

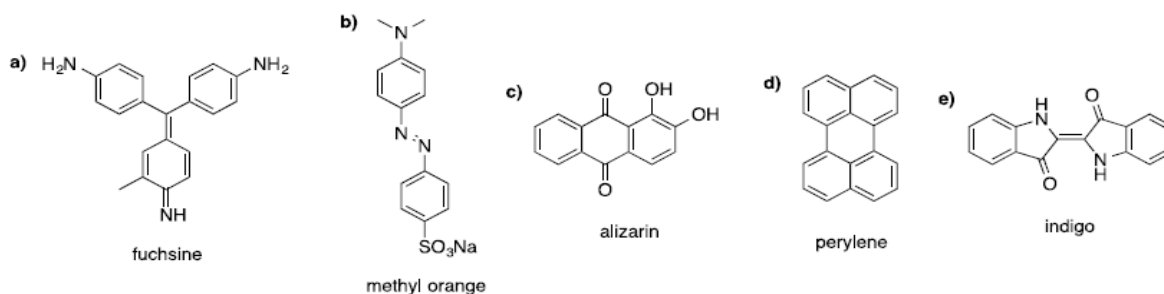
# Chapter One

## 1. 1 Introduction

Hair dyes are perhaps among the most commonly used cosmetics by elderly and the young alike - for concealing gray hair by the former or just for a fashion statement by the latter. The popularity of hair coloring can be gauged from the fact that the median age for debut was 16 years and nearly 75% of women and 18% of men had dyed their hair at some point in their lives according to a Danish population-based study [1] This rising trend of hair coloring has resulted in an increased prevalence of hair dye-associated adverse effects accounting for 5.3% of Danish persons who dyed their hair.[1] Similarly, 42% of the respondents reported adverse reactions from use of hair dyes and the mean age of hair dye debut was 27 years in an Indian study.[2] Hair dyes include a variety of coloring agents such as 2,7-naphthalenediol, 2-amino-4-methyl-*p*-aminophenol hydrochloride, 2-chloro-*p*-phenylenediamine, *N*-phenyl-*p*-phenylene diamine and *o*-aminophenol, *p*-aminophenol Although all these agents can cause allergic contact reactions, *p*-phenylene diamine (PPD) remains the most commonly implicated agent for the contact sensitivity. It is an aryl amine derivative first described by Hoffmann in 1863. It is an effective compound for hair dyes due to its low molecular weight, high protein-binding capacity, and ability to penetrate the hair shaft. Apart from being a common constituent in varying concentrations of nearly 70% of the hair colorants available worldwide, it is also present in dyes for henna tattoos, textiles, leather and fur, and black rubbers. Being a member of 1,4-substituted benzenes, it cross-reacts with para-amino benzoic acid (PABA), sulphonamides, para-amino salicylic acid, ester anesthetics, thiazides, sesquiterpene-lactone mix, and azo dyes, It is a potent contact sensitizer even in low concentration and considered a best indicator and useful patch test screening allergen for hair dye dermatitis. The reported prevalence of positive patch test reactions to PPD among<sup>1</sup>.

## 1.2 The definition of dyes

Natural and synthetic dyes are compounds of great interest since they play an important role in our everyday life. The broad variety of technical and industrial applications, which includes “classical” utilizations like dyeing of textiles and other consumer goods as well as rather new usages such as laser dyes and dyes for organic light emitting diodes (OLEDs), liquid crystal (LC) displays, optical data storage and fluorescent labeling, has produced a great deal of research in this field. The main driving force is the constant demand for improved dyeing efficiency or photochemical/photophysical properties while also focusing on eco-friendly procedure, reduced toxicity, and decreased production costs. A promising approach to fulfilling these requirements is the combination of dyes and polymeric materials. The great advantage of such systems is the controllability of many features like solubility, stability, and toxicity through appropriate choice of polymeric material. Widely applied and interesting representatives amongst the large number of dye categories are tri phenyl methane, azo, anthraquinone, perylene, and indigoid dyes (see Figure 1). Due to the fact that these compounds cover a large spectrum of applications, they are the main focus of the article<sup>2</sup>.



*Fig(1) Characteristic representatives of (a) triphenylmethane dyes, (b) azo dyes, (c) anthraquinone dyes, (d) perylene dyes, and (e) indigoid dyes.*

The major application of these stains is their use in the textile industry for dyeing nylon, wool, silk, cotton, etc., in the paper and leather industries, and in the food and cosmetics industries. Their high dyeing efficiency and the low light fastness are considered the major benefits of these stains. Their high dyeing efficiency and the low light fastness are considered the major benefits of these stains. The underlying structures of tri phenyl methane dyes are the colorless compounds tri phenyl methane and triphenylcarbinol, whose conversion into dyes is achieved

through the introduction of amino- or hydroxyl-groups stabilizing the cationic charge that serves as the chromophore. Depending on the resulting substitution pattern, mono amino-, di amino-, tri amino-, and hydroxyl-tri phenyl methane dyes are differentiated. Another valuable class of dyes is represented by perylenes, belonging to the group of olig (peri) naphthalene (rylene) chromophores. Due to their excellent physical and chemical properties, these compounds are widely used as laser markers, sensitizers in photovoltaic devices, and fluorescent labels . The basic chromophores of these stains are perylene and the photochemically more stable perylenetetracarboxdiimide. Since the latter derivative is of outstanding value for single molecule spectroscopy, it serves as a key structure for a variety of chromophores. Extension of the perylene motif with additional naphthalene units leads to larger chromophores such as terrylene and quaterrylene, 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. Additionally, the rare mineral hoelite is known to be a natural source of anthraquinone. Due to their high color fastness and stability, anthraquinone dyes are important compounds in printing processes and textile dyeing<sup>1</sup>.

Natural dyes are derived from natural resources and based upon their source of origin, these are broadly classified as plant, animal, mineral, and microbial dyes although plants are the major sources of natural dyes. As interest in natural dyes grew, information from the old literature was collected and traditional dyeing practices in different regions were documented and compiled by various researchers Historically, plants have been used for the extraction of a majority of natural dyes .Various plant parts including roots, leaves, twigs, stems, heartwood, bark, wood shavings, flowers, fruits, rinds, hulls, husks, and the like serve as natural dye sources. The famous natural blue dye, indigo is obtained from the leaves of the plant *indigofera tinctoria*. Some plant-derived dyes have other applications also, for example, as food ingredients and medicines in traditional medicine systems and hence a commercial supply chain of these dyes is in place. Some of the natural dyes were well known in the past for their dyeing properties and have remained in use even now, albeit on a small scale. A renewed interest in natural increased their commercial availability<sup>3</sup>.

S.No	Common name of the plant	Botanical name	Part used	Color obtained
1	Siam weeds	<i>Eupatorium odoratum</i>	Whole plant	Yellow
2	Goat weed	<i>Ageratum conyzoides</i>	Whole plant	Yellow
3	Jack fruit tree	<i>Atrocarpus heterophyllus</i>	Bark	Yellow
4	Gulmohar	<i>Delonix regia</i>	Flower	Olive green
5	Teak	<i>Tectona grandis</i>	Leaves	Yellow
6	Babool	<i>Acacia nilotica</i>	Leaves, bark	Yellow/brown
7	Water lilly	<i>Nymphaea alba</i>	Rhizomes	Blue
8	Dahlia	<i>Dahlia variabilis</i>	Flowers	Orange
9	Amla	<i>Emblica officinalis</i>	Bark, fruit	Grey
10	Indian Jujube Ber	<i>Ziziphus mauritiana</i>	Leaf	Pink
11	Drumstick	<i>Moringa pterygosperma</i>	Leaf	Yellow
12	Sausage tree	<i>Kigelia pinnata</i>	Petals, heartwood, bark	Yellow, pink
13	African tulip tree	<i>Spathodeacompanulata</i>	Flower	Yellow/orange
14	Tamarind	<i>Tamarindus indica</i>	Leaves, seeds	Yellow, brown
15	Golden dock	<i>Rumex maritmus</i>	Seeds	Brown
16	Eucalyptus	<i>Eucalyptus camaldulensis</i>	Bark	Yellow and brown
17	Red sandalwood	<i>Pterocarpus santalinus</i>	Wood	Red

**Table (1.1) some promising natural dye sources**

### 1.3 The uses of dyes

One of the most important and, technically most difficult, usage of dyes the cosmetic field concerns the dyeing of living hair to aesthetically satisfying shades and there is an ever present demand for better techniques and new dyes in this field . At the same time, a number of new ranges of textile dyes have recently appeared which may well contain individual dyes of value in the dyeing of hair and in the coloring of cosmetics. An attempt will be made to Describe some of these .dyes ,although commercial consideration unfortunately Prevent a full discussion of their chemical structures (BROWN, 1967).Also the dyes uses in medical field In order to achieve cancer-targeted NIR imaging, a number of researchers have designed and synthesized various ICG derivatives, which are modified with some functional groups available for further conjugation of cancer-specific ligands, such as folate,8,9 cyclic RGD peptide (cRGD, a target for the  $\alpha\beta3$  integrin)10,11 and concertargeting antibodies.12,13 Despite the fact that the conjugation strategies described above demonstrate some efficacy, the specificity for drug delivery, the potency of cancer therapeutics, and the potential for clinic application still remain

unsatisfactory the one hand, chemical conjugation may alter the functional activities of targeting ligands, imaging agents, or therapeutic agents.<sup>15</sup> On the other hand, conjugation strategy means additional synthetic steps and costs, more convoluted behavior and effects in vivo, and also greater regulatory hurdles in applying for clinic trials and extensive applications<sup>4</sup>.

