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Sustainable Dyes and Pigments

Bridging Tradition and Technology

Edited by Nasser Awwad and Ibrahim S. Yahia



Sustainable Dyes and Pigments - Bridging Tradition and Technology

*Edited by Nasser Awwad
and Ibrahim S. Yahia*

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Meet the editors



Dr. Awwad obtained his Ph.D. in inorganic and radiochemistry from Ain Shams University, Egypt, in 2000, and completed his postdoctoral work at Sandia National Laboratories in New Mexico, USA, in 2004. He was an Associate Professor of Radiochemistry and a Professor of Inorganic and Radiochemistry at the Egyptian Atomic Energy Authority in 2006 and 2011, respectively. He has been a professor at King Khalid University (KKU) in Saudi Arabia since 2011. He has authored eight book chapters, edited eight books, and published 372 papers in highly ranked journals. He has reviewed and supervised numerous Ph.D. and MSc students. He participated in twenty-five international conferences in South Korea, the United States, Lebanon, Saudi Arabia, Egypt, and India. He participated in six projects with King Abdulaziz City for Science and Technology (KACST), Saudi Arabia, and Sandia National Laboratories, focusing on the conditioning of radioactive sealed sources and wastewater treatment. Dr. Awwad is a leader and member of many research groups investigating the utilization of nanomaterials for the treatment of inorganic and organic pollutants. He is a member of the Arab Society of Forensic Sciences and Medicine and the Saudi Society for Clinical Chemistry. Professor Awwad has been recognized for his highly influential research, ranking him within the top 2% of most-cited scientists globally. This prestigious citation, based on data from Stanford University, has been sustained since 2021.



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**Adsorption Kinetics and Equilibrium Studies of Organic Dyes by Zeolites
from Aqueous Solutions**

*by Sharifah A.E. Asiri, Murad A. Eissa, Mohamed S. Hamdy and
Nasser S. Awwad*

Preface

This book is divided into two sections; the first section covers three topics. In the first chapter, the authors showed that the industry can achieve sustainable solutions by reclaiming natural dyeing and integrating traditional techniques with technological advancements such as digital printing, waterless dyeing, and biotechnology. Hence, the dye industry, a cornerstone of global economic and cultural heritage, remains vital and contributes to a sustainable future by harmonizing innovation with tradition. In the second chapter, it explores the limitations of natural dyes, which led to their steady decline and transition to modern-day synthetic dyes. Additionally, the authors discuss the various classifications of natural dyes and their corresponding chemical structures. In a third chapter, the authors explore the fundamental principles of supercritical CO₂ dyeing, emphasizing the critical properties required for dyes to achieve optimal solubility, thermal stability, and fiber affinity under high-pressure conditions. It also outlines the technical requirements necessary for industrial-scale applications, including specialized equipment, process optimization parameters, and fiber adaptability.

On the other hand, the second section covers four topics. In chapter 4, the authors stated that natural pigments, such as anthocyanins, can be incorporated into food packages to enhance shelf life due to their antioxidant and antimicrobial activities, among others. They have been applied in polymeric matrices to preserve the sensorial and nutritional properties of food, extending their shelf life. In Chapter 5, the authors present three applications of optical porphyrin-based sensors: continuous blood-oxygen measurements for use in intensive care units (ICUs), pressure-sensitive paint for aeronautical wind tunnel measurements, and pH imaging in cementitious materials. Their unique chemical and physical characteristics make them well-suited for long-term use as chemical sensors. In chapter 6, the authors studied the molecular conformation, Highest Occupied Molecular Orbital- Lowest Unoccupied Molecular Orbital (HOMO-LUMO) energy levels, UV-Vis absorption spectra, maximum absorption wavelength, and prediction of the proportion of components in the black dispersed dye composition using the optimized DFT/TD-DFT (time-dependent-density function theory) calculation method. In the last chapter, our team presents recent developments in efficient adsorbents for the removal of organic dyes, including Rhodamine B (RhB), Methyl Violet (MV), and Phenol Red (PR), which are essential for sustainable wastewater treatment. This study investigates the removal of these three dyes using both commercial and dealuminated zeolites, comparing their adsorption efficiencies.

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Section 1

Advanced Chromic Materials: From Molecular Design to Functional Applications

Chapter 1

Chemistry and Application of Natural Colourants

Ruma Chakrabarti

Abstract

This chapter dwells on the history of dyes and dyeing across from pre-historic times and early civilizations across the world to present day coloration and techniques. This chapter explores the limitation of natural dyes that lead to its steady decline and transition to the modern-day synthetic dyes. This chapter discusses the various classification of natural dyes and also the chemical structure of these dyes. The prevalent and common methods of application of natural dyes are also discussed along with the comparison of the impacts of the usage of the natural colourants as compared to the synthetic dyes. The scope of the use of natural dyes on the performance criteria of fastness, and the durability properties of these coloured materials during use are also touched upon. The revival of dyeing with natural dyeing techniques in recent days will be emphasised in the context of rising concerns about fast fashion and growing demand for circular economy. This will also focus on standardisation techniques for the dyes so as to establish consistency in the application process.

Keywords: natural colorants, annatto, turmeric, application on fabrics, properties, indigo

1. Introduction

Colours are an integral part of the universe that we live in. From our birth, we are associated with colours not only for its aesthetic appeal but also for our survival. Colours have a profound emotional and psychological impact on people and as such colours communicate energy, vibrancy, calm, and turbulence and various other emotions without any verbal or written words. Colour has been used as a toll to communicate danger, and also, colour has been used successfully by advertisers for branding their products. Colours like red are generally associated with passion, energy, and love, whereas blue denotes serenity and calmness. Till the mid-nineteenth century, textile coloration was derived from natural sources such as trees, rocks, and minerals. The invention of synthetic dyes with the first Synthetic dye “Mauvine” by Sir William Perkin in 1865 led to the advent of a large variety of colours that were readily available, had good fastness properties, could be standardised, and was reproducible with excellent colour yields [1]. This led to the gradual decline of the use of natural dyes and the techniques of natural dyeing practiced through the ages. Recent decade has

seen a gradual shift towards the use of natural dyes, as these dyes being sourced from nature is considered environmentally friendly with fewer negative impacts compared to synthetic dyes.

2. History of dyeing

The fascination of human beings with colouration of clothes can be traced back to the neolithic period, that is, during the pre-historic time that agriculture developed, and early man started living in settlements.

The first evidence of coloured textiles dated back to more than 30,000 years ago from the upper Palaeolithic period in the Dzudzuana caves located in the western part of the modern Republic of Georgia. Flax fibres coloured in black, grey, turquoise, and pink were found in this early settlement, which established the fact that some form of decorative coloration on fibres existed even way back in the Palaeolithic times.

Coloured textiles were also found in Catalhuyuk in Southern Antalya, Turkey. The fibres were of bast origin but not from Flax. People in Catalhuyuk used ochre that was derived from iron ore, a mineral source to colour the fabrics.

Dyeing of clothes was prevalent in many other ancient civilization, like Egyptian civilization, China, The Indus Valley civilization and the art flourished along the rivers of the ancient times, because as like the present day coloration of fabrics required the use of large quantities of water.

The only source of coloration during those times was from natural sources such as tress, insects, animals or other naturally occurring minerals or matter.

2.1 Ancient Egypt

In around 1828, a number of papyri were recovered from burial sites in Thebes near central Egypt. These papyri detailed the aspects of dyeing of textiles and also making of imitation materials like gold. These Papyri is known as the “Stockholm Papyri”. An interesting aspect of these Greco-Egyptian Papyri is the fact that these [2] recipes were primarily for the dyeing of wool, though Egypt Prehistoric textiles were based out of linen. This document establishes the mastery and understanding of the ancient Egyptian culture of mordants and its effect on various colours and dyeing.

2.2 Indus valley civilization and India

India has traditionally a vibrant history of use of natural dyes and dyeing [3]. These dyes and dyeing techniques along with mordanting techniques were closely guarded secrets practiced and maintained only by the traditional craftsman. The name of the dye “Indigo” refers to the India, where it was grown and the dyeing techniques developed [4].

The material of choice in the Indus Valley Civilization was cotton and was dyed with Indigo and Turmeric. In the excavation site of Mehr Garh, cotton seeds were found. The early weavers of this region used indigo-dyed blue yarn alternating with natural or bleached cotton. Also, evidence of use of other fibres such as wool, jute and flax was also obtained from these excavation sites [4].

The ancient Hindu Sanskrit texts, known as the Vedas dating back to 1500–500 BCE, have details about textiles and clothing worn at that time especially during ceremonies and also have reference to the use of different colours. These scriptures

provide us with evidence that dyeing techniques for creating vibrantly coloured fabrics existed and were practiced around that time in this region.

The technique of mechanical resists by tie and dye method popularly known as “Bandhani” also has its roots in India. This dyeing technique is still practiced by the traditional craftsman in India Today.

2.3 China and Japan

The technique of cultivating silk came to Japan from China and also the Japanese gradually developed the art of dyeing over a period of 2000 years. The process of creating colour began from the early stage is the formation of the cocoon. From the practice of feeding the silk worms on mulberry leaves or wild mulberry leaves, the silk obtained could be either white or yellow. For dyeing the silk material, the material was first bleached by boiling in Lian tree fruit. The fabric was then dyed by different dyes like:

Blue—Fermenting Indigo, black—iron vitriol, red—Madder root or Safflower, yellow—Jinzi Fruit.

Historical Japanese writings also reference a dye called “Bengala”, derived from iron oxide naturally occurring in the soil. Recognised as one of the earliest pigments used by humans, its application dates back to the Palaeolithic Age. The characteristic red hue of red soil is attributed to the presence of iron oxide. The term “Bengala” originates from the Bengal region, spanning parts of present-day India and Bangladesh, where its production and use gained prominence.

2.3.1 Chinese civilization

In China, detailed records were found about the dyes and the dyeing techniques from the Ming and Qing dynasties ranging from 1368 to 1644 to 1644–1911 respectively a period extending for more than seven centuries. These records provide important historical insights into the use of different natural substances to achieve the diverse and vibrant colours associated with Chinese silk and other textiles [5].

2.4 Middle East

Ancient Persians used rich vibrant colours sourced from *runas* obtained from *Rubia cordifolia* (madder), *red grain* (kermes or cochineal beetles), walnut, *neel* (indigo), vine leaves and other plant materials. Techniques of dyeing protein-based natural fibres such as wool and silk with these natural dyes were a part of the process of the making of woven and hand-knotted carpets. The earliest Persian carpets were made over 2000 years ago by nomadic tribes, and each tribe had their signature design and colour and was a reflection of their culture and also symbolism important for the tribe. The Safavid Carpets or the Royal carpets made during the Safavid Empire (1501–1736) are universally renowned for their intricate designs and colours.

The Phoenicians were known for their expertise in dyeing Tyrian Purple a dye that was extracted from sea snails.

The Middle East also introduced the Ikat style of dyeing. Ikat is a tie and dye technique where the yarns are dyed which are then later woven into fabrics to produce unique designs. Ikat style could be done on any set of yarns or on both, that is warp and weft.

Natural dyes, though effective in rendering colour to fibres of both animal and plant origin, were very fundamental in their range of shades and faded substantially with use. Natural dyes define all colourants that are derived from natural resources such as plant, animals, and minerals. These colourants are generally non-substantive in nature; that is, they are unable to form stable bonds with the fibre substrate and are dependent on chemicals known as “mordants” for their application. The mordant functions as a bridge which holds both the dyeing matter and the fabric together.

The process of using natural dyes from prehistoric times until around the mid-1800s remained undeterred till the invention of “Mauvine” by Sir William Perking in 1865, when he introduced the first synthetic dye. This and later invention of new dyes led to the slow decline and the use of natural dyes. This decline was assisted by some inherent drawbacks of the natural dyes itself like:

- Not readily available
- Suited mainly for natural fibres such as cotton, wool, silk, and linen—This played a very crucial role in the transition period, because in the late nineteenth century research across the globe focussed on making new man made and synthetic fibres. These fibres gained popularity among the masses as these synthetic fibres were more durable, readily available and was also low on maintenance. Inability to colour these fibres and in turn the availability of synthetic dyes with their bright hues and an almost inexhaustible colour palette provided a stark contrast in the choice of dyestuffs.
- Poor fastness properties like washing, water, rubbing.
- Poor colour (shade) reproducibility
- Lack of standardised formulations and dyeing techniques as the colourants itself could not be standardised and are subjected to the vagaries of nature.
- The natural dyes use metallic mordants to achieve fastness, some of which have since been found to impact adversely man and the environment. So the reigning concept of natural dyes being ecofriendly was not entirely correct.

But in the last few decades, there has been a steadily growing concern of the impact of synthetic dyes due to the use of harmful chemicals on human ecology, the environment—soil, water and air. These chemicals are present everywhere and we are exposed to them willingly or unwillingly [6]. The invasion of these chemicals is so rampant that these chemicals are now detected inside human bodies. With a growing awareness about these impacts, the last few decades have seen a resurgence in interest of natural dyes. Natural dyes have the advantage of being eco-conscious, non-carcinogenic, hypoallergenic, biodegradable, and safe for human use. The stakeholders in reviving interest in these traditional dyeing techniques are primarily associated with groups that have taken up natural dyeing as a hobby, NGOs who wish to promote and preserve traditional dyeing techniques of natural dyeing process, designers looking for an exclusive and a niche market, and of course the traditional dyers and printers who are in the process of practicing this are through generations. The stakeholders also have indicated and established opined the enhancement of

some additional functional properties as an unintended but desirable consequences such as UV protection, anti-bacterial properties [7–9], deodorising properties and mosquito repellent properties [10] by the use of natural dyes.

As we are aware the tinctorial and colouring aspect of the dye is directly dependent on the presence of certain functional groups within the dye structure. These functional groups produce colour by the absorption of certain wavelengths of light while reflecting specific wavelength of light in the visible spectrum. The reflected light rays are then processed by the eye through the light-sensitive cells known as rods and cones to give us a sensation of colour. These functional groups that are responsible for the colouring properties are known as chromophores. The word “chromophore” is derived from the Greek word “Chroma-meaning colour” and “phore-meaning carrier”. In essence “Chromophore” aptly means “carrier of colour”.

A viability of a colouring material to be used as a dye also requires that the colouring matter or the chromophore can attach to the fibre or form bonds with the textile substrate. The stronger the bonding between the fibre and the colouring matter the better are the overall fastness properties. The part of the dye molecule which is attached to the chromophore and is responsible for the bonding with the fibre substrate and also supports the chromophore in intensifying the colour is known as auxochrome.

Hence, to understand dyeing with natural dyes it is important to understand their chemical structure.

Classification of natural dyes: Historically, these dyes were sourced from natural sources and could be classified

1. Source of origin as:

- a. Vegetable origin: for example Madder, Indigo, Turmeric.
- b. Animal origin: Cochineal, Tyrian Blue.
- c. Mineral origin: Ochre, Malachite, Hematite.

Besides the above, classification can also be done in terms of their

2. Classification based on their Chemical structure:

- a. *Indigoids*: Indigoids are an interesting class of natural pigments that are available in plants and marine animals. Two extremely popular dyes of this class are Indigo and Tyrian Blue. Their structure is essentially a connecting structure of two Indole moieties. These family of natural dyes are composed of 13 members out of which Indigo is the most commonly used and also the most popular [11].

It has been found that natural indigo that is derived from *Indigofera tinctoria*, especially those used along with salts of Cu, has shown antibacterial activity against yeast and some strains of bacteria. Synthetic Indigo does not possess the antibacterial properties of natural Indigo.

- b. *Carotenoids*: Carotenoids are a class of naturally occurring pigments found extensively in nature. They are synthesised by various organisms including plants, algae, fungi and specific types of bacteria. These molecules are primarily of two types:

- i. Carotenes—These are hydrocarbon-based pigments and include compounds such as β -carotene, α -carotene and lycopene.
- ii. Xanthophylls—These are oxygenated carotenoids comprising pigments like lutein, zeaxanthin, astaxanthin, fucoxanthin and cryptoxanthin.

Carotenoids are an essential pigment present in photosynthetic organs of plants along with chlorophylls.

A total of 850 naturally known carotenoids were listed till 2018. In 1906, Zwet was able to separate the compounds carotene, xanthophyll and chlorophyll from green leaves using column chromatography. This feat was followed by Karrer and Khun who elucidated the structures of β -carotene, γ carotene and lycopene [12]. These pigments are heat stable but sensitive to pH and light.

- c. Anthraquinones: These dyes are derived from both plant and animal sources and have been used for dyeing of textiles from ancient times. They are one of the most common types of natural dyes and these phytopigments are responsible for lasting shades in the hue range from red to brown [12].
 - i. Plant anthraquinones: Historically, red anthraquinone dyes were most commonly obtained from the roots of plants in the Rubiaceae family, especially species of *Rubia* (madder). These plants have long been valued for producing vivid red shades on textiles when used with mordants, with evidence of their use by ancient Indians. Anthraquinones associated with madder dyestuffs have been detected in historic and archaeological fabrics across various regions globally. These dyes are not visible in the flowers, fruits or leaves of the plant but are mostly present in the roots and barks of the plant. They give colour in slightly alkaline conditions.
 - ii. Animal-based anthraquinones: These are derived from insects of the Coccidae family, like America/Mexican Cochineal and kermes. The primary colouring compound is Carminic acid and they produce colour in acidic medium.
- d. Tannins: These compounds act both as a natural dye and also a natural mordant in dyeing with natural dyes. They are present in barks, roots, leaves and seeds and act as a shield against predators. Some tannin-based natural dyes are derived from Pomegranate peels, Myrobalan, Heena, Tea and Catechu [13].
- e. Flavanoids: These are further classified as:
 - i. *Anthocyanidins and anthocyanins*—They produce fugitive colour and they are fugitive colourants with poor wash fastness with low thermal and chemical stability. These change colour when exposed to light, temperature and humidity. These pigments are available in petunia's, red cabbage and black beans.
 - ii. *Anthoxanthins*: They are pigments that produce a whiter shade in acidic medium which turns to yellower shades in neutral or alkaline pH. Examples are Buckhorn bark, berries, etc.

- f. Betanins: They contain the pigment Betalain which are water soluble pigments found in plants and mushrooms and are responsible for the red-violet coloration in beetroots. Betanin is a betalain pigment, together with isobetanin and other betacyanins. They are widely used as natural food colourant. Betalains from beetroot are either grouped into betacyanins, with reddish-violet hues, and betaxanthins, with yellow to orange hues [4]. These pigments are also associated with many inherent bioactive properties such as antioxidant activity, anti-inflammatory activity, immunomodulatory activity, and chemopreventive properties. Betanin is very pH sensitive [5, 6], and in acidic conditions, that is between pH 4 to 5, it is bright bluish-red; with increase in pH, it becomes blue-violet and degrades in alkaline pH by hydrolysis into a yellowish brown colour [10].

Betanin structure

- g. Dihydropyran-based: These are mainly two types of heterocyclic compounds with the general formula C_5H_8O . The di-hydro refers to the use of two hydrogen atoms which replaces in double bond in the parent compound pyran. These pigments are derived from Logwood and brazilwood with the colouring matter known as brazillin or haematoxylin and are responsible for dark shades in textile substrate [13].

3. Classification based on their application method:

- a. Mordant dyes: These are dyes which fixes to the textile fibres through a compound referred to as “mordant” as these dyes lack affinity for the fibre being dyed. The mordant molecule forms coordinate bonds with both the dye and the fabric. This bonding is enabled by electron-donating groups present in the mordant, allowing it to complex with metal salts such as aluminium or iron. Examples of mordant dyes include madder, fustic, Persian berries, kermes and cochineal.
- b. Vat dyes: These are dyes that are initially insoluble in water. To apply them, they are first reduced using sodium hydrosulphite and made soluble with the addition of an alkali. In this soluble form, the dye can be absorbed by the fibres. The actual colour develops only after the dye is oxidised, which regenerates the original insoluble dye *in situ* within the fibre matrix. This is followed by treatment with a hot soap solution to remove any unbound dye remaining on the fibre surface. A common example of a vat dye is indigo.
- c. Direct dyes: These dyes are characterised by their high affinity for the cellulosic fibres. These dyeing process with these dyes is carried out from dye bath maintained at boiling temperature. Pomegranate rind, turmeric, harda, etc., are some examples of direct natural dyes.
- d. Acid dyes: Acidic dyes are applied from an acidic dye bath. These dyes contain either sulphonic or carboxylic acid groups, allowing them to form electrovalent bonds with the amino groups found in protein-based fibres like silk or wool. The fastness properties of the dye are typically improved by a post-dyeing treatment process using tannic acid and is commonly referred to as back tanning. An example of an acid dye is saffron.

- e. Basic dyes: These dyes are also known as basic dyes and produce coloured cations upon ionisation, which form electrovalent bonds with the carboxyl (-COOH) groups present in fibres such as wool and silk. They are applied under neutral to slightly acidic conditions. However, these dyes have poor light fastness. An example of a basic dye is berberine.
 - f. Disperse dyes: These dyes are natural compounds known for their small molecular size, limited water solubility and lack of strong solubilising groups. Disperse dyes are typically used on hydrophobic synthetic fibres under neutral to mildly acidic pH. Their fastness properties can be enhanced through post-mordanting. Examples include lawsone, along with various flavone and anthraquinone-based dyes.
4. Another method of classification according to Bancroft in his book entitled “Treatise to Permanent Colours” [14], written more than 170 years ago was:
- a. Substantive dyes: The dyes which could colour the fabric/fibre directly. Examples: Indigo, turmeric
 - b. Adjective Dyes: These dyes are required to be mordanted with metallic salt or in the presence of metallic salt in the dye bath in order to dye the material. Without the mordant, the dye does not effectively bind to the fibre. Examples include logwood, madder, and cochineal.

This classification was later modified as direct dyes for substantive dyes and, mordant dyes as adjective dyes.

5. Hummel-classified natural dyes as:

- a. Monogenetic—These dyes produce a single colour and the mordants have no effect on the colour produced.
- b. Polygenetic—These dyes produce different colours with different mordants.

According to the colour or hue: The colour index natural dyes are classified according to their hues or the dominant colours. These dyes are mentioned in a separate section of the colour index. A total of 92 natural dyes are listed out of which the chemical structure of 67 of these dyes are disclosed [15, 16].

The number of dyes in each colour category is as follows:

- | | |
|-----------|---------|
| a. YELLOW | 28 dyes |
| b. ORANGE | 6 |
| c. RED | 32 |
| d. BLUE | 3 |
| e. GREEN | 5 |

f. BROWN 12

g. BLACK 6

Use of mordants in natural dyeing: Mordant in Latin means to “Bite” as it is believed that the mordant abrade away the substrate surface making the fibre more accessible to the dye molecule. Mordant is basically a compound, which can has affinity and also fix itself to the fibre and simultaneously also combine with the dyestuff. The mordant works as a bridge or link between the dyestuff and the fibre, which allows certain dyes with no affinity to be fixed on to the fibre [17, 18].

Properties of mordants:

A suitable mordant should fulfil the following criteria:

- Ensure high colour yield at an economical cost and a low dosage of application.
- Maintain or enhance the physical and fastness properties of the fibre and the dye; it should not negatively impact the dyed fabric but should ideally improve colour durability.
- It must not cause any adverse effect during processing like harmful fumes, allergies or environmental hazard.
- The resulting dyed fabric should be free from harmful chemicals [19, 20].

Types of mordants: Three types of mordants are commonly used:

a. Metal salts or metallic mordants. A variety of metal salts can be used for mordanting. The most effective ones are:

i. Alum—potassium aluminium sulphate— $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

ii. Copper—copper sulphate— CuSO_4

iii. Chromium—potassium dichromate— $\text{K}_2\text{Cr}_2\text{O}_7$

iv. Iron—ferrous sulphate— FeSO_4

v. Tin—stannous chloride— SnCl_2 .

vi. Stannic chloride— SnCl_4 .

These salts are very effective as a mordant but the use of the salts such as potassium aluminium sulphate (alum), potassium dichromate, ferrous sulphate, copper sulphate, stannous chloride and stannic chloride has been restricted due to the its toxicity to human beings and the ecosystem.

b. Tannins and tannic acid. Tannins are naturally occurring, high-molecular-weight polyphenolic compounds of vegetal origin, typically ranging between 500 and 3000 Da. They are rich in phenolic hydroxyl groups (1–2 per 100 Mw), which enable them to form cross-links with proteins and other macromolecules. This

unique property allows tannins to effectively modify substrates for improved dye adherence.

These compounds are known for their ability to precipitate proteins and are broadly classified into four structural types based on the nature and arrangement of their phenolic cores:

- i. Hydrolysable tannins: Found in plant materials such as myrobalan fruit, oak bark, gallnuts, pomegranate rind and sumac leaves. These tannins are esterified derivatives of gallic or ellagic acid.
- ii. Condensed tannins: Derived from flavonoid units such as catechin, a key component extracted from *Acacia catechu*.
- iii. Complex: Complex tannins have a molecular structure that are amalgamation of hydrolysable and condensed tannins which may include gallic, ellagic and catechin sub-units.
- iv. Phlorotannins: These are a rarer group of tanins, and are found primarily in brown algae and are composed of phloroglucinol units.

Tannins alone do not function as mordants. However, when a tannin-treated fabric is subsequently exposed to a metal salt solution (e.g., alum), aluminium ions are introduced into the fibre matrix. These ions are absorbed by the hydroxyl and carboxyl groups on the tannin-treated fabric, forming either a metal-complex or metal salt. The resulting tannin-metal complexes create active binding sites that significantly enhance the fabric's affinity for natural dyes. Therefore, while tannins themselves are not direct mordants, their role in forming metal-organic complexes is crucial in facilitating effective dye-fibre binding in natural dyeing processes.

- c. Oil or oil mordants: Oil-based mordants were associated with the traditional dyeing of Turkey Red, which is a vivid and durable red colour derived from madder. They form a complex with alum which is the main mordant. Since alum lacks strong affinity for cotton fibres and is water-soluble, it is prone to washing out during processing. These oil mordants are typically composed of natural oils rich in fatty acids, for example, palmitic, stearic, oleic and ricinoleic acids, along with the glyceride forms. The carboxylic acid groups ($-\text{COOH}$) of these fatty acids can react with metal ions from salts, forming metal carboxylates ($-\text{COOM}$), where M depicts the metal ion. Treating these oils with concentrated sulphuric acid leads to the formation of sulphonated oils, which possesses sulphonic acid groups ($-\text{SO}_3\text{H}$). The modified oils demonstrate the enhanced metal-binding capacity due to the ability of sulphonic acid groups to interact with metal salts, forming sulphonate-metal complexes ($-\text{SO}_3\text{M}$). These metal containing sulphonated oils can then effectively bind mordant dyes such as madder, producing a rich Turkey Red shade with excellent colour fastness and vibrancy [19, 20].

3. Methods of mordanting

Methods of mordanting: Traditionally and also till this date three methods of mordanting are used:

- i. *Pre-mordanting*: In this technique, the fabric or fibre is first treated with a mordant before the dyeing step. The material is initially placed in the mordant solution at room temperature, and the temperature is then gradually raised to the optimal range, typically between 70°C and 100°C. The mordanting process is carried out for approximately 45 minutes to an hour. After mordanting, the material is dried and then dyed using the appropriate dyeing procedure, followed by washing, soaping and final drying.
- ii. *Meta-mordanting or simultaneous mordanting*: This method involves carrying out mordanting and dyeing in a single step. The mordant is introduced directly into the dye bath, along with any necessary dyeing auxiliaries and additives. After the dyeing process is complete, the fabric is thoroughly rinsed and subjected to a soaping treatment. While this method is efficient due to its one-step nature, it may not be ideal for delicate fibres that are prone to damage.
- iii. *Post-mordanting*: In this method, the dyeing of the material is first carried out without the use of any mordant. The dyed material is then treated with a mordant solution in a separate bath. The treatment conditions vary depending on the type of mordant used. This method has different effect on the final shade obtained and also on the fastness properties of the dyed material. It is a preferred treatment method as the outcome of the final shade can be mostly controlled by the dyer [21, 22].

Colour fastness of materials dyed with natural dyes: Colour fastness refers to the fabric's ability to resist changes in its colour or prevent the transfer of dye to nearby white materials when exposed to external factors such as light, washing, rubbing, perspiration, and dry cleaning.

Among the various types of colour fastness, light fastness, wet fastness, and rubbing fastness are most commonly evaluated, as they directly affect the functional performance and durability of the dyed material. Fastness to perspiration is important when the material is worn as apparel or where a material has next to the skin contact.

Light fastness: The light fastness of many natural dyes—particularly those derived from flower petals—is generally rated as low to moderate. In comparison with synthetic dyes, natural dyes typically exhibit inferior stability when exposed to light. However, the use of mordants can enhance both the wash fastness and light fastness of these dyes.

Yellow dyes generally show lower fastness ratings, while *red, blue, brown and black plant-based dyes* tend to offer good to excellent resistance to light. This difference is largely due to the typically pale nature of yellow dyes derived from botanical sources, which results in lighter shades and lower colour yield on the fabric, making them more prone to fading when exposed to light. The brighter yellow shades obtained from turmeric have poor light fastness. Mordants play a major role in the lightfastness of yellow dyes. Yellow shades tend to fade more rapidly when treated with tin alum mordants compared to chrome, iron or copper mordants, which offer better protection against fading. Red dyes, typically derived from anthraquinone compounds, exhibit greater stability under light exposure and are therefore more light-resistant. Blue hues are most commonly obtained from indigo, which shows higher lightfastness on wool compared to cotton, and is also about 1–2 grades better than on silk. Brown and black dyes are often sourced from tannin-rich plants such as pomegranate peel

and myrobalan. Tannins form dark-coloured complexes when combined with ferrous sulphate, resulting in shades with good resistance to light.

Wash fastness: Natural dyes generally exhibit moderate resistance to washing. Alkaline components in detergents can negatively impact dye stability, particularly affecting yellow dyes, which tend to show only average wash performance. Red dyes are typically more stable during washing. Blue dyes, often derived from indigo, are applied in a soluble form but oxidise within the fibre to become insoluble, resulting in excellent wash fastness. Tannin-based black dyes, being large and complex molecules, have strong affinity for both cellulosic and protein fibres, contributing to their good resistance to washing. When applied to wool using metallic mordants, lac dye exhibits moderate to very good wash fastness. In comparison, *Babool* demonstrates consistently high wash fastness, whereas *Catechu* shows variability, ranging from good to very good wash fastness performance [23–27].

Rubbing fastness: For most natural dyes, the rubbing fastness rating ranges between moderate and good.

Extraction of natural dyes: Natural colourants can be extracted through different techniques. These techniques are selected based on the colour that is being extracted and the properties of the colouring compound. The different stages of any extraction of natural dye are:

1. The drying and grinding of colouring material.
2. The second stage of the process involves the choosing of a suitable solvent.
3. Finally, the extraction of the targeted dye material.

Some commonly used extraction methods are as follows:

- **Aqueous extraction:** In this technique, dry raw materials are first broken into smaller pieces or ground into a powder, and then soaked in water to help break down the cell structure. If fresh (wet) plant material is used, it is finely chopped or ground into a paste. This paste is then boiled, and the resulting liquid is filtered to remove any non-colouring residues, leaving behind the dye extract. Both dry and wet forms of raw material can be processed this way to obtain colour for various applications. However, aqueous extraction has certain drawbacks, including being time-intensive, requiring high temperatures and large amounts of water, and offering low dye yield. Additionally, heat-sensitive pigments may degrade at elevated temperatures, and only water-soluble dye components can be extracted using this method.
- **Acidic or alkaline extraction:** In this process, the extraction of the dye is done under acidic or alkaline medium. Dilute acid or alkali is used which for the hydrolysis of glycosides which results in better extraction [17, 18].
 - Acidic method is used in extraction of colouring matter from Tesu flower.
 - Alkaline extraction method is primarily used for extraction of materials containing phenolic groups; for example, safflower petals are extracted by this method.
- **Ultrasonic microwave extraction:** This technique involves subjecting plant materials to aqueous treatment under the influence of ultrasonic or microwave

energy. The use of high temperature and energy input allows for faster and more efficient extraction in a shorter duration. Dyes from sources like butterfly pea flowers and annatto seeds have been successfully extracted using this method.

- *Fermentation-based extraction*: This method utilises naturally occurring microorganisms within the plant material to facilitate dye release through fermentation. The microbial activity helps break down plant tissues, aiding in the dye's extraction. It is a traditional approach used for obtaining colours from plants such as turmeric, annatto, and indigo.
- *Enzymatic extraction*: Commercial enzymes such as cellulase, amylase and pectinase are employed to degrade the structural components—like cellulose, starch or pectin—in tough plant parts such as bark or roots. This breakdown assists in releasing the dye compounds more efficiently without damaging the dye integrity.
- *Solvent extraction*: This method uses organic solvents such as acetone, ethanol, ether, chloroform or petroleum-based agents to isolate dye molecules from plant matter. Compared to water-based extraction, this method typically yields a higher quality extract, requires lower processing temperatures, and significantly reduces water consumption.

Modern techniques of extraction: Contemporary extraction methods offer significant advantages over traditional approaches, primarily by enabling higher yields while maintaining lower operational costs. Some of the new methods of extraction are as follows:

- *Solid-phase micro-extraction (SPME)*: SPME is a solvent-free technique that integrates sampling, extraction, concentration and introduction of the analyte into the instrument in a single step. It is a non-exhaustive method where a small quantity of an extractive phase, which is supported on a solid substrate, is brought in contact with the sample for defined time period. The process operates on two principles: (a) distribution of the analyte between the sample matrix and the extractive coating, and (b) desorption of the concentrated analyte into the analytical instrument. This approach is simple and efficient, and minimises solvent usage while providing enriched target compounds.
- *Supercritical fluid extraction*: This technology of using super critical fluid for the extraction is as old as 1984. This extraction technique relies on the solubility of target dye compounds in supercritical fluids such as carbon dioxide, propane, butane or ethylene. Dye components are extracted by the help of a supercritical fluid under high pressure. It is an advanced separation technique that utilises the enhanced solvating power of gases when they are in a supercritical state, that is above their critical temperature and pressure. A supercritical fluid extraction is functionally composed of two processes: (1) extraction of analytes by use of the supercritical fluids and (2) separation of analytes from the supercritical fluid [28]. Super critical fluids are characterised by low viscosity and a high diffusion coefficient that enables easy penetration into sample particles and dissolve the soluble analytes. Among the supercritical fluids, carbon dioxide is preferred due to its relatively low critical temperature, non-flammable nature, minimal toxicity

and cost-effective availability in high purity. Typically, CO₂ is employed within a temperature range of 40–80°C and a pressure range of 35–75 MPa.

