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Research Article

A comprehensive study of natural and synthetic dyes: their properties, methods of preparation, and uses

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ABSTRACT

The use of natural dyes in the dying process was one of the oldest procedures used by the ancients. Obtaining dyes from natural sources means extracting them from plants and animals. Colors are derived from natural sources. Dyes can be divided into two categories: natural dyes and synthetic dyes. Synthetic dyes include saffron dyes and azo dyes, the latter being one of several types of organic compounds that are produced in large quantities through industrial processes. Dyeing is a process that involves the use of dyes in the dyeing process of textiles and food products. Fabrics are colored with different dyes for different types of fibers, while wool and silk are directly dyed with acidic and synthetic dyes. The food additives we are exposed to on a daily basis cause our bodies to produce toxins.

On the other hand, consumers have become more concerned about their food as a result of their understanding of the risks posed by these additives and the toxicity they contain. Dyes, natural dyes, azo dyes, and toxic dyes are just a few of the key terms.

1. INTRODUCTION

Dye is a chemical substance capable of binding to other substances, and the intense coloring of different materials is related to their chemical composition. The first coloring materials were of plant origin (foh, indigo...) and animal origin such as cochineal. Currently, dye has been developed in particular dyes that have an acidic and basic character, and dyes have been used in clothing and food. Dyes are divided into natural dyes and synthetic dyes that are classified into several types, including: saffron, carmine and azo... etc.

The latter constitute one of the largest classes of organic compounds prepared industrially, azo dyes are considered to have a wider range of use because they are easy to prepare. According to statistical data, we find that one million tons of these dyes are produced annually around the world. Where azo dyes are classified from a scientific point of view into: basic dyes, acidic dyes and direct dyes.

Since its inception, man has been fascinated by the beauty of nature and has tried to imitate it, as the color of animal skins and the materials from which clothing is made with natural dyes. Dyeing is used to decorate clothing and fabrics, where organic dyes are obtained from natural sources. Different categories of dyes are used for different types of fibers according to different stages of the textile production process, starting from loose fibers through spinning and fabric to finished garments where wool and silk are dyed with acid dyes and polyester threads are dyed with disperse dyes. Cotton is dyed with a variety of dyes, including vat dyes, synthetic dyes, direct dyes. In fact, the profound modification of the nature and composition of food and our eating habits has disrupted our metabolism, in addition to the food additives to which we are exposed almost daily, generating toxins in our bodies that are difficult to eliminate if the acceptable daily dose is not respected. On the other hand, today's consumer has become more knowledgeable and interested in his food, aware of the risks resulting from these additives, whether industrial or natural. Coloring food with natural dyes has been practiced since ancient times in the era of the Roman Empire, the Pharaohs of Egypt and the Middle Ages in order to treat the monotony of their diet by using everything natural such as turmeric.

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2. HISTORICAL OVERVIEW OF DYES:

Dyes have been applied in almost all areas of our daily life for dyeing clothes, food, cosmetics as well as paper printing etc. Textile dyes have been produced for more than 4000 years, the colors used were of natural plant, animal and mineral sources[1]. Synthetic dyes were discovered by Perkins which are aromatic compounds that provide a wide range of bright colors in 1856 when Perkin William discovered purple which is the first synthetic organic dye[2]. While trying to find a way to synthesize chitin which is a drug used to treat malaria. So Perkin Henry in his attempt to manufacture chitin produced a new material to generate the dye[3].

In 1871 Woufle prepared picric acid by treating the natural dye indigo with nitric acid, which led to the formation of the synthetic organic dye. Since then a large number of new chemical dyes have been introduced to the list of dyes. Synthetic dyes almost completely replaced natural dyes at the beginning of the twentieth century[4].

2.1 The concept of dyes:

It is a substance that changes the color of the medium in which it enters and is soluble in it. The dye can be of natural origin (animal, vegetable or mineral, in which case it is necessary to use separation methods (solvent extraction, distillation) It can also be produced by chemical synthesis[5], the dye is present in food, especially in drinks and sweets, and it is also used in dyeing clothes and is the main component of inks. For a substance to be a dye, some conditions must be met[6]:

- It must have a specific and stable color
- It must be able to dye the fabric directly or indirectly.
- When fixed on the fabric, it must not be quickly faded, meaning that it must be colorfast to light and must be resistant to the effect of water, and to some extent this gives it a better characteristic for dilute acids and alkalis (especially the latter due to the alkaline nature of washing soda). Many natural dyes have been known since ancient times, and they were obtained from animal and plant sources, while today's dyes are synthetic dyes prepared from aromatic organic compounds, and the only and main source, which is still the case today, is tar (Coal Tar) Coal Tar[7].

2.1.1 Colour:

Dyeing is a chemical compound that can absorb a specific wavelength of light within the visible range and reflect the rest, and the dye is a substance that has an affinity for a type of product, whether it is a plant, fabric, leather, or synthetic threads, and we need to apply dyes to the fabric in a liquid medium that may be water or liquefied air to be able to dissolve or spread, and then migrate towards the fabric and spread to the amorphous areas in the fibers (Amorphous area). When white light (7500-40000) falls on a material, the light is either completely reflected or completely absorbed. In the first case, the material appears white, and in the second case it appears black. If a specific percentage of the light is absorbed and the rest is reflected, the material has the colour of the reflected light. If only one (single) beam is absorbed, the material has the complementary colour of the colour of the absorbed beam. If a substance absorbs all visible light except one band which it reflects, the substance will have the color of that reflected band. Thus, a substance appears blue because it absorbs only the yellow part of the spectrum or because it absorbs all of the visible spectrum except blue[8]. The shades will also be distinctly different and there is no color pigment that reflects only one band of wavelengths. For example, malachite green reflects a light green color and also reflects to some extent red, blue, and violet. Many substances that appear colorless do have absorption spectra, but in these cases the absorption occurs in the sub-red or ultraviolet region rather than in the visible spectrum.

2.1.2 Causes of color and constitution: Relation Between Color & Constitution

Graebe and Lieberman noted in (1868) that organic coloring matter can be reduced to colorless compounds by reduction with hydrogen, for example, and that when the hydrogen atoms (added by reduction) are removed by oxidation, the original color returns again. Witt in (1876) was the first to note that color usually appears in an organic compound when that compound contains specific unsaturated groups. It is important to note that the carbonyl group is referred to as the unsaturated group and its presence in a compound does not give impetus to the desaturation process. As we will note later, a more appropriate term than the unsaturated group is the group with multiple bonds. Witt called these groups with multiple bonds chromophores. One of the most important and famous color-bearing pigment groups is Chromophore Groups. The structures of dyes are complex structures, and may be the most complex chemical compounds, but they share common features, as we mention from their components:

1. Aromatic rings: We may find in them monomeric benzene rings, or dinaphthalene, or trimeric anthracene[9].

2. Conjugation or conjugated double bonds: The specificity of these systems lies in increasing absorption and thus increasing radiation, especially light radiation. This is what makes compounds that carry this type of bonds colored as a result of the presence of conjugation or electronic resonance, especially if the number of bonds exceeds 7 double bonds,

which means that they contain hydrocarbon chains with a sequential system of single and double bonds, i.e. (=C-C=C-C=C-)[10], and we often need about five or six conjugated carbon atoms. This is so that they can absorb certain wavelengths to reflect the rest, as the bonding of electrons in their basic positions is weak, which enables them to travel and roam the entire area of the molecule once they take the energy they need to jump from one energy level to another of the light wave falling on the molecule, so that the electronic cloud covers the entire dye molecule as a result of absorbing selected wavelengths from the entire beam. For example: CN-N=N:

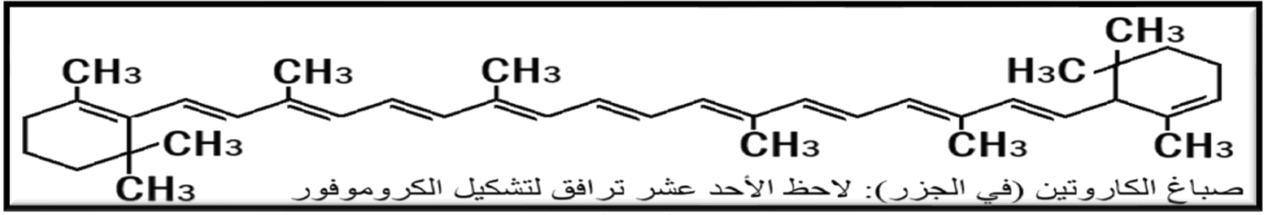


Fig 1: Chromophore structure

Thus, each pigment molecule contains two basic components, in addition to other supporting components, which are as follows:-

The pigment molecule can be represented as follows[11]:-

Pigment molecule = chromogen + oxochrome

Examples of color-giving groups (chromophores)

Nitroso group No (or = N – oH)

Nitro group (N)o_2 (or=No .oH)

Azo group N = N

Cthylene group C =C

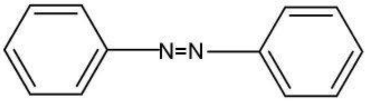
Carbonyl group C = O

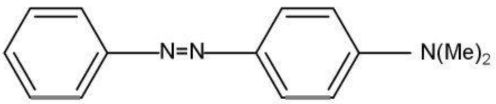
Thiocarbonyl group C =S

Carbon – nitrogen group C=NHand – CH = N

These groups are very important as dyes are classified according to their chemical composition based on the type of color donor group they contain. Examples of color deepening groups (oxochrome) NH2, -NHR, -NR2, -OH, -SO3H, -COOH

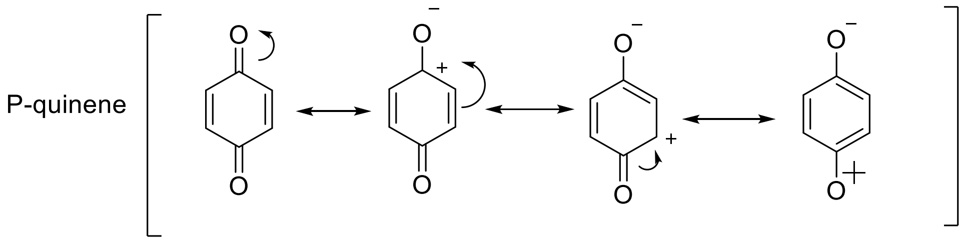
Some of these groups give positively charged ions like basic groups such as (C=+NMe,CI) and others give negatively charged ions and acidic groups such as (O-, -SO-3)[12]. In the case of the aromatic structure containing a chromophore, i.e. a color donor group only, a colored substance is produced but it is not useful and (compound I) is not used as a dye. When the same compound contains an oxochrome, i.e. a deepening group, the resulting compound is used as a dye (compound II). These groups, in addition to increasing the intensity of the color, improve the affinity and bonding between the dye molecules and the materials for which they are used:-

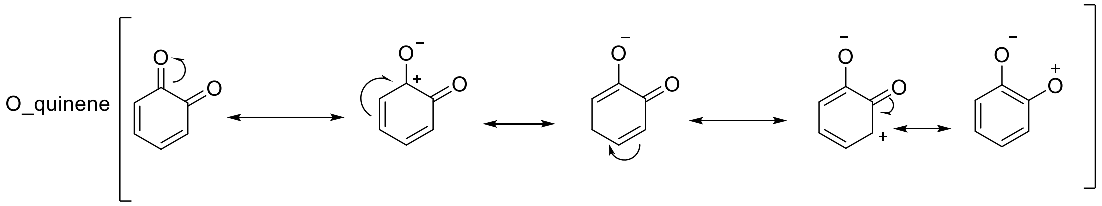




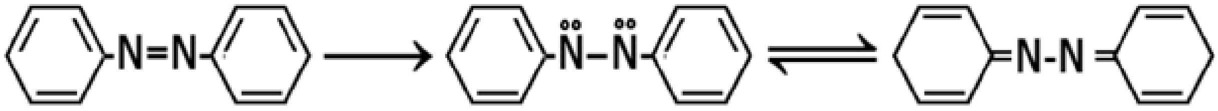
The most important factors that increase the intensity of color in dye molecules are:-

1. Increasing the number of color-donating groups, for example
   CH2 = CH2 CH3, (CH = CH) – CH3
   Yellow color, colorless
2. Increasing the number of color-deepening groups.
3. Increasing the molecular weight by increasing the deepening groups and aromatic rings.
4. Increasing the amount of unsaturation available in the aromatic rings and donor groups by a certain amount increases the resonance, which is an important factor in increasing the intensity of the color[13].
5. The presence of a donor group within the quinoniod structure.

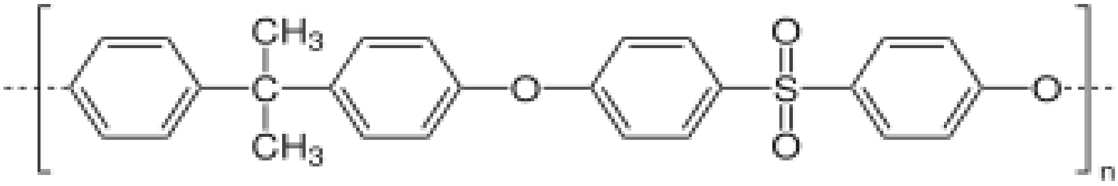




A. Chromophores: or color carrier, its task is to absorb the light beam. The most important chromophores are: nitro, nitrous, azo, carbonyl. Its task is to absorb light such as the groups (–N=O, -N=N-). For example, the chromophore (–N=N-) absorbs ultraviolet light around (3400) angstroms, while the orange azo benzene in open compounds absorbs around (3190-44501) angstroms because the association of the aromatic group (π) with the nitrogen electrons forms an extended chromophore group capable of light excitation at lower energies (i.e. at longer waves) through resonant excitation of the light-excited molecule[14]:



B. Auxochromes: or color assistant, its function is to displace the absorbed light cloud up to wavelengths that lead to increasing the depth of the color. It often plays a role in making the pigment molecules dissolve in water on the one hand and fixing the pigments on the fibers through a chemical reaction with them. Its function is to displace the absorbed band to increase the degree of color depth[15]. We mention the amino, hydroxyl, carboxyl, and sulfone groups among the auxochromes... These groups, due to their affinity for water, enhance the settlement rates (the regular distribution of pigment molecules over the entire dyed area), and improve the stability of the dyes due to the bonds they form according to the type of fabric between hydrogen, polar, ionic, or covalent bonds. The size of the dye molecule also plays an important role in the dyeing process. Small molecules can easily penetrate and spread in the fibers, and therefore it is easy for them to exit in the opposite direction, which increases the settlement rates. On the contrary, the larger the molecule, the more difficult it is to penetrate and the longer it takes, and thus its exit becomes more difficult, which leads to a decline in settlement and an increase in its stability in washing. The most important oxochromes are: amino groups, oxyhydroxyl, and sulfone. The following is the structure of the sulfone[16].



C. Batho-Chromic Groups: Or color enhancers, whose task is to change the color towards the longer wavelength, i.e. from red to violet.

D. Hypso-Chromic Groups: Their task is to change the color and shift the absorption towards the shorter wavelength, i.e. from red to violet.

