

A Green Approach- Ultrasonic Natural Dyeing of Cotton Fabric with Enzyme Pretreatments

Green Chemistry

- **Green chemistry**, also called sustainable chemistry, is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances.

Green Chemistry Principle

- [Paul Anastas](#), then of the [United States Environmental Protection Agency](#), and John C. Warner developed 12 principles of green chemistry, which help to explain what the definition means in practice. The principles cover such concepts as:
 - the design of processes to maximize the amount of raw material that ends up in the product;
 - the use of safe, environment-benign substances, including solvents, whenever possible;
 - the design of energy efficient processes;
 - the best form of waste disposal: not to create it in the first place.

The 12 principles are:

- It is better to prevent waste than to treat or clean up waste after it is formed.
- Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- Chemical products should be designed to preserve efficacy of function while reducing toxicity.
- The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

Continued

- Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.”
- A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.
- Reduce derivatives - Unnecessary derivatization (blocking group, protection/ deprotection, temporary modification) should be avoided whenever possible.
- Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
- Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
- Substances and the form of a substance used in a chemical process should be chosen to minimize potential for chemical accidents, including releases, explosions, and fires.

Abstract

- Natural dyeing is being itself a green chemistry process and when enzyme are used as pretreatment in an ultrasonic bath ,the process become even more ecofriendly and greener. Green chemistry applications in textile particularly in the field of dyeing include the utilization of a set of principles that reduce or eliminates the use or generation of hazardous substances in the design, manufacture and application .The mandate is ---
- Production and processing should be biodegradable,recyclable,renewable-source.
- Reduction and elimination of chemical hazardous and effluent.
- Energy efficiency and water conservation .

Introduction

Innovation in Natural dyeing due to advanced technology now available to the dyers has brought back old traditional dyeing once again into limelight. The main focus of research in this area covers four major issues –

- i) Extraction of Natural dye
- ii) Innovation in Dyeing
- iii) Effluent Management
- vi) Green approach- eliminating use of metal salts

Objective

To develop a green methodology for natural dyeing with an aim for better dye uptake and improved fastness properties of dyed fabric without using metal mordants, by the use of Enzymes.

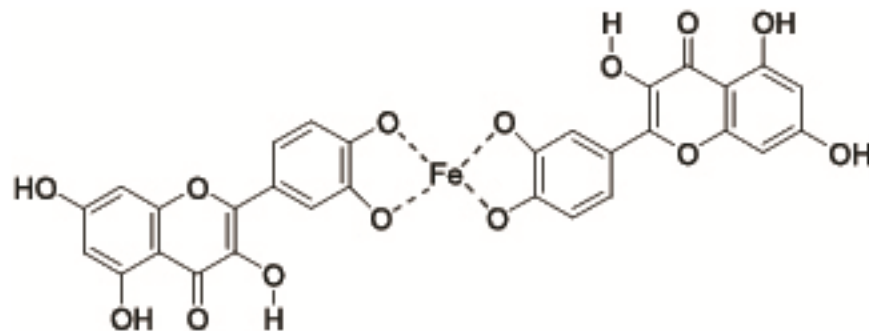
Pretreatment used

To make Natural dyes resistant, bright, appealing various pretreatments are done before dyeing and they are –