- Pressurised extraction method: This technique uses elevated temperature and moderate to high pressure range for better extraction of colouring component. In this process, the sample is first dispersed with sand or other inert materials. In the 2nd stage also known as the Static extraction stage, the solvent is introduced into the vessel containing the dispersed material. In the 3rd Stage also called the dynamic extraction stage, the solvent flows through the dispersed materials. The efficiency of the process is determined by the type of solvent, extraction temperature, pressure and nature of adsorbents [7, 29–31].

4. Conclusion

Nature is vivid in its colour palette and the use of natural products for dyeing has potential and a wide range of possibilities. The challenge is more intricately related to our present day lifestyle and the rampant increase in consumerism in the last few decades. With the advent of sophisticated machineries and state-of-the-art technologies, mass manufacturing and replication of bulk quantities of coloured textile materials are a reality that is readily and easily catered by synthetic dyes. To popularise and truly adapt natural dyes as an alternate method of coloration a paradigm shift in our mindset with respect to our consumption methods needs to be addressed.

The linear business models need to be shifted to circular business models. A return to the basics or to the consumption patterns of a few decades back needs to be rejuvenated and brought into style.

This also needs to be supported by contemporary research on natural dyes aimed to create a fuller palette of hues and colours along with addressing the poor fastness properties and lack of reproducibility in shade of natural dyes.

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Chapter 2

Introduction to Dyes

Maira Liaqat, Rana Rashad Mahmood Khan, Tahir Iqbal and Xian-Zhu Fu

Abstract

Dyes are chromatic chemicals that chemically adhere to substrates, bestowing vivid and long-lasting hues to things including fabrics, plastics, leather, and food. This chapter examines the historical development of dyes, tracing their ancient origins from natural sources such as plants, insects, and minerals to the groundbreaking invention of synthetic colors during the Industrial Revolution. The categorization of dyes into natural and synthetic types is examined along with their unique qualities, applications, and interactions with various fabrics. The importance of dyes encompasses various sectors, including textiles, art, and advanced technology applications. Dyes are essential in leather tanning, food and cosmetics, pharmaceuticals, and sustainable energy technologies such as dye-sensitized solar cells. The dye business plays a crucial role in worldwide economies, propelled by the demand for sustainable and high-performance colorants. Nonetheless, problems include environmental degradation, fluctuations in raw material prices, and the conservation of traditional dyeing methods.

Keywords: chemical compound, natural and synthetic dyes, ecofriendly, textile fabric, color fastness

1. Introduction

1.1 Definition of dye

A dye is a colored substance that possesses a unique ability to bind to a substrate and impart color to it. In other words, dyes are chromatic compounds typically used in a solvent to color materials such as textiles, plastics, leather, and food [1, 2]. They differ from pigments in that they are soluble and bind chemically to the substrate, requiring mordants (chemical fixatives) to enhance colorfastness and durability [3].

1.2 Historical overview of dyes

The history of dyes is a complex and fascinating narrative that intertwines with the development of human civilization. From the earliest use of natural pigments to the revolutionary discovery of synthetic dyes, the story of dyes reflects humanity's ingenuity, cultural practices, and scientific progress. Here we discuss in detail.

1.2.1 Ancient origins (prehistoric era to early civilizations—3000 BCE)

As early as the prehistoric era, there was a foundational era in human history where dyeing emerged as a critical cultural and technological innovation. Early humans, driven by the desire to express identity, status, and creativity, began harnessing natural resources to color textiles and artifacts [4]. Dyes derived from plants, insects, and minerals were extracted through rudimentary chemical processes, such as boiling, fermentation, and reduction. Archeological evidence indicates that natural pigments were used as early as 36,000 years ago with dyed flax fibers found in Georgia's Dzudzuana cave (30,000 years old) and indigo-dyed Peruvian textiles (6000 years old) [5–7]. In ancient Egypt, natural dyes like indigo, saffron, and madder were used to color linen, symbolizing spirituality and social status in Mesopotamia and China [8]. For example, yellow represented divinity while green signified rebirth. By 2600 BCE, China had advanced silk-dyeing techniques using cochineal and madder for vibrant hues [9]. The Silk Road (6400 km) facilitated the exchange of dyestuffs like indigo and saffron between east and west spreading dyeing knowledge globally. This era laid the groundwork for modern dye chemistry, blending artistry with empirical knowledge to transform raw materials into culturally significant colors [10].

1.2.2 Classical antiquity (golden age of dyes: 3000 BCE–500 CE)

In the classical antiquity period, the art of dyeing reached new heights with specific dyes becoming symbols of wealth, power, technological implication, and cultural identity [11]. Civilizations including the Egyptians, Greeks, Romans, Phoenicians, Indians, and Chinese mastered dyeing techniques from early chemical concepts such as solubility and coordination chemistry, oxidation–reduction processes. To get preferred colors like Tyrian purple from Murex Snails, the Phoenicians used sophisticated biochemical procedures that consisted of oxidation and reduction reactions. This bright color shows authority and riches. Woad, in the meanwhile, gave European cultures like the Celts beautiful blue tones, and madder roots gave Egypt and Persia rich reds. Saffron produced golden-yellow tints in the Mediterranean [12]. Alums, mainly used as a mordant, exposed an early understanding of coordination chemistry, which upgraded colorfastness and dye attachment. The combination of indigo from *Indigofera* plants and red dyes from lac insects in India demonstrated a profound understanding of organic chemistry and solubility [13]. These developments draw attention to the substantial degree of chemical expertise incorporated in conventional dye-making processes. The Chinese possessed advanced methods for dyeing silk, employing tannins and iron salts to achieve black hues through precipitation. This progress not only enhanced the value of textiles but also reflected social hierarchies, cultural identities, and economic power. The chemical understanding of this period explains how ancient painters were, in many aspects, the first practical chemists. Hence, this classical period opens the evolution of dye chemistry and its durable impact on human society.

1.2.3 Medieval and renaissance periods (500–1600 CE)

During the Middle Ages and Renaissance era, dye chemistry flourished, where painters created colorful fabrics that reflected religion, culture, and social status. While trade routes like the Silk Road and Hanseatic League extended access to exotic

materials like indigo and saffron, natural dyes like madder, woad, and cochineal ruled [14]. For the production of deeper and long-lasting colors, artists develop different methods such as resist dyeing, overdyeing, and the use of mordant application. The red color represented monarchy, while blue color the Virgin Mary. Cochineal's arrival from the Americas transformed European dyeing during the Renaissance [15, 16]. Beyond their surface appearance, these colors created cultural identity and economic power. Hence, the modern artificial dyes were founded in this era by a mix of artistic creativity, global commerce, and pragmatic experimentation.

1.2.4 Industrial revolution (1760–1840)

In this period, the Industrial Revolution changed the textile sector from initially labor-intensive natural colors to other mass-producing synthetic dyes. The first time was in 1856, when William Henry Perkin unintentionally discovered Mauveine, which produced coal tar-based synthetic dyes and produced bright and reliable colors formerly unreachable with natural sources like cochineal or indigo [17, 18]. Steam-powered dyeing machines and the mechanization of large-scale textile production quickly lower prices and improve accessibility. Factories with automated dyeing procedures thrived at this time. Hence, guaranteeing color stability in application and raising the need for reasonably priced colored fabrics. Furthermore, in this evolution, synthetic hues sometimes included hazardous chemicals that endangered the environment and impacted workers' well-being. The move to synthetic dyes affected the local economic and cultural legacy as fewer traditional craft dyeing techniques were needed.

1.2.5 Modern period (1900–Present) and beyond

The modern period has revolutionized dye chemistry obtained from industrial innovation, environmental challenges, sustainability, and a regeneration of traditional practices. Further, developments like digital printing and supercritical CO₂ dyeing reduce resource use and pollution [19]. In the meantime, natural dyes like cochineal and madder have been used again for sustainable practices and historical authenticity. Furthermore, in this period, plant-based extraction and safer mordants were used for the improvement of colorfastness and the reduction of toxicity. Furthermore, in the nineteenth century, many companies, like Winsor and Newton (founded in 1832), strongly focused on madder dye, emphasizing ongoing refinement of old pigments. In return, the late twentieth and early twenty-first centuries committed to reducing ecological impact through sustainable actions, including the development of eco-friendly dyes, biodegradable pigments, and closed-loop dyeing systems to reduce the waste [1]. Moreover, biotechnology plays an important role in the manufacturing of dyes with microorganisms, reducing reliance on petrochemicals. Hence, the rehabilitation of natural dyes and traditional dyeing techniques reflects a rising appreciation for cultural heritage and sustainability. This modern period has explored the opportunities of dye chemistry and emphasized the significance of balancing innovation with environmental applications.

2. Classification of dyes

The dyes are mainly classified into two main types. These are natural dyes and synthetic dyes [6]. These natural and synthetic dyes can be further classified according to

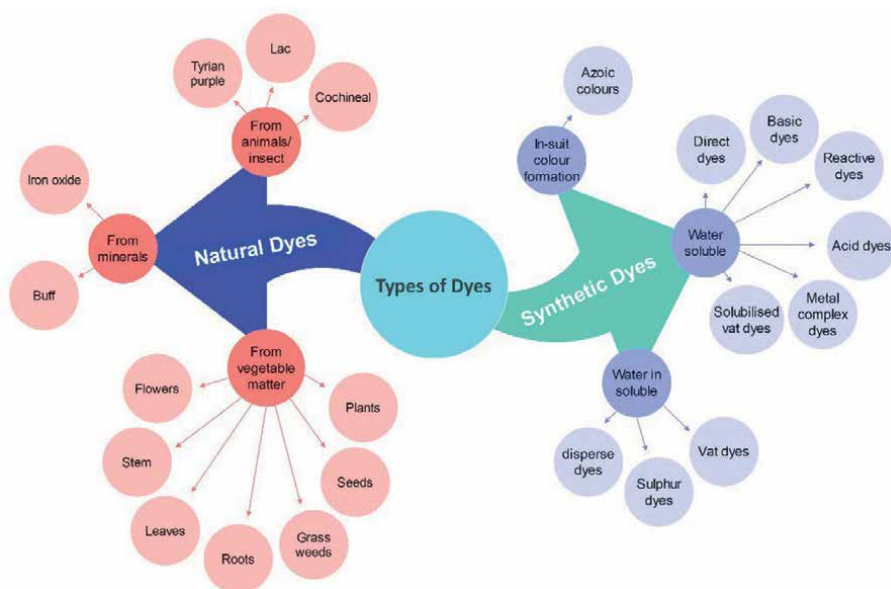


Figure 1.
Classification of dyes.

their source of origin, chemical structure, solubility, and application method. **Figure 1** explains the types of dyes. Each type has distinct characteristics and applications.

2.1 Natural dyes

Natural dyes are pigments derived from nature through organic and inorganic materials or sources such as plants, animals, and minerals [12, 20]. Natural dyes are mostly used due to their eco-friendly nature and a variety of colors through compounds like indigo, alizarin, and curcumin.

2.2 Synthetic dyes

Synthetic dyes are man-made colorants. Chemical synthesis adds different chemicals to natural colors to create these dyes [21]. The synthetic dyes provide an incredible range of vivid and stable hues. These dyes are further categorized as in-situ color creation, water-insoluble dyes, and water-soluble dyes. Synthetic dyes are mostly used in industries like textiles, printing inks, plastics, leather, pharmaceuticals, and food coloring because of their great behavior, including colorfastness, lightfastness, and cost efficiency [2, 22, 23].

3. Importance of dyes (textiles, art, and industry)

3.1 Textiles (the backbone of the dye industry)

Textiles form the foundation of the dye industry, acting as the primary material for applying dyes and significantly shaping its development [24]. Archeologically, mostly natural dyes were used to color fabrics. Nowadays, due to the wide variety

of textile fibers available, such as cotton, wool, polyester, etc., the demand for specialized dyes and cutting-edge dyeing techniques has increased [25]. The textile industry's requirement for vibrant, long-lasting, and sustainable colors has spurred modernizations in dye chemistry, such as reactive, disperse, acid, and vat dyes, as well as cutting-edge technologies like digital textile printing and waterless dyeing [26]. But challenges like environmental pollution from dye effluents have pressed the industry toward sustainable solutions, consisting of biodegradable dyes and eco-friendly processes [27]. In the Asia Pacific region, the global textile dye market is projected to grow gradually, driven by major textile manufacturing pivots and also enhanced by the value of sustainable practices. This mutual relationship between textiles and dyes fuels progress in both fields, with developments in smart and functional textiles further expanding the role of dyes. The relationship between these industries underscores the importance of chemistry in shaping the future of color, design, and sustainability while meeting the evolving needs of consumers and the environment.

3.1.1 Role of dyes in textile

Dyes are a key component of the textile sector since they help to provide materials used in technical textiles, home furnishings, and garments with different hues [28]. This not only satisfies the many aesthetic, functional, and cultural needs of consumers but also greatly improves the visual appeal, utility, and market competitiveness of these textile products over a wide range of uses [29]. Dyes are used in the garment sector to provide bright and long-lasting colors that fit customer tastes and fashion trends. Applied to a variety of natural and synthetic textiles like cotton, wool, polyester, and nylon, it creates garments with various hues and designs. Dyes are necessary in the home furnishings industry for coloring products like bed linens, upholstery, carpets, and curtains, hence enabling creative freedom and personalization. They assist in designing attractive and pleasant living areas. Dyes serve functional goals for technical textiles such as industrial fabrics, where they provide not only color but also particular functional qualities such as UV resistance and flame retardancy, medical textiles, vehicle interiors, and antimicrobial characteristics. Factors like the material being dyed, desired color, durability criteria, and legal issues influence the selection of dye type and formulation [30]. All things considered, dyes are essential in changing fabrics into flexible, useful, and aesthetically pleasing products that fit various industrial and consumer needs [31].

3.1.2 Dye-fiber interactions

The dye-fiber interactions are essential for the dyeing process, as the efficiency of a dye depends on its compatibility with the specific type of fiber being colored [24]. Each fiber, whether natural, synthetic, or blended, has exclusive chemical and physical properties that determine how it relates to dyes [32]. For example, cotton and other cellulosic fibers like cotton [33], linen, and rayon are best dyed with reactive or direct dyes, which form strong covalent bonds with the fiber, ensuring excellent wash fastness and also vibrant colors. Direct dyes, which depend on van der Waals forces and hydrogen bonding, are mostly used for cellulosic but are less colorfast unless treated with after-treatments. Protein fibers like wool and silk contain amino and carboxyl groups, making them perfect for acid dyes [34]. These dyes form ionic bonds with the positively charged amino groups in the fiber under acidic conditions, resulting in rich, durable colors. Metal-complex dyes are a subclass of acid dyes, mostly

used for wool to increase its lightfastness and wash fastness. Synthetic fibers such as polyester fibers have less affinity for most dyes and require disperse dyes, which are non-ionic and penetrate the hydrophobic fibers under high temperature and pressure. Similarly, nylon fiber has a high affinity for acid dyes, which form ionic bonds with the amino acids in the nylon. Disperse dyes and reactive dyes are mostly used for nylon, while acrylic fibers have a high affinity for acid dyes and disperse dyes and are typically colored with basic (cationic) dyes due to their negatively charged sites. Hence, matching dyes to fiber types is a crucial aspect of textile dyeing, as it ensures optimal dye-fiber interaction and colorfastness. The choice of dye and dyeing process focuses on the type of fibers, the desired colors, and the required colorfastness. By understanding the dye-fiber interactions, textile manufacturers can produce high-quality and durable dyed fabrics.

3.1.3 Properties of textile dye

Textile dyes are particular chemical compounds designed to impart color to fabrics. Their effectiveness depends on different properties that confirm optimal performance, durability, and sustainability [35, 36]. Here are some properties of textile dyes explained in detail.

3.1.3.1 Colorfastness

Colorfastness is the capacity of a dye to keep its hue under various external influences like washing, light, heat, and friction. Consumer pleasure depends on high colorfastness since it guarantees the fabric keeps its look over time. Primarily, three varieties of colorfastness exist.

- a. Lightfastness is the ability of the dye to resist fading under light exposure. Outdoor textiles and clothes that will be exposed to the sun rely on this.
- b. Wash fastness is the ability of the color to resist fading during washing. This is important for home textiles as well as for clothes that will be washed often.
- c. Rub fastness refers to a dye's ability to withstand fading when it is abraded or rubbed. This is especially important for items under friction, such as clothing and furniture.

3.1.3.2 Affinity for fiber

The affinity for fiber is an important property of textile dyes, describing their ability to interact with and adhere to specific types of fibers. This affinity has two types, i.e., chemical affinity and physical affinity.

3.1.3.2.1 Chemical affinity

Chemical affinity is the dye's ability to create notable chemical links with fiber, which is crucial for achieving long-lasting and permanent color. For example, reactive dyes have high chemical affinity for cotton fabric and form covalent connections that confirm strong color fixing. While the acid dyes are mostly drawn to wool and silk, bonding with ionic interactions.

3.1.3.2.2 Physical affinity

Physical affinity defines the ability of dye to bond with a fabric surface, which depends on its molecular structure. Smaller dye molecules easily penetrate the fabric surface, but large molecules cannot react with fibers easily. Hence, the color sticking is influenced by the fiber's porosity and surface texture.

3.1.3.3 Stability

Dye's stability is its capacity to resist fading, discoloration, and breakdown under different physical and chemical conditions. The stability of dye directly affects the lifetime and anti-aging look of coloring materials, including paper, leather, and textiles. Various parameters are used to assess dye stability. Thermal stability, chemical stability, light stability, pH stability, and eco-friendly surroundings are among these criteria.

3.1.3.3.1 Thermal stability

The thermal stability is a crucial factor affecting the type of textile dye. Dyes may compromise their structural integrity and diminish or deteriorate at elevated temperatures. High-performance dyes are ideal for industrial processes and applications demanding repeated exposure to elevated temperatures, as they preserve their color integrity even under extreme heat. Their exceptional thermal stability ensures uniform luminosity and reliable functionality even in challenging conditions.

3.1.3.3.2 Chemical stability

A significant factor is chemical stability. Chemical stability means a dye's ability to resist breaking down when it comes into contact with strong textile processing chemicals, like bleach or alkaline solutions used in mercerizing. This attribute ensures fabric quality and prevents undesirable fading throughout the manufacturing process. A chemically stable pigment in an acidic solution preserves its luminosity. The pigments employed in mercerizing also withstand the corrosive effects of sodium hydroxide. Ensuring colorfastness in demanding industrial processes requires significant endurance, as inferior dyes will degrade and undermine the outcome [37].

3.1.3.3.3 Light stability

A primary element is light stability. High-quality dyes will maintain their color in sunlight, ensuring the fabric preserves its natural hue. This attribute most significantly benefits outdoor textiles. A high light stability dye exhibits reduced susceptibility to fading. Therefore, they are perfect for goods needing long-term color maintenance under bright circumstances.

3.1.3.3.4 pH stability

The pH of the medium influenced the stability of a dye. Though some colors do better in neutral or alkaline settings, relatively few are stable in acidic ones. Keeping the right pH will help to ensure the longevity of the dye and its capacity to reach nice coloration. If the pH varies from the ideal range, it could cause a change in hue or color loss due to alterations in the dye's chemical structure.

3.1.3.3.5 Eco-friendliness

Low toxicity is emphasized by eco-friendly textile dyes to protect the health of consumers and employees, and their biodegradability allows for environmental breakdown, thereby reducing pollution [38, 39]. Additionally, by reducing pollution and degradation, these colors have a minor effect on the environment and contribute to the sustainability of the textile sector. Through the incorporation of characteristics like low toxicity, biodegradability, and reduced environmental effect, eco-friendly dyes enable safer production processes and align with international efforts to promote sustainable manufacturing practices.

3.1.3.4 Solubility

A dye's solubility means the dye is easily dispersed and forms a homogeneous solution in water or other solvents. Dye solubility mainly consists of two types. These are water solubility and solvent solubility.

3.1.3.4.1 Water solubility

If a dye is easily dissolved in water, then it is called water-soluble dye. Mostly during the dyeing process, the fabric is permitted to absorb the dye uniformly. For example, direct dyes need a constant color guarantee and suitable penetration of cellulose fibers so that the dye can be easily absorbed in water. Reactive dyes too rely on water solubility to enable their diffusion into the fiber and later chemical bonding. Too little solubility would cause the dye to clump or precipitate, hence producing uneven coloring and low colorfastness. Therefore, a major element is water solubility, which defines consistent and high-quality dyeing outcomes.

3.1.3.4.2 Solvent solubility

Solvent solubility is the capacity of dye to dissolve in organic solvents such as ionic liquids or supercritical CO₂ rather than water. Specialized dyeing methods such as solvent dyeing and supercritical CO₂ dyeing rely on non-aqueous solvents to deliver certain coloring effects or environmental advantages, so this characteristic is quite crucial. A dye's solubility in a solvent is affected by many elements, including the dye and solvent's polarity, the solvent's dielectric constant, temperature, and additive presence. Though supercritical CO₂ provides a sustainable alternative to water-based dyeing techniques, ionic liquids and deep eutectic solvents can greatly boost the solubility of natural dyes.

3.1.3.5 Compatibility

Dye compatibility is the capacity of a dye to interact with other dyes or chemicals in a dyeing system without producing negative effects. Two main factors are dye-to-dye compatibility and chemical compatibility [40].

3.1.3.5.1 Dye-to-dye compatibility

Compatibility of a dye is the ability of a dye to combine with other dyes without producing negative effects like uneven dyeing, color separation, or low colorfastness. This characteristic is important for making a broad spectrum of colors and tones. For

example, mostly cotton dyes mixed with other dyes smoothly make rich, fast, and bright colors. This characteristic helps the textile to achieve consistent, good quality results, expanding their color opportunities for different designs.

3.1.3.5.2 Chemical compatibility

The compatibility with other chemicals guarantees a dye's capacity to be utilized together with numerous chemicals usually used in the dyeing process, including salt, alkali, reducing agents, and other auxiliaries, without creating negative reactions. This quality is essential since the dye's interaction with these elements directly affects successful dyeing and colorfastness. Reactive dyeing, e.g., requires the dye to react with alkali chemicals, disrupting fiber connections. The color should also not degrade or produce undesired byproducts when applied with reducing agents.

3.1.3.6 Shade and color range

Important characteristics of textile dyes that directly affect their appropriateness for certain uses in the textile industry include color spectrum and shade constancy. The dye's broadest color spectrum lets it create a variety of hues, therefore sustaining the various color needs of the textile sector. This flexibility might allow the construction of vivid, diverse patterns that suit a range of consumer preferences and fashion trends. Conversely, regular shade declares that the dye produces a uniform hue across multiple applications and batches. This consistency guarantees the quality and homogeneity of the final product, thereby avoiding color fluctuations that can create dissatisfied consumers and inconsistent brand messages. Moreover, these features enable fabric manufacturers to create both creative and premium results.

3.1.4 Innovations in textile dyeing

Innovations in textile dyeing will be a remarkable convergence of science, technology, and sustainability, and will progress the industry, especially in the fields of digital printing and eco-friendly dyeing procedures. Digital textile printing is a method that has changed the way materials are dyed and designed. Utilizing inkjet technology to directly apply dyes onto fabrics presents a refined alternative to traditional dyeing methods, enabling unparalleled personalization, rapidity, and resource efficiency. This method is ideal for fast fashion and small-batch production, as it reduces waste by utilizing only the necessary dye, conserves water, and facilitates intricate designs and rapid color alterations. Eco-friendly dyeing techniques prioritize the utilization of natural, non-toxic, and biodegradable substances to mitigate their adverse effects on the environment [41]. Traditionally, textile dyeing is infamous for its high water use, chemical contamination, and production of hazardous wastewater. Business leaders and scholars are developing sustainable alternatives to help mitigate these issues. The remarkable advancement of natural dyes derived from plants, minerals, and microorganisms such as bacteria and fungi yields vibrant colors, requires minimal energy and water, is non-toxic, and exerts a negligible environmental impact [24].

Advancements in biotechnology have resulted in enzyme-based dyes and eco-friendly and more efficient auxiliary components [42]. The use of supercritical carbon dioxide as a solvent in waterless dyeing is a highly innovative approach. This approach involves subjecting CO₂ to a supercritical state, enabling it to function

as both a liquid and a gas, hence facilitating the penetration of colors into fabrics without the use of water. This technology conserves water and inhibits the discharge of toxic substances into ecosystems. Moreover, nanotechnology in textile dyeing has created new opportunities for enhancing dye fixation, color fastness, and fabric performance. Augmenting the utilization of colored materials further facilitates the incorporation of nanoparticles to produce consistent antimicrobial surfaces, UV-protective textiles, and self-cleaning fabrics. These advancements are not only theoretically intriguing but also significantly pertinent due to their fulfillment of the pressing demand for sustainable practices in the textile sector. Ultimately, digital printing and sustainable dyeing methods indicate a fundamental transformation in textile chemistry. The industry is progressing toward a future where modern technology and sustainable concepts can produce vibrant, high-quality textiles with minimal environmental impact. As academics, we must persist in scrutinizing these technologies, instruct the forthcoming generation of scientists, and propel the transition toward a more sustainable and efficient textile sector.

3.2 Art (dyes as a medium of creative expression)

Artists have used dyes as a medium of creative expression for generations, so offering a different spectrum of possibilities to create bright and important works [43]. Here is a look at dyes from different perspectives as a medium of artistic creative expression.

3.2.1 Historical use of dyes in art

Dyes have been a basis of human creativity, expressing both cultural expression and chemical innovation from prehistoric cave paintings to modern textile arts [44]. Early painters utilized certain biological materials such as iron oxides and charcoal to create earthy tones [45]. Narrative and symbolic ceremonies utilized these paints. As society changed, dyeing methods developed. For instance, whereas in Mesopotamia, Tyrian purple dye made from sea snails became a status symbol [46], the Egyptians created synthetic Egyptian blue for sacred pictures. China's mastery of indigo cultivation around 2400 BCE led to the evolution of silk-dyeing methods [32]. While ancient world arts give importance to West African mud cloth, Japanese shibori, Asian batik, and Indian bandhani, they investigated chemical ideas such as metal-ion complexes and solubility [47]. Europe during the Middle Ages saw colors like lead white and ultramarine, which were not synthetic but rather derived from natural sources. Perkin's invention of mauveine in the nineteenth century was a turning point, allowing bright, mass-produced color. Even now, dyes link art and chemistry by combining historical methods with modern materials science. This legacy emphasizes how, over tens of thousands of years, artistic vision and scientific developments have molded human.

3.2.2 Painting, printing, and fabric art

In painting, printing, and fabric art, dye is a medium that penetrates and chemically bonds with materials to produce bright, long-lasting, often translucent effects. Artists in painting can apply dyes on many surfaces like paper, fabric, or canvas using brushes or other instruments, much like they do paints. From transparent washes to opaque hues, dyes can be layered or diluted to produce various effects. Watercolor

dyes, for instance, dissolve in water and connect with cellulose fibers using hydrogen bonds, allowing them to produce fragile, translucent paintings with gentle color changes. Historically, oil painting used dyes like carmine. It includes combining dyes or pigments with drying oils that polymerize by oxidation, generating permanent, cross-linked films. For lightfastness, modern oil painting gives priority to synthetic pigments, e.g., cadmium red. Acrylics guarantee color permanence by using dyes spread in acrylic polymer emulsions, which create water-resistant films upon evaporation. Among the most noteworthy are quinacridone reds, synthetic dyes with planar aromatic structures that resist fading and produce strong chroma, and indigo, a vat dye needing reduction to leuco-indigo before oxidation to blue. These methods and materials show how chemistry from hydrogen bonding to polymerization influences the creative process as well as the lifetime of artworks. We also use dyes for printing and dyeing. Fabric art methods use dyes to color textiles by means of dip-dyeing, in which the fabric is submerged in a dye bath to obtain an equal hue or batik, which uses wax to resist the dye and produce detailed patterns. Common ways to transfer graphics onto fabric include dye block printing and screen printing. Techniques include screen printing, utilizing reactive dyes which create covalent connections with cellulose or disperse dyes which penetrate synthetics using hydrophobic interactions in printing. Block printing often uses mordants to increase dye-fiber affinity and sends dye pastes onto cloth. Under heat, digital printing uses sublimation dyes that bond with polyester fibers. In mixed media art, dyes can be used with other materials and methods. Used to stain or color metal, wood, or clay, they provide a splash of color and improve the general texture and visual appeal of the piece; e.g., dyes could be applied to a collage to produce a certain atmosphere or to blend various elements [48].

3.2.3 Importance of dyes in traditional art

Natural dyes have been absolutely crucial for the growth of cultural identity, customs, and artistic expression in a great spectrum of societies [43]. A UNESCO-recognized art form from Indonesia, batik uses natural colors like indigo in conjunction with wax-resist dyeing. More than only ornamental qualities, colors and designs have great cultural relevance; they visually explain stories. While elaborate decorations preserve local history and spiritual beliefs, blues are often connected with stability and our connection to nature. India's textile history provides beautiful examples. Rich in religious symbolism, the natural dyes used in Madhubani and Kalamkari paintings are made from indigenous plants using age-old traditions. During Hindu festivals, vivid reds and yellows are more than just decorative; they symbolize wealth, life, and divine favors. These constant color customs show how dyes connect cultural memory, identity, and religion, as well as being more than simply a source of color [7]. Cochineal represented power and divine favor in ceremonies and textiles made from insects important to Mesoamerican trade. Every design carries some cultural relevance. The dye used to color Malian African mud cloth, for example, is created from fermented mud and conjures ancestral stories and shared aspirations [49]. While the Japanese used indigo dyeing for confirmations of patience and tranquility, Chinese silk dyeing emphasizes meticulous craftsmanship using natural colors like madder and gardenia, which are basic to imperial art. Beyond looks, these hues express environmental balance, spiritual connectedness, and social hierarchy. Ancient Egyptians valued malachite and indigo for their mystical relevance in tomb decorations and ceremonies [50]. Natural dyes' comeback in artisan crafts and sustainable design

emphasizes their ongoing function in maintaining cultural legacy by linking contemporary efforts to old traditions, honoring the environment and human creativity.

3.2.4 Modern artistic evolutions

Changes in artificial and practical colors have had a major impact on modern art. By combining chemical innovation with artistic expression, these colors upsurge visual potential. Industrial synthetic dyes offer artists unmatched brilliance and longevity. Developed in 1907 and popularized in the 1930s, phthalocyanine blue gave Max Ernst a powerful lightfast replacement for conventional Prussian blue. Artists like Paul Cezanne and Seraphine Louis used synthetic alizarin as early as 1895 for its constant, strong hues. The strong molecular structures of these pigments absorb particular light wavelengths, hence generating bright hues that resist fading. Functional dyes such as thermochromic and photochromic pigments add dynamic interactive components to art. Some hues, e.g., exhibit reversible chemical interactions. Leuco dyes in thermochromic systems change between vibrant and colorless conditions, hence enabling artworks to react to environmental signals. Nanotechnology increases this interaction even more the structural color produced by nanostructured surfaces creates iridescent changes without pigments. Like Vant black, it absorbs 99.96% of light, therefore creating void-like images that change spatial awareness. Driven by environmentally friendly technologies, sustainability is getting more attention. Plant waste and low-impact synthetic-based bio pigments lower the need for hazardous heavy metals. Digital printing (inkjet-based) reduces waste by applying dyes pixel-by-pixel, while supercritical CO₂ fluid dyeing and other waterless dyeing techniques remove water pollution. Though they preserve creative diversity, these techniques tackle environmental issues. In the end, synthetic and functional dyes provide tools for bright, participatory, sustainable creation, exposing the harmony between chemistry and art. Although problems like degradation still exist, constant developments in analytical chemistry, bio-dyeing, and nanotechnology keep pushing creative boundaries and guarantee that the interaction between science and beauty stays dynamic and changing.

3.3 Industry (beyond textiles and art)

The applications of dyes go far beyond traditional sectors like textiles and art. Their optical, chemical, and interactive features inspire creativity in many other domains. Here is a brief overview of the use of dyes in different fields.

3.3.1 Printing and paper

The paper industry carefully selects dyes based on their chemical characteristics to impart specific aesthetic and functional qualities. By dissolving in water, direct dyes and sulfonated aromatic chemicals included in paper pulp during manufacture ensure a consistent color in products such as newsprint and office paper. Their capacity to engage with cellulose via hydrogen bonds produces long-lasting and vivid hues. Acid dyes in premium coated papers, greeting cards, and stationery need acidic conditions to attach to fibers, thus providing exact color control. Though they might show lower lightfastness, basic dyes are well-known for their strong pigmenting capacity, which lets them create bright colors for labels and ornamental materials, including gift wrapping. Fluorescent pigments absorb ultraviolet light and release visible wavelengths to brighten high-visibility items like neon sticky notes and security papers (banknotes). Apart from hue, functional additives improve paper

performance. Optical brighteners, which absorb UV radiation and re-emit blue light, help printing paper to look “whiter-than-white.” Embedded in specialist papers, pH indicators change color depending on acidity, therefore functioning analytically like litmus strips or industrial pH testing. These dyes and additives help papers meet many goals, from daily use to specialized ones. These dyes and additives demonstrate the connection between chemistry and design, thereby balancing sustainability, safety, and durability. Using dyes, printing produces high-quality images for packaging, newspapers, and magazines. Pigments in ink and paper coloring improve the look and functional qualities of paper products, enhancing their appeal and lifetime. Dyes in carriers such as solvents or resins impart color to materials, including paper, plastic, or textiles. Dissolving in organic solvents, solvent-based dyes are major dye types that generate high-intensity colors in conventional printing methods, often used in packaging. While they usually require fixatives to ensure durability, water-based dyes offer environmentally suitable substitutes for digital printing and food packaging with low volatile organic compounds (VOCs).

By forming covalent connections with cellulose, reactive dyes offer colorfastness in textile printing. UV-curable dyes cross-link under UV light to produce images resistant to scratches. Recent developments in ink technology have helped enhance performance and sustainability. For premium digital printing, nanoparticle dyes improve color depth and dispersion stability. E-readers utilize thermochromic and electrochromic inks, while smart inks combine biodegradable inks and plant-based dyes to create environmentally friendly packaging that supports the circular economy. These changes indicate a trend toward beneficial eco-friendly materials that nevertheless generate wonderful outcomes. The paper industry, therefore, relies on dyes to color paper products and manufacture high-quality inks. By enhancing its functional performance and visual appeal, its use increases the lifespan of the paper and its aesthetic appeal for many uses.

3.3.2 Leather tanning

Raw hides are converted into functional and visually appealing products through the complex interplay of chemical principles, craftsmanship, and innovative design referred to as leather dyeing. Contemporary advancements in dye chemistry prioritize sustainability and performance, aligning with stringent environmental regulations and evolving consumer preferences for eco-friendly products. To ensure that leather remains a durable, versatile, and eco-friendly material, the industry is increasingly using green energy methods such as biodegradable dyes and low-waste processes. There are different methods for leather dyeing and tanning. These are described below.

