THE PERFORMANCE OF PALM COIR PITH FOR METHYLENE BLUE DYE REMOVAL IN TEXTILE WASTEWATER

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ABSTRACT

Textile industry contributes a large amount of wastewater in Malaysia. It is also one of main sources that contribute to the water pollution. Hence, proper studies are needed to investigate the low-cost adsorbents used to remove the dye in textile wastewater. In this study, activated carbon, prepared from palm coir pith which is a waste product obtained throughout the extraction of coir fibre from husk were used as adsorbent for the removal of methylene blue. The palm coir pith was treated by using sulphuric acid and pyrolyzed in a muffle furnace for different temperature and times. There are three parameters considered to test the methylene blue which are pH of the methylene blue, adsorbance rate during adsorbing process and duration of the adsorbed substances staying inside the sample. The results show that in term of acidity, PCP that is pyrolyzed for 300 ^oC in 1 hour gives better improvement analysis which is 37.33 % compared to the others while in terms of clarity, the pyrolysis process in 4 hours at 300 ^oC gives good result compared to the others which is 89.31 %. Hence, it showed that activated carbon of palm coir pith could be used as low-cost alternatives to commercial activated carbon in textile wastewater treatment for the removal of basic dyes.

ABSTRAK

Industri tekstil menyumbang sejumlah besar air sisa di Malaysia. Ia juga merupakan salah satu sumber utama yang menyumbang kepada pencemaran air. Oleh itu, kajian yang betul yang diperlukan untuk menyiasat penyerapan kos rendah digunakan untuk membuang pewarna dalam air sisa tekstil. Dalam kajian ini, karbon diaktifkan, disediakan daripada sabut kelapa empulur yang merupakan bahan buangan yang diperolehi dalam pengeluaran gentian sabut daripada sekam yang telah digunakan sebagai penyerap untuk penyingkiran metilena biru. Empulur sabut kelapa dirawat dengan menggunakan asid sulfurik dan dibakar dalam relau meredam untuk suhu dan masa yang berlainan. Terdapat tiga parameter untuk menguji metilena biru iaitu pH metilena biru, kadar keserapan semasa proses dan tempoh bahan terjerap tinggal di dalam sampel. Hasil kajian menunjukkan bahawa dari segi keasidan, empulur sabut kelapa sawit yang dibakar untuk 300 ^{o}C dalam 1 jam memberikan analisis peningkatan yang lebih baik iaitu 37.33 % berbanding dengan yang lain manakala dari segi kejelasan, proses pirolisis dalam 4 jam pada 300 ^{o}C memberikan hasil yang baik berbanding dengan yang lain iaitu 89.31 %. Oleh itu, ia menunjukkan bahawa karbon teraktif daripada empulur sabut kelapa boleh digunakan sebagai alternatif kos rendah untuk komersial karbon diaktifkan dalam rawatan air sisa tekstil untuk penyingkiran pewarna asas.

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LIST OF SYMBOLS

Al^{3+}	Aluminium
Ca^{2+}	Calcium
Fe^{3+}	Ferric
Na_2S	Sodium sulphide
α	Thermal accommodation coefficient
τ	Average staying time
Γ	Surface concentration
θ	Fraction of surface covered
Σ	Specific surface area of the solid
σ^o	Area of a site

LIST OF ABBREVIATIONS

CI	Colour index
NIIR	National Institute of Industrial Research
AOP	Aspect Oriented Programming
IUPAC	International Union of Pure and Applied Chemistry
MB	Methylene blue
COD	Chemical oxygen demand
PCP	Palm coir pith
CAC	Commercial activated carbon
UV	Ultra violet

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Two thirds of the dyes manufactured are consumed from the textile industries. The consequence of batch processes in the dye-manufacturing and the dye-consuming industries is coloured wastewater. Effluents are discharged directly from the two percent of dyes that are produced and the other 10 % lost is during the process of textile colouration. Commonly, about 10 to 200 mg/L of dye concentration contains in the wastewater, as well as other organic and inorganic chemicals used in the dyeing process (Doble and Kumar, 2005).

