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INDUSTRIAL DYES FOR POLYMER MATERIALS: A REVIEW

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ABSTRACT

Dyeing is a process by which we fix the colour on textile, paper, leather etc. Dyes are primarily chemical compounds that connect themselves to fabrics or surfaces to pass on the colour. Demand for dyes is increased rapidly due to the growth in market size. Nowadays, dye-containing polymer are used in medicine, the gas separation process, etc., on the basis of their application and on the basis of source of material it is divided into major two components Natural dye and Synthetic dyes. The most challenging issue for the company's manufacturing dyes is the pollution caused by the dyes and their harmful effect on the environmental water. The pollution caused by the dyes in water reduces sunlight penetration due to which photosynthetic process is destroyed that becomes a threat to aquatic life. Till date, the annual production of more than 100,000 commercial dyes is 7×10^5tonnes/year. The treatment of wastewater can be done by the chemical method, physical method and biological method. Dye-bearing waste treatment by adsorption using low- cost alternative adsorbent is a demanding area as it has double benefits i.e. water treatment and waste management. Further, activated carbon from biomass has the advantage of offering an effective, low-cost replacement for non-renewable coal-based granular activated carbon, provided that they have similar or better adsorption efficiency.

Keywords : Low-Cost Adsorbents, Pigments, Dye-Containing Polymers .

1. INTRODUCTION

People have been drawn to the concept of colouring things and emphasizing their intrinsic qualities in textiles since the beginning of time. The molecules that make up natural and manmade dyes are particularly interesting because they are crucial to our daily lives[1]. There has been a

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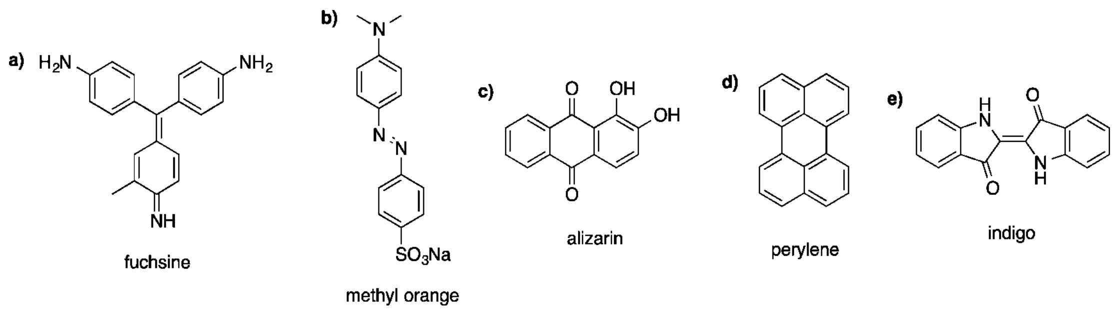
lot of research in this area due to the wide range of industrial and technical applications, including "traditional" ones such as dyeing textiles and other consumer items, as well as more contemporary ones like laser dyes and dyes for organic light-emitting diodes (OLEDs) and liquid crystal (LC) displays[2]. Lowered production costs and decreased toxicity are also prioritized along with ecologically sustainable practices.

The primary motivator is the ongoing need for increased colouring effectiveness. Along with focusing on environmentally sustainable practices, lowered production costs, and lower toxicity. The combination of dyes and polymeric materials is a potential strategy for achieving these goals, and it will be addressed in this book chapter. They are quite complex due to the wide range of dyes and chemicals utilized in an effort to produce more acceptable common colours of fabrics for a tough market[3]. During the last decade, environmental issues associated with dyestuff production and application have grown significantly. The great advantage of such systems is the controllability of many features, such as toxicity, stability, and solubility, through the appropriate choice of polymeric material. Azo, triphenylmethane, anthraquinone, indigoid, and perylene are among the several dye types that are widely used and intriguing representations. These compounds are the major subject of this study since they have a wide range of uses[4].



Triphenylmethane dyes have their importance to their cheapness and brilliance of colour with typical shades of red, violet, blue, and green. The major application of these stains is their use in the textile industry for dyeing nylon, wool, silk, cotton, *etc.*, in the paper, leather, food and cosmetics industries. Their high dyeing efficiency and the low light fastness are considered the major benefits of these stains[5]. The underlying structures of triphenylmethane dyes are the colourless compounds triphenylmethane and triphenylcarbinol, another important application of some triphenylmethane dyes is that they are used as indicator dyes due to their pH sensitivity, which is derived from their constitution. Some important examples of this class of dyes are phenolphthalein, fuchsine, and fluorescein.