3.3.2.1 Leather dyeing

There are five basic leather coloring methods. These are the aniline, pigment, drum, hand, and spray methods. Emphasizing natural textures by deep penetration into the leather’s fibers, the aniline dyeing procedure first preserves elasticity. Pigment dyeing is the second method, which consistently colors the surface and so provides longevity and fade resistance. The third method is drum dyeing which is perfect for large-scale manufacturing since it reaches thorough saturation using spinning drums. The fourth method is hand dyeing; it creates unique artisanal finishes by means of manual application. The fifth method is spray dyeing; it offers quick, uniform coverage for large surfaces, usually in industrial environments.

3.3.2.2 Leather tanning methods

The choice of dye and method depends on the leather's tanning process, which determines its structural properties and dye affinity. There are several leather tanning methods, such as vegetable tanning, chrome tanning, chrome-free tanning, synthetic tanning, aldehyde tanning, oil tanning, brain tanning, mineral tanning, and combination tanning.

3.3.2.2.1 Vegetable tanning

Vegetable tanning is a traditional leather-making process that uses natural tannins derived from plants such as oak bark, quebracho, and chestnut. These tannins chemically bond with the collagen fibers in the hide, stabilizing and cross-linking them to convert raw hide into durable leather. The process involves soaking the hide in water for cleaning, followed by immersion in vats with progressively stronger vegetable tanning solutions, a method that can take weeks or even months. The resulting leather has a natural, warm appearance, excellent breathability, and high durability, though it starts off stiff and softens over time while developing a rich patina. Still, as compared to other tanning techniques, it is more prone to water damage. Vegetable-tanned leather is often used in high-end items, including shoes, belts, handbags, and furniture upholstery, since it is attractive and durable.

3.3.2.2.2 Chrome tanning

Chromium (III) sulphate is utilized in chrome tanning, a modern and efficient leather manufacturing method, to maintain and strengthen the collagen fibers in the hide. The first phase of the process is regular hide preparation; next, immersion in a chromium salt solution with exactly controlled pH and temperature. Its flexible, permeable nature allows for dyeing, which leads to durable absorption and bright colors. Usually requiring just a few hours to many days, depending on the hide's thickness, chrome tanning is far faster than vegetable tanning. The resulting leather is quite strong, supple, and flexible. Its aptitude for bright dyeing and exceptional resilience to water and mildew are remarkable. The disposal of chromium-contaminated wastewater raises environmental issues, though. Apart from fashion items like purses, gloves, and outerwear, chrome-tanned leather makes up more than 85% of world production and is widely used in industrial uses requiring resilience and flexibility.

3.3.2.2.3 Chrome-free tanning

Ecologically conscious leather production, chrome-free tanning, uses safer substitutes like vegetable tannins, aldehydes, or synthetic chemicals in place of toxic chromium salts. This method lowers environmental and health concerns connected with conventional chrome tanning while producing soft, usable leather. Though usually slower and perhaps less water-resistant than chrome-tanned leather, chrome-free alternatives offer comparable flexibility and dyeability, with certain techniques producing biodegradable outcomes. In sustainable fashion, vehicle interiors, and luxury products, the leather is especially prized where eco-friendliness is a top priority. Although they might not be similar to chrome tanning in all performance criteria because of continuous developments in alternative tanning chemicals, businesses dedicated to balancing quality and environmental responsibility are finding

chrome-free tanning techniques more and more reasonable. Hence, this method is considered a greener method with an eco-friendly environment.

3.3.2.2.4 Synthetic tanning

Synthetic tanning, often known as artificial tanning, employs laboratory-produced organic compounds to replicate the advantages of traditional vegetable or chrome tanning while mitigating their disadvantages. Depending on the chemicals used, the method calls for processing hides under measured conditions with certain synthetic tanning agents. Usually more efficient than vegetable tanning, this technique yields more consistent outcomes. While sustaining the suppleness and elasticity natural in chrome-tanned leather, the resulting leather can be changed to increase chemical or water resistance. Many synthetic tanning chemicals have also been formulated to be more environmentally benign than conventional methods. Reducing toxicity and enhancing biodegradability help to achieve this. From daily needs to specialty items with particular performance criteria, synthetic tanning is also found in a great range of leather goods because of its flexibility and environmental friendliness.

3.3.2.2.5 Aldehyde tanning

Aldehyde tanning is a leather manufacturing technique that cross-links collagen fibers with reactive chemicals such as formaldehyde or glutaraldehyde, stabilizing the skin. This procedure processes the hide under controlled pH and temperature using an aldehyde solution, which accelerates the tanning process. As compared to vegetable-tanned leather, the resulting leather shows improved water resistance, better dimensional stability, and higher strength. The formaldehyde-based tanning technique is harmful and risks health and the environment. Its structural qualities are especially beneficial for industrial uses calling for robust leather, like specialist belts and industrial gloves.

3.3.2.2.6 Oil tanning

Oil tanning, an old leather-processing method also known as brain tanning, uses natural oils and fats, usually from animal brains, to soften and preserve hides. This method consists of soaking the hide and then lightly pressing oils into it. Smoking is typically used to define the therapy and improve preservation as well as to impart a certain color and earthy aroma. The resulting leather has an amazing natural feel and is incredibly soft, flexible, and breathable. On the other hand, its stain sensitivity and ongoing maintenance requirements are drawbacks. In Native American crafts and specialty leather goods like handbags and moccasins, where a soft and natural look is desired, this age-old technique is still highly prized. Hence, the oil tanning method is distinguished by its handmade quality and its association with traditional leather-working methods.

3.3.2.2.7 Combination tanning

By integrating the benefits of each approach, combination tanning creates leather with improved and tailored qualities using two or more tanning methods. For example, combining chrome and vegetable tanning produces leather that balances the hardness and natural look of vegetable-tanned hides with the softness of

chrome-tanned hides. A range of tanning chemicals are used in successive treatments during the process. Customized methods deliver the desired traits. While preserving a more natural appearance than chrome tanning by itself, this hybrid combined tanning approach offers higher water resistance than pure vegetable tanning. The outcome is a premium, flexible leather that may be exactly customized to fit certain requirements. Occasionally, combination tanning is utilized to obtain the extraordinary softness and polished natural appearance absolutely for high-end leather products such as luxury bags, shoes, and accessories. By maximizing both use and design, this technique demonstrates inventiveness in leather manufacture.

3.3.3 Food and cosmetics

Dyes play a multifaceted role in food, cosmetic, and personal care products, enhancing their visual appeal, aiding in brand identification, creating a sense of luxury, indicating specific functions, providing camouflage and correction, and influencing psychological and emotional well-being [38]. Their strategic use ensures that these products not only meet aesthetic standards but also cater to the diverse needs and preferences of consumers. Food dyes play a significant role in the food industry, enhancing the visual appeal, maintaining color consistency across batches, and marketability of various products. They play a key role in consumer perception, as color influences taste expectations and purchasing decisions. In food, both natural and synthetic dyes are used. They are particularly important in processed foods, i.e., ice cream, canned fruits, breakfast cereals, processed vegetables, beverages such as soft drinks, energy drinks, sports drinks, and flavored juices, baked goods, condiments, and candies. For example, the bright red dyes in candies mostly attract children, while natural-looking dyes in ready-to-eat meals make them more appetizing. The dyes are also essential in the cosmetic and personal care industry for enhancing visual appeal, providing color variety, offering functional benefits, aiding in brand identification, and influencing consumer psychology. Cosmetic goods, including lipsticks, eyeshadows, blushes, and nail polishes, use dyes in a variety of shades and colors. This allows consumers to choose colors that match their personal style, skin tone, and the occasion. High-quality vibrant dyes can give the impression of a luxurious and premium-quality product. Bright and intense colors in products like high-end lipsticks or eyeshadows can make consumers feel that they are using a top-of-the-line item. Furthermore, in hair coloring products, different colors may represent different levels of lightening or the specific shade of the final result. For skin base products like concealers and foundations, dyes are used to help hide flaws, dark circles, and other skin imperfections. They can also help the skin tone to change, making it more even and smooth. In psychological and emotional effects, hues have the ability to affect feelings and moods. The correct hue in cosmetics, for instance, can increase a person's confidence and make them feel more attractive; using a preferred shade of lipstick or eyeshadow can also have a good psychological impact, therefore enhancing the user's sense of self-assurance and organization.

3.3.4 Pharmaceuticals

In pharmaceuticals, dyes are quite important and diverse since they go well beyond basic coloring. Their uses range from medication formulation to patient safety to diagnostics to regulatory compliance; hence, they are absolutely vital in contemporary medicine. For example, as hospitals and pharmacies offer a large number

of drugs, dyes are used to color-code tablets, capsules, and liquid pills, allowing healthcare personnel to quickly identify several drugs. A frequent but major problem in healthcare environments, this lowers the likelihood of pharmaceutical mistakes. Dyes are also used to indicate medicinal strengths; for example, a lesser strength pill might be light colored, but a greater strength version of the same medication could be darker. This visual cue guarantees the right dose is given, hence supporting efficient treatment for patients as well as medical personnel. Dyes also have quite significant effects in enhancing the visual attractiveness of pharmaceutical items. The look of drugs can affect some adults as well as children and influence their desire to use them. Moreover, some dyes can show a drug's durability. Environmental variables, including pH, temperature, and humidity, can promote drug deterioration and cause them to change color. Dyes are also useful in medical diagnosis, for example, to stain pathological biological material. A straightforward method is hematoxylin and eosin (H&E) staining. While eosin colors the cytoplasm and extracellular matrix pink, hematoxylin colors the cell nuclei blue-purple. Pathologists can find various cell kinds, spot aberrant cell architectures, and diagnose cancers with this staining. Choosing the right antibiotic treatment depends on bacterial classification, which is done using other specialist stains such as Gram stains.

Fluorescent dyes are used in advanced diagnostic techniques such as flow cytometry and fluorescence microscopy. Fluorescence microscopy links these hues to particular chemicals or cells. Excited by a certain wavelength of light, they emit fluorescence, which allows researchers to examine the distribution and function of proteins within cells. Flow cytometry sorts and analyzes cells using fluorescent-tagged antibodies depending on their physical and chemical traits. Moreover, fluorescence is another technique. Often, guided surgery emphasizes tumors or other problematic regions using colors. This strategy allows doctors to precisely remove the sick area while maintaining healthy tissue. This process benefits patients by increasing the accuracy and success rate of treatments. Medical imaging also makes use of dyes as contrast agents. The digestive tract is X-rayed using barium sulfate. Coating the surfaces of the digestive organs allows medical personnel to identify issues like ulcers, polyps, or obstructions and enhances their appearance. Magnetic resonance imaging (MRI) increases the contrast between healthy and ill tissues by means of gadolinium-based contrast agents. This allows for precise diagnosis of conditions such as brain tumors and multiple sclerosis.

3.3.5 High-tech application

Functional dyes have transformed modern technology by means of advances in data storage, renewable energy, and biological imaging [51]. Modern uses depend on these molecularly designed, complex dyes since they are light-responsive, biocompatible, and conductive.

3.3.5.1 Optical data storage system

Functional dyes are mostly used due to their fast speed and maximum data storage density. CDs and DVDs, like other traditional optical discs, use dyes to produce a pattern of pits and lands that represent digital data. Conversely, new functional dyes permit more precise control over the recording and reading of data since they can absorb and emit light at particular wavelengths. This allows for the production of next-generation optical storage media, Blu-Ray discs that can hold far more data in

a smaller physical area. The employment of functional dyes in optical data storage is absolutely necessary to satisfy the rising need for large-capacity, quick-access storage options given the exponential increase of digital information. Moreover, functional dyes are meant to be quite durable under various environmental circumstances, hence guaranteeing long-term data storage. They withstand deterioration from elements like heat, light, and humidity that could finally lead to data loss. Archiving essential digital data, including historical records, scientific research, and cultural legacy artifacts, calls for these attributes.

3.3.5.2 Renewable energy

Functional dyes in solar cells boost the absorption of sunlight over a greater spectrum. Focusing on organic dyes, dye-sensitized solar cells (DSSCs) generate an electric current by means of photon collection and electron mobility. Tuning these dyes to absorb light at different wavelengths will assist in increasing their efficiency in converting solar energy into electrical power. By increasing the capacity of solar cells to collect light, functional dyes allow the creation of cheaper and more efficient solar energy systems. This depends on us reducing our reliance on fossil fuels and switching to a more sustainable energy future. Dyes are also a very inexpensive replacement for traditional silicon-based solar cells. The manufacture of DSSCs utilizing functional dyes is often less costly. Considering their low energy consumption and simple manufacturing process, DSSCs could be a sensible option for large-scale solar energy production. Therefore, the overall cost of solar cells is decreased by producing effective dyes from inexpensive and plentiful ingredients.

3.4 Dyes' economic and cultural impact

The dye industry has profoundly influenced human civilization and has been a foundation stone of global economic and cultural development. The evolution from the initial extraction of natural dyes in prehistoric eras to the extensive production of synthetic dyes in contemporary times has significantly influenced fashion trends, trade networks, and technological progress. A long time ago, dyeing was more than just a pragmatic need; it became a cultural symbol reflecting beliefs, identities, and history. This analysis will address the pressing challenges confronting the sector and the transformative potential that exists, while also exploring the multifaceted role of dyes in global economies and cultural heritage.

3.4.1 Financial benefits of the worldwide dye industry

International economies mostly focused on the dye sector because it produces employment and economic development. Expected to be worth USD 12.68 billion in 2024, the worldwide textile dye market is projected to upsurge at a compound annual growth rate (CAGR) of 6.1% to USD 21.61 billion by 2033 [52]. This expansion is fueled by various elements, including the increasing need for textiles caused by rapid urbanization, population increase, and greater discretionary money, particularly in developing nations [53]. Market revenue expansion is also being driven by the need for sustainable, eco-friendly, and long-lasting colors. Improvements in digital printing technology and the rising demand for specialty textiles, particularly technical and smart textiles, help the textile dye sector as well.

3.4.2 Cultural legacy

Many societies all throughout the world depend on traditional dyeing techniques, which are culturally important. Often handed down through time, these techniques are employed to produce conventional textiles, garments, and artifacts. Changed civilizations have employed natural dyes derived from plants, minerals, and insects for millennia to create unique and important colors. Keeping ethnic identity and traditional skills benefits local artisans and endorses environmentally responsible behavior. Projects are underway to document and bring back fading traditional skills to save this cultural legacy from industrialization and modernity.

3.4.3 Significance of dyes on consumer choice and fashion trends

By offering a broad variety of colors and tones that fit changing tastes and cultural expressions, dyes greatly affect customer choices and fashion trends. Often set by organizations like the Pantone Color Institute, color trends affect a wide range of goods consisting of cosmetics, accessories, and clothing [54]. Colors may be a strong weapon for designers to produce intended moods and stories in their collections since they can inspire certain feelings and interpretations. It is crucial to comprehend the psychological and cultural significance of colors, as different hues are associated with specific emotions or cultural implications. For instance, many link red with zeal and vitality, while blue is usually considered soothing and reliable. The growth of social media and digital media has also had a major influence on color preferences among fashion customers. Should it gain popularity among celebrities and influencers, the need for a certain type can be rapidly increased. Sustainability is becoming a pressing problem; hence, eco-friendly colors and materials are in more demand.

3.4.4 In global dye market challenges and prospects

Tight environmental rules, raw material price fluctuation, and supply chain interruptions are among the many issues the worldwide dye business confronts. Resource-demanding and waste-producing traditional dyeing methods drive more strict environmental rules and greater compliance expenses. Market income growth is hampered by the increasing availability of alternatives, including natural dyes and pigments, and the greater cost of dyes. Still, the business offers many possibilities. Advancements in dyeing technology, such as digital printing and waterless dyeing, are helping to increase the efficiency and sustainability of dyeing processes. Increased focus on sustainability is driving more interest in natural and eco-friendly dyes. Rising consumer knowledge of sustainable goods and the textile industry's growth in rising countries are driving the market.

4. Challenges and future directions

Many important problems in the dyeing sector need quick fixes and creative ideas. Dyeing's effects mostly include land degradation, water pollution, and worker health hazards; therefore, environmental concerns take first priority [55]. Dyeing operations' significant water use and use of chemicals call for strict environmental rules in places including China, North America, and Europe. Supply chain disruptions and



Figure 2.
Challenges and future directions.

changes in the prices of raw materials, including benzene, could affect the costs of textile dye production and price stability. As industrialization and the widespread use of synthetic dyes threaten the profitability of conventional dyeing techniques, cultural preservation becomes a major issue. The future of the dye industry lies in blending invention with history while also considering environmental concerns and sustainability. Emphasizing the development of affordable, scalable skills and sustainable production practices, technological innovation is absolutely vital. Implementing automation and digitalization methods, including machine learning, artificial intelligence, and the internet of things, is very vital if dyeing operations are to be more efficient and productive. Sustainable practices are essential; bio-based colors derived from bacteria, algae, and food waste, along with waterless dyeing techniques utilizing supercritical CO₂, are increasingly gaining popularity. Encouraging and supporting traditional dyeing methods facilitates cultural preservation and safeguards generations of cultural heritage. The dynamics of the global market will be significant; owing to rapid industrialization and rapidly increasing demand from countries such as China and India, the Asia-Pacific region is expected to command the biggest proportion of the dyes sector. The increasing demand for sustainable and eco-friendly dyes in North America and Europe offers new economic opportunities for creative and environmentally conscious dye makers. **Figure 2** explains challenges and future direction.

5. Conclusions

The dye business, encompassing natural pigments and synthetic dyes, has significantly influenced human civilization by addressing both practical and cultural needs. While it has catalyzed innovation in industry, art, and textiles, it presently encounters challenges related to cultural preservation and environmental sustainability. The industry can achieve sustainable solutions by reclaiming natural dyes and integrating

traditional techniques with technological advancements such as digital printing, waterless dyeing, and biotechnology. Hence, the dye industry, a cornerstone of global economic and cultural heritage, remains vital and contributes to a sustainable future by harmonizing innovation with tradition.

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Supercritical CO₂ Dyeing of Textiles: Dye Properties, Technical Requirements, and Industrial Perspectives

Ahmad Ibrahim, Hamid Lamoudan, Nathalie Gaudette, Justine Decaens, Valerio Izquierdo and Olivier Vermeersch

Abstract

Supercritical CO₂ dyeing represents a major innovation in sustainable textile processing, offering a water-free and energy-efficient alternative to conventional dyeing. This technology harnesses the unique solvent properties of carbon dioxide above its critical point, enabling efficient dye transport into synthetic fibers, particularly polyester, without generating wastewater or residual chemicals. For optimal performance, dyes must exhibit specific properties such as solubility in supercritical CO₂, high thermal stability, strong fiber affinity, and environmental compatibility. The process requires precise control of temperature, pressure, and dye concentration, along with specialized high-pressure equipment designed for industrial-scale operation. Despite its clear ecological benefits, large-scale adoption faces challenges, including high equipment costs and the limited availability of dyes compatible with CO₂-based systems. However, recent progress in dye molecular design, fluid dynamics modeling, and reactor optimization has significantly improved color yield, reproducibility, and economic feasibility. Supercritical CO₂ dyeing eliminates water usage, drastically reduces energy consumption, and minimizes chemical waste, achieving high coloration performance while aligning with global sustainability goals. Its application potential now extends beyond polyester to selected blends and high-performance fibers, supported by ongoing innovation in equipment design and dye chemistry. This chapter provides a comprehensive overview of the principles, technical requirements, and industrial outlook of supercritical CO₂ dyeing. It highlights how continuous advances in process engineering and green chemistry are paving the way for the broader adoption of this technology as a cornerstone of next-generation, eco-efficient textile manufacturing.

Keywords: sustainable dyeing, textile dyeing, dye solubility, fiber affinity, thermal stability, eco-friendly dyeing, high-pressure dyeing

1. Introduction

Textile dyeing is an important phase in textile production, where dye is used to increase the appearance of natural or synthetic fibers and to provide the specific properties. It is necessary for industries such as fashion, home goods, and technical textiles, the coloring process today presents important environmental and health challenges [1, 2]. This process requires huge amounts of water, usually between 100 and 150 liters per kg of clothing, mainly for soaking, dye determination, and rinsing. Unfortunately, most of this water is released without adequate treatment, which causes pollution in waterways, especially in areas with the weak environmental rules [3]. According to the UN Environment [4, 5], the textile industry contributes up to 20% of global water pollution through industrial waste. Dye, chemical additives, heavy metals and solvents used in dye can be toxic, non-biologically degradable and bio-accumulative, negative aquatic life, soil quality, and finally, can affect human health through food chains [6].

Moreover, the textiles manufacturing process accounts for a substantial share of global water usage, withdrawing around 93 billion cubic meters of water annually, claiming to be 4% of global freshwater resources [7] (AI. 1). In response to growing environmental concern and regulatory pressures, textile producers are constantly looking for resource efficient and sustainable textile processes to supplant water intensive methods. These efforts have led to the development of a range of resource efficient technologies such as supercritical carbon dioxide, plasma technology, Spin Dyeing, 3D printing, digital printing, enzymatic treatment, electrochemical dyeing, and ultrasonic treatment [8]. Among these technologies, Supercritical Carbon dioxide dyeing (scCO₂) has acquired significant focus for its potential to reduce environmental impact and increase resource efficiency.

Dyeing, particularly on synthetic fibers like polyester, demands elevated temperatures (up to 130°C for pressure-autoclave dyeing), resulting in significant energy consumption, especially in “aqueous” processes. The majority of this energy is derived from fossil fuels, leading to increased greenhouse gas emissions [9]. The discovery of options for traditional textile dyeing methods has only exceeded an industrial decision; it is now a strategic requirement that is driven by important factors such as regulatory pressure, environmental considerations, and increasing demand for stability. Governments and international organizations have implemented strict environmental rules in the textile industry, including the following:

- REACH (EU): This regulation limited or limits the use of thousands of dangerous chemicals, including many azofolols, heavy metals, and solvents often used in dyeing [10].
- ZDHC (zero emissions of hazardous chemicals): An industry initiative aims to eliminate the emissions of hazardous chemicals from textile production. AgeC Law (France), Law 25 (Quebec), Green [11].
- Deal (EU): These laws focus on regulating polluting practices, setting up recycling paths and encouraging eco-design in the textile field [12, 13].

Industries are now required to adapt their procedures in order to comply with increasingly strict environmental standards; failure to do so may result in penalties, loss of market access, or a decline in competitiveness [14]. The environmental impact

of textile dyeing has become unacceptable for much of society, largely due to the following issues [15–17]:

- Water pollution: Discharge of toxic effluents into rivers and water systems, including residual dyes, salts, surfactants, and effluents with extreme pH values.
- High carbon footprint: Significant energy consumption required to heat large volumes of water and to dry textiles after processing.
- Excessive water use: Heavy reliance on freshwater resources, often in regions already experiencing water scarcity. Reducing this impact has become increasingly critical in the context of climate change and the depletion of natural resources.

Today, both brands and consumers require more environmentally friendly products with specific criteria:

- Color durability without relapse.
- Reduced effects to reduce the environmental footprint of the finished product.
- Clean procedures that are compatible with chemical or mechanical recycling of textiles. In addition, openness about original and dyes has become an important buying criterion, especially in environmentally conscious market segments.

The introduction of supercritical CO₂ (scCO₂) as a solvent medium for dyeing polyester (PET) fibers can be attributed to early pioneering work in the field [18]. Supercritical fluids have the ability to dissolve organic molecules with hydrophobic characteristics, such as disperse dyes, which laid the foundation for the development of scCO₂ dyeing techniques [18]. Numerous studies have since investigated the dyeing of polyester in supercritical carbon dioxide, demonstrating the feasibility and performance of this approach [19, 20]. Beyond conventional dyeing, growing interest has emerged in functionalizing textile substrates through processes such as the impregnation of antimicrobial agents or photochromic compounds. It is also noteworthy that previous research examined the use of Disperse Orange 25—a dye sharing the same chemical structure as Coranger Orange PE3330—within the scCO₂ dyeing process. These investigations provided valuable insights into the solubility behavior of disperse dyes in the scCO₂ medium [21].

2. Supercritical CO₂

2.1 SCCO₂ as a solvent in textile dyeing process

Supercritical carbon dioxide (SCCO₂) functions as a nonpolar solvent, and since disperse dyes share this nonpolar character, the system naturally favors the dyeing of hydrophobic fibers such as polyester. Its distinctive features—low viscosity and high diffusivity—position scCO₂ as a strong candidate to replace the conventional aqueous dyeing techniques. A key aspect lies in its role as a molecular lubricant: In the supercritical state, CO₂ is able to swell and plasticize polyester, enhancing chain

mobility in the amorphous zones of the polymer structure [22]. Experimental findings indicate that the diffusivity of dyes in PET under scCO₂ conditions is nearly three orders of magnitude greater than in water-based systems, with the reported values of 6.0×10^{-16} compared to 2.3×10^{-17} m²/s [23, 24]. Such an increase highlights the efficiency of molecular transport in this medium.

Pressure-density relationships are also critical. Raising the pressure increases the density of CO₂, which strengthens interactions between the solvent and the dye molecules, thereby promoting solubility and diffusion into the fiber [25]. When the dye-fiber affinity is high, penetration is facilitated even under moderate pressures, which can shorten dyeing times; further increases in pressure do not necessarily yield added benefits. In contrast, dyes with weaker affinity exhibit lower uptake, as partitioning toward the CO₂ phase dominates.

The proximity to the critical point of CO₂ introduces additional complexity. Even slight temperature variations can trigger sharp density drops, reducing the solvating capacity of the medium. Under isobaric conditions, this translates into higher sublimation pressure of the dye coupled with reduced solvent density, leading to diminished dye solubility [26]. At lower pressures, elevated temperatures further limit solubility, whereas at higher pressures, both sublimation pressure and solubility rise together with temperature.

Overall, these observations emphasize the highly dynamic behavior of scCO₂ dyeing, where pressure and temperature act as decisive levers for process optimization.

2.2 Physicochemical properties

Supercritical CO₂ coloring is a cutting-edge technology that uses carbon dioxide in its supercritical state, an intermediate phase between gas and liquid, at a temperature above 31°C and is achieved by pressure over 73.8 bar [27]. In this condition, CO acts as a very effective solvent for hydrophobic dyes, especially they are used for synthetic fibers as polyester [28]. Unlike traditional dye methods, this approach eliminates water use, does not produce wastewater, and does not require supportive chemicals such as agents or dispensers [29]. In addition, more than 90% of the used CO₂ used can be recycled and recycled, making it an environmentally friendly alternative. Although the original costs of units are still high, the technology has a significant ability to reduce organic footprints of color colored, corresponding to new stability and regulatory standards [30, 31]. Despite these benefits, supercritical CO₂ dyeing is still mainly limited to research laboratories and small-scale production. The main barrier for broad adoption is optimal dye choices, and process advance and lack of knowledge about equipment design [32].

As described in **Figure 1**, the phase of carbon dioxide shows how the position changes with variation in temperature and pressure. At low temperatures and high pressure, CO₂ is present as a solid. Under moderate temperatures and high pressure, there is a liquid, while at high temperatures and low pressure it is present in the form of a gas. The two key points are highlighted: the triple point, where the solid, liquid, and gaseous phases of CO₂ coexist in equilibrium, and the critical point, which marks the conditions above which CO₂ becomes a supercritical fluid. In this supercritical stage, CO₂ shows both gas-like and liquid properties, making it valuable for applications such as dyeing, extraction, and cleaning.

The dye process works by dissolving colors in supercritical CO₂, which then takes the color into fiber. However, this can be difficult. If the dye is poorly soluble, there

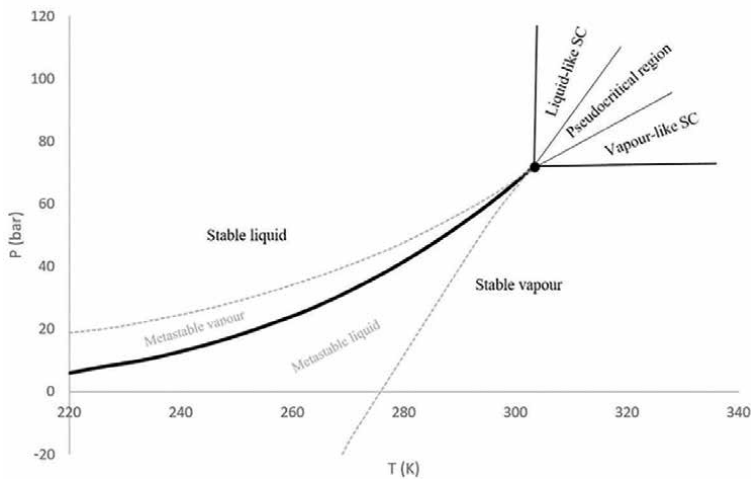


Figure 1.
Phase diagram of CO₂ showing the supercritical region [33].

may not be sufficient fasteners for the fiber sufficient for efficient production. On the other hand, if dissolved very well, it can remain in liquid instead of being binding to fiber, resulting in under-time material. In addition, different dyes interact with fiber in unique ways, which can lead to uneven dye distribution. This is why it is important to constantly understand the dye polarity and its behavior during the process to achieve high-quality results [34].

2.3 Key challenges faced in supercritical CO₂ dyeing

Supercritical CO₂ dyeing represents a highly promising sustainable alternative to conventional aqueous processes, but its adoption remains constrained by several critical challenges. Technically, the need for high-pressure, high-temperature equipment and the limited solubility or compatibility of many dye classes restrict large-scale implementation. From an economic perspective, the substantial initial investment and significant energy requirements can hinder uptake, particularly for small and medium enterprises. Environmentally, the true sustainability of the process depends strongly on the sourcing of CO₂ and the management of by-products. Overcoming these challenges through innovations in equipment design, dye chemistry, and renewable CO₂ sourcing will be essential to unlocking the full industrial potential of this technology. The main technical, economic, and environmental challenges associated with supercritical CO₂ dyeing are summarized in the following table, which highlights the current limitations of the process and the key factors that must be addressed for broader adoption.

Table 1 summarizes the key challenges faced in supercritical CO₂ dyeing, making it easier to understand the various technical, economic, and environmental issues associated with the process.

The supercritical CO₂ represents a state a cutting-edge approach to textile coloration that eliminates water use when providing energy efficiency and accurate color control. Unlike traditional water dyeing, SCCO₂ dyeing depends on the unique solvent properties of CO₂ over its significant temperature and pressure, so that it can act as both transport medium and an inflammatory agent for synthetic fibers. The

Challenge	Description	Impact
Technical challenges		
High pressure and temperature	The supercritical CO ₂ requires high-pressure application (7.38 MPa) and temperature (~ 31° C) to maintain its supercritical state. This requires special equipment [35].	Expensive and complex equipment is challenging to run small scale or adopt technology for new companies [35].
Dye solubility and efficiency	Some dyes may not be completely soluble in SCCO ₂ or require additional CO ₂ to increase solubility and coloring efficiency [36, 37].	A border in dye compatibility can affect the efficiency of the process, and the color structure may require additional chemicals or modifications [38].
Limited dye options	All types of dyes (e.g., reactive or VAT color) are not suitable for SCCO ₂ due to poor solubility in COO [39].	Limit the range of textiles that can be colored with SCCO ₂ , especially for natural fiber or fiber that requires special dyes [37].
Economic and scaling issues		
Initial investment	High starting costs are required to install super-critical COO dye systems, including special reactor, COO gas handling systems and pressure vessels [36].	High advance investments can prevent small companies or startups from using technology [40].
Energy consumption	Despite environmental benefits, this process requires significant energy to maintain supercritical conditions (temperature and pressure) [35].	Increased energy costs can deny certain environmental benefits if they are not adapted to efficiency affecting general stability.
Environmental concerns		
CO ₂ sourcing	Environmental benefits depend on the source of CO ₂ . If it is obtained from fossil fuels, the general stability of the process is compromised [36].	Using CO ₂ from non-renewable sources can reduce SCCO ₂ staining of green identification.
Waste and by-products	Although SCCO ₂ dyeing produces smaller products than traditional methods, some Sami sequences or additives can still produce waste [41].	The use of Sami sequences can cause chemical waste, although the volume is much smaller than the methods of traditional dyeing.

Table 1.
Key challenges faced in supercritical CO₂ dyeing.

efficiency of this method depends not only on the process such as temperature, pressure, and time, but also on the chemical properties of the colors themselves. Choosing colors with the compatible properties with SCCO₂ ensures effective solubility, uniform fiber penetration, and durable color performance.

2.4 Critical properties of dyes for supercritical CO₂ dyeing (SC CO₂)

The table above reveals the criteria required to choose appropriate dyes for dyeing. Considering the solubility, thermal stability, fiber compatibility, and environmental effects carefully, itself can adapt to dye, ensure similar dyeing and maintain the stability advantage that is inherent for supercritical COO processes. In addition, it supports focusing on fixed properties and reversality both commercial quality and experimental flexibility, making SCCO₂ a versatile and environmentally conscious alternative for traditional methods (Table 2).

Property	Requirement/feature	Reason/role in scCO ₂ dyeing	Example/notes
Solubility in scCO ₂ [42, 43]	Non-polar or hydrophobic structure; small to moderate molecular weight; alternative use of a co-solvent for polar dyes	ScCO ₂ is not-polar; the pigment should be effectively dissolved to move in fiber. Poor solubility reduces the color management and uniformity.	Dispers dyes (e.g., C. I. Dispers Red 60, Dispers Blue 79). Ethanol, such as ethanol, can partly improve the solubility of polar colors.
Thermal Stability [44]	Stable at 80–120°C (typical SCO) coloring area; resistant to pressure-induced changes	Prevents chemical decline or color changes under high temperatures and pressure; shadow maintains stability and fading.	The pigment should maintain chromism for integrity; Azo and anthraquinone colors are preferred.
Fiber affinity/compatibility [45]	Strong affinity for synthetic fibers (polyester, nylon); enhanced diffusivity in the fiber matrix	The uniform color ensures penetration; not-polar dyes spread effectively in hydrophobic polymers.	Polyester fiber: Scattered dye works well. Cotton or wool requires change or co-discomfort to improve recording.
Molecular diffusivity [46]	Small-to-moderate size molecules that can penetrate fiber amorphous regions	High diffusivity allows dyes to evenly distribute and reach deep fiber layers.	Larger or highly branched dyes diffuse poorly, causing uneven coloration.
Fastness properties [44]	High resistance to washing, rubbing, and light exposure	Maintains commercial quality and durability of dyed textiles.	Testing via ISO 105 standards for washing (ISO 105-C06), rubbing (ISO 105-X12), light (ISO 105-B02)
Environmental compatibility [47]	Minimal or no auxiliary chemicals; ideally no toxic co-solvents	Preserves the eco-friendly advantages of scCO ₂ ; reduces chemical effluent	Dyeing polyester with only CO ₂ avoids water pollution; small amounts of ethanol may be used to enhance solubility without environmental risk.
Reversibility/recoverability	Non-reactive dyes that can be removed if necessary	Facilitates recycling of dyes and CO ₂ ; supports circular processes	Important for experimental runs or for adjusting shade in industrial processes.