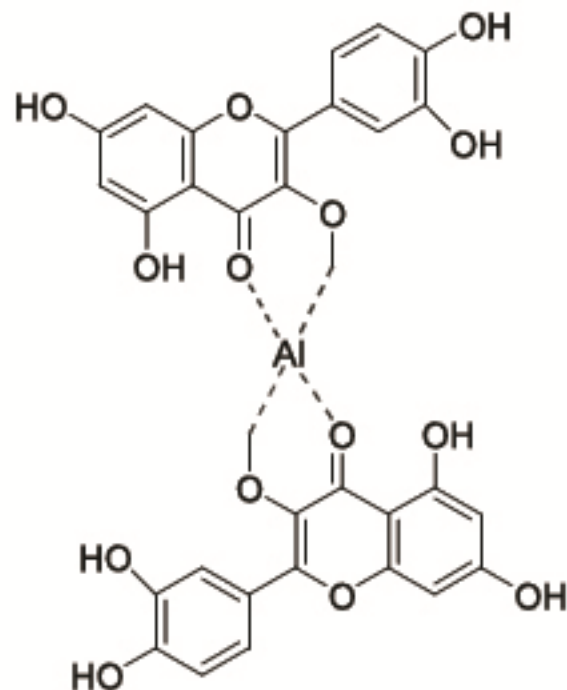
- Metal mordant such as alum, Ferrous sulphate, Copper sulphate, Stannic chloride, Stannous chloride, Potassium dichromate.
- Tannic acid ,Tartaric acid, Citric acid, acetic acid.
- Bio mordants –Enzyme, PEG and other Plant extract.

ROLE OF A MORDANT

The iron binding by phenolics increases with increasing number of –OH groups. A flavonoid ring B and a 3', 4'-dihydroxy group is required for Fe-binding (I)



In case of aluminium ion binding, the 3-hydroxychromane groups are required as shown in the structure (II).



Green Chemistry approach ENZYME

➤ **Some drawback of metal mordant :**

- Metal mordant highly pollute effluent generated from dye bath
- Metal mordant are not so effective when compared with enzyme.

➤ **Enzyme :**

- Enzymes are gaining an increasing role in textile wet processing due to their proven flexibility, reliability and concern about safety, energy and water conservation and environmental responsibility.
- Enzyme can be used in chemical as well as bio chemical process as they are most efficient under normal condition of temperature, pressure and pH.
- Enzyme are very specific with their action and they show results in reasonably good time and in a very cost effective manner .
- Enzymes are of bio origin thus make the process eco-friendliness.

TECHNOLOGY UPGRADATION

- Effective and efficient exploitation of new technology will keep us in competitiveness with the world.
- Utilization of Ultrasound energy for Extraction as well as Dyeing cotton, silk and wool with natural dyes is a definitive improvement and green approach in modern textile processing This has been developed by us in FEAT laboratory.

NEWER TECHNIQUE IN DYEING

- Sonicator dyeing--In sonicator dyeing when the fabric is dipped into the dye bath, the dye uptake is most rapid at the beginning and then slows down as the process continues.
- Due to higher dye uptake the effluent is fairly clear thus least amount of dye discharge.
- Sonication is not only an energy saving process but also helps in dramatically high dye uptake.

PROCESS ADOPTED FOR DYEING

- Pretreatment of Enzyme and then dyeing through conventional and sonication method.
- Two different processes were developed for dyeing. They are:
- One step (Enzyme +Tannic acid +Dyeing)
- Two steps (Enzyme +Tannic acid and then dyeing)

PRETREATMENT OF ENZYME THEN DYEING THROUGH SONICATION AND CONVENTIONAL METHOD

- a) The fabric /cotton was pretreated with enzyme as well as metal mordant separately for the sake of comparison.

- b) The pretreated fabrics (both with enzymes and mordants separately) were dyed with two natural dyes- catechu and tectona in sonicator bath at liquor ratio 30:1. The temperature of the dye bath was kept not higher than 45 °C and maintained at this level for 1 hour. In sonicator dyeing the process showed accelerated dye uptake. Conventional dyeing was also carried out simultaneously to compare the dye uptake.

