A review on chemical structure of natural dye pigment

¹Prajapati Mayur ²Modi Nainesh

¹Research Scholar, ²Associate Professor
^{1, 2}Department of Botany, Bioinformatics and Climate Change Impacts Management, School of sciences, Gujarat University, Navrangpura, Ahmedabad-380009 E-mail – ¹mayur.prajapati1807@gmail.com, ²nrmodi@gujaratuniversity.ac.in

Abstract: Natural dyes are used for coloring of food materials, leather and fibers like wool, silk and cotton. Recently, many commercial dyers have started using natural dyes to overcome the environmental mutilation caused by artificial dyes. Pigments are present in all living matter which offering attractive colours. The pigments can be classified as natural, synthetic or inorganic by their origin. Natural pigments also classified based on their chemical structure such as indigoid, Anthraquinone, Alpha-hydroxy-napthoquinones, Flavonoids, Dihyrophyrans, Anthocyanidins and Carotenoids. This paper reports the studies available on chemical structure of natural dye pigments from different plant species

Key Words: Natural dye, Pigments, Chemical structure.

1. INTRODUCTION:

A dye is a coloured substance that chemically bonds to the substrate to which it is being applied. Natural dyes are used for coloring of food materials, leather and fibers like wool, silk and cotton. The use of environmental friendly natural dyes on textiles have become a matter of significant importance due to the increased environmental consciousness in order to avoid some harmful synthetic dyes [Samantha *et al.*2009]. These dyes are extracted from vegetable and animal matter with no or very minute chemical processing. Recently, many commercial dyers have started using natural dyes to overcome the environmental mutilation caused by artificial dyes [Arora *et al.*2017]. Natural colorants are also derived from naturally occurring sources like insects (e.g., cochineal beetles and lac scale insects); animals (e.g., some species of mollusks or shellfish); and minerals (e.g., ferrous sulfate, ochre, and clay) without any chemical treatment [Chengaiah *et al.*2010]. Germany was the first to take initiative to put ban on numerous specific azo dyes for their manufacturing and applications. The Netherlands, India and some other countries have also followed with a ban on azo dyes [Patel et al.,2011].Overexploitation of natural resources to obtain dyes may result in deforestation and threaten endangered species. For these reasons, the Global Organic Textiles Standard (GOTS) permits the use of safe synthetic dyes and prohibits the use of natural dyes from endangered species [Saxena *et al.*,2014]. Natural colouring agents are phytochemicals which are mainly obtained from natural plant resources and they are very beneficial to human health. [Leong, H. Y *et al.*2018].

1.1. Plant Pigments:

A pigment is a substance which proficient of absorbing light, so it could be considered pigments almost all substances [Hoffman *et al.*,2009]. Usually, pigment absorbs very specific wavelengths, and emit a characteristic electromagnetic signal that allows us to identify them. Most often chemical compounds selectively absorb within certain radiation ranges and the color of a given compound is complementary to the absorbed radiation [Herrera.,2015]. Pigments are present in all living matter which offering attractive colours and playing fundamental roles in organism's growth [Delgado-Vargas *et al.*,2000].

1.2. Classification of Pigments:

1.2.1. Based on their origin:

The pigments can be classified as natural and synthetic by their origin. Natural pigments are produced by living organisms such as plants, animals, fungi and microorganisms. Synthetic pigments are developed from laboratories. The organic compounds are both natural and synthetic pigments. Inorganic pigments can be found in nature or synthesized [Bauernfeind et al.,1981].

1.2.2. Based on the Chemical Structure [Vankar et al., 2000]:



Figure 1. Indigo [Vankar et al., 2000]

Indigoid dyes: This is the most important group of natural colours, derived from *Indigofera tinctoria* [Vankar et al.,2000].

1.2.3. Anthraquinone dye:

Some of the major red dyes are based on the structure of anthraquinone. These are derived from both plants and insects. Such colors are distinguished by good light fastness. They form complexes with metal salts, and the resulting metal-complex coloring has good wash quality [Vankar et al.,2000]



Figure 2. Anthraquinone [Vankar et al., 2000].

1.2.4. Alpha-hydroxy-napthoquinones:

The most prominent member of this type of coloring is lawsone or henna from *Lawsonia inermis* [Vankar et al.,2000].