Table 2.
Critical properties of dyes influencing solubility, fiber affinity, and performance in supercritical CO₂ dyeing.

3. Dyeing process

In supercritical CO₂ dyeing, the process is carried out without the use of water, making it a cleaner and more sustainable alternative to conventional methods. The steps include preparing the textile, dissolving the dye in supercritical CO₂, transporting the dye molecules into the fiber matrix, and finally depressurizing to recover the CO₂ for reuse. Each stage is essential to achieve uniform dye penetration, strong fixation, and high-quality results. The diagram below (**Figure 2**) illustrates the overall process flow and the role of each step (**Figure 2**).

Process Flow describes each step of the dyeing process as shown in the diagram:

- CO₂ Bottle (Input): CO₂ is stored in a bottle and pumped into the system.

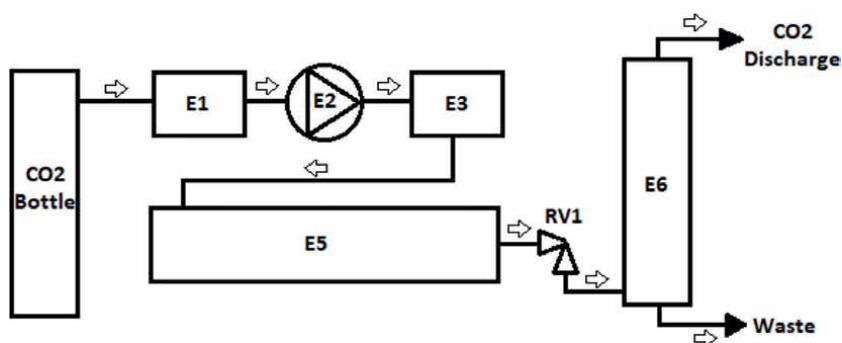


Figure 2.
Dyeing process (Top) and CO₂ dyeing equipment at CTT group (Bottom).

- E1 (CO₂ Pressurization): The CO₂ is pressurized to reach supercritical conditions.
- E2 (CO₂ Dosing/Control): CO₂ flow and pressure are carefully controlled to maintain supercritical conditions for dyeing.
- E3 (Dyeing Chamber): The textile material is placed in the chamber where supercritical CO₂ and dye interact, causing the dye to bond with the fabric.
- E5 (Dyeing Process Control): The dyeing parameters, such as temperature and pressure, are adjusted and monitored to ensure optimal dye absorption.

- RV1 (Flow Regulation Valve): CO₂ flow is regulated to maintain the desired pressure and volume during the dyeing process.
- E6 (Post-treatment and Waste Disposal): After dyeing, CO₂ is discharged, and any excess dye or waste is removed from the system.

3.1 Equipment description

- Supercritical CO₂ dyeing vessel: The dyeing vessel, as seen in the top-left image, has a volume of 250 mL ($V = 250 \text{ mL}$), which indicates that the chamber used to treat textiles with supercritical CO₂ is relatively small and can be used for laboratory-scale experiments or small batch production. This compact size makes it suitable for experimental purposes, where controlled conditions can be maintained.
- CO₂ tank: A CO₂ tank (seen in the middle-right of the image) is used to store and supply the CO₂ required for the supercritical dyeing process. The gas is pressurized and then injected into the dyeing vessel.
- Pressure and temperature control: The setup requires precise control over pressure and temperature. The image shows the working conditions of 250 bar pressure, 120°C temperature, maintained for 120 minutes. These parameters are critical for reaching the supercritical state of CO₂, where it behaves like both a liquid and a gas, allowing it to act as a solvent for the dye. This combination ensures the dye penetrates the fabric effectively.

3.2 Supercritical CO₂ dyeing process: Step-by-step

The supercritical CO₂ dyeing process begins with the careful preparation of the textile substrate, which may be in the form of fabric, yarn, or loose fiber. Before insertion into the dyeing system, the material is preloaded with dye through a controlled application method. In most cases, the textile is placed into a permeable container or wrapped with the dye powder to ensure that the dye is evenly distributed over the surface of the substrate. This initial step is crucial, as it facilitates homogeneous exposure of the textile to the dye once the supercritical medium is established. The prepared textile is then introduced into the supercritical CO₂ vessel, a highly specialized chamber designed to withstand both high pressures (typically around 250 bar) and elevated temperatures (up to 120°C). Inside the vessel, carbon dioxide is brought to its supercritical state, where it combines the solvent power of a liquid with the diffusivity of a gas. In this condition, CO₂ is capable of dissolving disperse dyes that would otherwise remain insoluble in aqueous systems, thereby enabling the efficient transport of dye molecules into the fiber matrix. The dyeing phase is generally maintained for approximately 120 minutes, providing sufficient time for the dye molecules to diffuse through the amorphous regions of the polymer and achieve uniform penetration. During this period, the textile undergoes swelling and plasticization facilitated by the supercritical CO₂, which enhances molecular mobility and promotes strong dye-fiber interactions. Upon completion of the dyeing cycle, the pressure inside the chamber is gradually released, and the CO₂ is recovered in its gaseous form for recycling. This controlled depressurization prevents damage to the textile structure while ensuring safe and efficient solvent recovery. The dyed textile is then removed from the vessel,



Figure 3.
Experimental setup for supercritical CO₂ dyeing [35].

with the color already firmly fixed within the fibers (**Figure 3**). The final product typically exhibits superior qualities compared to conventional aqueous dyeing, including enhanced color saturation, excellent uniformity, and improved fastness properties. The elimination of post-dyeing drying steps, combined with the recyclability of CO₂, further reduces environmental impact and operational costs, making this technique a promising and sustainable alternative for modern textile dyeing.

4. Factors influencing scCO₂ dyeing

4.1 Temperature

In supercritical carbon dioxide (scCO₂) dyeing, the critical point of CO₂ plays a decisive role in solubility and dyeing efficiency. Even small variations in temperature near the critical point can lead to substantial density changes, thereby reducing the solvating power of the medium. At lower pressures, solvent density decreases, and dye solubility diminishes with increasing temperature. Conversely, higher pressure enhances the sublimation pressure of the dye, thereby improving solubility as temperature increases. Polyethylene terephthalate (PET), being a semi-crystalline polymer, exhibits a glass transition temperature (T_g) that decreases with the elevated temperatures. This reduction in T_g facilitates significant CO₂ uptake by the PET fiber, which in turn enhances dye molecule penetration into the polymer matrix [26].

4.2 Pressure

An increase in scCO₂ pressure directly raises CO₂ density, thereby strengthening interactions between CO₂ molecules and dye molecules. As a result, dye solubility within the polymer matrix increases [25]. Polymer swelling is also intrinsically linked to system pressure, and higher pressures promote more extensive swelling, which facilitates easier penetration of dye molecules into the substrate.

However, dye uptake reaches a saturation point at elevated pressures. Beyond this point, further increases in pressure yield no significant improvement, emphasizing the need to identify the optimal pressure settings for each dye-polymer system [25].

Studies indicate that dye concentration and dye-fiber affinity are also crucial. For instance, at low dye concentrations, higher pressures may cause excessive dilution in the CO₂ medium, reducing dye penetration. In contrast, when dye-fiber affinity is strong, uptake occurs more rapidly, and higher pressure offers no added benefit. Conversely, dyes with poor affinity exhibit compromised uptake, as partitioning into the CO₂ phase becomes dominant [25].

4.3 Time

scCO₂ combines the characteristics of both liquids and gases. Its liquid-like density allows efficient dye dissolution, while its gas-like viscosity and high diffusivity enable significantly shorter dyeing times compared to aqueous methods [48]. Prolonged treatment periods further reduce the T_g of polymers such as PET (typically lowered by 20–30°C), increasing free volume in the amorphous regions and facilitating enhanced dye diffusion within the fiber matrix [26].

Nevertheless, extended exposure is not always beneficial. Overly long dyeing times may cause thermal degradation of both the polymer and the dye molecules. Therefore, careful optimization of temperature, pressure, and time is critical for achieving efficient dye uptake and maintaining polymer integrity. These parameters are particularly important when working with semi-crystalline fibers such as PET, and they are central to establishing eco-friendly and resource-efficient scCO₂ dyeing processes.

5. Economic and societal considerations

The adoption of supercritical carbon dioxide dyeing in industrial settings faces a major barrier in terms of high initial investment costs, which discourages many companies from establishing scCO₂ dyeing facilities. However, a broader and long-term perspective—beyond the short-term focus on setup and operational expenses—reveals the potential for transformative outcomes, resulting in eco-friendlier products and production processes. Compared to the conventional aqueous dyeing, scCO₂ dyeing has been shown to reduce operational costs by approximately 20% [5]. This economic advantage is largely attributed to shorter dyeing times and reduced energy consumption. Typical scCO₂ dyeing processes require only 2–3 hours, in contrast to the 3–4 hours often needed for aqueous methods. Furthermore, the drying step is eliminated, as CO₂ is released in its gaseous state, thereby generating additional energy savings. The water-free nature of scCO₂ dyeing also substantially lowers costs associated with water intake and wastewater treatment. For example, a study by DyeCoo reported operational costs for polyester (PET) dyeing with scCO₂ ranging between \$0.76 and \$1.37 per kilogram, lower than those of conventional aqueous dyeing. This reduction stems from the elimination of dyeing auxiliaries—such as dispersing agents, plasticizers, leveling agents, and carriers—which are not required in scCO₂ processes. Additionally, dye utilization efficiency is significantly improved, with dye losses of only ~1% in scCO₂ dyeing compared to ~10% in water-based systems [49]. Energy efficiency can be further optimized through careful process parameter control. For instance, research demonstrated that reducing dyeing pressure from 25 to 21 MPa at a constant temperature of 120°C decreased energy consumption from 201 to 184 kWh [50]. Such findings highlight the importance of fine-tuning operational conditions to balance performance with economic viability. From a logistical perspective, scCO₂ dyeing plants offer greater flexibility in terms of location. Unlike aqueous dyeing facilities, which must be established in water-accessible regions, scCO₂ installations can be sited independently,

reducing transportation needs and simplifying distribution. Finally, the societal and environmental dimensions of scCO_2 dyeing are significant. CO_2 , the primary solvent, is non-toxic and non-flammable, while the entire process requires zero water input. The use of chemicals is minimal, limited primarily to dyes and small amounts of biodegradable co-solvents such as acetone. These attributes not only reduce the ecological footprint of textile dyeing but also contribute to broader sustainability goals demanded by consumers and regulators alike.

6. Conclusion

In summary, supercritical CO_2 dyeing offers a promising alternative to conventional aqueous dyeing processes. It provides high-quality results through uniform color distribution and improved fastness while reducing environmental burdens. By eliminating water use, lowering energy demand, minimizing chemical discharge, and enabling CO_2 recycling, this technology aligns with the growing need for sustainable and efficient textile production.

In the future, super-critical CO_2 provides important promises of bringing revolution in the dye textile industry, especially when it comes to stability. As technological advances continue, we can expect to see more cost-effective, short equipment, so the process can be available to small manufacturers and even independent designers. Innovation in dye chemistry, including the development of new dyes compatible with SCCO_2 , will increase the efficiency and versatility of the process. In addition, integration of SC-CCO_2 with other durable technologies that integrate dye-like recycling systems with closed loop or biodegradable dye-FISH can also reduce environmental footprints. As the consumer's demand for environmentally friendly products increases and the regulator pressure increases, it may be more widespread to use supercritical CO_2 coloring and contribute to a more durable and spherical textile industry. However, challenges related to scalability, energy consumption, and source of CO_2 are still necessary to address their ability to unlock their ability to completely. With continuous research and investment, Supercritical CO_2 dyeing has the opportunity to have a game switch for the future of the textile industry.

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Section 2

Packaging Innovation

Anthocyanins as Natural Pigments in the Development of Intelligent Films and Active Packaging: Opportunities for Food Quality and Safety

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Abstract

Anthocyanins are natural, water-soluble pigments that belong to the flavonoid family, widely distributed in fruits, vegetables, cereals, and tubers. Their relevance in food and cosmetics has increased significantly due to their natural origin, pH-dependent color variability, and well-documented health benefits, including antioxidant, anti-inflammatory, antimicrobial, cardioprotective, neuroprotective, and antidiabetic activities. Compared to synthetic colorants, anthocyanins represent a safer and more sustainable alternative, although their lower stability and higher production costs currently limit their industrial application. Recent advances in extraction and encapsulation techniques have improved the efficiency, stability, and functionality of these compounds, facilitating their incorporation into biodegradable polymeric matrices. This chapter reviews the main sources, extraction methods, structural characteristics, and biological properties of anthocyanins, as well as their application in developing active and intelligent packaging. The use of pH-sensitive films based on anthocyanins as visual indicators of food freshness and quality is highlighted, owing to their halochromic properties. Furthermore, integrating anthocyanins into biodegradable packaging enhances protection against oxidation and microbial growth, extends shelf life, and reduces the need for synthetic additives. Overall, anthocyanins are emerging as key compounds for innovation in food packaging, aligning with current trends toward sustainability, food safety, and consumer preference for natural ingredients.

Keywords: anthocyanins, extraction methods, biological properties, smart and active packaging, biological sensors

1. Introduction

In recent years, natural colors have gained notable interest in the food and cosmetic industries, particularly anthocyanins. This is mainly due to their natural origin and health benefits, which contrast with those of synthetic colorants. According to the report of Mordor Intelligence, global demand of anthocyanins grows quickly, impulse by a significant preference of consumers toward natural products and regulatory restrictions imposed to synthetic colorants for their possible risks to human health, such as red 40 and red 20, prohibited in Japan, Australia, and the European Union [1].

Anthocyanins are distinguished by a pH-dependent color from red to blue tones, and exhibit antioxidant and functional properties. However, synthetic colorants present higher stability regarding light, temperature, and pH changes, which eases their application in industrial processes for products that require extended shelf life. Also, synthetic colorants are cheaper and offer a wide range of colors, while anthocyanins have a higher cost and lower stability, limiting their applications to certain products [2, 3].

Regarding the toxicological effects, several synthetic colorants have been associated with adverse reactions like allergies, hyperactivity in children, and possible carcinogenic effects. These concerns have led to more strict regulations for implementing synthetic colors and an increasing interest in natural colorants, especially anthocyanins, which are considered safe and of low environmental impact. To assess these demands, the industry invests in developing technologies to improve their stability and functionality, such as encapsulation and derivative pigments synthesis, to expand anthocyanins' commercial applications [4–6].

A comparison of the general characteristics of natural and synthetic colorants is included in **Table 1**.

Characteristic	Anthocyanins (natural colorants)	Synthetic colorants
Source	Fruits, flowers, and vegetables	Chemically produced in a laboratory
Color	pH-dependent (red to blue)	Intense and stable color, pH-independent
Stability	Sensitive to light, temperature, and pH	High stability to light, heat, and pH
Functional properties	Antioxidant, anti-inflammatory, and health benefits	Generally, without functional benefits
Safety and toxicity	Generally safe with low toxicity	Some are related to allergies, toxicity, and adverse effects
Applications	Functional food, natural cosmetics, supplements	Processed food and beverages, cosmetics, and textiles
Cost	Higher costs due to extraction methods	More economical, easily produced
Regulation	Favored in normative regulations	Restrictions in some countries

Table 1.
Comparison of natural colorants (anthocyanins) and synthetic colorants.

2. Anthocyanin sources

Anthocyanins are hydrophilic pigments that belong to the flavonoid family and are widely distributed in the plant kingdom. They are characterized by presenting distinctive red, purple, and blue colors. They are obtained from natural sources, such as fruits, flowers, and tissues from vegetables. These colors are not static, but change depending on the pH of the environment. In this regard, red tones are predominant on acidic pH, while alkaline environments produce blue colors [7, 8]. In **Figure 1**, the structural diversity of anthocyanins and their chemical structures, which exert a significant influence on physicochemical stability and bioavailability, is depicted. This is due to a substitution in the B ring, which is characterized by the presence of hydroxyl (OH-) or methoxy (OCH₃) groups, the acylation degree, and the type of carbohydrate bound to the aglycone. Lastly, some of the most representative anthocyanins obtained from natural sources are shown.

Anthocyanins have been isolated and recognized from several sources, predominantly from fruits, vegetables, cereals, and tubers. Some of the fruits that have been identified as rich in anthocyanins are blueberry, strawberry, Chagalapoli, and capulin. In the blueberry (*Vaccinium corymbosum* L.) fresh pulp, the main anthocyanins found are malvidin-3-glucoside, petunidin-3-glucoside, and delphinidin-3-glucoside [9]. On the other hand, acylated anthocyanins of complex structure from purple potato (*Solanum tuberosum* L. var. Vitelotte), such as peonidin-3-(p-coumaroyl)-rutinoside-5-glucoside and malvidin 3-rutinoside-5-glucoside, have been identified [10]. Chagalapoli (*Ardisia compressa* K.) is a fruit native to Mexico that has exhibited

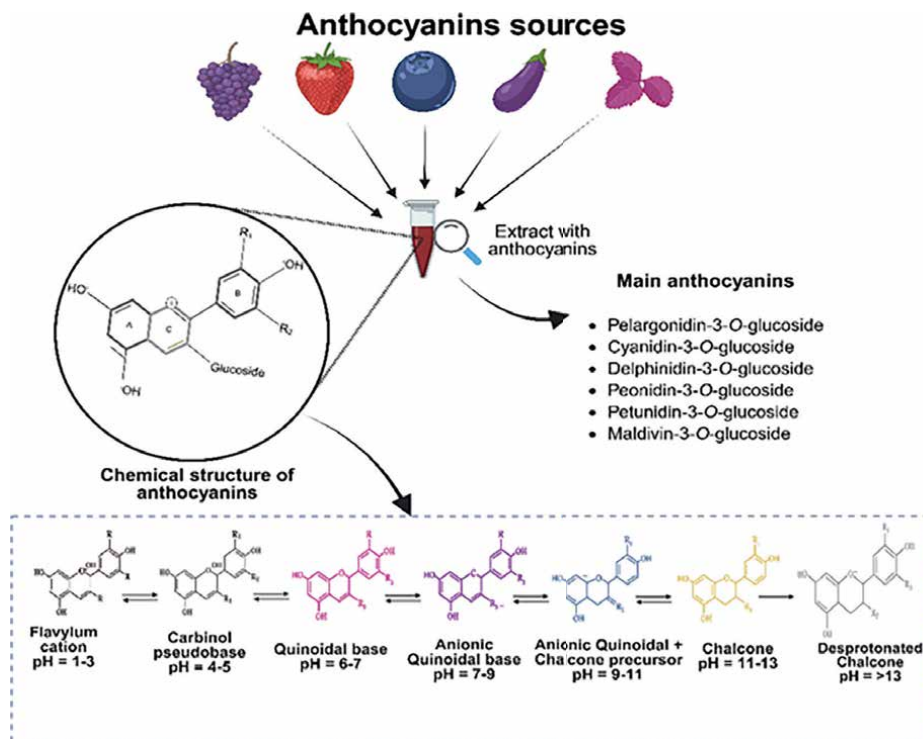


Figure 1.
Sources, chemical structures, and transformations of anthocyanins regarding pH.

an anthocyanidin profile mainly composed of galactosidic derivatives that include malvidin, petunidin, delphinidin, cyanidin, and peonidin [11]. At the same time, cyanidin-3-O-glucoside has been identified in fresh capulin juice (*Prunus serotina* subsp. capuli) with chromatographic techniques [12]. In another study, over 50 structures of anthocyanins were found in strawberry (*Fragaria × ananassa*) detected with ultra-high-performance liquid chromatography-mass spectrometry (UHPLC-MS), among which pelargonidin-3-O-sophoroside-5-O-glucoside and cyanidin-3-O-galactoside were found [13].

Among plants, herbs like *Ocimum sanctum* L. (Tulsi) have been manifested with potential for sources of anthocyanins, which have been identified with spectroscopic techniques [14]. The other vegetable is purple onion (*Allium cepa* L.), with compounds like cyanidin-3-glucoside (C3G) and peonidin-3-glucoside identified with chromatographic techniques [1].

3. Extraction methods and role of solvents

Typical techniques used to extract anthocyanins include maceration, ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE), and enzymatic procedures [2–4]. UAE has demonstrated superior efficiency in multiple extractions of natural compounds from different sources like blueberry (*Vaccinium corymbosum* L.), purple yam (*Dioscorea alata*), and purple onion (*Allium cepa* L.). It has been attributed to cavitation phenomena that promote cellular disruption in moderate conditions (< 50°C) and minimize thermal degradation of the compounds of interest [4]. On the other hand, compounds obtained from eggplant (*Solanum melongena* L.) with multifrequency UAE (25 + 40 + 70 kHz) were 2.94 times higher than those from conventional methods [5].

In other studies that used MAE on purple basil (*Ocimum sanctum* L.), an accelerated extraction of 2–4 minutes was achieved, with a reduction of organic solvents applied [14]. The extraction and preservation of cyanidin-3-O-glucoside from capulin (*Prunus serotina* subsp. capuli) during blending and filtering was achieved without the addition of solvents [12]. Acidified hydroalcoholic formulations continue to be the dominant preparation for extraction procedures, due to their efficiency and food compatibility, as it has been evaluated in black rice (*Oryza sativa* L.), purple potato (*Solanum tuberosum* L.), and purple cabbage (*Brassica oleracea* var. capitata) [6]. Also, acidifying extraction methods (pH of 2–3) are essential for cation stabilization, such as flavylum [15].

Recent advances in extraction methods include combined technologies like Ultrasound-Assisted Enzymatic Extraction (UAEE), and Ultrasound-Assisted Deep Eutectic Solvent Extraction (UADESE), which optimize the efficiency and reduce environmental impact. Some examples have been applied to wastes from blueberry wine, blackberry, black carrot, and black rice bran [16, 17].

The extracts are characterized with spectrophotometric techniques (differential pH method) or chromatographic (ultra-high-performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS)) techniques to provide information regarding the efficiency of extraction and purity of the bioactive compounds recovered [18]. Consequently, the selection procedure must consider not only the yield and purity, but also the stability of anthocyanins, the solvent used, the application of anthocyanins in the industrial field, and feasibility throughout the process [19].

Table 2 lists anthocyanins, extraction sources, parameters, and procedures applied.

Anthocyanin	Source	Content	Extraction method	Solvent and conditions	Advantages	Reference
Cyanidin-3-glucoside (C3G), peonidin-3-glucoside	Black rice bran	1231–5101 mg C3G eq/100 g	Batch solvent extraction	Acidified ethanol (HCl), powdering, freeze-drying	High stability, pH sensitivity	[20]
Complex anthocyanin profile	Red cabbage leaves	5% v/v in hydrogel	Maceration	Ethanol (7:3), pH 2.0, soaking for 24 h (5°C)	Simple, economical, reproducible	[21]
Petunidin (51.6%), malvidin-3-O-glucoside (18.0%)	Purple sweet potato	208.55 mg/L	Ultrasound-assisted extraction (UAE)	Ethanol 2.5% in citric acid, ultrasound 30 minutes (45°C)	Stable acylated anthocyanins	[10]
Malvidin-3-glucoside, petunidin-3-glucoside	Blueberry pulp	84.9 mg/100 g	Ultrasound-assisted extraction (UAE)	Methanol (80:20), pH 3.0, ultrasound 30 minutes (15°C)	High efficiency, low temperature	[9]
Cyanidin-3-glucoside equivalent	Purple yam tuber	0.44–1.44 mg/g	Ultrasound-assisted extraction (UAE)	Ethanol (80:20), ultrasound 10–30 minutes (30–60°C)	2.5 higher yield than Soxhlet	[22]
9 anthocyanins (cyanidin and peonidin derivatives)	Red onion bulb	2.15mg/g	Optimized ultrasound-assisted extraction	Methanol (57%), pH 2, ultrasound 10 minutes (60°C)	Box-Behnken optimization, fast	[1]
Total anthocyanins (not individually specified)	Purple basil	47.50 mg/100 g fresh sample	Microwave-assisted extraction (MAE)	Water acidified with 0.1% HCl	Simple, eco-friendly, fast extraction	[14]
Total monomeric anthocyanins (as C3G equivalent)	Eggplant peels	5.88 mg C3G/100 g dry weight	Multifrequency ultrasound-assisted extraction	Ethanol 53.6% (v/v), slightly acidified	Energy efficient, enhanced cavitation effect	[5]

Table 2.
Major anthocyanins in food sources and parameters for extraction methods.

4. Biological properties of anthocyanins

Due to their natural sources, biodegradability, and beneficial effects, anthocyanins have gained popularity as natural pigments in the food, cosmetics, and pharmaceutical industries. They present an alternative to synthetic colorants that potentially harm the environment and human health. To this day, anthocyanins have been added to beverages, dairy, confectionery, and cosmetic products; particularly, they can be implemented in smart packaging to evaluate food quality [9, 10, 23].

Some biological properties of anthocyanins are antioxidant, anti-inflammatory, antimicrobial, cardioprotective, neuroprotective, and antidiabetic. The evidence has demonstrated that the effect is related to chemical structure and concentration [14, 15, 17].

Wang et al. [24] evaluated the antioxidant capacity of diverse anthocyanidins and their glucosides with the ORAC (Oxygen Radical Absorbance Capacity) method, finding that cyanidin-3-glucoside exhibits 12,500 μmol of Trolox equivalent per gram ($\mu\text{mol TE/g}$), surpassing other anthocyanins like pelargonidin (3600 $\mu\text{mol TE/g}$) and malvidin (8200 $\mu\text{mol TE/g}$). The presence of hydroxyl groups in the B ring, such as cyanidin, increases the antioxidant capacity, but other structural factors also influence this activity.

Other studies have estimated that aurantinidin has an antioxidant capacity of 9000 $\mu\text{mol TE/g}$. On the other hand, delphinidin, which has three hydroxyl groups, exhibits lower values, which indicate a complex relation between structure and functionality [25]. Natural extracts from *Vaccinium floribundum* have shown an EC_{50} (half-maximal effective concentration) of 2520 $\mu\text{g/mL}$ at the 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay, confirming their high antioxidant activity [26].

Also, anthocyanins affect the production of molecules associated with inflammation, such as vascular cell adhesion molecule 1 (VCAM-1) and intercellular adhesion molecule 1 (ICAM-1), which reduces inflammation of blood vessels and enhances endothelial function, helping to prevent heart diseases [27, 28]. Clinical studies and animal models' evaluation have confirmed that consuming anthocyanins prevents low-density lipoprotein (LDL) oxidation and regulates arterial pressure, reducing the risks of atherosclerosis [29, 30].

The anthocyanins extracted from strawberry, blackberry, and blueberry have exhibited antibacterial and antifungal properties against pathogenic Gram-negative bacteria and fungi. Also, their antioxidant capacity has been confirmed with low EC_{50} values for DPPH assays, which reinforce their multifunctional bioactive compounds [26, 31]. These effects are attributed to the capacity of anthocyanins to interact with cellular membranes and block vital enzymes for microorganisms. Other investigations have proved that anthocyanins can inhibit pathogenic bacteria like *Escherichia coli*, *Listeria monocytogenes*, *Salmonella typhimurium*, and *Staphylococcus aureus* in different tests [32]. It has been suggested that these molecules act through membrane alteration, as well as enzyme and nucleic acid synthesis [33, 34]. This property highlights the potential of anthocyanins in the design of smart packaging for the food industry [35, 36]. The pelargonidin anthocyanin stimulates insulin secretion and improves sensitivity, which is relevant for diabetes control [25, 31]. On the other hand, delphinidin and blueberry extracts have shown benefits for brain function, improving thinking capacity and reducing cellular damage [25, 37].

The increase in polyphenol intake, such as anthocyanins, helps beneficial bacteria to grow, including *Bifidobacterium* spp. [38], and *Lactobacillus* spp. [39], which in consequence reduces endotoxemia, relieves inflammation, and restores cellular permeability [40]. In **Table 3**, a relation between anthocyanins and their biological properties is presented.

Anthocyanin	Source	Antioxidant evaluation	IC ₅₀ (µg/mL or µM)	Biological effect	Reference
Cyanidin-3-glucoside Malvidin	Blueberry (<i>Vaccinium</i> spp.)	ORAC: 12,500 µmol TE/g	8.2 µM (DPPH)	Anti-inflammatory, antidiabetic, antimicrobial	[24, 41]
Pelargonidin Cyanidin	Strawberry (<i>Fragaria × ananassa</i>)	ORAC: 3600 µmol TE/g	12.5 µM (DPPH)	Insulin secretion stimulation	[24, 42]
Malvidin Petunidin Peonidin	Grape (<i>Vitis vinifera</i>)	ORAC: 8200 µmol TE/g	10.7 µM (DPPH)	Cardioprotective, immunological modulatory	[24]
Aurantidin Delphinidin	Citric (<i>Citrus</i> spp.)	ORAC ~9000 µmol TE/g (theoretical)	ND	Anti-inflammatory, metabolic modulatory	[42]
Delphinidin Cyanidin Petunidin	Berries	ORAC: 7000 µmol TE/g (estimated)	7.9 µM (DPPH)	Neuroprotective, antioxidant	[43]
Cyanidin Delphinidin Petunidin	Bluebell (<i>Vaccinium floribundum</i>)	EC50 DPPH: 2520 µg/mL	2520 µg/mL (DPPH)	Antimicrobial	[44]
Punicalagin Cyanidin Delphinidin	Pomegranate (<i>Punica granatum</i>)	TEAC: 5000 µmol TE/g	13.1 µg/mL (DPPH)	Antioxidant, anti-inflammatory	[45]
Pelargonidin Cyanidin	Strawberry and blackberry (<i>Fragaria × ananassa</i> and <i>Rubus fruticosus</i>)	Bacterial inhibition	ND	Antimicrobial	[46]
Cyanidin-3-glucoside Pelargonidin Delphinidin	Purple maize (<i>Zea mays</i> L. var. purple)	Antioxidant and antimutagenic assay	19.6 µg/mL (DPPH)	Antiproliferative, anti-inflammatory	[47]
Cyanidin Delphinidin	Mashua (<i>Tropaeolum tuberosum</i>)	FRAP and DPPH antioxidant capacity	15.2 µg/mL (DPPH)	Physicochemical and antioxidant properties	[48]

Anthocyanin	Source	Antioxidant evaluation	IC ₅₀ (µg/mL or µM)	Biological effect	Reference
Cyanidin Malvidin	Blueberry (<i>Vaccinium</i> spp.)	ORAC: 9800 µmol TE/g	9.1 µg/mL (DPPH)	Neuroprotective, improvement of cognition	[47]
Malvidin Peonidin	Red grape (<i>Vitis vinifera</i>)	ORAC: 10,200 µmol TE/g	11.3 µg/mL (DPPH)	Cardioprotective, antioxidant	[49]
Cyanidin Delphinidin Petunidin	Red flowers	DPPH IC ₅₀ : 34.89 ± 0.98 µg/mL	34.89 ± 0.98 µg/mL	Metal chelating, anti-sickling	[50]

Table 3.
Biological properties and quantitative values of anthocyanins.

5. Active and smart packaging for food quality

Food packaging has been an essential method for years for preservation, facilitating transportation and storage, and in some cases, providing relevant information about the product to the consumer [51, 52]. Traditionally, plastic packages fabricated from synthetic polymers have prevailed due to their mechanical, barrier, and thermal properties [53]. These materials protect the food against external factors like moisture, oxygen, light, microorganisms, and mechanical stress [51].

Although polymeric materials for packaging exhibit multiple advantages, they have limitations mainly because they are not biodegradable, are challenging to recycle, and cause environmental pollution [53, 54]. As an alternative, biodegradable films based on natural materials are being implemented [54–56]. These films protect the food and work as smart and active packaging, which helps to extend shelf life and control the food's freshness.

According to the European Food Safety Authority [57], active packages are materials that interact with the food or the environment, releasing or absorbing substances that preserve the quality or extend shelf life. These smart packaging monitor the state of the packaged food, providing information about safety and freshness. For this, in recent years, the use of natural components to develop these films has increased because they are safe and non-toxic for human health [56]. **Table 4** summarizes active and smart packaging, comparing their characteristics.

Description	Intelligent packaging	Active packaging
Characteristics	Monitors the condition of the food and provides visual signals regarding food quality. The system does not directly interact with the food [58].	Protects and extends product shelf life. Directly interacts with the food and the surrounding environment [59].
Mechanism	The system incorporates sensors or reactive materials that change color or send signals. These sensors detect gas signals (H ₂ , O ₂ , NO ₂ , NH ₃ , CO ₂), pH level, temperature, and leakage [54, 59].	Oxygen scavengers, CO ₂ releasers and absorbers, moisture absorbers, ethylene extractors, ethanol releasers, and antioxidant and antimicrobial releasers. [60].
Main Uses	Freshness indicators, temperature sensors, and smart labels [58].	Release or absorption of bioactive compounds into the food or its environment. This phenomenon is known as Bility [54].
Natural compounds used in coatings	Anthocyanins, flavonoids, and polyphenols (colorimetric sensors) [58].	Anthocyanins, ascorbic acid, tocopherols, phenolic compounds (antioxidants and antimicrobials), and polyphenols (colorimetric sensors) [59].
Examples	pH indicators, time-temperature indicators, gas sensors, and leakage sensors. Color change, QR codes with information, gas sensors [61]. 	Oxygen absorbers, antimicrobial releasers, and moisture regulators [54]. 

Table 4.
Active and smart packaging comparison.

6. Food spoilage

Food spoilage is a global problem that impacts public health and the economic sector. Annual losses are estimated to range between 6.5 and 34.9 billion U.S. dollars. On the other hand, the Food and Agriculture Organization of the United Nations (FAO) estimates that global food waste amounts to approximately 1.3 billion tons annually [62]. According to the World Health Organization (WHO) data, foodborne diseases are the leading cause of mortality worldwide; they cause 600 million cases of illness and 420,000 deaths globally. Of these deaths, 125,000 occur annually in children under 5 years of age [63].