ROLE OF ULTRASOUND ENERGY

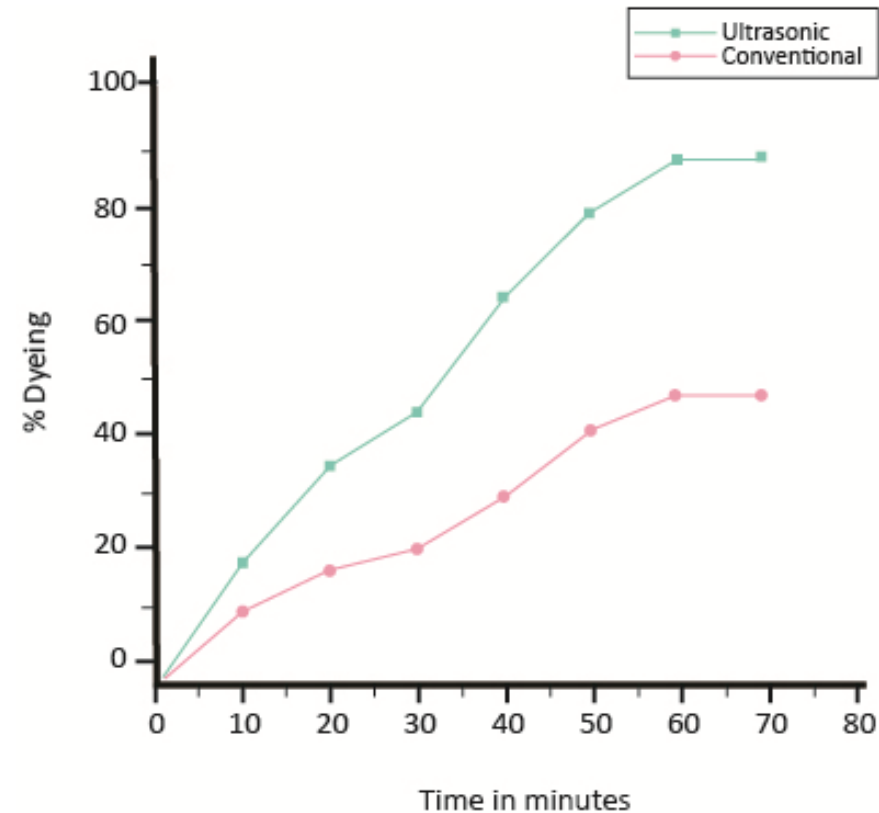
Utilization of ultrasound energy for dyeing has the following advantages

- The sonicator used is of 20kHz frequency which is suitable for inducing cavitations
- Cavitation which causes formation and collapse of micro bubbles is very effective in dye extraction of air sensitive substrates.
- The micro bubbles which are unstable slowly grow in the process of oscillation, finally implode generating momentary localized high pressure & temperature, thus helping in better and faster dye uptake.

