International Journal for Multidisciplinary Research (IJFMR)

E-ISSN: 2582-2160 ● Website: www.ijfmr.com ● Email: editor@ijfmr.com

Analysis of the Structural and Photophysical Properties of Dyes

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Graphical Abstract

Abstract

Dyes and pigments have the power to make the world a more beautiful place. With a long history of use, they have diverse applications in various industries, including food, textiles, artifacts, and paper. This has led to extensive research on developing natural colorants from natural sources. The benefits of using natural colorants are numerous. They are eco-friendly, safe, and easily obtained from renewable sources. Natural colorants are also soft, lustrous, and soothing to the human eye. Additionally, they do not pose health hazards and offer no disposal problems. India is a rich source of natural colorants, with an estimated 500 varieties of colorant-producing plants. This mini-review explores fundamental aspects of colorants, including their classification, chemical constituents, newer methods of production and extraction, and prospects. Furthermore, coumarin and its derivatives have emerged as versatile compounds with various biological and pharmacological applications, including anti-inflammatory, antifungal, and antibacterial properties. This review highlights the use of coumarin derivatives as dyes and their impacts on the environment and human health.

Keywords: Coumarin derivatives, biological, pharmacological, colorant.

1. Introduction

1.1 The Global Scenario of Textile Dyes and Its Environmental Impact

A maximum of the chemicals used in textile dyes harm every area of our ecosystem. According to the 2022 study on global textile chemical consumption [1], almost all countries use these textile chemicals. The textile industries are the primary users of these dyes. The following pie chart illustrates how the United States consumes main textile chemicals compared to other nations in 2022 nearly half of the world. The USA is the world's biggest user of textile chemicals, and the country is currently subject to stringent environmental regulations that compel dye manufacturers to close their facilities. The closure of American industrial facilities has increased India's chances of breaking through globally [1]. Because of their characteristics and the massive amount of wastewater they generate, the textile industries are considered to be among the most polluting industrial sectors **Figure 1**.

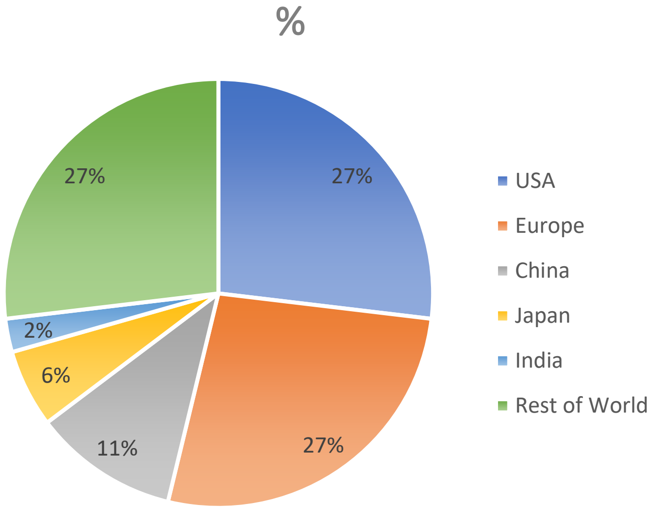


Figure 1 Textile Consumption by Region

1.2 WHO Data Textile

There is a growing global shift towards the application of non-allergenic, antimicrobial, and eco-friendly dyes in the textile industry. These nature-based dyes, derived from plants, and animals without chemical processing, are preferred for their non-toxic properties and renewable sources, making them more eco-friendly [2]. Although natural dyes have lower tinctorial strength and light fastness compared to synthetic dyes, they are favored for specialized applications due to the harmful environmental effects of metallic mordants used in synthetic dyes. The textile industry is a significant global sector, contributing about 2 trillion dollars in sales and representing 8% of total global exports. It employs around 35 million people worldwide, playing a crucial role in providing jobs and supporting livelihoods [3]. While the dye manufacturing segment is a small part of the chemical industry, it plays an essential role in the textile supply chain, especially in creating vibrant fabrics for the fashion and garment sectors. The worldwide manufacturing of synthetic dyes is approximately 810,000 tons per year, but around 10.5-15% of these dyes are lost during textile manufacturing processes. Synthetic dyes are widely utilized in various industries, including textiles, cosmetics, food, paper printing, pharmaceuticals, and leather. These dyes are classified into several categories, such as acid, reactive, direct, basic, vat, dispersion, metal complex, mordant, and sulfur dyes. In textile production, over 11,000 dyes are in use, with about 75% being azo dyes, which are complex and synthetic [4], [5]. Synthetic dyes play a crucial role in the textile industry by offering vibrant, long-lasting colors for different fabric types. However, a major challenge persists in the form of dye loss during production. The classification of synthetic dyes is essential in understanding their distinct properties,[6] which are vital for the creation of textiles and other products. Given their significance, synthetic dyes continue to be a key focus of research in both academic and industrial fields. One major environmental concern is the incomplete fixation of dyes onto textile fibers during the dyeing process, which contributes to pollution. Reducing the residual dye in textile wastewater has become a critical challenge. Dyes, which are organic chemicals, are used to add color to fabrics. Unlike pigments, which are finely ground solid dyes typically containing carbon that is either suspended in a liquid or mixed with other substances like ink or paint, pigments can be inorganic or organic compounds without containing carbon. Most pigments produce brighter colors and may be insoluble in the medium used [7]. The human fascination with color has deep historical roots, driven by both aesthetic and practical reasons. Dyes and colorants have been important in trade for centuries, and color remains a vital element in the development of nearly all retail products. Today, there are approximately 9,100 colorants available, with over 51,200 trade names in use. This vast variety of colorants reflects the diverse range of hues and chemical properties desired, with the color of the dye primarily determined by its molecular structure. Dyes can be obtained through chemical processes or from natural sources. A notable feature of these substances is that, unlike paint, they do not merely coat the surface of fibers but penetrate the material itself. This is possible because dye molecules are smaller than the pores in the fiber [8]. Dye molecules have a shape resembling flat ribbons, which allows them to penetrate the polymer structure of the fiber when immersed in the dye bath. Additionally, the strong force of attraction held between the dye and the fiber, helps the dye to remain within the fiber due to cohesive forces [9]. Many natural dyes contain chromones, flavonoids, and coumarin cores, which offer antimicrobial and UV-protective properties. To address the challenges posed by dye effluents, it is essential to develop natural dyes with excellent heat resistance and color retention **(Figure 2)**.

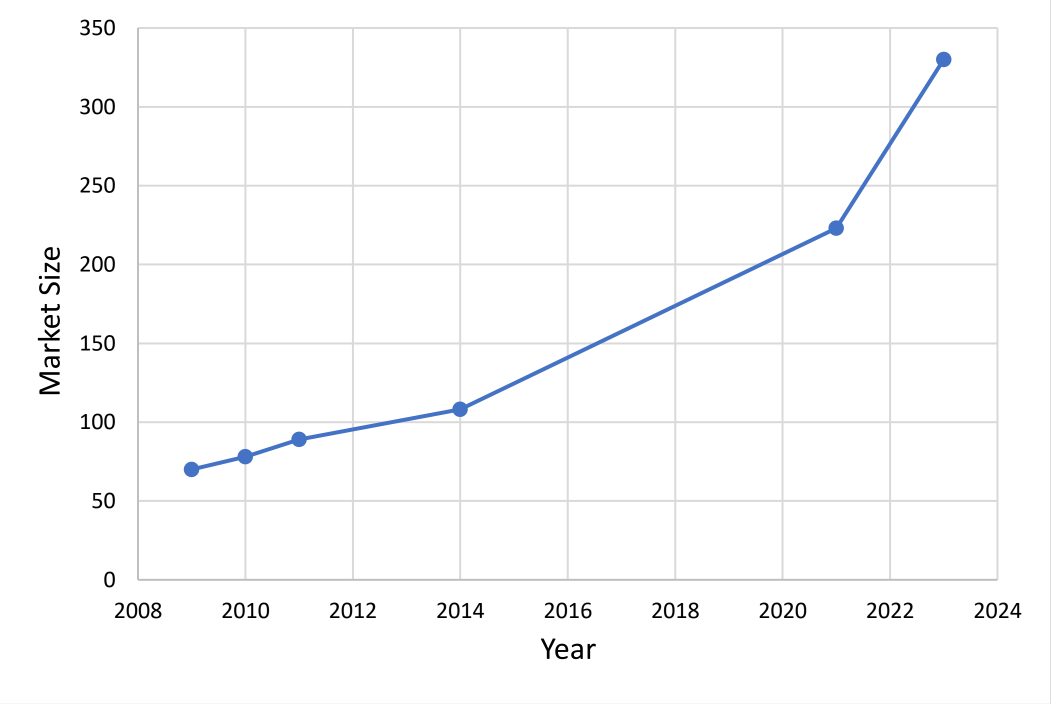


Figure 1 Textile Market Rate Year Wise

1.3 Textile Dyeing Unit in Tripura

There are 780 textile dying units in the Indian city of Tirupur; 335 of them are active at the moment. Regretfully, until 2007, the Noyal River and the Orathupalayam dam across it had significantly higher TDS and chloride levels due to the units' discharge of partially treated and untreated effluent into the river. As a result, the High Court ordered in 2007 that the dyeing facilities install zero liquid discharge (ZLD) plants and cease all effluent flow into the river. Since the majority of these facilities operated on a modest scale, a number of them joined forces to establish common effluent treatment plants (CETPs), which combine biological, physicochemical, and reverse osmosis (RO) plants with refuse management systems to achieve zero lateral discharge (ZLD). The wastewater from Tirupur's textile dyeing and bleaching factories is now treated by 58 individual effluent treatment plants (IETPs) and 25 CETPs.

