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นางสาวกาญจนา ลือพงษ์

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INVESTIGATION ON REMOVAL OF RESIDUAL DYESTUFF IN EFFLUENT FROM YARN DYEING PROCESS BY PHYSICAL AND CHEMICAL METHODS

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ในการศึกษานี้แบ่งการศึกษาออกเป็น 2 ทฤษฎี โดยมีวัตถุประสงค์หลักในการลดความเข้มของน้ำสีที่เหลือจากขบวนการฟอกย้อม ทั้ง 2 วิธีการนี้คือการบำบัดด้วยวิธีทางเคมีโดยอาศัยปฏิกิริยาออกซิเดชันและปฏิกิริยารีดักชัน ในการทำลายพันธะของโครงสร้างที่มีสี ส่วนวิธีทางกายภาพจะอาศัยการดูดซับโดยผ่านตัวถ่านกัมมันต์ ตัวแปรที่เกี่ยวข้องในการศึกษานี้ได้แก่ ผลของสารช่วยย้อม ความเข้มของสี สภาวะของน้ำย้อม และประเภทของสีที่ใช้ในการศึกษา

ในการบำบัดด้วยวิธีทางเคมีปัจจัยที่มีผลต่อการบำบัดคือโครงสร้างสี และลักษณะเฉพาะตัวของสี การกำจัดสีจะอาศัยปฏิกิริยารีดักชันในการเปลี่ยนโครงสร้างมีสีในแต่ละตัวสี โดยการสลายพันธะคู่ทำให้เกิดโครงสร้างที่ไม่มีสี สารรีดักชันที่ใช้ในการทดลองคือ โซเดียมไดไธออไนท์ (Sodium dithionite) ประสิทธิภาพการบำบัดเรียงตามประเภทของสีได้ดังนี้ สีไดเร็กท์ > สีแอซิด > สีรีแอคทีฟ > สีเบสิค > สีดิสเพิร์ส เวลาในการบำบัด 30 นาที ส่วนการบำบัดทางกายภาพปัจจัยที่มีผลได้แก่ สภาวะของน้ำย้อม เวลาที่ใช้ในการกรอง และปริมาณถ่านกัมมันต์ ในการศึกษาพบว่าสภาวะที่ดีที่สุดในการกรองคือสภาวะที่เป็นกรด ใช้เวลาในการกรองอยู่ที่ 1-2 ชั่วโมง ปริมาณถ่านกัมมันต์ 100-200 กรัม/น้ำเสีย 1 ลิตร ประสิทธิภาพการบำบัดสามารถเรียงประเภทของสีได้ดังนี้ สีเบสิค > สีแอวิด > สีดิสเพิร์ส > สีไดเร็กท์ > สีรีแอคทีฟ แต่อย่างไรก็ตาม การเลือกวิธีการบำบัดแบบใดนั้น จะมีความแตกต่างกันไป ขึ้นอยู่กับขนาดของโรงงาน ปริมาณน้ำย้อมที่ปล่อยออกมาและค่าบำบัดต่อหน่วยที่เกิดขึ้น

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต
สาขาวิชา วิศวกรรมเคมี ลายมือชื่ออาจารย์ที่ปรึกษา
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KEY WORD: DYESTUFF/ EFFLUENT / DECOLOURATION/ PRETREATMENT

KANCHANA LUEPONG : INVESTIGATION ON REMOVAL OF RESIDUAL DYESTUFF IN EFFLUENT FROM YARN DYEING PROCESS BY PHYSICAL AND CHEMICAL METHODS.THESIS ADVISOR: ASST. PROF. SASITHORN BOON-LONG, Dr.3eme Cycle, THESIS CO-ADVISOR : PHICHITPHOL JAROENSAPYANANT, 114 pp. ISBN: 974-17-4128-6

In this experimental study two methods of pretreatment of effluents from dyeing processes were investigated. The main objective was to reduce the colour strength of the effluents. The first method was chemical pretreatment using oxidation and reduction to destroy the conjugate double bonding system of the chromophore structure. The other method was the physical pretreatment using activated carbon to adsorb the colourant. The parameters studies were chemical auxiliaries, colour strength, conditions and types of dyestuff.

Results of chemical pretreatment showed that the factors effecting the reaction were dye structure and characteristics of the dyes. The removal of colour strength was achieved by using reduction reaction to change the chromophore structure of each dyestuff by destroying the conjugate double bonding system forming non chromophore structure. Sodium dithionite was used for reduction. It was found that colour strength removal efficiency is direct >acid > reactive > basic > disperse. The reduction time was 30 minutes. Factors effecting the physical treatment were conditions of the dyeing solution, time of treatment and height of activated carbon. It was found that the most suitable solution condition was acidic in nature, time of contact between 1-2 hours and amount of activated carbon is 100 – 200 gram/liter of dye effluent. The dye removal efficiency is basic > acid > disperse > direct > reactive. However, the choice of treatment method varies, depending on the size of the plant, amount of effluent released and unit cost of treatment.

Department	Chemical Engineering	Student's signature…………………………...
Field of study	Chemical engineering	Advisor's signature………………………..
Academic year	2003	Co-advisor's signature…………………….

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Finally, I would like to express my deepest thanks to my lovely family, my brothers and my sister for their helpfulness, care and endless encouragement.

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CHAPTER I

INTRODUCTION

Since the establishment of the synthetic dye industry with Perkin's synthesis of mauvein in 1856, generations of chemists have applied their minds to the challenge of designing dyes for an ever-widening range of fibre substrates and application methods. The large number of dyes in use today bears witness to their creativity and innovation in successfully meeting this challenge and satisfying the dyer's demands for simple, reproducible application processes, and the consumer's need for quality products of reasonable price.

Dyes are required to show a high degree of chemical and photolytic stability in order to fulfil the fastness requirements of both retails and consumers. One sequence of this stability is that they are not readily degraded under the aerobic conditions prevailing in the biological treatment plant at a sewage treatment works. The impacts of dyes on the environment is

1. Toxic to stream life
2. Oxygen depletion in stream water
3. Physical impletion of stream condition
4. Preventing the dispersion of light on the stream so that water plant can not synthesize light.

Table 1 Effluents from Dye Manufacturing

(milligrains per liter, except for pH)   Parameter Maximum value

pH	6-9
BOD	30
COD	150
TSS	50
Oil and grease	10
Phenol	0.5
Chromium (hexavalent)	0.1
Copper	0.5
Zinc	2
AOX	1
Toxic organics such bezidine (each)	0.05

Note: Effluent requirements are for direct discharge to surface waters

At the present time, textile activities are in constant expansion showing a high pollutant potential. They have long been a large and important group of industrial chemicals, and are used in many products such as paper, leather, and foodstuffs.

Dye effluents are extremely variable in composition, due to the large number of dyes and other chemicals used in dyeing processes. Dyes often receive the most attention from researchers interested in textile effluents treatment process because of their colour, as well as the toxicity of the raw materials used to synthesize dyes.

There are in the region of 3,000 different dyes available on the commercial market, and more than half of these dyes are azo compounds and derivatives followed by groups of dyes with a common structure element containing, e.g. an anthraquinone, triphenylmethyl-methane or phatalocyanine moiety. The biological activity of dyes can differ greatly in spite of their similar structure, so their toxicological properties cannot be generalized by reference to one group only.

One of the major factors determining the release of a dye to the environment is its degree of fixation on the substrate. Since fixation is clearly dependent on individual circumstances and governed by several factors including depth of shade, application method and liquor ratio. It is therefore impossible to give a definitive set of it. Table 2 represents the summary of the data available.

Table 2 Estimated degree of fixation for different dye/fibre combination

Dye Class	**Fibre**	**Degree of Fixation (%)**	**Loss to effluent (%)**
Acid	Polyamide	80-95	5-20
Basic	Acrylic	95-100	0-5
Direct	Cellulose	70-95	5-30
Disperse	Polyester	90-100	0-10
Reactive	Cellulose	50-90	10-50
Sulphur	Cellulose	60-90	10-40
Vat	Celllulose	80-95	5-20

The problem of coloured effluent has become identified particularly with the dyeing of cellulose fibres (notably cotton, which accounts for almost 50% of the total fibre consumed by the textile industry worldwide). For all dye/fibre combinations the degree of fixation decrease with increase depth of shade.

In Thailand there are 4554 textile plants, 355 of which are dyeing processing plants. More than 24% of the textile plants are situated in Bangkok area, about 33% in Samut Prakarn and 25% in Samut Sakorn and Nakorn Pratom area. Most of the plants are situated in a very populated environment with the country’s important rives flowing through them.

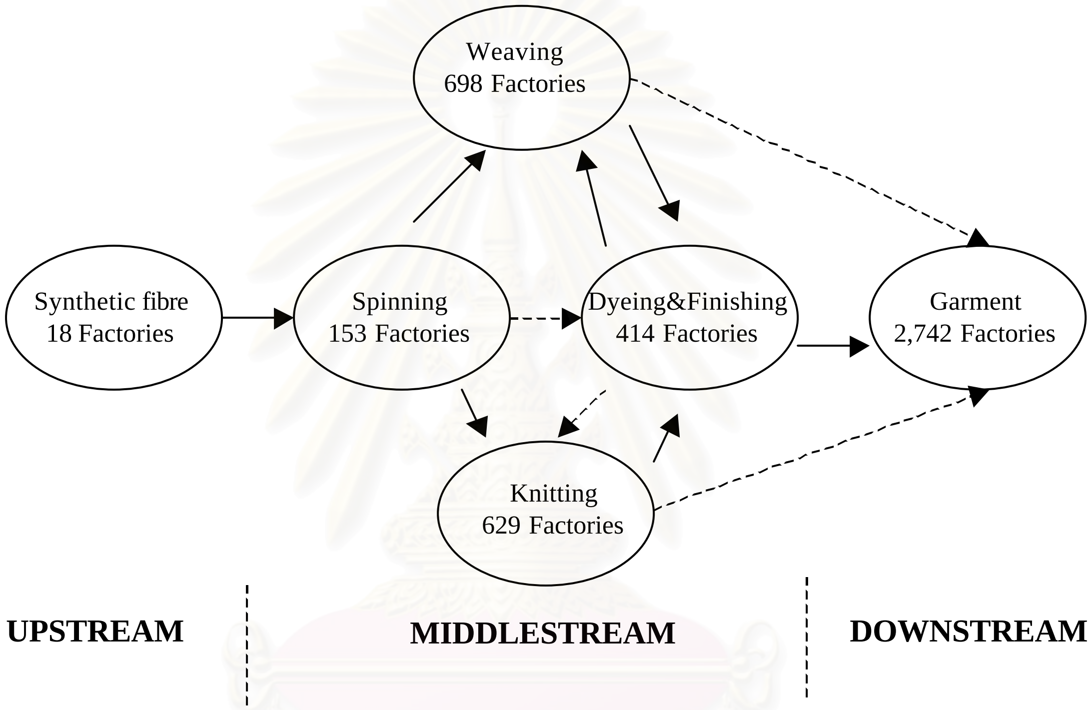


Figure 1 Textile Industry in Thailand
(Source: www.thaitextile.org, January 2003)

From the impact of wastewater emerging from dyeing processes on the environment mentioned earlier, it is found that this problem is difficult to solve. Treatment of wastewater to remove dyestuff in effluents using many methods have been attempted, however the cost of treatment is still high and at present there are many types of dyes and treatment differs on the type of dye used.

Objectives of the work

The main objective of the present work is to carry out a series of experiments to remove residual dyestuff in effluents from dyeing processes by physical and chemical methods.

The main objective can be broken down into the following:

1. To develop the experimental techniques necessary to carry out the experiments.
2. To select suitable adsorbent and oxidizing agent or reducing agent for use in the experiments.
3. To study the effect of colour strength of the dyes used in the dyeing process.

Scope of the work

In order to achieve the objectives mentioned above, the physical pretreatment experiments were carried out in the apparatus shown in Figure 8. Activated carbon was used as the adsorbent. While, chemical pretreatment experiments were carried out using standard glassware in the laboratory. The oxidizing agent used were Hydrogen peroxide (H_2O_2 , 50% w/w) and Sodium hypochlorite (NaOCl), and the reducing agent used was Sodium dithionite (hydro) ($Na_2S_2O_4$). The effluents employed were from various dyeing processes. The effluents can be categories into two types, those with auxiliaries and those without auxiliaries.

CHAPTER II
LITERATURE REVIEW AND METHOD

2.1 Literature Review

One of the earliest studies reported on the use of the Andco electrochemical system to treat textile wastewater was by Demmin and Uhrich. Their studies, which focused on the treatment of effluent from dyebaths containing a variety of classes of dyestuffs using an iron cell, achieved reductions in biochemical oxygen demand (BOD), Chemical oxygen demand (COD), total suspended solids (TSS), heavy metals, and colour, with efficiencies as high as 90%.

Tincher, Weinberg, Stephens and Weinberg used the same technology to study the decontamination of simulated acid dyebaths, simulated solutions of stain-blocking agents (in which a “phenolic resin” was the main active ingredient), influent to a treatment plant, effluent from a carpet dyeing facility, and effluent from a wastewater treatment plant. An iron cell, which was shown to remove acid dyes at an efficiency of more than 80%, was used. A greater percent colour removal occurred following treatment of the mill effluent than following treatment of the influent, although it was not clear whether that difference was real or it was the result of an experimental error. The authors reported reductions in COD and organic contaminants, as well as in stain-blocking agents, from the carpet dyeing facility.

Following a study on the potential for recycling electrochemically treated disperse dye effluent, Wilcock and Hay reported substantial decolourization and detoxification of disperse dye effluent following treatment with iron electrodes. Reuse of the treated effluent (following up to eight consecutive laboratory dyeings) resulted in first-quality dyeings.

A paper by Wilcock, Brewster, and Tincher reported results from three case studies in which the Andco system effectively decolourized effluents containing metal complex disperse, and acid dyestuffs. The case study that involved the removal of metal complex dyestuffs confirmed the removal of chromium irons as well as the dyestuffs. The studies that focused on disperse and acid dyes demonstrated the success of reusing the treated dyebaths, a strategy that can significantly minimize the quantity of effluent discharged into the environment without compromising dyeing quality.