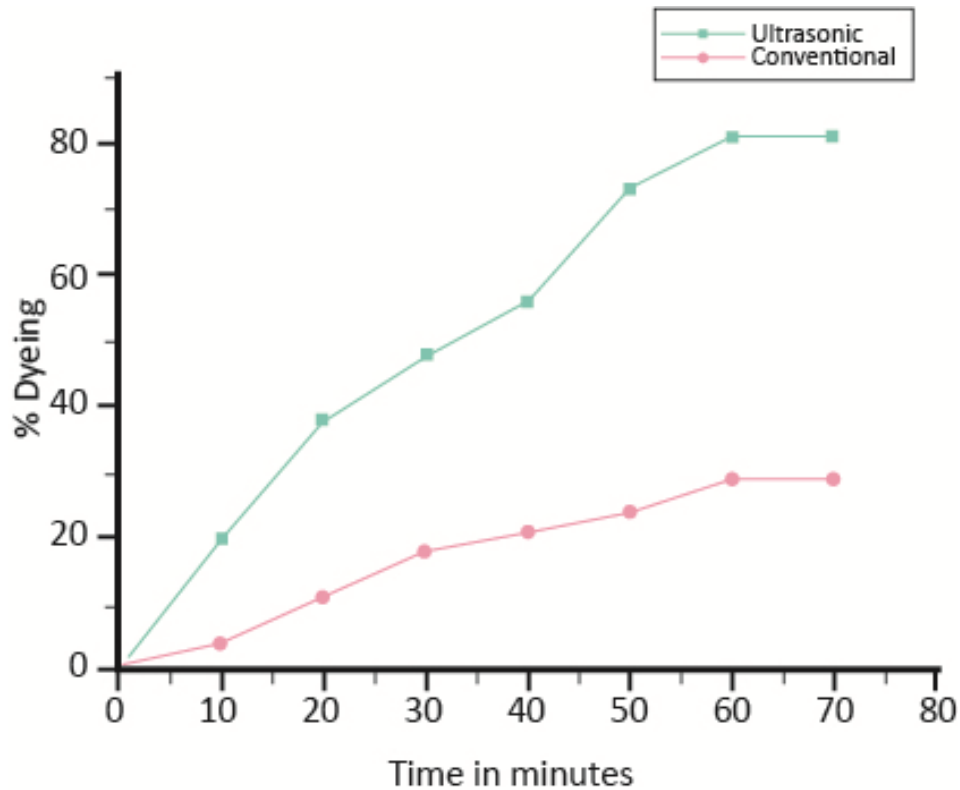
EFFECT OF SONICATION

The effect of sonication was studied by ease of dye uptake through UV-Visible spectrometer by measuring the absorbance of the dye bath solution before and after dyeing and was compared by similar measurements of conventional dyeing and the difference can be seen in next slide.

