Studies of Banana SAP used as mordant for natural dye

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INTRODUCTION

India has a rich biodiversity and it is not only one of the world's twelve mega diversity countries, but also one of the eight major center of origin and diversitification of domesticated places. It has approximately 490,000 plant species of which about 17,500 are angiosperms more than 400 are domesticated crop species and almost an equal number their wild relatives. Thus, India harbor a wealth of useful germplasm resources and there is no doubt that the plant kingdom is a treasure-house of diverse natural products. One such product from nature is the dye.

Natural dyes are dyes or colorants derived from plants, invertebrates, or minerals. The majority of natural dyes are vegetable dyes from plant sources – roots, berries, bark, leaves, flower and wood and other organic sources such as fungi and lichens. Natural dyes are known for their use in colouring of food substrate, leather, wood as well as natural fibers like wool, silk, cotton and flax as major areas of application since ancient times.

Natural dyes produce an extraordinary diversity of rich and colours that complement each other. Natural dyes from plants may also have dozens of compounds and their properties vary with soil type and dyes are one of the most important uses of the plants, as they are related with cultural practices, rituals, arts and crafts, fabrics and to satisfy personal embodiment, however, dye yielding plants have not received significant attention the weather. Synthetic dyes are produced at high temperature and pressure from chemicals isolated from petroleum derivatives. During the manufacturing process of dyes many carcinogenic chemicals are used which leads to formation of toxic by-products. These by- products are discharge in rivers and ponds or left in open. Hence cause severe water and atmospheric pollution. The production of synthetic chemical dyestuffs has become big business, but unfortunately the production and use of these synthetic dyes is one of the world's most polluting industries. Conventional synthetic dyes present health risks to those working with them and to those who wear them, as well as damaging the environment in a number of ways. The dyes in solution are absorbed by the fibers. The process of transferring the dye from the water to the fiber is called exhaustion or "fixation rate", with 100% exhaustion meaning there is no dye left in the dyebath solution. Most conventional dyes have an exhaustion rate of 80%, meaning the dyestuff which is not affixed to the fiber is flushed into our rivers with the spent process water. Each year the global textile industry discharges 40,000 – 50,000 tons of dye into our rivers, and more than 200,000 tons of salt. One of the most pressing issues today is the lack of fresh drinking water, and as one of the most polluting industries, textiles – and especially the dyeing of textiles – is responsible for many instances of pollution making fresh water undrinkable. The 40,000 to 50,000 tons of synthetic dyestuffs expelled into our rivers are complex chemical formulations containing some things that are very toxic to us, such as heavy metals (like lead, mercury, chromium, zinc, cobalt and copper), benzene and formaldehyde. Many certifications, such as the new Global Organic

MORDANTS

A mordant is a substance used to set dyes on fabrics or tissue sections by forming a coordination complex with the dye which then attaches to the fabric or tissue. It may be used for dyeing fabrics, or for intensifying stains in cell or tissue preparations. The term is derived from the Latin *mordere*, to bite.

Effects of Chemical Mordant

BANANA PSEUDOSTEM SAP AS MORDANT

In India, banana is cultivated on 5.65 lakh ha area and the leading states are Maharashtra (0.54 lakh ha), Gujarat (0.49 lakh ha), Tamil Nadu (0.82 lakh ha), Andhra Pradesh (0.56 lakh ha), Karnataka (0.42 lakh ha) and Kerala (0.59 lakh ha). In addition to fruit production, huge quantity of biomass (pseudostem, leaves, suckers etc.) is generated. Presently, this biomass is discarded as waste.

ORIGIN OF BANANA

Alexander the Great discovered the taste of the banana in the valleys of India in 327 BC. The existence of an organized banana plantation could be found in China in 200 AD. The word banana is of West African origin, and passed into English via Spanish or Portuguese.

Museceae

Musaceae is a botanical name for a family of flowering plants. The family is native to the tropics of Africa and Asia. The plants have a large herbaceous growth habit with leaves with overlapping basal sheaths that form a pseudostem making some members appear to be woody trees.