1.4 Source of Wastewater during Dyeing

The textile industry is a sector involved in wet fabric processing, which includes processes such as mercerizing, bleaching, de-sizing process, scouring process, dyeing process, printing process, and finishing process, among others. Various chemicals are required at each stage, including strong acids, alkalis, sodium hypochlorite, inorganic chlorinated compounds, and organic substances like dyes, starch, finishing agents, bleaching agents, surface-active chemicals, thickening agents wetting agents, dispersing agents, metal salts. Different types of dyes are used during the dyeing process to add color to the products, with multiple colors often employed to enhance their visual appeal. In Tripura, the primary output of the textile industry includes power looms, towels, pullovers, and napkins made from raw cotton. A detailed list of processing stages and the associated pollutants is provided in **Table 1**.

Table 1 Wastewater Generation Process and Nature of Wastewater

Process	Nature of Wastewater
Sizing	High BOD
De-Sizing	High BOD, COD, Dissolved Solid
Bleaching	Excessive Alkalinity, Suspended Solid
Mercerizing	High in pH and Dissolved Solid
Dyeing	Strong in Color
Printing	Strong in Color, High BOD & Suspended Solid

1.5 Pollution Potential in Textile Dyeing Units

Water is heavily consumed by the textile industry, particularly during the dyeing and finishing stages. Regretfully, textile factories are regarded as one of the most polluting industrial sectors because of the amount of water they use and the type of effluent they produce. Variations in parameters, including pH, color, salinity, chemical and biochemical oxygen demand (BOD), and p*H*, are characteristics of wastewaters from textile industries. The wastewater's composition is determined by the kinds of chemicals, dyes, and organic compounds that are employed in both wet and dry processing. Particularly during the dyeing process, unfixed dyes are thought to be lost to the environment to the tune of 20% to 50%. Since dyes and pigments are designed to withstand biodegradation and persist in the atmosphere for longer periods, the removal of color from wastewater poses a significant challenge to the textile industry. As a result, unutilized salts like sodium chloride and sulfate accumulate and raise the TDS level. The effluent is also extremely poisonous due to the presence of sulfur, naphthol, vat dyes, chromium compounds, heavy metals, and other auxiliary chemicals. There may also include harmful substances including non-biodegradable coloring chemicals, softeners based on hydrocarbons, and dye-fixing agents based on formaldehyde. Textile mill effluent frequently has a high pH and temperature, and the addition of colloidal debris, colors, and oily scum makes the effluent more turbid and smells bad.

1.6 Impact of Dyes

1.6.1 Water

The most common organic pollutant in untreated effluents from the textile industry is textile dye [10]. Azo dyes, which comprise more than 50% of textile dyes, are the most widely used in the industry [11], [12]. Between 15% and 50% of these azo dyes, which do not properly bind with fabrics, can be released into wastewater due to inefficient dyeing processes [13], [14]. Although textile industries can often treat their wastewater and break down the azo dyes, many neglect this step, discharging untreated effluents directly into water bodies. This poses a significant threat to the environment and living organisms, leading to harmful consequences. In many developing countries, farmers have historically used untreated industrial effluents mixed with wastewater for irrigation, which has led to a decline in soil quality and reduced crop germination, as shown by studies from M.A.S. Jiku in 2021 and S. Ao in 2022 [6,15]. Azo dyes in water lessen the light penetration, which affects the growth of aquatic organisms. Additionally, these dyes when engulfed by fish and other organisms generate toxic compounds that impact negatively on their health and the health of their predators [4]. Azo dyes, often found in industrial effluents **(Figure 3)**, can also be absorbed by humans and other mammals through skin contact or consumption, leading to harmful effects [3]. In the human stomach, azo dyes can be converted by intestinal bacteria into harmful amino acids, causing tissue damage throughout the body[16]. Research by R. Kishor in 2021 also demonstrated that bacteria from human skin can decompose azo dyes, generating carcinogenic amines (R. Kishor, 2021). Given the rapid growth of the textile industry and the large volumes of wastewater containing dyes, effective management strategies are essential to prevent ecosystem contamination and ensure sustainability. However, selecting the appropriate treatment technology requires considering various inorganic and organic compounds, their toxicity, and the permissible discharge limits[17]. Introducing textile dyes into aquatic environments negatively affects aquatic plants, particularly by absorbing and reflecting sunlight, which blocks light from reaching the photic zone and disrupts photosynthesis, leading to changes in aquatic ecosystems [18,19]. The discharge of dye-laden wastewater can also cause allergic reactions, dermatitis, skin irritations, cancers, and mutations in humans, in addition to degrading water quality, causing unpleasant odors, and discoloration, making the water hazardous[3]. The elevated concentration of textile dyes in water depletes oxygen levels, obstructs sunlight, and interferes with the biological processes of aquatic organisms[20]. Azo dyes, in particular, are highly resistant to conventional physical and chemical degradation methods, with 50-70% being toxic, carcinogenic, and challenging to treat[21]. Eutrophication caused by the uncontrolled release of mineral elements disrupts photosynthesis in aquatic plants, creating long-term risks [22]. Consuming fish and other aquatic organisms contaminated with dyes can lead to symptoms like abdominal pain, elevated body temperature, and high blood pressure. Wastewater containing textile pigments and dyes is characterized by intense color, fluctuating pH levels, and extreme concentrations of biological oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), and suspended particles. These particles can hinder water movement through fish gills, leading to stunted growth or mortality[23]. Prolonged exposure to textile effluents can reduce a fish's food intake, lower protein, carbohydrate, and fat levels, and slow its growth. Reactive azo dyes can cause genotoxic effects, increasing the occurrence of micronuclei in adult fish and gill micronuclei in juvenile fish. Hypoxia induced by dye contamination weakens the immune system of fish, making them more susceptible to diseases, and consuming contaminated fish can significantly affect human health[24]. The release of organic substances, such as dyes and pigments, disrupts natural bacterial processes that regulate oxygen consumption in water[25]. Stagnant aquatic environments may experience oxygen depletion due to the bacterial breakdown of organic matter, which can exhaust oxygen levels in water (Lin Y, 2008). The accumulation of organic debris in watercourses can lead to undesirable tastes, bacterial growth, foul odors, and discoloration[26]. According to Lim Y.B. (2010), dyes in concentrations as low as 5 grams per liter can alter the appearance of water, affecting its transparency and sunlight penetration, which disrupts photosynthesis in aquatic plants[27]. Synthetic organic dyes, being resistant to conventional biological degradation, persist in the environment for long periods[28]. Unsaturated dye molecules are generally less persistent than saturated dye compounds, and the stability of aromatic compounds increases with the number of substituents, especially halogen groups[29]. Microalgae, which are vital primary producers in aquatic ecosystems, are particularly vulnerable to dye contamination. The presence of textile dyes inhibits their growth and disrupts the transfer of nutrients and energy within aquatic systems. Dye contamination in rivers, lakes, and oceans negatively impacts microalgae growth, pigmentation, protein content, and nutrient levels. Due to their increased sensitivity to toxic substances, algae are often used as indicators of pollution[30]. Methylene Blue, a commonly used cationic dye, can generate cancer-causing aromatic amines like benzidine. Studies on the microorganisms, which are ecologically and nutritionally significant, have shown that exposure to Methylene Blue reduces growth rates, protein levels, and pigment content, while also inhibiting chlorophyll production, affecting photosynthesis[31]. Aquatic macrophytes, plants that thrive in or around water, are increasingly used as ecological indicators to assess the toxicity of textile dyes. Various growth parameters, such as dry weight, frond count, and chlorophyll content, are affected by dye toxicity, underscoring the need to evaluate dye effects on aquatic habitats[32]. The toxicity of textile dyes significantly impacts these parameters, stressing the importance of using macrophytes for ecological assessments. Additional research is needed to fully understand the mechanisms of dye toxicity in microalgae and macrophytes and to develop more effective strategies to reduce their harmful impacts. Studies have indicated that dyes can inhibit the growth of aquatic macrophytes, often by causing oxidative stress or disrupting electron transport in chloroplasts[33]. A study examining the effects of Congo Red and Gentian Violet dyes on biogenic amine production in *Lemna minor* revealed that these dyes suppressed growth and chlorophyll production, with Gentian Violet having a stronger effect due to its interference with biogenic amine biosynthesis. The findings suggest that measuring decarboxylase activity and biogenic amine levels could be early indicators of phytotoxicity[34].