ULTRASONIC vs CONVENTIONAL DYEING



Ultrasonic dyeing with Catechu



Ultrasonic dyeing with Tectona

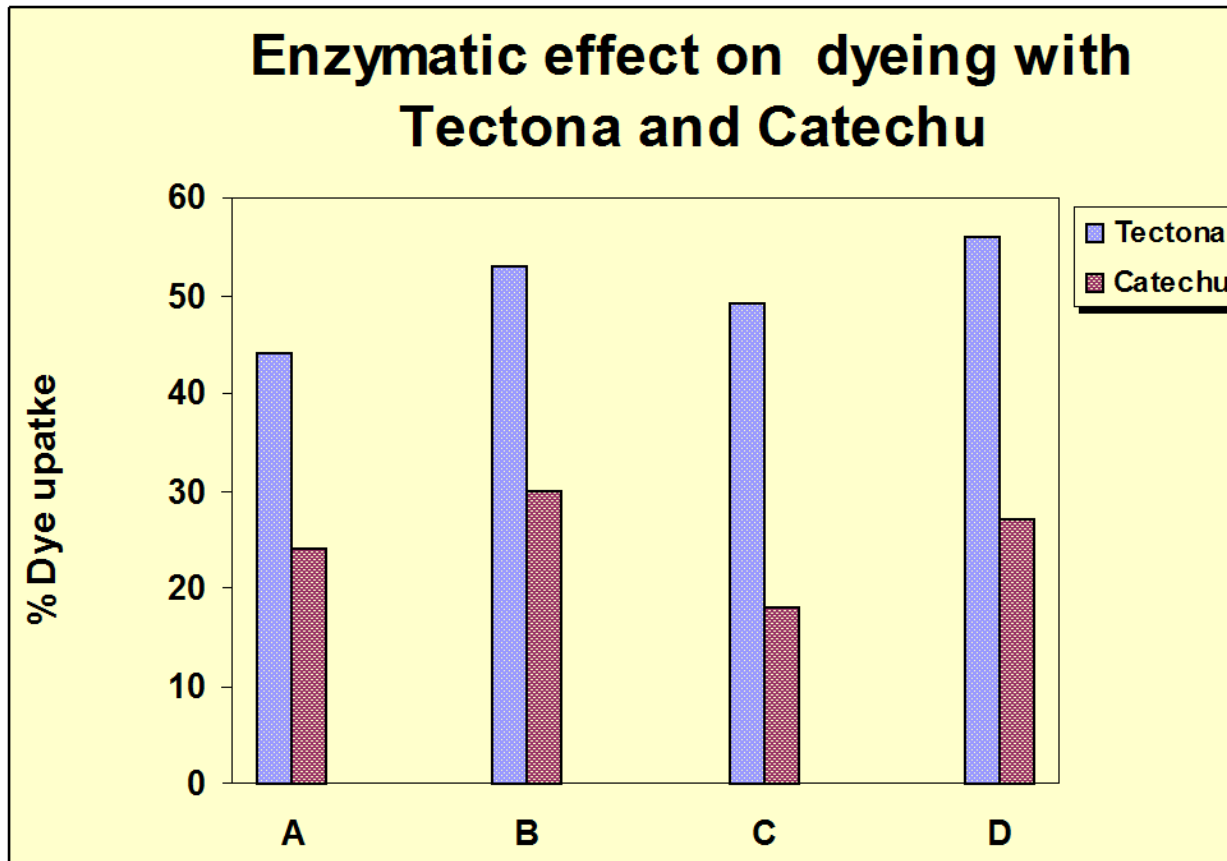
COLOR MEASUREMENTS - CIE LAB VALUES

CIE lab values of catechu and tectona dyed fabric pretreated with enzyme

| Dye | Enzyme | L* | a* | b* | Wash fast IS-687-79 | Light fast IS-2454-85 |
|------------|---------------|-----------|-----------|-----------|--------------------------------|----------------------------------|
| Catechu | Pro-Amyl | 50.033 | 10.403 | 30.504 | 4-5 | 4-5 |
| Catechu | Diasterease | 53.061 | 6.562 | 20.500 | 4-5 | 4-5 |
| Catechu | Lipase | 51.330 | 7.345 | 25.367 | 4-5 | 4-5 |
| Tectona | Diasterease | 60.234 | 10.002 | 25.303 | 4-5 | 4-5 |
| Teactona | Pro-Amyl | 61.221 | 9.005 | 22.453 | 4-5 | 4-5 |
| Tectona | Lipase | 62.439 | 8.222 | 21.566 | 4-5 | 4-5 |

CIELab values for catechu dyed fabric pretreated with metal mordants

| Mordant | L* | a* | b* | Wash fast IS-687-79 | Light fast IS-2454-85 |
|-------------------|-----------|-----------|-----------|--------------------------------|----------------------------------|
| Alum | 61.061 | -0.562 | 10.500 | 4 | 4 |
| Stannic chloride | 57.882 | 12.968 | 35.522 | 4 | 4 |
| Stannous chloride | 55.600 | 10.588 | 29.203 | 4 | 4 |
| Ferrous sulphate | 50.033 | 10.403 | 30.504 | 3-4 | 4 |
| Copper sulphate | 52.886 | 12.522 | 34.107 | 3-4 | 3-4 |
| Pot. dichromate | 48.402 | 14.536 | 32.278 | 3-4 | 3-4 |



