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Utilization of Nasturtium officinale R. Br. dye available in Kashmir valley for value added paper and products: A way forward towards green chemistry

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ABSTRACT

Natural dye from Nasturtium officinale R.Br. available in Kashmir valley in abundance has been reconnoitred for its solicitation in paper dyeing. The extraction of natural dye was carried out using aqueous and organic solvents. Extracted dye was initially studied for the presence of anthocyanin, carotenoid, and chlorophyll content. The l results revealed that test species recorded highest per cent yield with ethanol and lowest with ethyl acetate solvent. Aqueous extract being eco-friendly in nature was applied on 12 % alkaline peroxide pulp of Amaranthus hybridus species. the resulted dyed paper strength properties was compared with undyed paper and it has been found that natural dyed paper has better strength properties. Overall results revealed that Nasturtium officinale R.Br. can be used as potent dye yielding plant for pulp and paper industryfor colouring value added products. The application of this natural dye may offer the great potential for producing different shades to retain its eco-friendly credentials by replacing the synthetic dyes.

Keywords: Amarathus hybridus; Aqueous solvent; Nasturtium officinale R.Br. organic solvents, strength properties.

I. INTRODUCTION

Now a day, the fortification of surroundings has turned into a challenge for the many manufacturing units. Across the world, environmental regulations are becoming stricter and forcing the shift of technology towards less or practically non-polluting areas of technological development. Dyeing industry is under increasing pressure to curtail the impairment to the environment, which is caused by their manufacture, application processes and their run-offs. Synthetic dyestuffs have also come under severe blame on the grounds of producing deadly and allergic reactions to individuals and also cause carcinogenicity and inhibition of benthic photosynthesis [1].

Ecological complications from the coloring of paper arose after industrialization, when old natural dyes were replaced by synthetic dyes. Synthetic dyes are intended to resist chemicals and progress the value of

the produce but are tenacious in the environs [2]. Maximum synthetic dyes are carcinogenic, highly toxic in nature and cause allergic dermatitis, skin irritation and mutation to humans [3]. Pollution of water due to synthetic dye molecules causes harm to the surroundings and has adversarial effects on community health [4]. 10- 50 per cent colorant is getting loss into the surroundings [5; 6; 7]. Some dyes are highly toxic and mutagenic and also decrease light penetration and photosynthetic activity, causing oxygen deficiency and limiting beneficial uses such as recreation, drinking and irrigation [5; 7].

Worldwide concern over the carcinogenic effects, toxicity and allergic reactions associated with synthetic dyes interest, the revival of natural dyes is increasing day by day [1]. Furthermore, many countries have already obligatory stringent environmental standards over synthetic dyes. the resurgence interest in natural dyes is actually due to increased consumer awareness in terms of minimal environmental and health impact versus synthetic dyes and revival of old practice of coloration with natural dyestuffs [8]; 9] .

In sight of the deleterious effects of the synthetic dyes and lack of knowledge of natural materials for dyeing, there is calamitous need to explore out new cheaper dye sources from the biodiversity wealth and extraction methods for producing sufficient quantities of viable safe natural pigments and dyes. Therefore, it becomes necessary to develop new techniques of coloration and standardize these processes with the help of modern scientific inputs so that natural dyes can offer themselves as an effective ecofriendly option to their synthetic counter parts. For this *Nasturtium officinale* R.Br. finds an important application in paper industry. Kashmir valley exhibits a prodigious degree of plant diversity. Many workers have contributed to ethno botany and plant diversity studies of the state but dye yielding potential and their application on paper of the flora has not been studied so far. Hence, the study titled "Utilization of *Nasturtium officinale* R. Br. dye available in Kashmir valley for value added paper and products: A way forward towards green chemistry." is proposed.

II.MATERIALS AND METHODS

Plant material for paper making and dyeing was collected from Srinagar and Kulgam districts of Kashmir province of J&K state. The experimental material comprised of 12 % alkaline peroxide pulp *Amaranthus hybridus* for papermaking, petals of *Nasturtium officinale* R.Br. for dye extraction.