Foods are composed of macronutrients, such as carbohydrates, lipids, and proteins. **Figure 2A** illustrates that other components, like vitamins, minerals, and water, also contribute to the composition of foods. The deterioration of lipids and proteins (**Figure 2A**) is due to the decomposition of these nutrients; as a consequence, they cease to be harmless and become potentially dangerous elements for human consumption. The manifestation of food spoilage is the perception of unpleasant odors or flavors. Deterioration is caused by microbial, chemical, or physical processes, and to a lesser extent by pests, such as insects and rodents [64, 65].

For example, the degradation of carbohydrates produces acids, primarily lactic acids, alcohols, and mixtures of CO_2 and H_2 or CO_2 . In the case of proteins, they can decompose to the point of putrefaction, which generates unpleasant odors. The degradation of fats is called rancidity and can be hydrolytic or oxidative [65].

Food degradation mainly occurs due to microbial contamination; in this context, microorganisms alter the food, which provides the necessary nutrients for their proliferation, and favorable environmental conditions promote their growth. The microorganisms that commonly decompose food are mainly bacteria, yeasts, and molds (**Figure 2B**) [65, 66].

Microbial contamination is visibly present as slime and colonies, as well as texture alterations caused by the degradation of proteins, carbohydrates, and lipids [66]. These microorganisms can be found in the air, soil, surfaces, walls, wrappers, and others [67, 68].

Chemical deterioration, on the other hand, encompasses lipid oxidation, enzymatic reactions such as the Maillard reaction, chemical hydrolysis, and other chemical changes that compromise food quality. These reactions are influenced by the nature and composition of the foods, as well as by environmental factors, such as air, light, and heat [65].

Physical factors include variations in temperature, humidity, and mechanical damage; these can, on their own, deteriorate food. However, they also contribute to chemical and microbiological deterioration. Environmental factors encompass temperature, humidity, light, oxygen, and certain gases (**Figure 2C**). For example, heat facilitates the proliferation of numerous mesophilic microorganisms [66].

The decomposition reactions of food can produce molecules, such as acids, gases, amines, ammonia, toxins, and other chemical compounds. Some of these generated molecules or microorganisms are responsible for various diseases [67, 68].

Foodborne illnesses are generally classified into intoxications, infections, and toxicoinfections. Intoxication occurs when an organism develops in food and produces a toxin. Infection occurs when consuming food contaminated with pathogenic microorganisms. Toxicoinfection refers to the production of a toxin in the organism by a microbe ingested through food. Among the pathogenic bacteria transmitted

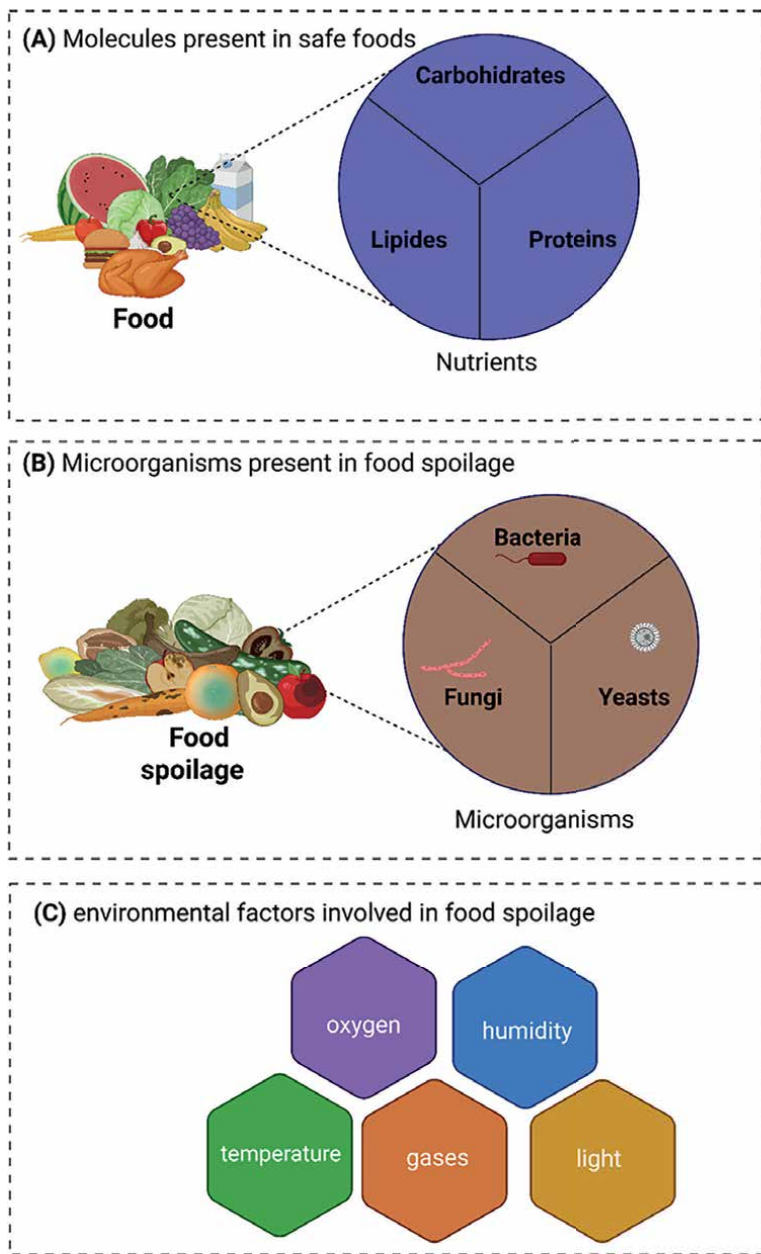


Figure 2.
Food spoilage factors: (A) Nutrients in food; (B) Presence of microorganisms; (C) Environmental factors.

through food, the most resistant are those capable of forming spores. This capacity allows them to withstand extreme conditions, including conventional preservation methods. Therefore, they are potentially dangerous. For example, mesophilic spore-forming bacteria belong to the taxonomic groups of the order *Bacillales* and the genus *Clostridium*. *Bacillus*, *Clostridium*, *Sporolactobacillus*, *Sporosarcina*, and *Desulfotomaculum* can create endospores [66].

In addition to bacteria, viruses and parasites also cause certain foodborne illnesses, where they act as a passive medium in the transmission. Among the human pathogenic viruses transmitted by food are norovirus, rotavirus, sapovirus, astrovirus, adenovirus, hepatitis A virus, and hepatitis E virus [69]. Diseases caused by food contaminated with parasites are mainly transmitted through the consumption of meat and vegetable products contaminated by human or animal feces and have not received adequate thermal treatment. Some examples of these parasites include worms like *Trichinella*, *Taenia*, *Anisakis*, and *Diphyllobothrium latum*, as well as small organisms like *Cryptosporidium* spp., *Giardia intestinalis*, and *Cyclospora cayetanensis* [66, 69]. All these pathogens generally cause mild and self-limiting gastrointestinal illnesses, although they can lead to severe acute diseases and potentially fatal complications. Around 2–3% of foodborne illness cases have complications, such as arthritis, hemolytic uremic syndrome (HUS), mental retardation, heart problems, or Guillain-Barré syndrome, which causes neuromuscular paralysis without visible injury [66, 69].

An example of a food that harbors pathogenic microorganisms is chicken meat, in which *Salmonella* spp. and *Campylobacter jejuni* predominate, two of the most prevalent bacteria worldwide responsible for diarrheal diseases. These pathogenic bacteria are transmitted through food contaminated with fecal matter from the same animal [70, 71]. Other types of bacteria found in meat products include *Staphylococcus aureus*, *Clostridium perfringens*, *Yersinia enterocolitica*, *Acinetobacter*, *Moraxella*, *Pseudomonas*, *Shewanella*, *Micrococcus*, *Flavobacterium*, and yeasts.

7. Anthocyanins in active and smart packaging of food

Due to the biological properties of anthocyanins, especially antibacterial and antioxidant capacity, they are considered bioactive compounds. When they are incorporated in coatings for food, they acquire the biological activity, categorizing them as a bioactive film [51, 53].

7.1 Active packaging

To prevent food spoilage, antioxidant capacity is a desirable property in packages, since it inhibits the oxidation of food, increasing its shelf life. Considering this, anthocyanins have been incorporated in packaging films and have been proven to preserve the nutritional value of food, maintaining its quality [51, 52, 55].

It has been found that adding anthocyanins to polymeric matrices improves multiple physicochemical characteristics of package films, including traction resistance, elongation, water solubility, UV-ray blocking, and water vapor and oxygen barrier. These improvements are due to the interaction of the polymer with the anthocyanins [51, 53, 54]. The functional and technological behavior of these films depends on the nature of the interactions [51].

For foods that contain lipids, oxidation is a process that spoils them, leading to rancidity. Anthocyanins act with oxidant agents, preventing the oxidation of lipids [51, 54]. Regarding antimicrobial activity, anthocyanins exhibit this property mainly in two mechanisms: one implicates the inactivation of proteins through hydrogen bonds, while in the other, they interrupt bacterial metabolism and membrane stability by reducing pH and proton gradient, which reduces nutrient uptake and leads to cellular death [56, 61]. It has been demonstrated that this activity is more effective with Gram-positive bacteria, due to their structure of cell walls [55, 56].

7.2 Smart packaging

Food spoilage involves modifications of pH and acidity. Also, these modifications affect the sensorial properties [72–74]. These parameters can be used for monitoring food spoilage and its life cycle in real time. For instance, fresh milk has a pH between 6.4 and 6.8; when spoilage develops, this parameter drops to 4.0 and 5.0 [52, 75, 76]. Smart packaging can detect the quality of dairy products with visual indicators based on compounds that change their color with variations of pH, which can be associated with spoilage [52, 77].

Yong et al. [78] developed a film with anthocyanins from purple and black eggplant incorporated in a chitosan matrix. These films reduced the amount of light that reached the food, and the color changed from light purple to green when the pH passed from 2 to 13. The formulations with 2 and 3% of the extract controlled the spoilage of pasteurized milk. Also, the compounds of the eggplant extracts improved the antioxidant activity and the polymeric matrix mechanical characteristics.

On the other hand, Tirtashi et al. [72] designed a film of chitosan and cellulose with anthocyanins extracted from black carrot. The films showed higher swelling and water solubility, which indicates that the films were more hydrophilic due to the interaction between the anthocyanins and the chitosan. The films detected milk spoilage with a progressive color change, turning from blue to purple at 24 hours, and to pink-violet at 48 hours, keeping the milk at 20°C.

Similarly, Goodarzi et al. [73] formulated a film based on chitosan and starch with anthocyanins of black carrot. This coat presented a high stability of color during a month under diverse conditions of temperature and light. The incorporation of anthocyanins did not modify the swelling and solubility in water, but transitions of color defined by the pH (from pink to blue at acidic and alkaline pH, respectively) were shown, with gray colors at pH above 10. The color changes exhibited in milk were related to pH changes and the produced rancidity, which reinforces the incorporation of anthocyanins for monitoring freshness in food.

Mushtaq et al. [79] proposed a smart film based on zein with pomegranate peel extract rich in anthocyanins. This extract helped to preserve the barrier properties of the polymeric matrix against moisture and gas interchange. Also, it retarded the oxidation reactions of lipids and proteins, maintaining the sensorial properties of cheese.

In another study, a mixture of carboxymethylcellulose, polyvinyl pyrrolidone, guar gum, and bacterial cellulose, in combination with anthocyanins from red cabbage, was applied to evaluate the shelf life of Gouda cheese. Films located inside the package showed a pink color at the initial contact with the cheese due to the presence of organic acids. As time passed, color was an intense red, associated with the accumulation of acids and pH reduction produced during storage at 4°C [80].

The colorimetric response of anthocyanins to pH changes makes them a promising candidate as natural indicators to monitor the freshness and quality of foods [51]. In **Figure 3**, a representation of anthocyanins incorporated as smart or active films is shown.

7.3 Potential of anthocyanins as sensors

As has been described previously, anthocyanins present a specific color depending on the pH of the environment, which suggests a possible application as a sensor to monitor the quality of foods [51]. When food undergoes spoilage, it releases

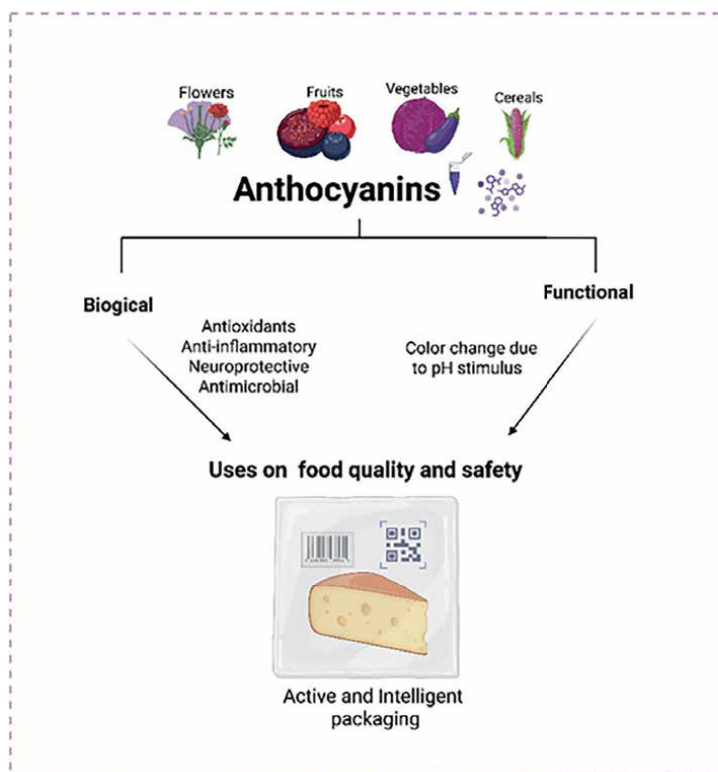


Figure 3.
Application of anthocyanins as active and smart packaging.

metabolites such as acids, gases, amines, and ammonia (associated with microbial spoilage) that alter the pH of the food matrix [51, 54]. These changes are evidenced by anthocyanins incorporated in smart films, which give consumers information about the quality state of food [51, 55].

Other components responsible for food spoilage, like ethylene, water, or CO₂, can interact with anthocyanins. With the diverse compounds that anthocyanins can react to produce different colors, they can be applied as sensors [51, 55]. Several indicators that use anthocyanins can be used depending on their substrate; they can be time-temperature sensors, colorimetric sensors, gas detectors (O₂ and CO₂), and pH indicators [55, 61].

Figure 4 illustrates the function of a food sensor based on anthocyanins.

Biological and chemical sensors function when chemical or microbiological changes occur in the food environment; also, their main objective is to supervise food quality during storage, identifying fluctuations in the surroundings such as pH change due to the formation of acidic or alkaline compounds [81, 82].

Figure 5 depicts the interaction of an analyte from samples of safe and spoiled food, according to the color response. Some chemical sensors that function as pH indicators incorporate synthetic pigments like methyl red, bromocresol purple, alizarin red, and bromophenol blue, which can interact with the pH variations in the food environment. Nevertheless, these colorants have been associated with toxicological effects, such as carcinogenicity and mutagenicity, so their application in the food industry is restricted [82, 83]. For this, the use of biological sensors has gained great interest since natural pigments are obtained from

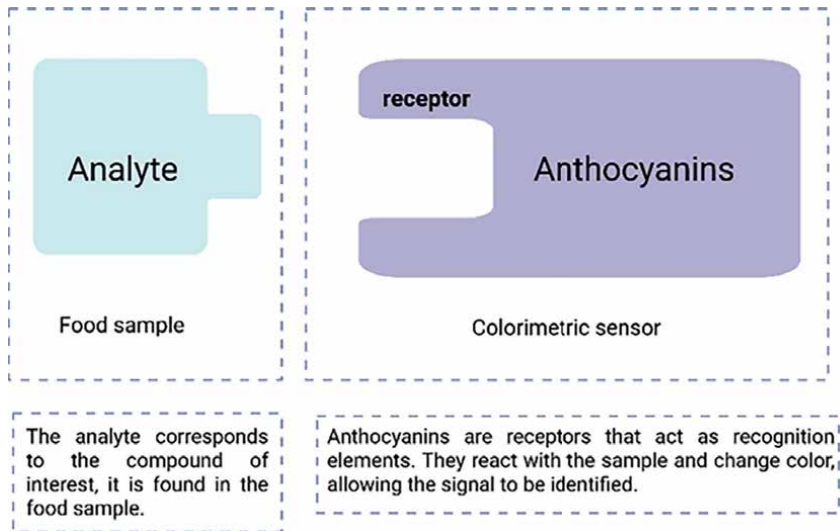


Figure 4.
Elements and functionality of an anthocyanin-based sensor.

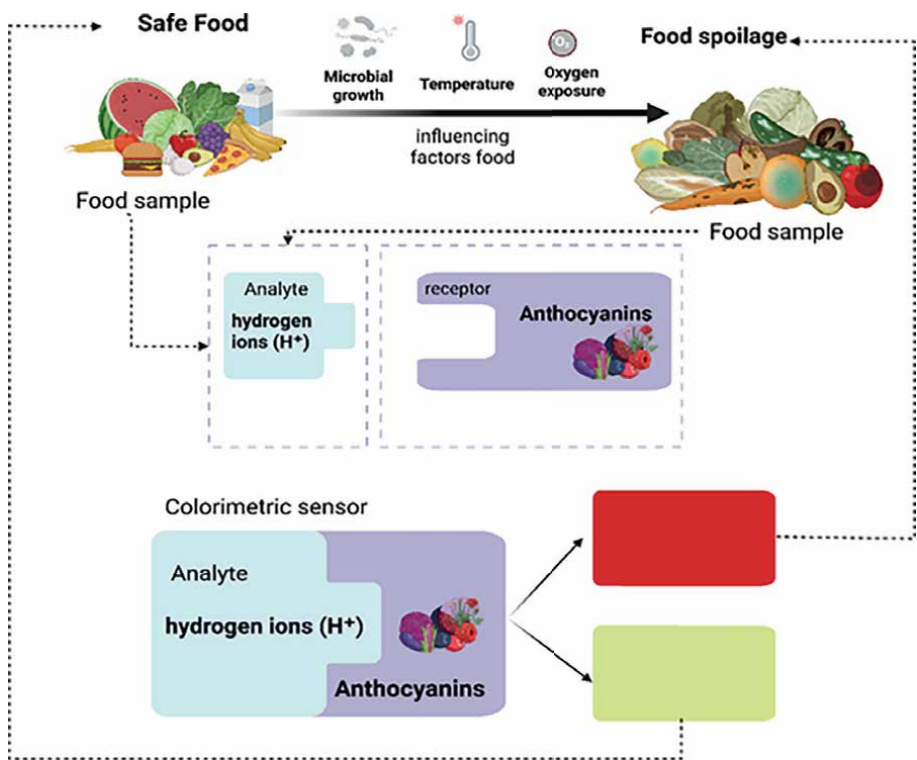


Figure 5.
Anthocyanins as sensors for the determination of food quality.

sustainable sources like plants and fruits. Also, these pigments are safe for consumption and possess bioactive characteristics that improve the quality of foods when they are contained in packages [84–86].

The application of different anthocyanins from different sources in food is summarized in **Table 5**.

Anthocyanin	Source	Biological properties	Functional properties	Application	Reference
Delphinidin-3-(p-coumaroyl)-rutinoside-5-glucoside and delphinidin-3-O-glucoside	Purple and black eggplant peel	Antioxidant	UV barrier and pH sensitive	Smart sensor for organic acids in pasteurized milk	[78]
Cyanidin-3-O-glucoside	Black carrot	—	pH sensitive	Smart sensor for lactic acid in pasteurized milk	[73]
Cyanidin-3-O-glucoside, malvidin-3-O-glucoside, petunidin-3-O-glucoside	Blueberry	—	pH sensitive	Smart sensor for lactic acid in pasteurized milk	[87]
Cyanidin-3-O-glucoside	Red cabbage	Antimicrobial	pH sensitive	Smart sensor for lactic acid in pasteurized milk	[88]
Cyanidin-3-O-glucoside, delphinidin-3-O-glucoside, malvidin-3-O-glucoside	Red cabbage	—	pH sensitive	—	[74]
Cyanidin-3-O-glucoside, delphinidin-3-O-glucoside	Blueberry	—	pH sensitive	Smart sensor for lactic acid in pasteurized milk	[89]
Cyanidin-3-O-glucoside, delphinidin-3-O-glucoside	Mulberries	—	UV barrier and pH sensitive	Smart sensor for organic acids in pasteurized milk	[81]
Cyanidin-3-O-glucoside	Blueberry	—	pH sensitive	Smart sensor for organic acids in pasteurized milk	[90]
Cyanidin-3-O-glucoside	Purple cabbage	—	pH sensitive	—	[91]
Cyanidin-3-O-glucoside	Pomegranate peel	Antioxidant and antimicrobial	—	Active sensor to extend the shelf life of Kalari cheese	[79]
Cyanidin-3-O-glucoside	Red cabbage	—	pH sensitive	Smart sensor for organic acids in Gouda cheese	[80]
Cyanidin-3-O-glucoside	Pomegranate peel	—	pH sensitive	Smart sensor for lactic acid in cream cheese	[92]

Anthocyanin	Source	Biological properties	Functional properties	Application	Reference
Cyanidin-3-O-glucoside, delphinidin-3-O-glucoside	Elderberry	Antioxidant and antimicrobial	UV barrier and pH sensitive	Active and smart sensor in fresh cheese	[93]
Cyanidin-3-O-glucoside	Red cabbage	—	pH sensitive	Smart sensor for organic acids in Gouda cheese	[80]
Cyanidin-3-O-glucoside	Pomegranate peel	—	pH sensitive	Smart sensor for lactic acid in cream cheese	[92]
Cyanidin-3-O-glucoside, pelargonidin-3-glucoside	Elderberry	Antioxidant and antimicrobial	UV barrier and pH sensitive	Active and smart sensor in fresh cheese	[93]

Table 5.
Anthocyanins are used as active compounds and quality monitors in foods.

8. Conclusions and perspectives

Current challenges for the food industry are related to producing nutritious and safe food. The spoilage associated with the growth of microorganisms and the production of acidic components may lead to economic losses and public health issues.

In this regard, natural pigments like anthocyanins can be implemented in food packages to improve shelf life due to their antioxidant and antimicrobial activities, among others. They have been applied in polymeric matrices to preserve the sensorial and nutritional properties of food, extending their shelf life. Also, anthocyanins exhibit a color dependent on the pH of the environment, which can be used as sensors to monitor food quality. There are several sources, like plants and fruits, that provide anthocyanins; even agroindustry wastes can produce extracts rich in this pigment. The valorization of these byproducts could contribute to reducing contamination.

Some challenges that research and industry must address in this regard include the optimization of the extraction method and the immobilization of anthocyanins in different matrices, creating new and eco-friendly packages that will provide consumers with information about food quality, which, in consequence, could prevent food-associated diseases.

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Conflict of interest

The authors declare no conflict of interest.

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Porphyrin Optical Sensing: Three Applications

Gamal Khalil

Abstract

Porphyrin derivatives play an important role in various applications, including optical chemical sensors. The electronic structure of the inner 16-membered ring in porphyrins, which consists of 18 electrons, governs their key optical features. Different classes of porphyrin molecules provide a diverse range of ring structures and substitutions, which can be effectively utilized to tune or modify specific spectral properties. Additionally, these properties are influenced by chemical modifications or changes in the pyrrole rings. Porphyrin is a highly symmetrical molecule with two pairs of low-energy excited states: quasi-forbidden Q states in the visible region and strongly allowed B states in the near-UV region. Over the past 30 years, our research group, in collaboration with other organizations, has played a key role in developing a wide array of optical porphyrin-based sensors by exploring the complex spectral properties of porphyrin derivatives. Here, we present three applications of optical porphyrin-based sensors: continuous blood-oxygen measurements for intensive care unit (ICU) use, pressure-sensitive paint for aeronautic wind tunnel measurement, and pH imaging in cementitious materials.

Keywords: blood-oxygen, dissolved-oxygen, luminescence-barometry, pressure-sensitive paint, concrete pH

1. Introduction

Porphyrins and their derivatives have been successfully applied in various fields, particularly as optical chemical sensors [1–7]. This class of molecules offers a wide range of ring structures and substitutions that can be fine-tuned to modify desired spectral properties. The electronic structure of the inner 16-membered ring, containing 18 electrons, is primarily responsible for the molecule's key optical features. These properties can be further influenced by chemical modifications to the pyrrole rings. Porphyrins are highly symmetrical molecules, featuring two pairs of low-energy excited states: the quasi-forbidden Q states in the visible spectrum and the strongly allowed B states in the near UV region.

Chemical substitutions on the porphyrin ring can reduce symmetry, affecting both the intensity and the spectral position of the Q-transition, often shifting it to longer wavelengths. Various groups, such as carboxylic, amine, sulfonyl, phenyl, alkyl,

ether, nitro, and others, have been attached to the porphyrin's external skeleton [8]. Generally, substituting chemically similar groups has only minor effects on the optical spectra. However, more significant changes in wavelength and absorbance can be achieved through charge-transfer perturbation. For instance, a charge-transfer effect can be induced by attaching an electron-donating group to one pyrrole ring and an electron-withdrawing group to the opposite ring. This effect is amplified when donor groups are substituted at high electron-density positions, while withdrawing groups are placed at low electron-density positions. Additionally, porphyrins can chelate with a wide range of metal ions.

The 2-fold symmetry of free-base porphyrins arises because the four central nitrogen atoms are bound to only two hydrogen atoms. Replacing these hydrogen atoms with a metal ion restores 4-fold symmetry. Chelation with metal ions typically reduces the number of absorption bands and causes a spectral shift, which can be red or blue, depending on the substituents. While metal substitution generally has a minimal impact on the absorption spectra, it significantly affects the emission spectra. This phenomenon has been extensively reviewed by Gouterman [9]. For example, chromium porphyrins exhibit anomalous near-infrared (NIR) luminescence, attributed to emissions from two quasi-states: the quartet and sextet. Notably, the luminescence of chromium porphyrins is temperature dependent [10]. Lanthanide porphyrins have absorption spectra similar to other closed shell metalloporphyrins [11], though their emission spectra vary depending on the lanthanide ion. For instance, ytterbium, neodymium, and erbium porphyrins show line emissions at 970 nm, 890 nm, and 1530 nm, respectively, which are assigned to f-f transitions of the lanthanide ion [12]. In contrast, gadolinium porphyrin exhibits broad π - π^* emission from the porphyrin triplet state, with a spectral shift to the NIR region displaying vibronic structures from 650 nm to beyond 1100 nm [13]. This spectral shift has made gadolinium porphyrin complexes potential candidates for NIR oxygen sensing materials.

The high quantum yield and short triplet-state lifetime of platinum porphyrins [14] have proven useful in many practical applications. The strong electronic interaction between platinum's filled d-orbitals and porphyrin's empty d-orbitals, combined with platinum's strong spin-orbit coupling, leads to nearly 100% triplet quantum yield and 90% phosphorescent emission yield.

A method for monitoring oxygen concentration, based on oxygen quenching of platinum porphyrin phosphorescence, was originally developed at the University of Washington for blood oxygen monitoring [15]. This method relies on the Stern-Volmer equation [16]. The luminescence lifetime of platinum porphyrins is matched with the oxygen diffusion rate in the polymer to produce measurable changes in luminescence intensity or lifetime in response to oxygen pressure. Platinum tetrakis(perfluorophenyl)porphyrin (PtTFPP) is the most widely used dye for oxygen sensing [17–22]. The perfluoro-substitution on the porphyrin ring raises oxidation potential and reduces electron density, improving photostability and sensor longevity [23, 24]. Tetra(pentafluorophenyl)porphyrins also exhibit significantly less concentration quenching compared to non-fluorinated porphyrins, such as octaethylporphyrins [25].

A new porphyrin species, known as porpholactone, was serendipitously produced during the synthesis of silver tetra(pentafluorophenyl)porphine. In porpholactone, one of the pyrrole rings is oxidized, converting a CH=CH bond to a -O-(C=O)- group, and replacing the pyrrolic subunit with an oxazolidone, forming an azlactone ring [26–28]. This novel structure has led to new applications in sensor engineering. For

example, platinum tetra(pentafluorophenyl)-porpholactone (PtTFPL) has a red-shifted phosphorescence emission spectrum at 740 nm and has been successfully used as a photostable oxygen sensor. The bathochromic shift of PtTFPL allows for the inclusion of additional sensors or reference dyes without spectral overlap [29, 30]. Furthermore, the absorption and emission spectra of PtTFPL exhibit additional bathochromic shifts in the presence of a base. This effect is attributed to the combined influence of fluorinated substituents and the lactone group, which acidifies the PtTFPL ring and allows for deprotonation with base addition. This class of lactones has demonstrated reversible spectral changes in response to pH, with a strong dynamic range between pH 11 and pH 13.5. This discovery enabled an optical method for high-resolution, real-time pH measurements in Portland cement concrete, offering a new tool to study pH-dependent degradation and hydration reactions in cement-based composites.

Over the past 30 years, our research group at the University of Washington, in collaboration with other organizations, has advanced the development of a diverse range of optical porphyrin-based sensors through discovery and fundamental understanding of porphyrin spectral properties. Three key applications will be discussed: continuous blood oxygen measurements for ICU use, pressure-sensitive paint for aeronautic wind tunnel measurements, and pH imaging in cementitious materials.

2. Blood oxygen measurement

Measurement of arterial blood pH, partial pressure of carbon dioxide (PCO_2) and partial pressure of oxygen (PO_2) is an indispensable tool in the management of critically ill patients. Because of the rapidity that these variables can change, it is very desirable to obtain a reliable measurement quickly. A blood sample may undergo significant changes from the time it is removed from the body until it reaches the sensors of a laboratory blood gas instrument. Therefore, blood gas results may not adequately reflect the patient's current oxygenation status [31–35]. It has been the goal of the medical community to produce sensors that could be placed unobtrusively in the blood stream so that uncertainty could be reduced, and timeliness improved [36–39]. Advances in miniaturization of sensor technology have led to the development of continuous, invasive blood gas technology where sensors, introduced through a catheter, can measure arterial blood in situ. The very nature of this technology has the potential to mitigate many of the concerns regarding discrete blood gas measurements as well as provide immediate, real-time assessments of patient acid/base and oxygenation status.

A fiber optic-based sensor probe has been developed to allow for the continuous measurement of pH, PCO_2 and PO_2 . The probe is made of three 120 μm diameter poly-methyl methacrylate optical fiber for each parameter. They are bundled with a thermocouple in a sheath that is intended to fit inside a 20 g plastic cannula [40–42]. Both pH and carbon dioxide sensors are absorbance-based with a reflector to return the incident light. The pH sensor is made of phenol red dye covalently linked to a hydrophilic polymer [43]. The carbon dioxide sensor embodies a modified Severinghaus principle in which bicarbonate is mixed with a pH indicator dye [44]. The PO_2 sensor is based on phosphorescence quenching of platinum porphyrin (PtTFPP) mixed with a hydrophobic gas permeable polymer and dipped on the end of an optical fiber. Light at the excitation wavelength of PtTFPP (400 nm) is pulsed down the fiber and the dye emits a 650 nm wavelength in response. The oxygen

concentration is proportional to the ratio of two luminescent decay times of the PtTFPP emission. The three fiber optic sensors and a thermocouple are then integrated into a sensor bundle. The thermocouple is included to measure the probe site temperature allowing for correction of the blood gases to 37° C.

The arterial blood gas probe is a sterile, disposable fiberoptic device designed for insertion into arterial blood flow. The measurement technology is designed to minimize transient motion artifacts common to some fiberoptic devices specifically using reference wavelengths and ratio metric algorithms which compensate for non-catastrophic light loss due to optical fiber motion. The probe undergoes a two-point calibration process prior to measurement. The probe calibration data are then coupled with specifically designed algorithms which transform the optical signals to the desired outputs of blood pH, and gases. Extensive bench evaluation to characterize the system performance was done first in buffer then in vitro blood loop testing. Probe in vitro performance specifications values of; accuracy, drift, response time, and resolution are used to screen the probes before use. The system has demonstrated accuracy and linearity comparable to the electrochemical sensing-based blood gas instruments commonly used in clinical laboratories. A set of probes reading values for 72 hours were compared to the average of 3 laboratory instruments readings. The average accuracy observed (standard deviation) for pH unit was 0.022 (0.037), PCO₂ torr was 1.2 (2.1) and PO₂ was -2.5% (7.4%). It should be noted that laboratory instrument calibrates automatically every 30 minutes while the probe only once at the beginning and one point update every 24 hours. Animal testing to verify in vivo efficacy and safety was carried out. Animal results show precision of +/-0.023 pH unit, +/- 2.3 mm Hg PCO₂, and +/- 6.3% mm Hg PO₂. These results are consistent with the American College of Pathologists proficiency standard [45].

The fiberoptic system was found to measure arterial blood gases and pH with acceptable clinical accuracy. However, comparing conventional laboratory technology with real time in situ measurement is a challenge when introducing new measuring concepts. Clinical studies revealed some performance limitations, including compromised performance under states of flush interference and thrombus occlusion of sensor membranes. For example, in the event of low arterial blood flow, the saline flush solution is not fully cleared away. As a result, the sensors measure a mixture of blood and saline. The resulting flush interference produces measurements that are not clinically relevant [46]. Several companies have demonstrated this technical accomplishment, however solutions to the physiologic problem of getting adequate samples to the sensors still need to be addressed.

3. Pressure sensitive paint

In the design of new airplanes, a “loads model” is created to study pressure distributions across aerodynamic surfaces. This is traditionally performed by drilling numerous small holes along the airflow path and using multitube manometers or pressure transducers to measure the pressures at specific locations. These pressure taps then provide a lift distribution map, which is essential for engineering the support structure and other key features of airplanes. However, creating a loads model can be expensive—costing millions of dollars—and is time consuming.

Several years ago, our research group developed a more flexible method called luminescence barometry [47]. This technique enables continuous pressure mapping across aerodynamic surfaces using luminescent paint. The paint contains a

phosphorescent compound, typically platinum porphyrin (PtTFPP), dissolved in an oxygen-permeable polymer and is referred to as pressure-sensitive paint (PSP). When a surface painted with PSP is illuminated with blue light, it emits red luminescence, the intensity of which is inversely proportional to the surface pressure, and oxygen quenching of the resulting phosphorescence enables this relationship. This is because oxygen concentration remains constant regardless of the total pressure. Finally, luminescence images are captured using a CCD camera and processed on a computer to provide 2D surface pressure maps.

PSP enables high-resolution pressure distributions in wind tunnel environments. Comprehensive reviews on this method have been published [48–52]. Compared to traditional pressure-tap methods, PSP offers significant advantages, such as speeding up the design process and reducing costs. PSP can produce a near-continuous pressure map (up to 1000×1000 pixels) in contrast to the limited number of fixed-pressure tap locations. Furthermore, PSP enables the capture of data from areas where installing pressure taps is not feasible, such as thin sections of a wing model.