From the previous studies by the researchers, it was showed that around 15 % of produced synthetic dyes per year have been lost during manufacturing and processing operations that involve the production and handling with many organic compounds dangerous to human health. A very severe environmental problem caused from wastewaters originated from dye production and application industries because of the aesthetic nature due to fact that the colouration is visible even in a low dye concentration (Lewinsky, 2007).

Therefore, adequate treatment must be conduct to safeguard human health and the environment (Twardowska et al., 2004). In general, wastewater treatment methods can be broadly categorize into biological, physical and chemical (Forgacs et al., 2004). Yet, biological methods by itself are often unsuitable because of the low rates of biological degradation. For the physical treatment, also makes them unsatisfactorily effective and very costly due to the requested further treatment of generated secondary waste due to the regeneration of inactive adsorbents (Lewinsky, 2007).

Effluent characteristics like concentration of dye, temperature, pH, the economic involves, flow, volume and the social factor are factors that must be considered to choose the treatment for dye removal (Dwivedi et al., 2008). The current research explored its removal method based on adsorption technique. Adsorption is a process, which molecules or ions retained on the surface of solids by chemical or physical bonding. Adsorption appears to be an attractive process compared with other methods because of its high efficiency, easy handling, low cost and available for different adsorbents (El Qada et al., 2008). Reactive dyes can also removed from wastewaters by adsorption on various natural organic materials such as cellulose, sugarcane bagasse, rice husk, coconut husk and alternatively cheap adsorbents (Karcher et al., 2001).

Coir pith, a waste product obtained throughout the extraction of coir fibre from husk is filled with root stimulating hormones. Coir pith is very light, highly hygroscopic and highly compressible. There are a few application of coir pith. They are act as activated carbon, and after fungal degradation, they can be used as organic fertilizer and can be considered as a substitute for soil (NIIR Board of Consultants & Engineers, 2014). Since coir pith can act as activated carbon, hence this study is to investigate the performance of palm coir pith as adsorbent for the removal of methylene blue dye.

1.2 PROBLEM STATEMENT

Textile industry and its wastewaters is one of the main sources of severe pollution problems worldwide. In particular, the discharge of coloured effluent into the environment is undesirable, due to their colour and many dyes from wastewater are toxic or mutagenic to life (Santos et al., 2007). The total dye consumption of the textile industry worldwide is in excess of 10^7 kg/year, and an estimated 90 % of this ends up on fabrics. Consequently, 1000 tonnes/year or more of dyes are discharged into waste streams by the textile industry worldwide (Ahmad et al., 2007).

Adsorption is one of the processes, which other than being widely used for dye removal; also have wide applicability in wastewater treatment (Bansal and Goyal, 2005). The term adsorption refers to a process wherein a material is concentrated at a solid surface from its liquid or gaseous surroundings (Mishra et al., 2013). Among several chemical and physical methods, the adsorption is superior to other techniques. This is because it is sludgefree clean operation and removes the dyes completely even from a dilute solution (Malik, 2003).

The components of coir fibre are water soluble (5.25 %), pectin & related compounds (3.30 %), hemi-cellulose (0.25 %), cellulose (43.44 %), lignin (45.84 %) and ash (2.22 %) (NIIR Board of Consultants & Engineers, 2014). Coir is the fibre from the husk. The husk can be divided into coir fibres and coir pith or pulp, which is a coir dust that has been a waste product. Although the characteristics of coir pith is biodegradable but it can take up to 20 years to decompose (Resh, 2012). Hence, for the palm coir pith, it is the same part as coconut coir pith but for different plant, which is palm.

1.3 OBJECTIVES

The objectives of this study are:

(i) To investigate the potential of palm coir pith with different pyrolysis temperature in adsorbing methylene blue.

(ii) To study the acidity and clarity of methylene blue solution after being treated with palm coir pith adsorbents.