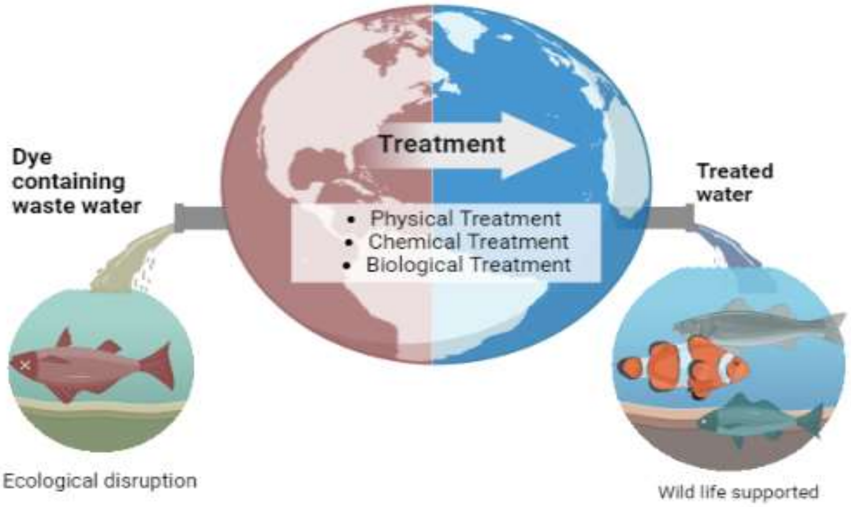


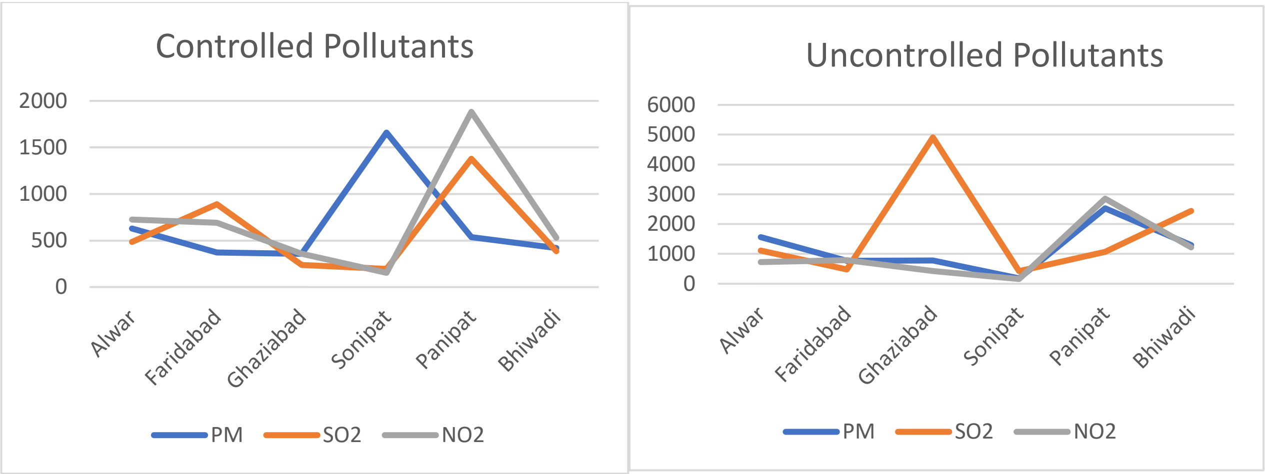
Figure 2 Dye Effluents Cause Water Pollution

1.6.2 Dye’s Impact on Air

It is crucial to note that the textile industry ranks as the second largest reason for global pollution due to its air emissions. While there are various speculations regarding the types and quantities of air pollutants generated by textile processes, it remains challenging to accurately collect, analyze, or determine the exact nature and volume of air pollution associated with these activities. Maximum air pollutants in textile operations are caused by the release of carbon dioxide, aerosol fumes, toxic gases, and volatile organic compounds (VOCs), which are emitted as both visible and invisible smoke, often accompanied by a strong, unpleasant odor. Additionally, air pollution can arise from other processes such as printing, dyeing, fabric preparation, and wastewater treatment. Textile drying processes release hydrocarbons, while methods involving mineral oil drying and high-temperature curing produce dangerous combinations of formaldehyde, acids, and softeners. The primary pollutants from textile operations are acetic acid and formaldehyde, both of which have significant harmful effects. These toxic gases can cause damage to humans and animals, as well as degrade the quality of the environment. As a result, textile industries have become a major source of pollution, as shown in **Table 2** and **Figure 4**.

Table 1 Pollution Loaded from Major Polluting Industrial Sector

District	**Sector**	**Major Fuel**	**Pollutants (tonnes/year)**					
			Controlled			Uncontrolled		
Alwar	Distillery	Agr	530	383	725	1551	383	725
Faridabad	Metal	Liquid Fuel	373	891	591	772	3907	793
Ghaziabad	Textile	Coal	357	239	355	180	323	323
Sonipat	Automobile	Liquid Fuel	1559	195	285	775	1057	198
Panipat	Textile	Wood	535	1378	1882	2530	2337	2853
Bhiwadi	Textile/Pharma	Coal	553	318	570	1257	1038	1102


Controlled Pollutants
Uncontrolled Pollutants

Source: CSE 2019-22 based on data provided by SPCB

Figure 3 Comparison of Pollutants

1.6.3 Impact of Dyes on Soil

Textile dyes and their associated waste can negatively impact the chemical composition of soil and disrupt the balance of soil microorganisms. These organic pollutants also harm plant growth, particularly by affecting processes such as blooming and germination [35]. Key indicators of plant health and development following exposure to textile dyes include seed germination rate, seedling height, and survival. Additionally, the presence of healthy green shoots signifies that the plants are actively producing dry matter through photosynthesis, indicating a high chlorophyll concentration and robust photosynthetic activity. According to Z. Wan (2017), a higher concentration of solid materials in industrial wastewater containing dyes has a more harmful effect on plant growth. The increased concentration of materials in contaminated wastewater depletes dissolved oxygen and disrupts osmotic balance, further harming seedlings[36]. Elevated levels of dissolved solids can also lower chlorophyll concentrations in plants, impairing photosynthesis, and slowing plant growth, which leads to a reduced accumulation of dry matter.[7]. Studies have shown that high levels of abscisic acid can degrade chlorophyll and impede plant growth by interfering with the production of new chlorophyll. Furthermore, textile dye effluents have been associated with elevated proline levels in plants, suggesting that these dyes are triggering stress. The presence of azo dyes in industrial wastewater can result in genotoxic effects in Allium cepa seeds, causing chromosomal abnormalities, micronucleus formation, and cell death, particularly in the meristematic cells of A. cepa when exposed to low proportion of Black Dye Commercial Product[37].

1.6.4 Dye's Impact on Human Health

Textile dyes, which are known for their high toxicity and carcinogenic effects, have been associated with various health issues in both humans and animals[38,39]. Exposure to these dyes can lead to numerous health problems, including skin irritation and nervous system disorders, as shown in **Figure 5**. Additionally, enzyme cofactor substitution can deactivate enzymes, resulting in further health complications[40]. Ingesting or inhaling textile dyes can irritate the skin and eyes, especially when exposed to dust. Workers handling reactive dyes are at an increased risk of allergic reactions such as contact dermatitis, allergic conjunctivitis, rhinitis, and occupational asthma. When a reactive dye binds to human serum albumin, it acts as an antigen, triggering the production of Immunoglobulin E (IgE) antibodies, which attach to histamine. According to V. Suryavathi (2005), the textile industry faces exposure to harmful substances that can impact ovulation and spermatogenesis. Azo dyes, derived from benzidine and its derivatives, are commonly used in textiles, paper, and leather industries. Research has shown a link between these compounds and bladder cancer in humans. In animals, azo dyes are metabolized by intestinal bacteria into their parent amines, which are easily absorbed by the gastrointestinal tract[41], and these amines are present in both human and animal urine. Studies have shown that textile dyes like Reactive Green 19, Disperse Red 1, and Reactive Blue 2 can have long-term harmful effects on human health. D.M. Leme (2015) found that Reactive Green 19 showed harmful effects depending on the dosage, while Reactive Blue 2 and Disperse Red 1 were not toxic. These dyes, widely used across industries, can accumulate in the environment, especially in freshwater organisms such as fish and algae[36]. A. Korpi (2009) reports that the concentration of hazardous chemicals in humans can be up to 1100 times higher than their original levels in water. When organic compounds combine with chlorine during water treatment, trihalomethanes are produced, which help eliminate harmful microbes but may also have adverse health effects[12]. Prolonged exposure to specific chemicals can lead to cancers of the bladder, colon, and colorectal, as well as immune system suppression[17,42]. Azo dyes, including Sudan I, are mutagenic and frequently used in the textile and food industries. Disperse Red 1 dye is mutagenic in human liver cells (HepG2) and lymphocytes, enhancing the occurrence of micronuclei, which indicates mutagenic activity[43]. Disperse Orange 1 has been shown to cause DNA damage through base-pair substitutions and frameshift mutations, disrupting the genetic code, and exhibiting cytotoxic effects by triggering apoptosis in HepG2 cells[44]. Direct Blue 13 produces a carcinogenic amine when it interacts with bacterial species on human skin. At the same time, Disperse Yellow 7 and similar dyes break down in natural water bodies to form carcinogenic amines[45]. Azure B, a positively charged dye, can intercalate between DNA and RNA strands, potentially inhibiting monoamine oxidase A, an enzyme crucial for human behavior. It also affects enzymes like glutathione reductase, which is essential for maintaining cellular redox balance. Triphenylmethane dyes, such as Basic Red 9, are widely used in textiles, leather, paper, and ink, but they can generate harmful aromatic amines when degraded under anaerobic conditions. Exposure to these dyes can lead to allergic dermatitis, skin irritation, genetic mutations, and cancer[46]. Crystal Violet, a triarylmethane dye, can cause mitotic poisoning, chromosomal damage, and abnormal cell accumulation during the metaphase stage. It has been linked to reticular cell sarcoma in various organs, including the bladder and vagina, and can cause chemical cystitis, skin irritation, digestive discomfort, as well as respiratory and renal failure[46]. Despite regulatory efforts, over 100 of the 3000 dyes tested for toxicity are still commercially available, posing a risk of cancer-causing amines[47]. The illegal disposal of toxic dyes by small-scale textile mills, often motivated by the pursuit of low-cost labor for the export market, presents a significant environmental hazard. Bioremediation technologies offer a promising solution, supporting sustainable development and promoting environmentally friendly economic growth and human health[48].