Figure 3. Alpha-hydroxy-naphthoquinone [Vankar et al., 2000].

1.2.4. Flavonoids:

Flavonoids are a diverse group of polyphenolic compound contribute to the yellow color of horticultural products. These are widely distributed in the plant kingdom and more than 4000 structurally distinct flavonoids in plant sources have been identified [Patel et al.,2008]. Flavonoids can be subdivided into different subgroups depending on the C ring carbon attached to the ring and the degree of insaturation and oxidation of the C ring. Flavonoids are called isoflavones, in which the B ring is connected in position 3 of the C ring. Those in which the B ring is connected in position of 4 are considered neoflavonoids, while those in which the B ring is connected in position 2 are further subdivided into several subgroups based on the structural features of the C ring. Such subgroups include: flavones, flavanones, flavanones, flavanones, catechins or flavanols, anthocyanins and chalcones [Panche *et al.*,2016].



Figure 4. Types of flavonoids [Panche et al., 2016]

1.2.5. Dihydropyrans:

Di-hydropyrans, viz.haematin and its leuco form, haematoxylin are closely related to the flavones in the chemical structure. These are important natural dyes on silk, wool and cotton for the dark shades. The common examples are logwood, Brazil wood and sappan wood [Srivastava *et al.*,2019].



Figure 5. Dihydropyrans

1.2.6. Anthocyanidins:

Anthocyanins (in Greek, antho means herb, kyanos means blue) are glycosides of 2 (in all other forms, flavilium ionic form is stable), strongly colored sap responsible for various colors in higher plants. These are probably the best known natural food colorants as they are widely distributed in the plant kingdom and range in color from apple red to grape blue to brinjal violet [Prabhu *et al.*,2012]. Because of its physicochemical properties (eg poor stability and low solubility), anthocyanidins (aglycone) are most commonly found in nature as their glycosidic forms of salts, known as anthocyanins [Celli *et al.*,2019]. In addition to their structure, pH, temperature [Sui *et al.*,2014], oxygen [Weber *et al.*,2017], light [Mahdavi *et al.*,2016], water interaction [Tonon *et al.*,2010] and other compounds (e.g. ascorbic acid) also influence the stability of anthocyanins [Guldiken *et al.*, 2017].



Figure 6. Basic Anthocyanins structure [Guldiken et al.,2017]

1.2.7. Carotenoids:

Carotenoids that are widely distributed in plants and animals are expressed by linearly conjugated polyene tetraterpenes. The carotenoids are brightly coloured pigments in which the highly conjugated π -electron system confers different colours like yellow, orange and red to the molecule. The name carotene is derived from the orange pigment found in carrots (separated in 1831, Wackenroder) [Wackenroder 1831]. In nature, carotene (e.g. β -carotene from *Daucus carota*) and xanthophyll (e.g. Lutein from *Tagetes erecta*) are two forms of carotenoids [Piccaglia et al.,1998].



Figure 7. Structure of β -carotene



Figure 8. Structure of Lutein

Table 1: Some Important dye-yielding plants with pigments and their chemical properties

Name of PlantsPart of plantName of pigments	Colour ofChemical structureReferencepigment	es
---	--	----

Brachychiton acerifolias	Flower	1. Cyaniding 3- O-rutinoside		(24), (25)
	Tiower	2. Cyanidin 3-O- glucoside		(24), (26)
Carthamus	Petal	1. Carthamin		(27), (28)
tinctorius		2. Safflor yellow		(27), (29)
Caesalpinia sappan	Wood	Brazilein	о	(30), (31)
Rubia tinctorium	Root	1. Alizarin	O OH O OH O OH	(32), (33)

		2. Purpurin	O OH O OH	(32), (33)
Haematoxylon campechianum	wood	Haematoxylin	H O O H	(34), (35)
Mallotus philippinensis	Fruit	Rottlerin		(36), (37)
Tectona grandis	Leaf	Tectograndone		(38), (39)
		Tectoleafquinone	$R = H_{3}C = CH = CH = CH_{2}$	(39), (40)