## 1.4 Hair dyes

A great majority of the dyes used in hair coloring are known as oxidation hair dyes. A much smaller number of the commercial hair dyes are synthetic dyes that have affinity for protein substrates such as wool. Oxidation dyes, the more permanent of the two groups, are produced directly on the hair by oxidizing aromatic diamines such as *para*-phenylene diamine or 2,5-diaminotoluene with an oxidizing agent. Suitable diamines have been referred to as “primary intermediates” and the oxidizing agents (e.g. hydrogen peroxide) as “developers.” Other useful primary intermediates are amino diphenyl amines, amino methyl phenols, and *para*-aminophenol.

When used alone, the primary intermediates provide a very limited shade-range following their oxidation on hair. To enhance the range of available hair colors, the primary intermediates are oxidized in the presence of suitable “couplers.” While most couplers do not produce colors when exposed to developers alone, they give a wide range of shades on hair when applied in combination with primary intermediates. Appropriate couplers include 3-aminophenol, resorcinol, and  $\alpha$ -naphthol the chemistry associated with the oxidation of primary intermediates is now reasonably well known. For *para*-phenylene diamine and *para*-aminophenol, oxidation-induced self-coupling proceeds via the process outlined in Fig. 18, where it can be seen that permanent hair-dye formation involves oxidation followed by coupling to give type-15 structures. This provides chemistry representative of combinations arising from joining an  $\alpha$ -naphthol-based coupler and a sulfonated *N*-phenyl-*para* phenylene di amine primary intermediate to produce experimental dyes 18 and 19. This chemistry also illustrates the fact that oxidation dyes are often mixtures rather than single products it is an effective compound for hair dyes due to its low molecular weight, high protein-binding capacity, and ability to penetrate the hair shaft. Apart from being a common constituent in varying concentrations of nearly 70% of the hair colorants available worldwide, it is also present in dyes for

henna tattoos, textiles, leather and fur, and black rubbers. Being a member of 1,4-substituted benzenes, it cross-reacts with para-amino benzoic acid (PABA), sulphonamides, para-amino salicylic acid, ester anesthetics, thiazides, sesquiterpene-lactone mix, and azo dyes. It is a potent contact sensitizer even in low concentration and considered a best indicator and useful patch test screening allergen for hair dye dermatitis. The reported prevalence of positive patch test reactions to PPD among dermatitis patients is 4.4% in Asia, 4.1% in Europe, 6.0% in North America, and 11.5% in India. The clinical features of hair dye dermatitis vary from mild contact dermatitis localized to one body site (hand dermatitis) or disseminated generalized dermatitis to severe life-threatening complications such as contact urticarial /angioedema, rhinitis/bronchospasm/asthma, and renal toxicity. The most common clinical presentations include contact dermatitis localized to sites of contact or photo exposed skin, periorbital dermatitis, airborne contact dermatitis, hand dermatitis, and rarely erythema multi form-like lesions. In this pilot study, we present our clinico-epidemiological observations and patch test results of PPD contact sensitivity in patients suspected to have hair dye dermatitis. (Mrinal Gupta, 2015). Hair is an essential feature that plays a key role in self-perception. Sometimes, it also expresses people's personality. Hair style can be created and modified through hair cosmetics, including hair conditioning, hair straightening, hair waving and hair coloring cosmetic products. Hair graying is a natural part of aging, which occurs in approximately 50% of the people over 50 years old. Therefore, the product of hair coloring is the one of the most important cosmetics for modern people. Some of the temporary hair dyes can be obtained from natural resources, such as henna from *Law Sonia inermis* Linn. Semi-permanent hair dyes are generally synthetic and are typically composed of relatively low molecular weight coal tar materials. These dyes can diffuse freely in and out of the cortex and remain on the hair longer than a temporary dye. Permanent hair dyes are the most frequently used on hair; this is due to the persistence and darkness effects it has on the hair. For permanent hair dyes, the oxidation procedures are dependent on three main components, *i.e.*, primary intermediates, couplers and oxidants. Thus, during the hair dying process, the hair must firstly be bleached with a mixture containing ammonium/sodium persulfate and hydrogen peroxide. After the hairs are bleached, the dye formation reactions will occur by primary intermediates (such as *p*-phenylene di amines) with couplers

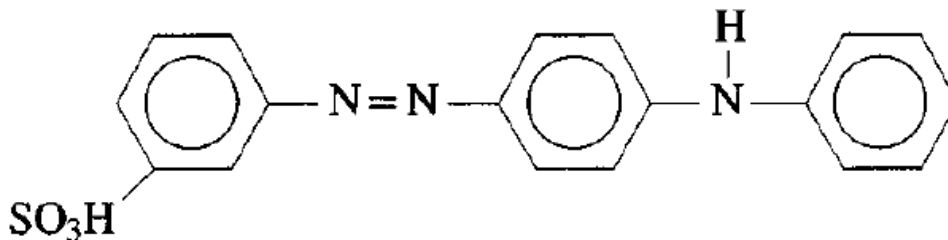
to attain the final hair color. The commonly used couplers are resorcinol and *m*-amino phenols these steps may have adverse effects that can damage both the hair and the skin cells. Therefore, the effects of such components of hair dyes on cells are very important for their safety. The chemical structures of selected hair dyes are shown in Figure (2)<sup>5</sup>.

## 1-5. Classification of Dyes

Dyes may be classified according to their chemical structure or the method by which they are applied to the substrate. The dye manufacturers and dye chemists prefer the former approach of classifying dyes according to the chemical type. The dye users, however, prefer the latter approach of classification according to the application method.

### 1-5-1. Acid dyes

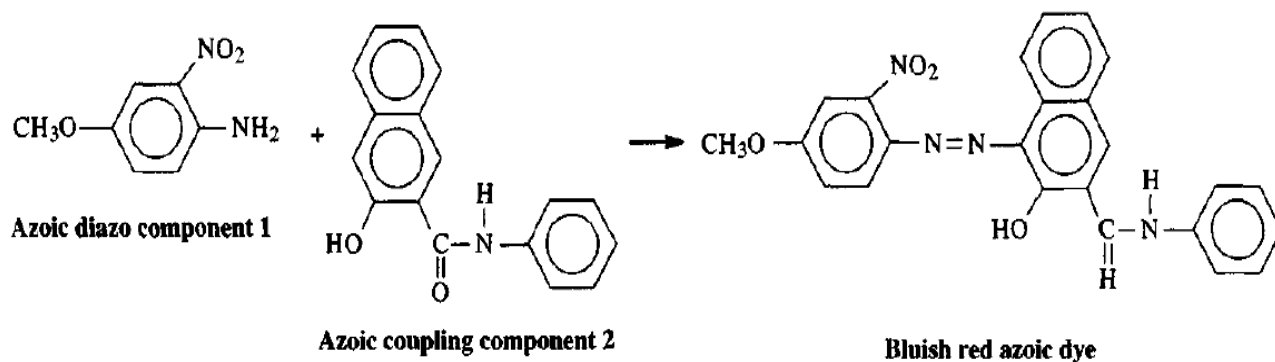
Acid dyes are water-soluble anionic dyes, containing one or more sulfonic acid substituent or other acidic groups. An example of the class is acid yellow 36.



Acid dyes are applied from acidic dye baths to nylon, silk, wool, and modified acrylics. They are also used to some extent for paper, leather, ink-jet printing, food, and cosmetics.