E. Chromogens**:** These are the aromatic groups to which the chromophores are attached. Dr. Zou Linfer collects the relationship of all these components together in the form: Research for a hundred years has depended on what was established by White in 1876, which we can summarize as follows: In order for a chemical compound to have the ability to color, it must contain basic groups, which are chromophores, whose association is based on the principle of conjugation of double bonds. When the chromophore is able to give color to the compound, we call it oxochrome. Recently, the naming of oxochrome has been adopted as an electron donor, such as the groups $(NH)_2^-$-,OH^-,O^-, and the naming of anti-oxochrome as groups and groups that take electrons. Based on the above, linear chromophores with conjugated ring systems form what we call chromogens. We find in industrial research on dyes that most of the basic building blocks of color compounds are artificial, and they differ from each other in the barriers or functions of their exchanges and some other secondary details[17]. It is important to note that the human eye senses light waves in the range of wavelengths 4000 - 8000 angstroms or 10^{-8} cm, and the color that the eye sees depends or is related to the light source first, whether it is sunlight or a normal or colored lamp, and then the ray reflected from the colored material that the eye perceives. So if a white color falls on an object and appears to us to be orange, the reason is that it reflected the orange and absorbed the rest. We see in Figure 3 the apparent change in color with the change in the light source, or what is called metamerism. Making the color deep (in color chemistry) means changing the color according to the following:
Yellow → Orange - Red - Purple → Violet → Blue → Green → Black
Since visible color is complementary to the absorbed band, the pseudochromic groups shift the maximum absorption from violet to red [18] (i.e. they lower the frequency of the absorbed light)[19] and conversely, the hypsochromic groups shift the maximum absorption from red to violet (i.e. they raise the frequency of the absorbed light). In order for a substance to act as a pigment, it must be able to fix itself or have the ability to attach to the tissue. There are no chromogens that act as pigments because the presence of a salt-forming group is necessary. Auxochromes and similar groups, regardless of their properties as auxochromes (in order to make the color deep, their presence is necessary to make the chromogen a pigment. Thus, auxochromes do two things. The sulphonic acid groups and the carboxyl-group have very little or no auxochromic properties, but their presence makes the chromogen a pigment. In addition, the sulphonic acid group makes the pigment soluble in water, and the carboxyl-group usually helps the pigment to form fixed pigments.

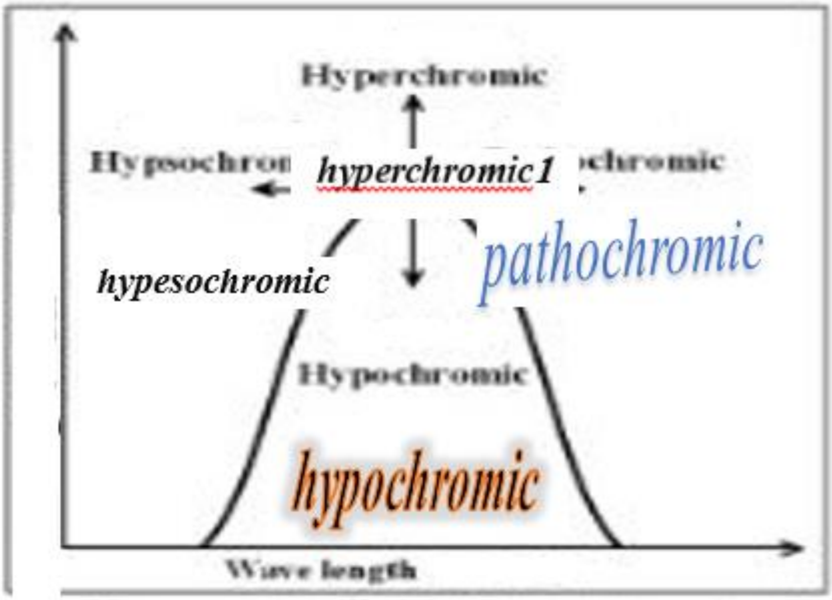


Fig 2: Wavelength and absorption coefficient change with absorption band change.

2.2 Theories of Pigments

1- Theory of the origin of color: There are many theories of pigment construction and the scientific situation has not settled in explaining the phenomenon of color and linking it to the chemical structure due to the abnormal cases of each theory. However, there are broad lines and some observed phenomena that can be summarized as: -

- The molecule should be relatively large in size and contain pi electrons.
- There must be compatibility of the double bond system in the molecule so that the electron cloud can resonate and move over the entire molecule with the least light energy it can reach. The example of Carbocyanine explains these observations. If the increase in the value of N leads to the transmission of the absorbed color according to Table (I).

TABLE I. INCREASE IN THE N VALUE OF THE ABSORBED COLOR TRANSMISSION

n value	zero	1	2	3
Reflected color	yellow	red	blue	green

2- Dyeing theory: Dye: A compound capable of bonding in some way with the fibers to be dyed, giving them color. The chemical compound acquires color when it has the ability to absorb a certain band of visible light and reflect the rest. Dr. Heinrich Zulfiers states in his book The Chemistry of Color: The appearance of color depends on a group of physical, chemical, physiological and psychological factors, and the part of the light that a person sees is in a range of wavelengths between 700 - 400 nanometers. Gases, liquids and solids can absorb all the light or reflect part of it to pass through gases, liquids or glassy solids. The light emitted by a light source or reflected from a reflective surface begins to interact chemically and photochemically after reaching the retina of the eye, which leads to the transmission of information from it to the brain to reach what is called visual perception[20].

2.3 Nomenclature of Dyes:

There is no systematic nomenclature for dyes. Many dyes have names given to them by manufacturers, so it is common to find a dye with multiple names. Usually, each dye has a name or trade name. The color gradation is indicated by letters, for example: Y or G = yellow, 0 = orange, R = red, B = blue. Sometimes the letter is repeated, and the number of letters indicates the intensity and strength of the color. For example, methyl violet 6B is a very dark purple color (close to blue. Sometimes the letters have other meanings, such as alizarin blue D, where D here means that this dye colors cotton directly, fuchsine S, where S indicates that the dye is acidic. The letter F is sometimes used to indicate that the dye is fast in light. To avoid the difficulty of choosing a regular and unified nomenclature, the Society of Dyers and colorists has proposed a color guide in which each dye is identified and its color number .

2.4 Classification of Dyes:

Dyes are classified according to their composition and chemical structure, or according to their use on fabric. The first classification has theoretical value for the chemist but is less important for the dyer who is primarily concerned with the interaction of the dye with the fabric or fiber to be dyed.

2.4.1 Chemical Classification:

The composition and chemical structure of dyes is so diverse that it is difficult to classify them into distinct groups. Dyes are classified according to the type of chromophore group they contain into:-

2.4.1.1 Nitro Dyes.

These dyes contain a nitro group as a chromophore and a hydroxyl group usually an oxychrome.

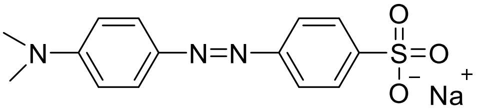
2.4.1.2 Nitrous Dyes.

In these dyes, the chromophore has a nitroso group and the auxochrome has a hydroxyl group[21].

2.4.1.3 Azo dyes

Azo dyes are the largest group of synthetically prepared organic dyes[22]. They have the ability to add distinctive colors to fibers. The prepared colored compounds are characterized by their ability to bind to the material to be dyed, giving it bright colors. Some of them are not affected by washing, oxygen, acids, or bases. The azo group consists of two adjacent nitrogen atoms linked by a double bond (-N = N-). Its hybridization is (Sp2). It is linked to aliphatic or aromatic carbon atoms. These dyes can be monoazo such as (Monoaz0) or diazo such as (Diazo) and can also contain more than two azo groups as in triazo dyes such as (Triazo).