A study by McClung and Lemley considered the mechanism by which electrochemical treatment might occur and attempted to identify the breakdown products that could be released into the environment or be contained within the recycled decolourized effluent. Using high-performance liquid chromatography (HPLC) techniques, these researchers determined that the electrochemical removal of pure dye from an aqueous solution resulted from adsorption and/or degradation of the dyestuff itself, following interaction with iron electrodes. In the same study, degradation of one of the two azo dyes that were studied resulted in the formation of aniline. The degradation products of the second azo dye studied were not characterized. No breakdown products were found in the decolourized effluent that originally contained an anthraquinone dyestuff. No attempt was made to examine the efficacy of electrochemical treatment of the non dyestuff components normally found in a commercial dyestuff formulation.

Wilcock and co-workers treated disperse dye effluent with an aluminum cell instead of more common iron cell and reported that the mechanism by which decolourization occurred involved physical adsorption rather than dye degradation. The difference between the integrity of the colourants in this study and the dye degradation reported by McClung and Lemley was explained by the choice of electrode in the two studies. The aluminum electrodes cannot act as a reducing agent since aluminum enters solution in a single valence state. In contrast, the iron electrodes used by McClung and Lemley cause the release of ferrous iron, which is capable of acting as a reducing agent to cause dye degradation. The results of the aluminum study further indicated that quinolone dyes were easier to decolourize than either anthraquinone or azo dye, and that dyes with similar chemical structures reacted in a similar manner to electrochemical treatment. Dispersing agents of the lignin sulfonate type were shown to be more completely removed from the effluent along with the disperse dyes than were those of the naphthalene sulfonate type. The authors concluded that colourant, dispersing agent, and other components of commercial dyebath formulations probably all influence the efficacy of electrochemical treatment.

Nilsun H. Ince studied for critical effect of hydrogen peroxide in photochemical dye degradation by advance oxidation processes (AOP) catalyzed by a source of UV light and a powerful oxidant is a promising alternative for the effective removal of colour and refractory organics from the effluent. A crucial feature in designing such systems is the optimization of operating conditions (such as UV and oxidant dosages), which yield maximum removal at acceptable costs. The present study describes a modeling approach to keep the oxidant dosage at the most effective level to sustain maximum rate of dye removal at the selected experimental conditions. The method of study involved monitoring the rate of dye degradation in a synthetic azo dye solution of nearly constant concentration during irradiation by a medium pressure light source and varying H_2O_2 dosages, followed by predicting a mathematical relation between the pseudo-first order rate constant and the effective H_2O_2 to dye, or the light fraction absorbed by hydrogen peroxide within the UV emission spectra of the light source.

Keith K.H. Choy, Gordon Mckay, John F.Porter studied the adsorption of three acid dyes, namely, Acid Red 114, Polar Yellow and Polar Blue RAWL, onto activated carbon. Equilibrium isotherms were measured for three single component systems (AB, AR, AY) and one binary component system (AB + AY). The isotherms were determined by shaking 0.05 g activated carbon, particle size range 500 – 710 μm, with 0.05 dm^3 dye solution of initial concentrations from 10 to 250 mg/dm^3. A constant temperature agitating 400-rpm shaking water bath was used and the temperature maintained at 20±2 ^oC. A contact time of 21 days was required to achieved equilibrium. Analysis of data was carried out in two stages. (a) In single component analysis, the experimental isotherm data were analyzed using Langmuir, Freundlich, Redlich-Peterson, Temkin and Dubinin-Radushkevich equations for each individual dye. The monolayer adsorption capacities are 101.0 mg Acid Red per g carbon , 100.9 mg Acid Blue per g carbon and 128.8 mg Acid Yellow per g carbon. (b) In multi component analysis, one binary system has been analysed using an extended from of the Langmuir equation. The correlation between theoretical data and experimental data had limited success due to competitive and interactive effects between the dyes and dye-surface interactions.

Jiasheng Cao Liping Wei, Qingguo Huang Liansheng Wang, Shuokui Han presented the reducing degradation kinetics of five azo dyes, Acid orange II, Acid orange GG, Acid red 3B and Orange I, by zero-valent iron power in aqueous solution. It showed that the degradation is a two-step reaction, with the first step being reversible. Solution acidity and iron surface area are the factors greatly influencing the degradation rates, and with increasing acidity and iron surface area, the degradation rates increase.

L.C.Morais, O.Mfreitas, E.P.Goncalves, L.T.Vasconcelos and C.G. Gonzales Beca attempted to solve the pollution problem caused by the presence of reactive dyes in textile effluents, was undertaken. Owing to the fact that eucalyptus bark is a very abundant and inexpensive forest residue in the authors' country, Portugal, it was decided to experiment with it as a potential adsorbent for a certain type of the supra cited pollutants used in cellulose fibres dyeing (Remazol BB). In order to study the variables that define the process, 2^4 and 2^5 factorial experimentations were carried out, in two stages. In the first one, the variables selected were: temperature, initial pH, sodium chloride concentration and initial dye concentration/bark concentration ratio. Tests showed that the last parameter did not describe the adsorption process, another stage followed, keeping the first three variables and substituting initial dye concentration and bark concentration separately for their ratio. It was verified that all the variables studied had significant influence on the adsorption process at a level of 1% probability. The influence order was: initial dye concentration > bark concentration > initial pH > sodium chloride concentration > temperature. Parallel adsorption tests, under similar conditions, carried out with a commercial activated carbon and with eucalyptus bark, showed the adsorption capacity of eucalyptus bark to be about half of that of the activated carbon. It is considered that the results obtained are quite encouraging, though there is still a long way to go before definitive conclusions may be drawn.

2.2 Methods of Wastewater Pretreatment

Dye wastewater are extremely variable in composition, due to the large number of dyes and other chemicals used in dyeing processes. In general, the composition of a particular wastewater, in addition to site-specific conditions, dictates the most appropriate treatment method. Detailed wastewater characterization is therefore, an integral step in selecting wastewater treatment methodologies. Dyes often receive the most attention from researchers interested in textile wastewater treatment processes because of their colour, as well as the toxicity of some of the raw materials used to synthesize dyes (e.g., certain aromatic amines used to produce azo dyes) however, they are often not the largest contributor to the waste stream.

Pretreatment processes in the textile dyeing industry are generally designed to remove colour from the wastewater . The methods for wastewater pretreatment are

1. Physical pretreatment: such as sedimentation, filtration and adsorption. The advantage of these are high efficiency but use a long time and high cost for maintenance.
2. Chemical pretreatment: such as neutralization by using chemical adjustment. This method uses shorter time but contaminants remained in the treated wastewater
3. Biological pretreatment: such as using bacteria to digest the organic compound. Although this method is friendly, but it cannot reduce the colour of the effluent and is not suitable for use in the textile industry.

2.2.1 Physical pretreatment

Physical pretreatment is the most used adsorption pretreatment method. There are many types of adsorbents used, but the most well known is activated carbon (AC).

Activated carbon is the generic term used to describe a family of carbonaceous adsorbents with a highly crystalline form and extensively developed internal pore structure. A wide variety of activated carbon products is available exhibiting markedly different characteristics depending upon the raw material and activation technique used in their production. In selecting an activated carbon, it is important to have some understanding of its characteristics. Many natural substances of base materials are used to make activated carbon. The most common of these are wood, coal, lignite, and coconut shell. The base material is first subjected to a heating process called carbonization. This initial treatment forms a fixed carbon mass full of tiny pores. The carbonized base material is then activated by a second heat - steam treatment (200-1600 ^{o}C) while regulating oxygen and carbon dioxide levels. Activation creates a fast internal pore network and imparts certain surface chemistries (functional groups) inside each particle. Thus activation gives carbon its unique filtering characteristics. The carbon product may be supplied as granular activated carbon (GAC), powdered activated carbon (PAC), or in pelleted form (compressed PAC). Some carbons are activated or washed with phosphoric acid, zinc chloride, or potassium hydroxide. These chemically treated activated carbons are unsuitable for use in the aquarium. These products could leach phosphate (an algae promoter), heavy metals, or alter pH.

Activated carbon is similar to crude graphite--the material used in pencils. Along with diamonds, activated carbon and graphite are both forms of carbon and contain almost no nitrogen, hydrogen, halogens, sulfur or oxygen. From a chemist's perspective, activated carbon is an imperfect form of graphite. This imperfect structure results in a high degree of porosity and more than a million-fold range of pore sizes, from visible cracks and crevices to gaps and voids of molecular dimensions. Porosity is what distinguishes activated carbon and makes it "activated." Intermolecular attractions in the smallest pores result in adsorption forces. Carbon adsorption forces work like gravity, but on a molecular scale. They cause a reaction similar to precipitation, in which adsorbates are removed from solution or vapor stream. To develop a strong adsorption force, either the distance between the carbon platelets and the adsorbate must be decreased (by reducing its pore size), or the number of carbon atoms in the structure must be increased (by raising the density of the carbon). Physical adsorption enables activated carbon to remove taste and odor-causing organic compounds, volatile organic compounds (VOCs), trihalomethanes (THMs) and other halocarbons from process water and vapor streams.

The important properties of activated carbon:

Surface area (BET N_2) - measurement, using nitrogen (N_2), of the extent of the pore surface developed within the matrix of the activated carbon. Used as a primary indicator of the activity level, based on the principle that the greater the surface area, the higher the number of adsorptive sites available.

Pore size distribution - determination of the pore size distribution of an activated carbon is an extremely useful way of understanding the performance characteristics of the material. The International Union of Pure and Applied Chemistry (IUPAC) defines the pore size distribution as: Micropores $r < 1$nm, Mesopores r 1-25nm, Macropores $r > 25$nm, The macropores are used as the entrance to the activated carbon, the mesopores for transportation and the micropores for adsorption. View of pore structure - scanning electron microscope

Iodine number - measurement of the porosity of an activated carbon by adsorption of iodine from solution.

Carbon tetrachloride activity(CTC) - measurement of the porosity of an activated carbon by the adsorption of saturated carbon tetrachloride vapor.

Hardness - an important factor in system design, filter life and product handling. There are large differences in the hardness of activated carbons, depending on the raw material and activity level.

Bulk Density - should be carefully considered when filling fixed volumes as it can have considerable commercial implications. The backwashed and drained density will show a lower value due to the water film between the particles of activated carbon.

Particle size distribution - the finer the particle size of an activated carbon, the better the access to the surface area and the faster the rate of adsorption kinetics. In vapor phase systems this needs to be considered against pressure drop, which will affect energy cost. Careful consideration of particle size distribution can provide significant operating benefits.

Adsorption is a process where a solid is used for removing a soluble substance from the water. In this process activated carbon is the solid. Activated carbon is produced specifically so as to achieve a very big internal surface (between 500 - 1500 m^2/g). This big internal surface makes activated carbon ideal for adsorption.

AC works by attracting and holding certain chemicals as water passes through it. AC is a highly porous material, therefore, it has an extremely high surface area for contaminant adsorption. The equivalent surface area of 1 pound of AC ranges from 60 to 150 acres. AC is made of tiny clusters of carbon atoms stacked upon one another. The carbon source is a variety of materials, such as peanut shells or coal. The raw carbon source is slowly heated in the absence of air to produce a high carbonaceous material. The carbon is activated by passing oxidizing gases through the material at extremely high temperatures. The activation process produces the pores that result in such high adsorptive properties. The adsorption process depends on the following factors: (1) physical properties of the AC, such as pore size distribution and surface area; (2) the chemical nature of the carbon source, or the amount of oxygen and hydrogen associated with it; (3) chemical composition and concentration of the contaminant; (4) the temperature and pH of the water; and (5) the flow rate or time exposure of water to AC.

Physical Properties of AC, forces of physical attraction or adsorption of contaminants to the pore walls is the most important AC filtration process. The amount and distribution of pores play key roles in determining how well contaminants are filtered. The best filtration occurs when pores are barely large enough to admit the contaminant molecule (Figure 2). Because contaminants come in all different sizes, they are attracted differently depending on pore size of the filter. In general AC filters are most effective in removing contaminants that have relatively large molecules (most organic chemicals). Type of raw carbon material and its method of activation will affect types of contaminants that are adsorbed. This is largely due to the influence that raw material and activation have on pore size and distribution.

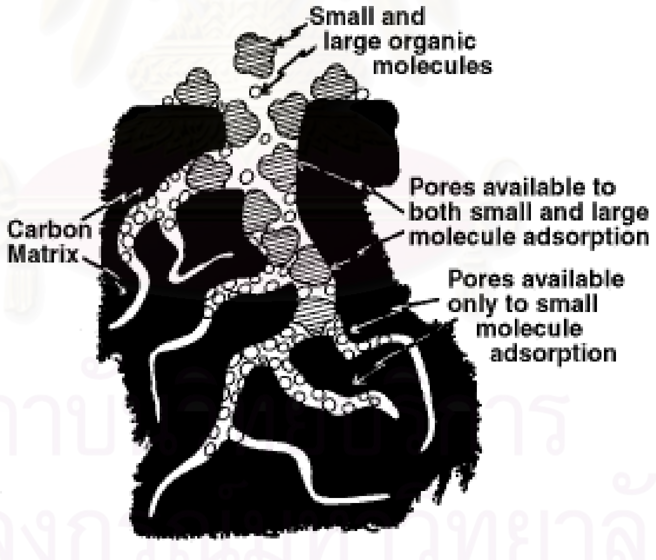


Figure 2. Molecular screening in the micropores of an activated carbon filter. (after G. L. Culp and R. L. Culp)

Chemical reactions and forms of chemicals are closely related to pH and temperature. Adsorption usually increases as pH and temperature decrease. When pH and temperature are lowered many organic chemicals are in a more adsorbable form. The process of adsorption is also influenced by the length of time that the AC is in contact with the contaminant in the water. Increasing contact time allows greater amounts of contaminant to be removed from the water. Contact is improved by increasing the amount of AC in the filter and reducing the flow rate of water through the filter.