2.1 Preparation of dyeing material

The shade dried fresh plant material of *Nasturtium officinale* R.Br. was washed with water to remove dirt and other adhering materials.

2.2 Quantification of pigments

2.2.1 Total anthocyanin content

For anthocyanins estimation method of Fuleki and Francis (1968) [10] was followed.

2.2.2 Total chlorophyll and carotenoids

Chlorophylls and carotenoid content were estimated by Hiscox and Israelstam (1979) [11] and Arnon (1949) [12].

2.3 Extraction and dye yield% of selected plant species

2.3.1 Aqueous extraction of dye

Extraction of dye from selected test species was performed by Soxhlet apparatus using distilled water as solvent. For 100 gram plant material 1 litre of distilled water was used. The material was kept for reflux for about 8 hours at 80-85^{o}C. The liquid extract was evaporated at 65^{o}C in a rotary vacuum evaporator to one fourth of its original volume to get the final extract for dyeing [13].

2.3.2 Alcoholic extraction of dye

Alcoholic extraction of dye from selected test species was performed by Soxhlet apparatus at 80-85^{o}C for 8 hours using different organic solvents ethanol, benzene petroleum ether, methanol ethyl acetate and iso propyl alcohol having different polarities. The material to liquor ratio was kept 10:100 ratio in boiling flask of 500 ml capacity. The reflux was repeated till no trace of color in solvent was seen. The extract was collected by filtering the solution through fritted glass assembly. The liquid extract was evaporated at 65^{o}C in a rotary vacuum evaporator to one fourth of its original volume to get the final extract for dyeing [13.

2.4 Dyeing of pulp

Natural dye extracts were used for the dyeing of pulp using conventional process. The simple impregnation of the pulp in the dye bath is defined as conventional dyeing or stock dyeing. The extracted dye solution (3%) was added to beaten pulp in different dosages and stirred for 5-10 minutes for better mixing and retention of dye on pulp. Dyeing conditions includes 20- 25 ^{o}C dyeing temperature (Td) and 15 minutes residence time (Tr). The dyeing was realized using a liquor ratio of 55:1 ml/g. [14].

2.5 Production of laboratory sheets and evaluation of paper properties (undyed)

Laboratory sheets from undyed pulp were formed and were tested by standard TAPPI testing methods.

2.5 Production of laboratory sheets and evaluation of paper properties (dyed)

Laboratory sheets from dyed pulp were formed and were tested by standard TAPPI testing methods.

Laboratory handsheets of 60 GSM (g/m^2) were formed from undyed and dyed pulp on sheet former by Standard TAPPI testing method T221 cm-99. The hand sheets were conditioned at 27 ºC and 65 per cent relative humidity for 24 hours in accordance with standard TAPPI testing method T402 sp-98. After conditioning, the physical strength properties were evaluated as per the Standard testing methods. Tensile index by T494 om-01, tear index by T414 om-98, burst index of handsheets was measured by method T 403 om-97, double fold numbers by T423 cm-98 and brightness was calculated according to the ISO 2470-1