1.4 SCOPE OF STUDY

The scope of this study is the adsorbent used for removal of methylene blue in this study is by using palm coir pith. Palm coir pith was collected from Kilang Sawit Lepar Hilir, Gambang, Pahang. For the preparation of palm coir pith adsorbent, there are two types of actication process. The first one is chemical activation process by using 13 M of sulphuric acid to prepare acid-activated palm coir pith adsorbent. Second, is physical treatment or called as thermal treatment. For thermal treatment, the palm coir pith was pyrolyzed at different temperature and activation time, which are 300 ^{o}C in 1 hour, 300 ^{o}C in 4 hours, 400 ^{o}C in 4 hours and 600 ^{o}C in 4 hours. Laboratory testing was done to determine the acidity and clarity of methylene blue solution after being treated with palm coir pith adsorbents. For methylene blue analysis, the wavelength used was 665 nm by using UV-Visible Spectrophotometer.

1.5 SIGNIFICANT OF STUDY

This study should be done to determine whether palm coir pith can be used as an adsorbent to remove dyes from textile wastewater. The adsorption process provides an attractive alternative treatment, especially if the adsorbent is economical and readily available. The activated carbon is the most popular adsorbent and has been used with great achievement. The investigation of performance of palm coir pith as an activated carbon can be used in filtration process to treat polluted water.

By using palm coir pith as an activated carbon, the cost of treatment process can be decrease and this method is simple than the usual water treatment in our country. Furthermore, this research can help industry to improve their treatment process especially for wastewater treatment, removal of heavy metal and nocuous ion or dye removal.

This project should help the society since dye waste is one of the reasons of human illness and environmental degradation. All the organic materials present in wastewater from a textile industry are at great concern in water treatment because they counter with many disinfectants mainly chlorine. Those chemicals in water will be evaporated and mix with the air we inhale or being absorbed through our skin. Later, it will show up as allergic reactions and may cause damage to children even before birth (Kant, 2012). Thus, this project is relevant to human safety, health and environment.

CHAPTER 2

LITERATURE REVIEW

2.1 DYE

Dyes are extremely coloured substances that can be used to create a significant degree of coloration when dispersed in or reacted with other materials by a process which, at least shortly, destroys the crystal structure of the substances. This latter point distinguishes dyes from pigments that are usually applied in an aggregated or crystalline- insoluble form. The products of synthetic organic chemistry are called as modern dyes. Dyes need to have high colour intensity and produce dyeing of some permanence to be a commercial interest. The degree of permanence compulsory differs with the end use of the dyes material (NPCS Board of Consultants & Engineers, 2009).

The characteristics of dyes with relation to the properties of the materials to be dyes must reflect by both the dyer and the dye manufacturer. In overall, dyes must be selected and applied so that, colour excepted, a least of change is produced in the properties of the substrate. It is required, therefore, to consider the chemistry of textile fibres as a background for an understanding the chemistry of dyes (NPCS Board of Consultants & Engineers, 2009). Almost all of the dye compounds commonly used for dyeing textile fibres has these characteristics. They are first, can absorb very strongly at wavelengths in the visible spectrum. Second, they are composed of polyaromatic compounds and water soluble in their applied form; except for disperse dyes, vat dyes and pigments. Next, they are substantive to certain fibres and are resistant to biological degradation. The last characteristics means that dyes passed out in textile effluents are slight affected by conventional biological waste treatments (Christie, 2007).

Textile dyes can be categorized in numerous ways. Previously, the dyes were divided into (a) Natural dyes, the dyes extracted from vegetable and animal resources and primarily used in textile processing until 1856, and (b) Synthetic textile dyes, which were originally discovered in 1856. Recently, textile dyes are mainly classified in two different categories, which are based on their application characteristics and based on their chemical structure. Examples of textile dyes based on their application characteristics are Colour Index (CI) Generic name such as mordant, acid, direct, basic, reactive, disperse, azo insoluble, pigment, vat and sulphur dye. Next, examples of textile dyes based on their chemical structure are Constitution Number (CI) such as azo, nitro, diphenylmethane, carotenoid, acridine, xanthene, indamine, quinolone, amino- and hydroxyl ketone, sulphur, indigoid, anthraquinone, inorganic pigment, phthalocyanine, etc. (Malik et al., 2013).

Although dyes are useful, but it can be categorized as problematic compounds because they can contaminate the environment otherwise they been treated nicely. Dye is water-soluble and cannot be remove simply from the wastewater although using biological wastewater treatment (Panswad and Luangdilok, 2000; Forgacs et al., 2004). There are two key of dye molecule, which are the chromophores and auxochromes. Chromophores are used for produce the colour and auxochromes to give the molecule soluble in the water and increased affinity toward the fibres. Figure 2.1 presents example of the presence of chromophores and auxochromes in Basic Blue 9 while Table 2.1 shows the properties of dye and usage.