Examples of substances are well adsorbed by activated carbon are

- Non-biodegradable organic compounds
- Adsorbable Organic Halogens (AOX)
- Toxicity
- Colour
- Inhibitory compounds for biological treatment systems
- Aromatic compounds
- Chlorinated/halogenated organic compounds
- Pesticides

Activated carbon is an expensive product. In most of the cases the cost of replacing the saturated carbon would be prohibitive. It should therefore be regenerated, and four methods have been developed for this purpose:

- Steam regeneration

This method is restricted to regenerating carbon which has only retained a few very volatile products.

- Thermal regeneration

By pyrolysis and burning off of adsorbed organic substances. In order to avoid igniting the carbon, it is heated to about 800 °C in a controlled atmosphere. This is the widely used method and regenerates the carbon very well, but it has two disadvantages, it requires considerable investment in either a multiple-hearth furnace and it causes high carbon losses.

- Chemical regeneration

Some process based on the action of a solvent used at a temperature of approximately 100 °C and with a high pH.

- Biological regeneration

This method of regeneration has not yet been applied on an industrial scale.

2.2.2 Chemical pretreatment

For chemical pretreatment in this study we will discuss 2 reactions. One reaction is oxidation and the other is reduction.

1. Oxidation: The reaction causes accumulation of oxygen or extraction of hydrogen. These are compounds which either add oxygen to, subtract hydrogen from, or take electrons away from other chemical compounds. The overall effect may be either the loss of negative charge or the gain of a positive charge. Such reactions are called oxidation. Oxidation is essentially the opposite of reduction. Many dyes may be effectively decolourized using chemical oxidizing agents. Chlorine-in the form of a liquid or gas, chlorine water, or hypochlorite-is often used to decolourize wastewater. However, chlorine is viewed with increasing disfavor because it has the potential for generating toxic chlorinated organics that are harmful to both humans and the environment.

Apart from the factors determining the chemical process (i.e. time, temperature, catalysts and other additives present) the result of the oxidation of cellulose depends greatly on the pH conditions of the bleaching solution. Two kinds of oxy cellulose can be produced during the process of oxidizing discolouring

The conjugated system of the coloured substance is destroyed, and the resultant radicals undergo a chemical reaction with the nascent (very reactive) oxygen liberated by the oxidising agent. The nascent oxygen is designated as ‘O’. The general oxidizing agent used for textile is Sodium hypochlorite (NaOCl) , it’s an alkaline salt (strong alkali with weak acid) and is relatively stable. In the presence of any acid, it immediately forms hypochlorous acid :

$$NaOCl + H^{+} \longrightarrow HOCl + Na^{+}$$

[sodium hypochlorite + hydrogen $\longrightarrow$ hypochlorous acid + sodium ion]

Hypochlorous acid (HOCl) is thermodynamically unstable and can decompose on textile surfaces to produce hydrogen chloride and nascent oxygen

$$HOCl \longrightarrow HCl + 'O'$$

[hypochlorous acid ⟶ hydrogen chloride + nascent oxygen]

The developing nascent oxygen is the bleaching agent. The pH of the solution become acidic due to the production of hydrogen chloride (HCl). Under acid conditions, chlorine gas and water are formed; the gas combines with water and, in the third step provides nascent oxygen.

Hydrogen peroxide hydrogen peroxide is the most frequently applied textile bleaching agent. The properties is water-clear, colourless and odorless, weakly acidic (normally stabilised with sulphuric acid). At the room temperature, the bleaching effect of hydrogen peroxide within the chosen test period of 30 min is slight. When the catalyst comes in contact with hydrogen peroxide, it turns the hydrogen peroxide (H_2O_2) into water (H_2O) and oxygen gas (O_2).

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

(hydrogenperoxide ⟶ water + oxygen)

The chemical pretreatment, except for hydrogen peroxide pretreatment was effective in removing colour. But it was effective in removing BOD_5 (21% removal).

2. Reduction: The reaction has the effect of adding hydrogen or removing oxygen. Reducing agents are used for several purposes in bleaching: to discoloured stains and dirt, and to convert them into water-soluble products by reduction. It is widely known that azo dyes undergo conversion to aromatic amine. For many dyes, particularly azo dyes, chemical reduction is an effective decolourization technique. The most commonly used chemical reducing agent is sodium dithionite, Thiourea dioxide (also known as formamidine sulfinic (FAS, acid) Sodium borohydride, Sodium formaldehydesulfosylate, and Tin (II) chloride are additional reducing agents for treating dye effluent. Sodium dithionite ($Na_2S_2O_4$) still often referred to by the incorrect name ‘sodium hydrosulphite’ is a strong reducing agent, which is used as a standard agent for the colour yield and quality of dyeing. The advantages are adequate

reduction potential for vat, sulphur and indigo dyed and has good liquor stability of the attached liquor. On the other hand, when it is contaminated in the wastewater it will hinder the biological breakdown of wastewater and leads to strong oxygen depletion, over-reduction at higher dyeing temperature and making the process more expensive. The decomposition of sodium dithionite proceeds as follows ;

$$Na_2S_2O_4 + H_2O \longrightarrow NaHSO_2 + NaHSO_3$$

[Sodium dithionite + water → sodium sulphoxylate + sodium hydrogen sulphite]

The reducing effect is carried out by the developing sodium hydrogen sulphite. Decomposition of sodium dithionite is accelerated in mildly acidic conditions

Consideration for reduce dye by chemical method

1. Dyestuff
2. Colour strength

2.3 Dyestuff

Dyes are coloured compounds which can bond to natural and synthetic fibres and make them coloured. Dyes owe much of their character to the presence of aromatic ring structures which, in the case of direct dyes, are mainly derivatives of benzene and napthalene. The aromatic rings are drawn as hexagons, one for benzene, two side by side for napthalene. Each line represents a carbon-carbon bond, and all the carbon atom lie in one plane. The hexagons give rise to the idea that dye structural formulae resemble chicken wire.

Table 3 Some combinations of colour absorbed and observed for various wavelengths of light

Apparent colour of solid	Absorption beam (nm)
Yellow	400 – 430
Orange	430 – 480
Red	480 – 550
Violet	550 – 600
Blue	600 – 700

Classification of dyes

Dyes can be classified according to their chemical structure and method of application. Classification according to chemical structure can be based on the characteristic chromophoric group of the dye (e.g. azo group); the chromophoric structure (e.g.anthraquinones or flavonoids); the characteristic components (e.g. the presence of reactive groups in reactive dyes). Dyes can be grouped according to their method of application as follows.

1. Dyes which dissolve in water. Examples include direct dyes, acid dyes (including 1:1 and 1:2 metal complex dyes), basic dyes and disperse dyes. Dyes belonging to this group remain water-soluble even after dyeing. The wash-fastness of this group of dyes is never 100%.

2. Dyes which dissolve in water but form non-water-soluble dyestuffs in the fibre after dyeing. Examples include sulphur dyes, vat dyes, azoic dyes. This group may have good fastness properties.

3. Mordant dyes. This group forms complexes with the metals of mordants; mordants are water-soluble salts of various metals applied before, during or after dyeing. Mordants dyes usually exhibit excellent wash fastness.

4. Reactive dyes. These dyes bond to fibres by covalent bonds. Their washfastness varies depending on the dye used, and they can have excellent washfastness.

5. Pigments. These are usually applied with binding media, which bond them to the surface of fibres. They are applied in printing or painting. Their washfastness depends mainly on the properties of the binding medium employed.

Table 4 Classification of dyes according to their chemical structure and method of application.

Dye class	**Chemical structure**	**Fibre**
Direct	Salts of sulphonic or Carboxilic acid, Mono, Dipolyalcohol, Azo compounds, Anthraquinone, Oxazine	Cotton, Rayon, and other cellulosics
Acid	Salts of organic bases, Anthraquinones, Azines, Polycyclic compounds, Nitro compounds, Azo compounds	Silk, Wool, Acrylic, Nylon
Basic	Salt of sulphonic or Carboxylic acids, Azo compounds	Wool, Silk, Nylon, Acrylic, Spandex
Disperse	Non-ionic with limited solubility, Monoazo and Bisazo compounds, Polycyclic compounds, nitro and nitroso compounds	Acetate, Polyester, Nylon, Acrylic
Reactive	Form covalent bonds with bonds with fibre: Monoazo, Aanthraquinone, Phthalocyanines	Cotton, Rayon, Wool

The dyes and the fibres of organic substrate contain sufficient amount of polar functional groups to attract each other and form primary or secondary bonds can occur between the dye and substrate if suitable groups in the dye and fibre close enough to each other. The main aim of dyeing is to achieve the closest possible proximity between the dye and fibre. Dyestuff can diffuse close to the substrate when that substrate is swollen. To achieve this swollen state, dyeing is usually carried out in hot water in presence of surface-active agents and various additives, such as salts. As the start of dyeing, salts also serve to decrease the repulsion between the dye and functional groups of the substrate of similar polarity/charge. The heating of the dyebath serves not only to swell the fibres but also to aid diffusion of dye. The properties of the main classes of dyestuff are discussed below. The dyes are grouped according to their method of application. Each type (dye class) is illustrated by representative dyes, characteristic of those found in textile.

Direct dyes: The dye within this section are those which were originally designed and marketed for primary purpose of dyeing cotton and are defined by Societ’s Terms and Definitions Committee as ‘Anionic dye substantive to cellulose when applied from an aqueous bath containing an electrolyte’. They provide the simplest means of colouring cellulosic materials since they are normally applied from a neutral or slightly alkaline bath, at or near the boil, to which sodium chloride or sulphate is added in such quantities and at such intervals of time appropriate to the dyeing properties of individual dyes. The majority of direct dyes belong to the Dis-,Tris- and Polyazo classes, the remainder being Monoazo, Stibene, Oxazine, Thiazol and Phthalocyanine compounds. Direct dyes bond to fibres with secondary bonds. They are usually large, linear, flat, water-soluble molecules. Direct dyes diffuse into the fibres from hot water solutions. The flat shape of this class of dye facilitates effective diffusion and gives them an affinity for cellulose fibres. Direct dyes are particularly suitable for dyeing cellulose fibres because the many polar hydroxyl side groups of the cellulose form hydrogen secondary bonds with the polar auxochrome groups of the dyestuff.

Vital substituents of direct dyes are the sodium sulphonate groups,-SO_3 Na, attached to the benzene or naphthalene rings.It is the sulfonate group which gives most direct dyes the property of water solubility so imperative to dyeing. When dyes containing these groups are placed in water they ionize into sodium cations and coloured sulfonate anions which are positively and negatively charged respectively i.e., Na^+ and -SO_3^- both of which are extremely attractive to water and become heavily hydrated (surrounded) by water molecules. There are usually from two to four -but can be from one to five-sulfonate groups as an intrinsic part of any direct dye molecule. The number of these groups is a major factor in determining how strongly the dye is attracted to water. This roughly translates into how soluble the dye is, and how much electrolyte is needed to force the dye out of the water and onto the fibre during dyeing. Most direct dye molecule could be described by a general formula:

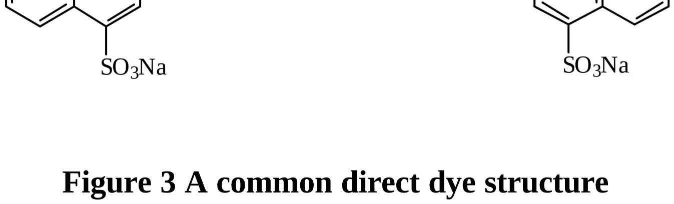


Figure 3 A common direct dye structure

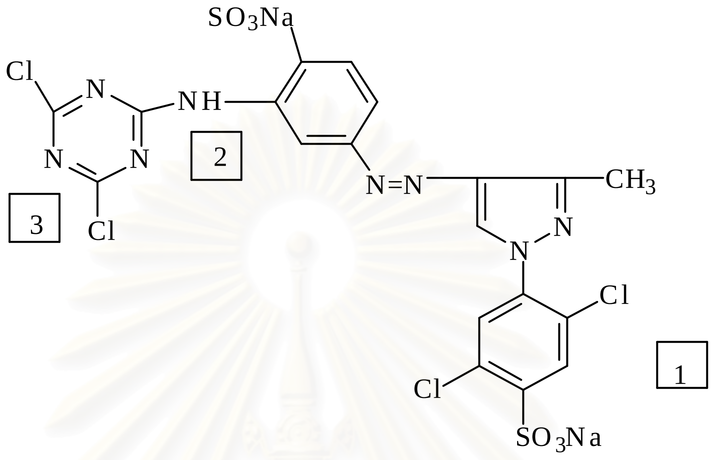
Commercial textile dyes are not pure coloured products. Finishing and standardization of dyes involves much expertise and hard work. The quality of this endeavor, which is an added cost, could make all the difference between as easy to use product of consistent high quality and a superficially cheaper, inconsistent product which could be nothing but trouble and added expense to a dyeing operation.

There are many factors for direct dye dyeing; the main is electrolytes (i.e. salts, such as sodium chloride or sulphate) are often added to dyebaths to decrease the repulsion between the polar groups of cellulosic fibres and dyestuffs of similar polarity and to increase the swelling of fibres. After the spontaneous formation of secondary bonds the fibre-dye complex is in a stable electronic state. The polar auxochrome groups of the dyestuff form hydrogen secondary bonds with the polar functional groups of the fibre while the non-polar parts of the planar molecule are kept in place by van der Waals forces. Natural direct dyes are common for cellulosics but rare for silk or wool.