The azo dyes are aromatic compounds which have one or more -N=N- groups. Synthetic dyes made from these aromatic compounds is used in several economic sectors. These artificially coloured compounds are employed in several industries, including the food, textile, paper, and leather sectors, as well as other sectors as additives in various goods. Azo dyes are widely used in the food business because they give processed meals a noticeable look and make them appealing to consumers[6]. Perylene or perilene is a polycyclic aromatic hydrocarbon with the chemical formula $C_{20}H_{12}$, occurring as a brown solid. Its derivatives may be carcinogenic, and it is considered to be a hazardous pollutant. In cell membrane cytochemistry, perylene is used as a fluorescent lipid probe[7]. Due to their excellent physical and chemical properties, these compounds are widely used as laser markers, sensitizers in photovoltaic devices, and fluorescent labels which also offer a large number of applications.

Stains belonging to the class of anthraquinone based dyes are prepared via introduction of various substituents to anthraquinone, which is readily available via oxidation of anthracene. Due to their high color fastness and stability, anthraquinone dyes are important compounds in printing processes and textile dyeing[8]. An interesting aspect is their potential use in cross-dyeing processes since they exhibit a high affinity to silk and wool while leaving cellulose fibers unaffected. Furthermore, the electronic properties of these dyes make them valuable candidates for photosensitizers and solar energy storage devices.

For almost 5000 years, indigo has been utilised as a vat dye in the textile industry, making it one of the oldest natural dyes[9]. These days, it is preferred to use the precursor indoxyl, which is produced when formaldehyde, aniline, and sodium cyanide combine. Two keto functionalities and a double bond in the α-position make up the indigoid chromophore. The molecules' general planarity makes them poorly soluble in water and the majority of organic solvents. The most crucial Tyran Indigo carmine and purple indigo derivatives are utilised as food colouring agents, colouring agents, and anti-cancer medications.

This chapter discusses the properties of dyeing in a general manner. The classification of dyes, preparation techniques, methods. The following chapters will present considerably more detailed discussion regarding industrial dyeing with reference to principles.

2. CLASSIFICATION

Ionic bonds are also formed by the dyes for these substrates inside the polymer matrix. Since polymers like poly (acrylonitrile) have a negative (anionic) charge in their structure, the ionic character of the interacting substances is opposite. Thus, positive (cationic) charged dyes are utilized in this situation. Due to the inability of cellulosic, polyester, or polyamide polymers to form an ionic connection with them, these dyes have no affinity for these materials. The first synthetic dye, Mauveine was a basic dye that was used to colour silk, although cationic dyes may also be used to colour protein fibres.

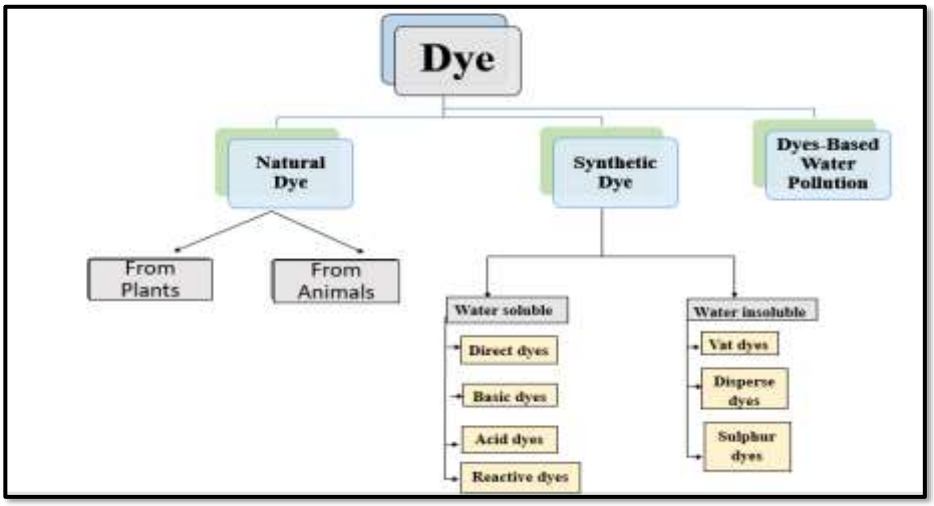


Fig.1. Classification of Dye

2.1 Natural Dyes

Natural dyes are pigments that come from minerals, invertebrates, or plants. Vegetable dyes derived from plants, including roots, berries, bark, leaves, and wood, as well as other biological sources like fungus, make up the bulk of all natural colours. For e.g. Alizarine (obtained from Madder plant), Blue dye (Indigo), Red dye or Carmine red (Carmic acid) obtained from coccus cacti, cochineal (obtained from Insect).To extract the dye components into solution with the water, the dye material is heated in a pot of water. The dye-able materials are then added to the pot and heated until the desired colour is obtained. Before spinning or weaving ("dyed in the wool"), after spinning ("yarn-dyed"), or after weaving ("piece-dyed"), textile fibre can be coloured[10].