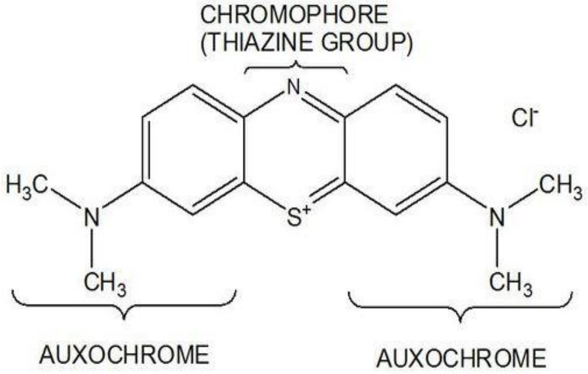

Figure 2.1: Example of the presence of chromophores and auxochromes in Basic Blue 9

Source: Lachheb (2002)

Table 2.1: Properties of dye and usage

Type of dye	Usage	Principle Chemical Classes
Acid dyes	Nylon, wool, silk, modified acrylics and to some extent for paper, leather, ink-jet printing, food and cosmetics.	Azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro.
Cationic dyes	Paper, polyacrylonitrile, modified nylons, modified polyesters, cation dyeable polyethylene terephthalate and to some extent in medicine.	Diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine and acridine.
Disperse dyes	Mainly on polyester and to some extent on nylon, cellulose, cellulose acetate and acrylic fibres.	Azo, anthraquinone, styryl, nitro and benzodifuranone groups.
Direct dyes	Dyeing of cotton and rayon, paper, leather and to some extent to nylon.	Polyazo compounds, along with some stilbenes, phthalocyanines and oxazines.
Reactive dyes	Cotton and other cellulosics, but are also used to a small extent on wool and nylon.	Azo, anthraquinone, triarylmethane, phthalocyanine, formazan, oxazine, etc.
Solvent dyes	Plastics, gasoline, lubricants, oils, and waxes.	Predominantly azo and anthraquinone, but phthalocyanine and triarylmethane are also used.
Sulphur dyes	Cotton and rayon and have limited use with polyamide fibers, silk, leather, paper and wood.	Have intermediate structures.
Vat dyes	Cotton mainly to cellulosic fibers as soluble leuco salts and for rayon and wool too.	Anthraquinone (including polycyclic quinones) and indigoids.
Mordant dyes	Wool, leather, natural fibers after pretreating with metals and anodized aluminium.	Azo and anthraquinone.

Source : Christie (2007)

2.1.1 Classification of Dyes

Dyes, are classified according to application method, for the convenience of the dyer. The best classification method available is that used in the CI, a publication sponsored by the society of dyers and colourists (England) and the American Association of Textile Chemist and Colorists (NPCS Board of Consultants & Engineers, 2009).

2.1.1.1 Acid Dyes

Acid dyes are used on silk, wool (protein fibres), and some rayon and synthetic (noncellulosic) fibres. They are made of diverse colour-imparting chemical groups, such as azo or anthraquinone chemicals that are bound to a sulfonic acid group. The sulfonic acid percentage of the molecule has affinity to the basic amino groups originate in these fabrics. During the process, the dye is made more acidic with sulphuric, acetic or formic acid baths to rise the dye’s affinity to fabric (Greenberg, 2003). These dyestuffs involve an acidic solution to charge the positive ions onto the fibre. They show decent colourfastness, although appropriateness of use is variable, meaning the dye must be used selectively according to the textile end-use (Nielson, 2007). Example of acid dyes is Acid Yellow 36 (metanil yellow) structure shown in Figure 2.2 below.

