University of Thi-Qar Journal of Science (UTsci)
ISSN Onlin:2709-0256, ISSN Print: 1991-8690 Volume (8), No.1

Classifications, Advantages, Disadvantages, Toxicity Effects of Natural and Synthetic Dyes: A review

Sajda .S. Affat

Department of Chemistry/College of Science/
University of Thi-Qar
Thi-Qar/ Iraq.
sajida.j_mschem@sci.utq.edu.iq

***Abstract*— Dyes are complex organic compounds, which are used by various industries to colour their products. Natural and synthetic dyes are compounds of great interest since they play an important role in our everyday life. The broad variety of technical and industrial applications, which is used for dyeing or printing of textile, paper, leather and other materials. Some of these dyes are toxic, carcinogenic and can cause skin and eye irritation. Many carcinogenic and allergic synthetic dyes are banned now. Many dyes, though not banned yet, may not be completely safe. Most synthetic dyes are not biodegradable; they accumulate on lands and in river causing ecological problems. Dyes from natural resources such as vegetables, animals and minerals were popular before the invention of synthetic dyes. The efforts have been made to substitute harmful synthetic dyes with natural counterpart. However, natural dyes should be selected with caution – some are neither eco-friendly nor good performer. This review paper provides extensive literature information about dyes, its classification, advantages, disadvantages and toxicity effects.**

Keywords— Dyes, natural dyes, synthetic dyes, mordents, toxicity

I. I. INTRODUCTION

Dyes are colored compounds, which are widely used in textiles, printing, rubber, cosmetics, plastics, leather industries to color their products. Mainly dyes are classified into anionic, cationic, and non-ionic dyes. Among all the dyes using in industries, textile industries placed in the first position in using of dyes for coloration of fiber (Reisch, 1996). Chemists have been intrigued by the relationship between the color of a dye and its molecular structure. Because of these early days, the subject has been of special academic interest to those fascinated by the origin of color in organic molecules. In addition, an understanding of color and constitution relationships has always been of critical importance in the design of new dyes, perhaps the most notable early contribution to the science of the color referred to as the chromophore and the auxochromes (Goodwin, 1982). The theory built on the principle of chromophore is commonly an electron-withdrawing group. Auxochromes are usually electron-releasing groups and they are linked to one another through a conjugated system. In essence, the concept of the donor-acceptor chromogen was born. Furthermore, it was observed that a bathochromic-shift of the color, *i.e.* the absorption band shifted to longer wavelength, might be obtained by increasing the electron-withdrawing power of the chromophore, by increasing the electron-releasing power of the auxochromes and by extending the length of the conjugation. The chromophore and auxochrome theory is proposed as a simple method for explaining the origin of color in dye molecules, although it lacks rigorous theoretical justification. The most important chromophores, as defined in this way, are the carbonyl (C=O), diazo (-N=N-) (Affat, et al., 2018; Affat, et al., 2018), azomethine (-CH=N) (Afatt et al., 2012) and nitro (NO_2) groups. Other groups increase the intensity of the color and shift the absorption to longer wavelengths of light, including hydroxyl (OH) and amino (NR_2) groups. The concept may be applied to most chemical classes of dye, including azo, carbonyl, azomethine and nitro dyes (Bailey, et al., 1989; Salleh, et al., 2011). Dye bearing effluents from these industries are characterized by its high colour, organic content and hazardous as well (Dawood, et. al. 2014).
Dyes can be produced from natural or synthetic sources as shown below.

A. Natural dyes

Natural dyes are organic compounds are derived from naturally occurring sources such as plants (e.g., indigo and saffron); 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 (Kadolph, 2008). A spectrum of beautiful natural colours ranging from yellow to black exists in the above sources. Various organic and inorganic molecules (pigments) exhibit these colours and their mixtures are due to the absorption of light in the visible region of 400-800 nm. This absorption of light depends on the structure or constituents of the colouring pigment/molecules contain various chromophores present in the dye yielding plant to display the plethora of colours (Bhat, et al., 2005). The use of natural products together with their therapeutic properties is as ancient as human

civilization and for a long time, mineral, plant and animal products were the main sources of drugs (Hernandez-Ceruelos, et al., 2002). Natural dyes are mostly non-substantive and must be applied on textiles by the help of mordants, usually a metallic salt, having an affinity for both the colouring matter and the fibre (Samanta, et al., 2009). Some natural dyes have low level of toxicity as well. Certain natural dyes may have detectable mutagenic effects (Choudhury, et al., 2018).