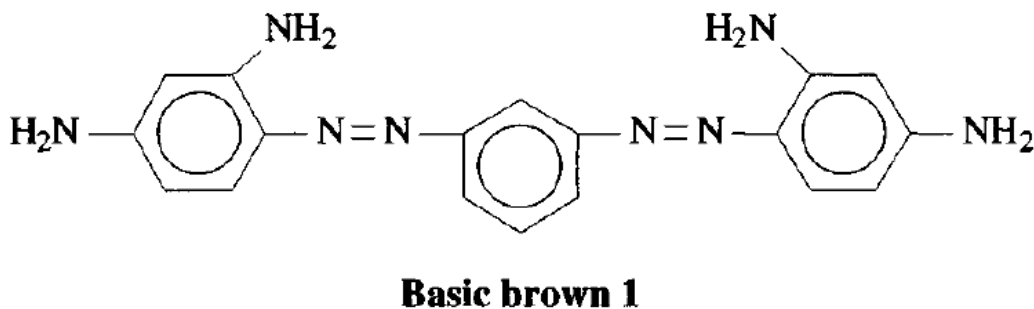
### 1-5-2. Azonic dyes

Azo dyes contain at least one azo group ( $\text{—N=N—}$ ) attached to one or often two aromatic rings. They are produced in textile fibers (usually cotton, rayon, and polyester) by diazotization of a primary aromatic amine followed by coupling of the resulting di azonium salt with an electron-rich nucleophile (azo coupling). A variety of hues can be obtained by proper choice of di azo and coupling components. The production of bluish red azoic dye from the following two components is an example.



### 1.5-3. Basic (cationic) dyes

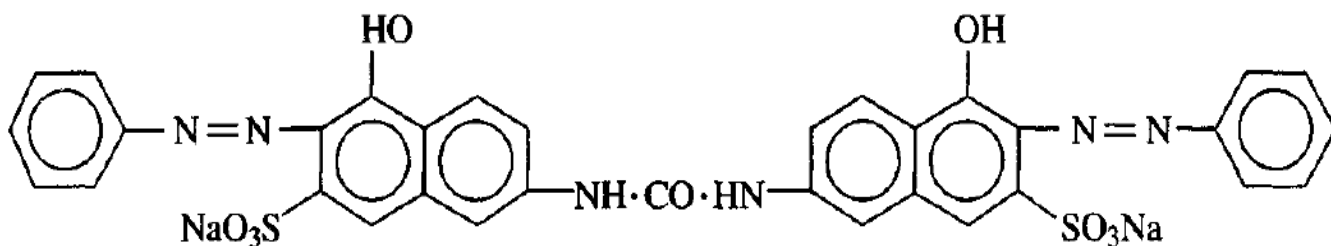
Basic dyes are water-soluble and produce colored cations in solution. They are mostly amino and substituted amino compounds soluble in acid and made insoluble by the solution being made basic. They become attached to the fibers by formation of salt linkages (ionic bonds) with anionic groups in the fiber. They are used to dye paper, polyacrylonitrile, modified nylons, and modified polyesters. In solvents other than water, they form writing and printing inks. The principal chemical classes are triaryl methane or xanthenes. Basic brown 1 is an example of a cationic dye that is readily protonated under the pH 2 to 5 conditions of dyeing.



### 1-5-4. Direct dyes

Direct dyes are water-soluble anionic dyes, but are not classified as acid dyes because the acid groups are not the means of attachment to the fiber. They are used for the direct dyeing of cotton and regenerated cellulose, paper, and leather. They are also used to dye union goods (mixed cotton, and wool or silk) and to a lesser extent nylon fiber. Most adding common salt or Glauber's salt. The presence of excess sodium ions favors establishment of equilibrium with a minimum of dye remaining in the dye bath. Direct orange 26 is a typical direct dye.



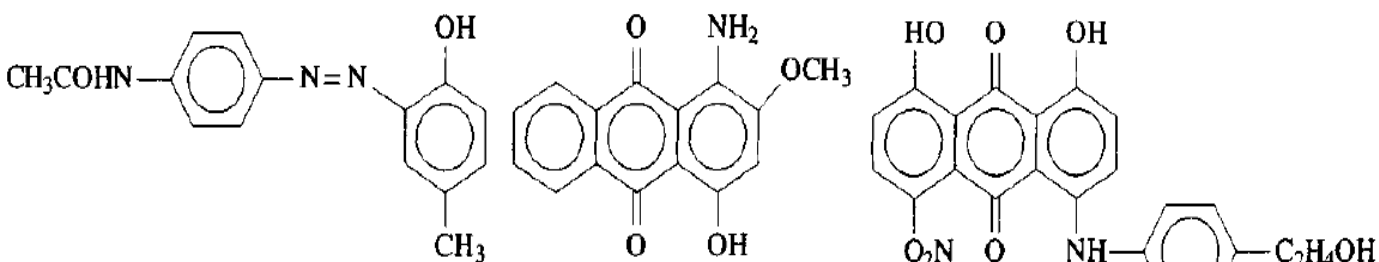


**Direct orange 26**

### 1-5-5. Disperse dyes

Disperse dyes are substantially water-insoluble non-ionic dyes for application to synthetic hydrophobic fibers from aqueous dispersions. Disperse dyes are applied as very finely divided materials that are adsorbed onto the fibers with which they then form a solid solution.

Dispersed dyes are primarily used for polyester and acetate fibers. Simple soluble azo, styryl benzodi furanone, and insoluble anthraquinone are the most common disperse dyes. Disperse yellow 3, disperse red 4, and disperse blue 27 are good examples of disperse dyes:



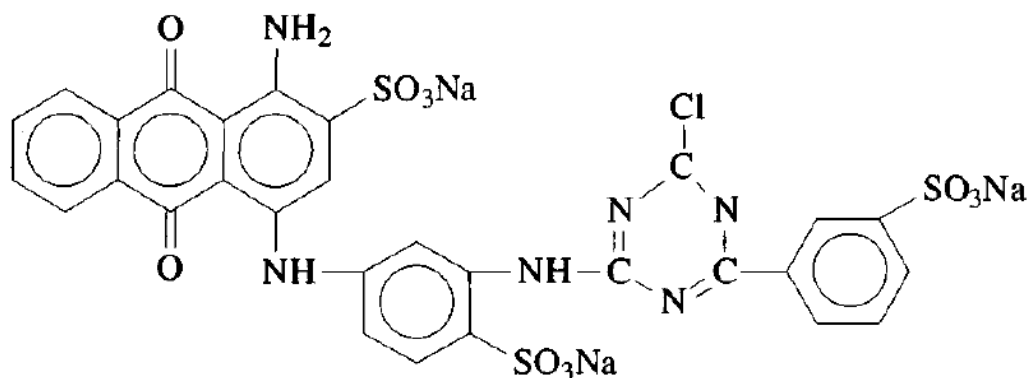
**Disperse yellow 3**

**Disperse red 4**

**Disperse blue 27**

### 1-5-6. Fiber-reactive dyes

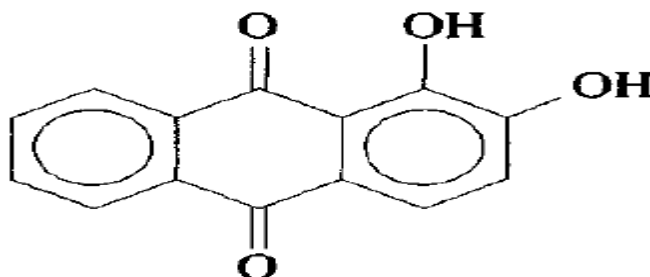
These dyes react with the cellulosic fiber to form a covalent bond. This produces dyed fiber with extremely high wash fastness properties. Cotton, rayon, and some nylons are dyed by this relatively simple dye. The principal chemical classes of reactive dyes are azo, tri phenyloxazine, phthalocyanine, formazan, and anthraquinone. An example of this type is the reactive blue 5 dye shown below



**Reactive blue 5**

### 1-5-7. Mordant dyes

Some dyes combine with metal salts (mordanting) to form insoluble coloured complexes (lakes). These materials are usually used for the dyeing of cotton, wool, or other protein fiber. The fiber is first treated with an aluminum, chromium, and iron salt and then contacted with a lake-forming dye (azo and anthraquinone derivatives). The metallic precipitate is formed in the fiber producing very fast colours highly resistant to both light and washing.



**Mordant red 11**

Mordant dyes have declined in importance because easier methods using developing dyes and vat dyes have replaced this process.