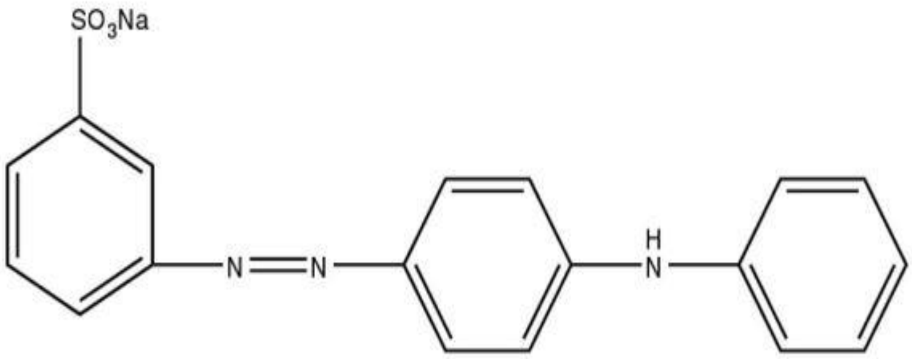

Figure 2.2: Acid Yellow 36 (metanil yellow) structure

Source: Sabnis (2007)

2.1.1.2 Basic Dyes

Basic dyes or cationic dyes are used for fabrics with protein fibres (wool and silk) and cellulose fibres mordant with tannic acid. Some of these dyes may be related with allergic skin reactions. Example of basic dyes that are suspected carcinogens are Basic Orange 2 and Basic Violet 10 (Greenberg, 2003). Basic dye owe their name to the presence of aromatic amino (basic) groups, and in this case a cationic amino group is present. Normally, they have outstanding brightness and colour strength, especially among the triarylmethane types. Figure 2.3 shows the structure of Basic Blue 22 as a basic dye while Figure 2.4 shows the structure of Basic Violet 3 that has a mobile cation that produces resonance structures of comparable energy (Kent, 2010).

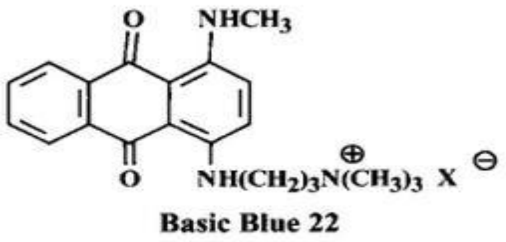

Figure 2.3: Structure of Basic Blue 22

Source: Kent (2010)

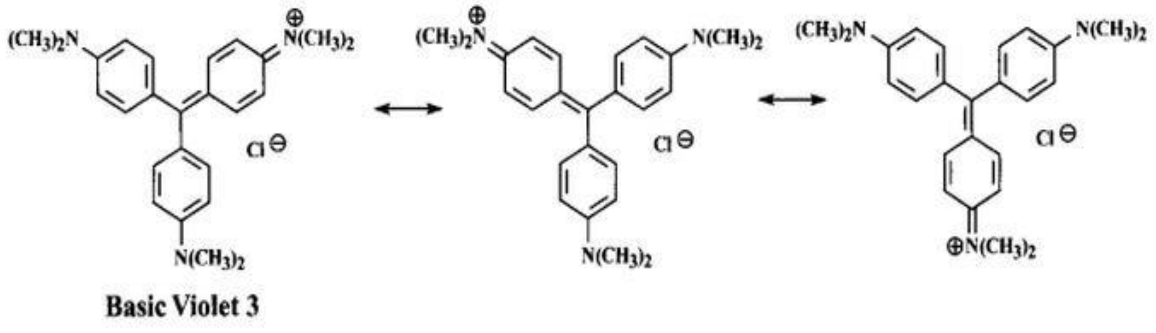

Figure 2.4: Structure of Basic Violet 3 has a mobile cation that produces resonance structures of comparable energy

Source: Kent (2010)

2.1.1.3 Direct Dyes

Direct dyes are anionic materials. They are very alike to acid dyes but with greater molecular weight. They are applied to pure cellulosic substrates from neutral to weakly alkaline baths (pH 8) or to blends from weakly acidic baths (pH 6) by a certain procedures. These dyes require only about 2-20 g/L of salt, typically common salt or Glauber's salt. If proper temperature and salt concentrations are used, dye bath exhaustion is typically 85% or better. Direct dyes bind to cellulose at nonspecific dye sites on the surface of naturally occurring crystalline areas within the fibre. The binding mechanism is hydrogen bonding or van der Waals forces. This provides for weak binding (typically 2 kcal/mol). Normally, direct dyes have low aquatic toxicity and better solubility. Some of direct dyes, contain metals which is notably turquoise and green dyes (Andrady, 2003).