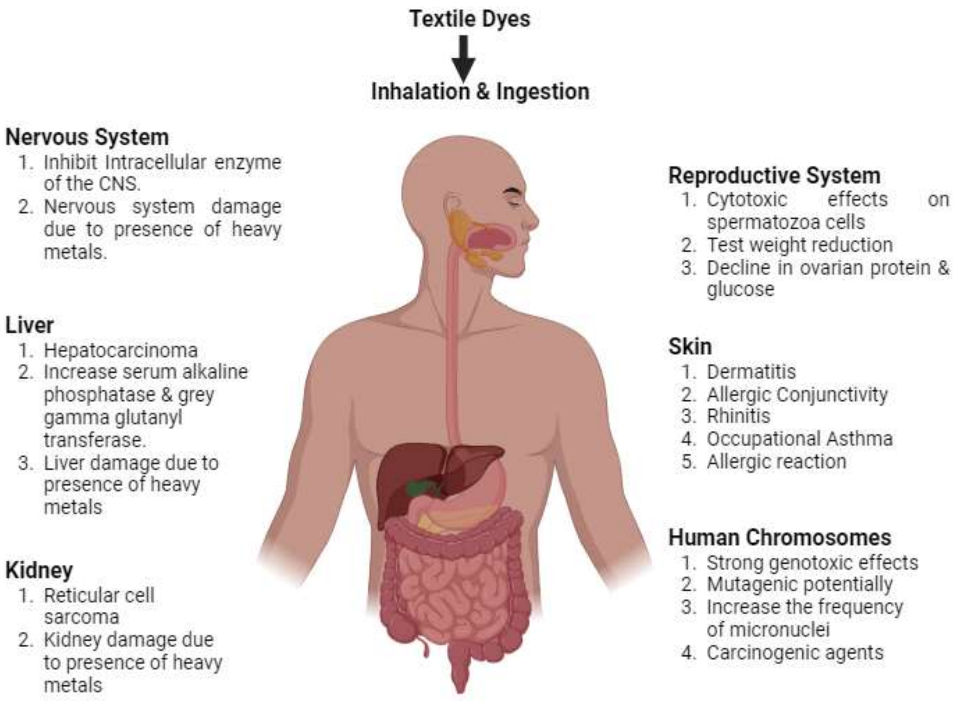


Figure 4 Impact of Dyes on the Human Body

1.7 History of Dyes

Before the 1850s, dyes were mainly derived from natural sources such as plants, trees, lichens, and insects. Evidence from North African tombs shows that dyeing practices date back over 5,000 years. Ancient hieroglyphs detail the methods used to extract and apply these natural dyes. Although there were numerous attempts to extract dyes from brightly colored plants and flowers, only a few natural dyes became widely used due to their limited durability. According to Abhahart (2019), many of these attempts failed because natural dyes are often unstable and exist in complex mixtures that were difficult to separate using the primitive techniques available at the time. However, research in the 1850s laid the foundation for the development of synthetic dyes, and by 1950, synthetic dyes had largely taken over the market[49].

Some of the most notable natural dyes include alizarin, indigo, and henna **Figure 6**. Alizarin is a crimson pigment extracted from the roots of the madder plant (*Rubia tinctorium*). Two other significant red dyes come from scale insects: Kermes, derived from the *Coccus ilicis* (or *Kermes ilicis*) insect that infests the Kermes oak [50], and cochineal, obtained from the *Dactylopius coccus* insect found on prickly pear cacti in Mexico. It takes approximately 320,000 cochineal insects to produce a kilogram of dye. The key components of these dyes' kermes and carminic acids were found to be similar by 1950. Many natural colorants are water-soluble due to sugar residues, though these sugars are often removed during the isolation process[51]. Indigotin considered one of the oldest known dyes, is a blue pigment derived from the *Isatis tinctoria* herb in Europe and the *Indigofera tinctoria* plant in Asia. Both alizarin and indigo are highly valued for their dyeing properties, with indigo, in particular, being the preferred dye for denim, although synthetic indigo has now largely replaced its natural form[52].

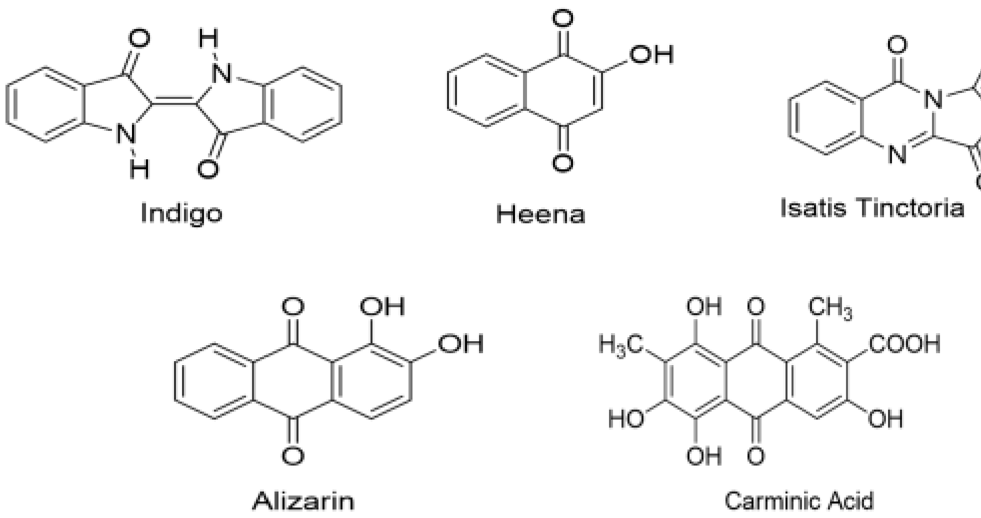

Indigo
Heena
Isatis Tinctoria
Alizarin
Carminic Acid

Figure 5 Natural Based Dyes

A derivative of indigo, Tyrian purple **Figure 7**, was produced by the Phoenicians using the glands of *Murex brandaris*, a type of snail found in the Mediterranean Sea. It took 10,000 snails to produce just 1.5 grams of dye, a result of 15,000 experiments conducted in 1910. Known as royal purple throughout history, this dye was reserved for royalty, emperors, and high priests, as mentioned in the Hebrew Bible and depicted in mosaics celebrating Roman emperors in Ravenna. The Mediterranean purple industry eventually faded as the Eastern Roman Empire declined in the 1550s.

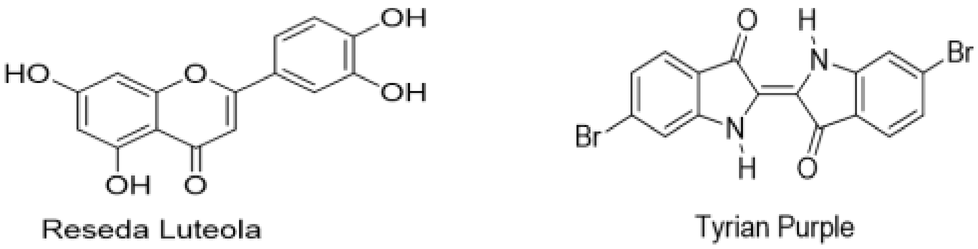

Reseda Luteola
Tyrian Purple

Figure 6 Structure of Indigo

The process of producing yellow dye involves extracting Angelini G.L. from the leaves of the weld plant (*Reseda luteola*) and quercetin from the bark of *Quercus tinctoria*, a North American oak. Flavonoid compounds, predominantly found in higher plants, are responsible for the vivid colors in many flowers. These compounds can produce nearly all the colors of the spectrum, except for green. The color Lincoln green, often associated with Robin Hood and his band of Merry Men, is derived from the yellow crystalline pigment luteolin[53]. Carotenoids, which produce yellow to red hues, are present in all green plants. Lycopene, the pigment responsible for the red color in tomatoes, is the source of all carotenoids. Crocetin, a natural yellow dye that has been used for centuries, is derived from the stigmas of *Crocus sativus* and is unquestionably a derivative of lycopene. Flavonoid and carotenoid colorants that would have been stable under ancient extraction methods are exceptionally rare **Figure 8**.