Azo compounds have strong and clear colors such as yellow, red and orange. Therefore, they are used as dyes. The most common of them is (DIAZO), an example of which is the compound methyl orange, which is used as an indicator in acid-base reactions:-



The colors of azo dyes are affected by their chemical composition, number, and the nature of the substituent groups. For example, the simplest azo dyes are yellow. The depth of the color increases with the increase in the number of chromophore groups (color carriers) or with the increase in the molecular weight of the dye, turning red, then violet, then green. The presence of electron-repellent substituents on the benzene rings carrying the chromophore group leads to an increase in the intensity of the color carried by the chromophore group. These auxiliary groups are called exochromes, meaning color sterilizers, and are arranged according to the intensity of their effect as follows[23]: -
- OR < OH < NH2 < NHR < NR2

2.4.1.4 Anthraquinone dyes (Indanthrene dyes) INDANTHRENE

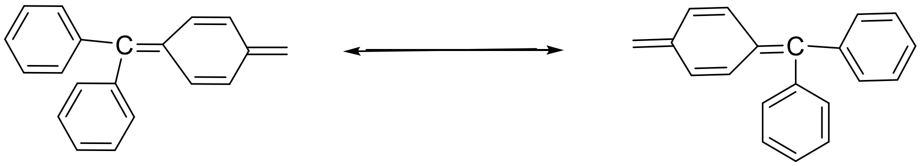
They are important dyes discovered in 1905. The simplest example of these dyes is INDANTHRONE dye

2.4.1.5 Indigo dyes

The best representation of this type of dyes is indigo dye. It is found in several species of a plant family called Indicovary and is grown in India, Java, China and Central Africa. The dye is not found in plants in a free form, but rather in the form of indoxyl combined with glucose in a glycoside bond called indican. To obtain the dye, the plant is picked early and immersed in water at 50°C for several days until it ferments and the enzymes are released and the indican is decomposed into indoxyl and glucose, then air is passed through. In the presence of alkalis, the indoxyl is oxidized and the dye separates in the form of blue flakes that are filtered and then boiled with water for several minutes to prevent further fermentation, then filtered and dried. Since indigo dye is insoluble in water and does not have the ability to bind to textiles, it is transformed into what is called water-soluble white indigo, which has a high affinity for textiles. This is achieved by carefully reducing indigo in an alkaline medium. The two carbonic groups are reduced to two phenolic hydroxide groups that can form soluble sodium salts in the presence of sodium hydroxide. Before dyeing is done, the textiles are dipped in the hot alkaline solution of white indigo, then removed from the dyeing bath and exposed to the effect of air. The white indigo is oxidized very easily by the oxygen in the air and is transformed again into the blue dye that is insoluble in water. This dye is mainly used in dyeing cotton textiles and textiles made of industrial iron. It is characterized by high stability to light and washing. This method cannot be used in dyeing textiles sensitive to alkalis such as wool and silk[24].

2.4.1.6 Triphenylmethane dyes

Triphenylmethane dyes are among the oldest types of dyes and have bright colors in the red, violet, blue, and green range. The color-bearing system consists of a central carbon atom linked to three aromatic rings to give a number of stable resinous structures in which the chromophore includes the quinoid system and the reciprocal bonds.



The color gradation and its properties depend on the number and nature of the color deepening groups NR2, OH – where R is hydrogen, acetyl, phenyl, or both in the three para positions. In the absence of any acidic group in the molecule. Then the di- and tri-aminotriphenylmethane dyes are called cationic dyes. The presence of acidic sulfonic groups makes them soluble in water, and then the dyes are negatively ionic (ANIONIC) in the presence of hydroxyl groups as color deepening groups adjacent to the carboxyl groups and give the properties of fixed dyes[25].

2.4.2 Classification of dyes according to application: Classification According to Application

1. Acid Dyes: They are sodium salts of sulfonic acids and nitrophenols. These dyes directly dye animal tissues and fabrics but not plant ones, so they are widely used on silk and wool[26].

2. Basic Dyes: These are salts of bases (colored bases with hydrochloric acid or zinc chloride. These dyes are used directly on animal tissues as well as plant tissues that have been fixed by tannic acid. They are often used on cotton and silk[27].
3. Substantive dyes - Direct Dyes: Direct dyes that do not require a fixative and directly dye animal and plant tissues (fibers).
4. Adjective dyes (Mordan dyes): They do not directly dye plant and animal fibers, but they require a fixative. If the dye is acidic, the fixative must be basic, and if the dye is basic, the fixative must be acidic. For acid dyes, the fixatives are metallic hydroxides, and for basic dyes, the fixatives usually used are tannic acid and tannic acid: a mixture of organic tanning substances found in oak leaves, tea, etc. It is a light yellow amorphous powder that dissolves in water and glycerin. It is used in tanning leather, as a color fixative during dyeing, and as an antiseptic in medicine. For metallic fixation, the fabric is dipped and immersed in a solution of metallic salt and the (fiber) filled (applied) is then immersed in a solution of the dye, this gives and results in an insoluble colored fixative dye which is fixed when washed. For the second fixation, the fabric is immersed in a bath of tannin, but since fixative dyes are dark and tend to be unstable dyes, this results in a more insoluble and shiny fixative dye. The color of the fixative dye depends on the metal used and the most common metals used are chromium, aluminum, iron and tin. Dye fixatives are believed to be internally complex compounds (chelate compounds) formed between the substrate and the dye. Most of the fixed dyes owe their specific properties to the presence of a hydroxyl group[28].
5. Vat Dyes: These dyes are insoluble in water, but are reduced by the alkali sodium hyposulfite (dithionate) to alkali-soluble compounds which are easily re-oxidized to dye. These reduced compounds are sometimes white or colorless and are therefore called leuco compounds. They directly stain both animal and plant tissues. Vat dyes are often used on cotton fabrics.
6. Ingrain or Developed dyes: Their color appears in the fabric and they are divided into three groups:
    - Ice-color: Usually used on cotton fabrics by immersing the fabric in the secondary component (phenol) or (amine for azo dyes) and the dye is developed by immersion in a diazonium salt solution. The name ice-clours was given because the dialysis and coupling are done at low temperatures.
    - Direct cotton dye containing a free amino group is used on the fabric and is subjected to a dialysis process by immersing it in a nitrous acid solution, followed by immersing it in a solution of a secondary component phenol or amine, and then the azo dye is produced and presented.
    - Aniline Black: It is produced by oxidation of hydrochloroaniline, either by oxidation of fabric impregnated with amine salt, or by heating the fabric with a solution of hydrochloroaniline containing an agent (oxidation of potassium chlorate and vanadium salts as a mediator)[29].
7. Sulphur Dyes: These are dyes containing sulfur and are soluble in aqueous sodium sulfate, and are used comprehensively and widely for plant tissues, and the dye is generated in the fabric by oxidation in the air or by oxidation with dilute aqueous potassium dichromate.
8. Rayon Dyes: Rayon Viscose rayon and ammoniacal copper oxide silk can be dyed in the usual way, while acetate rayon requires special dyes and techniques as well.
9. Organic Dyes: These dyes are not dyes in that they dye tissues, but rather solid materials that are usually insoluble in water and are used to color paint and varnish. Some dyes have been prepared to be soluble in water and then used as dyes, such as Phthalo cyanine dyes[30].

2.5 Physical and chemical properties that affect color:

a) Effect of pH:
Some dyes are composed of chemical compounds that are sensitive to acidity and their acidic form has a color that differs from their basic form, such as anthocyanin, which is pink-red in color, but in the basic medium it has a yellow-green color and in the neutral solution it has a purple color, as a result of the change in its colors with the change in the medium in which it is placed, so anthocyanin is used as a colored indicator of acidity[31].

b) Effect of solvent:
The color of the dye can depend on the solvent in which it is dissolved. For example, iodine is brown in color, so if it is placed in an aqueous solution, it becomes yellow-orange, but if the solvent changes, its color changes. When cyclohexane is used, it gives a purple color [27].

c) Effect of temperature:

d) Materials whose color depends on temperature are called thermochromates, such as liquid crystals or inks used to combat counterfeiting of banknotes. When the temperature of the ink used increases, the color changes[27].

e) Effect of concentration:

The concentration of the dye dissolved in a solvent does not affect the color of the solution, but it affects the dye itself, i.e. the higher its concentration, the darker the color of the dye. In general, a specific value must be chosen for the solution and the dye. Therefore, it is generally agreed that the concentration of dyes should be weak in solutions so that we can change the physicochemical properties of the solutions. X) Chemical composition

Dyes resulting from chemical composition absorb a color of white light and the rest of the colors are reflected. For example, when the red color is absorbed, according to the color wheel, the color of the dye solution appears green[27].