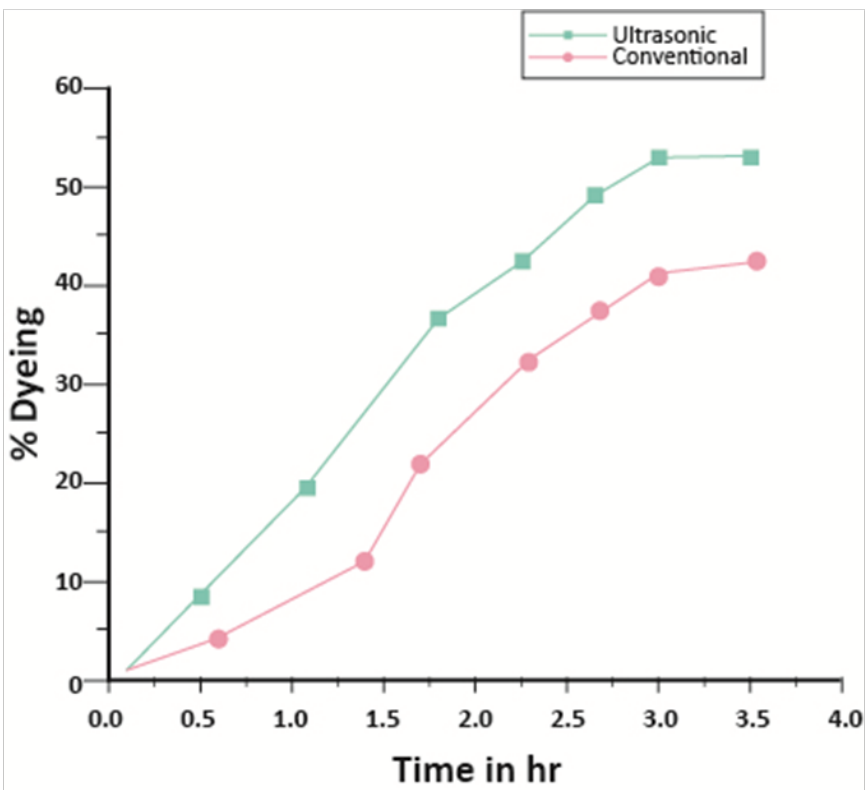
A-----Without treatment, B-----Protease and Amylase
C-----Lipase, D-----Diasterease

Dye enzyme compatibility was also assessed and it was found the protease & amylase combination is suited for catechu ,while diasterease is suited for tectona .