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III.RESULTS AND DISCUSSION

The data presented in Table1 revealed that photosynthetic pigments (anthocyanins, carotenoids and chlorophyll) in test species varied significantly. Anthocyanins are water-soluble vacuolar pigments of higher plants abundant in juvenile and senescing plants. Anthocyanins are glycosides of anthocyanidins (also called aglycones) and sugars and span quite a range of colour hues and give rise to the blue, purple, red, orange colour to flowers and fruits of many plants. The absorption spectra of anthocyanins of plant tissues indicate a strong overlapping of anthocyanins, chlorophyll and carotenoids [15] Lee and Graham, 1986). Anthocyanin synthesis in vegetative organs is induced by different environmental factors [16] Chalker, 1999) and anthocyanins concentration increases during senescence [17]. In the present study total anthocyanin content value in *Nasturtium officinale* R.Br. petals was recorded 71.67 mg/100g. Carotenoids are lipid soluble, yellow, orange and red pigments found in all higher plants. The distinctive yellow colours of light-harvesting carotenoids become more apparent in leaves during autumn when chlorophyll degrades revealing their strong colours. Carotenoids are required for the correct assembly of photosystems [18; 19]. Carotenoids content to the tune of 0.07 mg/g fw was recorded in *Nasturtium officinale* R.Br. petals. Chlorophyll is the green pigment utilized by all higher plants for photosynthesis in response to available sunlight. Chlorophyll is a fat soluble tetrapyrrole pigment, occurring in chloroplasts of green plants, photosynthetic bacteria and algae [20]. It plays a fundamental role in the photosynthesis, being capable of converting sunlight into chemical energy. The most important forms of chlorophyll are chlorophyll a and chlorophyll b, occurring in an approximate ratio of 3:1 [21]. 0.39 mg/g fw chlorophyll content was recorded in *Nasturtium officinale* R.Br. petals. The difference in the pigment (anthocyanin, carotenoids, chlorophyll) contents can be attributed to an integration of genetic and environmental factors which affect the photochemistry, biochemistry, physical diffusion of CO_2 into chloroplasts and activities of non-photosynthetic plant tissues [22]. Photosynthetic efficiency is affected by diverse plant and site factors e.g. properties of leaves, plant architecture, duration of photosynthesis, photosynthesis by organs other than leaves, soil factors such as soil moisture, nutrient availability, and CO_2 released in soil respiration and ambient climatic factors such as air temperature, wind speed, CO_2 concentration, relative humidity, angle of sun, and nature of radiation and thus makes an difference in the composition of the pigments.

Table 1. Quantification of pigments *Nasturtium officinale* R.Br.

Parameter	Quantity
Anthocyanins (mg/100 g)	71.67
carotenoids (mg/g fw)	0.07
Chlorophyll (mg/g fw)	0.39

Dye yield is the quantity of dye extract obtained after evaporation of water from the extracted dye solution. The per cent yield of dye extract of the selected plant material varied ranging between 0.72 to 23.39% (Table 2). Petals of *Nasturtium officinale* R.Br. recorded highest (23.39%) per cent yield with metanol and lowest (0.72%)

was recorded with ethyl acetate solvent. The low extraction yield of test species with ethyl acetate comply with the studies conducted by [23] Angelini *et al*. (1997) and may be probably due to dissolution of only free aglycones [24]. Similar results were observed by the study carried out by [25]. The variation in yield of the dye extract may be attributed to the difference in dissolution of dye and the polarity index of the solvent [26; 27]. The high extraction yield of *Nasturtium officinale* R.Br. with organic polar solvents in comparison to non-polar or less polar solvents showed that the test species contain high amount of organic polar component [26]. The results are well in agreement with the study conducted by Bushra *et al*. (2009) [28, 26; 27].

Table 2: Yield (%) of dye extracts of test species

Solvents	Test species
	Nasturtium officinale R.Br.
Petroleum ether	1.12
Benzene	15.91
Chloroform	1.52
Ethyl acetate	0.72
Ethanol	17.97
Methanol	23.39
Water	1.97

Impact of natural dye had significant influence on tensile strength value of *Nasturtium officinale* R.Br. paper (Table 3). *Amaranthus hybridus* paper exhibited highest (24.16 N.m/g) tensile index with addition of dye and lowest (21.85 N.m/g) was shown without dyeing. This may be attributed to the efficient binding of dye molecules to the cellulosic fibre by forming chemical bridge between dye and fibre through mordant, which gets fixed on the fibre and helps in fixation of natural dyes thus increases the tensile strength properties by addition of dyes and with the addition of mordant [29; 26]. *Nasturtium officinale* R.Br. also contains carotenoids, flavonoids and triterpenic alcohols, both in their free and esterified forms [25]. Flavonoids are considered favoured bio compounds as chemotaxonomic markers in plants because they show large structural diversity and are chemically stable [25]. During dyeing of cellulosic fibres, the amount of the dye taken up required agent, to acquire a more fixation (30]