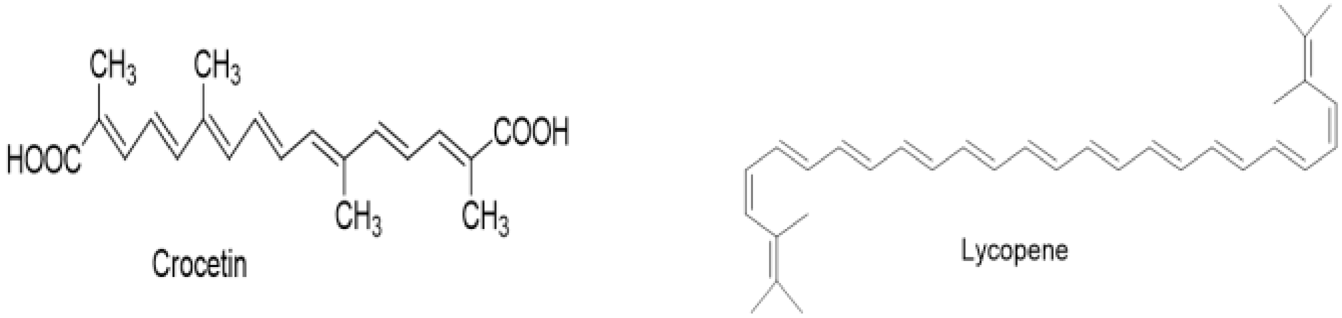


Figure 7 Structure of Flavonoids and Carotenoids Colorants

1.8 Classification of Dyes

Insects, minerals, and plant debris are examples of natural sources of dyes. Petrochemical feedstock can also be used to make dyes in factories. Using coal tar, Perkin created the first synthetic dye, Mauveine. When it comes to natural dyes, indigo is well-known for its vivid blue hue, which is produced by the fermentation of plant leaves. The red lac dye is made from lac, a small insect's resinous defensive secretion.

1.8.1 Dyes Can Be Classified into Different Categories Based on the Application on Fabric:

Direct Dyes: Water-soluble dyes are used to dye fabrics directly in an aqueous solution. The process of dyeing fabrics involves several steps, such as soaking the fabric in a dye solution, removing the excess dye, and drying the fabric for further analysis. Since polar dyes are attracted to a wide range of fiber, including cotton, silk, jute, linen, and so on, direct dyes can be applied to these materials. Rather than forming a chemical link, these dyes bind to cellulosic fiber via weak hydrogen bonds and Vander Waals forces. Because of their lengthy length and flat structure **Figure 9**, Vander-Waals molecules can lie beside cellulose fiber, increasing the possibility that hydrogen bonds, dipoles, and Vander-Waals will form[54].

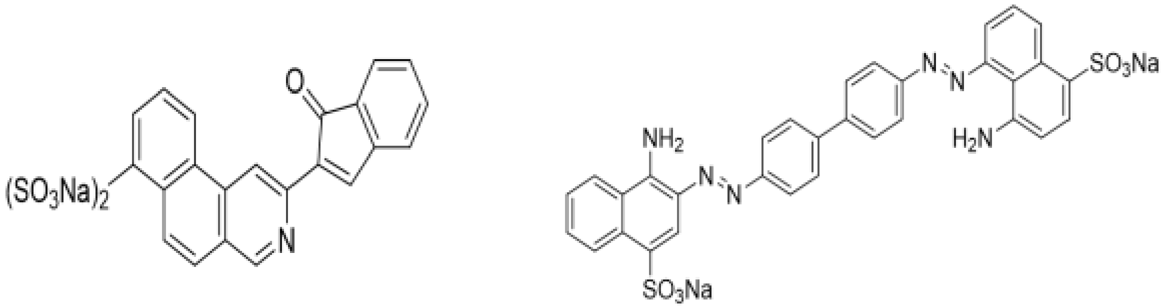
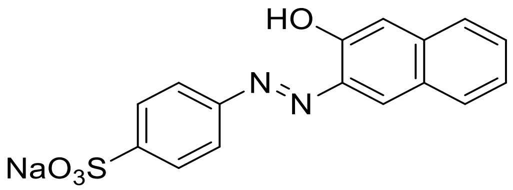


Figure 8 Direct Dyes

Direct Dyes are further classified into two categories:

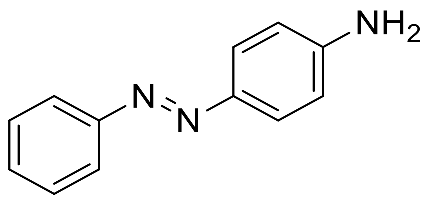
Acidic dye: Anionic dyes contain acidic groups such as SO_3H and COOH, which confer anionic properties on the dye molecule. These dyes are commonly used on protein fibers such as wool and silk, owing to the specific chemical properties of these fibers. Notably, acidic groups in the anionic dyes facilitate the formation of direct bonds with basic groups in fiber, allowing for efficient dyeing of the fiber. This is because the acidic groups can react with the basic groups of the fiber, forming a strong bond **Figure 10**.



sodium (*E*)-4-((3-hydroxynaphthalen-2-yl)diazenyl)benzenesulfonate

Figure 9 Acidic Dye

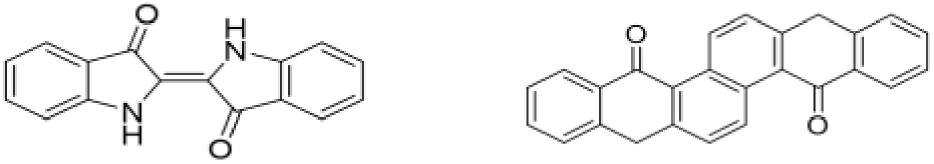
Basic dyes: Cationic dyes contain cationic groups composed of basic radicals such as groups NH_2, NHR, and NR_2. As they are obtained directly from nature, these dyes are mainly used for cotton fiber since they are a natural element in the fabric **Figure 11**.



(*E*)-4-(phenyldiazenyl)aniline

Figure 10 Basic Dye

Vat Dyes: Natural coloring materials are used in the Vat dyeing method. They are dissolved through fermentation and submerged in wooden vessels. This process takes place while the dye is being preserved in the wooden vessel. It is crucial to remember that vat dyes cannot be applied directly to fabric since they are not soluble in water. Instead, they must be applied to the fabric after being dissolved in a solvent. It is important to note that cellulosic fabrics are the only materials that can be dyed using vat dyes. Because of their special characteristics, they must go through a certain procedure to dissolve in a certain solvent before being applied to cloth. We call this procedure "vatting." In general, the textile industry relies on the vat dyeing process, a sophisticated and specialized method for coloring materials, to produce high-quality results **Figure 12**, [55].



Vat blue

Vat orange

Figure 11 Vat Dyes

Mordant Dyes: These colors are insoluble in water. The third material serves as a cohesive agent that secures the dye onto the fabric. In the dyeing process, fibers are immersed in a mordant, dried, and then immersed again in the dye solution. The mordant forms a complex with the dye and gets deposited onto the fiber, giving it a permanent shade by reacting with it. Basic mordants like metal salts such as $Fe(OH)_3$

and $Al(OH)_3$ are used for acid dyes, while basic dyes require an acid mordant, such as phosphoric acid or tannic acid. Alizarin is a good example of a mordant dye. It gives different colors when used with different materials. For instance, Al and Sn salts produce a red color. On the other hand, Cr mordant produces brownish-red tones; Fe mordant produces black violets **Figure 13**.

1,2-dihydroxy-3-nitroanthracene-9,10-dione

1,2-dihydroxyanthracene-9,10-dione

Figure 12 Mordant Dyes

Azo dye: These colors are applied directly to the fiber through a process involving diazotization and coupling at low temperatures. The fabric is first soaked in an alkaline phenol solution, dried, and then immersed in a cold diazonium salt solution. The dye is developed by directly dyeing the fiber with the azo dye. These dyes are also referred to as "Ice colors" because they appear to form at low temperatures within the fabric, resulting in a dye that develops close to water. The process of creating these dyes can be reversed as well. In this case, an amine solution is applied to the fabric, which is then diazotized and developed using an alkaline phenol solution after immersion. This type of dye is also known as "ingrain dye." These dyes have proven especially effective in producing printed fabrics **Figure 14** [43].

(*E*)-1-((4-nitrophenyl)diazenyl)naphthalen-2-ol

(*E*)-4-(phenyldiazenyl)benzene-1,3-diamine

Figure 13 Azo Dyes

Disperse Dye: Disperse dyes are a type of insoluble dye that is capable of dissolving certain synthetic fibers. Typically, these dyes are administered in the form of a finely divided dye dispersed in a soap solution in the presence of a solubilizing agent, such as phenol, cresol, or benzoic acid, within a dispersion of finely divided dye. The absorption of dye into the fiber requires high temperatures and pressures to facilitate the process. Synthetic fiber, such as acetate rayon, Dacron, Nylon, and others, are dyed using dispersed dyes **Figure 15** [56].