1) Classification of Natural dyes

They are classified by various ways namely (Yusuf, et al., 2012):

(a) Based on sources of origin (Bhattacharyya, 2010). Depending on the source of origin, natural dyes are of three groups:

1) Vegetable/Plant Origin
2) Insect/Animal Origin
3) Mineral Origin: The most important mineral pigments of various colours are as follows (Choudhury, et al., 2018):

- Red Pigments
- Yellow Pigments
- Green pigments
- White Pigments
- Black Pigments

(b) Based on solubility natural dyes are classed intotwo groups namely:

1) Soluble natural dyes
2) Insoluble natural dyes

(c) Based on substantively: natural dyes can be classified into two groups:

1) Substantive. e.g. Turmeric.
2) Adjective natural dyes . e.g. logwood, Substantive dyes can dye the fibrous materials , directly without mordant. e.g. Turmeric.

(d) Based on colours formed with various, natural dyes can be classed into two groups namely:

1) Monogenetic: Produce only one colour irrespective of mordant present in the fibre.
2) Polygenetic natural dyes, produce different colours with different mordant (e.g. logwood, alizarin, fustic and cochineal).

(e) Based on chemical constitution (Bhattacharyya, 2010; Mussak, & Bechtold, 2009; Bechtold, & Mussak, 2009) (figure 1):

1) Indigoids (a)
2) Beberine (b)
3) Carotenoids (c)
4) Quinonoids (d)
5) Flavonoids (e)
6) Dihydropyran-based Dyes (f)
7) Betailains (g)
8) Tannins (h)

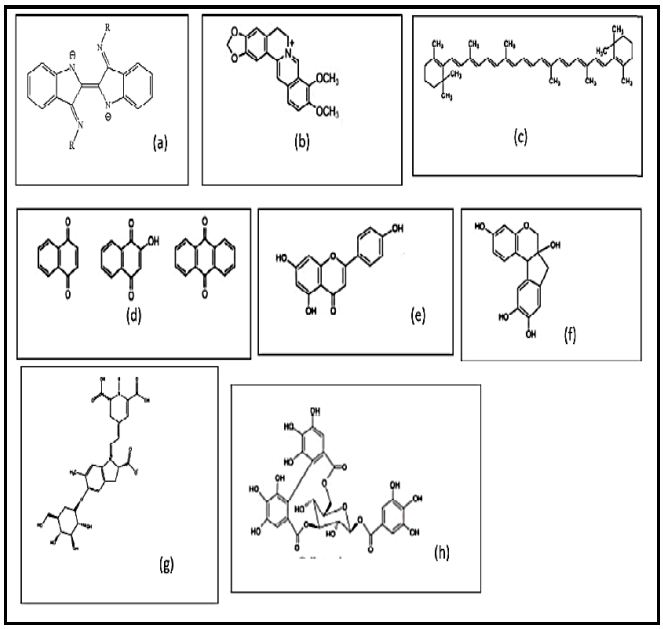


Fig.1. Chemical structures of various chemical classes of natural dyes: (a) Indigoids, (b) Berberine, (c) Carotenoids, (d) flavonoids, (f) dihydropyran based, (g) betalain and (h) Tannins

(f) Classification according to the method of application to:

1) Substantive dyes can further be classified as direct, acid, basic (figure 2).
2) Non-substantive dyes can be bound to a material for which it otherwise has little or no affinity by the addition of a mordant, a chemical that increases the interaction between dye and fibre. This classical definition of mordant dyes has been extended to cover all those dyes, which can form complex with the metal mordant. Most of these dyes yield different shades or colours with different mordents.