2.1.1 From Plants

There are four sources from which natural dyes are available, specialized plant and animal sources. Many plants and some animals have been identified as potentially rich in natural dye contents, and some of them have been used for natural dyeing. Normally natural dyes are extracted from the roots, stems, leaves, flowers, fruits of various plants, dried bodies of certain insects and minerals.

2.1.2 From Vegetables

Some 200 years ago, the industrial fur dyeing industry was founded using vegetable dyes made from extracts of logwood, redwood, and fustic. Salts of iron, chromium, or copper are used for mordanting. To guarantee adequate oxidation and lack, the dyeing procedure is repeated multiple times, and in between applications, the fur skins are hung out in a humid environment. Nowadays, it is rare to employ vegetable dyes. Iron or copper salts, for example, may occasionally be used to lighten natural hair.

2.2 Synthetic Dyes

Petrochemical compounds, which are marketed as liquids, powders, pastes, or

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granules, are the source of most synthetic colors[11]. A range of colour pigments and tints, ease of manipulation, resilience against many external variables, cost-effective energy use, and rapid and uniform colouring with the different fabric classes mentioned in the preceding section are only a few of their potentials[12]. Therefore, when untreated or partially treated synthetic materials are released into the environment, most Colours have detrimental impacts[13]. Up to 15% of applied colours may escape from the textile fibres and end up in wastewater due to the high water consumption of the dyeing, fixing, washing, and other processes involved in textile dyeing.

2.2.1 Water Soluble

One of the top producers and suppliers of water-based dyes worldwide is Colour (or water-soluble dyes). There are many different types of water-soluble dyes and colourants, some of which are described below with details on their functions and features.

1. Basic Dyes

Basic colours, often known as "cationic dyes" are natural water soluble. These classes of dyes are distinguished by their vivid hues. It is mostly used on acrylic, wool, silk, and polyester fibres.

2. Acid Dyes

Acid dyes are the only option when it comes to dying wool and other animal fibres. They are frequently used on nylon when a high level of wash fastness is required.

3. Direct dyes

Moreover, they are known as "substantive dyes". Majority of them are azo compounds with sulphonic acid and sodium salts. These are soluble anionic chemicals under water, and its main application is for colouring cotton.

4. Reactive Dyes

The dyes in this class are the most commonly employed on cellulosic (cotton) for the same purpose and are the largest ones when it comes to producing the necessary brilliant colours. Reactive dyes are also excellent for use with nylon, wool, and silk.

2.2.2 Water Insoluble Dyes

Water-insoluble dyes are applied in a reduced soluble state, and after being absorbed into the fibre, they reoxidize to their original insoluble form.

1. Disperse Dyes

Disperse dyes are mostly used to colour polyester since they have the feature of being insoluble in water. One of the less common uses is dyeing synthetic fibres like polyamides and cellulose acetate[14].

1. Sulphur Dyes

Sulfur Dyes Cotton is typically dyed with Sulphur to provide cost-effective dark hues. They are quite resistant and work well for washing but struggle in the sun. They often offer extremely low chlorine fastness.

2.3 Dyes-Based Water Pollution

Because synthetic dyes have such a wide range of uses in the textile, paper, leather, paint, cosmetics, pharmaceutical, and food sectors, there is a constant need for them among the world's expanding population. Up to 10,000 different dyes are used globally, and their combined output each year is around 7×10^5 metric tons. Textile sector contributes more than any other industry to the environmental release of dye effluents[15].

One of the main environmental hazards is wastewater discharge from dye production plants. Dyeing alters the colour of water, which prevents photosynthesis by reducing light penetration and disrupting the aquatic life forms' primary food source[16].

3. PREPARATION TECHNIQUES

Covalent or non-covalent binding mechanisms can result in the creation of dye-polymer conjugates. Non-covalent binding can happen through a variety of interactions, including ionic and dipole-dipole interactions as well as through the formation of inclusion complexes.

3.1 Non-Covalent Attachment

Non-covalent attachment describes how molecules associate through weaker forces—such as hydrogen bonds, van der Waals attractions, electrostatic interactions, and hydrophobic effects—rather than by forming true covalent bonds. Because these interactions are reversible and generally gentle, non-covalent strategies enhance biocompatibility, allow for straightforward surface functionalization.