1-amino-4-hydroxyanthracene-9,10-dione

1,4-bis(methylamino)anthracene-9,10-dione

Figure 14 Disperse Dyes

1.8.2 Dyes are categorized based on the Chromophore group:

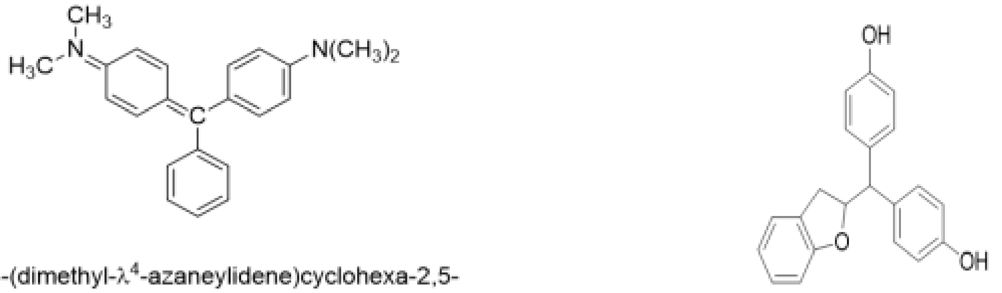
Nitro Dyes: Nitro dyes are a type of dyes that have chromophores consisting of nitro and hydroxyl groups. The nitro group, a functional group comprising a nitrogen atom linked to two oxygen atoms, gives the dye a yellow or orange color. Conversely, the hydroxyl group is accountable for the dye's ability to dissolve in water. An instance of a nitro dye is naphthol, frequently employed in the textile sector to color cotton and other types of natural fiber **Figure 16**.


sodium 2,4-dinitro-7-sulfonaphthalen-1-olate

1-nitrosonaphthalen-2-ol

Figure 15 Nitro Dyes

Triarylmethane Dyes: Triarylmethane dyes are a group of artificial dyes distinguished by the inclusion of triphenylmethane as the central component in their chemical composition. These dyes are extensively utilized in the textile business because of their capacity to bestow vivid and saturated hues on garments. The backbone of these dyes contains three aromatic rings that are fused at the center by a carbon atom. Additionally, these dyes contain aminated or hydroxyl groups, which act as auxochromes, enhancing their ability to absorb light and produce bright colors **Figure 17** [57]**.**


4-((4-(dimethyl-λ^4-azaneylidene)cyclohexa-2,5-dien-1-ylidene)(phenyl)methyl)-*N*,*N*-dimethylaniline

4,4'-((2,3-dihydrobenzofuran-2-yl)methylene)diphenol

Figure 16 Triarylmethane Dyes

Anthraquinone Dyes: Anthraquinone is a basic structure found in dyes. It is important to note that anthraquinone itself is colorless, but when an electron donor group has been added to the first, fourth, fifth, and eighth positions, it becomes suitable for the formation of color. There are two classes of anthraquinone dyes: Natural anthraquinone dyes and synthetic anthraquinone dyes. Natural dye anthraquinone is obtained from the environment, whereas anthraquinone sulphonate and nitroanthraquinone dyes are synthetic dyes, obtained through sulphonation and nitration of anthraquinone, respectively **Figure 18** [58].

sodium 4,8-diamino-1,5-dihydroxy-9,10-dioxo-9,10-dihydroanthracene-2,6-disulfonate

sodium 4,8-diamino-1,5-dihydroxy-9,10-dioxo-9,10-dihydroanthracene-2,6-disulfonate

Figure 17 Anthraquinone Dyes

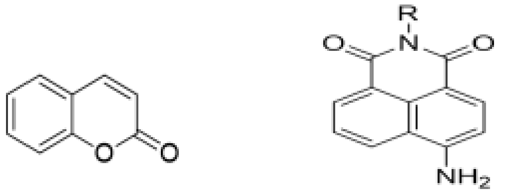
Indigo Dyes: Indigo dye, also known as Indigofera tinctoria, is a natural dye that has been used for centuries to color textiles. This deep blue dye is primarily sourced from the leaves of the Indigofera plant, which is native to tropical regions of Asia and Africa. The dyeing process involves fermenting the leaves in water to release the blue pigment, which is then extracted and processed into a powder form. The color of Indigo dye comes from the chemical compound indigotin, which is formed by combining and bonding multiple double bonds together. This gives the dye its characteristic deep blue hue, which can range from a pale blue to a dark, almost black shade depending on the concentration of the indigotin. Indigo dye is a crystalline powder that is soluble in a variety of solvents such as DMSO and sulfuric acid. It is primarily used for dyeing denim fabrics and clothes due to its ability to create long-lasting, fade-resistant blue colors. In addition to its use in the textile industry, indigo dye has also been used for medicinal purposes in traditional medicine practices. Overall, Indigo dye is a versatile and valuable natural product that has played an important role in cultures and industries worldwide **Figure 19**.

(*E*)-[2,2'-biindolinylidene]-3,3'-dione

1,2-dihydroxyanthracene-9,10-dione

Figure 18 Indigo Dyes

Fluorescent Dyes: Fluorophores dyes, are molecules that do not contain any protein. These dyes have a unique property of absorbing light at a specific wavelength and then re-emitting light at a longer wavelength after absorption. This process, known as an optical transaction, results in the emission of light that originates from the optical transaction. Fluorophores are also known as charge-transfer dyes or charge-transfer pigments. They are used in various applications, including bioimaging and medical diagnosis. Examples of fluorophores include rhodamines, which are widely used in fluorescence microscopy, cyanines, which are used in DNA sequencing, and coumarins, which are used in detecting fatty acids and amines **Figure 20** [59].



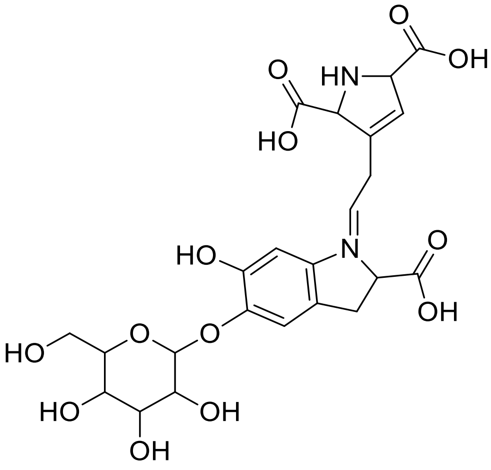
2*H*-chromen-2-one

Napthalimides

Figure 19 Fluorescent Dyes

1.8.3 Classification of Dyes Based on Application:

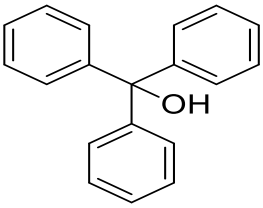
Food Dye: Food-based dyes are chemically substantialized in the food and beverage sector to provide color to different food items. These colors are offered in liquid and powder forms and are used to enhance the visual attractiveness of food, making it more enticing to consumers. The main objective of food dyes is to augment the visual aspect of the meal, rendering it more aesthetically pleasing and attractive to the observer. Food dyes can be categorized into two groups: natural and synthetic. Food dyes or colorants sourced from plant, animal, or mineral sources are known as natural. They are generally considered safer and healthier than synthetic food dyes but have some limitations. They are less vibrant and less stable than synthetic dyes, and they can also be more expensive. On the other hand, synthetic food dyes are artificially manufactured from petroleum-based chemicals. They are widely used in the food industry because they are more colorful, stable, and cost-effective than natural dyes. Synthetic food dyes provide a wider range of color options, and they are also easier to use in processing. However, studies have shown that synthetic food dyes may have harmful effects on human health, especially in children. These dyes have been linked to food intolerance and hyperactivity in children that resemble symptoms of ADHD. As a result, many countries around the world have banned the use of synthetic food dyes in their food products. In conclusion, food dyes are an essential part of the food and beverage industry, as they help to enhance the appearance of food products and make them more attractive to consumers. However, synthetic food dyes should be carefully monitored and regulated to ensure that they do not pose any health risks to consumers, particularly children **Figure 21**[60].



Betanin

Figure 20 Food Dye

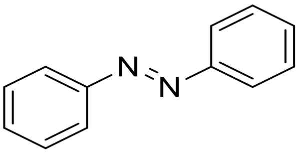
air Dye: Hair dyes are used to color hair by targeting the melanin in the hair follicles. Melanin is the pigment that gives hair its natural color, and variations in its concentration, such as eumelanin and pheomelanin, can cause changes in hair color. Hair dyes are often preferred in such cases. Eugene Schueller was the first person to discover synthetic hair dye. A chemical reaction occurs when hair dye is applied, allowing the dye to penetrate the hair follicles. However, this can cause a variety of side effects, such as hair loss, roughness of the hair, and eye allergies **Figure 22**.