3. METHODS OF PREPARING DYES

1. Nitro Dyes ;

   The simplest nitro dye is picric acid, which was first prepared by Wolf (1771 AD) who noticed its ability and power to dye silk bright yellow, but the color is not fixed. Other nitro dyes include Mortius yellow and Manchester yellow, which is 4:2 dinitro-I-naphthol, and was prepared by nitro-I-naphthol-4:2 disulfonic acid (picric acid). It was used as a sodium, calcium, or ammonium salt, but it is not fixed and rises easily from the fabric. Therefore, it was replaced by naphthol yellow. It is 4:2 dinitro-I-naphthol-7-sulfonic acid (potassium or sodium salt II). This compound is the most important nitro dye and is now prepared by nitration of naphthol-7:4:2 trisulfonic acid or 4-nitro-I-naphthol-7:2 disulfonic acid. This dye has been widely used as an acid dye for wool and silk.

   (III) GG Lithol fast yellow: It is a dye used as a non-toxic substance for chrome yellow (lead chromate). It is prepared by condensation of -P-ch loro-O-nitroauilire with formaldehyde[32].
2. Nitroso dyes:

   Nitroso dyes are prepared by the action of nitrous acid on phenols and naphthols. Only para-nitroso compounds are useful and beneficial and are often used in the form of iron green fixed dyes in dyeing and printing such as fost green O which is prepared by the action of nitrous acid on resorcinol and the oxime formula is what gives and destroys fixed dyes. [28] (The oxime dye is fixed and stabilized by a hydrogen bond between the molecules). There are also other dyes such as Gambine R (2-Nitrous-1-Naphthol (I) and Gambiney (1-Nitrous-2-Naphthol (II).

   There are also other dyes such as Gambine R (2-Nitrous-1-Naphthol (I) and Gambiney 1-Nitrous-2-Naphthol (II).
3. Preparation of azo dyes :

   Azo dyes can be prepared in several ways. The most important of these methods is the method of coupling between the diazonium salt. Either with an aromatic amine, phenol or naphthol. In the second example, a diazonium salt can be made from the azo dye and then another coupling can be made with phenol or another amine. Thus, an azo dye containing two or more azo groups can be obtained. Thus, different colors and molecules with high molecular weights can be obtained.
4. Anthraquinone basin dyes (andanthrene dyes) Indanthrene :

   The simplest example of these dyes is INDANTHRONE dye which is prepared by melting 2-aminoanthraquinone with potassium hydroxide and potassium nitrate at a temperature of (200-150 C). However, if the melting occurs at a higher temperature, another dye is formed, which is FLAVANTHRONE. These dyes are very similar to indigo dyes, as they do not dissolve in water, but are reduced by sodium hydrosulfite in an alkaline solution to soluble hydroquinone salts. To dye textiles with these dyes, they are dipped in the solution of these dyes in their reduced form, then exposed to air, so the dye oxidizes and precipitates inside the tissues. These dyes are characterized by high stability to light and washing[33].

   Since wool and silk are proteins and are connected by concentrated alkaline solutions, these dyes are mainly used in dyeing cotton and other cellulosic fibers. BENZANTHRONE is also a member of this series. These dyes are derived from benzanthrone, which is prepared by heating ANTHRONE with glycerol at 120°C and in the presence of sulfuric acid, then acrolein, which is formed as an intermediate compound that condenses with the methylene group in the Anthrone molecule. The resulting compound decomposes at position 1, forming a new benzene ring[29].

   - Flavanthrone: Benzanthrone itself is not considered a vat dye, but when it is melted with alkalis, it undergoes a binary union accompanied by dehydration and dimerization, forming violanthrone, which gives an important series of vat dyes that are used especially in dyeing cotton fabrics.
   - anthrone benzanthrone: The number and types of anthrine dyes increased with the discovery of an economical method for the yellowing of phthalic anhydride and ortho-xylene, which are used as raw materials for the yellowing of anthraquinone.
5. Preparation of indigo dyes:

A number of chemists participated in the study of indigo dye, and Bayer's research played a prominent role in determining the structure and synthesis of this dye. Karl Hyman developed two methods for preparing indigo, the first in 1890 and the second in 1893.

a) From the cyclization of phenylclassine to indoxyl :

Phenylclassine, which is prepared from the condensation of aniline with chloroacetic acid, can be cyclized by fusing with bases to form indoxyl, which forms indigo when oxidized by air under basic conditions. The disadvantages of this method are that the cyclization takes place at a high temperature of 300°C, which reduces the yield. Sodium amide was used as a cyclization agent to make the cyclization take place at a lower temperature of 180-200°C, thus increasing the yield. This method is also expensive and difficult to solve because it relies on aniline, which is prepared from benzene. indigo, indoxyl [29].

b) From the oxidation of naphthalene:-

Naphthalene is oxidized in the presence of mercury to phthalic anhydride, which is converted to phthalimide by passing ammonia over its molten state. Phthalimide is converted to anthranilic acid by the Hofmann reaction. When anthranilic acid is treated with chloroacetic acid, it turns into PHENYI GIYCINE 6-0- CARBOXYLICACID. When this acid is melted with an alkaline substance, water separates and the ring is closed, forming indoxylic acid. This acid is a B-Ketoacid that loses carbon dioxide, forming indoxyl. When air is passed through this solution, indoxyl is oxidized to indigo, which precipitates as a blue precipitate. From an economic point of view, the second method is more important because naphthalene has a much smaller ring than aniline. Various modifications have been introduced to this method, where naphthalene is oxidized to phthalic anhydride by atmospheric oxygen in the presence of vanadium pentoxide V_2O_5 as a catalyst. The color of indigo dye is not greatly affected by the presence of substituents. More stable dyes to light and friction have been prepared by brominating or chlorinating indigo dye. In this case, the halogens take positions 5-, 7-, 5. However, replacing the benzene ring with a naphthalene or anthracene ring results in brown, green, and gray dyes. Different colored dyes have also been prepared by making various modifications to the composition of indigo dye. For example, THIOINDIGO was prepared, which contains sulfur instead of nitrogen and is red in color and is used to dye cotton textiles. This dye is prepared by melting 2-CARBOXY PHENYL THIOGLYCOLIC ACID with potassium hydroxide. Several THIOINDIGO substituents have also been prepared, and they have colors ranging from orange to red. 30 In the period 1909-1911, Friedlander studied the animal pigment known as Tyrian red and determined its composition. He proved that it is a di-bromo-indeco compound in which the two halogens are located in the 6- - 6 position.

6. Triphenylmethane Dyes :

One of the most important positive anionic (basic) dyes among the Diaminotriphenylmethane dyes is Malachite Green, which is prepared by the condensation reaction of one mole of benzaldehyde with two moles of dimethylaniline (N-N-Dimethylaniline) in a hydrochloric acid solution at 100°C for 8 to 10 hours. At the end of the reaction, the soluble base (Leuco Base) is formed, and the white granules are filtered and washed, and dissolved in dilute hydrochloric acid and the temperature is lowered to zero degrees Celsius by adding ice. With continuous mechanical stirring, the theoretical amount of lead dioxide (newly yellowed by hypochlorite on the lead nitrate solution) is added as quickly as possible. Sodium sulfate solution is added to precipitate the lead sulfate, which is removed by filtration. The dark green precipitate containing the dye hydrochloride, is treated with sodium - to precipitate the carbinol base to the dye by adding acid and separates as a di-salt. Malachite green is used for dyeing cotton with an acidic fixative, and the lightfastness and other factors are poor when used for cotton. However, all these specifications improve and become good when used for light and other factors are poor when used for cotton. However, all these specifications improve and become good when used for acrylonitrile and are used for leather and paper. Another important example of this type is crystal violet, which is an example of a triaminotriphenylmethane dye and has a special manufacturing method to give the following chemical composition in an acidic medium (see its weighting forms under basic dyes)[31].