Table 5 Percentage distribution of chemical classes in direct dye hue sectors

Chemical class	**Distribution in hue sector/%**								
	Yellow	**Orange**	**Red**	**Violet**	**Blue**	**Green**	**Brown**	**Black**	**% of all direct dyes**
Monoazo	4	7	14	4		8	3		5
Disazo	58	58	71	83	52	21	22	23	49
Polyazo	8	16	10	3	31	64	67	68	33
Copper-complex azo			3	9	12	4	1	8	5
Stilbene	17	23	2			1	7	1	5
Thiazole	13	1							1
Dioxazine				1	3				1
Phthalocyanine					2	2			1

Reactive dye: The very high wash fastness of reactive dyes is due to the covalent bond formed between the dye and the fibre during dyeing. The general structure of reactive dyes is shown in Figure 4 below by describing C.I.Reactive yellow 1.



1. Chromophoric part
2. Bridge
3. Reactive group

Figure 4 A common reactive dye structure

The chrophoric part can be an azo compound or an anthraquinone; it can also be a premordanted or a phthalocyanine compound. The bridge couples the chromophoric part and the reactive group. The reactive group can undergo a substitution or addition reaction with suitable functional groups of the fibre. Chlorinated compounds form covalent bonds by a substitution reaction. Reactive dyes containing unsaturated reactive groups are used to facilitate the addition reaction.

Table 6 Percentage distribution of chemical classes in reactive dye hue sectors

Chemical class	Distribution in hue sector/%								
	Yellow	Orange	Red	Violet	Blue	Green	Brown	Black	% of all reactive dyes
Unmetallised azo	97	90	90	63	20	16	57	42	66
Metal-complex azo	2	10	9	32	17	5	43	55	15
Anthaquinone				5	34	37		3	10
Phthalocyanine					27	42			8
Miscellaneous	1		1		2				1

Disperse dyes: Dyes with extremely low solubility in water which, in finely dispersed state, are used for dyeing polyester, acetate, triacetate, polyamide, polyacrylonitrile, modacrylic and polyvinyl chloride fibres. Both azo and anthraquinone disperse dyes can differ considerably in molecular weight. These dyes are practically insoluble in cold water due to the absence of any solubilizing groups in the molecule. Disperse dyes are applied in the form of fine aqueous. The size of the dispersed dye particles is in the region of approx.0.5-1µm. Because of their hydrophobic character, disperse dyes have an affinity for the likewise hydrophobic synthetic fibres. The dye particles are able to penetrate the fibre during dyeing in a molecularly dispersed state are produced with various chemical structures.

Disperse dyes were developed for dyeing acetate fibres. They are small, non-water-soluble or slightly water –soluble coloured compounds. The finely ground dye can be used from its dispersion, and is usually effective with synthetic fibres, which can resist the high temperature required by the dyeing process. There is a wide range of disperse dyes; those with azo chromophoric structures are well known.

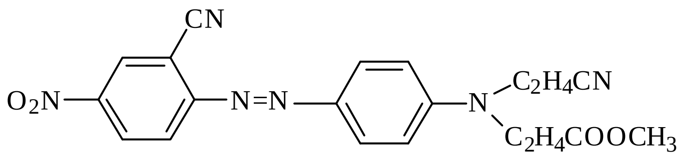


Figure 5 A common disperse dye structure

Table 7 Percentage distribution of chemical classes in disperse dye hue sectors

Chemical class	Distribution in hue sector/%								
	Yellow	Orange	Red	Violet	Blue	Green	Brown	Black	% of all disperse dyes
Azo	48	92	73	47	27	30	100	100	59
Anthraquinone	6	2	25	53	72	65			32
Nitro	16	3							3
Aminoketone	8	2	1		1	5			2
Methine	14								2
Quinophthalone	4								1
Miscellaneous	4	1	1						1

Acid dyes: Acid (anionic) dyes are mainly alkali salts of sulphonic and/or carboxylic acids (containing SO_3H ,COOH or OH groups). Acid dyes have good water solubility and excellent affinity for wool, silk , and polyamide fibres. The name acid dyes is derived from the fact that for centuries, some water soluble dyes have been more readily applied to wool and silk from aqueous dyebaths containing acids in the form of neutral dyebaths. The acid dyes represent an important dye class for these fibres. They are easily dyed, have generally good leveling properties, and produce uniformly exhausted, well penetrating dyeings. Acid dyes exhaust directly from neutral to strongly acidic dyebaths. Acid dyes are important dyes for natural protein fibres as well as various synthetic fibre e.g. polyamide and even, to some extent for cellulosic fibres. This class of dye has a strong affinity for the protonated amine groups of protein fibres. The name originates from the dyeing process, in which acids (usually acetic acid, occasionally sulphuric acid) are added to the dyebath. This is required to protonate the amino groups of polyamide fibres and the proteins of silk or wool fibres. The acid dye ionize (dissociates) to a negatively charged anion in water, which can bond to the positively-charged protonated amino groups of protein fibres by salt linkages. In addition to the salt linkages, hydrogen, dipole and van der Waals bonds are also formed between the dye and the fibre polymer. Most modern acid dyes are applied in the form of their sodium salt, which can be easily ionized. The salt linkages between protein fibres and acid dyes are formed in following way. Most synthesized acid dyes depend on pendant sulfonate salt groups,-SO_3Na, for their solubility as do the direct dyes.

There are three common acid dyeing methods. Equalizing acid dyes have good migration properties and are applied from a strong acid dyebath (made with sulphuric acid) containing sodium sulphate (Glauber’s salt), which controls the leveling (equal distribution) of the dye. Intermediate acid dyes have poor migration properties in strong acid solution, and they are therefore applied under weak acid conditions (made with acetic acid). Milling acid dyes are applied from a dyebath containing ammonium sulphate or ammonium acetate at an almost neutral pH, which turns to acid on evaporation of the ammonia.

Early work on the mechanism of acid dye uptake by wool gave rise to the hypothesis that under acid conditions, the cationic hydrogen ions, being small and able to diffuse readily, are first absorbed from the dyebath by water swollen fibre and become associated with the amino groups to give cationic ammonium groups,-$NH3^+$. The dye anions, being rather large, diffuse relatively slowly into the fibre, but because they alone are substantive, they will eventually displace all the smaller and less or non substantive anions which rushed in first.

A generalized mechanism for acid dyeing based primary on the coulombic (electrostatic) attraction of anionic dyes by oppositely charged sites in the fibres has the benefit of simplicity and can be used to qualitatively explain the different ionic types of leveling agents suitable for use when dyeing wool, silk and nylon. But such a mechanism is not entirely valid, and it cannot fully explain the widely known phenomena of over dyeing or the blocking of one dye from the fibre by another. The variety of coloured anionic structures suitable for application to wool, silk and nylon, with their localized hydrophobic and hydrophilic locations within the fibre molecules, calls for a dyeing mechanism which can take into account both ionic and hydrophobic dye-fibre bonding. The majority of natural plant and insect dyes can be applied as acid (anionic) dyes.

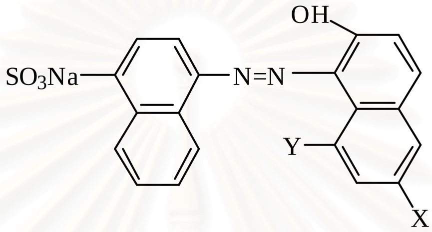


Figure 6 A common acid dye structure

Table 8 Percentage distribution of chemical classes in acid dye hue sectors

Chemical class	Distribution in hue sector/%								
	Yellow	Orange	Red	Violet	Blue	Green	Brown	Black	% of all acid dyes
Unmetallised azo	65	55	64	22	17	15	79	47	48
Metal-complex azo	31	42	29	44	21	39	13	46	31
Anthraquinone			2	18	36	22	3	3	10
Triarylmethane				12	16	16			5
Xanthene	1	1	4	3					2
Azine		1	1	1	4			1	1
Phthalocyanine					5	1			1
Nitro	1	1					5		1
Miscellaneous	2				1	7		3	1

Basic dyes: Basic dyes are water-soluble and contain cationic groups. The positive charge on the dyes may be localized on a quarternary ammonium group or delocalized over the entire aromatic structure (such as in triarylmethanes, methines, xanthenes and other hetroocyclic systems). These dyes are applied primarily to acrylics and occasionally to polyester and polyamide fibres. Although basic dyes gave brillant colours on wool, silk and cellulosic fibres, they had poor fastness properties on these types of fibres. Thus, they fell into disuse until it was discovered that they were quite suitable for application to acrylic fibres.

Basic dyes ionize in water to cations, and show great affinity to the ionized carboxyl groups of protein fibres. Neutral or slightly alkaline conditions promote the ionization of the carboxyl end and side group of proteins into negative charged groups. This can be achieved at a pH above the isoelectric region of protein fibres of silk or wool. A buffer of acetic acid and sodium acetate is added to the dyebath to provide a slightly alkaline pH. Many modern basic dyes become positive ions after the ionization of the halogen ion attached to their positively charges protonated amino groups. In the dyeing process, salt linkage are formed between the negatively charged carboxyl the negatively charged carboxyl residue and the positively charged ion of the dye.

As noted earlier, these dyes are of historical interest because the first synthetic dye mauve (prepared by sir William Henry Perkin) is a basic dye with an azine ring structure. Other cationic dyes of historical interest include the triphenylmethane dyes, Crystal Violet and Malachrite Green. Important chemical classes of basic dyes include; methines, xanthenes , azine and azo dyes with cationic groups.

It is usually necessary to scour acrylic fabrics to remove additives present from knitting or weaving processing to obtain uniform dyeing. Acrylic fabrics dyes slowly below their glass transition temperature (generally 70 –80 ^{o}C), then extremely rapidly above it and are difficult to level by migration unless cationic retarders are used as auxiliaries in the bath with the basic dye.

The only natural dye that belongs to this dye class is berberine. Many synthetic basic dyes were introduced in the second half of the nineteenth century, such as fuchsine.

Cellulose fibres can be dyed with basic dyes after having been impregnated with tannins (galic and ellagic acid), which provide the ionizable carboxyl groups in the material.

The common structure of basic dye used in this study is cynanine, these dyes, classifield as methines. These characteristically contain a conjugated system through one or more methine (-CN=) groups terminating with heterocyclic atoms.

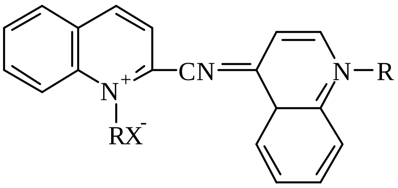


Figure 7 A common basic dye structure

Table 9 Percentage distribution of chemical classes in basic dye hue sectors

Chemical class	Distribution in hue sector/%								
	Yellow	Orange	Red	Violet	Blue	Green	Brown	Black	% of all basic dyes
Azo	33	51	55	38	34	12	100	60	43
Methine	41	13	23	21	2	10			17
Triarylmethane			5	18	23	56			11
Acridine	12	36							7
Anthraquinone				5	15				5
Azine			6	13	5			20	5
Oxazine					11			20	3
Xanthene			11	5					3
Miscellaneous	14				10	22			6

2.4 Colour strength

The subject of colour, with all its ramifications, is huge. Many textbooks have written about it and fortunately some of the more useful works to textile chemist, dyers and colourist are quite recent. Others, of great historical and research interest to colour physicists, are not of significant value to textile which occasionally frustrates some colour scientists. Colour Technology in the Textile Industry, an edited collection of papers on specific topics, is perhaps the most immediately useful reference, but rapid advances in equipment and computing capability have dated some of the papers. The collection is being updated by a subcommittee of AATCC Committee RA36, Colour Measurement Test Methods.

The technique of measuring the percentages of incident light transmitted by solutions or reflected by objects are known as transmittance and reflectance spectrophotometry. Instruments designed for making such measurement are spectrophotometers. The seemingly astonishing variety of tasks performed by colour systems (computer/spectrophotometer combination) is due primarily to the multitude of ways in which computer hardware and software can handle spectrophotometric data.

It is important to appreciate the three principle factors which control the colour appearance of an object. They are the nature of the object, the nature of the light illuminating the object and the nature of the observer (or detector)

The light: Without light there is no colour. But the radiant energy of a light source can be distributed in an infinite number of ways across the wavelengths of the visible region.

The object: The characteristics of colour and appearance of an object depend on the extent to which its scatters, reflects, transmits and absorbs light of different wavelengths in visible region (400-700 nm)

The Detector: Throughout history the most important colour detector and the final arbiter in commercial colour disputes has been the human observation. It is therefore importance to understand something of this human observer, as well as about the instruments designed to produce numerical value which relate to the responses of the human observation.

On the other hand, commercial reflectance spectrophotometers are not without variables of their own, and they can have an almost bewildering variety of features. These include different light sources, different geometric double or single beam optics, whether the whole visible spectrum is scanned continuously, or measured only at 5,10 or (in some cases) 20 nm intervals. Spectrophotometers which measure at selected points of the spectrum are known as abridged. However, fortunately, the accuracy and precision of commercially available instruments has improved over the years to the level where the largest majority, if properly used and maintained are sufficient for most textile colour purposes.

Not all compounds absorb light in the visible region of the electromagnetic spectrum. Many colourless compounds exist (transparent to all wavelengths of visible light), but those materials that do absorb in the visible range are especially important to people because they are the substances responsible for all the colour in the world that can see.

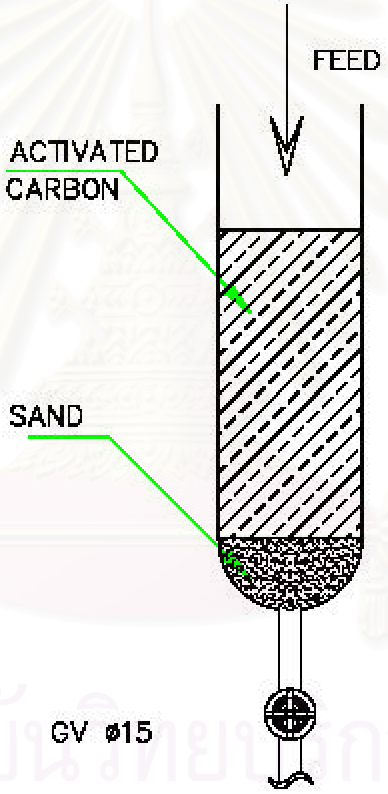
In this study the interaction of visible light with molecules will be studied by use of a particular dye in solution. Absorption of the dye solution at all wavelength of visible light will also be determined.