Triphenylmethanol

Figure 21 Hair Dye

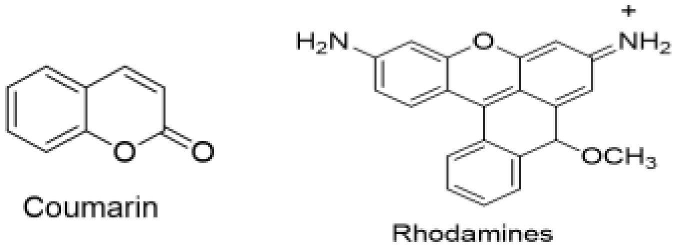
Biomedical Dye: Dyes are a crucial component in the production of drugs as they provide color to the medication. However, their role extends beyond that, as they also play a significant role in medical testing. One test that utilizes dyes is Fluorescein, which is used to produce accurate results for a specific purpose. This test involves using a dye to highlight certain parts of the body, allowing medical professionals to diagnose and treat certain conditions. Apart from medical testing, dyes are also widely used in the medical field for various purposes. For instance, they are used as drug colorants to help differentiate between different medications and their dosages. They are also used in vital staining, which is a technique used to highlight specific cells or tissues in a sample. Additionally, dyes are used in tracing, where they are used to track the movement of certain substances in the body. Moreover, dyes are used in chemotherapeutics to help identify cancerous cells in the body. Azo dyes, in particular, are mainly used as medicinal dyes due to their ability to produce bright and vibrant colors. Overall, the use of dyes in medicine is critical and has proven to be invaluable in the diagnosis and treatment of various medical conditions **Figure 23** [30,61].



Azo Dye

Figure 22 Biomedical Dye

Laser Dye: Laser dyes like coumarin and rhodamines are used as lasers in specific mediums. The color emitted by the laser dye depends on the medium. Coumarin emits in the green region of the spectrum, whereas rhodamines emit in the yellow-red region. However, laser dyes are generally toxic in nature due to the solvent in which they are dissolved, causing many carcinogenic and mutagenic effects on the human body. Examples of laser dyes are Coumarin and Rhodamines **Figure 24**.



Coumarin Rhodamines

Figure 23 Laser Dye

1.9 Dyeing

The dyeing process occurs when a dye interacts with a fiber and infiltrates its inner structure. This process involves two primary stages: adsorption, where the dye transfers from the aqueous solution to the fiber's surface, and diffusion, where the dye moves deeper into the fiber. Dyeing can also include the precipitation of dyes within the fiber (as seen with vat dyes) or a chemical reaction between the dye and fiber (as with reactive dyes). Printing, which involves applying different colors to fabric to form a pattern, is considered a form of partial dyeing from a coloration perspective. Both dyeing and printing are intricate processes influenced by factors such as fiber types, yarn or fabric structures, dye types, chemical auxiliaries, and dyeing technologies (Berns B. M., 2000). These factors can be mathematically described using the kinetics of dyeing or dyeing equilibria. The concept of the dyeing curve explains the dyeing phenomena, and the optimization and uniformity of color are also tied to kinetic processes, making kinetic dyeing an essential aspect. Additionally, the functional groups present in both the fiber and the dye significantly impact the dyeing process[62].

1.10 Chemistry of Dyeing

Dyes are most effective on natural fibers like cotton, nylon, wool, silk, polyester, jute, etc. Among these, wool is the easiest to dye, followed by cotton. Nearly all of these fibers require mordant, a substance that helps bond the dye to the fabric. The key to successful dyeing is selecting the right dye from the appropriate source to achieve beautiful tones and colorfast results. The binding of dyes to fibers is a complex process that involves direct bonding, hydrogen bonds, and hydrophobic interactions between dye to fabric. Mordants act like a bridge between the dye and the fiber that enhances the dye's staining ability and improves its fastness properties. Mordants incorporated insoluble dye compounds within the fiber. An example of alizarin's interaction with Nylon-5, which also contains peptide linkages. Additionally, the chemistry between dyes and fabric materials is influenced by the hydrophilic/hydrophobic properties of the fabric and the formation of salt linkages between functional groups on the dye and fabric [52].

1.10.1 Mechanism of Dyeing

There are four steps in the dyeing process, and each one can regulate both the rate and the outcome of the dying.

1. Dye transfer to the fiber surface via the dye bath.
2. Dye substance adsorption at the fabric.
3. Dyestuff diffusion via the fiber's interior structure.
4. The dye molecules' anchoring and fixing in the proper places.

1. **Dye transfer to the fiber surface via the dye bath**: A dyeing machine uses a pump to transfer the dye-alcohol mixture to the fiber during the dyeing process. Convective diffusion refers to the macroscopic speed at which the dye molecules move [63]. The liquid speed increases from zero at the

fiber surface to the bulk phase value, as there is no macroscopic flow at the fabric surface. This creates a hydrodynamic boundary layer, which is a liquid layer that flows from the fabric surface into the dye bath. The gradient in dye concentration formed in this region is called the diffusional boundary layer, and it is approximately ten times thinner than the hydrodynamic boundary layer[50]. This liquid layer marks the final stage of the dye molecule's journey from the liquid to the fiber surface, where it is limited by diffusion. If the process is diffusion-controlled, the dye uptake rate increases linearly over time. When diffusion within the fiber is fast and the boundary layer at the fiber surface is thick, liquid diffusion plays a more significant role at lower dye-liquor flow rates. The rate of dye uptake is not influenced by the convective speed of the dye, which is generally faster than the adsorption rate at the fiber surface. However, as the thickness of the boundary layer decreases with lower flow rates, increasing the liquid flow can result in a higher depletion rate. It is also possible that liquid diffusion controls the process only during specific dyeing stages.

2. **Dye substance adsorption at the fabric** - The dye molecules in the dye bath migrate in the direction of the fiber during the first stage of the dyeing process, and those that are closest to the fiber surface get adsorbed on it. These molecules form an incredibly thin layer on the fiber surface. The dye molecules that remain within the dye bathwill be adsorbed as long as this adsorbed layer moves further into the fiber. A schematic representation of a fiber **Figure 25** shows the adsorption of dye molecules on the surface of the fiber [64].

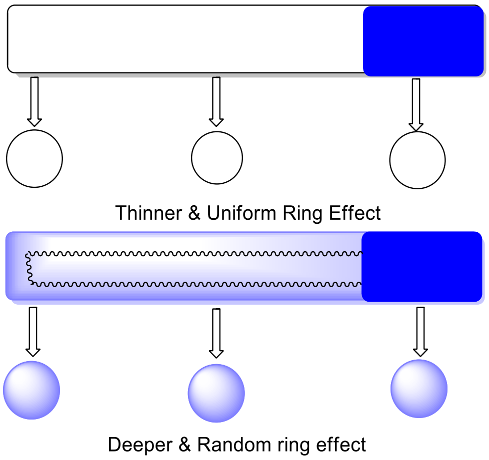


Figure 24 Adsorption of Dye on fabric

3. **Dyestuff diffusion via the fiber's interior structure:** The diffusion mechanism for cellulosic and direct dyes is widely accepted as the transfer of dye from an aqueous solution through the adsorption on and migration over capillary surfaces [65], also known as pores. The dye attaches to the pores in a dynamic reversible equilibrium that exists between the dyes in the water of the pores and the adsorbed dye molecules[66]. The process of dye transfer involves three stages, with the slowest being the diffusion from the fiber surface into the interior, also known as film diffusion. This is different from liquid diffusion in the boundary layer and determines the overall rate of dye transfer. However, the situation for direct dyes on cotton is often different, as explained in the next section. The diffusion in the fiber is several orders of magnitude slower than in water, primarily due to the greater mechanical obstruction to movement caused by the fiber and the stronger physicochemical attractions between the fiber and the dye[67].

4. **The dye molecules' anchoring and fixing in the proper places**: In the final stage of dyeing, known as fixation, the dye molecules find appropriate locations within the fiber and become anchored there. The strength and type of forces used to hold the dye molecules in place vary depending on the connection between the dye and the fiber.

Bonds Between the Fiber and the Dye –

The coloration of dye is contingent upon the characteristics of both the dye and the fiber. The dye molecule is affixed to the fiber using forces that can be classified as:

1. Vanderwall forces
2. Hydrogen bond
3. Ionic bond
4. Covalent bond

Van der Waal forces: When the electrons of one atom and the nucleus of another atom come close enough, feeble forces of attraction exist between them. These forces are referred to as Van der Waal forces. While each force may be weak on its own, when combined, they are deemed powerful enough to be the primary attraction forces between dye and fiber. Specifically, the bonding of dispersion dyes to polyester fiber is achieved through the utilization of Van der Waal forces.

Hydrogen bond: Some atoms found in dye molecules have gentle forces of attraction that only manifest when they are near other atoms in the fiber. If these forces are strong enough, they create a chemical connection. Cellulose fiber can hydrogen-bond certain direct and vat dyes.

Salt linkages or Ionic bonds: When a dyestuff is dissolved in a solution, its molecules separate into positive and negative charged particles called ions. One of these ions is colored, depending on the type of dyestuff. The colored ion can be either cationic (carrying a positive charge) or anionic (forming bonds). For instance, when the anionic ($-SO_3$) groups in an acid dyestuff come in proximity to a cationic ($-NH_3^+$) group in wool, silk, or nylon, the resulting bond can be a salt linkage or a covalent bond.