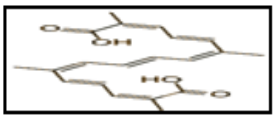
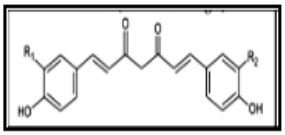
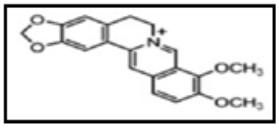
Dyes	Examples of dyes	Chemical structure's example	Applications of dyes
Acid dyes	Saffron, lac	Saffron 	Silk , wool, food cosmetic industry
Direct dyes	Turmeric, safflower	Turmeric 	Cotton, wool, silk
Basic dyes	Berberine	Berberine 	Silk, wool

Fig.2. Classification of naturel dyes based on applications

2) Advantages of Natural Dyes

1. Minimal impact on environment: As of natural origin, natural dyes are not harmful to the environment. This makes it very appealing to the

consumers. Natural dyes are biodegradable and disposing them do not create pollution.
2. Renewable: Natural dyes are obtained from renewable sources assuring no harm to the environment.
3. Chemical reactions: No or little chemical reactions are involved during dye preparation.
4. Disposal: No disposal problems.
5. Natural shades: If you're going for a soft hue or soothing shade, natural dyes can help you achieve that look.
6. Safe: Some natural dyes, such as carmine found in lipsticks, will not cause harm or health problems when ingested (Choudhury, et al., 2018).

3) Disadvantages of Natural Dyes

1. Cost: A larger amount of natural dyes may be needed in order to dye a specific amount of fabric as opposed to synthetic dyes. For instance, one gram of cotton may be dyed with just five grams of synthetic dye, whereas 230 grams of natural dye are needed to dye the same amount of material. Since that is the case, using natural dyes is more expensive than synthetic dyes.
2. Standardization: Difficult to standardize and to blend.
3. Poor brightness and fastness properties: Colour pay-off from natural dyes tends to fade quickly. More so, quality may not be as consistent as what synthetic dyes can deliver.
4. Availability: Another issue with natural dyes is their availability. It can be difficult to produce because the availability of raw materials can vary from season to season, place, and species, whereas synthetic dyes can be produced in laboratories all year round.
5. Fixation: Inadequate degree of fixation.
6. Lengthy dyeing procedure.
7. Reproducibility: Poor reproducibility of shade
8. Solubility: Poor solubility in water and tedious extraction procedure may be necessary.
9. Harmful Effects: Natural dyes can also be harmful to some extent. Logwood has ingredients, hematein and hematoxylin, that can be have harmful effects when inhaled, ingested, or absorbed through the skin. Bloodroot, another natural dye source, can cause irritation and inflammation when inhaled. More so, natural dyes may need mordants for application. While these substances help the dye stick to fabrics, they can also be toxic. Example of mordants used in natural dyes are aluminium, copper, iron, and chrome (Choudhury, et al., 2018; Keycolour, 2016). Textile dyeing and finishing in a green way can be achieved by using chemical-free dyes made from plants, marine invertebrates (like sea urchins and starfish), algae, bacteria, and fungi. These herbal dyes are not only bio-degradable but also posses' medicinal properties. Plants, fruits, barks, stems, minerals, and herbs are used to make fabrics with anti-bacterial, anti-inflammatory, and anti- allergic fabrics. However, it is difficult to get all desirable shades and to get good color fastness properties.

B. Synthetic dyes

Synthetic dyes are extensively used in wide range of industries amongst which textile processing industries are the major consumers (Keharia, & Madamwar, 2003).