3.1.1 Sugar-Based Polymers

Sugar-based (macro)molecules are ideal materials for the supramolecular attachment of dyes due to the abundance of polar substituents that allow the formation of dipolar interactions with suitable substrates. Such oligo-/polysaccharides can be obtained from natural products (e.g., starch, cellulose, chitosan) or from chemical linkage of monomeric subunits.

In the primary studies, the polymers were done by the cross-linking of β-cyclodextrin and starch respectively, with hexamethylene diisocyanate[17-18]. For both types of polymers, the major effects resulting in adsorption of the dyes were found to be hydrogen bonds formed between hydroxyl and amine groups located at polymers and the sulfonate moieties of the azo dyes.

3.1.2 Synthetic Polymers

Several other polymers were discovered to adsorb dye molecules through ionic or dipole-dipole interactions in addition to the sugar-based compounds[19]. Fiber-like polymeric materials were formed from the combination of a positively charged perylenediimide derivative and a negatively charged copper-phthalocyanide derivative. Both compounds are stacked into helices to form polymeric structures, which are then stabilized by a mix of coulomb coupling and charge transfer interactions. Another system that also involves electrostatic interactions consists of poly (acrylic acid-co-acylamide) hydrogels and the cationic dye methyl violet[20]. Adsorption of the dyes to the polymer was found to occur via hydrogen bonding or dipole–dipole interactions. However, it was observed that the diffusion process is hindered by comparatively strong dye-dye interactions. This issue was resolved by utilizing a dye combination.

3.1.3 Covalent Attachment

The research contains numerous synthesis methods that enable the covalent implantation of dye molecules in polymeric materials. These typically fall into the following categories of approaches:

1. Polymerization of coloured monomers.
2. Polycondensation or (cross)coupling reactions of adequate dyes/dye derivatives.

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3. Polymer-analogous attachment of dye molecules to preformed polymers.
4. Preparation of high molecular weight derivatives of single chromophores.

An overview of the different polymerization techniques and the accessible materials will be given in the following paragraphs.

3.2 Polymerization of Colored Monomers

A useful method for creating dye-containing polymers is to transform dye molecules into polymerizable compounds and then (co) polymerize those derivatives.

There are several known cases of azo dyes being transformed into radically polymerizable compounds. Acrylated azo dyes for materials used in non-linear optics are an interesting case. The preparation of a methacrylate-based azo dye monomer within three reaction steps was addressed in another survey[21]. Tyramine was methacrylated in the first stage by being exposed to methacrylic anhydride. The resultant substance was next combined with methacrylated tyramine. The resulting azo pigment monomer was copolymerized with N, and N-dimethylacrylamide and added to polymers. The copolymer's complexation behaviour in the presence of copper ions was also investigated. Polymerizable triphenylmethane dyes is the polymerizable phenolphthalein derivative which was obtained through the reaction of phenolphthalein with *N*- (hydroxymethyl) acrylamide[22-23].

3.2.1 Polycondensation and (Cross) Coupling Reactions of Adequate Dye Derivatives Multiple studies have shown the enormous potential of polycondensation. For instance, sebacoyl chloride was used in interfacial polycondensation processes with a number of azo dyes and an anthraquinone dye[24]. Comparing the UV-Vis spectra of the polymers to those of their low-molecular-weight equivalents, it was discovered that the maxima shifted when the solvent systems changed. The coupling of dihalogenated derivatives with appropriate comonomers, which produces copolymers, is another popular method of adding perylene colours to polymeric materials. A range of these copolymers were shown, where the perylene moieties were either end limit units at the end of the polymer chain or any of the polymer backbone or pendant side groups[25].

3.2.2 Polymer-Analogous Attachment of Dye Molecules to Preformed Polymers

The existence of functional side groups bound to the polymeric backbone that can easily react with functional groups of small molecules is required for the polymer-analogous attachment of dyes. This attachment can cause noticeable alterations to the chromophoric system, depending on the dye's molecular structure and type of reactive side group.

4. APPLICATIONS

A growing number of technical and medical uses for synthetic dyes, particularly those involving polymer linked dyes, are being pursued due to their adaptable qualities and rising environmental awareness. In comparison to low-molecular compounds, enhanced quality characteristics like high colour fastness in textile dyeing appear to be as advantageous as reduced toxicity or the potential for greater recovery and reusability. Therefore, colour impression in paintings or cloth dyeing are not the only common use

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for dye-containing polymers.