Covalent bonds: Covalent bonds are a form of chemical bonding that generates exceptionally robust forces that are challenging to disrupt under typical circumstances. An instance of covalent bonding occurs when cellulose is linked to a reactive dye by the formation of chemical bonds with the suitable atom. Different dyes show different affinity towards different fabrics as shown in **Table 3**

Table 2 Different Dyes Having an Affinity towards Different Fabric

Fiber	Dye	Dye-fiber bond
Cellulosic fiber: Cotton, rayon, jute	Direct dye, Vat dye, Sulfur dye, Reactive dye	Vander walls force of attraction, Hydrogen bonds, and Covalent forces
Protein Polyamide: Wool, Silk, Nylon	Acid dye, Reactive dye	Ionic and Covalent bonds
Polyesters and Acrylic	Disperse dye	Vander walls, Hydrogen, and Ionic bonds

1.11 Coumarin as a Dye

Coumarin, 1,2-benzopyrone, or o-hydroxycinnamic acid-8 lactone was discovered in 1822 by Vogel, it was first isolated from tonka beans (Dipteryx odorata). Chemically, coumarin (2*H*-1-benzopyran-2-one) is part of the lactone subgroup, which includes two key structures: benzo-α-pyrone (commonly known as coumarin) and benzo-γ-pyrone (known as chromone). These compounds differ in the position of the carbonyl group on the pyrone ring position 1st in coumarin and position 2nd in chromone. Coumarin derivatives are widely used in pharmaceuticals and medicine due to their significant dyeing, optical, and biological properties, which play a role in developing new drug therapies, and dyeing processes. Over the years, various methods for synthesizing substituted coumarins have been developed, though plant-derived coumarin typically produces higher-quality compounds. Some derivatives also contain fused furan rings or other structural variations. Coumarins are known for their six-membered ring structure attached to the coumarin core and are recognized as biologically active heterocycles. In the context of industrial development, the production and use of coumarin and its derivatives can also serve as a measure of a country's economic advancement. Azo compounds are extensively utilized in various applications owing to their distinctive characteristics. Azo dyes can color various materials such as cotton, wool, silk, linen, viscose rayon, distemper, printing ink, and even edibles. Some azo dyes also have useful therapeutic effects. Azo compounds became widely used in medical chemistry with the discovery of the powerful antibacterial activities of sulphanilamide, the active metabolite of the azo dye Prontosil Rubrum. Sulfa medicines, such as sulphasalazine, continue to be utilized for the treatment of Crohn's disease and ulcerative colitis, despite the widespread adoption of penicillin antibiotics in most antimicrobial contexts[68]. Synthetic dyes provide challenges in terms of degradation because of their strong resistance to heat and light, and their decomposition in the environment can lead to the production of cancer-causing effects on living creatures. The discharge from textile factories is a significant source of water contamination. To tackle these problems, it is necessary to produce eco-friendly colors through synthesis. Coumarins are a specific class of heterocyclic compounds that incorporate oxygen as a constituent of the heterocyclic ring. Benzopyrones are a type of heterocyclic compound that is formed when a pyrone ring is fused with a benzene nucleus. There are two different types of benzopyrones: benzo-α-pyrones or 2*H*-chromene-2-one, which are popularly known as coumarins, and benzo-γ-pyrones or 4*H*-chromene-3-one, which are called chromones **Figure 26**. The sole distinction is in the placement of the carbonyl group within the heterocyclic ring.

2*H*-chromen-2-one

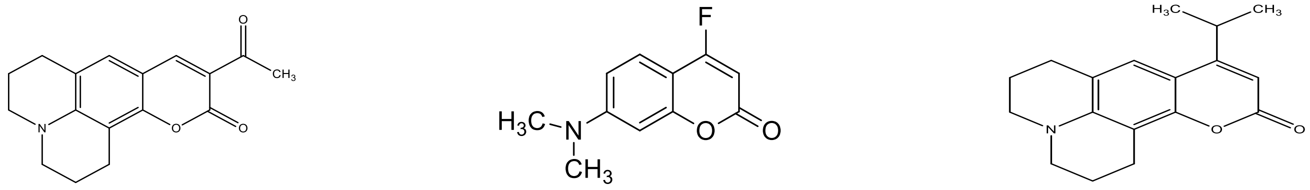
4*H*-chromen-4-one

(1) (2)

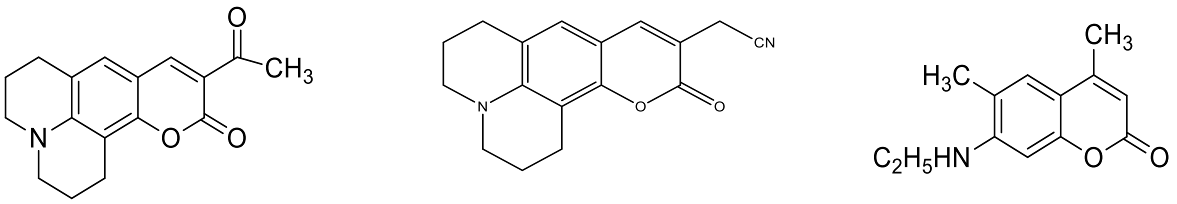
Figure 25 Types of Chromones

Coumarins are organic molecules found abundantly in plants as secondary metabolites. These compounds are significant due to their notable characteristics, including antibacterial qualities, their ability to function as fluorescence biosensors, and their capacity for dyeing[69]. Coumarins possess many synthetic and modifiable characteristics, rendering them indispensable for specific applications. Unsubstituted coumarin is white. However, when coumarins have strong electron-donating groups, their absorbance causes a shift towards longer wavelengths in the UV-visible area. This shift leads to colors that range from yellow to orange to red. Coumarins possess characteristics of both fluorophores and chromophores, rendering them very desirable in the commercial polymer industry.

Coumarin Azo compounds exhibit intense coloration and are extensively utilized as dyes and pigments across diverse applications. These areas encompass textile dyeing, non-linear and photo-switching dyes, chemical analysis, pharmaceuticals, photochromic materials, photoelectronic, and optical information storage. Chemists have long been intrigued by the synthesis of coumarin dyes due to the presence of this heterocyclic nucleus in various natural compounds. These colors are also valuable in chemical, biological, physical, and medicinal contexts. While coumarin itself does not exhibit fluorescence, the introduction of an electron-withdrawing group, such as a diazotized aromatic amine or an acetyl group, greatly enhances its fluorescence. Due to their straightforward production, coumarins are often amenable to chemical modification. The research on coumarin-based dyes, which consist of heterocyclic diazo components, has been thorough due to their strong coloring ability and exceptional brightness. Coumarin derivatives serve as an inhibitor of yellowing and as a fluorescent brightening agent in different paper grades employed for printing and writing purposes. These paper grades are manufactured using both coated and uncoated wood-free papers. Coumarin and its derivatives are frequently employed as a fluorescent chemical in solar cells [70]. Moreover, coumarin is extensively employed as a fluorescent indicator for measuring pH levels and can also be utilized for detecting both metal ions and anions. Coumarin is an inexpensive and highly specific chemical that enables precise identification of harmful heavy metals, anions, and enzymes. Coumarin laser dyes are predominantly employed for pigmenting substrates in the realms of biological and medical research, as well as in the domains of non-linear optics and optical data storage systems [71]. The literature mentions several commercially available coumarin laser dyes, such as coumarin 102, coumarin 355, coumarin 2, coumarin 3, coumarin 152A, coumarin 152, coumarin 522, coumarin 500, and others as shown in **Figure 27**.



Coumarin 7 **Coumarin 35** **Coumarin 102**



Coumarin 33 **Coumarin 337** **Coumarin 338**

Figure 26 Commercial-Based Coumarin Dyes

Coumarin dyes have poor photostability and degrade when exposed to laser light, leading to the formation of by-products that can absorb light in the laser zone, resulting in undesirable effects. Additionally, the intensity of the coumarin laser dye beam is limited by saturation and cannot be increased beyond a certain pump power threshold due to its photo-quenching effect. Despite these limitations, coumarin is widely used as a fluorescent chemosensor in environmental chemistry, analytical chemistry, and medicinal science. This is due to the benefits of coumarin, which is composed of benzopyrone, including a high fluorescence quantum yield, a large Stokes shift, excellent light stability, and low toxicity. Coumarin is commonly used to detect anions such as cyanide, fluoride, pyrophosphate, benzoate, and metal ions like Hg (II), Cu (II), Zn (II), Ni (II), Co (II), Pb (II), Fe (II), and Al (III). Modifying the coumarin structure can lead to shifts in the fluorescence band. For example, introducing a methyl group at the 3th position of 7-hydroxy coumarin results in a spectral redshift. Similarly, placing electron-repelling groups at positions 3th, 5th, or 7th, or electron-attracting groups at the 3rd position, can cause the fluorescence band to shift to a higher wavelength. Mercury, which poses significant environmental and health risks, can be detected using a coumarin-thiazole benzo-crown ether-based chemosensor. This sensor takes advantage of the strong coordination between Hg (II) and the crown oxygen and thiazole nitrogen [72].

1.12 Conclusions

Based on a literature survey, it was discovered that existing coumarin dyes tend to lose their original color and fade when exposed to high temperatures and light. Some coumarin dyes were found to have suboptimal dyeing characteristics. It was observed that the existing azo coumarin dyes use mordant during the dyeing process. The use of mordant causes many harmful effects to the environment by increasing water pollution. Our goal is to study coumarin-based dyes that display consistent dyeing and fluorescent properties. Our research explores how conjugation affects the dyeing properties of newly synthesized coumarin derivatives.

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