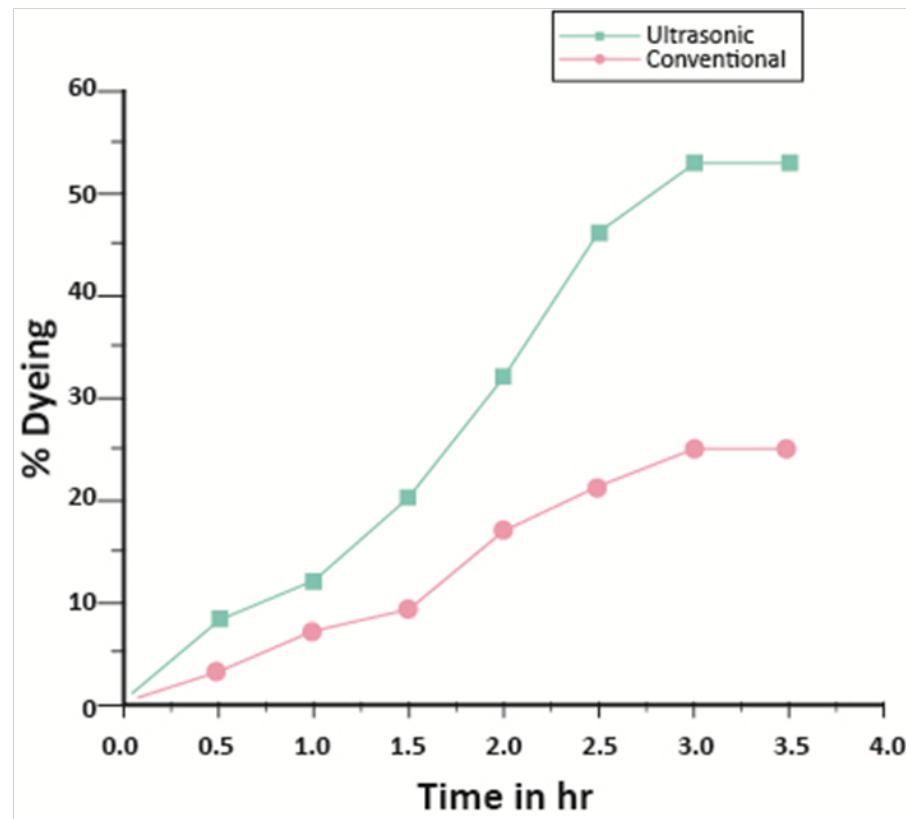
ONE STEP AND TWO STEP PROCESS

- i) The dyes, tannic acid and the enzymes (in the ratio of 2 % dye , 1 % tannic acid and 1 % enzymes) were all taken in one bath and the moist fabric was dipped for 3 hours at temperature 30-40°C. The dyed fabrics were dipped in dye-fix solution (2 %) for 1 hour and then it was rinsed thoroughly in tap water and allowed to dry in open air.
- ii) The tannic acid and the enzymes (in the ratio of 1 % tannic acid and 1 % enzymes) were first treated onto taken in one bath and the moist fabric was dipped for 3 hours at temperature 30-40°C. The dyed fabrics were dipped in dye-fix solution (2 %) for 1 hour and then it was rinsed thoroughly in tap water and allowed to dry in open air.

ULTRASONIC vs CONVENTIONAL DYEING



Ultrasonic dyeing with Punica



Ultrasonic dyeing with Terminalia

COLOR MEASUREMENTS - CIE LAB VALUES

Effect of different enzymes on the colorimetric data obtained for tannic acid/enzyme/ Punica granatum dye

| Dye-Enzyme-TA | L* | a* | b* | C | H |
|---------------|--------|-------|--------|--------|--------|
| Control | 58.066 | 6.510 | 32.319 | 32.968 | 78.580 |
| PG-Pro-Amy-TA | 56.956 | 5.745 | 29.984 | 30.529 | 79.122 |
| PG-Dias-TA | 58.089 | 6.072 | 32.259 | 32.816 | 79.305 |
| PG-Lipa-TA | 57.604 | 6.349 | 31.330 | 31.967 | 78.573 |

Effect of different enzymes on the colorimetric data obtained for tannic acid/enzyme/ Rheum emodi dye

| Dye-Enzyme-TA | L* | a* | b* | C | H |
|---------------|--------|--------|--------|--------|--------|
| Control | 51.510 | 11.940 | 28.486 | 30.887 | 67.232 |
| RE-Pro-Amy-TA | 51.606 | 12.468 | 28.594 | 31.194 | 66.414 |
| RE-Dias-TA | 52.164 | 12.866 | 29.971 | 32.616 | 66.740 |
| RE-Lipa-TA | 52.867 | 14.196 | 31.641 | 34.680 | 65.810 |

FASTNESS TESTING

Fastness properties of dyed cotton fabrics under conventional heating and ultrasonic conditions of enzyme and Punica

| Dyeing methods | Wash–perspiration–rubbing–light | | | | | |
|----------------|---------------------------------|-----------------------|----------------------|--------------------|--------------------|-----|
| | WF | Per _{acidic} | Per _{basic} | Rub _{dry} | Rub _{wet} | LF |
| Conventional | 3–4 | 4 | 3–4 | 2–3 | 2-3 | 4 |
| Ultrasonic | 4 | 4 | 4 | 3-4 | 3-4 | 4-5 |

Fastness properties of dyed cotton fabrics under conventional heating and ultrasonic conditions of enzyme and terminalia

| Dyeing methods | Wash–perspiration–rubbing–light | | | | | |
|----------------|---------------------------------|-----------------------|----------------------|--------------------|--------------------|----|
| | WF | Per _{acidic} | Per _{basic} | Rub _{dry} | Rub _{wet} | LF |
| Conventional | 4 | 4 | 3–4 | 3-4 | 3-4 | 4 |
| Ultrasonic | 4-5 | 4 | 4 | 4 | 3-4 | 5 |

WF = wash fastness, LF = light fastness

CONCLUSION

Our main focus of research study is utilization of enzymes in natural dyeing, a green approach to textile processing for betterment of dye uptake and improvement of fastness properties. The innovation that we have made is to use enzymes and high mechanical agitation such as sonicator and studied its advantages over metal mordants.

Textile dyeing with natural dyes- fiber, fabric or garments all show better dye uptake after enzymatic pretreatment, it also eliminates the use of metal mordants and shows better wash fastness and light fastness.