7. Xanthen Dyes :

The main heterocyclic system characteristic of this class is xanthine (XAN - THEN), the nature of each dye depends on the nature of the color deepening groups and other substituent groups present in the molecule. The chromophore includes stable resonant structures. The compounds of this group have bright, radiant colors, ranging from red to greenish yellow. The most important examples of this type are fluorescein and eosin, which is a tetrabromine derivative of the former.

Fluorescein is prepared by heating anhydrous phthalic acid with resorcinol in a ratio of 1/2 mole in an iron vessel where the temperature is regulated at about 220 °C for about seven hours in the presence of anhydrous zinc chloride. The molten metal is then dissolved in sodium hydroxide and the product is precipitated by acidification, forming a yellow powder that is luminous (luminous) with a greenish-yellow color in a basic medium. Another example of xanthine dyes is Rhodamine B, which is prepared by the reaction of anhydrous phthalic acid with 3-diethylaminophenol to produce the compound, RHODAMINE B C.I BASIC VILET 10[36].

8. Phthaleins Dyes:

   This class of dyes is derived from ortho-carboxylic acid compounds of tri-phenyl-methanol and therefore they are similar in composition to tri-phenyl-methane dyes. These dyes are prepared by the condensation of phthalic anhydride with phenolic compounds and most of these dyes are used as indicators. 1. Phenolphthalein: It is one of the simplest and most important members of this series and is prepared by heating phthalic anhydride (1 mol) with phenol (2 mol) in the presence of sulfuric acid. The anhydride ring turns into a cyclic lactone, and under the influence of alkalis, the lactone ring opens to form a carbinol, which loses a water molecule, forming a pink quinoide anion. Adding acid reverses the reaction and the color disappears, and this is the basis for its use as an indicator. The most important use of phenolphthalein is as an indicator, and since it is effective in softening the intestines, it is used in medicine as a laxative. Tetra-iodo-phenolphthalein, which is prepared by iodination of phenolphthalein in a basic medium, is used to stain the gallbladder when photographed with X-rays because the heavy iodine atoms accumulate in the gallbladder and block the rays. [32].

9. Sulfophthaleins :

   They are modified phthaleins in which the carboxylic acid group is replaced by a sulfonic acid group. The simplest dyes in this series are prepared by condensing phenols with O-SULFOBENZOIC ANHYDRIDE. Most sulfophthaleins are used as indicators. For example, the indicator BROMO PHENOL BLUE is tetra-bromo-sulfophthalein.

   A. Fluorescein: sometimes called resorcinolphthalein. The reaction involves condensation to form phthalene followed by the elimination of a second water molecule from the two hydroxyl groups at the ortho position to form a new heterogeneous ring called Benzopyran Xanthene. Fluorescein is an orange powder that dissolves in alkaline solutions to form a yellow solution and a green fluorescence that is clearly visible even when the solution contains one part of fluorescein per 40 million parts of water. Therefore, it is used to study and monitor waterways, groundwater, and to identify sources of water pollution. Fluorescein was also used during World War II to dye clothes and pilots' belts as a sign to identify pilots lost at sea. This dye helped save the lives of many pilots. [33]
   B. Mercurochrome: When di-bromo-fluorescein is treated with mercury acetate then with sodium hydroxide solution, the appearance known as mercurochrome is formed, which is the sodium salt HYDROXY MERCURI DIBROMO FLUORESCEIN [37].
   C. EOSI: It is the sodium salt of tetra-bromo-fluorescein and is prepared by fermenting fluorescein in the presence of glacial acetic acid and is used to dye wool a bright red color and is also used in the manufacture of red ink.

10. Other types of dyes:

    - Sulfur-dyes: Sulfur dyes rank second after azo dyes in terms of the amount produced annually, if they constitute about 20% of the total amount of industrial dyes produced. The reason for the spread of these dyes is their low price and their very high stability. They are very similar to indigo dyes in their price, stability, quantity produced, and method of use. The first sulfur dyes that were prepared were by heating sawdust or bran with sulfur. These dyes were yellow or brown in color. Then, derivatives of benzene and naphthalene were used to prepare sulfur dyes of various colors[38]. These dyes are prepared in basins by heating derivatives of phenols and aromatic amines with sulfur and sodium sulfide, where the latter works to reduce the dye resulting from the reaction, which is in an insoluble form, and converts it into a soluble dye that has a high affinity for fibers. The fibers to be dyed are immersed in this basin, and after removing the fibers from the basin and exposing them to air, the dyes reappear inside the fibers. Most sulfur dyes have an unknown chemical composition. Sulfur dyes are only used to dye cotton fibers because they are used in the presence of sodium sulfide, which attacks protein and ester fibers. One of the most important representatives of these dyes is SULFUR BLACK, which is manufactured in quantities greater than any other single dye. It is prepared by heating 2,4-di-nitro-phenol with sulfur and sodium sulfide [35].
    - Aniline black dyes:

      It is a complex dye with a dark black color and has high stability to the effect of washing, light, oxidizing and reducing agents. It is prepared directly inside the fibers, where the cotton fibers are immersed in a bath containing aniline hydrochloride, an oxidizing agent (KCIO3)[39], a catalyst (copper or vanadium salts) and an electrolyte (NACI). Then they are removed from the bath and dried, where the fibers appear in a dark greenish black color. To increase their stability to the effect of reducing agents, the fibers are immersed again in a bath containing aniline and dichromate acid, then removed from the bath and dried, so the fibers acquire a dark black color.
    - Dyes soluble in alcohols and oils

A number of colored compounds that do not contain sulfonic acid groups are soluble in organic solvents and are therefore used to color gasoline, plastics, oils, fats and waxes. Synthetic fibers are colored by adding these dyes to the solutions or melts of these fibers before spinning.

- Dyes for food and medicine

  A number of dyes are toxic substances and some of them cause cancer. Therefore, dyes used in coloring food, medicine and other household items must be safe. These dyes are approved by the Food and Drug Administration, which advises against using dyes in coloring food because a number of approved dyes have subsequently been proven to be unsafe[40].
- Reactive dyes

  We mentioned earlier that the difficulties that accompany the process of dyeing cotton fibers are due to the fact that they do not contain active groups (except for hydroxyl groups) that help to bind them to the dyes. Despite the possibility of dyeing cotton with a number of direct dyes, most of these dyes have poor stability. Also, the basin dyes that are mostly used in dyeing cotton, despite their high stability, the method of using them is complicated. In 1956, a new type of cotton dyes appeared that is characterized by high stability to the effect of washing and light, called reactive dyes. These dyes are characterized by the fact that their chromophore group contains a group that can bind to the fibers by means of a covalent bond that works to keep the dye permanently bound to the fibers. The first step in preparing these dyes begins with the reaction of cyanuric chloride (CHBVIDE) with any dye containing an amine group through which the active group is connected. Usually, dyes with a beautiful bright color are used for this purpose, but they are not used alone due to their low stability. Therefore, any type of dye can be used, but the most important types used are azo and anthraquinone dyes. After the reaction with cyanuric chloride, a dye is formed that contains a triazine ring with one or two active chlorine atoms. Such a dye has the ability to react chemically with the hydroxyl groups present in cellulose. The bond that forms between cellulose fibers and active dyes can be generally expressed as [36].
- Phthalocyanines dyes

  A number of English chemists noticed that when phthalamide was prepared from the reaction of ammonia with phthalic anhydride in copper containers, the resulting phthalamide contained a blue substance. Later, it was noticed that the same substance was produced from heating O-PHTHALONITRILE with copper salts. Thus, an important type of dye was discovered by chance, which is used in the preparation of dyes, in the manufacture of printing ink, in the manufacture of dyes used in drawing and decoration, and in the coloring of synthetic fibers[41].