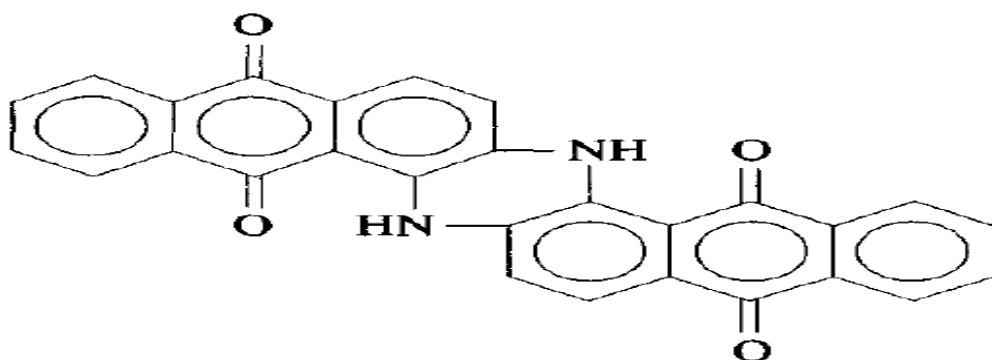
### 1-5-8. Sulfur dyes

Sulfur dyes are applied to cotton from an alkaline reducing bath with sodium sulfide as the reducing agent. These dyes are water-insoluble but they are soluble in their reduced form and exhibit affinity for cellulose. They dye by adsorption; but on exposure to air, they are oxidized to reform the original insoluble dye inside the fiber. The cost is low and they have good fastness to light,

washings, and acids. The actual structures of sulfur dyes are largely unknown although it is considered that they possess sulfur-containing heterocyclic rings.

### 1-5-9. Vat dyes

The vat dyes are insoluble complex polycyclic molecules based on the quinone structure (keto-forms). They are reduced with sodium hydrosulfite in a strongly alkaline medium to give soluble leuco forms that have a great affinity for cellulose. After the reduced dye has been absorbed on the fiber, the leuco forms are reoxidized to the insoluble keto forms. The dyeings produced in this way have high wash and light-fastness. An example of a vat dye is vat blue 4 (indanthrene)<sup>6</sup>.



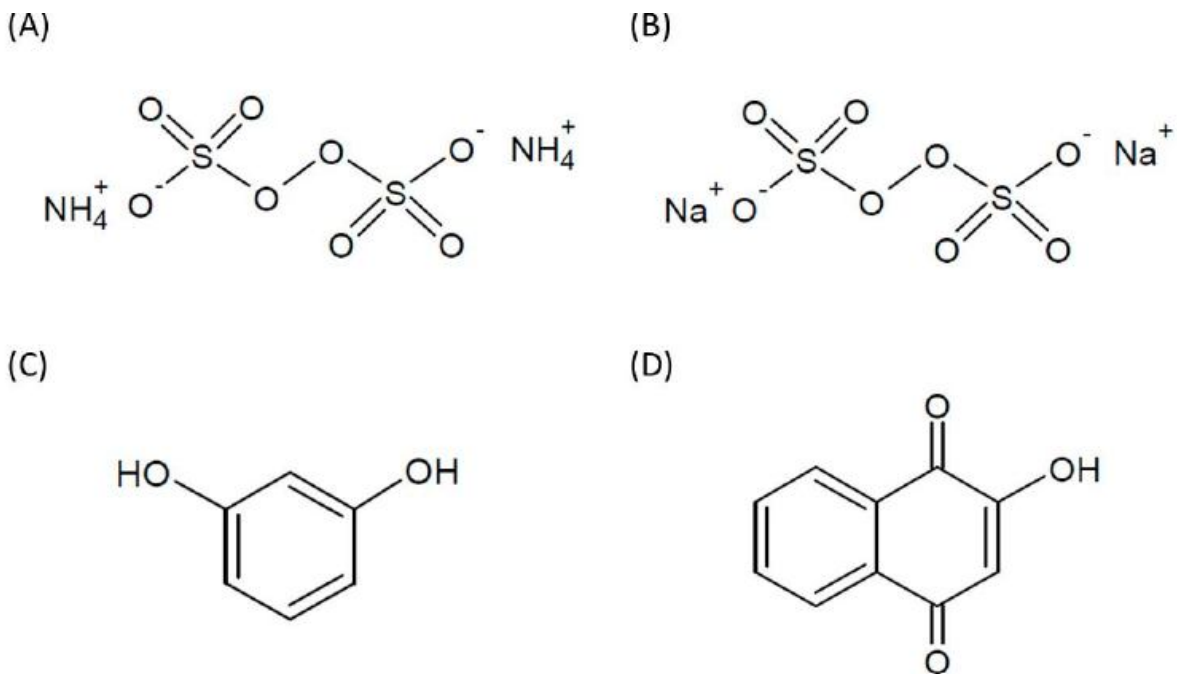
**Vat blue 4**

### 1-5-10. Solvent dyes

These dyes are water-insoluble but soluble in alcohols, chlorinated hydrocarbons, or liquid ammonia. They are used for coloring synthetics, plastics, gasoline, oils, and waxes. The dyes are predominantly azo and anthraquinone, but phthalocyanine and triarylmethane dyes are also used. Perchloroethylene is the preferred solvent.

### 1-5-11. Oxidation dyes

These dyes are produced on the substrate by oxidation of colorless compounds such as aromatic amines and phenols. For example, aniline may be oxidized in cotton with sodium bichromate to produce aniline black. The color produced by aniline black is characterized by a full bluish black shade and excellent fastness. However, oxidation dyes are rapidly decreasing in importance because aniline, other aromatic amines, and bichromate that are used for oxidation, are toxic.



**fig(2) Chemical structures of (A) ammonium persulfate; (B) sodium persulfate; (C) resorcinol and (D) lawsone.**

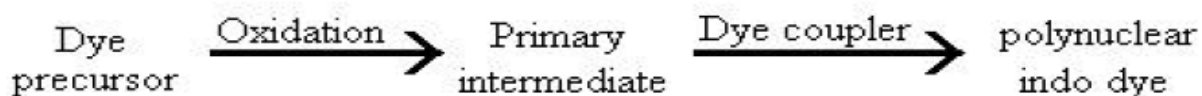
## 1-6. Permanent and demi-permanent hair colour

Permanent hair colouring product is formulated with two different components of precursor-coupler base and oxidizing base. The precursor-coupler base consists of surfactants, alkaline, reducing agent, precursors, couplers, and water.

The oxidizing base consists of an oxidizing agent (e.g. peroxide), stabilizer for the peroxide, and surfactants. Since the peroxide is unstable in alkaline solution, the precursor-coupler base and the oxidizing base have to be formulated separately for product storage<sup>7</sup>.

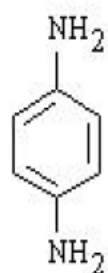
Surfactants are used to help in dissolving the precursors and couplers, to assist in spreading the dye evenly over the hair, and to thicken the product, so it does not drip easily while applying the product<sup>7</sup>. Alkaline solution is required to facilitate the oxidation reaction, and the reducing agent to inhibit oxidation of precursors by air. The surfactant in the oxidizing base works as a thickener by the surfactants precipitating on dilution when the two components are mixed together, resulting in a much thicker mixture<sup>8</sup>. Dyes for permanent colouring are achieved

by an oxidation reaction of a dye precursor followed by a reaction with a dye coupler. Schematic of the reaction of an oxidation dye is shown below  
Schematic of oxidative hair dyeing reaction

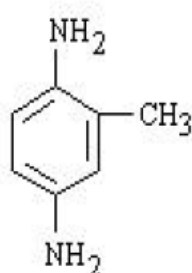


The common oxidation reagents are hydrogen peroxide and ammonium hydroxide, and the primary intermediates are usually Ortho- or para-substituted amino aromatic compounds. Dye couplers are electron-rich aromatic phenols or amines. The structures below show some sample dye precursors and dye couplers, respectively. Combination of different dye precursors and dye couplers gives different colouring effect.

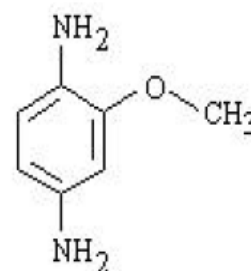
Examples of dye precursors.