Luminescence barometry, developed in collaboration with NASA Ames and Boeing, is now widely accepted in the aerodynamics community and is used in wind tunnels around the world. Commercial paint formulations, test equipment, and software are readily available [53].

The advantages of luminescence barometry over traditional pressure-measurement methods include the following: (a) High spatial resolution, limited only by the imaging device or optics; (b) ease of application and reapplication of the PSP; (c) elimination of the need to alter the wing by drilling holes; (d) fast response times; and (e) the ability to integrate surface pressure maps to determine aerodynamic loads, thereby eliminating the need for heavily instrumented loads models. (f) Finally, surface flow features such as shock locations and boundary layer separations can often be observed in raw images, making the technique a valuable visualization tool during testing.

PSP applications continue to expand [54–56]. However, this method has some drawbacks, including (a) sensitivity to temperature; (b) the need for a reference image taken with wind tunnel fans off; however, this image may not align perfectly with the image taken when fans are on, requiring additional corrections; and (c) self-illumination, where light reflects off different parts of the object being tested, compromising the results.

Temperature dependence of Pt-porphyrin-based oxygen sensors varies depending on the polymer matrix. For example, PtTFPP sensors made with Poly(Bisphenol A-carbonate) and polystyrene have measured temperature coefficients of $-1.3\%/^{\circ}\text{C}$ and $-0.9\%/^{\circ}\text{C}$, respectively. To address this temperature dependency, our research group synthesized a fluorinated acrylic polymer, FIB [57], which is a random copolymer of heptafluoro-*n*-butyl methacrylate and hexafluoroisopropyl methacrylate. PtTFPP sensors made with the FIB polymer have a dynamic range of 0.9, a 95% response time of less than one second, and a temperature dependency of $-0.5\%/^{\circ}\text{C}$ [58–60]. Notably, the FIB-based porphyrin sensors exhibited the same temperature dependence at any oxygen or pressure concentration, thereby simplifying the correction process.

To further mitigate the temperature effects and model motion during measurements, a dual-luminophore PSP system was developed. This system uses two dyes that are excited at the same wavelength but are emitted at different wavelengths. The luminescence of one dye is quenched by oxygen, whereas that of the other serves as a reference to correct excitation and intensity changes. The advantages

of dual-luminophore PSP systems, including a dual-luminophore PSP composed of an oxygen-sensitive NIR molecule (PtTFPL) and oxygen-insensitive molecule (MgTFPP), have been demonstrated [29, 30, 61–64]. This system, tested with a two-camera setup at ISSI of Dayton, Ohio, and NRC of Canada for automotive model testing, produced near-ideal PSP measurements, with a pressure sensitivity of 4.5% per psi and a temperature dependency of less than $-0.1\%/^{\circ}\text{C}$. This ratiometric method has proven to deliver reliable and robust oxygen pressure sensors.

4. pH imaging in cementitious materials

Cement-based materials like concrete have highly alkaline pore fluids, and the pH of these fluids is critical in both fresh and hardened states. The pH affects the rate of cement hydration, the morphology of crystalline and amorphous products in cement hydrates, early aging, as well as the overall strength and durability of concrete structures. Both cement and steel reinforcing bars are continuously exposed to environmental conditions that influence their surface and internal pH environments. Notably, reactions such as concrete carbonation and alkali-silica reactions are significant under ambient conditions, leading to concrete expansion and oxide formation on steel reinforcing bars. Therefore, monitoring internal pH levels is essential for designing, assessing the health of, and implementing remedial measures for concrete infrastructure [65–69]. Direct pH measurements in the target range of approximately pH 11 to 13 are currently not feasible. Existing methods for assessing internal pH levels involve extracting pore fluids, which only provide bulk information. The only method available for spatially resolved data indicates whether the pH is above or below 10, without further specificity. To address this limitation, we have developed an optical imaging method capable of directly assessing the spatial distribution of pH in the range of pH 11 to 13.5. This approach utilizes a porphyrinoid high-pH indicator, specifically the PtTFPL complex [70]. Porpholactones demonstrate a unique reversible dynamic range between approximately pH 11 and 13. This behavior is attributed to a nucleophilic attack by hydroxide (OH^-) ions on the lactone carbonyl, which significantly alters the optical properties of the porpholactones. Upon hydroxide attack, new peaks appear in the UV-vis spectra, spaced more than 100 nm apart from the original porpholactones' spectra, which have high extinction coefficients. In PtTFPL, this hydroxide interaction collapses the visible absorption bands into a single broad, red-shifted band with a reduction in extinction coefficient. These spectral changes are reversible when the base is neutralized. The porpholactone molecules are embedded in a hydrophilic polymer or polymer blend to create "High pH sensing paint." This paint is applied to the concrete surface, and the optical signal is processed through two band-pass filters and captured by a digital camera. The resulting spectral behavior allows for ratiometric sensing, making the measurements independent of indicator concentration, significantly enhancing practical applications. The camera intensities are processed into images revealing the pH distribution across the fractured concrete surface [71–74]. Porpholactones and their metal derivatives are highly suitable as high-pH sensors, capable of operating within this elevated pH range. The method is technically robust, simple, and convenient. Several factors directly influence sensor performance, including (i) the use of different polymer carriers for the sensor molecule and (ii) the incorporation of particle pigments to enhance ionic transport. The pH dynamic sensing range can

be fine-tuned by altering the central metal atoms or modifying the aryl groups. New porpholactone derivatives with favorable chemical and physical properties have been synthesized and evaluated. These derivatives exhibit excellent solubility, high chemical stability, and some are becoming readily available for various diagnostic infrastructure applications [75–81].

5. Conclusion

Porphyrin compounds are macrocyclic organic molecules, several of which play essential roles in natural energy conversion systems such as photosynthesis and oxygen transport. Their unique chemical and physical characteristics make them well suited for long-term use as chemical sensors. Key advantages include Long-Term Stability: Porphyrins exhibit inherent chemical stability due to their aromatic structure, Favorable Optical Properties: Their electronic structures enable strong optical absorption and emission, facilitating easy excitation and detection and Synthetic Flexibility: While many porphyrins are commercially available, they can also be readily synthesized and modified, enabling precise “tuning” of their chemical or optical properties. The extensive body of research on porphyrin offers a wide variety of ring structures and substitution patterns, providing a versatile platform for tailoring spectral properties to specific sensing applications.

Over the past 30 years, our research group at the University of Washington, in collaboration with various partner organizations, has advanced the development of a wide range of optical porphyrin-based sensors by uncovering and deepening the fundamental understanding of their spectral properties. This chapter highlights a select three key applications: continuous blood oxygen monitoring in intensive care units, pressure-sensitive paint for aerodynamic testing in wind tunnels, and pH imaging in cementitious materials.

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Optimization of Component Proportions in Ultra Black Dispersed Dye Composition and Application of Quantum Chemical Calculation in Performance Prediction of Disperse Dyes

Liu Yue

Abstract

Black dispersed dye is a type of dye used in textile dyeing that consumes a large amount. It is composed of dispersed dye components with different structures combined in a certain proportion and occupies a high proportion in the development of new dispersed dye varieties. The chemical structure and mixing ratio of each component directly affect the color performance of the black dispersed dye composition. This chapter explores the influence of the chemical structure and mixing ratio of each component in the black dispersed dye composition on the color performance of the black dispersed dye composition. In recent years, the continuous improvement of new technologies, including quantum chemistry theory, has provided an intuitive quantitative approach for the study of the correlation between the structure and properties of dispersed dyes. This chapter studied the molecular conformation, HOMO-LUMO energy levels, UV-Vis absorption spectra, and maximum absorption wavelength of experimental dispersed dyes using the optimized DFT/TD-DFT calculation method. The results indicate that the type, quantity, and position of halogen substituent groups have a significant impact on the excited state orbitals, energy gaps, and spectral properties of dispersed dye molecules. A prediction and optimization model for the maximum absorption wavelength of dispersed dyes was established through quantum chemical calculations of dispersed dye molecules and multivariate fitting regression of experimental data. This model has good consistency in predicting the maximum absorption wavelength of dispersed dyes in monoazo orange systems. Research has shown that optimal quantum chemical density functional theory can provide better technical support for the molecular design and innovative research of new dispersed dyes.

Keywords: disperse dyes, UV-visible absorption spectrum, maximum absorption wavelength, black dispersed dye composition, component ratio prediction, quantum chemistry calculations

1. Introduction

Disperse dyes are specialized coloring agents used for dyeing or printing textiles made of polyethylene terephthalate fibers (referred to as polyester fibers). In order to adapt to the special polymer chemical structure of polyester fibers, which are dense and lack water-soluble groups, dispersed dyes usually exist in the form of nonionic dyes with small molecular weight and are difficult to dissolve in water. During dyeing, they rely on dispersants to suspend in the dye solution, diffuse into the intermolecular gaps of polyester macromolecules in a molecular state, and combine with hydrophobic fibers through van der Waals forces, hydrogen bonds, and dipole forces [1]. With the rapid industrial application of polyester fibers, the variety and production volume of dispersed dyes have developed rapidly, gradually becoming the largest dye variety in the textile industry since the 1970s [2]. The application of various emerging technologies, including quantum chemical computing technology, provides strong technical support for the innovative development of new dyes at the molecular structure design level.

In recent decades, also benefiting from modern technology, quantum chemical calculations, especially those based on density function theory (DFT), have been used increasingly in the research of various materials, including dyes. Both color and properties depend on the structure of dyes. So, it has become a trend to apply the powerful DFT method to explore many aspects of dyes, such as dye synthesis and dye optical properties [3, 4]. At the same time, keeping an excellent balance between accuracy and efficiency, the time-dependent-density function theory (TD-DFT) method has become the most common means for investigating the optical properties of organic molecules [5]. From the research of Jacquemin and his team [6], we can know that after multivariate fitting, the results calculated by PBE0 and B3LYP functional, the dye's estimated value of the maximum absorption wavelength ($\lambda_{\max}$) was more accurate. Although the vertical excitation calculation results obtained by using B3LYP and PBE0 functional alone are usually relatively precise and reasonable [7]. B3LYP functional with 20% Hartree-Fock (HF) exchange and PBE0 functional with 25% HF exchange are both global hybrid functionals [8]. The proportion of HF in this kind is constant globally, that is, the proportion of HF exchange remains unchanged when the distance between two electrons is arbitrary. Moreover, another commonly used method is the range-separated hybrid functionals, such as CAM-B3LYP. This kind has segmented control of precise HF exchanges between long-range and short-range, and the proportion of exchanges increases with the increase of the distance between electrons. A statement had been pointed out that the long-range corrected functional CAM-B3LYP, the frequently used one in the study of dyes' transition [9], was the most suitable for simulating disperse dye molecules [10]. In addition to the choice of function, the influence of the solvent on solutes' spectra needs to be considered in the calculation. A general approach is to combine the TD-DFT method with a solvation model [11]. The most used one among them is the polarizable continuum model (PCM), which regards the environment as a polarizable continuous medium and estimates its effects with limited computational resources and costs [12]. Therefore, based on the theory of quantum chemistry, it is of practical significance to explore and predict the spectral absorption properties of dispersed dyes according to their chemical structures. This chapter discusses the influence of the chemical structure and mixing ratio of each component in black dispersed dye compositions on the color properties of black dispersed dye compositions and explores the

optimization of deep dyeing black dispersed dye compositions using the color triangle method. By studying the effects of changes in the type, quantity, and position of halogen groups in the structure of dispersed dyes on their spectral properties, we aim to explore the application of quantum chemical calculations in the study of dispersed dye properties.

2. Analysis of the progress of dispersed dye production from invention patents

The development of dispersed dyes is closely related to the high demand for textiles, especially polyester fiber textiles, from various countries around the world over the years. At the same time, it also benefits from the application of dispersed dye production technology and innovation in new varieties. However, in the research and application of new dispersed dye varieties, innovation in the synthesis of dispersed dyes with new molecular structures does not account for the largest proportion. In order to better understand the technology and product R&D trends related to the production of disperse dyes, we used “disperse AND dyes” as the search keyword to make statistics on disperse dye invention patents under the category C09B (organic dyes or related compounds used to manufacture dyes; mordant; lake) on the website of the China National Intellectual Property Administration of China (CNIPA) [13, 14]. The time period was from January 1, 1985, to April 4, 2025. The patent documents searched involved 954 authorized invention patents related to the research and development of disperse dyes, including some invention patents applied for and granted by foreign companies in China. The changes in the number of 689 dispersed dyes and their related authorized invention patents over the years are shown in **Figure 1**.

According to the number of patent authorizations in the year of application, the number of patent authorizations was less than 10 before 2003. After 2004, it slowly fluctuated and increased, reaching its maximum in 2014. In 2015, it began to decline. Since then, the average annual number of invention patent authorizations has been about 45, and its development trend is basically synchronized with the development

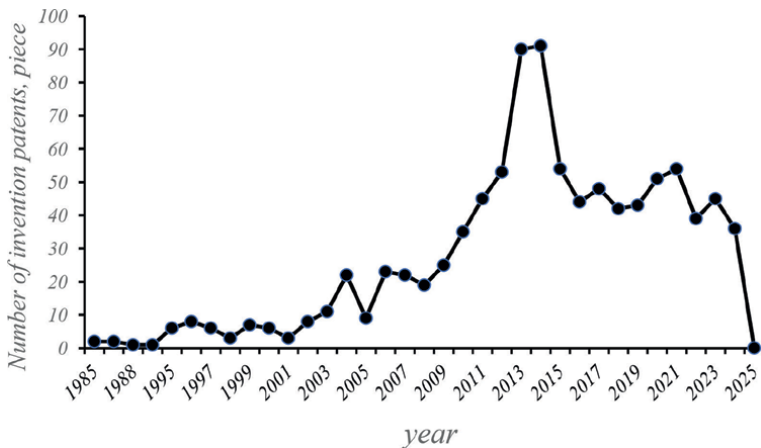


Figure 1.
Invention patents' trend related to disperse dyes under C09B classification in China.

trend of polyester fibers. Considering that the substantive examination period from application to authorization for invention patents generally takes 2–3 years or even 5 years, based on the recent situation of dispersed dye invention patent authorization, the number of dispersed dye invention patent authorizations tends to slow down in the short term.

The analysis of technical subject data for four major categories of patents, including production and processing processes, dye compositions, dye monomers, and other technical subjects, is shown in **Figure 2**.

From **Figure 2**, it can be seen that among the tested invention patents, the proportion of dispersed dye composition patents is as high as 62%, far higher than the other three themes such as dye monomer theme, indicating the significant influence of factors such as dye new structure synthesis technology or dye innovation cost. Nevertheless, the innovation of high-performance dye monomers remains the foundation for obtaining dye compositions with better application performance.

2.1 Disperse dye monomer

Disperse dye monomers are mainly divided into azo, anthraquinone, and non-azo heterocyclic compounds according to their main chemical structures. Among the 197 dispersed dye monomer patents retrieved, the majority are azo-based. In the classification of aromatic azo compounds, almost all are monoazo aniline. In the classification of heterocyclic azo, heterocycles such as benzothiazole/benzothiazole and phthalimide are mainly used. 80% of the research on these dye monomers focuses on improving the selection of substituents in the main structure, such as substituents on the benzene ring and N atom of azo coupling components, aniline, and substituents on the heterocyclic or benzene ring of diazo components. Related studies have shown that Ref. [15], when benzothiazole is used as a diazo component and N-substituted aniline is used as a coupling component, dyes with ethyl and benzyl substituents have good alkali stability and excellent color fastness.

According to the annual distribution data of authorized patents for dispersed dye monomers, the number of authorized patents for this technology subject accounted for about 59% of the total during the same period in 2003 and earlier. Afterwards, this proportion decreased to about 18%. After a high investment in the structural research

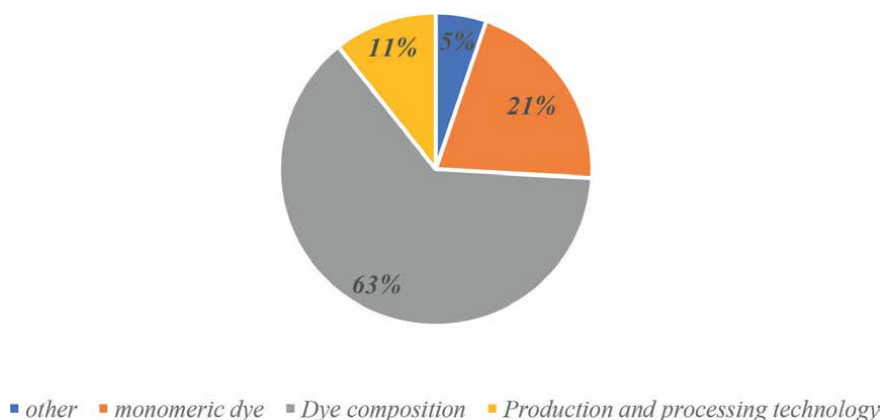


Figure 2.
Technology topic's distribution of authorized invention patents from 1985 to 2025.

and development of dispersed dyes in the early stage, the existing dye structure reserve serves as the basic technical support for the enterprise, which is sufficient to maintain its long-term development. The short-term development of new dye monomers will no longer be the focus of the enterprise's current development, but will instead focus on improving the performance of existing dye varieties, such as new dye combinations and formulas, in order to better suit the enterprise's market expansion and maximize profits. In the specific patents mentioned above, the focus of the development of new structured dispersed dyes is mainly on: including those that can be applied to supercritical CO₂ dyeing, polyester cotton short process same bath dyeing, and other new energy-saving and emission reducing printing and dyeing processes, as well as dispersed active dyes suitable for the printing and dyeing of new synthetic hydrophobic fibers, high alkali resistant, fluorine-containing, water-soluble, diazo-based, and other types of dispersed dyes. In order to cater to the current hot topic of supercritical fluid dyeing and processing technology with broad prospects, dispersed and reactive dyes are connected through bridging. This new structure of dispersed reactive dyes can exhibit better dyeing effects for blended textiles in environmentally friendly supercritical CO₂ dyeing [16, 17].

2.2 Disperse dye composition

The combination of dispersed dyes is a new dye product composed of suitable different dye monomers through dye compounding technology, known as blended dispersed dyes. The appropriate combination can maximize the synergistic effect between blended dyes and have better performance [18]. With the reduction of dye monomer structure development and its limitations in dyeing deep and dark colors and other dyeing properties, the synergistic effect of dye compounding has become a trend and focus of industry research in recent years. Between 2004 and 2025, the number of authorized invention patents related to dye compositions accounted for as much as 63% of the total number of patents during the same period, while this figure was only 25% between 1985 and 2003. About 75% of these dispersed dye composition patents are used to optimize application performance, such as deep color, color fastness, dye uptake, and uniformity. Other purposes include improving the environmental performance of dyes, replacing banned dyes, and meeting the high dyeing requirements of ultrafine polyester, polyester ammonia, and other fibers.

The upgrading of consumer health protection and the continuous improvement of environmental protection requirements by printing and dyeing enterprises have put forward stricter requirements for harmful substance content limits in the dye production and application industry [19]. Therefore, highly environmentally friendly dyes are a necessary research path for dye companies to adhere to green and stable development in the long term under the new situation, and they are also an inevitable trend for the future development of dispersed dyes.

Production enterprises generally promote the efficiency of dyes through the design of dye structures and the screening of dye components. In dye composition patents, nearly half of them choose to blend aromatic and heterocyclic azo dyes, mainly heterocyclic azo structural dyes, which have a certain dark effect due to the presence of electron-withdrawing heterocycles. Combined with the design and selection of substituents on the main structure and the synergistic effect of other dye components, various problems in dye applications can be well solved. Regarding the chromatography of dye compositions, the blue series is the most involved in these patents, followed by the blue black dark series that can adjust color changes

according to component ratios, while the number of patents for pure color series, such as black, red, and yellow, is basically similar.

2.3 Production and processing technology of dispersed dyes

The invention patents related to the production and processing technology of dispersed dyes involve new synthetic processes, commercial posttreatment processes, microcapsule preparation processes, and raw material recycling. Overall, nearly half of the patents in this topic aim to address the improvement of clean production processes, such as controlling harmful substance residues in dyes, energy conservation and consumption reduction, and reducing three wastes. This not only simplifies the process and facilitates operation but also improves the quality of dye products, resulting in better economic benefits. At the same time, optimizing the application performance, such as dyeing properties and color fastness, from the production and processing technology of dyes is also a research focus for enterprises.

In the synthesis of new processes, most patents propose more environmentally friendly and clean synthesis methods with better product performance, including methods such as raw material selection and ratio adjustment, process parameter adjustment, reaction system environment setting, etc., which reduce the three wastes in production, improve the yield, and enhance the quality of dyes. As a result, enterprises can reduce costs and increase profits. In the commercialization process, more than half of the patents focus on the preparation of liquid dispersed dyes, mainly on different control processes to improve the stability of dye quality. This is the dye production enterprises' grasp of the urgent demand for production automation and cleanliness from downstream printing and dyeing enterprises in the industrial chain. Disperse dyes of this formulation omit spray drying [20] in production and chemical process in use, making the production and application process simpler.

The preparation methods and applications of dispersed dye microcapsules have been extensively explored in academia [21]. Although there is currently no effective production technology in industrialization, the use of microcapsule dyes can make the printing and dyeing process more environmentally friendly and clean, with better printing and dyeing quality. Its significant characteristics indicate its great potential for development.

2.4 Other technical topics

Invention patents related to other technical topics mainly involve dye dispersants and crystal form control, which have a high degree of overlap with the refinement and commercial processing of dispersed dyes. Dispersants are crucial for the particle size, dispersion stability, and other application properties of dispersed dyes [22]. Among these patents, the majority focus on modifying and optimizing lignin-based dispersants that are widely available and low-cost, in order to reduce their adverse effects on fiber staining and azo dye reduction during use. The unstable crystal structure of dispersed dyes can cause performance problems such as poor high-temperature dispersibility of dyes [23], resulting in uneven color, color spots, and other defects in printed and dyed products. Therefore, crystal transformation is a necessary process in the synthesis and production of dispersed dyes. Stabilizing the crystal structure is beneficial for improving the quality of dispersed dyes and achieving better printing and dyeing results in applications. Therefore, the control process of dispersed dye crystal form is considered one of the key technologies for enterprise production.

3. Research on the optimization and application of component proportions in ultra black dispersed dye composition

Among various dyed polyethylene terephthalate fiber textiles, the hanging and flowing black polyester textiles are highly favored by consumers due to their noble and elegant visual effects. The black dispersed dyes used for dyeing are mostly composed of different dispersed dyes mixed in a certain proportion [24–26]. However, many commercial black dispersed dyes have shortcomings such as color cast and shallow black depth in dyeing polyester textiles due to the structure and compatibility of their mixed components [27]. To improve the above shortcomings, it is recommended to select dispersed dye components with high light absorption and excellent compatibility, and to obtain a black dispersed dye composition with deep dyeing and stable color through color triangle blending dyeing experiments. The proportion of each component is a good choice.

3.1 Optimization of component proportions in black dispersed dye composition by color triangulation method

3.1.1 Establishment of color triangle method

The design scheme for the color triangle study is shown in **Figure 3**, where R represents Disperse Purple SE-E, Y represents Disperse Orange SE-G, and B represents Disperse Blue SE-F. The total concentration of the mixed staining is 3% o.w.f, and the numerical numbers in the figure represent the corresponding color triangle staining sample numbers. Use a datacolor colorimeter to test the color information of the dyed sample. Obtain the required dark black color formula based on color information such as $L^* a^* b^*$ value and K/S value of the mixed and dispersed dye dyed sample [28, 29].

Dyeing experimental process: fabric wetting, extrusion drying → dyeing (adjusting the pH of the dyeing bath with glacial acetic acid to 4.5–5.5, bath ratio 1:30, dyeing at room temperature, heating at a rate of $2^{\circ}\text{C}\cdot\text{min}^{-1}$ to 130°C , holding for 45 minutes, then cooling to 80°C) → hot water washing → reduction cleaning ($2\text{ g}\cdot\text{L}^{-1}$ of sodium

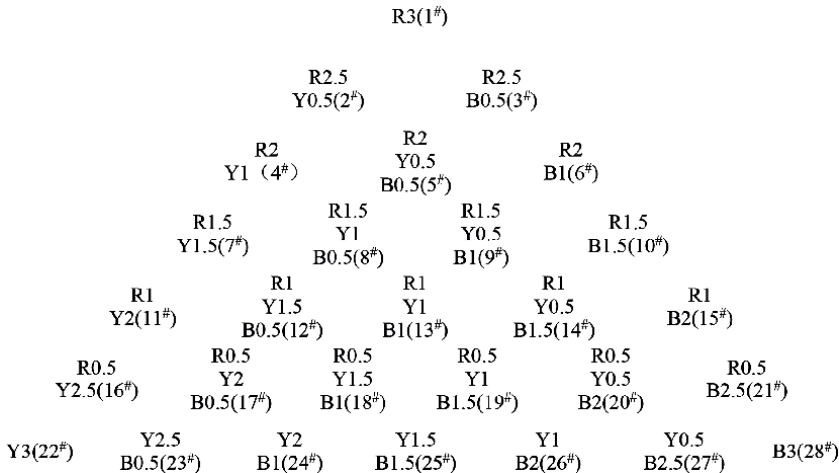


Figure 3.
Color triangle mixing experiment.

carbonate, 2 g·L⁻¹ of caustic soda, bath ratio 1:30, 80°C × 5 min) → water washing → soap washing (2 g·L⁻¹ of sodium carbonate, 5 g·L⁻¹ of soap powder, bath ratio 1:30, 95°C, 10 minutes) → drying (80°C).

3.1.2 Compatibility study of components in black dispersed dye composition

The residual liquid method can be used to obtain the relative dye uptake of each component of the black dispersed dye composition. However, after fabric dyeing, it still needs to go through processes such as water washing and reduction cleaning to wash away the floating color. The reducing agent used in reduction cleaning may damage the dye structure, causing a significant change in its maximum absorption wavelength. To obtain the accurate experimental results, the dimethylformamide (DMF) stripping method is used to test the concentration of each component of the black dispersed dye composition [30].

Weigh 0.1000 ± 0.0001 g of the sample and place it in a small test tube containing 10 ml DMF. Keep it at 130°C in an oil bath for 15 minutes and transfer the peeled dye solution to a 100 ml volumetric flask. Repeat the above steps three times. By the third time, the stripping solution no longer has obvious color. Finally, dilute the volumetric flask with DMF, shake well, and measure its absorbance using a UV-2450 UV visible spectrophotometer.

According to Lambert Beer's law, the absorbance of dispersed dyes has additive properties. Therefore, the total absorbance of a solution at different wavelengths should be the sum of the absorbance of each dye component at that wavelength [31, 32], that is:

At the wavelength of λ_1 , the formula for calculating absorbance is:

$$A_{(\lambda_1)} = A_{1(\lambda_1)} + A_{2(\lambda_1)} + A_{3(\lambda_1)} = K_{1(\lambda_1)}C_1L + K_{2(\lambda_1)}C_2L + K_{3(\lambda_1)}C_3L \quad (1)$$

Similarly, at the wavelength of λ_2 , the formula for calculating absorbance is:

$$A_{(\lambda_2)} = A_{1(\lambda_2)} + A_{2(\lambda_2)} + A_{3(\lambda_2)} = K_{1(\lambda_2)}C_1L + K_{2(\lambda_2)}C_2L + K_{3(\lambda_2)}C_3L \quad (2)$$

Similarly, at the wavelength of λ_3 , the absorbance calculation formula is:

$$A_{(\lambda_3)} = A_{1(\lambda_3)} + A_{2(\lambda_3)} + A_{3(\lambda_3)} = K_{1(\lambda_3)}C_1L + K_{2(\lambda_3)}C_2L + K_{3(\lambda_3)}C_3L \quad (3)$$

Under the condition of known values of A, K, and L, the C values of each dye component in the solution, that is, the concentrations of each component, can be obtained through simultaneous equations.

The results of the first color triangle blending dyeing experiment are shown in **Table 1**.

In the table, C represents the chromaticity in the CIELCH color space and also represents the distance of the color sample from the center point of the ab color graph. The smaller the value, the closer the color point is to the center point in the ab two-dimensional plane. Similarly, a smaller L value indicates that the dyed fabric is darker [33].

From the above experimental data, it can be seen that in the first mixed color triangle, the C values of the black dispersed dye combinations numbered 12, 13, 17, 18, 19, 24, 25, and 26 dyed samples are all less than 3.5. Therefore, it can be inferred

Experiment number	L	a	b	C	K/S
1	16.76	9.98	-17.43	20.08	25.09
2	15.95	5.26	-7.36	9.05	25.85
3	16.08	7.72	-16.06	17.82	26.35
4	15.50	4.05	-3.06	5.08	26.37
5	16.03	3.31	-7.45	8.15	25.13
6	16.40	6.76	-15.96	17.34	25.74
7	16.37	4.41	-1.04	4.53	24.45
8	15.17	1.76	-3.44	3.87	26.77
9	15.06	2.21	-6.80	7.15	27.62
10	16.21	5.33	-14.47	15.42	26.08
11	17.28	6.12	1.54	6.31	23.331
12	15.40	1.02	-1.34	1.69	25.96
13	15.66	0.63	-3.43	3.49	25.70
14	15.82	1.46	-6.68	6.84	25.88
15	15.94	4.42	-14.16	14.84	27.52
16	18.75	10.52	5.89	12.06	25.74
17	17.20	0.99	1.07	1.47	22.79
18	16.13	-0.24	-1.28	1.30	24.51
19	15.95	-0.11	-3.21	3.22	25.38
20	16.21	0.43	-6.62	6.63	25.75
21	16.74	3.10	-14.91	15.23	26.95
22	39.78	40.74	42.24	58.69	25.56
23	19.86	1.61	6.47	6.67	23.54
24	17.46	-1.43	1.44	2.04	22.87
25	16.50	-1.47	-0.84	1.70	24.76
26	16.63	-1.52	-2.51	2.94	24.76
27	17.14	-1.63	-6.08	6.30	25.29
28	18.52	-0.09	-16.65	16.65	26.13

Table 1.
Color test data of the first dyeing sample of the experimental black dispersed dye composition.

that when the total concentration is 3% o.w.f, R (Disperse Purple SE-E) varies within the range of 0–1.4 (the proportion of dye concentration in the mixed components,% o.w.f, the same below), Y (Disperse Orange SE-G) varies within the range of 0.6–2.4, and B (Disperse Blue SE-F) varies within the range of 0.1–2.4, resulting in a darker color visual effect. Following a similar experimental cycle, a black dispersed dye composition with a lower brightness value L (i.e. darker color) can be obtained.

The data shows that during the fourth blending, the C values of the dyed samples were all less than 1, and the magnitude of the change further tended to be smaller. Among all the dyed samples, sample 8 has the lowest L value of 15.92 and the highest K/S value of 24.74, indicating a darker visual color. Therefore, the optimal ratio for blending dyes can be determined as formula 8, which is Disperse Purple SE-E: Disperse Orange SE-G: Disperse Blue SE-F=0.50:1.85:0.65.

3.2 Compatibility performance of components in experimental black disperse dye composition

Due to the additive nature of the absorbance of each component of the black dispersed dye composition, and the influence of concentration changes on the absorbance of dispersed dyes, it is necessary to clarify the corresponding absorbance of the same dispersed dye at different wavelengths and concentrations. When testing pure DMF solvent with a UV2450 UV visible spectrophotometer, the maximum absorption wavelengths λ_{max} of Disperse Orange SE-G, Disperse Purple SE-E, and Disperse Blue SE-F are 466 nm, 565 nm, and 597 nm, respectively. The absorption linearity data of the three dispersed dye components in the black dispersed dye composition at their respective maximum wavelengths are shown in **Table 2**.

From the absorption standard curves of various dispersed dyes in **Table 2**, it can be seen that the linear correlation coefficients between concentration and absorbance of each single component dispersed dye are all within the range of 0.999, indicating a high linear correlation. According to the relevant data in the table, the extinction coefficient K values in formulas (1), (2), and (3) can be calculated for different dyes under corresponding conditions. The corresponding relationships between the “concentration—absorbance” of a single dispersed dye at different wavelengths are as follows:

1. At a wavelength of 466nm: Disperse Purple SE-E, $A_{\text{Purple (466nm)}} = 8.9168C_{\text{(Purple E)}}$; Disperse Orange SE-G, $A_{\text{Orange (466nm)}} = 35.786C_{\text{(Orange G)}}$; Disperse Blue SE-F, $A_{\text{Blue (466nm)}} = 6.6089C_{\text{(Blue F)}}$
2. At a wavelength of 565nm: Disperse Purple SE-E, $A_{\text{Purple (565nm)}} = 41.218C_{\text{(Purple E)}}$; Disperse Orange SE-G, $A_{\text{Orange (565nm)}} = 2.8606C_{\text{(Orange G)}}$; Disperse Blue SE-F, $A_{\text{Blue (565nm)}} = 32.8C_{\text{(Blue F)}}$
3. At a wavelength of 597nm: Disperse Purple SE-E, $A_{\text{Purple (597nm)}} = 32.108C_{\text{(Purple E)}}$; Disperse Orange SE-G, $A_{\text{Orange (597nm)}} = 0.6368C_{\text{(Orange G)}}$; Disperse Blue SE-F, $A_{\text{Blue (597nm)}} = 37.535C_{\text{(Blue F)}}$

Types of dyes	test wavelength(nm)	linear relationship	linear correlation(R^2)
Dispersed Blue SE-F	597.0	$Y = 37.575x$	0.9998
	466.0	$Y = 6.6089x$	0.9994
	565.0	$Y = 32.800x$	0.9996
Dispersed Orange SE-G	466.0	$Y = 35.786x$	0.9990
	565.0	$Y = 2.8606x$	0.9992
	597.0	$Y = 0.6368x$	0.9994
Dispersed Purple SE-E	466.0	$Y = 8.9168x$	0.9998
	597.0	$Y = 32.108x$	0.9991
	565.0	$Y = 41.218x$	0.9993

Table 2.

The absorption standard curve and linear data of each component in the black dispersed dye composition at its maximum wavelength.

After stripping the black dispersed dye composition obtained from the 3% o.w.f color triangle, the absorbance of the stripping solution was measured at different wavelengths as $A_{466\text{nm}} = 0.729$; $A_{466\text{nm}} = 0.458$; $A_{466\text{nm}} = 0.404$. By substituting the above data into the simultaneous equations (1), (2), and (3) described earlier, the calculation yields $C_{(\text{Purple E})}$: $C_{(\text{Orange G})}$: $C_{(\text{Blue F})} = 0.4872:1.7989:0.6308$. This ratio is very close to the concentration ratios of the various blending components in the dyeing formula: Disperse Purple SE-E: Disperse Orange SE-G: Disperse Blue SE-F=0.50:1.85:0.65. Considering experimental errors, it indicates that the various components of the experimental black dispersed dye composition have good compatibility.