Most of direct dyes do not have good washfastness and lightfastness. Their dyeings on cotton are often treated with a chemical agent, in what is normally known as after treatment process. There are three most generally used after treatment methods which are cationic fixatives, copper sulfate or diazotization and coupling reactions. Cationic fixatives and diazotization and coupling reactions are designed to boost washfastness and are illustrated in Figure 2.5 (Kent, 2010).

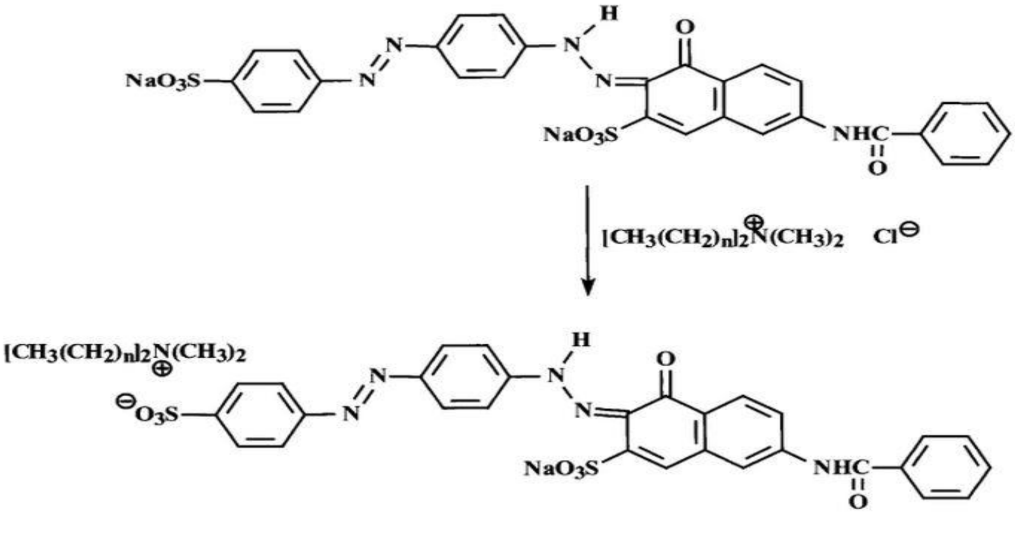

Figure 2.5: Use of a cationic fixative to enhance direct dye washfastness

Source: Kent (2010)

2.1.1.4 Mordant Dyes

Mordant dyes require a pre-treatment of the fibre with a mordant material designed to bind the dye. The mordant becomes attached to the fibre and then chains with the dye to form an insoluble complex called a “lake”. An example of a mordant is aluminium hydroxide that has been precipitated on cotton fibre. This mordant is proficient of binding such dyes as Mordant Red 11 in Figure 2.6 by formation of an aluminium “lake”. Mordant dyes have weakened in importance mainly because their use is no longer necessary. Equal or superior results can be obtained with other classes of dyes at less expense in time and labour (NPCS Board of Consultants & Engineers, 2009).

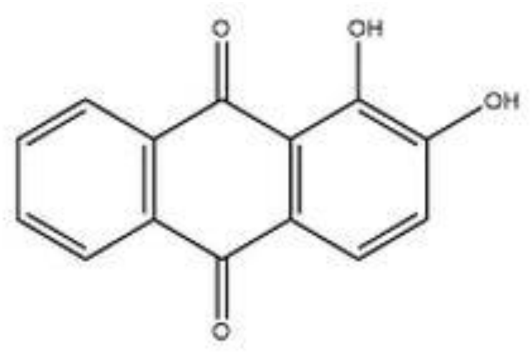

Figure 2.6: The structure of Mordant Red 11

Source: Sabnis (2007)