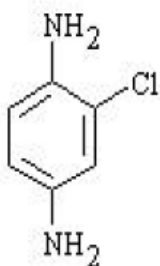
p-Phenylenediamine



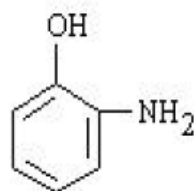
Toluene-2,5-diamine



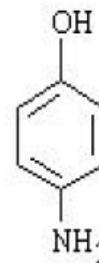
2-Methoxy-p-phenylenediamine



2-Chloro-p-phenylenediamine

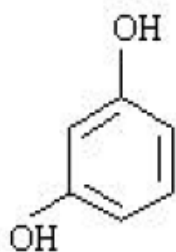


o-Aminophenol

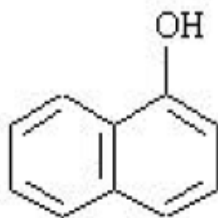


p-Aminophenol

Example of dye couplers



Resorcinol



1-Naphtol



Hydroquinone

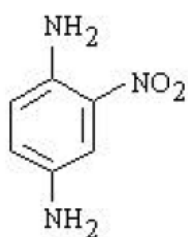
Studies have been done to control the primary intermediates. Several allergic dermatitis and nephrotoxic effect have been related to amino phenols and 1,4-Benzene amine, whereas some dye intermediates are toxic compounds and carcinogenic. However additions of cationic surfactants of tetra decyl tri methyl ammonium bromide (TTAB) or hexa decyltrimethylammonium bromide (CTAB) allow the separation of these hazardous intermediates<sup>9</sup>.

Semi-permanent hair colouring is similar to the permanent hair colouring in term of oxidative dyes but resembles the lasting properties of a semi-permanent hair color. The amount of peroxide is less and therefore offers less damage to the hair. semi-permanent hair colouring products do not require any peroxide or mixing. The formulation consists of solvents, surfactants, amide, fragrance, and acid or alkali.

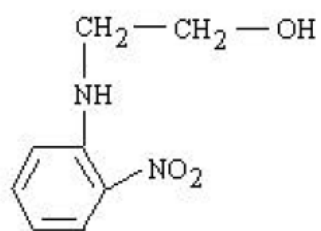
The solvents most commonly used are water and glycols or glycol derivatives, and the purpose of the acid or alkali is to adjust the PH. The types of dyes used are neutral aromatic amine, nitro aromatic amine, or anthraquinone derivatives.

The dyes can be classified as mono-, di-, or tri nuclear (ring) dyes. Studies have shown that small mononuclear hair dyes has a higher rate of rinsing out. Larger dyes are able to reach more hindered position in the hair shaft and therefore the hair colour lasts longer<sup>7</sup>.

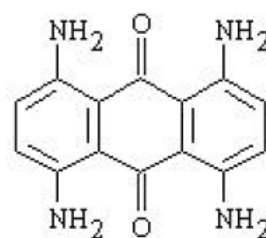
Examples of semi-permanent dyes. <sup>7</sup>.



2-Nitro-p-phenylenediamine  
(red)



HC yellow No. 2



Disperse blue 1

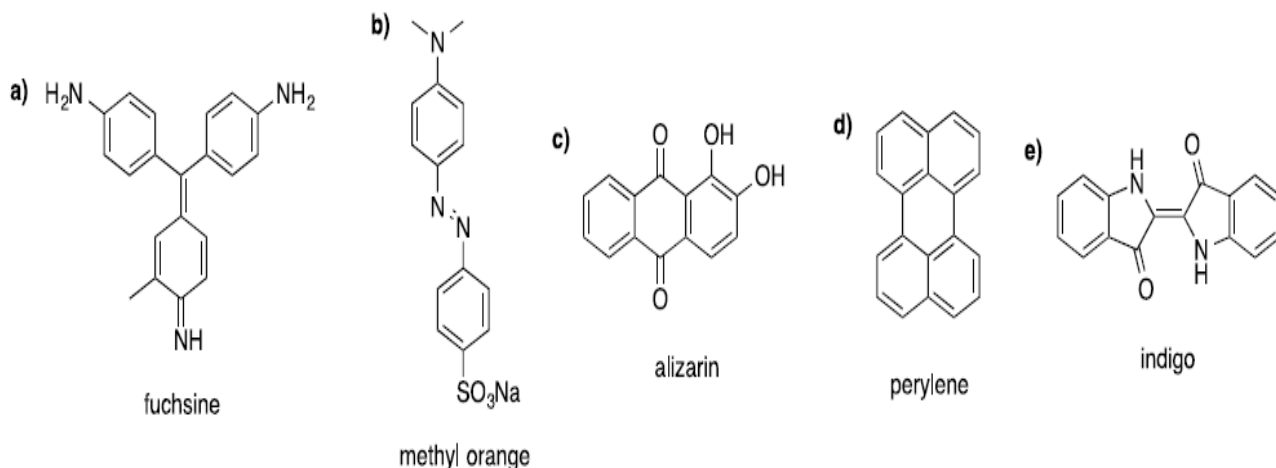
## 1.7 Synthesis of dyes:

Natural and synthetic dyes are compounds of great interest since they play an important role in our everyday life. The broad variety of technical and industrial applications, which includes “classical” utilizations like dyeing of textiles and other consumer goods as well as rather new usages such as laser dyes and dyes for organic light emitting diodes (OLEDs), liquid crystal (LC) displays, optical data storage and fluorescent labeling, has produced a great deal of research in this field. The main driving force is the constant demand for improved dyeing efficiency, or photochemical/photophysical properties, while also focusing on eco-friendly procedures, reduced toxicity, and decreased production costs, a promising approach to fulfilling these requirements is the combination of dyes and polymeric materials, which will be highlighted in this review. The great advantage of such systems is the controllability of many features like solubility, stability, and toxicity through appropriate choice of polymeric material. Widely applied and interesting representatives amongst the large number of dye categories are triphenylmethane, azo, anthraquinone, perylene, and indigoid dyes (Fig. 2). Due to the fact that these compounds cover a large spectrum of applications, they are the main focus of this article.

Azo dyes are numerically the most important class of dyes since more than 50% of all dyes listed in the Color Index are azo dyes. Covering all shades of color, azo dyes are used for dyeing textiles, paper, leather, rubber or even foodstuffs. Some examples of indicators, drugs, and histological staining agents are known as well. Since there are no naturally occurring azo dye derivatives, their synthesis usually involves two steps: diazotization and azo coupling, the latter of which requires a nucleophilic or anionoid center present in the coupling partner [13]. Regarding the spatial arrangement of the azo group, two configurations—*cis* and *trans*—are possible. The UV-induced conversion to the *cis*-configuration is a well-investigated phenomenon that allows these compounds to be used for optical storage. Another valuable class of dyes is represented by perylenes, belonging to the group of oligo(peri)naphthalene (rylene) chromophores. Due to their excellent physical and chemical properties, these compounds are widely used as laser markers, sensitizers in photovoltaic devices, and fluorescent labels. The basic chromophores of these stains are perylene and the photochemically more stable perylenetetracarboxydiimide. Since the latter derivative is of outstanding value for



single molecule spectroscopy, it serves as a key structure for a variety of chromophores. Extension of the perylene motif with additional naphthalene units leads to larger chromophores such as terrylene and quaterylene, which also offer a large number of applications<sup>2</sup>.



**fig(3) Characteristic representatives of (a) tri phenyl methane dyes, (b) azo dyes, (c) anthraquinone dyes, (d) perylene dyes, and (e) indigoid dyes.**

## 1.8 The effect of PPD:

Hair dyes are widely used by men and women in the United States, and are known to frequently contain potent contact allergens. Recent reports in the media have highlighted cases of significant morbidity, and It is known that *p*-phenylene di amine (PPD) is a frequent ingredient in hair dye products sold in Europe, as illustrated by two recent market surveys from Spain and Sweden. PPD is a potent contact sensitizer, and relatively high and stable prevalence rates of contact allergy to PPD are observed in European dermatitis patients. Furthermore, the literature has also highlighted cases of additional adverse events associated with PPD exposure, including: immediate hypersensitivity reactions, systemic toxicity following ingestion, hair loss, and a potentially increased risk of malignancy. A better understanding of the common ingredients in consumer hair dye products is important, because the definitive treatment for allergic hair dye substances categorized as potent skin sensitizers was compiled on the basis of assessments by