3.3 Enhancement performance of experimental black dispersed dye composition

We conducted dyeing enhancement experiments on the black dispersed dye composition obtained from the experiment at different concentrations. As a comparison, a comparative dyeing experiment was conducted using commercially available black dispersed dyes. The experimental results are shown in **Table 3**.

Comparing the experimental results in **Table 3**, it can be found that the lifting power of the experimental blended dye and the brightness value of the dyed fabric are significantly better than those of the commercial liquid black at the same concentration. The brightness value of the experimental formula dye sample has reached $L^* = 14.62$ at 8% o.w.f concentration, while the brightness value of the commercial liquid black dispersed dye currently used by the enterprise under the same dyeing conditions is $L^* = 15.91$ at 10% o.w.f concentration, indicating that the experimental blended black dispersed dye can achieve the dyeing effect of deep black polyester textiles at lower dye concentrations.

Concentration (% o.w.f)	Experimental black dispersed dye composition		Commercial black dispersed dye	
	L	K/S	L	K/S
0.125	50.17	2.476		
0.250	40.79	4.642		
0.500	32.43	8.177		
1.000	23.72	15.15	29.82	13.78
2.000	17.40	22.59	21.61	17.09
3.000	15.54	25.44	19.01	18.49
4.000	15.18	25.94	17.43	22.91
5.000	15.10	25.93	16.84	23.35
6.000	14.70	25.94	16.42	23.71
7.000	14.74	26.63	16.35	23.99
8.000	14.62	26.90	16.12	24.04
9.000			16.06	24.20
10.00			15.91	24.55

Table 3.
Dyeing lifting power of experimental blending black disperse dye.

Types of dyed samples	L*	a*	b*	C
Enterprise dyeing samples	14.80	0.17	−0.18	0.25
Experimental dyeing sample	13.77	0.22	−0.16	0.28

Table 4.

Color testing data of experimental black dye combination and commercial black dye dyed samples.

3.4 Dyeing performance of experimental black dispersed dye composition

To compare the dyeing effect of the experimental black dispersed dye combination with commercial dispersed dyes, the dyed samples of polyethylene terephthalate fiber enterprise dyed textiles (8% o.w.f) and deepened were compared with the color measurement data of the experimental black dispersed dye combination dyed samples at a concentration of 6% o.w.f. The results are shown in **Table 4**.

Table 4 shows that the color performance of enterprise dyed samples with 8% o.w.f dye concentration and already subjected to darkening treatment is similar to that of samples dyed with 6% o.w.f experimental black dispersed dye composition concentration. However, the brightness value L^* of the dyed samples obtained from the experiment is significantly lower, and the visual effect of the apparent color is darker.

4. Application of quantum chemical calculation in the study of dispersed dye

The molecular structure of dispersed dyes is closely related to their maximum absorption wavelength, color, and other properties, which determine the application value of dispersed dyes. The correlation between the structure of material molecules and their corresponding energy levels is a research field in quantum chemistry. The application of quantum chemistry theory and its related computational applications in dye innovation research has received increasing attention. The application of quantum chemistry theory and its related computational programs in dye substructure design and color performance prediction has become a hot research topic, providing strong support for the interaction mechanism between dyes and fibers, as well as the design and development of new dyes [34–36].

Gaussian [37–39] is currently the most widely used computational software application in quantum chemistry. Among them, Chem3D [40] is mainly used for drawing and analyzing the 3D chemical structure of molecules, as well as conducting molecular dynamics simulations and structural optimization. Open Babel [41–43] is a chemical toolbox that can be used to process various chemical data languages. Confab is a functional module in Open Babel, mainly used in the fields of chemical informatics and molecular modeling. Screening low-energy conformations helps users find the most stable molecular conformation. XTB [44, 45] is used to calculate the geometric structure, electronic properties, and energy of molecular systems, providing a tool that strikes a balance between computational speed and accuracy. Geometries, frequencies, non-covalent interactions extended tight binding (GFN xTB) is a semiempirical quantum chemistry method. Although its accuracy may not

be as good as full quantum chemistry methods in some cases, it can provide efficient and accurate geometric optimization, frequency calculation, and non-covalent interaction description. At the same time, xTB can achieve rapid pre-optimization of conformational batches and obtain rough energy. Crest [46–48] is a tool based on the GFN method, particularly suitable for use in conjunction with the GFN2 xTB [49, 50] method, which can more fully utilize computing resources and significantly reduce computation time. Molclus [51] is a program for cluster configuration search and molecular configuration search, which can control the details of configuration search and is extremely convenient for data modification, continuation, and recalculation. Multiwfn [52] is an electronic wave function analysis program widely used in post-processing analysis of quantum chemistry calculations and can flexibly and efficiently analyze the results of quantum chemistry calculations.

In the process of quantum chemistry calculations, the vertical excitation calculation method is used to simulate UV-Vis absorption of dispersed dyes with different structures. The software programs used include Gaussian 16 C01, Chem3D, Crest, Xtb, OpenBabel, Multiwfn, Molclus, Visual Merchandising (VMD), Origin [53], etc.

Generate initial conformations for each structure using the Confab program in OpenBabel, use crest to call xTb for batch optimization under the GFN2 xTB method, and use the isostat program in Molclus to screen conformations in order of energy from low to high. Under the calculation conditions of Solvation Model Density (SMD) solvent model (N,N-Dimethylformamide [DMF] solvent) and functional basis set combination of B3LYP/6-31G * [54, 55] in Gaussian, the ground state structure optimization and vibration analysis of each molecular structure were carried out for the batch with the lowest energy, and D3 (BJ) [56] dispersion correction was used.

In quantum chemistry calculations, van der Waals forces and dispersion forces play important roles in intermolecular interactions. These interactions involve fluctuations in the electron cloud, leading to the generation of instantaneous dipole moments and multipole moments in molecules, resulting in different forces. Dispersion correction is a method for more accurate correction of the calculation results under the influence of van der Waals forces and dispersion forces, among which D3 (BJ) is currently the commonly used dispersion correction method.

Each conformation underwent structural optimization and vibration analysis, and high-precision single-point calculations were performed under M06-2X/def2-TZVPP [57, 58], and the corresponding free energy was obtained by adding it to the free energy thermal correction. Calculate the proportion of Boltzmann distribution for each structure, select conformations with a proportion of not less than 5%, and then calculate the excited states of these conformations.

For accuracy considerations, the basis set for excited state calculation is selected as the def2-TZVP basis set for the multiatom macromolecular system. Due to the lack of a dispersion function in the basis set, the accuracy of its calculation results may decrease. Therefore, a dispersion function is added to the def2-TZVP basis set in a manner to ensure the accuracy of the calculation results [59].

By using Gaussian and related auxiliary programs to study the correlation between the structure of dispersed dyes and their maximum absorption wavelength, good support can be provided for predicting and optimizing dye performance in the development process of new dyes.

5. Quantum chemical calculation study on the influence of halogen-substituted groups on the spectral absorption properties of disperse dyes

5.1 Molecular conformation calculation of dispersed dyes

Taking the C.I. Disperse Orange 44 monoazo dye and similar structured dispersed dyes as an example, each containing different types, quantities, and positions of halogen-substituted groups. The molecular structure of the dye is shown in **Table 5**. Quantum chemical calculations were performed on experimental dispersed dyes with different structures using Gaussian-related programs. The differences in the types, numbers, and positions of halogen-substituted groups in the dispersed dye structures were explored, and their effects on the molecular structure conformation, molecular orbitals, excited state orbital transitions, contribution rates, absorption spectra, maximum absorption wavelengths, and other related properties of the dyes were investigated.

Due to the thermal motion of molecules at finite temperatures, these motions have a significant impact on the energy and properties of the molecules. Therefore, for the thermal correction of free energy, it is necessary to consider the additional energy contribution of molecular motion at room temperature (i.e., 298.15 K), in order to obtain free energy close to room temperature and make theoretical calculation data more realistic.

By using the Boltzmann distribution ratio, these energy differences were converted into the relative proportion of conformations. Due to the smaller proportion of conformations with a Boltzmann distribution ratio of less than 5% at 298.15 K, and the dominance of lower energy conformations, which are more important for describing the ground and excited state properties of molecules, conformations with a Boltzmann distribution ratio of not less than 5% at 298.15 K were selected for each structure. The results are shown in **Table 6**.

From the data in **Table 6**, it can be seen that the conformational free energies of each molecule are different, which means that there are differences in the stability of different molecular conformations under the same conditions. Lower free energy usually indicates a more stable conformation. The energy data in **Table 6** shows that the

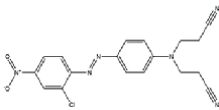
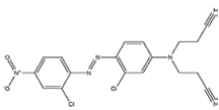
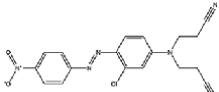
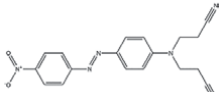
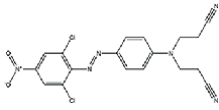
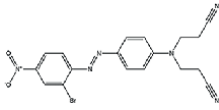
Dye molecule code	Chemical structure	Dye molecule code	Chemical structure
S1		S4	
S2		S5	
S3		S6	

Table 5.
Study the molecular structure of dispersed dyes for research purposes.

Dye molecule code	conformation	Free energy (a.u)	Relative energy ΔE (kcal/mol)	Boltzmann distribution ratio (%)
S1	1	-1 633.693 765	0.00	44.01
	2	-1 633.693 673	0.06	39.93
	3	-1 633.692 375	0.87	10.10
S2	1	-1 633.702 440	0.00	99.53
S3	1	-2 093.305 205	0.00	64.11
	2	-2 093.304 201	0.63	22.14
	3	-2 093.303 598	1.01	11.69
S4	1	-2 093.303 867	0.00	58.05
	2	-2 093.302 969	0.56	22.43
	3	-2 093.302 747	0.70	17.73
S5	1	-1 174.089 548	0.00	92.5%
	2	-1 174.086 924	1.65	5.74%
S6	1	-3 747.693 142	0.00	93.06%

Table 6.
The energy and Boltzmann distribution ratio of different conformations in various structures.

types, quantities, and positions of certain substituents in the molecular structure have a significant impact on the energy and conformational stability of the molecule.

For example, the conformational energies of S1, S3, and S4 structures are relatively close, indicating the existence of multiple stable conformations in S1, S3, and S4. The proportion of Boltzmann distribution in S3 and S4 is higher than that in S1, and the highest proportion of Boltzmann distribution in S3 and S4 has a lower conformational free energy than S1, indicating that adding a Cl substituent to S1 in S3 and S4 helps to increase the stability of the molecule. The reason is that the strong electron attraction effect of Cl atoms leads to their Boltzmann distribution being more concentrated in the same dominant conformation. Compared to the S1 conformational distribution, the main conformational distributions of S3 and S4 are concentrated in the first conformation (64.11, 58.05%), indicating that multiple Cl substituents may be more conducive to regulating the electron density of the molecule, resulting in a more stable conformation. Cl substituents with symmetry or electronic effects enhance the stability of the molecule. Compared to S1, the conformation of the S5 molecule without Cl substituents is more uniform, resulting in the highest proportion of Boltzmann distribution in S5 conformation reaching 92.57%.

Compared with S1, the Boltzmann distribution of the first conformation of S2 is 99.53%, accounting for almost the entire Boltzmann distribution proportion, indicating that S2 has a nearly unique conformation due to the same Cl substituent but different positions. In contrast, S3, which is also a dual Cl substituent S4. Although there are some differences in the distribution positions of the two Cl groups, the conformational free energy and Boltzmann distribution ratio of the molecules are relatively close, indicating that the introduction of double Cl substituents at different positions increases the complexity of the dye molecule, making its conformational distribution more dispersed and introducing more conformational possibilities. However, in terms of the final result, the strong electronegativity of

Cl substituents has a much greater impact on the electron cloud of dye molecules than their distribution positions. Comparing the effects of individual Cl substituents on the Boltzmann distribution of conformation in S1 and S2, the different positions of substituents have a significant impact on the minute conformation or molecular stability.

The structure of S6 is similar to that of S1, except that the substituent is a Br atom. From the perspective of electronegativity, the electronegativity of Cl substituents is higher than that of Br substituents, but the spatial volume of the latter is higher than that of the former. The result is that the conformation with the highest proportion of Boltzmann distribution in S6 occupies a high proportion of 93.06%, which is much higher than the dispersed distribution of S1 structure. The reason is that compared with Cl, Br has lower electronegativity but larger spatial volume, and its comprehensive influence is much lower than that of Cl substituents.

The different molecular conformations and their resulting differences in light absorption properties determine the main characteristic of the molecular absorption spectrum, namely its chromogenic properties.

5.2 HOMO and LUMO orbital energies of dispersed dyes

In quantum chemistry, Highest Occupied Molecular Orbital (HOMO) orbitals represent the part of a molecule that is most likely to lose electrons, while Lowest Unoccupied Molecular Orbital (LUMO) orbitals represent the part that is most likely to gain electrons. The HOMO and LUMO orbital energy and bandgap (E_g) data of the conformation with the highest proportion of Boltzmann distribution for each dye molecule structure are shown in **Table 7**. The HOMO energy reflects the electron donating ability of a molecule, and the higher the value, the more likely the molecule is to lose electrons. The LUMO energy reflects the ability of a molecule to accept electrons, and the lower the value, the easier it is for the molecule to accept electrons. The energy gap $E_g = E_{LUMO} - E_{HOMO}$, which is the energy difference between LUMO and HOMO, is related to the optical absorption of dye molecules. The smaller the energy gap, the lower the light energy absorbed by the molecule, so the molecule will absorb monochromatic light of longer wavelengths.

The double Cl substituent has a higher electron-withdrawing effect compared to the single Cl substituent, stronger constraints on electron spillover or activity ability, and significantly improves the molecular orbital energy level. From the data in **Table 7**, it can be seen that the energy gaps of S3 and S4 structure molecules are both larger than S1, while the energy gaps of S5 and S6 structure molecules are smaller

Dye molecule code	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
S1	-5.739 2	-3.148 6	2.590 6
S2	-6.085 0	-3.446 9	2.638 1
S3	-6.076 6	-3.413 7	2.662 9
S4	-6.155 8	-3.431 4	2.724 4
S5	-5.944 1	-3.378 3	2.565 8
S6	-5.992 5	-3.495 0	2.497 5

Table 7.
HOMO and LUMO orbital energies of dispersed dye molecules.

than S1, resulting in a blue shift in the absorption spectra of S3 and S4 structure molecules compared to S1 structure dispersed dyes. The absorption spectra of S5 and S5 structural molecules exhibit a red shift tendency.

Considering the -NO₂ substituent on the left side of the dye molecule and the -N, N-cyanoethyl structure on the right side, compared with the S2 structure molecule, the Cl substituent in the S2 structure is located at the benzene ring position in the middle of the dye molecule. The electron absorption performance of the Cl atom on the balance of the conjugated electron cloud of the entire dye molecule is lower than that of the S1 structure molecule. Therefore, the energy gap of the S2 structure molecule is larger than that of S1. In terms of light absorption performance, S2 can absorb shorter wavelengths of light than S1, leaning toward the ultraviolet region.

The energy gap of S3 and S4 structural molecules is greater than that of S1, indicating that compared with a single Cl substituent, the double Cl substituent further reduces the degree of freedom of the electron cloud, suppresses the conjugation effect of π -electrons, and leads to a larger energy gap. Compared with the S4 structure, the two Cl substituents in the S3 structure molecule are located on both sides of the same benzene ring at the end. Theoretically, its electronegativity has a certain offsetting effect, but its constraint effect on the entire molecular electron cloud is lower than that of the S4 structure. Therefore, its energy gap is lower than that of the S4 structure. Therefore, in terms of light absorption performance, S4 can absorb shorter wavelengths of light than S3, and its light absorption ability tends to be in the ultraviolet region.

S5, without the electron attraction effect of Cl substituents, means that the electron cloud is more freely distributed, and the conjugation effect is stronger. Its energy gap is lower than that of S1, S2, S3, and S4. Without Cl substituents, S5 has a slightly longer wavelength for absorbing monochromatic light compared to S1, S2, S3, and S4.

Compared with S1, S6 has a Br substituent, which has a lower electronegativity than the Cl substituent. The larger polarization effect of the Br substituent lowers the energy level, resulting in a lower HOMO orbital energy of S6 than S1. Similarly, the HOMO orbital energy of S6 is lower than that of S5 without a substituent. The energy gap of S6 is slightly smaller than that of S1, suggesting that Br substituents are more effective in reducing excitation energy compared to Cl substituents. Similarly, the energy gap of S6 is slightly smaller than that of S5, resulting in a longer absorption wavelength of S6 than both S1 and S5.

In summary, the introduction of different types, quantities, and positions of halogen-substituted groups into the structure of dye molecules can lead to varying degrees of constraint on the electronic cloud of the entire dye molecule and the conjugation effect of π -electrons. Therefore, in terms of light absorption performance, it results in changes in the wavelength of light that can be absorbed.

5.3 Excited state orbital transitions and their contribution rates of dispersed dyes

The excited state calculation was performed on the conformation with the highest proportion of Boltzmann distribution for different molecular structures, and the main orbital transitions and contribution rates in the excited state were obtained. The results are shown in **Table 8**.

From the data in the table, it can be seen that the HOMO to LUMO transitions of different molecular structures account for the main contribution in multiple molecules, especially in S2, S5, and S6, where the contribution rate of HOMO>LUMO

Dye molecule code	Main orbital transition
S1	HOMO -> LUMO (63.0%) HOMO-1 -> LUMO+1 (11.0%), HOMO -> LUMO+1 (10.4%)
S2	HOMO -> LUMO (85.9%) HOMO -> LUMO+1 (7.6%)
S3	HOMO -> LUMO (58.1%) HOMO -> LUMO+1 (13.5%) HOMO-1-> LUMO+1 (12.9%) HOMO-4 -> LUMO (6.3%)
S4	HOMO -> LUMO (59.6%) HOMO-1 -> LUMO +1 (13.6%) HOMO -> LUMO +1 (7.7%) HOMO-1 -> LUMO (7.1%) HOMO-4 -> LUMO (5.9%)
S5	HOMO -> LUMO (84.4%) HOMO -> LUMO +1 (8.6%)
S6	HOMO -> LUMO (86.6%) HOMO -> LUMO +1 (7.7%)

Table 8.
Main orbital transitions and contribution rates in the excited states of each structure.

transitions is over 80%. This indicates that the main electronic excitation of these molecules is the direct transition from HOMO to LUMO, and the main absorption band of these molecules in the spectrum is caused by this transition, with $\pi \rightarrow \pi^*$ transitions being the main ones. Therefore, it can be inferred that the absorption spectra of these molecules are mainly influenced by the size of the HOMO-LUMO bandgap, which is consistent with the bandgap data in **Table 7** previously.

In the S1, S3, and S4 transitions, in addition to the HOMO ->LUMO transition, the HOMO-1->LUMO+1 transition also has a high contribution rate (e.g., in S4, the HOMO-1->LUMO+1 contribution rate is 13.6%). Prove that these molecules not only exhibit absorption peaks caused by HOMO ->LUMO transitions in the spectrum but may also exhibit secondary absorption peaks caused by HOMO-1->LUMO+1 transitions. These secondary absorptions may result in wider absorption bands, increasing the optical absorption range of the molecule.

The data shows that the HOMO ->LUMO transition contribution rates of S3 and S4 are relatively low (58.1 and 59.6%, respectively), while HOMO ->LUMO+1 and HOMO-1->LUMO+1 also have significant contributions. This indicates that lower energy electrons in the excited states of these molecules also participate in the transition, which in turn affects the electron distribution and molecular optical properties of the excited states. This means that S3 and S4 may have multiple electronic transition paths in their excited states, which can affect their optical behavior.

A higher HOMO ->LUMO contribution rate usually means that the molecular electron excitation is more concentrated, and there will not be too many complex transition paths, which may make the molecule more stable in the excited state. Based on the previous Boltzmann distribution data, the proportion of Boltzmann distribution in S2, S5, and S6 is relatively high, and their HOMO ->LUMO contribution rates are also significant, which further confirms their stability in the excited state.

5.4 Molecular absorption spectra and maximum absorption wavelengths of dispersed dyes

Different molecular conformations have different spectra. By calculating the proportion-weighted average of the Boltzmann distribution, all possible molecular conformational information can be integrated to obtain a more comprehensive spectrum. Import the output files of conformational excited states obtained by Gaussian calculation of different Boltzmann distribution ratios for each structure into Multiwfn, and plot the UV-Vis spectra after averaging the conformational weights. The results are shown in **Figure 4**.

From **Figure 4**, it can be seen that the absorption spectrum of the S3 structured dye molecule is slightly to the left of S1, and its maximum absorption wavelength is also slightly smaller than S1, confirming the blue shift trend caused by the larger energy gap of S3, which is consistent with the analysis in 3.2. The double Cl substituent

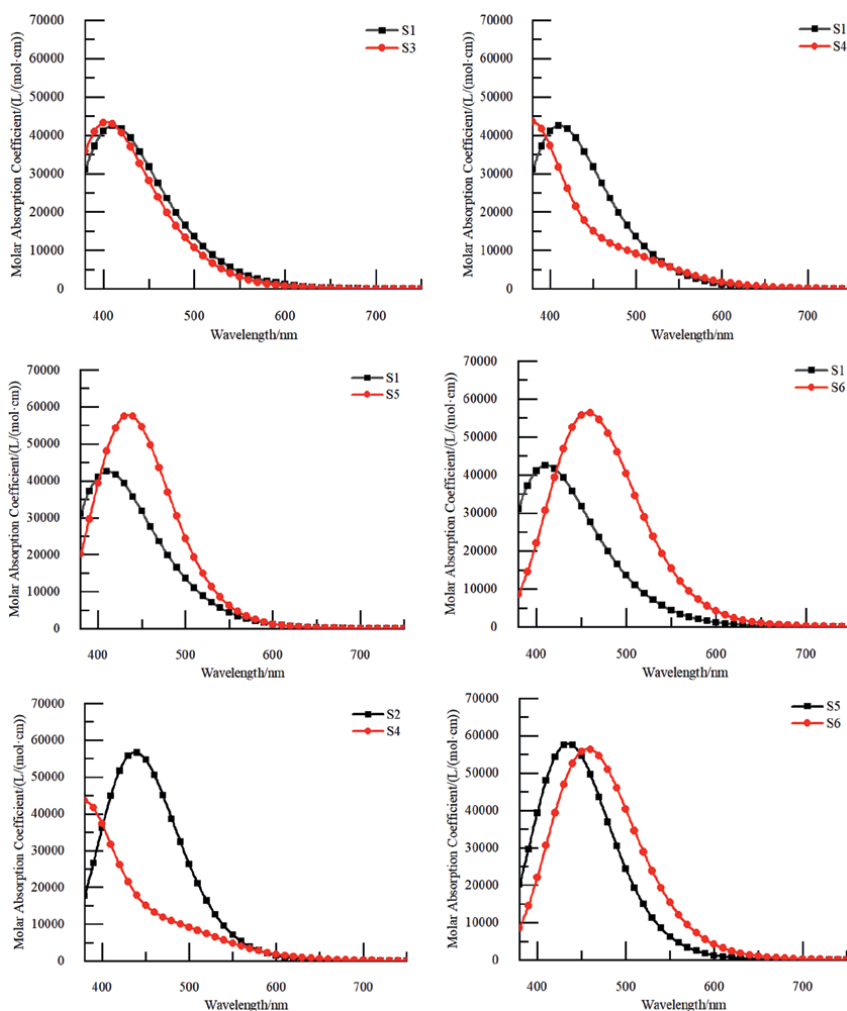


Figure 4.
Conformation-weighted average UV-visible absorption spectra of each structure.

of the S4 structure dye molecule results in a larger energy gap of the dye molecule, causing its absorption peak to shift to the left and toward shorter wavelengths than that of S1. This result is consistent with previous theoretical predictions, leading to a significant blue shift. The performance of S5 structural dye molecules is exactly the opposite, with its absorption peak significantly shifted to the right compared to S1, appearing in the longer wavelength region. This indicates that after removing the Cl substituent, the conjugated system is enhanced, the energy gap is reduced, and the absorption spectrum is redshifted, which is consistent with the theoretical predictions. The absorption peak of S6 structural dye molecules is significantly shifted to the right compared to the absorption peak of S1, and the red shift phenomenon is significant, which is consistent with the polarization enhancement of Br and the electron conjugation effect, consistent with theoretical analysis. The influence of the double Cl substituents on the S4 structure dye molecule results in its absorption peak appearing to the left of the S2 absorption peak, confirming the blue shift phenomenon, consistent with theoretical analysis, indicating that the symmetrical distribution of double Cl substitution enhances the energy gap. The absorption peak of S6 has shifted to the right compared to the absorption peak of S5, showing a significant red shift. This indicates that the introduction of Br reduces the energy gap and shifts the absorption spectrum toward longer wavelengths, consistent with theoretical predictions.

Calculate the excited states of different molecular structures and obtain their maximum absorption wavelengths. The relevant data are listed in **Table 9**. Based on the maximum absorption wavelength in the table and combined with previous data analysis, it can be seen that the size relationship of the maximum absorption wavelength between different structures is the same as the previously inferred gap size relationship based on HOMO and LUMO orbital energies. The smaller the HOMO-LUMO gap of a molecule, the longer its maximum absorption wavelength. For example, S6 has the smallest energy gap of 2.4975 eV, so its maximum absorption wavelength is 457 nm, which is the longest absorption wavelength among all molecules, consistent with the size of the energy gap. On the contrary, S4 has the largest HOMO-LUMO energy gap at 2.7244 eV, and its maximum absorption wavelength is shorter at 380 nm, which conforms to the rule that molecules with larger energy gaps have shorter absorption wavelengths.

The calculation results show that different types, quantities, and positions of substituent groups have significant effects on the distribution, energy gap, and color of the HOMO and LUMO orbitals of dye molecules, which is consistent with the quantum absorption theory of molecular energy levels. Molecules containing halogen atoms exhibit longer absorption wavelengths and stronger optical activity. By changing the number and position of substituents in the molecular structure, the absorption wavelength and chromogenic properties of dyes can be effectively adjusted, which provides useful assistance for the design and performance prediction of dispersed dye molecules.

Dye molecule code	Maximum absorption wavelength $\lambda_{\text{cal/nm}}$	Dye molecule code	Maximum absorption wavelength $\lambda_{\text{cal/nm}}$
S1	408.00	S4	380
S2	430.00	S5	435

Table 9.

Calculated value of the maximum absorption wavelength of each structure.

6. Conclusion and prospect

Disperse dyes, as the most consumed coloring agent for textile dyeing, have been widely used in textile dyeing and printing processing. Among them, dispersed dye compositions represented by black dispersed dyes account for a relatively high proportion in the development of new varieties of dispersed dyes. The chemical structure and mixing ratio of each component directly affect the color performance of black dispersed dye compositions. It is a good choice to select dispersed dye components with high light absorption and excellent compatibility, and to obtain a black dispersed dye composition with dye depth and color stability through color triangle blending dyeing experiments.

Through the optimized DFT/TD-DFT calculation method, the study on the HOMO-LUMO energy levels, electronic transition paths, bandgap sizes, UV-Vis absorption spectra, and maximum absorption wavelengths of dispersed dye molecules with different structures shows that the type, quantity, and position of halogen-substituted groups have a significant impact on the HOMO and LUMO orbital distribution, bandgap, and color presentation of dispersed dye molecules. By changing the substituents in the molecular structure of dyes, the absorption wavelength and spectral properties of dispersed dyes can be purposefully adjusted.

There is an optimized maximum absorption wavelength fitting prediction model between the theoretical calculation data and test data of dispersed dyes, but the prediction model has significant differences in predicting the maximum absorption wavelength of dispersed dyes with different structures. The predicted maximum absorption wavelength of the orange-based dispersed dye with a single diazo structure in the research case is close to the measured value.

The fitting equation established through multiple regression analysis of the calculated and experimental values of the maximum absorption wavelength of dispersed dyes is used to predict the proportion of black dispersed dye composition components using DB291, DO61, and DR73 dispersed dye components. The optimal value of black dispersed dye composition components under the brightness target can be obtained. The dyeing experiments on black dispersed dye compositions with different proportions show that the predicted improvement, color fastness, and dyeing performance of black dispersed dye compositions, especially the brightness value, are better, with unique black visual effects.

By further fitting and optimizing the selected quantum chemical density functional module and prediction model, it is possible to predict the maximum absorption wavelength of dispersed dyes and the composition ratio of black dispersed dye combinations within a certain accuracy range, providing good technical support for the design and innovative research of new dispersed dyes.

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Adsorption Kinetics and Equilibrium Studies of Organic Dyes by Zeolites from Aqueous Solutions

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Abstract

The recent development of efficient adsorbents for the removal of organic dyes, including Rhodamine B (RhB), Methyl Violet (MV), and Phenol Red (PR), has become essential for sustainable wastewater treatment. This study investigates the removal of these three dyes using both commercial and dealuminated zeolites, comparing their adsorption efficiencies. The zeolites utilized in this study include H-ZSM-5, H-Y, H-beta, ferrierite, and mordenite. The research explores the utilization of dealuminated zeolite materials as promising candidates for dye degradation, leveraging their unique combination of high surface area, molecular sieving properties, and ability to host photoactive components. The investigation focuses on the mechanistic pathways of dye removal under ambient conditions, with particular emphasis on the role of dealuminated zeolite framework characteristics in facilitating the adsorption process. Spectroscopic analysis was used to identify the removal efficiency of intermediate products to elucidate the distinct degradation pathways for each dye. The commercial H-Y zeolite demonstrated the highest capacity for MV (4.95 mg/g), while dealuminated H-beta was most effective for RhB (2.25 mg/g). Dealuminated ferrierite showed the best PR adsorption (0.60 mg/g), with Freundlich modeling ($R^2 > 0.98$) indicating heterogeneous binding. The Langmuir model fitted MV adsorption exceptionally well ($R^2 > 0.99$). The results highlight how zeolite type and modification significantly influence dye adsorption efficiency, with commercial zeolites excelling for MV and dealuminated variants performing better for RhB and PR removal. This study aims to provide insights into the adsorbent's material degradation capability for environmental remediation applications.

Keywords: dealuminated zeolite, dye removal, methyl violet, rhodamine B, phenol red

1. Introduction

Artificial dyes exemplify one of the fundamental classes of pollutants discharged into a hydrous ambiance, foremost due to their spacious use in textile,

pharmaceutical, cosmetic, and paper manufacturing. Complicated aromatic structures that render them extremely steady and reluctant to natural decay processes, thereby posing serious environmental and health hazards, often describe these compounds [1]. Rhodamine B (RhB), phenol red (PR), and methyl violet (MV) are dyes known for their toxicity and environmental stability, and numerous studies and research have been conducted to eliminate these dyes in water treatment processes.

Rhodamine B (RhB) is a cationic dye belonging to the xanthene group, structurally related to fluorescein compounds [2]. It is vastly exercised in manufacturing and scientific implementations, including plastic and paper industrialization and cosmetic formations, and as a fluorescent tracer in molecular biology and analytical chemistry, but it can have harmful effects on living things with long-term exposure [3]. These adverse effects raise concerns about the need of prompting researchers to explore safer alternatives and methods for its degradation. The dye exhibits strong photophysical properties, with absorption generally occurring between 540 and 550 nm and fluorescence emission in range 570–590 nm, rendering it extremely appropriate for imaging and detecting applications [4]. Nonetheless, its mild calorific and photochemical stability restrict its application under severe environmental circumstances. As a result, research is focused on understanding its ecological fate and improving processes for its removal from polluted water systems [5].

The synthetic dye phenol red (PR), sometimes called phenolsulfonphthalein, has long been used mainly for pH measurement but also for a variety of other industrial, food preservation, and scientific purposes. Because this dye is resistant to degradation and may be detrimental to aquatic habitats, recent research has examined the possibility of integrating it into new materials and its interactions with ecosystems [6]. One of the serious environmental impacts of phenol red (PR) is its easy leakage into water and the difficulty of removing it from contaminated water due to its high stability and resistance to degradation. This poses challenges in wastewater treatment. However, some research has made great strides toward improving its deterioration [7]. In short, phenol red has several scientific applications, but its environmental impact limits its use. This necessitates unique treatment options that contribute to the development of effective degradation processes for this dye, thereby striking a balance between convenience of use and environmental sustainability [8].

Methyl violet (MV) is a class of synthetic cationic dyes made from triphenylmethane compounds. This class includes several analogues, including methyl violet 2B, 6B, and 10B (crystal violet). These compounds are widely used in industrial sectors such as paper, paints, textiles, and inks. The chemical structure of methyl violet dye includes numerous aromatic rings and amine groups, making it water-soluble and highly reactive with negatively charged materials [9]. The dye's negative impacts on the environment and human health have attracted attention. Its presence in wastewater is of concern due to its potential mutagenic, cytotoxic and carcinogenic effects according to a number of toxicological evaluations. Furthermore, prolonged exposure to wastewater contaminated with MV can cause enzyme inhibition, oxidative stress, bioaccumulation in food chains, and other harmful impacts on aquatic life [10]. Because of their molecular stability and biodegradability, nanoparticles are sometimes difficult to remove using conventional processing methods such as membrane filtering, coagulation and flocculation, and biodegradation. This limitation has contributed to accelerating the development of advanced processing technologies. Among these methods, biosorption techniques using algae or fungal biomass, photodegradation using metal oxides, and adsorption using nanomaterials have demonstrated very promising results. In practical wastewater systems, these technologies strive not only

to achieve high removal, but also to achieve cost-effectiveness and environmental sustainability [11].

Eliminating such dyes from aqueous environments is crucial for universal health and ecological safeguards. Among diverse approaches, adsorption features due to its operational naivety, low cost, and loud elimination qualification. This process involves the gathering of dye molecules on the surface of a solid substance, with the execution heavily affected by the surface characteristics of the adsorbent [12].

There are many compounds that have been used in the process of adsorption of hazardous dyes and treatment of polluted water. Zeolites are composed of microporous crystalline aluminum silicates that used for this propose. They possess distinctive and unique properties, including their high surface area, stable pore sizes, and ion exchange efficiency. Render them exceptionally appropriate for the adsorption of diverse organic and inorganic contaminants. The negatively charged structure of zeolites, arising from the isomorphous substitution of Al^{3+} for Si^{4+} , facilitates robust electrostatic interactions with cationic dyes, primarily methyl violet (MV) and rhodamine B (RhB). Furthermore, zeolites can be chemically or physically modified to enhance their adsorption capacity, therefore augmenting their effectiveness in environmental remediation [13].