Advantages of copper phthalonitrile dye:-

1- Its color is bright blue.
2- It has high thermal stability.
3- It is stable towards melting bases and hot concentrated hydrochloric acid.
4- It dissolves in concentrated sulfuric acid but can be recovered by dilution [37].
5- It does not dissolve in organic solvents.
6- Its derivatives containing sulfonic acid groups are soluble in water and can be used as dyes for fabrics and fibers.

After that, it was possible to prepare copper phthalonitrile substitutes by heating O-Phthalonitrile substitutes, with copper salts, and it was also possible to prepare a number of more complex phthalocyanines that are characterized by a number of good specifications by using other metals.

4.USES AND IMPORTANCE OF DYEING

4.1 The first type of natural dyes:

Natural dyes are considered the first dyes used by humans, as they were extracted from:

- Roots, leaves and seeds of plants.
- And from some insects as animal sources.
- As for the mineral sources, they were natural well water, and their defect was that they caused weak fibers. They are divided into plant dyes and animal dyes[42].

Vegetable dyes: There are several types, which are[43]:

A. Blue indigo dye (Indigo): This dye, with its distinctive color and stability, is extracted from the leaves of the indigo plant, which grows in hot tropical climates.
B. Yellow saffron dye (Saffron): It was extracted from the saffron plant, which was planted abundantly by the ancient Greeks and Romans, and they extracted the dye from the female parts of its flower.
C. Red Brazil wood dye (Brazil wood): One of the red wood trees, and a bright red dye is extracted from the wood.

Th- Red Logwood Dye: A large tropical tree whose wood produces a range of dyes in purple, violet and black.

Animal Dyes: Ancient man knew animal dyes, but they were expensive, and therefore were limited to the rich only, and their colors were more intense and gave more stability. Some of these dyes include[44]:

a) Fish Scales: A cheap dye, purple in color, extracted from the scales of some fish on the island of Crete.
b) Cochineal (Kermes): An ornamental insect that lives on the leaves of low shrubs, its body is dried and ground into a bright red powder.
c) Coceus cacti: A Mexican worm, often living close to the cactus plant, and its body juice is still used to produce a bright red dye. Despite the better performance of synthetic dyes, the use of natural dyes on textiles has recently become more popular due to the following reasons:
    i. Wide availability of natural dyes in India and the Indian subcontinent as they have the potential to produce large quantities of dyes.
    ii. Growing awareness about the allergy and toxic effects of some synthetic dyes, and awareness of natural dyes.
    iii. The ancient and traditional technique of dyeing with natural dyes provides livelihood to artisans, with the potential to generate employment opportunities.
    iv. To provide employment opportunities and sustainable income to the weaker section of the population in rural and semi-urban areas. Archaeological studies for the conservation and restoration of ancient textile caches using naturally dyed textiles. More reports of scientific study on the methods of applying natural dyeing to textiles are available. The production of synthetic dyes is based on petrochemical source, and some synthetic dyes contain toxic amines, which are carcinogenic and not environmentally friendly. The current global consumption of textiles is estimated at around 30 million tons, and this huge amount of required textile materials cannot be dyed with natural dye alone. Therefore, the use of safe synthetic dyes is essential. Natural dyes consume 75% of the 48,000 tons of dyes produced. Although the sales of natural dyes are very small, their production is increasing. Dyes are not used regularly because they are not easily available, and therefore natural dyeing has become more expensive than synthetic dyes. However, researchers are working on finding a cost-effective way to dye naturally, but at the moment the search is ongoing to obtain shades that are repeatable and have a stable color[45].

- Many countries in the world currently import naturally dyed textiles. Therefore, the demand for natural dyes has increased and the use of synthetic dyes has decreased significantly due to their toxicity. Naturally dyed products are comfortable due to their light colors and their healthy properties are non-allergenic. The use of natural dyes will also provide more job opportunities.
- The production of synthetic chemicals involves many chemical reactions that require high energy and as a result we get unwanted by-products and the discharge of these toxic or environmentally unfriendly by-products into rivers, ponds, and into the atmosphere has led to environmental pollution. Natural dyes often lack uniformity and color repetition due to the lack of scientific information on the methods of applying natural dyes and also their unavailability in large quantities. Natural dyes often do not give the necessary color stability due to the cost of color stabilizers. Antimicrobials caused by dyeing and UV damage to natural dyes must be detected[46].

4.2 Second: Food dyes

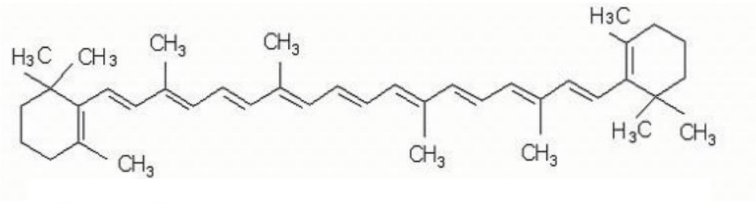
Color is the first distinguishing feature of food and has an immediate effect on the eyesight and minds of consumers. Attractive color is linked to quality and unattractive color is rejected. Food colors are substances that are added to enhance the aesthetic appearance of foods, making them more attractive and increasing the appetite value of food products for consumers, especially children.

- Flavonoid dyes: They include many compounds that are widespread in nature, such as quercetin and the most commercially used anthocyanin, which is symbolized by E163 (European number). More than 200 anthocyanin substances have been identified, twenty of which are found in black grapes, which are considered the main source of anthocyanin dye used in food coloring. Figure .
- The most common anthocyanin pigments are as follows
- Pellagronidin, found in some types of corn.
- Cyanidin, found in grape peels and residues, red cabbage, some types of corn and other fruits[42].
- Delphinidin, found in grape peels and raisins.
- Petiotidine, found in grape peels.
- Biconidine, found in corn and hawthorn.
- Malvidin, found in grape peels.

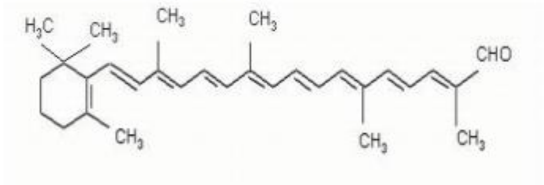
- The color of anthocyanin pigments is affected by the pH. In an acidic medium, their color is red, and the higher the pH, the bluer the color becomes. Anthocyanins are color-fast at pH.
- Carotenoid pigments:

  The carotenoids are the most common pigments in nature and are responsible for the yellow, orange and red colours of many fruits, vegetables, flowers, fungi and some animals. More than 400 pigments have been identified as belonging to the carotenoid group. The most common are bixin, lutein, violaxanthin, beta-carotene, lycopene and apocarotenoids. Carotenoids are sometimes found associated with proteins, canthaxanthin and astaxanthin. Most carotenoids contain 40 carbon atoms and their structural formula includes eight isoprene units. The attractive colours of carotenoids are due to their presence of adjacent and conjugated carbon double bonds[41].

***β*- Carotene**



***β*-apo-8'-carotenal**



Some carotenoids have been synthetically synthesized as pure pigments soluble in water or fat. In general, all carotenoids are soluble in fat to some extent and are added to foods at concentrations of less than 10 ppm pure pigment. The following are some carotenoid pigments.