4.1. Waste Water Treatment

In addition to being used in the manufacturing sectors, dyes are also essential in the paper making process, plastics, cosmetics, medicine, and biology. Furthermore, the gradually rising frequency of dye pollutants, which cause undesirable colour contaminations and occasionally have harmful impacts on both people and animals, is also having an increasingly negative impact on the environment. Polymers are utilized in a variety of wastewater treatment procedures that involve dye contaminants. Dye-containing polymers can be utilized for the detection of metal contaminants in wastewater from factories because of the dyes' reactivity to plastics and a variety of low-molecular-weight molecules, or indeed inorganic compounds. Lead is being used more frequently in industry, which results in high levels of wastewater pollution and harmful effects on people. Early research demonstrated the remarkable leading ion selectivity of some anthraquinone equivalents[26-27].

4.1. Paintings and Textiles

For hundreds of years, paint and fabric colouring have been the most well-known uses of dyes. The majority of dyeing techniques are only capable of attaching non-covalently to textile fibres like nylon, wool, silk, and cotton[28,23]. Applications for usage as a batch colour or pigments are restricted due to their poor mobility for most media. In today's world, indigo continues to be utilized to make blue jeans, but as indigo derivatives are only available in blue tones, they have progressively taken indigo's position. Triphenylmethane and azo dyes both tend to exhibit good attachment to textile fibres. Both natural cotton and silk along with synthetic fabrics like nylon may be coloured successfully.

4.2. Medicine

Due to their physicochemical characteristics and visual impact, dyes are crucial in

medical applications. It is crucial to choose non-toxic derivatives because this frequently includes administrations inside the human body. Rheumatoid arthritis treatment might be in vivo medical use for polymer-attached dyes. Synthetic eye transplants, which are intended to cure iris deficiencies by enhancing vision and lowering glare, are a great example of polymers in medicine that are very application-oriented. The use of polymer-attached dyes that can be polymerized, bridged, and then sharpened to the desired iris shape is therefore necessary.

4.3. Photochemistry

As many of them show nonlinear optical properties, and liquid crystallinity, including birefringence, azo dyes are among the most significant dye groups inside the planet[29]. Their capacity to transform from the less unstable trans-configuration to the much more durable cis-configuration upon exposure to UV or visible light adds to these qualities. As a result, they have several uses in photochemistry, including visual storage systems[30- 32].

4.4. Optical Sensors

Polymer-attached dyes have a variety of different uses, such as electrochemistry or scientific analysis, in addition to being used in pharmaceuticals, artwork, wastewater treatment, and photochemistry. Polymer-attached phenolphthalein is an illustration of polymer-attached dyes, which refer to the optical properties of the dye and may be employed as pH-sensitive material for analytical reasons. Chromogenic materials, such as mechanochromic, photochromic, and thermochromic have just recently emerged as a new category of dye-containing polymers in the late 1990s.

4.5. Electrochemical and Optoelectronic Applications

Polymer chemistry is currently having an increasing impact on electrochemistry. Due to their solubility in organic solvents and poor sustainable development, many ionic compounds with excellent capacity and cyclabilities fall in price[33]. It can therefore be utilized as a modified electrode for a biosensor, electrocatalyst, or electrochemically controlled release device[34]. Organic light-emitting diodes which may be utilized as a filled, rising and low-drive voltage material for flat-panel screens, are a relatively recent area of study in polymers mixed with dyes[35]. These polymers must be homogeneous, silky, and flexible sheets lacking tiny holes as well as thermally stable and incapable of crystallizing[36-38]. For instance, polymer-attached dyes have several benefits over inorganic LEDs, including low manufacturing costs, superior ease of processing, and strong electronic and chemical safety.

CONCLUSIONS

Electrochemistry, organic light-emitting diodes, waste water treatment, and therapeutic applications like ocular implants or in vivo testing are just a few of the many fields that employ covalent or supramolecular polymer-attached dyes. Even though dye-containing polymers already offer a sizable field of compounds for modern applications, there is always a need for more research and development, particularly to maximize advancements in sustainability, technology, and environmental awareness. Furthermore, as polymeric compounds are more affordable and environmentally benign while exhibiting better qualities, technological problems like organic light-emitting diodes are an important area for additional research. Azo dyes currently account for the greatest volume of dye chemistry production, and their relative significance might potentially rise in the future. Azo dyes are frequently utilized in a wide range of industries, including the food, pharmaceutical, paper, cosmetics, textile, and leather sectors. Deeply coloured azo dyes are produced when diazonium ions combine with aromatic amines, phenols, or naphthols in a process known as azo coupling.

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