The table reveals that the dyed *Amaranthus hybridus* paper showed the highest (5.92 $mN.m^2/g$) tear index while as undyed *Amaranthus hybridus* paper showed the lowest (5.87$mN.m^2/g$) tear index. This is probably due to better fibre bonding and better interaction of *Amaranthus hybridus* fibres with the dye molecule as indicated by higher tear index. The complexation of iron centered ion involved carboxylic group of cellulose

fibre of test species with the phenolic group of natural dye, giving more enhancement of tear index properties [31]. Natural dyes enhance the tear index very much than synthetic dyes because of relatively higher possibility of hydrogen bond formation than synthetic dyes [26].

The examination of the data in table 3 indicates that that the dyed *Amaranthus hybridus* paper showed the highest (1.79 kPa.m^2/g) burst index while as undyed showed the lowest burst index (1.56 kPa.m^2/g). This may due to more feasibility of dye molecules with the fibres of test species for hydrogen bonding [29; 26]. In the dyeing of adjective colours, the mordant, having the stronger chemical affinity to the colouring matter, plays the role of the cellulose [32]. The enhancement of burst index with the addition of mordant may be attributed that the addition of mordant helps in fixation of more and more dyes which increases the bonding between the dye molecule and fibre surface hence increases the burst index properties [27]. The presence of chemical compounds (tannin, flavonoids, resins) in dyeing test species explains their great affinity to the cellulosic fibres. This affinity can be increased by means of mordant which favours the bonding of dye molecule with the cellulosic fibre surfaces [32].

The data indicated that folding endurance (Double fold number) was recorded highest (37) in dyed *Amaranthus hybridus* dyed paper and lowest (33) folding endurance (Double fold number) was recorded in undyed paper. The paramount results obtained by *Nasturtium officinale* R.Br. dye may be credited to the effecient binding of dye molecules to the cellulosic fibre by forming chemical bridge between dye and fibre through mordant, which get fixed on the fibre and help in fixation of natural dyes thus increases the folding endurance properties by addition of dyes and with the mordant [29; 26]. The presence of chemical compounds in dyeing test species explains their great affinity to the cellulosic fibres [32].

Application of natural dye showed noteworthy effect on brightness percentage value of *Amaranthus hybridus* dyed paper. The data presented in Table 3 indicated that ISO brightness percentage was highest (29.13%) without the addition of dye and lowest (54.94%) with addition of dye. Addition of dye helps in fixation of more and more dyes which increases the bonding between the dye molecule and fibre surface hence decreases the brightness [27].

Table 3. Paper properties of undyed and dyed of *Amaranthus hybridus*

	Paper properties				
Paper sample	Tensile Index, N.m/g	Tear Index, $mN.m^2/g$	Burst Index, $kPa.m^2/g$	Double Fold, No.	ISO brightness, %
Nasturtium officinale R.Br. dyed	67.33	7.51	3.83	1091	27.57
12 % APP undyed	65.20	7.10	3.60	1048	59.9

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V.CONCLUSION

- Per cent yield of dye extract was recorded highest in *Nasturtium officinale* R.Br. with metanol and lowest with ethyl acetate solvent. Aqueous extract of selected natural dye applied on 12% APP pulp enhanced the strength properties of paper to a greater extent.
- The affinity of the dyes recorded best on *Amaranthus hybridus*. However dyed samples showed better dye quality and strength properties than undyed samples.

Thus, it is concluded from the present study that dye extracted from *Nasturtium officinale* R.Br. can be used for the dyeing of *Amaranthus hybridus* paper adopting stock dyeing method. The selected dye showed major influence on the strength properties of paper can be used for attaining the varieties of beautiful shades.

Utilization of these species for paper production and for paper dyeing shall help in environmental conservation in terms of reducing the stress on forest resources and pollution caused by synthetic dyes.

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