the European Commission's Scientific Committee on Consumer Products (SCCP) and the Scientific Committee on Consumer Safety (SC (Geeta Ahlawat, n.d.)cs ) of animal data, and ranking by quantitative structure–activity relationships . All hair dye substances that had been categorized as strong or extreme skin sensitizers by the SCCP and SCCS and/or strong or moderate skin sensitizers.<sup>10</sup> . Other branded hair dyes like 'Godrej', Kesh kala, color mate etc. are available in powder or liquid forms. The concentration of active substance para phenyldi amine, varies from 70 to 90% in stone hair dye and 2 to 10% in branded dyes, which are used for coloring the grey hair black. The stone hair dye is very cheap and freely available, making it an attractive option for suicidal intent. It is brownish to black colored solid which is partially soluble in water and easily soluble in hydrogen peroxide. PPD is a good hydrogen donor and is metabolized by electron oxidation to an active radical by cytochrome P 4 5 0 peroxidase to form a reactive benzoquinone diamine. This is further oxidized to a trimer known as Brandowaski's base, a compound reported to cause anaphylaxis as well as being strongly mutagenic. Oral ingestion of PPD causes mainly two types of toxic effects; the first manifestation is angioneurotic edema presenting as rapid development of severe edema of the face, neck, pharynx, tongue and larynx with respiratory distress sometimes requiring emergency tracheostomy. The time of onset of symptoms after ingestion was about 4 to 6 h and at the time of admission, majority of the patients are presented with acute angioneurotic edema of the head and neck and wooden hard swollen protruded tongue with swelling of pharynx and larynx, and these are typical diagnostic feature of acute hair dye poisoning. Initial insult is due to local irritation of the mucous membrane and the skin, causing intense edema. Edema of the eyes may be very severe and may cause exophthalmos. Muscle pain was the next most common presentation of hair dye poisoning following angioneurotic edema. Limbs are usually swollen, tender and stiff. Muscle pain typically occurs about 10 to 12 h after ingestion of hair dye. Acute hair dye poisoning leads to rhabdomyolysis and muscle necrosis. Patients pass chocolate brown color urine which along with typical orofacial swelling is diagnostic of acute hair dye poisoning specially in those cases where history of dye ingestion is lacking. This chocolate is brown colour of urine is due to the presence of myoglobin and hemoglobinuria. In the later phase, rhabdomyolysis and acute tubular necrosis supervene. The myoglobin released because of rhabdomyolysis and muscle necrosis which reach the renal tubules and clog them, leading to pathologic features of acute tubular necrosis

responsible for oliguria and acute renal failure. Acute renal failure was seen as the late cause of death in acute hair dye poisoning cases. Tubular obstruction by myoglobin casts is regarded as the principal mechanism for producing ARF.

### **1-9. Toxicity of PPD**

The dermatological properties of PPD have been studied for more than 50 years, but the systemic toxicity was discovered more recently. The systemic toxicity associated with topical application indicated absorption of small amounts of some hair dye ingredients. That is why the European Economic Community posed regulations on the concentration of PPD in hair dye formulations which should not be more than 6 %. In the field of industry the employees exposure to PPD should not exceed  $0.1 \text{ mg/m}^3$  in the working atmosphere in any eight hours work shift of a forty hours working week.

Application of hair dye formulation for long time may result in apparent typical PPD toxicity. The major problem of PPD toxicity results from ingestion of the pure stuff (99%) for suicidal, homicidal or by mistake. However there were some cases reported as a result of topical application during hair dying using pure stuff or while practising henna

## 1-10. Colouring process

Human hair is primarily proteinaceous and contains a large percentage of oxidizable groups. The external layer of the hair, called the cuticula contains a large portion of amorphous keratin, a hair fiber. This undamaged cuticula that contains a few polar groups, is strongly hydrophobic, and contains negatively charge ionic groups<sup>11</sup>.

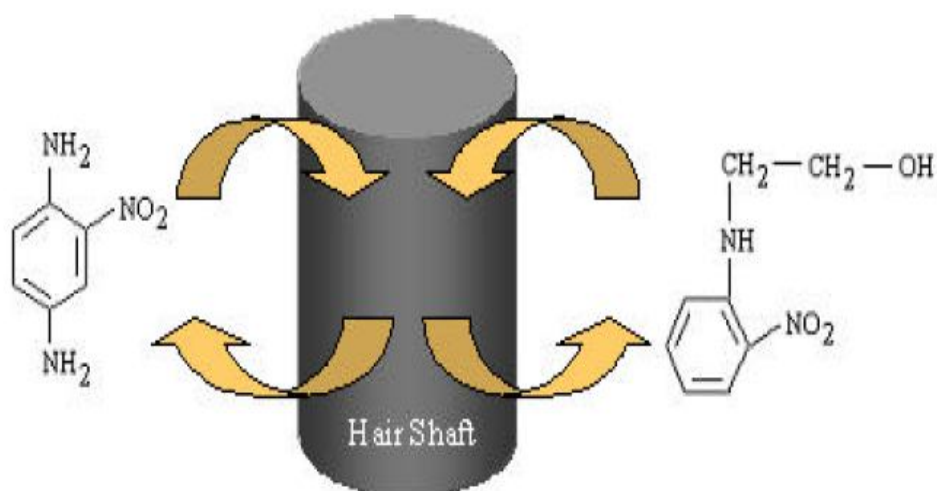
The reaction step of the dye with the hair fibers can be summarized in the following four phases:

1. Diffusion through solution
2. Adsorption or interaction at the fiber surface
3. Diffusion or transport into the fibers
4. Reaction at internal sites in the fibers.

The diffusion of dyes into the fibers can be assumed as diffusion into a cylinder from a solution of limited volume or from an “Infinite Bath”. Both approximations give an accurate diffusion coefficient. However, the temperature, molecular size of the dye, cross- linking density of the fibers, fiber swelling, and exposure time plays a critical role in colour deposition<sup>12</sup>.

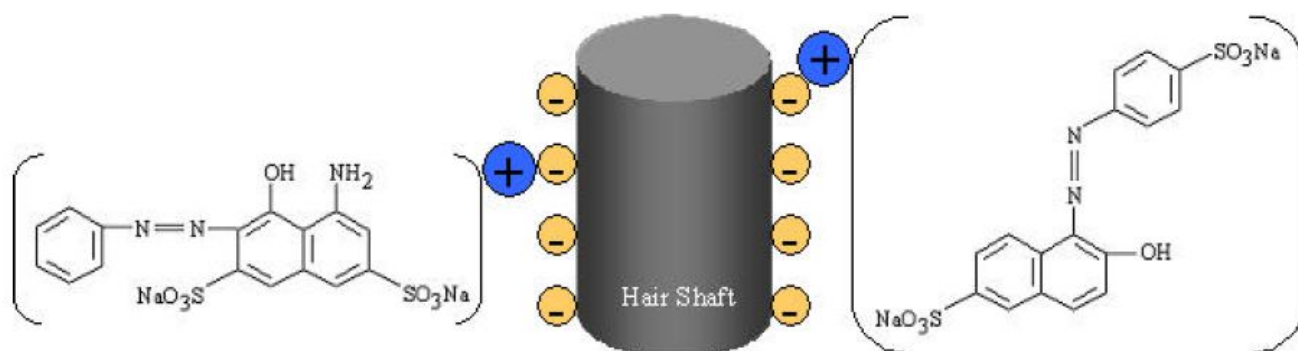
In the presence of an oxidative dye (permanent hair coloring), the hair goes through an oxidative degradation of disulfide bonds to polar sulfonic acid groups<sup>11</sup>.

Semi-permanent dyes are small enough to enter the hair shaft. As the hair is being washed, the dye leaves the hair shaft as the hair returns to its original colour<sup>12</sup>.



The cationic dyes used in temporary colouring are too large of a molecule to enter the hair shaft. Instead, the molecules stick onto the hair shaft as a result of the net negative charge on the hair surface. Since the temporary dyes stick to the surface of the hair, it is easily removed by one to three washes. However, if the hair has been chemically treated (e.g. permanent hair colouring) prior to the application of the temporary dye, the hair becomes more porous and allows the dye to penetrate into the hair shaft, resulting in the hair colour to last longer.

The cationic basic dye is attracted to the surface of the hair shaft. After a few washes, the dye will leave the hair surface<sup>12</sup>.



of the dyes in this class are polyazo compounds, along with some stilbenes, phthalocyanines, and oxazines. The solubility of the dye in the dye bath is often reduced by

## Chapter Two Material and Methods

### 2-1. Sampling

Two types of commercial hair dye from local market in Khartoum Sudan ( $s_1$ ), soft color ( $s_2$ ), Amir.

#### Reagents and chemicals:

- Commercial hair dye and Sudanese henna samples
- Distilled water
- Potassium Bromide

#### Equipment and apparatus

- UV.VIS spectrophotometer
- IR (84005 Shimadzu- Japan)
- Flask
- Beakers
- Pipette
- Sensitive Balance

#### Reagents and chemicals

- PPD standard
- Hair dye and henna samples
- Distilled water

### 2-2. Determination of P-phenylenedi amine (PPD) in hair dye and henna by IR spectrophotometry.

Mixed about 0.05gram of sample with 0.5 gram K Br and grinding till hemogounce and passage to 5 tons for 30s , the pellet passage to light .

Characterization was performed using an Infrared spectrophotometer FT,IR 84005 Shimadzu , in wavelength 4000 to 400  $\text{cm}^{-1}$ .