Mordant dyes are used on acrylic, some olefins, rayon, wool, silk and polyesters. This dye type ionically charges or adheres to metallic substances rather than to the fibre, so the fabric may be pre-treated with a mordant, which is a metal compound. A multiplicity of mordant dyes is known as premetalized dye when the dyestuff is varied with the metallic substance, removing the need to pre-treat with metalized solution. Colourfastness rises during cleaning. Mordant dyes are good for lightfastness too. Colours are dull rather than brilliant (Nielson, 2007). The mordant commonly used are potassium aluminium sulphate (alum), ammonia, oxalic acid, tannic acid (tannin) etc. The adverse effects of these agents include allergic sensitization, skin and mucous membrane irritation, and possible carcinogenesis (Greenberg, 2003)

2.1.1.5 Vat Dyes

Vat dyes are insoluble. They are reduced with sodium hydrosulphite in intensely alkaline medium to give a soluble form that has affinity for cellulose. This decreasing process was formerly carried out in wooden vats, giving rise to the name vat dye. The original insoluble dye is reformed by oxidation with air or chemicals after the reduced dye has been absorbed in fibre. The dyeing formed in this way are very fast to washing, and, in most cases, the dyes are intended to be fast to light and bleaching as well (NPCS Board of Consultants & Engineers, 2009).

Vat dyes have mainly anthraquinone (82 %) or indigoid/thiondigoid (9 %) structures, with the former having much better fastness properties. The anthraquinone vat dyes exhibit a bathochromic colour shift upon reduction to their leuco forms, whereas the indigoids exhibit a hypsochromic shift. Example of the two structural types is shown in Figure 2.7. Anthraquinone vat dyes having a single anthraquinone unit exist; however, those with the best fastness properties seem to have the equivalent of two anthraquinone units (Kent, 2010).

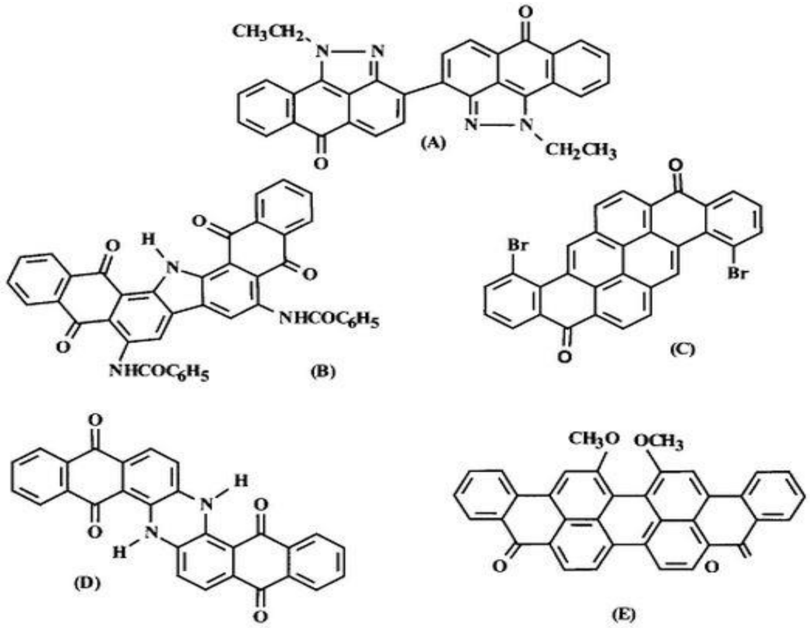

Figure 2.7: Representative anthraquinone vat dye structure: CI Vat Red 13 (A), Vat Black 27 (B), Vat Orange 2 (C), Vat Blue 4 (D) and Vat Green 1 (E)

Source: Kent (2010)

2.1.1.6 Azo Dyes

Azo dyes are produced inside textile fibres, usually cotton, by azo connection. The dye is firmly occluded and is fast to washing. A variation of hues can be obtained by proper select of diazo and coupling components. In the usual process for the development of azoic dyes, the fibre is first impregnated with an alkaline solution of the coupling component. Next, they are treated with a solution of the diazonium compound. Finally, the dyed goods are soaped and rinsed. The diazonium compound may be produced in the dyehouse by diazotization of the azoic diazo component, or it may be obtained as a stabilized complex for ready for use. Zinc double salts, diazoamino compounds and nitrosamines are examples of stabilized diazonium complexes (NPCS Board of Consultants & Engineers, 2009).