CHAPTER III

EXPERIMENTAL WORK

In this study, experiments were performed by 2 methods, physical and chemical methods. For the physical method activated carbon was used as the adsorbate, and for the chemical method oxidizing agents H_2O_2 and NaOCl were used for oxidation and reducing agent $Na_2S_2O_4$ was used for reduction.

The batch apparatus shown in Figure 8 below was used to perform the physical pretreatment experiments. It consisted of a PVC column with I.D. 4 inches.



- Feed referred to 1 liter dye effluent
- Activated carbon is the adsorbate
- Sand was used to filter the water
- GV ϕ 15 referred to gate valve

Figure 8 Apparatus for physical pretreatment

For the chemical pretreatment experiments, an ordinary 250 ml. Erlenmeyer Flask was used.

The sequence of our study is shown below.

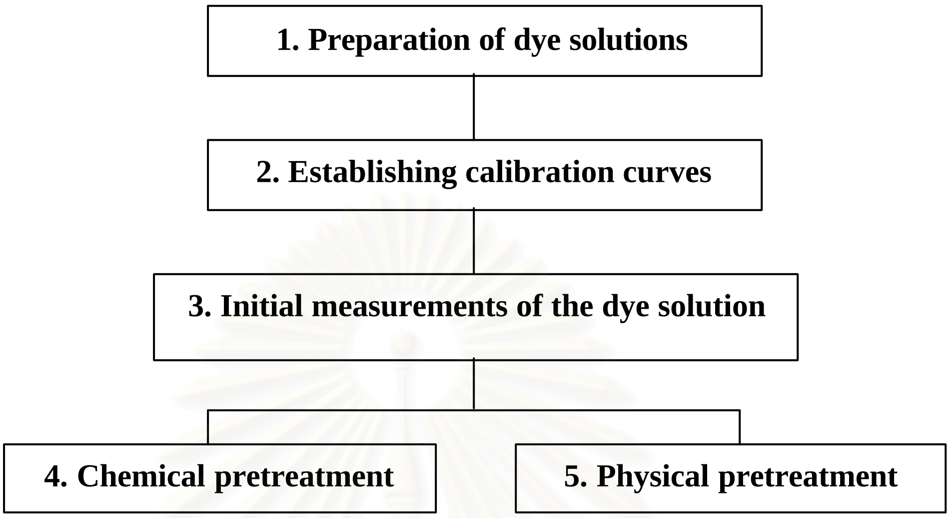


Figure 9 Flow diagram of experimental work

3.1 Preparation of dye solutions

Dye solutions from dyeing processes at concentrations of 0.5%, 1.0% and 2.0 % shade of weight fabric (owf) were prepared in a 100 liter Circular Jet apparatus. In this study two important studies were performed, treatment of dye solutions containing auxiliaries and solutions without auxiliaries. Preparation sequences of dye solutions are shown in Figures 10 -12, depending on the type of dye used.

1. Direct dye

Direct dyes are particularly suitable for dyeing cellulose fibres. About 20 gm/l of sodium sulphate (chemical auxiliaries) was added. Chemical auxiliaries helped to reduce the charges between the dye and the fibres, thus enhancing the dyeing process.

Commercial name : Mapra direct red 8BL 180%

Shade of colour : Bright red

C.I. Number : C.I. Direct red 81

Structure : Disazo

maximum wavelength , (nm) λ_{max} : 510 (with auxiliaries), 508.8 (without auxiliaries)

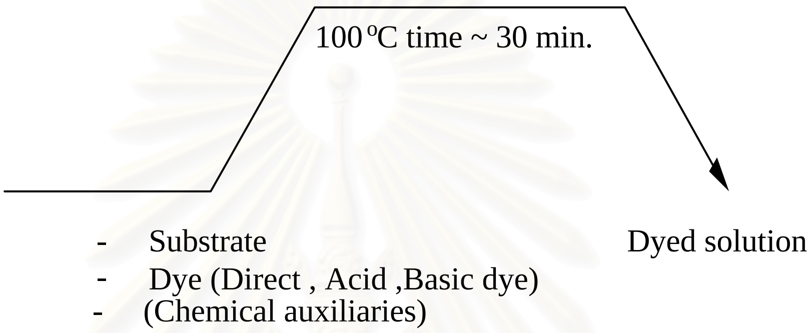


Figure 10 Dyeing processes of Direct, Acid and Basic dyes

2. <u>Reactive dye</u>

This type of dye is particularly suitable for dyeing cellulose fibres. In order to adjust dyeing process conditions, chemical auxiliaries which consisted of 20 gm/l sodium sulphate and 20 gm/l sodium carbonate were added to the dye solution. During dyeing process covalent bonds formed between the dye and the fibres.

Commercial name : Polative red HE-7-BN

Shade of colour : Bright bluish red

C.I. Number : C.I. Reactive red 141

Structure : Disazo

maximum wavelength (nm), λmax : 520.2 (with auxiliaries), 544 (without auxiliaries)

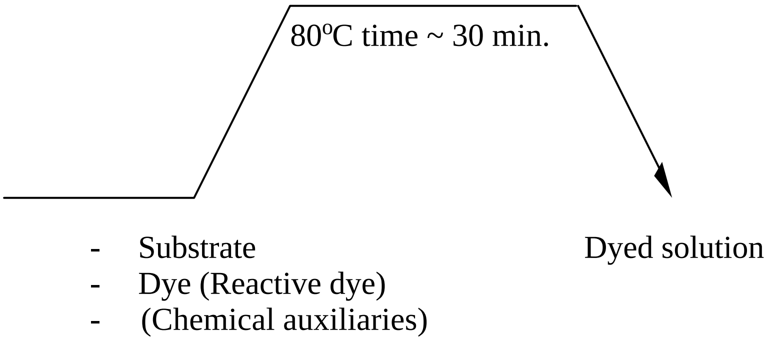


Figure 11 Dyeing process of Reactive dye

3 Disperse dye

Disperse dyes have extremely low solubility in water, and in finely dispersed state, are used for dyeing polyester, acetate, triacetate, polyamide, polyacrylonitrile, modacrylic and polyvinyl chloride fibres. It is most used to dye polyester fibres. Conditions for dyeing is that the dyeing solution has to be acidic, so we added about 3% owf of acetic acid, which is a chemical auxiliaries, to the dye.

Commercial name : Polacron red S2-GFL 200%

Shade of colour : Bluis red

C.I. Number : C.I. Disperse red 167

Structure : Azo

Maximum wavelength (nm), λ_{max} : 502.6 (with auxiliaries),
463.8 (without auxiliaries)

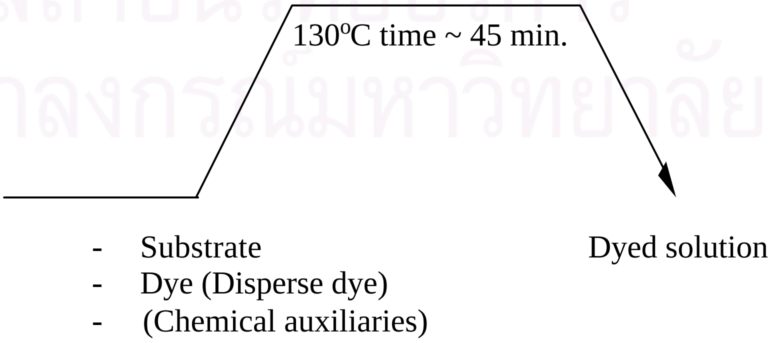


Figure 12 Dyeing process of Disperse dye

4. Acid dye

Acid (anionic) dyes are mainly alkali salts of sulphonic and/or carboxylic acids (containing SO_3H ,COOH or OH groups). Acid dyes have good water solubility and excellent affinity for wool, silk , and polyamide fibres. In this study we used acid dye to dye nylon fibres. In order to enhance the dyeing process of nylon, the solution condition had to be adjusted to acidic in nature. Therefore, about 3% owf acetic acid (chemical auxialiaries) was added to the dye. The dyeing process is similar to the process using direct dye, Figure 10.

Commercial name : Polynyl red MBN

Shade of colour : Bluish red

C.I. Number : C.I.Acid red 131

Structure : Monoazo

Maximum wavelength (nm), λ_{max} : 564.6 (with auxiliaries),
562.4 (with auxiliaries)

5. Basic dye

Basic dyes are water-soluble and contain cationic groups. The positive charge on the dyes may be localized on a quarternary ammonium group or delocalized over the entire aromatic structure (such as in triarylmethanes, methines, xanthenes and other hetroocyclic systems). These dyes are applied primarily to acrylics and occasionally to polyester and polyamide fibres. In this study basic dye was used to dye acrylic fibres. To enhance the dyeing process the dyeing solution had to be acidic, so about 3% owf acetic acid was added to the solution. The dyeing process is similar to the process using direct dye, Figure 10.

Commercial name : Concord Dacryl red 4G 200%

Shade of colour : Bright red

C.I. Number : C.I. Basic red 14

Structure : Cynanine

Maximum wavelength (nm), λ_{max} : 514.6 (with auxiliaries),
512.8 (without auxiliaries)

3.2 Establishing the calibration curve for each dye

Dye solutions at various concentrations were prepared in distilled water. For direct dye, reactive dye, disperse dye and acid dye, concentrations of the dye solutions prepared were 0.001, 0.002, 0.003, 0.004 and 0.005 %w/v in distilled water. However, for basic dye, the concentrations were lower because this dye has high brightness so the absorbance would be more than 2.5 %w/v. In theory this value is unacceptable. The absorbance of the dye solutions were measured using a UV spectrophotometer. The results obtained were used to establish the calibration curve for each dye.

1. Direct dye

Concentration (%w/v)	Absorbance (%w/v)	
	with auxiliaries	without auxiliaries
0.000	0.000	0.000
0.001	0.471	0.517
0.002	0.856	0.806
0.003	1.150	1.113
0.004	1.492	1.370
0.005	1.839	1.700

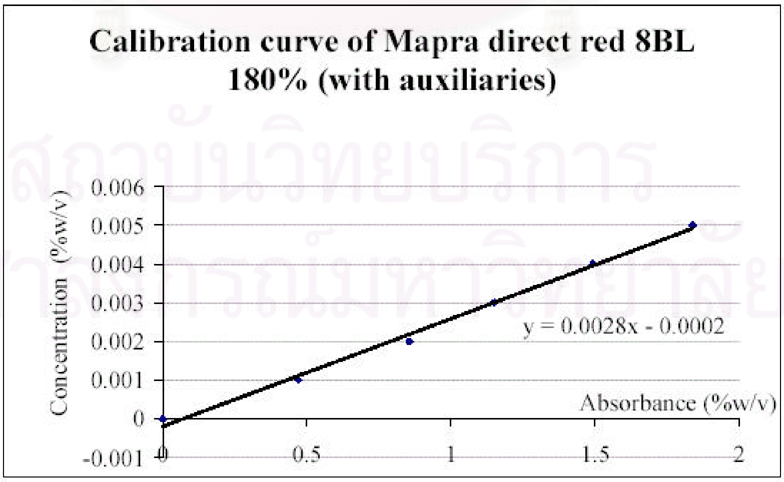


Figure 13 Calibration curve of Mapra direct red 8BL 180% (with auxiliaries)

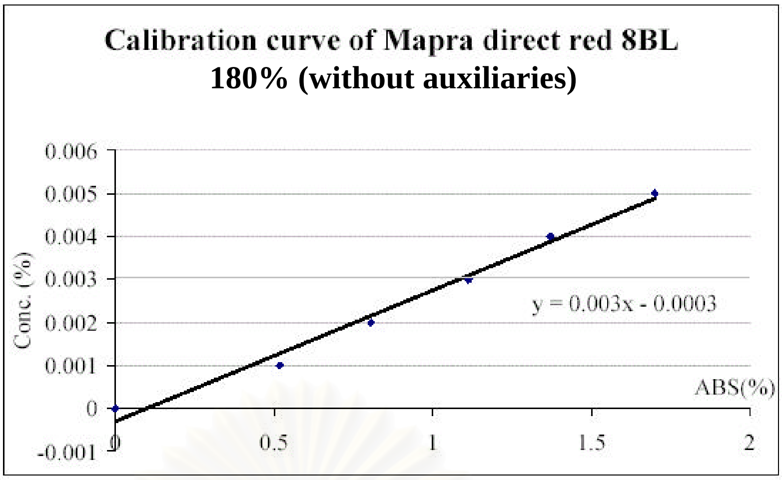


Figure 14 Calibration curve of Mapra direct red 8BL 180% (without auxiliaries)

2. Reactive dye

Concentration (%w/v)	Absorbance (%w/v)	
	with auxiliaries	without auxiliaries
0.000	0.000	0.000
0.001	0.135	0.212
0.002	0.296	0.404
0.003	0.454	0.596
0.004	0.643	0.788
0.005	0.841	0.981

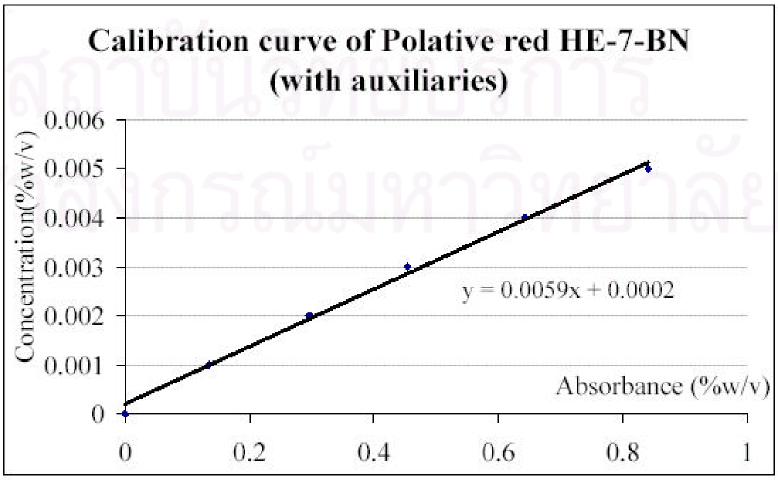


Figure 15 Calibration curve of Polative red HE-7-BN (with auxiliaries)