Genus Musa

The genus *Musa* was first described by the pre-Linnean Rumphius. The name may derive from *mauz {mouz* or *moz)* the Arabic word for the banana fruit, but it was accepted by Linnaeus because it could have been in commemoration of Antonius Musa

Review of Literature

6.Work done on Banana pseudostem

The banana pseudo stem has been reported to contain high quality starch (Shantha and siddappa, 1970). The banana Pseudo-stem show satisfactory physical properties, such as relatively high tensile strength and stiffness, which indicate its prospect as a promising fibre material. The application of natural fibers including banana Pseudo-stem has been proved promising in various technical fields, such as replacing synthetic fibers as reinforcement in various composites used in automobile parts (Pothan and Thomas ,2003) Ammayappan *et al.* (2004),studied the natural dye from pseudostem of banana for silk. The result revealed that pseudostem of banana contain 2-3% dye, which gives vanilla cream colour without mordanting and with mordants gave different colour only in pale and light shade on silk fabric. Each plant produces a single bunch of fruits.After harvesting, the bare Pseudo-stem are cut and thus, several tons of banana Pseudo-stem are produced daily on the plantations (Cordeiro *et al.*, 2004). In general, banana Pseudo-stem is an abundant natural resource in subtropical and tropical regions and has potential for providing profitable product such as manure(Ultra et at.2005). Anirudhan(2006) and Noeline (2005) studied new absorbent systems containing banana Pseudo-stem. These absorbent systems, which can remove phosphate from wastewater, exhibit high absorption potential and satisfactory recyclability. Zainudin (2009) studied the thermal behavior of banana Pseudo-stem (BSP) filled unplastisized polyvinyl chloride (UPVC) composites. From the study, the thermal stability of the composites was found to be higher than that of BPS fiber and the UPVC matrix. The physicochemical properties of plantain *(Musa paradisiaca)* and banana *(Musa sapientum)* pseudostem wastes have been determined. The results showed that the green plantain and banana pseudostem wastes contain high amount of carbohydrate which can be converted into sugar (glucose) by saccharification and fermentation into alcohol (biofuel), it can also be used in the paper making and in the preparation of cellulose derivatives; both samples have very high moisture content.(Akpabio *et al.*,2012)

MATERIALS AND METHODS

7.1 Chemicals and Reagents

Iodine solution, Benedict's reagent, Barfoed's reagent, Seliwanoff's solution, Sulfuric acid, Acetic acid, Acetone, Sodium hydroxide, Fehling's reagent A, Fehling's reagent B, Cotton fabric, Alum, Myrobalan, *Butea* flowers dye, Folin Phenol reagent, Sodium carbonate solution.

7.2 Instrumentation

Hot air oven, Water bath, Desiccators, pH meter, Weighing machine, Spectrophotometer

7.3 Sample site

Banana plant pseudostem sap was collected from Raver Tehsil (Maharastra) just near Burhanpur (M.P.).

7.4 Sampling Process

The pointed end of the knife was pushed tangentially into the stem. The incision were left to bleed for 24 h and stored in a wide mouth plastic bottle in refrigerator until use.

7.5 Pseudostem sap colour:

Pseudostem sap is thick liquid and very light brown or dusty in colour.

Fig 1

8. Analysis of the composition of the Banana pseudostem sap:

Qualitative analysis for carbohydrate by Cole's method,(Cole,1933).

Quantitative analysis of carbohydrate:

8.1Molisch's Test: In a test tube, 2 ml. of the test solution and 2 drops of α-naphthol solution were added. The tube was carefully inclined and conc. H_2SO_4 were poured drop wise, using a dropper, along the sides of the tube. Violet colour at the junction of two liquids was observed.

8.2 Fehling's Test: In a test tube 2 ml. of the test solution and add equal volumes of Fehling A and Fehling B were added and placed it in a boiling water bath for few minutes. When the content of test tube started boiling, they were mixed together and observed for any change in colour or precipitate formation. The production of yellow or brownish –red precipitate of cuprous oxide indicated the presence of reducing sugars in the given sample.

8.3 Benedict's Test: To 2 ml. of Benedict's regent, 5 drops of the test solution were added and mixed well. The test tube were placed in a boiling water bath for 5 minutes after that the solution were cooled and observed for any change in colour or precipitate formation. The colour change from blue to green, yellow, orange or red (depending upon the amount of reducing sugar present in test sample) were observed.