1) Classification of Synthetic dyes

Dyes are broadly classified into (Le Coz, 2005; Hernández-Montoya, et al., 2013; Forgacs, et al., 2004):
a) Cationic
b) Anionic
c) Non-ionic dyes

Perkin was the pioneer in producing man made organic dye, mauve, as early as 1856. The first synthetic organic dye was produced in 1871 when Woulfe prepared picric acid by treating the natural dye, indigo with nitric acid. Since then several new chemical dyes have been added to the ever increasing list of dyes (Mathur, et al., 2006). Synthetic dyes today have evolved into a multi-billion dollar industry. Almost all the colors that you see today are synthetic dyes, and they are widely used for dyeing and printing in a broad range of industries. The synthetic dyes can be named according to the chemical structure of their particular chromophoric group. For example, diphenylmethane derivatives, triphenylmethane compounds, oxazine compounds, xanthene compounds, azo dyes to name a few. Most of the synthetic dyes with a few exception are aromatic organic compounds which can be divided into groups like ionic (acidic) and cationic (basic) dyes (Anonymous, 2008). Pigments are chemical compounds that reflect only certain wavelengths of visible light. This makes them appear colorful. Flowers, corals, and even animal skin contain pigments, which give them their colors. More important than their reflection of light is the ability of pigments to absorb certain wavelengths. Because they interact with light to absorb certain wavelengths, pigments are useful to plants and other autotrophs-organisms that make their own food using photosynthesis. In plants, algae, and cyanobacteria, pigments are the means by which the energy of sunlight is captured for photosynthesis. However, since each pigment reacts with only a narrow range of the spectrum, there is usually a need to produce several kinds of pigments, each of a different color, to capture more of the sun's energy (Anonymous, 2013). Dye effluents are produced because dyes do not have a complete degree of fixation to fiber during dyeing and finishing processes (Pang, et al., 2013). Dye based effluents can cause a serious hazards to the water stream and environment due to their synthetic origin and complex molecular structures which decrease their ability to biodegrade. There are various types of dyes used in various industries such as acid dyes, reactive dyes, basic dyes, azo dyes, direct dyes, vat dyes and disperse dyes (Demirbas, 2009). More dyes are water soluble except disperse dyes and vat dyes. Many dyes contain traces of metals such as copper, zinc, lead, chromium and cobalt in their aqueous solution except vat and disperse dyes. Dye bearing effluents from these industries are characterized by its high colour, organic content and hazardous as well. It is estimated that more than 100,000 commercial dyes are known with an annual production of more than $7x10^5$ tonnes per year (Gupta, et al., 2013). Synthetic dyes are usually added to food stuffs and soft drinks. They improve appearance, color and texture. This class of com- pounds has been added legally into foods since the 1880s to make food more attractive for customers. However, some synthetic colorants can be pathogenic, particularly if they are excessively consumed (El-Shahawi, et al., 2013; Pourreza, et al., 2011).

Anionic dyes include various dyes' groups such as acid dyes, reactive dyes, azo dyes and direct dyes while cationic dyes are the basic dyes.

The dyes may be classified according to application or dyers point of view as follows (figure 3):

1) Direct dyes
2) Acid dyes including metal complex
3) Basic or Cationic Dyes
4) Chrome mordant dyes
5) Azoic dyes
6) Sulphur dyes
7) Vat dyes
8) Reactive dyes
9) Disperse dyes