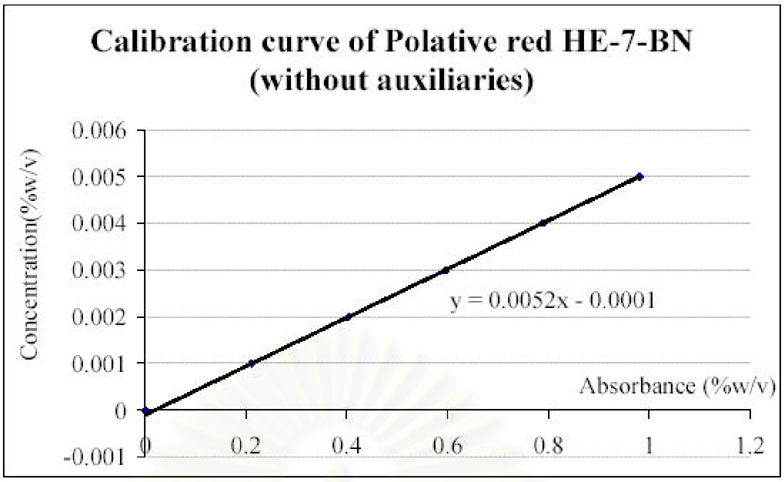


Figure 16 Calibration curve of Polative red HE-7-BN (without auxiliaries)

3. Disperse dye

Concentration (%w/v)	Absorbance (%w/v)	
	with auxiliaries	without auxiliaries
0.000	0.000	0.000
0.001	0.134	0.073
0.002	0.251	0.186
0.003	0.361	0.244
0.004	0.481	0.331
0.005	0.569	0.414

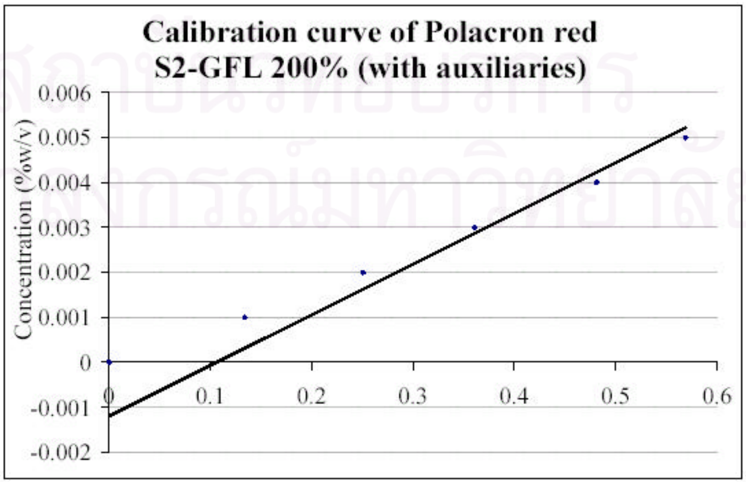


Figure 17 Calibration curve of Polacron red S2-GFL 200% (with auxiliaries)

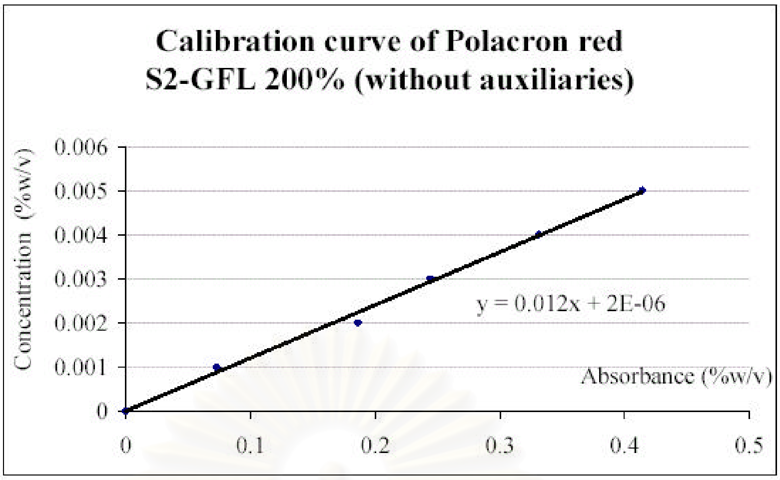


Figure 18 Calibration curve of Polacron red S2-GFL 200% (without auxiliaries)

4. Acid dye

Concentration (%w/v)	**Absorbance (%w/v)**	
	with auxiliaries	without auxiliaries
0.000	0.001	-0.023
0.001	0.348	0.272
0.002	0.627	0.496
0.003	0.897	0.754
0.004	1.12	0.963
0.005	1.382	1.197

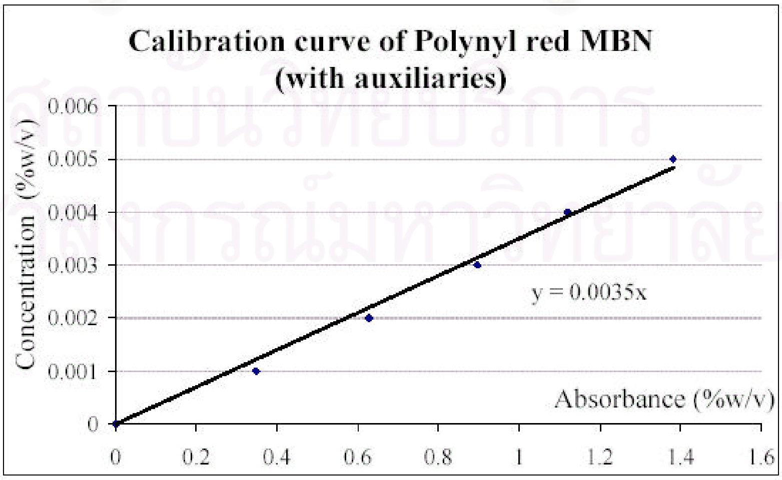


Figure 19 Calibration curve of Polynyl red MBN (with auxiliaries)

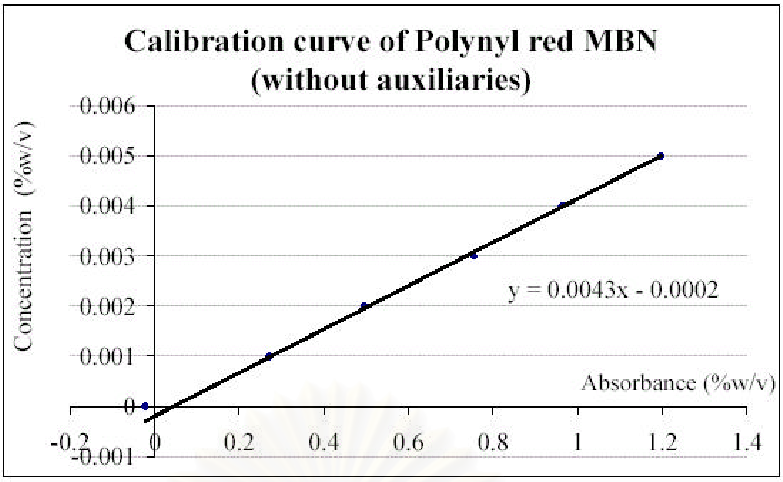


Figure 20 Calibration curve of Polynyl red MBN (without auxiliaries)

5. Basic dye

Concentration (%w/v)	Absorbance (%w/v)
0	-0.011
0.00025	0.197
0.00050	0.407
0.00075	0.584
0.00100	0.824
0.00125	1.163

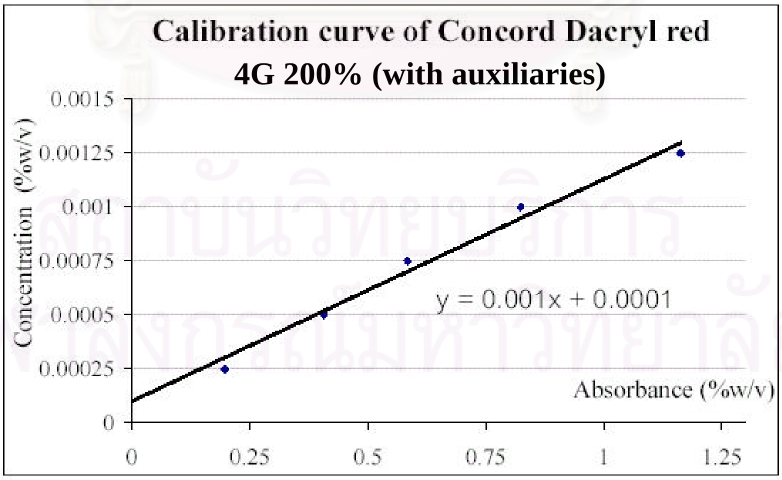


Figure 21 Calibration curve of Concord Dacryl red 4G 200% (with auxiliaries)

-without auxiliaries

Concentration (%w/v)	Absorbance (%w/v)
0	0
0.0005	0.352
0.001	0.755
0.0015	1.045
0.002	1.473
0.0025	1.817

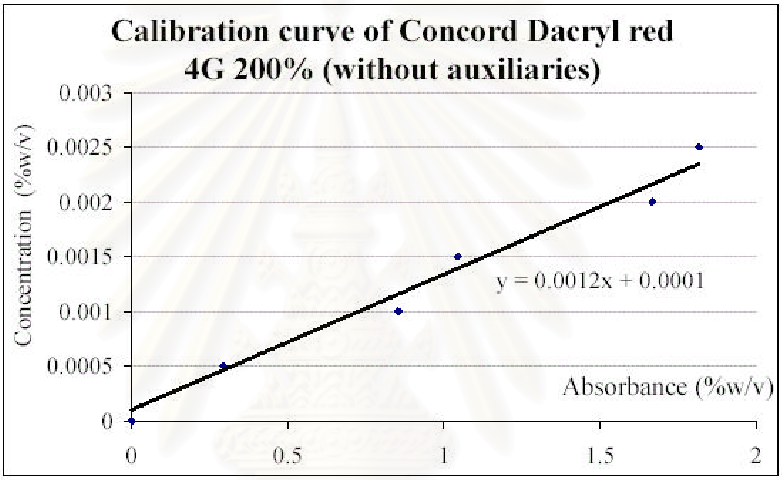


Figure 22 Calibration curve of Concord Dacryl red 4G 200% (without auxiliaries)

3.3 Measuring the dyed solution before pretreatment.

Firstly, pH value and colour strength of dye solutions at maximum wavelength of the dye must be measured before pretreatment. For this study the values of pH and colour strength were measured for three different concentrations, being at 0.5% shade, 1.0% shade and 2.0% shade.

Table 10 Colour strength of dye solution before pretreatment

Classification	Concentration	pH value	Colour strength (%w/v)
Direct with auxiliaries	0.5	7.65	0.0004
	1.0	7.82	0.0026
	2.0	7.56	0.0049
Direct without auxiliaries	0.5	8.28	0.0023
	1.0	8.06	0.0050
	2.0	8.06	0.0072
Reactive with auxiliaries	0.5	11.59	0.0017
	1.0	11.59	0.0040
	2.0	11.63	0.0074
Reactive without auxiliaries	0.5	8.14	0.0023
	1.0	7.85	0.0048
	2.0	7.97	0.0081
Disperse with auxiliaries	0.5	7.65	0.0013
	1.0	6.92	0.0018
	2.0	6.64	0.0039
Disperse without auxiliaries	0.5	8.1	0.0025
	1.0	8.51	0.0029
	2.0	8.35	0.0097
Acid with auxiliaries	0.5	4.17	0.0000
	1.0	4.23	0.0000
	2.0	4.59	0.0031
Acid without auxiliaries	0.5	8.57	0.0037
	1.0	8.67	0.0080
	2.0	8.79	0.1010
Basic with auxiliaries	0.5	3.75	0.0002
	1.0	4.81	0.0021
	2.0	4.75	0.0026
Basic without auxiliaries	0.5	3.75	0.0004
	1.0	4.81	0.0030
	2.0	4.75	0.0036

When all the essential data of various dyes to be used in our study are known, pretreatment could be performed via chemical and physical means. The main objective of pretreatment was to reduce the colour strength of the dye effluent. Factors studied were dye type, chemical auxiliaries, colour strength, and condition.

3.4 Chemical pretreatment

Chemical pretreatment experiments were performed by using the method of oxidation and reduction. Hydrogen peroxide and sodium hypochlorite were used as oxidizing agents and sodium dithionite was used as reducing agent. The experiments were carried out in a 250 ml Erlenmeyer flask. For each experiment 100 cc of the dye solution prepared previously was first introduced into the flask, then oxidizing agents or reducing agents were added. The amount of the chemicals added varied from 1 – 15 g/l. The reaction was allowed to go to completion, that is, when no further change in the reaction occurred. The time taken was about 30 minutes. For each experiment the the colour strength was measured and the degradation rate of the model pollutant was calculated from the calibration curves determined earlier. The results were as follow:

1. Direct dye

Table 11 Oxidation –Reduction (with auxiliaries)

Amount of Chemical (g/l)	Colour strength (%w/v)								
	0.0004			0.0026			0.0049		
	H_2O_2	NaOCl	$Na_2S_2O_4$	H_2O_2	NaOCl	$Na_2S_2O_4$	H_2O_2	NaOCl	$Na_2S_2O_4$
0	0.0004	0.0004	0.0004	0.0026	0.0026	0.0026	0.0049	0.0049	0.0049
1		0.0004	0.0000		0.0042	0.0000		0.0046	0.0000
2	0.0007	0.0004	0.0000	0.0016	0.0030	0.0000	0.0013	0.0041	0.0000
3		0.0004	0.0000		0.0020	0.0000		0.0039	0.0000
4	0.0006	0.0004	0.0000	0.0013	0.0013	0.0000	0.0003	0.0032	0.0000

Table 11 (Cont.)