- Beta-carotene: exists in two forms, the first is soluble in water and fat and the second is soluble in water
- Apocarotenal: exists either in a form soluble in water or fat and has poor resistance to oxidation
- Canthaxanthin: does not dissolve in water and slightly soluble in fat and is used to color many foods such as sugary sweets. These three carotenoid compounds have been evaluated.
- Red pepper: does not dissolve in water and is soluble in fat and the color it gives ranges from red to orange. In addition to the color, sweet red pepper gives a spicy taste to the products to which it is added. Therefore, its addition as a colorant is limited to a few foods.
- Saffron: It gives a bright yellow color, dissolves in water and does not dissolve in fat, and is stable to light and oxidation. The most important pigments found in saffron are quercetin.
- Porphyrin pigments: Porphyrin pigments are found in nature and are responsible for the green color in plants and are produced from chlorophyll and chlorophyllin.
- Betalain pigments: It is a water-soluble pigment and is responsible for the red and yellow colors and is found in beets. The main pigment found in beet juice is betanin, which is red, as well as jaxanthin, which is yellow. The stability of the red pigment of beets is low to light, heat, and sulfur dioxide, and it is stable at a pH of 3.
- Quininoid pigments: It is found in roots, some types of wood, and some insects, and gives colors ranging from yellow to brown and red.
- Riboflavin pigments: It is vitamin B2 and is found as a yellow pigment in milk and yeast. The bulk of commercially available riboflavin is synthetically synthesized and is poorly soluble in water and fat, has a bitter taste, and is poorly stable to light and bases. It is classified in the international list under number 101 and is used to color cereal products and sugary sweets. The sodium salt of riboflavin phosphate is used as a coloring agent and is synthesized synthetically. It is more soluble and less bitter than riboflavin [46].

Melanoidin dyes: Caramel and malt caramel fall under the melanoidin dye. Caramel: It dissolves in water and alcohol. The international list includes three types of caramel. The first is made by the ammonia method, the second by the ammonia sulfite method, and the third by the normal method. Caramel gives a red-brown color and is considered to be stable to light, heat, and oxidation. It is used to color soft drinks, alcoholic beverages, sugary sweets, dairy products, ice cream, pickles, and appetizers.

- Malt: It gives a brown color and is stable to light, heat, and oxidation, and has the same uses as caramel. Turmeric dyes: It gives a bright yellow color and the dye is extracted from the underground stems (rhizomes) of the turmeric plant. Curcumin is considered the main dye in turmeric. Curcumin is considered to have weak stability to light, medium stability to oxidation and bases, and good stability to heat and acids. It has the international number 100. Safflower dyes: It is called Carathmas yellow, and is obtained from the petals of safflower flowers. It gives a yellow color and has good stability to light, heat, oxidation and changes in pH. Safflumin A dye is considered one of the most important safflower dyes and is soluble in water. Safflower is used to color soft drinks[47].
- Color stabilizers and food coloring aids and their toxicity to humans:
  The following table shows seven color stabilizers as mentioned in the international list, and these include cupric sulphate, potassium nitrate and nitrite, and sodium nitrate and nitrite. The table also contains some materials that maintain color stability in foodstuffs, and these include magnesium chloride and acidic magnesium carbonate. Examples of these include poorly soluble polyvinyl pyrrolidine, as well as coloring aids such as ferrous gluconate and magnesium hydroxide[52].
- Food dye toxicity:
  Many studies have shown that food dyes are the main source of food poisoning. They also have health effects as they target the liver, kidneys, and heart and work to destroy red blood cells in the body and reduce the percentage of Ca in the bones. Many studies have also confirmed that coloring materials are not absorbed during the digestion process and negatively affect the absorption of proteins in the body, so we addressed the toxicity of some dyes in this study[53].
- Tartrazine dye E102:
  A yellow azo dye that is soluble in water. In 2009, the European Food Safety Authority published an evaluation that this dye is able to directly affect DNA and the experiment was conducted on mice and the study conducted by was approved. It was also found that this dye has an effect on the estrogen hormone. Also, continuous intake of tartrazine leads to liver fibrosis, especially in women after menopause[54].
- Quinoline Yellow 104 E:
  A water-soluble yellow ionic dye, the toxicity of quinoline yellow was repeatedly evaluated by the ECFA in 1975-1978 and in 1984, studies by the Scientific Committee on Food established that the substance is safe at the usual daily dose of 0-10 mg/kg. In 2009, the European Financial Supervision Authority (EFSA) evaluated new evidence and noted that quinoline yellow exhibits mild genotoxic properties in lymphocytes. Furthermore, this dye has been shown to be able to inhibit red blood cells and plasma[55].
- Sunset Yellow E110 :
  A water-soluble monochromatic anionic dye giving an orange color. This dye was evaluated by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) in 1982 and by the SCF in 1984.
- Indigo Carmine E132:
  A water-soluble blue anionic dye. The toxicity of indigo carmine was first evaluated by JECFA which estimated the daily dose at 10-2.5 mg/kg in 1969. This value was increased to 50 mg/kg in 1975.
- Brilliant Blue E133:
  A water-soluble triphenylmethane anionic dye, known as Bluel. The toxicity of brilliant blue was evaluated by JECFA in 1970 and also by the SCF in 1975[50].

4.3 Third: Uses of dyes

1- Direct dyes: They are used for tissues of plant origin and are used in a neutral medium Mild alkaline. Also used for dyeing wool, natural linen and leather[56].
2- Acid dyes: Used for dyeing animal tissues (hair, wool, skin) in an acidic or neutral medium.
3- Chromo-acid dyes: These are acidic dyes with a specific composition and do not give color except in the presence of chromium ions. They are used for dyeing wool in a manner identical to the previous method. Chlorine salts are added to form a safe dye (sodium chloride or potassium)[57].
4- Multi-mineral dyes: Used for animal tissues (wool, hair, skin) and the dyes contain in their molecules mineral elements such as chromium, iron and copper. The famous dyes (Neolan, Arkalan, Sebalan, etc.) belong to this group and their method of use is similar to acid dyes.
5- Auxiliary dyes: Suitable for wool and cotton, but their uses in industry are now few.
6- Basic dyes: They are used to dye cotton and give bright colors in small quantities, but they are not stable to the effect of light and are used to give a shade to some colors only.

7- Sulfur dyes: They are used to dye plant tissues, and the use of this type of dyes that are insoluble in water requires converting them into soluble dyes by treating them with sodium sulfate, and this dye is stable and resistant to light and washing[58].

8- Oxidative dyes: They are often used to dye plant tissues (cotton - linen) and these dyes are characterized by their high resistance to external influences and their extreme vitality. These dyes are insoluble in water and require, as in sulfur dyes, converting them into permanent dyes by heating them with sodium and sodium hydrosulfite. Then by oxidizing them on the fabric, we get the color.

5. CONCLUSION

This study highlights the historical significance, classification, and various applications of both natural and synthetic dyes. Natural dyes, derived from plant, animal, and mineral sources, were historically prominent but gradually replaced by synthetic dyes due to their vibrant colors, ease of production, and industrial scalability. Synthetic dyes, especially azo and vat dyes, dominate the modern textile and food industries, offering a wider spectrum of colors and better stability.

Despite the advantages of synthetic dyes, recent concerns about environmental pollution, toxic by-products, and the carcinogenic nature of some dyes have reignited interest in natural dyes. This resurgence, coupled with the growing awareness of eco-friendly alternatives, presents an opportunity to develop cost-effective and sustainable dyeing processes. The study further underscores the complex chemistry behind dye molecules, their interaction with fibers, and their behavior under different environmental conditions. Future research should focus on improving the accessibility of natural dyes and addressing the limitations of both natural and synthetic dyes to meet the growing demands of modern industries while prioritizing health and environmental safety.

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