8.4 Barfoed's Test: To 2 ml. of the test solution about 2 ml. Barfoed's reagent were added. Mixed well and boiled for one minute in the water bath. The solution were allowed to stand for few minutes. Formation of a red precipitate of cuprous oxide in the bottom and along the sides of the test tube immediately, indicated the presence of monosaccharide.Since Barfoed's reagent is weakly acidic, it is reduce only by monosaccharides.

8.5 Seliwanoff 's Test: To 2 ml. of Seliwanoff's reagent, two drops of test solution were added and mixture was heated to just boiling. A Cherry red condensation product was observed indicating the presence of ketoses in the test sample.

8.6 Iodine Test: 2 drops of iodine solution were added to about 2 ml. of the

test solution. A blue black colour was observed which is indicative of presence of polysaccharides.

9. Chemical analysis

9.1 Sample preparation:

A petriplate previously cleaned and dried in an oven was weighed on an analytical balance to 0.01 g. 30 gm of banana pseudostem sap was placed on the petriplate. The sap was dried in oven at 60°C for 24 hours with the cover off. Then the petriplate was removed and placed in the desiccator for 15 minutes to cool, before weighing. Procedure is referred from TAPPI Standard.

9.2 Determination of Holocellulose content (TAPPI Standard T 222os – 74) :

2 g of air dried sawdust was weighed accurately. The sawdust was transferred quantitatively to a 250 ml conical flask. 100 ml water, 1.5g sodium chloride and 5 ml of 10% acetic acid were added and the flask was placed in a water bath maintained at 70°C, swirling the content of the flask at least once every five minutes. The flask was kept closed with a small, inverted Erlenmeyer flask. 5 ml of 10% acetic acid was added after 30 minutes. 1.5g sodium chloride was added after further 30 minutes. Alternative acetic acid and sodium chloride at 30 minutes were continued, after last addition of sodium chloride. The mixture was heated for 30 minutes after last addition of sodium chloride. The suspension was cooled in an ice bath. Residue was filtered into a weighed fruited glass crucible (medium or coarse porosity) and washed with iced distilled water and finally washed with acetone. The residue was air-dried (allowed the residue to strand in the open laboratory for a day or two until it is free of acetone) Covered it with a perforated aluminium foil. The sample was transferred to a desiccator and weighed at daily intervals until the sample reached constant weight. The moisture content was determined on a 0.5 g sample which is afterward. The following formula was used to determine the holocellulose content in pseudostem: Holocellulose content in pseudostem sap (percent)

$$= \frac{W_4 - W_3}{100 \times W_2} \times (100 - W_1)$$

where,

W_1 = extractive free content (percent)

W_2 = weight of oven- dried extractive free sample (grams)

W_3 = weight of oven dried crucible (grams)

W_4= weight of oven- dried residue and crucible (grams)

9.3 Determination of Cellulose content (TAPPI Standard T203 om- 93):

Weigh 1 gm of a holocellulose sample and placed in 200 ml beaker. Add 25 ml of 17.5% sodium hydroxide and stir. After 4 minutes, smash for 5 minutes. After 16 minutes, add 25 ml of distilled water and stir for 1 minute. After 5 minutes, filter with a preweighed glass filtering crucible and wash with distilled water until neutral. Add 40 ml of 10% acetic acid and hold for 5 minutes. Weigh the residue to calculate the α-cellulose content.

α-cellulose content in pseudostem sap (percent) $= \frac{W_4 - W_3}{100 \times W_2} \times W_1$

where,

W_1 = Holocellulose content (percent).

W_2 = weight of oven- dried holocellulose sample (grams).

W_3 = weight of oven dried cruicible (grams).

W_4 = weight of oven dried residue and crucible (grams).

9.4 Determination of Hemicellulose:

Hemicellulose was calculated by subtracting cellulose from holocellulose.