Amount of Chemical (g/l)	Colour strength (%w/v)								
	0.0004			0.0026			0.0049		
	H_2O_2	NaOCl	$Na_2S_2O_4$	H_2O_2	NaOCl	$Na_2S_2O_4$	H_2O_2	NaOCl	$Na_2S_2O_4$
5		0.0004	0.0000		0.0006	0.0000		0.0025	0.0000
6	0.0006	0.0000	0.0000	0.0011	0.0001	0.0000	0.0001	0.0027	0.0000
7		0.0000	0.0000		0.0000	0.0000		0.0024	0.0000
8	0.0004	0.0000	0.0000	0.0010	0.0000	0.0000	0.0001	0.0018	0.0000
9		0.0000	0.0000		0.0000	0.0000		0.0012	0.0000
10	0.0000	0.0000	0.0000	0.0009	0.0000	0.0000	0.0000	0.0008	0.0000
11		0.0000	0.0000		0.0000	0.0000		0.0006	0.0000
12	0.0000	0.0000	0.0000	0.0010	0.0000	0.0000	0.0000	0.0005	0.0000
13		0.0000	0.0000		0.0000	0.0000		0.0004	0.0000
14	0.0000	0.0000	0.0000	0.0008	0.0000	0.0000	0.0000	0.0004	0.0000
15		0.0000	0.0000		0.0000	0.0000		0.0004	0.0000
16	0.0000			0.0007			0.0000		
18	0.0000			0.0009			0.0000		
20	0.0000			0.0007			0.0000		
22	0.0000			0.0007			0.0000		
24	0.0000			0.0006			0.0000		
26	0.0000			0.0006			0.0000		
28	0.0000			0.0006			0.0000		
30	0.0000			0.0006			0.0000		

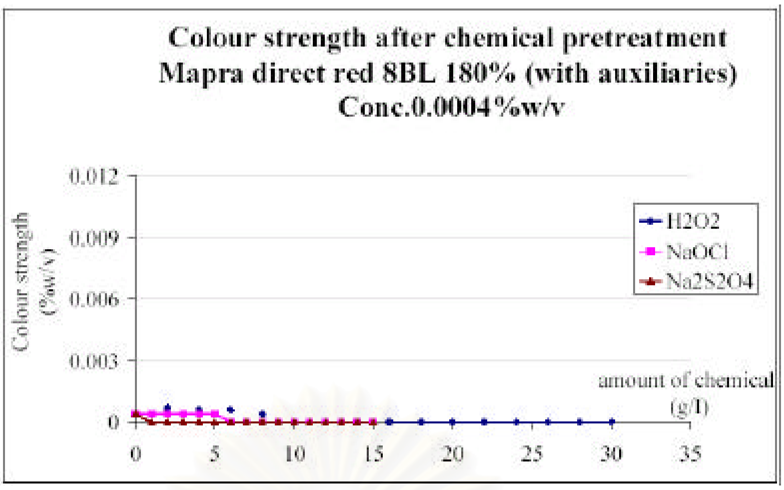


Figure 23 Colour strength after chemical pretreatment Mapradirect red 8BL 180% (with auxiliaries) Conc.0.0004%w/v

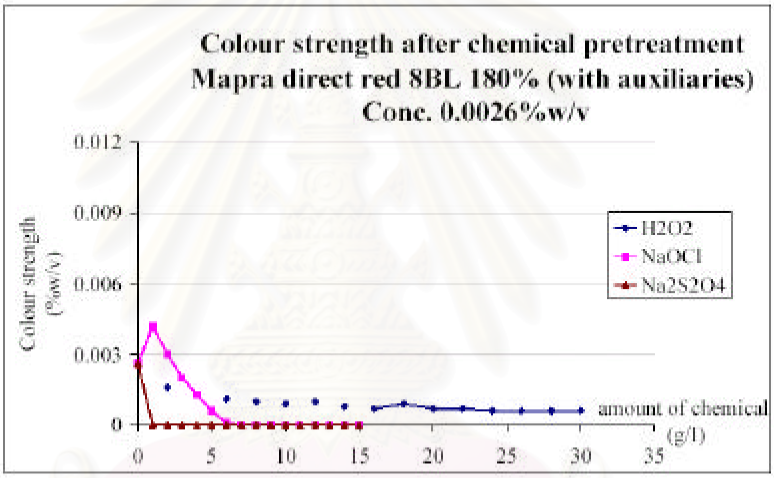


Figure 24 Colour strength after chemical pretreatment Mapradirect red 8BL 180% (with auxiliaries) Conc.0.0026%w/v

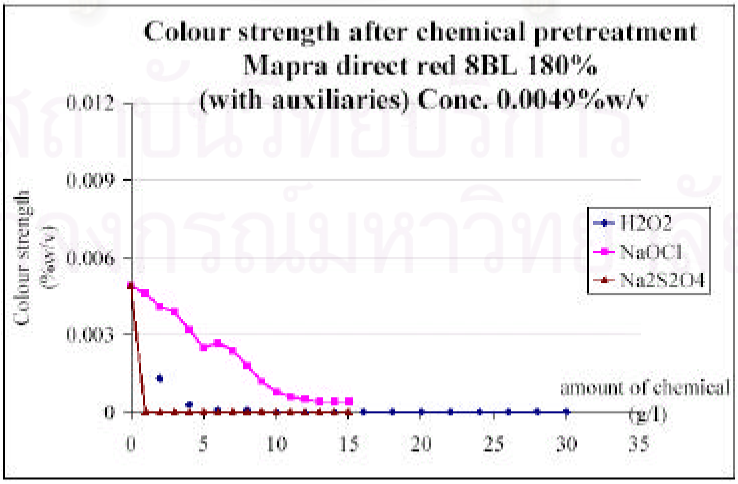


Figure 25 Colour strength after chemical pretreatment Mapradirect red 8BL 180% (with auxiliaries) Conc.0.0049%w/v

Table 12 Oxidation –Reduction (without auxiliaries)

Amount of Chemical (g/l)	Colour strength (%w/v)								
	0.0023			0.0050			0.0072		
	H_2O_2	NaOCl	$Na_2S_2O_4$	H_2O_2	NaOCl	$Na_2S_2O_4$	H_2O_2	NaOCl	$Na_2S_2O_4$
0	0.0023	0.0023	0.0023	0.0050	0.0050	0.0050	0.0072	0.0072	0.0072
1		0.0018	0.0000		0.0042	0.0000		0.0072	0.0000
2	0.0008	0.0011	0.0000	0.0019	0.0030	0.0000	0.0055	0.0072	0.0000
3		0.0005	0.0000		0.0020	0.0000		0.0072	0.0000
4	0.0004	0.0004	0.0000	0.0009	0.0013	0.0000	0.0036	0.0065	0.0000
5		0.0000	0.0000		0.0006	0.0000		0.0063	0.0000
6	0.0004	0.0000	0.0000	0.0006	0.0001	0.0000	0.003	0.0055	0.0000
7		0.0000	0.0000		0.0000	0.0000		0.0047	0.0000
8	0.0003	0.0000	0.0000	0.0004	0.0000	0.0000	0.0023	0.0050	0.0000
9		0.0000	0.0000		0.0000	0.0000		0.0047	0.0000
10	0.0001	0.0000	0.0000	0.0003	0.0000	0.0000	0.0023	0.0042	0.0000
11		0.0000	0.0000		0.0000	0.0000		0.0025	0.0000
12	0.0002	0.0000	0.0000	0.0004	0.0000	0.0000	0.0021	0.0018	0.0000
13		0.0000	0.0000		0.0000	0.0000		0.0011	0.0000
14	0.0002	0.0000	0.0000	0.0002	0.0000	0.0000	0.002	0.0009	0.0000
15		0.0000	0.0000		0.0000	0.0000		0.0004	0.0000
16	0.0001			0.0001			0.0017		
18	0.0001			0.0001			0.0015		
20	0.0001			0.0001			0.0014		
22	0.0000			0.0001			0.0012		
24	0.0000			0.0001			0.0011		
26	0.0000			0.0000			0.0009		
28	0.0000			0.0000			0.0009		
30	0.0000			0.0000			0.0009		

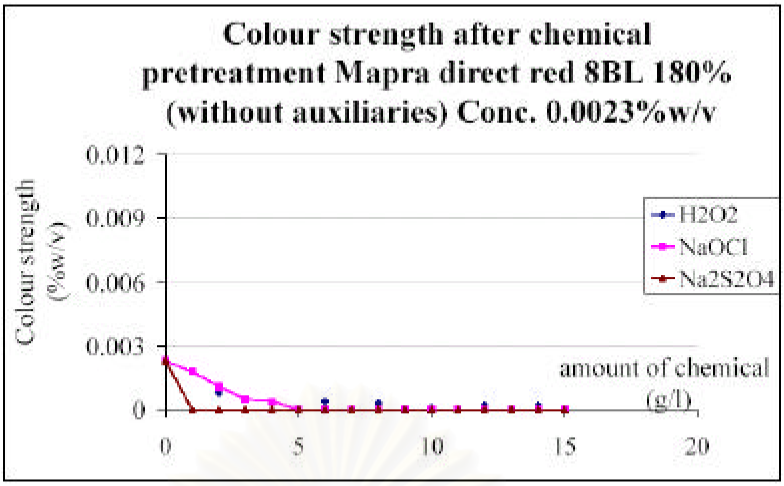


Figure 26 Colour strength after chemical pretreatment Mapradirect red 8BL 180% (without auxiliaries) Conc.0.0023%w/v

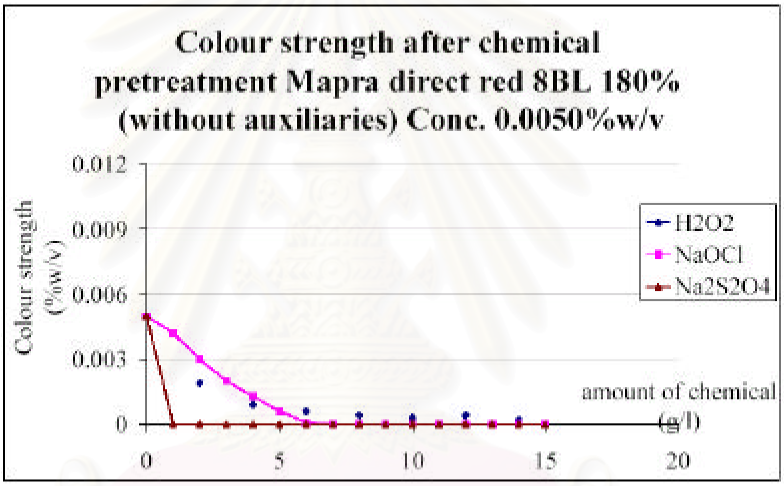


Figure 27 Colour strength after chemical pretreatment Mapradirect red 8BL 180% (without auxiliaries) Conc.0.0050%w/v

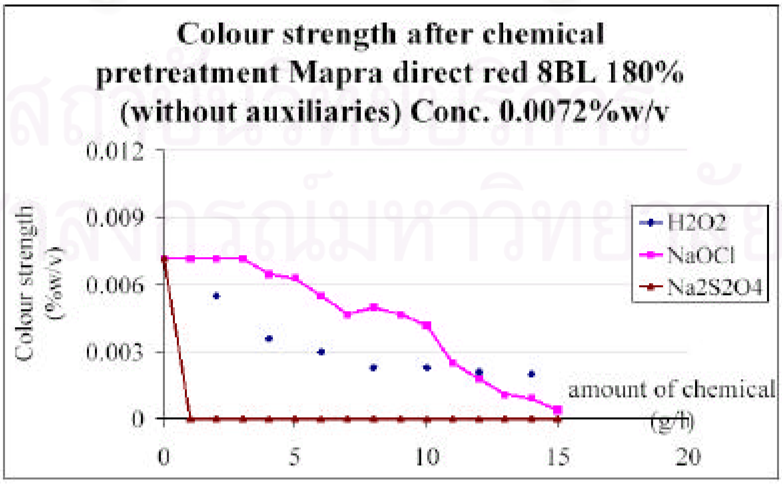


Fig. 28 Colour strength after chemical pretreatment Mapradirect red 8BL 180% (without auxiliaries) Conc.0.0072%w/v

2. Reactive dye

Table 13 Oxidation –Reduction (with auxiliaries)

Amount of chemical (g/l)	**Colour strength (%w/v)**								
	0.0017			**0.0040**			**0.0074**		
	H_2O_2	**NaOCl**	**$Na_2S_2O_4$**	**H_2O_2**	**NaOCl**	**$Na_2S_2O_4$**	**H_2O_2**	**NaOCl**	**$Na_2S_2O_4$**
0	0.0017	0.0017	0.0017	0.0040	0.0040	0.0040	0.0074	0.0074	0.0074
0.25			0.0007			0.0009			0.0005
0.5			0.0007			0.0008			0.0004
0.75			0.0007			0.0007			0.0005
1	0.0018	0.002	0.0007	0.0039	0.0038	0.0009	0.0065	0.0071	0.0004
1.25			0.0007			0.0007			0.0004
1.5			0.0007			0.0008			0.0005
1.75			0.0007			0.0008			0.0005
2	0.0018	0.002	0.0006	0.0038	0.0036	0.0007	0.0072	0.0071	0.0005
2.25			0.0006			0.0007			0.0005
2.5			0.0006			0.0007			0.0005
2.75			0.0006			0.0007			0.0005
3	0.0016	0.0018	0.0006	0.0036	0.0034	0.0007	0.0065	0.007	0.0005
3.25			0.0006			0.0007			0.0005
3.5			0.0006			0.0007			0.0005
3.75			0.0006			0.0007			0.0005
4	0.0017	0.0016		0.0036	0.0034		0.0065	0.0068	
5	0.0016	0.0015		0.0036	0.0034		0.0061	0.0065	
6	0.0017	0.0014		0.0036	0.0033		0.0062	0.0065	
7	0.0016	0.0012		0.0035	0.0031		0.0062	0.0063	
8	0.0017	0.0012		0.0035	0.003		0.0061	0.0061	
9	0.0016	0.0011		0.0028	0.0028		0.0066	0.0061	
10	0.0017	0.0011		0.0028	0.0028		0.0065	0.006	
11	0.0017	0.0009		0.0026	0.0026		0.0065	0.0058	
12	0.0016	0.0009		0.0026	0.0026		0.0066	0.0057	
13	0.0017	0.0006		0.0025	0.0025		0.0067	0.0055	
14	0.0017	0.0006		0.0025	0.0025		0.0065	0.0054	
15	0.0016	0.0006		0.0023	0.0023		0.0065	0.0052	