### 2-3. Determination of P-phenylene di amine in hair dye and henna by UV-VIS spectrophotometry

Standard preparation

A stock solution of 2 ppm P-phenylene di amine standard material was prepared by weighting 0.0005 g from P-phenylene di amine and transferred into 250ml conical flask then completed to mark(250ml) by distilled water.

The following concentrations was prepared from the stock solution by dilution 0.2ppm ,0.3 ppm ,0.4 ppm,0.5 ppm 0.6 ppm and 0.7 ppm

## **2-4. Identification the P-phenylene di amine (PPD) in hair dye and henna by TLC chromatography**

### **Equipment and apparatus**

- Thin layer Chromatography (TLC) Plates
- Test tube
- Measuring cylinder
- Tank
- Capillary tube
- Balance

### **Reagents and chemicals**

- Commercial hair dye and henna samples
- Toluene
- Acetone
- Chloroform
- Ethanol 98%

### **Preparation of PPD standard**

#### **Procedure:**

A 0.5g of PPD dye and henna samples were weighted and taken in test tubes, and then 10ml of 98% Ethanol were added to each test tube. The solution of samples solution and standards solution were taken by capillary tube and then were spotted on the thin layer Chromatographic Plate (TLC).

Mobile phase designed for the active separation of the constituents was acetone-chloroform-toluene in the ratio of 35:25:40 (v/v). The plate was placed into the tank which contains the mobile phase and the tank was covered. The mobile phase was left to scanned on the plate; the plate was removed, dried and inspected visually in comparison with the standard for presence of PPD in study samples. The retardation factor values of each sample and standard were calculated.

# Chapter Three

## The results

### 3.1 IR

The infrared spectra of the samples  $s_1$  and  $s_2$  shown in fig () and () it that lie in the literature wave number ranges of vibration absorption of N-H stretching, benzene ring, N-H bending, C-H bending, C-N aromatic amine and para-substituent amine functional groups.

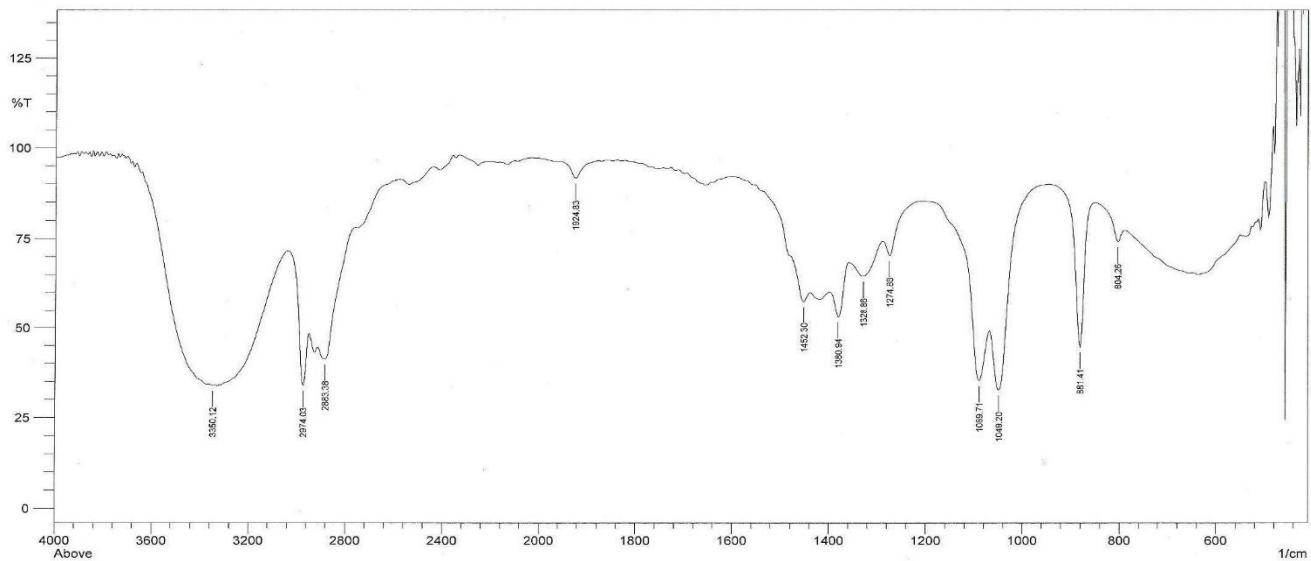
**Table 3.1: IR spectrophotometric analysis of henna sample ( $s_1$ )**

Function group	observed value	Literature value
N-Hstr	3350.12	3500 -3300
Benzene ring	1452.30	near1600,1500-1450
C-H bend	1380.94	~1450
C-N aromatic amine	1089.71-1049	1360 – 1250
Para-substituent compound	881.41	860-800

**Table 3.2: IR spectrophotometric analysis of henna sample ( $s_2$ )**

Function group	observed value	Literature value
N-Hstr	3394.48	3500 -3300
Benzene ring	1596.95	near1600,1500-1450
C-H bend	1446.51	~1450
C-N aromatic amine	1490.87-1446.51	1360 – 1250
Para-substituent compound	754.12	860-800