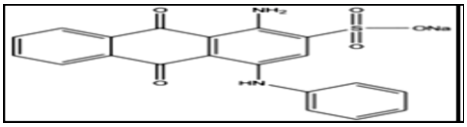
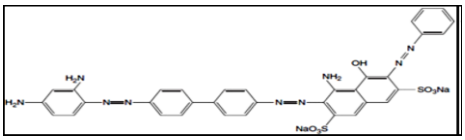
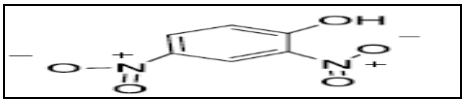
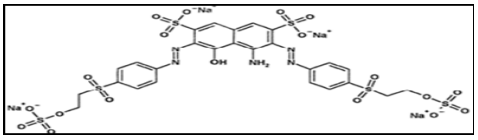
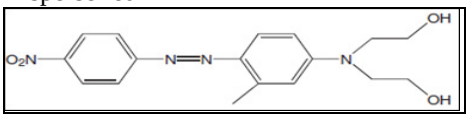
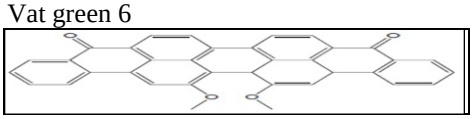
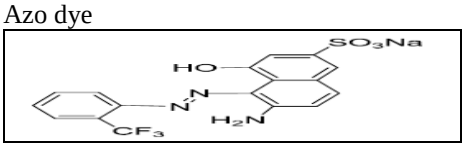
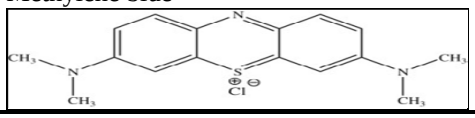
Dyes	Examples of dyes	Chemical structure's example	Applications of dyes
Acid dyes	Congo red Methyl (orange and red) Orange (I,II) Acid (blue, black, violet, yellow)	Acid blue 25 	Wool, silk, nylon (polyamide) Polyurethane, fibers
Direct dyes	Martius yellow, Direct black Direct orange, Direct blue, Direct violet, Direct red	Direct black 38 	Cotton, wool, flax, silk, leather in (alkaline or netural bath)
Sulfur dyes	Sulfur black Leuco sulfur black	Sulfur black 	Cellulosic, fibers
Reactive dyes	Reactive red, Reactive blue Reactive yellow, Reactive black, Remazol (blue, yellow, red, etc)	Reactive black 5 	Cellulosic, fibres wool, polyamide
Disperse dyes	Disperse blue Disperse red Disperse orange Disperse yellow Disperse brown	Disperse red 17 	Polyamide, fibers polyesters, Nylon polyacrylonitriles
Vat dyes	Indigo, Benzanthrone Vat blue, Vat green	Vat green 6 	Wool, flax, wool, rayon fibers
Azoic dyes	Mono azo dyes, diazo dyes, triazo dyes	Azo dye 	Textile, cosmetic, leather, paper paint, food industries
Basic dyes	Methylene blue, Basic red, Basic brown Basic blue, Crystal violet, Aniline yellow, Brilliant green	Methylene blue 	Polyester, wool , silk mod-acrylic nylon

Fig. 3. Classification of synthetic dyes based on applications

2) Advantages of Synthetic dyes

1. The limitation of natural dyes became louder, with the advent of synthetic dyes, such as Lesser availability of dye producing materials due to difficulty in collection or lack of organized plantation/farming of the dye-plants, poor color yield, complexity of dying process, non-reproducibility of shades, limited number of dyes, sometimes Inadequate fastness properties, these problems encountered with natural dyes, and the development of synthetic dyes came in to existence. When collapse due to the advent of synthetic dyes led to the collapse of the huge natural dye industry.

2. The development of synthetic dyes at the beginning of the twentieth century led to a more complete level of quality and more reproducible techniques of application.

3. Synthetic dyes are readily available at low cost, resulting in a less costly rug to produce. Density of weave also adds to quality and therefore to the cost. A low cost rug will be likely woven with synthetic dyes, on brittle, machine (not hand-

4. Basic spun) wool, and have a looser weave.

and disperse dyes have high exhaustion properties - hence, less polluting. Azoic and solubilizing vat aren't used in large

quantities. Pigments are water-insoluble and can be separated easily from effluent.

5. Synthetic dyes often produce garish, stark or muddy colors.

3) Disadvantages of Synthetic dyes

1. Synthetic dyes tend to remain quite stable to common oxidation and reduction processes as per their designing and so are very difficult to remove from textile industry effluents; natural dyes are biodegradable without the use of any oxidant or reductant. **2.** Synthetic dyes, if at all degraded, are full of byproducts that are directly or indirectly proven health hazards; such hazardous compounds have so far not been detected in the natural dye degraded byproducts. It is possible that natural dyes completely degrade under natural conditions. **3.** Synthetic dyes based effluents can cause a serious hazard to the water stream and environment due to their synthetic origin and complex molecular structures, which decrease their ability to biodegrade.