Azoic dyes are also known as naphthol dyes, because all employ a naphthol component in their formation. They also can be produced in batch or continuous processes. They are best known for their capability to provide cost-effective wet fast orange and red shades on cotton. A generic azoid dye structure is shown in Figure 2.8 (Kent, 2010).

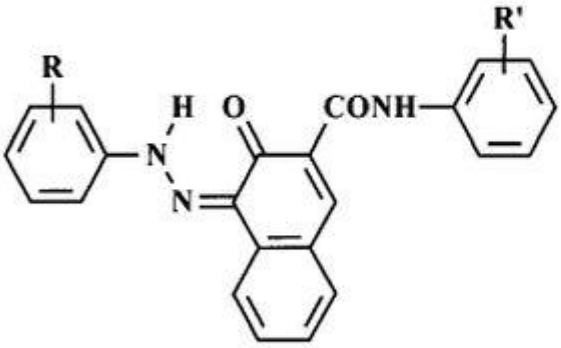

Figure 2.8: Generic structure for azoid dyes, where R and R'=alkyl, alkoxy, halo and nitro groups

Source: Kent (2010)

Special techniques have been developed for the use of azoic dyes on synthetic fibers. It is sometimes possible to apply both the diazo component and the coupling component simultaneously from aqueous dispersion (NPCS Board of Consultants & Engineers, 2009).

2.1.1.7 Sulfur Dyes

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Sulfur dyes are insoluble dyes which must be reduced with sodium sulphide before use. They are soluble and show affinity for cellulose in the reduced form. They dye by adsorption, as well as the direct dyes, but they are oxidized to reform the original insoluble dye inside the fiber upon contact to air. Thus, they become very resistant to removal by washing unlike the direct dye (NPCS Board of Consultants & Engineers, 2009).

Due to tremendously low solubility, the accurate structures of most sulphur dyes remain unknown. Much of what we know about sulphur dye structures ascends from the characterization of certain degradation products or reaction precursors. Based on that, it has been conceivable to determine that structures of the type shown in Figure 2.9 are covered in this dye class. A key common feature of sulphur dyes is the existence of sulphide ($-S_n-$) bonds. This feature makes dye application from an aqueous medium possible (Kent, 2010).

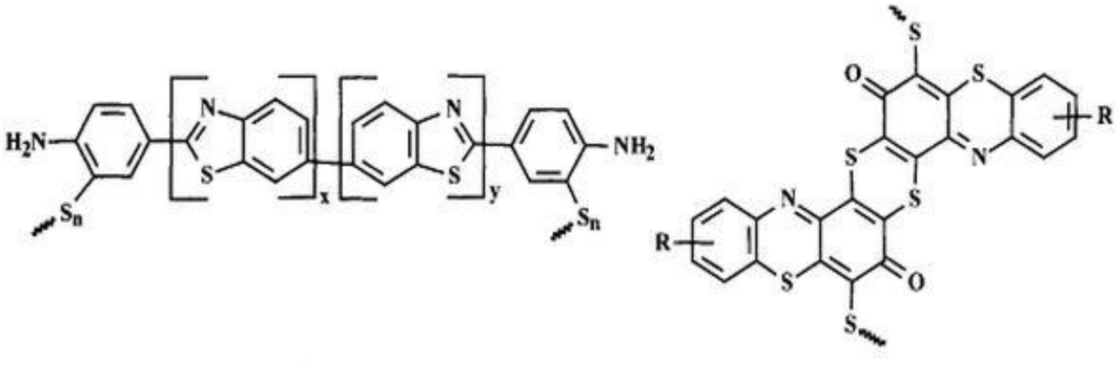

Figure 2.9: Examples of sulphur yellow (left) and red (right) dye structures

Source: Kent (2010)

The reaction of sulphur dyes with sodium sulphide (Na_2S) at $pH > 10$ effects the reduction of the sulphide bonds, giving their water-soluble forms. The reduced forms act like direct dyes, in that they exhaust onto cotton in the existence of salt. The reduced dyes are reoxidized to their water-insoluble forms once applied, hence, giving dyeings with good washfastness (Kent, 2010).