Hemicellulose content in banana pseudostem sap (percent) = $P_1 - P_2$

Where,

P_1= Holocellulose content (percent)

P_2 = Cellulose content (percent)

9.5 Determination of Lignin content (TAPPI standard T 222 om – 06) :

2 grams of sawdust was weighed out accurately in weighing bottle and transferred in a 100 ml beaker. 40 ml of cold (10-15 °C) 72% sulphuric acids was added carefully with a pipet and the mixture was stirred with a small glass rod. After the specimen is dispersed, cover the beaker with watch glass and keep it in a bath at 20 °C for 2 hours. Stir the materials frequently during this time to ensure complete solution. Add about 300 to 400 ml of water to a flask and transfer to material from the beaker to the flask. Rinse and dilute with water to 3% concentration of sulfuric acid, to a total volume of 1540 ml. Boil The solution for 4 hours, maintaining constant volume by addition of hot water. Allow the insoluble material (lignin) to settle keeping the flask in an inclined position. Without stirring up the precipitate, decant or siphon off the supernatant solution through a filtering crucible. Wash the lignin with hot water. Dry the crucible with lignin in an oven at 105°C to the constant weight. Cooled in a desiccator and weighed.

Lignin content in Banana pseudostem sap (percent) $= \frac{W_4 - W_3}{100 \times W_2} \times (100 - W_1)$

where,

W_1 = extractive free content (percent).

W_2 = Weight of oven dried extractive- free sample (grams).

W_3 = weight of oven dried crucible (grams).

W_4 = weight of oven dried residue and crucible (grams).

9.6 Tannin content:

The tannins were determined by Folin and Ciocalteu method. 0.1 ml of the sample extract was added with 7.5 ml of distilled water and adds 0.5 ml of Folin Phenol reagent, 1 ml of 35% sodium carbonate solution and dilute to 10 ml with distilled water. The mixture was shaken well, kept at room temperature for 30 min and absorbance was measured at 725 nm. Blank was prepared with water instead of the sample. A set of standard solutions of gallic acid is treated in the same manner as described earlier and read against a blank.

10. Dyeing procedure

10.1 Fabric sample

Pure cotton fabric with plain weave is used. The fabric sample is used with 2 gm owf (oven weight of fabric)

10.2 Dye extraction

In this method, dye from flowers powder were extracted by preparing an aqueous solution of flowers (10 g in 100 ml distilled water) and the extraction process was carried out at a temperature range of 80-85°C for 90 minutes. Extract was then filtered through a piece of cloth to yield the natural dye.

Table 1

CONDITION FOR EXTRACTION OF NATURAL DYE

Solvent	Temperature (°C)	Time (minutes)
Distilled water	80-85	90

Figure 2 *Butea* floewers

from Butea flowers

10.3 Biomordanting

The cotton fabric were mordanted using different amounts of banana pseudostem sap as mordant solution (10, 20, 30, 40 and 50 % owf) at 80 °C and M:L= 1:30 for 90 minute.

10.4 Pre-mordanting:

In this method, 5 cotton samples were pretreated with the Banana sap with different concentration 10, 20, 30, 40 and 50 % for 90 minutes at 80̊C. The pretreated cotton fabric was introduced into the dye bath containing required amount of dye extract and water. The dyeing was carried out for 90 minutes at 80℃. The dyed samples were taken out, squeezed and dried at room temperature.

TABLE 2

CONDITION FOR DYEING

Fabric	Mordant concentration	Dye concentration	Temperature (ºC)	Time (min)	M:L ratio
Cotton	10%	20%	80ºC	90	1:30
	20%				
	30%				
	40%				
	50%				

10.5 Simultaneous Mordanting:

Simultaneous Mordanting was done with the help of method in which , the 5 cotton samples were dyed with dye extract as well as the Banana sap with different percent 10, 20, 30, 40 and 50 % for 90 minutes at 80̊ c simultaneously. The dyed samples were taken out, squeezed and dried at room temperature.

10.6 Post Mordanting: 5 cotton fabrics was introduced into the dye bath containing required amount of dye extract and water for post mordanting method. The dyeing was carried out for90 minutes at 80℃. The dyed samples were taken out, squeezed and treated with the Banana sap with different percent 10, 20, 30, 40 and 50 % for 90 minutes at 80̊C.

Table 3

Qualitative tests used for carbohydrate analysis

No	Test	Observation	Inference
1	**Molisch's test**	Positve	Presence of carbohydrates

2	**Iodine test**	Negative	Absence of Starch
3	**Fehlings test**	Positive	Presence of reducing sugars
4	**Benedict's test**	Negative	Absence of reducing sugars
5	**Barfoed's test**	Positive	Presence of reducing sugars
6	**Seliwanoff's test**	Positive	Presence of ketose Presence of aldoses

The carbohydrate analysis test was shown positive results for presence of reducing sugars in table 3.