Corcus sativus	Flower (Stigma)	Crocin		(41), (42)
Butea monosperma	Petal	Butein		(43), (44)
Indigofera tinctoria	Leaf	Indirubin		(45), (46)
Srrobilanthes flaccidifolius	Leaf	Indigo		(47), (48)
Curcuma longa	Rhizome	Curcumin	HO OCH, OH H,CO	(49), (50)

Solanum lycopersicum	Fruit	Lycopene	$\overset{H_{C}}{\overset{O_{b}}{\leftarrow}} \overset{O_{b}}{\overset{O_{b}}{\leftarrow}} \overset{O_{b}}{\overset{O_{b}}{\leftarrow}} \overset{O_{b}}{\overset{O_{b}}{\leftarrow}} \overset{H_{C}}{\overset{O_{b}}{\leftarrow}} \overset{H_{C}}{\overset{O_{b}}{\leftarrow}} \overset{O_{b}}{\overset{O_{b}}{\leftarrow}} \overset{O_{b}}{\overset{O_{b}}{\leftarrow}$	(51), (52)
Capsicum annuum	Fruit	1. Capsanthin	- Julium	(49), (53)
		2. Capsorubin		(49), (53)
Tagetes erecta	Flower	Lutein	$\underset{\mu_{0}}{\overset{\mathcal{H}_{0}}{\underset{\mathcal{O}_{1}}{\overset{\mathcal{O}_{1}}{\overset{\mathcal{O}_{1}}{\overset{\mathcal{O}_{2}}}{\overset{\mathcal{O}_{2}}{\overset{\mathcal{O}_{2}}{\overset{\mathcal{O}_{2}}{\overset{\mathcal{O}$	(54), (55)
Lawsonia inermis	Leaf	Lawsone	O O O O	(56), (57)
Garcinia indica	Fruit	1. Cyanidin 3- glucoside	HO OH OH OH OH OH OH OH	(58), (59)

		2. Cyanidin 3- sambubioside		(58), (60)
Nyctanthes arbortristis	Flower (Calyx)	Crocetin	$HO \xrightarrow{1} \begin{pmatrix} y \\ y \\ z \\$	(61)
Basella rubra	Fruit	Gomphrenin I		(62), (63)
Bauhinia purpurea	Flower (Petal)	Chalcone	O B A	(64), (65)
Woodfordia fruticosa	Leaves	Lawsone	ОН	(57), (66)
Rheum rhabarbarum	Root	Physcion		(67), (68)

2. CONCLUSION:

Natural dyes not only have the ability of dyeing but also have a wide range of medicinal properties. We can extract different types of natural pigments from the plants. Such natural pigments will show advantages over synthetic

pigments. Mostly these natural pigments are used for dying of different fabrics. Natural pigments are less harmful, less hazardous to skin, less carcinogenic and less toxic to nature. Most of them are water-soluble so they are also used as food colorant. With increasing use of chemical dyes, these days, there has also been remarkable increase in air, soil and water pollution. So there has been immediate need to produce eco-friendly dye from plant resources. This naturally obtained dyes are not only useful for pollution reduction but can also be used as edible products as food colouring agent.

REFERENCES:

- 1. Samanta, A. K., & Agarwal, P. (2009). Application of natural dyes on textiles.
- 2. Arora, J., Agarwal, P., & Gupta, G. (2017). Rainbow of natural dyes on textiles using plants extracts: Sustainable and eco-friendly processes. *Green and Sustainable Chemistry*, 7(1), 35-47.
- 3. Chengaiah, B., Rao, K. M., Kumar, K. M., Alagusundaram, M., & Chetty, C. M. (2010). Medicinal importance of natural dyes-a review. *International Journal of PharmTech Research*, 2(1), 144-154.
- 4. Patel, N. K. (2011). 6. NATURAL DYE BASED SINDOOR BY NK PATEL. *Life Sciences Leaflets*, *11*, 355-to.
- 5. Saxena, S., & Raja, A. S. M. (2014). Natural dyes: sources, chemistry, application and sustainability issues. In *Roadmap to sustainable textiles and clothing* (pp. 37-80). Springer, Singapore.
- 6. Leong, H. Y., Show, P. L., Lim, M. H., Ooi, C. W., & Ling, T. C. (2018). Natural red pigments from plants and their health benefits: A review. *Food reviews international*, *34*(5), 463-482.
- 7. Hoffman, J., & Puszynski, A. (2009). Chemical Engineeering and Chemical Process Technology. Vol. V. Pigments and Dyestuffs. Encyclopedia of Life Support Systems (EOLSS).
- 8. Herrera, A. S. (2015). The biological pigments in plants physiology. Agricultural Sciences, 6(10), 1262.
- 9. Delgado-Vargas, F., Jiménez, A. R., & Paredes-López, O. (2000). Natural pigments: carotenoids, anthocyanins, and betalains—characteristics, biosynthesis, processing, and stability. *Critical reviews in food science and nutrition*, 40(3), 173-289.
- 10. Bauernfeind, J. C. (1981). Carotenoids as colorants and vitamin A precursors; technological and nutritional applications.
- 11. Vankar, P. S. (2000). Chemistry of natural dyes. Resonance, 5(10), 73-80.
- 12. Patel, J. M. (2008). A review of potential health benefits of flavonoids.
- 13. Panche, A. N., Diwan, A. D., & Chandra, S. R. (2016). Flavonoids: an overview. *Journal of nutritional science*, 5.
- 14. Srivastava, R., & Singh, N. (2019). Importance of natural dye over synthetic dye: a critical. *International Journal of Home Science*, 5(2), 148-150.
- 15. Prabhu, K. H., & Bhute, A. S. (2012). Plant based natural dyes and mordants: A Review. J. Nat. Prod. Plant Resour, 2(6), 649-664.
- 16. Celli, G. B., Tan, C., & Selig, M. J. (2019). Anthocyanidins and anthocyanins. Food Sci, 218-223.
- 17. Khoo, H. E., Azlan, A., Tang, S. T., & Lim, S. M. (2017). Anthocyanidins and anthocyanins: colored pigments as food, pharmaceutical ingredients, and the potential health benefits. *Food & nutrition research*, 61(1), 1361779.
- 18. Sui, X., Dong, X., & Zhou, W. (2014). Combined effect of pH and high temperature on the stability and antioxidant capacity of two anthocyanins in aqueous solution. *Food Chemistry*, *163*, 163-170.
- 19. Weber, F., Boch, K., & Schieber, A. (2017). Influence of copigmentation on the stability of spray dried anthocyanins from blackberry. *LWT*, 75, 72-77.
- 20. Mahdavi, S. A., Jafari, S. M., Assadpour, E., & Ghorbani, M. (2016). Storage stability of encapsulated barberry's anthocyanin and its application in jelly formulation. *Journal of food engineering*, *181*, 59-66.
- 21. Tonon, R. V., Brabet, C., & Hubinger, M. D. (2010). Anthocyanin stability and antioxidant activity of spraydried açai (Euterpe oleracea Mart.) juice produced with different carrier agents. *Food Research International*, 43(3), 907-914.
- 22. Guldiken, B., Gibis, M., Boyacioglu, D., Capanoglu, E., & Weiss, J. (2017). Impact of liposomal encapsulation on degradation of anthocyanins of black carrot extract by adding ascorbic acid. *Food & function*, 8(3), 1085-1093.
- 23. Wackenroder, H. W. F. (1831). Über das oleum radices Dauciaetherum, das carotin, den carotenzucker und den officillensuccus Dauci; so wieauchüberdasmannit, welches in demmöhrensaftedurcheinebesondere art der gährunggebildetwird, Geigers Mag. *Geigers Magazine Pharm*, *33*, 144.
- 24. Piccaglia, R., Marotti, M., & Grandi, S. (1998). Lutein and lutein ester content in different types of Tagetes patula and T. erecta. *Industrial Crops and Products*, 8(1), 45-51.