4. Many carcinogenic and allergic synthetic dyes are banned now. Many dyes, though not banned yet, may not be completely safe.

5. Most synthetic dyes are not biodegradable; they accumulate on lands and in river causing ecological problems.

C. Toxicity effects of dyes

Not all synthetic dyes are not harmful, for example, fibre-reactive dyes are dyes that form covalent bond to the fibres like cotton, rayon, and soy. There are not requiring harmful mordants. The toxicity of a dye considers the structure of the dye rather than the dyeing process. Heavy metals containing dyes and cancer-producing dyes cause high impact and are objectionable. Dyes that cause allergic reactions are not considered low impact. Dyes that pass eco- standards such as bluesign, GOTS, OekoTex 100 and Cradle to cradle and are compliant to the ZDHC MRSL have been assessed thoroughly for toxicity and should be chosen over dyes that have not. Acute toxicity involves oral ingestion and inhalation; the main problems of acute toxicity with textile dyes are skin irritation and skin sensitization, caused mainly by reactive dyes for cotton and viscose, few acid dyes for polyamide fibres and disperse dyes for polyester, polyamide and acetate rayon.

1. The reactive dyes which have proved to cause respiratory trouble and/or skin sensitization in workers on occupational exposure has been identified by ETAD (Chavan, 2013).. In order to minimize the risk of exposure to these dyes, dye dust should be avoided. This may be achieved by using liquid dyes, low-dusting formulations and by using the appropriate personal protective equipment. After dyeing and fixation, reactive dyes have completely different toxicological properties because the reactive group is no longer present and the high wash fastness of the dyed fabric ensures that no dye is exposed to the skin of the wearer. Consequently, consumers wearing textiles dyed with reactive dyes have reported no cases of allergic reactions. **2.** Disperse dyes, showing low perspiration fastness, are responsible for causing allergic reactions. Polyester dyed with disperse dyes does not in general pose a problem since the perspiration fastness is high. However, problems can arise with polyamide or acetate rayon dyed with disperse dyes since the low perspiration fastness allows the dyes to migrate to the skin. Basic dye are toxic and can cause allergic dermatitis, skin irritation, mutations and even cancer (Eren, 2009).

3. Cationic dyes can cause increased in heart rate, shock, vomiting, cyanosis, jaundice, quadriplegia, heinz body formation and tissue necrosis in humans (Vadivelan, & Kumar, 2005).

4. Anionic dyes have negative ions due to the excess presence of the OH- ions in aqueous solution. Anionic dyes are water soluble and they include acid dyes, azo dyes, direct dyes and reactive dyes. Reactive dyes attach to their substrates by a chemical reaction (hydrolysis of the reactive groups in the water) that forms a covalent bond between the molecule of dye and that of the fibre (Demirbas, 2009). Anionic dyes removal is the most challenging task as they produced very bright colours in water and show acidic properties.

5. Reactive dyes contain reactive groups such as vinyl sulphone, chlorotriazine, trichloropyrimidine,and difluorochloro-pyrimidine that covalently bonded with the fiber during the dyeing process (Labanda, et al., 2009). Moreover, azo dyes represent the largest class of reactive dyes used in the textile industry followed by anthraquinone and phthalocyanine classes (Wu, et al., 2008). Azo dyes have the largest variety of dyes and under anaerobic conditions, the dye's linkage can be reduced to form aromatic amines which are colourless but can be toxic and carcinogenic (Yaneva, & Georgieva, 2012). It was estimated that 130 of 3,200 azo dyes in use can form carcinogenic aromatic amines during degradation process (Yaneva, & Georgieva, 2012).

II. CONCLUSION

Hence this review presents gives the classification, advantage, disadvantage and toxicity effects for natural and synthetic dyes. Each dye class is described in detail giving more specific information regarding the chemistry of the dye class. The efforts have been made to substitute harmful synthetic dyes with natural counterpart. However, natural dyes should be selected with caution – some are neither eco-friendly nor good performer.

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