-8, 7, 7-8 grades on blue scale in this test. Thus it is clear that dyed fabrics using natural reducing agents- apple and cabbage show better results in color fastness to light test and mostly closer values to the excellent grade 8 for sodium dithionite reduced dyed samples.

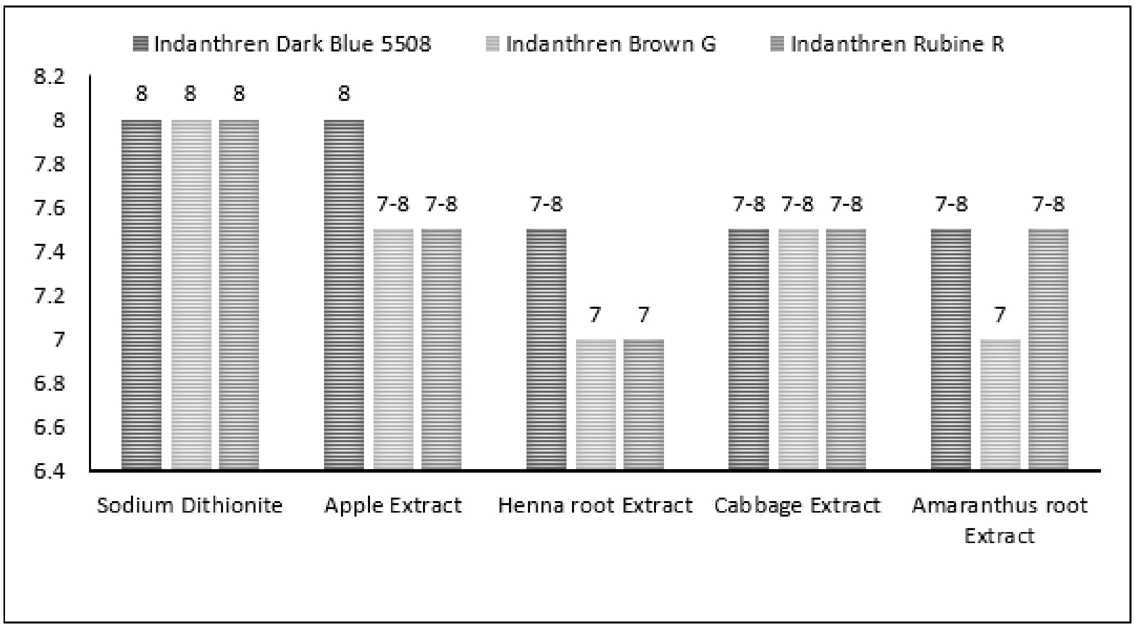

Figure 7: Light fastness (Xenon Arc Light).

3.7. Ecological performance measurement of effluent

It has been seen in the below table that the ecological parameters in mg/L values for effluents from conventional process with Sodium dithionite reduction are slight above the standards for public sewer disposal effluents. On the other hand, effluent load values from four different natural reducing agents are within national standard values for public sewer disposal effluents. This tabular analysis also shows that the replacement of Sodium dithionite with natural reducing agents generates effluents with toxicity values for environment within acceptable range. More specifically, pH of the waste water needs to be within 6-9 while Hydrose reduced effluents gives pH near to 8 but Henna and Apple reduced effluents are within 6-7. Again for BOD value analysis, at 20 °C, it needs to be below than 250 mg/L for public sewer wastage water according to National standards, Ministry of Environment and Forest, Bangladesh [32]. Here it is seen that dyeing effluents for four natural reducing agents BOD (mg/L) value are below than 250mg/L while Hydrose reduced effluent gives BOD value slightly above to 250 mg/L.

Table 7: Ecological parameters of Effluents after dyeing with Indanthren vat dyes.

Effluents after dyeing fabric with Indanthrene Dark Blue 5508 Dyes					
Ecological Parameters	Sodium Dithionite	Apple Extract	Hena root extract	Cabbage Extract	Amaranthus root Extract
pH	8	6.5	7	7.5	6.8
BOD (mg/L)	255	185	193	200	178
COD (mg/L)	400	375	360	392	370
DO (mg/L)	7	6.3	5.7	5	5
TDS (mg/L)	2030	1800	1750	1800	1760
Effluents after dyeing fabric with Indanthrene Brown G Dyes					
Ecological Parameters	Sodium Dithionite	Apple Extract	Hena root extract	Cabbage Extract	Amaranthus root Extract
pH	7.3	6.5	7.2	7	7.5
BOD (mg/L)	240	200	186	210	183
COD (mg/L)	410	372	350	375	368
DO (mg/L)	6.7	5.5	5	5	4.8
TDS (mg/L)	1900	1850	1800	1760	1830
Effluents after dyeing fabric with Indanthrene Rubine R Dyes					
Ecological Parameters	Sodium Dithionite	Apple Extract	Hena root extract	Cabbage Extract	Amaranthus root Extract
pH	7.8	6.0	6.8	6.8	7.7
BOD (mg/L)	250	190	190	210	185
COD (mg/L)	410	390	365	390	380
DO (mg/L)	7.3	6	5.5	5.7	5.3
TDS (mg/L)	2010	1830	1760	1790	1820

4. Conclusions

This study shows an opportunity to replace sodium dithionite (commercial name- hydrose) in reduction process (vatting) of vat dyes with several plant extracts. From previous related works, it has been seen many attempts to replace environmentally unfriendly hydrose by fruit extracts or glucose. But the application of plant extracts in vat dye reduction, including initial characteristic study of introducing reducing agents prior dyeing, is a novel work. The FTIR spectra made certainty to have reducing capacity in the three plant extracts. In addition, the reduction potential measurement yields a way to assume an approximate quantity of reducing agent for required reduction potential achievement. The spectrophotometric results of this eco-friendly dyeing approach has revealed that dyed fabric using apple and henna root extract for reduction gives better color strength (K/S value is 25.63 and 21.20, respectively while 28.50 for hyrose in reduction of Indanthren Dark Blue 5508). For the other two dyes, among three plant extracts, henna root extract reduced dyeing shows closer results in color strength to apple as well as to hydrose. In addition, from metamerism measurement, henna shows satisfactory results under four different light sources and the other two plant extracts also gives lower metamerism index values. The colorfastness properties of different dyed fabrics using the natural reducing agents show very good grading range (7-8) for color fastness to light and (4-5) for color fastness to rubbing, but in respect to color fastness to wash and color fastness to perspiration, dyed fabrics using plant extracts for vat dye reduction, gives moderate to good results. Moreover, the effluent test from conventional as well as natural extracts-based dyeing of vat dyes shows that natural extracts based processes gives effluents with pH, BOD, COD, TDS and DO values within acceptable range for public sewer while hydrose reduced dyeing wastes includes higher BOD, COD and DO values than standard limit.

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