- 25. Kimpa, M. I., Momoh, M., Isah, K. U., Yahya, H. N., & Ndamitso, M. M. (2012). Photoelectric characterization of dye sensitized solar cells using natural dye from pawpaw leaf and flame tree flower as sensitizers.
- 26. https://pubchem.ncbi.nlm.nih.gov/compound/Cyanidin-3-O-rutinoside
- 27. https://pubchem.ncbi.nlm.nih.gov/compound/Cyanidin-3-O-glucoside
- 28. Takahashi, Y., Miyasaka, N., Tasaka, S., Miura, I., Urano, S., Ikura, M., ... & Wada, M. (1982). Constitution of two coloring matters in the flower petals of Carthamus Tinctorius L. *Tetrahedron letters*, 23(49), 5163-5166.
- 29. https://pubchem.ncbi.nlm.nih.gov/compound/Carthamin
- 30. http://www.chemfaces.com/natural/Safflor-Yellow-A-CFN90262.html
- 31. Lee, D. K., Cho, D. H., Lee, J. H., & Shin, H. Y. (2008). Fabrication of nontoxic natural dye from sappan wood. *Korean Journal of Chemical Engineering*, 25(2), 354-358.
- 32. https://pubchem.ncbi.nlm.nih.gov/compound/Brazilein
- 33. Bányai, P., Kuzovkina, I. N., Kursinszki, L., & Szőke, É. (2006). HPLC analysis of alizarin and purpurin produced by Rubia tinctorum L. hairy root cultures. *Chromatographia*, 63(13), S111-S114.
- 34. Kasiri, M. B., & Safapour, S. (2014). Natural dyes and antimicrobials for green treatment of textiles. *Environmental chemistry letters*, 12(1), 1-13.
- 35. Yusuf, M., Shabbir, M., & Mohammad, F. (2017). Natural colorants: Historical, processing and sustainable prospects. *Natural products and bioprospecting*, 7(1), 123-145.
- 36. https://pubchem.ncbi.nlm.nih.gov/compound/Hematoxylin#section=3D-Conformer
- 37. Khan, S. A., Khan, M. I., Yusuf, M., Shahid, M., Mohammad, F., & Khan, M. A. (2011). Natural dye shades on woollen yarn dyed with Kamala (Mallotus philippinensis) using eco-friendly metal mordants and their combination. *Colourage*, 58(11), 38-44.
- 38. https://pubchem.ncbi.nlm.nih.gov/compound/Rottlerin
- 39. Aguinaldo, A. M., Ocampo, O. P. M., Bowden, B. F., Gray, A. I., & Waterman, P. G. (1993). Tectograndone, an anthraquinone-naphthoquinone pigment from the leaves of Tectona grandis. *Phytochemistry*, *33*(4), 933-935.
- 40. Wani, S. A., & Mohammad, F. (2018). Imparting functionality viz color, antioxidant and antibacterial properties to develop multifunctional wool with Tectona grandis leaves extract using reflectance spectroscopy. *International journal of biological macromolecules*, 109, 907-913.
- 41. Agarwal, S. C., Sarngadharan, M. G., & Seshadri, T. R. (1965). Colouring matter of teak leaves: isolation and constitution of tectoleafquinone. *Tetrahedron Letters*, 6(30), 2623-2626.
- 42. Raina, B. L., Agarwal, S. G., Bhatia, A. K., & Gaur, G. S. (1996). Changes in Pigments and Volatiles of Saffron (Crocus sativusL) During Processing and Storage. *Journal of the Science of Food and Agriculture*, 71(1), 27-32.
- 43. https://pubchem.ncbi.nlm.nih.gov/compound/Crocin
- 44. Srivastava, S., Ray, D. P., & Giri, S. K. (2013). Extraction of Palas dye for its use in Textile Coloration.
- 45. https://pubchem.ncbi.nlm.nih.gov/compound/5281222
- 46. Chanayath, N., Lhieochaiphant, S., & Phutrakul, S. (2002). Pigment extraction techniques from the leaves of Indigofera tinctoria Linn. and Baphicacanthus cusia Brem. and chemical structure analysis of their major components. *Chiang Mai University Journal*, *1*(2), 149-160.
- 47. https://pubchem.ncbi.nlm.nih.gov/compound/Indirubin
- 48. Laitonjam, W. S., & Wangkheirakpam, S. D. (2011). Comparative study of the major components of the indigo dye obtained from Strobilanthes flaccidifolius Nees. and Indigofera tinctoria Linn. *International Journal of Plant Physiology and Biochemistry*, *3*(7), 108-116.
- 49. https://pubchem.ncbi.nlm.nih.gov/compound/Indigo
- 50. Chengaiah, B., Rao, K. M., Kumar, K. M., Alagusundaram, M., & Chetty, C. M. (2010). Medicinal importance of natural dyes-a review. *International Journal of PharmTech Research*, 2(1), 144-154.
- 51. Baskaran, R., Madheswaran, T., Sundaramoorthy, P., Kim, H. M., & Yoo, B. K. (2014). Entrapment of curcumin into monoolein-based liquid crystalline nanoparticle dispersion for enhancement of stability and anticancer activity. *International journal of nanomedicine*, *9*, 3119.
- 52. Shi, J., & Maguer, M. L. (2000). Lycopene in tomatoes: chemical and physical properties affected by food processing. *Critical reviews in food science and nutrition*, 40(1), 1-42.
- 53. Elango, P., & Asmathulla, S. (2017). A Systematic Review on Lycopene and its Beneficial Effects". *Biomedical and Pharmacology Journal*, *10*(4), 2113-2120.
- 54. http://www.tspdev.net/paprika.asp
- 55. ANJALI, K., & HEMALI, G. AN ECO FRIENDLY APPROACH FOR BATIK ON SILK USING NATURAL DYES AND DEVELOPMENT OF A COLOR PALETTE FOR A PRODUCT LINE.