4.2 pH test

pH refers to acidity and alkalinity. It is measure of hydrogen ion (H^+) in the Banana pseudostem sap. Banana pseudostem sap pH was obtaining **6.2** .

Table 4.2
Chemical composition of banana pseudostem sap

Content	Value(%)
Holocellulose	5.51%
Hemicelluloses	5.424%
Cellulose	0.086%
Lignin	1.44%
Tannin	4.06%

In table 4.2 Chemical composition of banana pseudostem sap was analysed and different contents calculated in percent basis. Holocellulose, hemicellulose, cellulose, lignin and tannin were main contents in banana pseudostem sap which was used as a mordant in dyeing process. Holocellulose includes alpha cellulose and hemicellulose. Cellulose content in banana pseudostem sap was very low. Cellulose is a homopolysaccharide composed of β-D-glucopyranose units which are linked together by (1→4)-glycosidic bonds. Cellulose molecules are completely linear and have a strong tendency to form intra- and intermolecular hydrogen bonds. Hemicelluloses are heterogeneous polysaccharides, like cellulose, most hemicelluloses function as supporting materials in the cell walls [Sjostrom 1981].

However banana pseudostem sap had lower lignin i.e. 1.44% content than wood but its glue like quality is important for dyeing process. Banana pseudostem sap has 2.06% of tannin. Tannin is defined as naturally occurring water soluble polyphenolic compounds of high molecular weight (about 500-3000) containing phenolic hydroxyl groups to enable them to form effective crosslink between proteins and other macromolecules.

Discussion

1. Chemical compositions confirm the presence of following contents on percent basis in banana pseudostem sap. They are holocellulose, hemicelllulose, cellulose, lignin and tannin. These compounds are the substances which can give the fixing properties to the banana pseudostem sap. Tannin are the most important ingredients which are the most important ingredients which are necessary for mordanting with natural dyes.
2. Fastness properties of cotton dyed sample will be explained and described in the next research paper because some further work related washing is going on. In banana pseudo stem sap it has been confirmed by laboratory research work that tannin content is present in banana sap mordant. Cotton is less suitable for natural dyes. There are some natural dyes that was work on cotton, however especially if mordanted with tannins.Cotton is the second most consumed fiber worldwide, behind polyester

CONCLUSION

In banana crop, after harvesting the bare pseudostem remains in several tons as a waste. Fiber can be produced for paper industry, fabrics or yarn industry etc. But usually they are disposed of by burning in fields which creates another air pollution problem. Larger amount of solid waste increases pollution load in environment. In this connection, present study deals with the use of banana pseudostem sap as a mordant to utilize a large quantity of biomass. The remaining material can be used as fiber, green manure, as a source of carbohydrate for production of starch, sugar and alcohol. Synthetic mordants cause many health hazards in society due to irruption of problems like skin and eye irritation, inflammation, more damage to wounds and abrasions, possibility to enter in blood stream etc. Analysis of chemical composition of banana pseudostem sap revealed the presence of holocellulose including hemicellulose and cellulose. Cellulosic material are homopolysaccharides and have a strong tendency to form intra and inter molecular hydrogen bonds which certainly responsible to improve the bonding capacity of dye to fabric. On the other hand lignin and tannin contents are also present in banana pseudostem sap. Lignin's glue like property is acting as a binding agent in the dyeing process. If we talk about tannin content of pseudostem sap, then we can say it provides carboxylic group to cotton fabric to bind with dye molecule and thus increasing absorption capacity of fabric. The overall results show that banana pseudostem sap not only gives natural source of mordant but also improves the all qualities of dyeing process. The study carried out gives significant result use of because natural dyes helps to preserve the traditional art of dyeing and definitely will improve the popularity of natural material.The process of extraction of banana pseudostem sap and its use as a mordant was found to be cost effective as compared to the cost of chemical mordants in local market.If above concern has become fruitful it will give a way to grow more plants for greater use of dyes and mordants in textile industries, which will help to solve the problem of unemployment.The use of natural dyes and mordants in ecofriendly manner also giving conservation of plants as well as environment.

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