The modernistic research has evidenced the advantage of natural and synthetic zeolites in removing RhB, PR, and MV from polluted waters. For example, Moroccan natural zeolites showed high adsorption capacities for methyl violet, with performance affected by pH, contact time, and dye concentration [14]. Several operating conditions for RhB removal using modified zeolites and mineral complexes have been investigated, focusing on variables such as temperature and ionic strength [15, 16]. Although phenol red has received little attention, its structural similarity to other phenol dyes suggests that zeolites with the right surface chemistry may be able to adsorb it effectively.

The interaction processes between dyes and zeolite surfaces may include hydrogen bonding, van der Waals forces, ion exchange, and π - π stacking, depending on the nature of both dye and zeolite. Materials engineering progressions have been fulfilled in the preparation of nano-sized zeolites, hybrid composites, and functionalized surfaces that manifest to have selectivity and kinetic properties. These modifications aim to ride the confines of classical adsorbents and support renovation [13]. Zeolites continue to be the subject of much scientific research. This study will address the complex interplay between adsorption kinetics and structural properties of the zeolite materials.

2. Materials and methods

2.1 Materials

Zeolite were purchased from zeolyst, Rhodamine B (RhB), phenol red (PR), and methyl violet (MV) were purchased from Sigma Aldrich.

2.2 Methods

2.2.1 Dealuminated zeolite synthesis

Zeolites were refluxed in 13 M HNO_3 (20 mL/1gram of zeolite) at 100°C for 20 hours. The treated samples were then rinsed extensively with deionized water (500 mL/g zeolite) and dried in oven at 100°C overnight [17].

3. Instrumentation

The dye-adsorption studies were evaluated by a (UV-1800 model) Spectrophotometer in the wavelength ranging from 400 to 800 nm.

3.1 Adsorption experiment

The adsorption of Rhodamine B (RhB), phenolic red (PR), and methyl violet (MV) on zeolite was carried out by the batch method. Initially, 0.1 g of the zeolite was immersed in 60 mL of the dye solution with stirring constantly. The initial concentration of dye was constant at 10 mgL⁻¹. At certain time intervals, the dye solutions were filtered and evaluated using a UV-visible spectrophotometer at $\lambda_{\text{max}} = 558$ nm for (RhB), 432 nm for (PR), and 554 nm (MV). whereas the equilibrium adsorption capacity (q_e) and removal percentage (%) was calculated, Eqs. (1) and (2).

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where C_0 is the initial dye concentration (mg L⁻¹) and C_e is the final concentration (mg L⁻¹), respectively, where V refers to solution volume and m is the weight of the zeolite in grams.

3.2 Adsorption kinetics

The adsorption mechanism of dyes on the zeolites was described by pseudo-first order (PFO), pseudo- second order (PSO) and intra-particle diffusion models (IPD).

The linearized form of the model is stated below:

$$\text{Log}(q_e - q_t) = \text{log } q_e - \frac{K_1 t}{2.303} \quad (3)$$

$$\frac{t}{q_e} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

$$q_t = K_{id} t^{1/2} + C \quad (5)$$

Here, q_t (mg g⁻¹) and q_e (mg g⁻¹) are the adsorption capacity at time and equilibrium, respectively. K_1 and K_2 are the PFO and PSO rate constant which is expressed in min⁻¹ and g mg⁻¹ min⁻¹. Where K_{id} is the intraparticle diffusion constant (mg min^{1/2} g⁻¹) while C is the intercept. The kinetic parameters along with the correlation coefficient, are calculated (**Tables 1–3**).

3.3 Isothermal studies

The equilibrium adsorption explained by Langmuir and Freundlich isotherm model. The non-linearized Langmuir model is expressed as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

Adsorption isotherm model of Phenolic Red (PR)								
Adsorbents	Langmuir					Freundlich		
	$q_{\max}$	K_L	R	S.D	n	K_f	R^2	S.D
<i>Commercial zeolite</i>								
<i>Ferrierite</i>	0.162	0.004	0.825	1.157	-0.438	149.0	0.994	0.077
<i>Dealuminated zeolite</i>								
<i>Ferrierite</i>	0.603	0.081	0.978	0.100	-0.484	96.87	0.987	0.095

Table 1.
Adsorption isotherm models parameters of sorption of (PR) onto zeolite.

where q_e represents the equilibrium adsorption capacity of the adsorbate (mg g^{-1}), where $q_{\max}$ (mg g^{-1}) indicates the maximum monolayer adsorption capacity. K_L represents the Langmuir constant (L mg^{-1}). C_e is the equilibrium concentration of the adsorbate (mg L^{-1}). The linear form of the Langmuir isotherm model is presented in Eq. (7).

$$\frac{C_e}{q_e} = \left(\frac{C_e}{q_m} \right) + \left(\frac{1}{K_L * q_m} \right) \quad (7)$$

The slope and the intercept of the plot of C_e/q_e vs. C_e gives the values of q_m and K_L , respectively. The Langmuir separation factor (R_L) expressed as follows:

$$K_L = \frac{1}{1 + K_L C_0} \quad (8)$$

Feasibility and reversibility of the adsorption process measured by R_L . The linear representation of the Freundlich isotherm is given by:

$$\ln(q_e) = \ln K_f + \frac{1}{n} * \ln(C_e) \quad (9)$$

K_f and n values are Freundlich adsorption isotherm constants are obtained from the linear plot of the Freundlich isotherm.

4. Result and discussions

4.1 Dyes removal performance of commercial and dealuminated zeolite

The sorption behavior of Rhodamine B (RhB), Methyl Violet (MV), and Phenol Red (PR) dyes onto commercial and dealuminated zeolites revealed critical insights into adsorption mechanisms, kinetics, and the impact of zeolite modification. The investigation underscored the interplay between dye-zeolite interactions, structural properties of adsorbents, and operational parameters such as contact time which was investigated at different time intervals from 1 to 120 mints to demonstrate the influence of contact time on the degrading efficiency of the adsorbent while keeping all other parameters constant such as (initial concentration, dosage, RT), one example

Adsorption kinetics Rhodamine B (RhB)											
Adsorbents	Kinetic model										
	PFO			PSO			IPD				
	parameters			parameters			parameters				
	K ₁	q _e	R ²	S.D	K ₂	q _e	R ²	S.D	K _{ad}	C	S.D
<i>H-beta</i>	<i>Commercial zeolite</i>										
	0.020	2.11	0.939	0.002	16.87	6.581	0.963	0.01	0.774	0.332	0.087
<i>Mordenite</i>	<i>Dealuminated zeolite</i>										
	0.020	1.444	0.660	0.006	11.877	2.385	0.975	0.029	0.310	1.972	0.094
<i>H-beta</i>	0.076	3.179	0.881	0.010	76.251	6.088	0.999	0.0009	0.38801	2.281	0.088

Table 2.
Kinetic models parameters for adsorption of RhB onto zeolite.

Adsorption kinetics Methyl Violet (MV)												
Adsorbents	Kinetic model											
	PFO				PSO				IPD			
	parameters				parameters				parameters			
	K ₁	q _e	R ²	S.D	K ₂	q _e	R ²	S.D	K _{id}	C	R ²	S.D
Commercial zeolite												
<i>Ferrierite</i>	0.017	0.920	0.823	0.017	566.47	5.589	0.999	0.0006	0.061	5.096	0.815	0.014
<i>H-Y</i>	0.097	0.576	0.750	0.027	330.8	5.908	0.999	0.0008	0.092	5.063	0.865	0.020
<i>H- beta</i>	0.105	0.422	0.857	0.028	5.9	935.4	0.999	0.0001	0.086	5.248	0.791	0.005
Dealuminated zeolite												
<i>Mordenite</i>	0.055	1.492	0.931	0.006	59.29	6.275	0.991	0.0059	0.308	0.92	0.637	0.080
<i>H-beta</i>	0.300	5.179	0.931	0.010	4.383	3.892	0.846	0.044	0.538	1.826	0.801	0.001

Table 3.
Kinetic models parameters for adsorption of MV onto zeolite.

mentioned is the effect of shaking time on the sorption percentage of H-beta zeolite both commercial and dealuminated form on the RhB, MV, PR solutions (**Figure 1**).

4.2 Effect of shaking time and zeolite structure

The time-dependent adsorption profiles demonstrated that equilibrium was reached within 120 minutes for most zeolite systems, with dealuminated zeolites often exhibiting faster kinetics (**Tables 2–4**). The results demonstrate that the extending contact time further differentiated zeolite performance. The results in this work have been summaries in term investing which catalyst expected to reach the optimum faster.

Initially at 30 mints a comparative analysis of zeolite types for dye adsorption was conducted to reveals critical insights into their efficiency, mechanism, and kinetics, the sorption percentages varied significantly among the zeolites highlighting differences in their structural and surface properties (**Table 5**). For instance, Rhodamine B (RhB), dealuminated H-beta demonstrated superior performance (93.6%) compared to its commercial counterpart (76.6%), likely due to enhanced porosity or active site accessibility (**Table 5**).

Additionally, Methyl Violet (MV) exhibited exceptional removal rates, with commercial H-Y (97.9%) and dealuminated H-beta (99.6%) achieving near-complete adsorption, suggesting strong affinity between MV and these frameworks. This disparity can be attributed to variations in pore size, surface area, and cation exchange capacity, which influence the accessibility of dye molecules to active sites. Larger surface areas and mesoporous structures likely enhanced Zeolite's performance, enabling rapid dye uptake within the short timeframe. However, dealuminated mordenite showed poor MV uptake (49.3%), possibly due to structural constraints or reduced active sites post-dealumination.

At 120 minutes, prolonged contact time further differentiated performance trends, some zeolites reached near-total removal whereas some are not, and this result emphasizes the dye's recalcitrance (**Figure 2**).

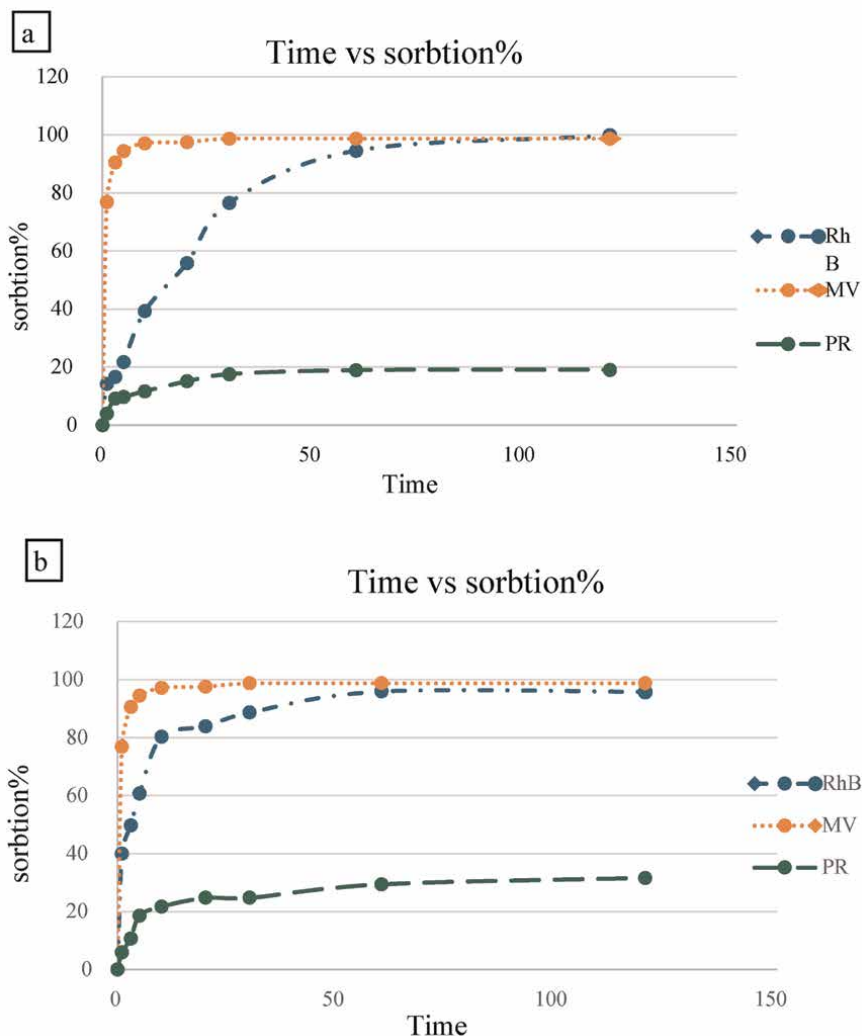


Figure 1. Effect of shaking time on the sorption percentage of a. H-beta b. dealuminated H-beta on the RhB, MV, PR solutions.

In term of Phenol Red (PR) this dye display consistently low sorption across zeolites, with minor improvements in dealuminated ferrierite (43.6%) compared to its commercial form (36.6%), indicating limited interaction between PR and the tested zeolites. These results underscore the critical role of zeolite-dye compatibility and the selective benefits of dealumination in optimizing adsorption. Although, it was observed from the phenol red dye UV spectrum analysis formation of peak while decrease in peak in the degradation at the same time, accompanied by a color shift from orange to red upon reaction with H-Y, this likely results from protonation-induced structural changes in the dye. As the Phenol red known as sulfonephthalein pH indicator, which may undergo protonation at its phenol oxygen when interacting with H-Y's protons, it might shift its equilibrium from the deprotonated quinoid form (longer-wavelength absorption, red) to a protonated benzenoid-like structure. It is also suggested that the H-Y stabilizes a resonance enhanced intermediate possibly a

Adsorption kinetics Phenolic Red (PR)												
Adsorbents	Kinetic model											
	PFO				PSO				IPD			
	parameters				parameters				parameters			
	K	qe	R ²	S.D	K ₂	qe	R ²	S.D	K _{id}	C	R ²	S.D
Commercial zeolite												
<i>Ferrierite</i>	0.094	0.599	0.914	0.007	3.510	2.270	0.999	0.0006	0.141	1.003	0.815	0.014
Dealuminated zeolite												
<i>Ferrierite</i>	0.077	2.688	0.839	0.006	5.051	2.274	0.998	0.006	0.037	0.113	0.801	0.001

Table 4.
Kinetic models parameters for adsorption of PR onto zeolite.

Zeolite type	Sorbent	Dye type	Sorption (%)
Commercial	H-beta	Rhodamine B	76.6
Dealuminated	H-beta	Rhodamine B	93.6
Commercial	H-Y	Methyl Violet	97.9
Dealuminated	Mordenite	Methyl Violet	49.2
Dealuminated	H-beta	Methyl Violet	99.6
Commercial	Ferrierite	Phenolic Red	36.6
Dealuminated	Ferrierite	Phenolic Red	38.0

Table 5.
Various of zeolites which has significant sorption%.

tautomer or charge-transfer complex that retains or extends conjugation from the unexpected red coloration, leading to a new absorption peak in the visible region (500–600 nm) (**Figure 3**). It is likely that the decreasing degradation peak reflects the successful dye's consumption, while the formation of the peak at the region 500–600 nm corresponds to the emergence of this protonated product with altered electronic properties, aligning with the observed spectral and color changes.

4.3 Adsorption isotherms: Langmuir vs. Freundlich

The relationship between initial dye concentration and adsorption capacity demonstrated that increasing concentration generally improved uptake until saturation occurred. The adsorption data fitted with both Langmuir and Freundlich isotherm models, though the Langmuir model showed marginally better correlation (higher R² values) for most zeolites. (**Tables 1, 6 and 7**), the result implies monolayer adsorption on homogeneous surfaces, where active sites are uniformly distributed. However, some zeolites show negative fit to the Freundlich model suggests some heterogeneity in its surface which may be due to defects or mixed-phase compositions. So, the monolayer coverage makes the Langmuir dominance aligns with the high sorption

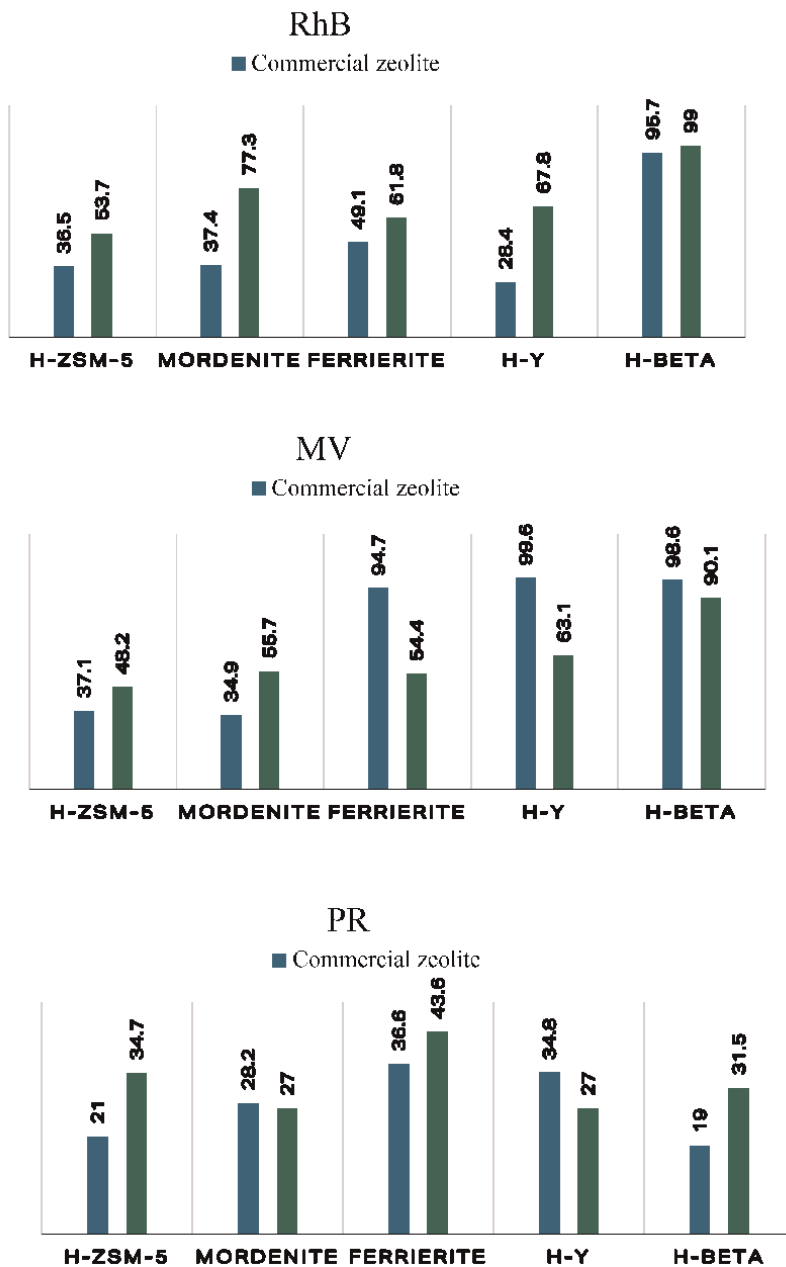


Figure 2.
summary of sorption% of dyes onto all tested zeolite types.

percentages in short durations which maximizes dye removal. Whereas moderate K_d values (e.g., 8.84 for dealuminated H-beta/Rhodamine B) suggest multilayer adsorption.

Dealumination generally improved kinetic rates, but it might be not for enhancing adsorption capacity. For example, the Phenol red dye, dealuminated ferrierite achieved a $q_e = 2.67$ mg/g, marginally higher than its commercial counterpart ($q_e = 2.27$ mg/g),

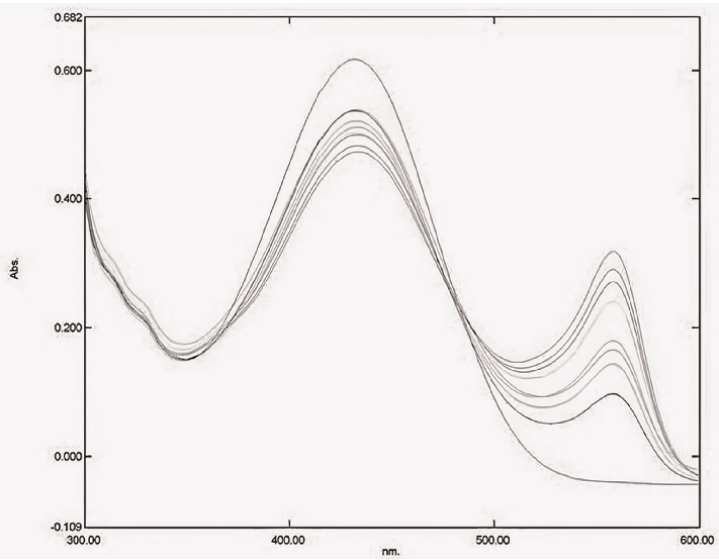


Figure 3.
UV spectrum for H-Y in PR.

Adsorption isotherm model of Rhodamine B (RhB)								
Adsorbents	Langmuir				Freundlich			
	$q_{\max}$	K_L	R^2	S.D	n	K_f	R^2	S.D
Commercial zeolite								
H-beta	1.038	0.624	0.836	0.122	-1.254	7.369	0.878	0.132
Dealuminated zeolite								
Mordenite	1.788	1.797	0.940	0.057	-1.484	8.710	0.914	0.084
H-beta	2.252	8.846	0.925	0.0513	-1.760	6.941	0.908	0.104

Table 6.
Adsorption isotherm models parameters of sorption of (RhB) onto zeolite.

Adsorption isotherm model of Methyl violet (MV)								
Adsorbents	Langmuir				Freundlich			
	$q_{\max}$	K_L	R^2	S.D	n	K_f	R^2	S.D
Commercial zeolite								
Ferrierite	4.674	2.170	0.998	0.003	-8.697	5.355	0.952	0.010
H-Y	4.951	5.907	0.997	0.004	-6.710	5.398	0.993	0.006
H-beta	4.572	1.360	0.996	0.005	-1.560	5.199	0.830	0.013
Dealuminated zeolite								
H-beta	3.048	6.671	0.974	0.023	-8.489	4.403	0.704	0.038
Mordenite	0.770	0.160	0.952	0.129	-0.630	37.797	0.968	0.140

Table 7.
Adsorption isotherm models parameters of sorption of (MV) onto zeolite.

which may due like to increased mesoporosity in the structure. However, commercial zeolites outperformed dealuminated ones in some cases (e.g., RhB on H-beta), indicating that dye molecular size and zeolite pore architecture must align. Corroborated these trends, with dealuminated zeolites showing superior distribution coefficients (K_d) for MV and PR, indicative of stronger affinities (**Tables 1, 6 and 7**).

Looking at the adsorption isotherms (Langmuir and Freundlich), the data indicates which model fits better for each dye-zeolite combination. The Langmuir model suggests monolayer adsorption, whereas Freundlich indicates multilayer adsorption on heterogeneous surfaces. For example, RhB onto H-beta shows a good fit with Langmuir, implying a homogeneous surface. However, the Freundlich model for dealuminated Mordenite might suggest surface heterogeneity after dealumination. The fitted parameter along with the correlation coefficient (R^2) is exhibited. A good agreement of the experimental adsorption capacity is noted for both models (**Tables 1, 6 and 7**). As, the Langmuir model provided the best fit for RhB adsorption onto H-beta ($R^2 = 0.999$), indicating monolayer adsorption on homogeneous surfaces. This shift underscores how dealumination introduces surface heterogeneity. However, commercial H-beta unexpectedly exhibited a higher equilibrium adsorption capacity ($q_e = 6.58 \text{ mg/g}$) compared to dealuminated H-beta ($q_e = 6.09 \text{ mg/g}$), implying that dealumination may alter pore geometry in ways that hinder adsorption for certain dyes. Therefore, the result indicates that both multilayer and monolayer adsorption were involved in the adsorption capacity process.

4.4 Kinetic models and mechanisms

The kinetic models (PFO, PSO, IPD) provide insights into the adsorption mechanism. The PSO model having higher R^2 values for most cases implies chemisorption is the rate-limiting step. However, some adsorbents like commercial H-Y for MV show exceptionally high K_2 values, which might indicate rapid adsorption. The possible reasons for these variations are differences in zeolite pore size, surface charge, or interaction with dye molecules. (**Table 2–4**), presents the effect of contact time on (a) PFO (b) PSO (c) IPD models (concentration of dye solution 10 ppm, contact time 120 mins, temperature 25°C).

The rate constant is a critical parameter in adsorption kinetics as it quantifies the speed of the adsorption process. From the Rhodamine B (RhB) Adsorption, the PFO of commercial (H-beta) $K_1 = 0.020 \text{ min}^{-1}$ suggests slow adsorption (**Figure 4**), typical for physisorption or weak interactions. However, the PSO presents high 16.872 g/mg. min indicates rapid chemisorption which may cause by strong electrostatic or covalent bonding. Moreover, Ferrierite (MV) shows a moderate fit ($R^2 = 0.824$) with $K_1 = 0.018 \text{ min}^{-1}$, indicating a slow approach to equilibrium. While, H-Y (MV) has a higher $K_1 = 0.098 \text{ min}^{-1}$ compared to Ferrierite, implying faster initial adsorption. Mordenite (RhB) has $R^2 = 0.660$, indicating a poor fit it may be due to chemisorption dominates. IPD resulted moderate diffusion rate, suggesting pore penetration is not the rate-limiting step. Also, dealuminated H-beta $K_1 = 0.076 \text{ min}^{-1}$ increases extremely high, indicating ultra-fast chemisorption (**Tables 5, 6, and 7**).

The PSO model ($R^2 > 0.99$) deduced across most systems implies chemisorption as the rate-limiting step, driven by electrostatic or covalent interactions between dye molecules and zeolite active sites. The adsorption of MV onto ferrierite showed a very high R^2 value (greater than 0.99), probably because the positively charged dye fits

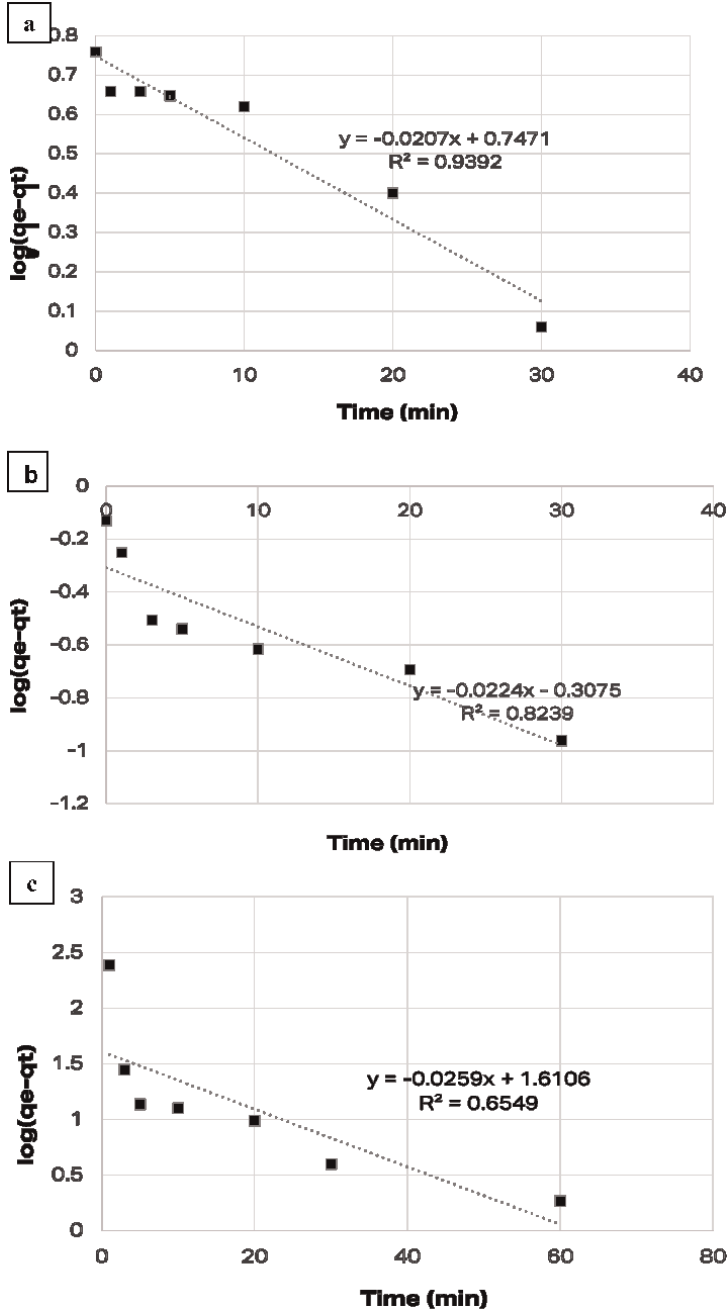


Figure 4.
Pseudo-First Order (PFO) a. Commercial H-beta (RhB) b. Commercial Ferrierite (MV) c. Commercial Mordenite (RhB) removal.

well with the negatively charged structure of the zeolite. For example, the commercial H-beta zeolite achieved RhB removal with a pseudo-second order (PSO) rate constant, while its dealuminated counterpart showed a significantly higher rate constant (Figure 5); this observation indicates that active site accessibility is enhanced after

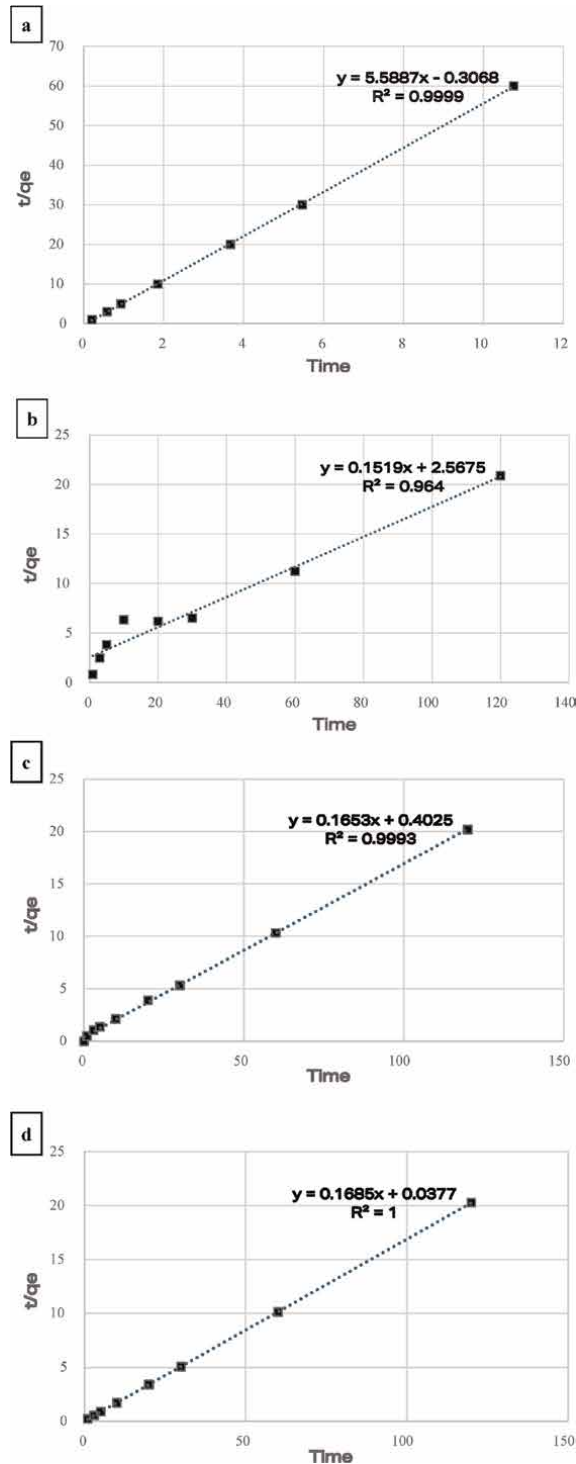


Figure 5. Pseudo-second order (PSO) kinetics for: (a) commercial ferrierite zeolite in the removal of methylene violet (MV); (b) commercial H-beta zeolite in the removal of rhodamine B (RhB); (c) dealuminated H-beta zeolite in the removal of RhB; (d) commercial H-beta zeolite in the removal of MV.

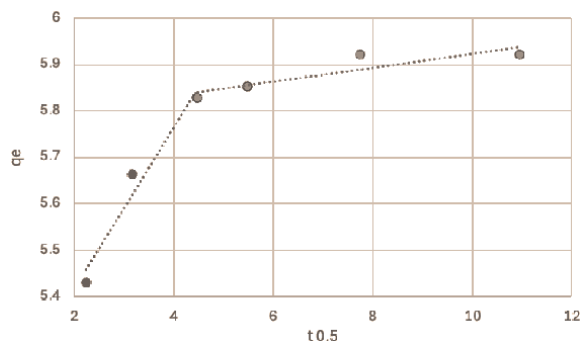


Figure 6.
 The Intra-particle diffusion (IPD) shows multi-stage adsorption processes.

dealumination. This modification may cause increased surface area or pore volume, facilitating dye diffusion.

The Pseudo-Second Order (PSO) model consistently provides the best fit across all dyes and adsorbents, with R^2 values often exceeding 0.99 and low S.D. This suggests that the adsorption kinetics are likely governed by chemisorption **Figure 6**. In addition, Pseudo-First Order (PFO) and Intraparticle Diffusion (IPD) models show variable fits, with some cases (e.g., Mordenite for RhB) having poor R^2 values (**Table 1**). This indicates that these models may not fully capture the adsorption mechanisms for certain adsorbents.

The Intra-particle diffusion (IPD) plots further revealed multi-stage adsorption processes (**Figure 6**), first Stage corresponds to the rapid adsorption of adsorbate molecules onto the external surface or macropores of the zeolite, whereas the second Stage reflects slower diffusion of adsorbate molecules into the micropores or internal sites of the zeolite were initial surface adsorption transitions to slower pore diffusion. The boundary layer parameter C (e.g., $C = 5.25$ for H-beta-MV) indicated a resistance, highlighting the impact of structural density in commercial zeolites, potentially due to their denser structures.

5. Conclusions

The study explores zeolite-dye interactions, focusing on optimizing adsorbent design for wastewater treatment. Top performers include H-beta, H-Y, Mordenite, and Ferrierite, which are effective, tunable adsorbents for targeted dye removal. The kinetic results showed that the PSO is more fitted than other model with maximum adsorption capacity (18.2 mg/g). The zeolite catalyst performance, governed by chemisorption and structural adaptability, positions them as promising candidates for scalable wastewater treatment solutions. The study suggests further refinement of dealumination protocols and investigation of pH, temperature, and regeneration potential to enhance real-world applicability.

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