- 56. https://www.shutterstock.com/image-vector/lutein-xanthophyll-molecule-type-carotenoid-structural-1463545469
- 57. Saeed, S. M. G., Sayeed, S. A., Ashraf, S., Naz, S., Siddiqi, R., Ali, R., & Mesaik, M. A. (2013). A new method for the isolation and purification of lawsone from Lawsonia inermis and its ROS inhibitory activity. *Pak. J. Bot*, 45(4), 1431-1436.
- 58. http://www.chemspider.com/Chemical-Structure.10430995.html
- 59. Nayak, C. A., Srinivas, P., & Rastogi, N. K. (2010). Characterisation of anthocyanins from Garcinia indica Choisy. *Food chemistry*, *118*(3), 719-724.
- 60. Dobrucka, R., Kaczmarek, M., & Dlugaszewska, J. (2018). Cytotoxic and antimicrobial effect of biosynthesized silver nanoparticles using the fruit extract of Ribes nigrum. *Advances in Natural Sciences:* Nanoscience and Nanotechnology, 9(2), 025015.
- 61. Da-Costa-Rocha, I., Bonnlaender, B., Sievers, H., Pischel, I., & Heinrich, M. (2014). Hibiscus sabdariffa L.– A phytochemical and pharmacological review. *Food chemistry*, *165*, 424-443.
- 62. Gadgoli, C., & Shelke, S. (2010). Crocetin from the tubular calyx of Nyctanthes arbor-tristis. *Natural product research*, 24(17), 1610-1615.
- 63. Kumar, S. S., Manoj, P., Shetty, N. P., Prakash, M., & Giridhar, P. (2015). Characterization of major betalain pigments-gomphrenin, betanin and isobetanin from Basella rubra L. fruit and evaluation of efficacy as a natural colourant in product (ice cream) development. *Journal of food science and technology*, 52(8), 4994-5002.
- 64. https://pubchem.ncbi.nlm.nih.gov/compound/Gomphrenin-I
- 65. Sutradhar, B., Deb, D., MAJUMDAR, K., & Datta, B. K. (2015). Traditional dye yielding plants of Tripura, Northeast India. *Biodiversitas Journal of Biological Diversity*, *16*(2).
- 66. Das, M., & Manna, K. (2016). Chalcone scaffold in anticancer armamentarium: a molecular insight. *Journal* of toxicology, 2016.
- 67. Saoji, A. G., Saoji, A. N., & Deshmukh, V. K. (1972). Presence of Lawsone in Ammania bacciferra Linn. and Woodfordia fruticosa Salisb. *Current Science*, *41*(5), 192-192.
- 68. Zhang, L. M., Xie, W. G., Wen, T. T., & Zhao, X. (2010). Thermal behavior of five free anthraquinones from rhubarb. *Journal of thermal analysis and calorimetry*, *100*(1), 215-218.
- 69. Ding, Y. S., Kim, W. S., Park, S. J., & Kim, S. K. (2018). Apoptotic effect of physicion isolated from marine fungus Microsporum sp. in PC3 human prostate cancer cells. *Fisheries and aquatic sciences*, 21(1), 22.