Fig(3.1) IR for S<sub>1</sub>

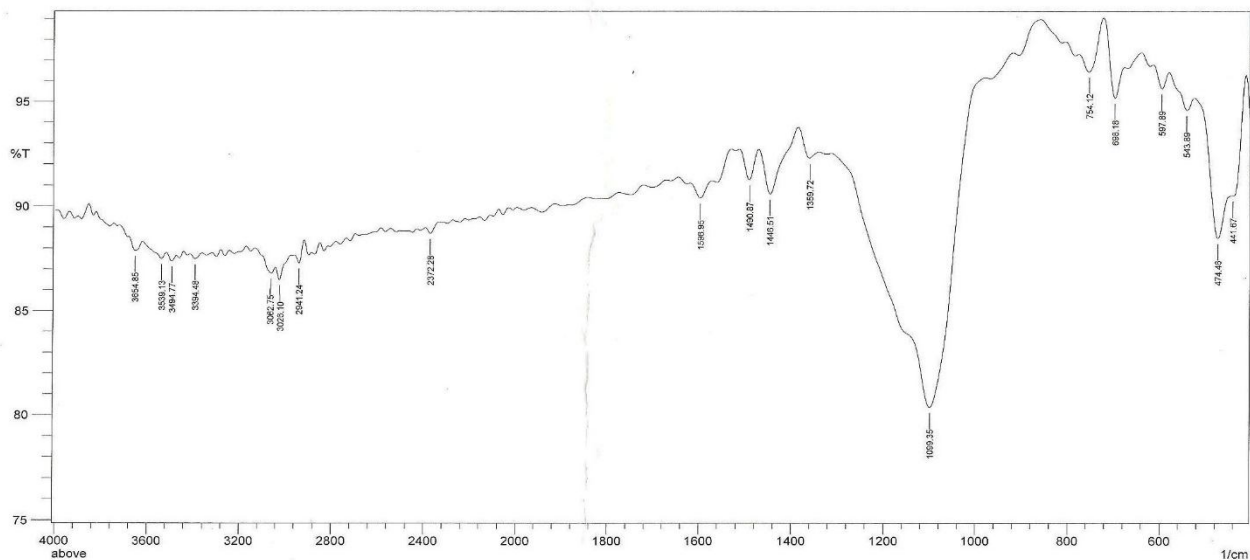
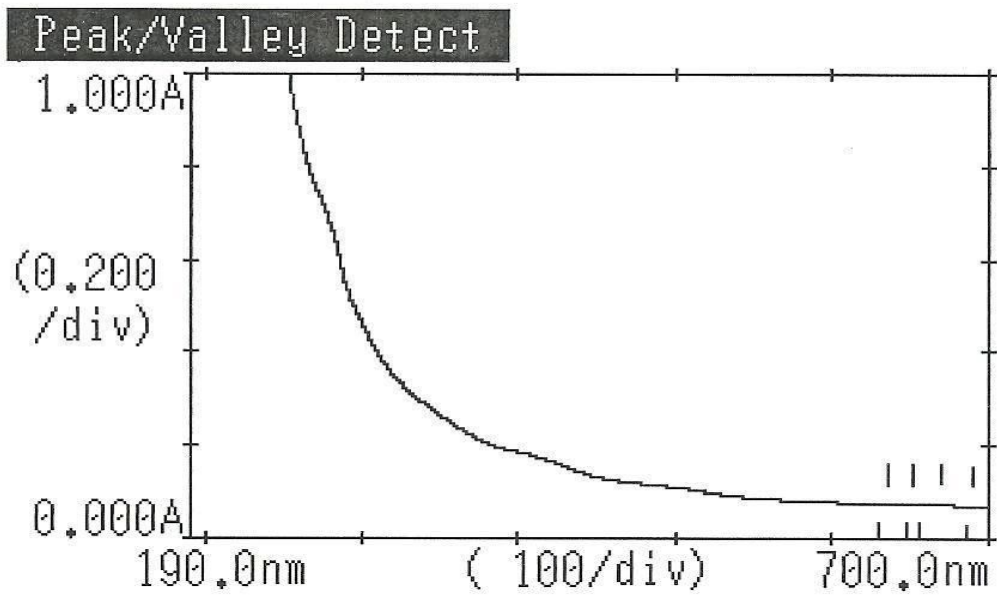
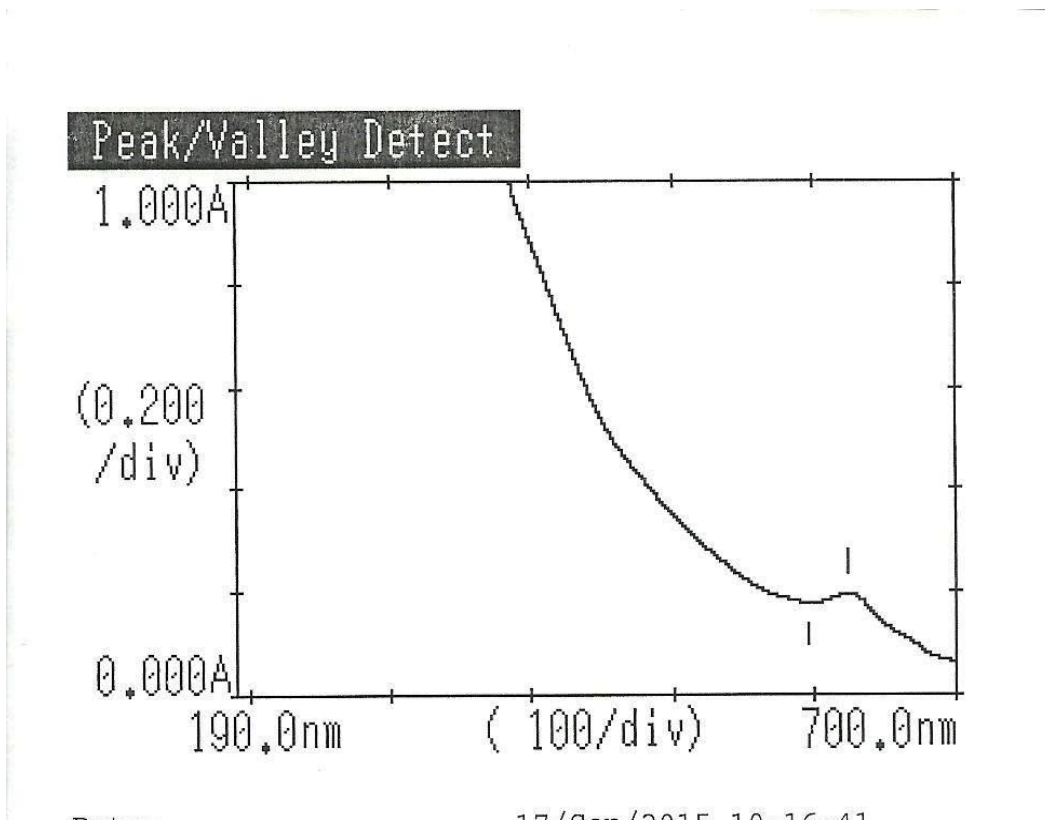


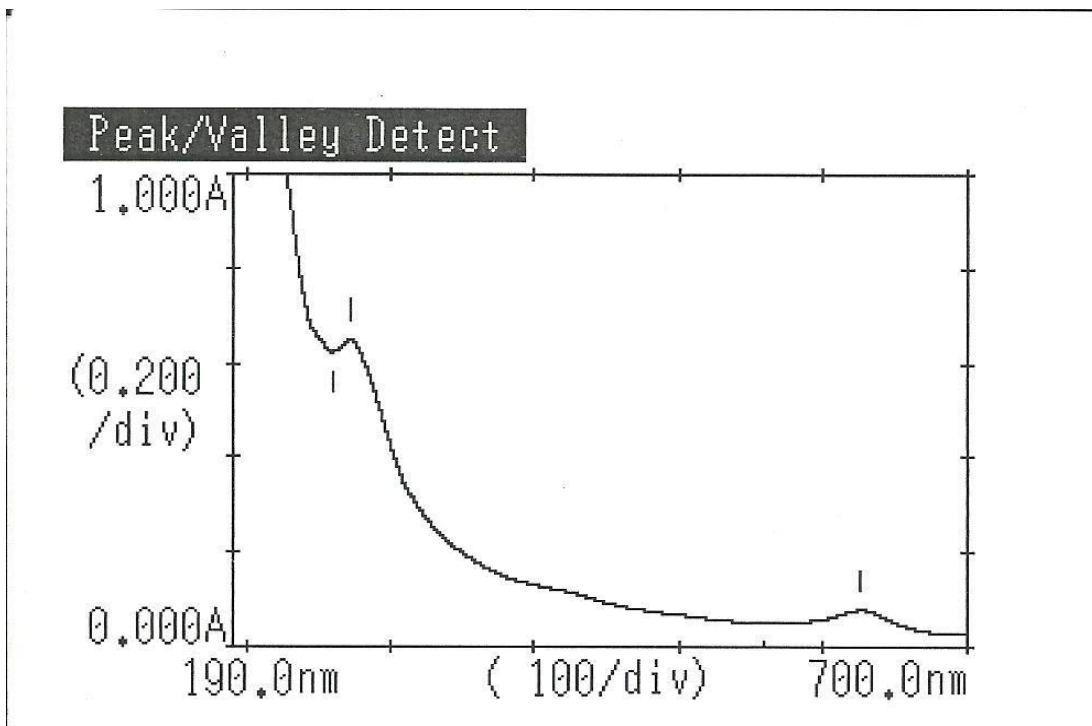
Fig (3.2) IR for S<sub>2</sub>



Fig(3.3) UV for S<sub>1</sub> With absorbed at 190 to 700nm



Fig(3.4) UV for S<sub>1</sub> With absorbed at 190 to 700nm



Fig(3.5) UV for S<sub>2</sub> With absorbed at 190 to 700nm

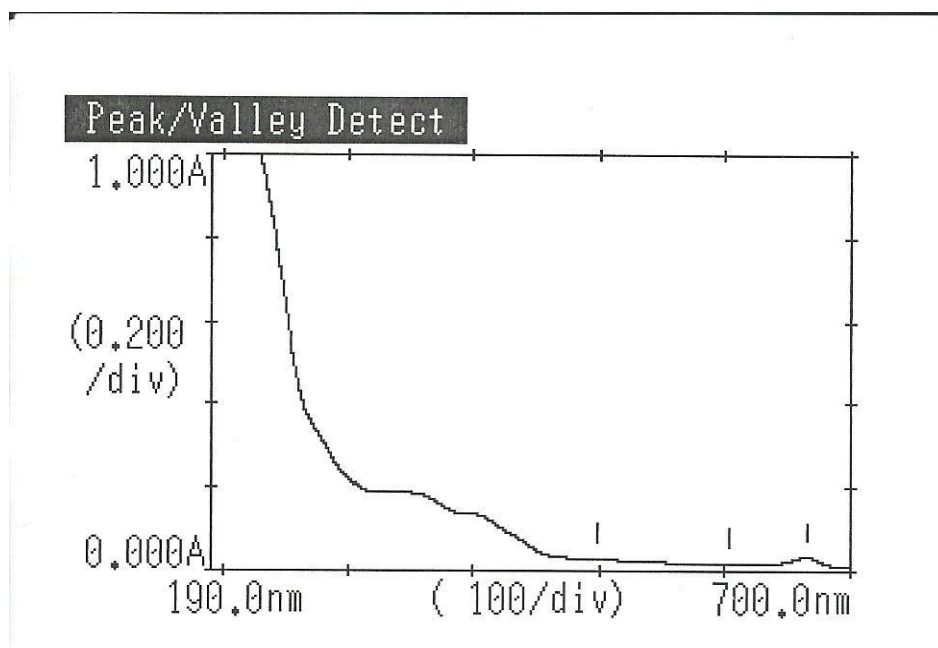


Fig (3.6) UV for S<sub>1</sub> With absorbed at 700 to 190nm

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