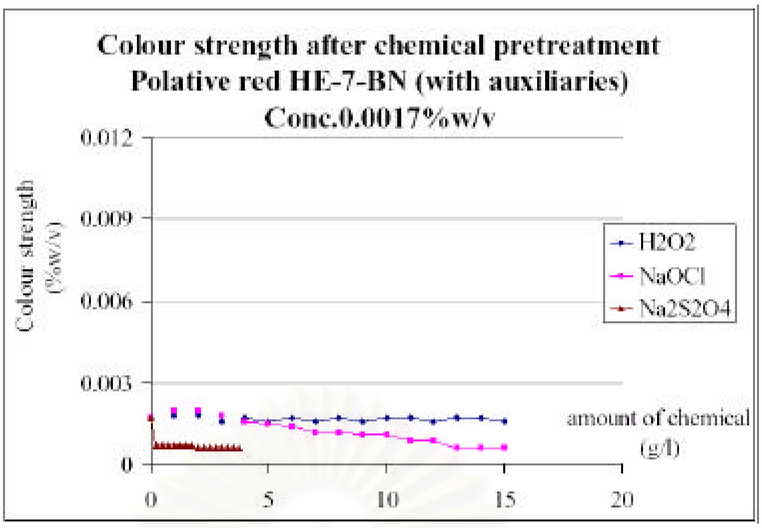


Figure 29 Colour strength after chemical pretreatment Polative red HE-7-BN (with auxiliaries) Conc.0.0017%w/v

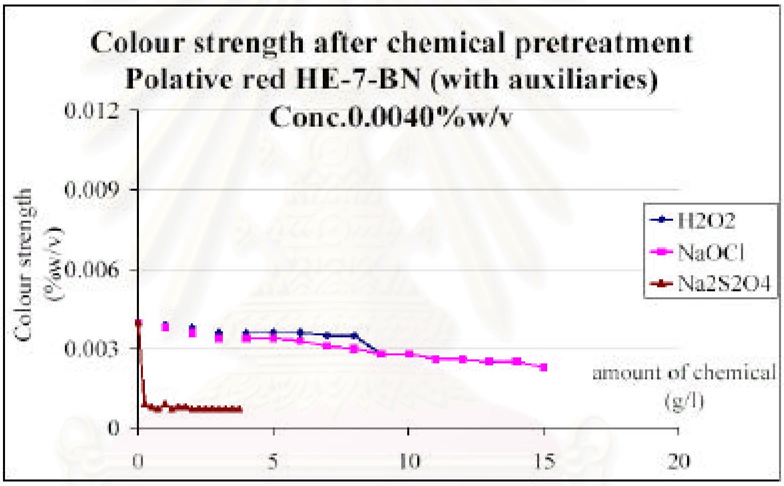


Figure 30 Colour strength after chemical pretreatment Polative red HE-7-BN (with auxiliaries) Conc.0.0040%w/v

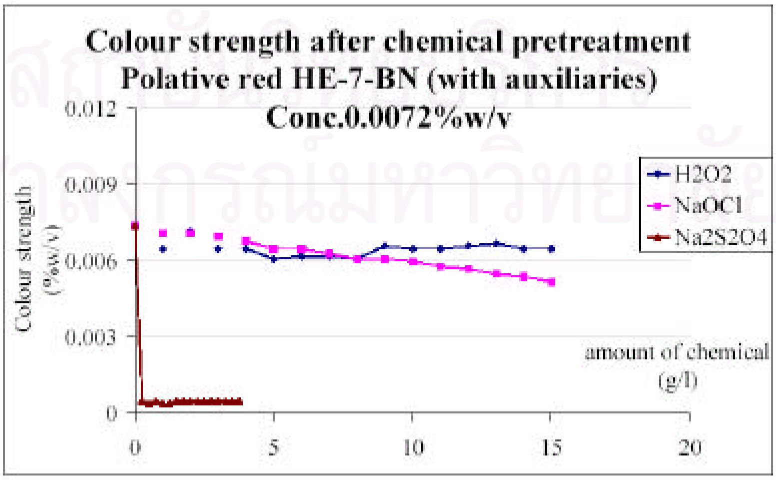


Figure 31 Colour strength after chemical pretreatment Polative red HE-7BN (with auxiliaries) Conc. 0.0074%w/v

Table 14 Oxidation –Reduction (without auxiliaries)

Amount of chemical (g/l)	**Colour strength (%w/v)**								
	0.0023			**0.0048**			**0.0081**		
	H_2O_2	**NaOCl**	**$Na_2S_2O_4$**	**H_2O_2**	**NaOCl**	**$Na_2S_2O_4$**	**H_2O_2**	**NaOCl**	**$Na_2S_2O_4$**
0	0.0023	0.0023	0.0023	0.0048	0.0048	0.0048	0.0081	0.0081	0.0081
0.25			0.0000			0.0000			0.0000
0.5			0.0000			0.0000			0.0000
0.75			0.0000			0.0000			0.0000
1	0.0014	0.0015	0.0000	0.0040	0.0041	0.0000	0.0063	0.0077	0.0000
1.25			0.0000			0.0000			0.0000
1.5			0.0000			0.0000			0.0000
1.75			0.0000			0.0000			0.0000
2	0.0011	0.0015	0.0000	0.0037	0.0040	0.0000	0.0056	0.0065	0.0000
2.25			0.0000			0.0000			0.0000
2.5			0.0000			0.0000			0.0000
2.75			0.0000			0.0000			0.0000
3	0.0018	0.0014	0.0000	0.0037	0.0042	0.0000	0.0056	0.0065	0.0000
3.25			0.0000			0.0000			0.0000
3.5			0.0000			0.0000			0.0000
3.75			0.0000			0.0000			0.0000
4	0.0009	0.0014		0.0034	0.0042		0.0056	0.0068	
5	0.0009	0.0015		0.0033	0.0041		0.0055	0.0065	
6	0.0009	0.0013		0.0034	0.0041		0.0052	0.0066	
7	0.0008	0.0013		0.0033	0.0040		0.0059	0.0065	
8	0.0008	0.0014		0.0034	0.0039		0.0052	0.0065	
9	0.0008	0.0014		0.0033	0.0038		0.0058	0.0065	
10	0.0008	0.0013		0.0033	0.0039		0.0056	0.0065	
11	0.0008	0.0013		0.0033	0.0036		0.0053	0.0065	
12	0.0008	0.0013		0.0033	0.0038		0.0053	0.0065	
13	0.0008	0.0013		0.0033	0.0036		0.0053	0.0065	
14	0.0008	0.0013		0.0033	0.0036		0.0053	0.0065	
15	0.0008	0.0013		0.0033	0.0036		0.0053	0.0062	

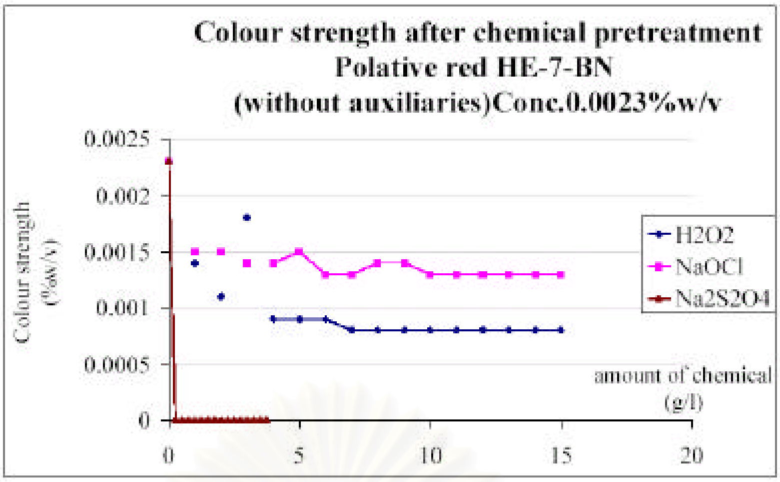


Figure 32 Colour strength after chemical pretreatment Polative red HE-7-BN (without auxiliaries) Conc.0.0023%w/v

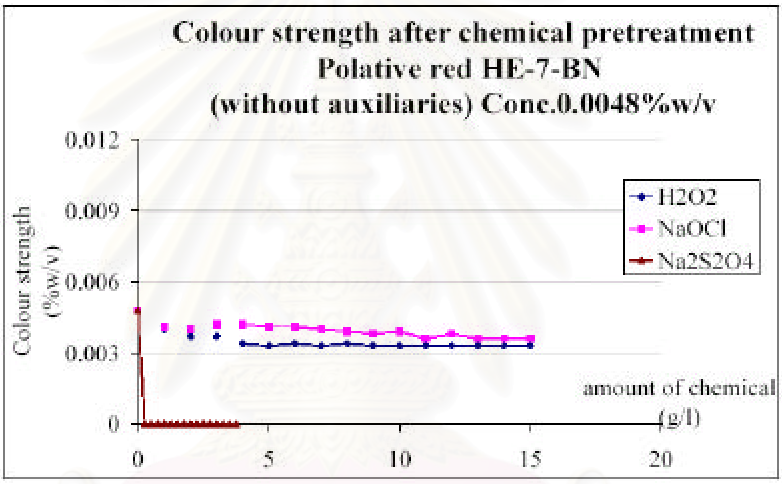


Figure 33 Colour strength after chemical pretreatment Polative red HE-7-BN (without auxiliaries) Conc.0.0048%w/v

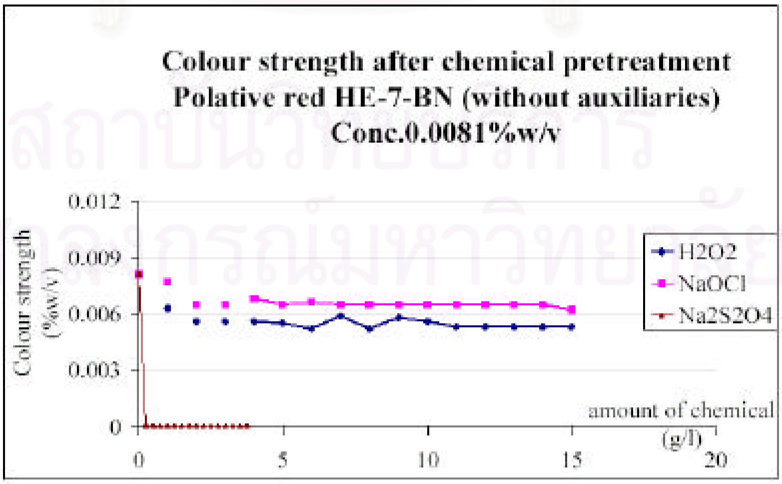


Figure 34 Colour strength after chemical pretreatment Polative red HE-7-BN (without auxiliaries) Conc.0.0081%w/v

Note: In chemical pretreatment of effluents using reactive dye showed that the dye was self-reacted. The dye colour changed to yellowish. The reduction reaction occurred very quickly when only a small amount of reducing was used. Auxiliaries had no effect on the chemical pretreatment.

4.3 Disperse dye

Table 15 Oxidation –Reduction (with auxiliaries)

Amount of Chemical (g/l)	Colour strength (%w/v)								
	0.0013			0.0018			0.0039		
	H_2O_2	NaOCl	$Na_2S_2O_4$	H_2O_2	NaOCl	$Na_2S_2O_4$	H_2O_2	NaOCl	$Na_2S_2O_4$
0	0.0013	0.0013	0.0013	0.0018	0.0018	0.0018	0.0039	0.0039	0.0039
1	0.0024	0.002	0.0005	0.0013	0.0015	0.0007	0.0013	0.0040	0.0017
2	0.0020	0.0019	0.0005	0.0011	0.0013	0.0005	0.0015	0.0039	0.0014
3	0.0024	0.0018	0.0004	0.0009	0.0012	0.0005	0.0014	0.0040	0.0011
4	0.0019	0.0018	0.0005	0.0011	0.0012	0.0004	0.0014	0.0039	0.0012
5	0.0026	0.0019	0.0005	0.0009	0.0012	0.0004	0.0013	0.0039	0.0011
6	0.0020	0.0018	0.0005	0.0009	0.0011	0.0004	0.0013	0.0039	0.0011
7	0.0035	0.0018	0.0005	0.0013	0.0010	0.0004	0.0013	0.0037	0.0011
8	0.0023	0.0018	0.0004	0.0009	0.0010	0.0003	0.0012	0.0036	0.0011
9	0.0022	0.0017	0.0004	0.0009	0.0007	0.0003	0.0012	0.0036	0.0011
10	0.0026	0.0017	0.0003	0.0010	0.0009	0.0003	0.0012	0.0036	0.0011
11	0.0017	0.0016	0.0003	0.0010	0.0010	0.0003	0.0012	0.0035	0.0011
12	0.0020	0.0015	0.0003	0.0011	0.0009	0.0003	0.0011	0.0034	0.0011
13	0.0013	0.0015	0.0003	0.0010	0.0008	0.0003	0.0011	0.0034	0.0011
14	0.0015	0.0015	0.0003	0.0011	0.0009	0.0003	0.0011	0.0035	0.0011
15	0.0011	0.0014	0.0003	0.0010	0.0008	0.0003	0.0011	0.0034	0.0011

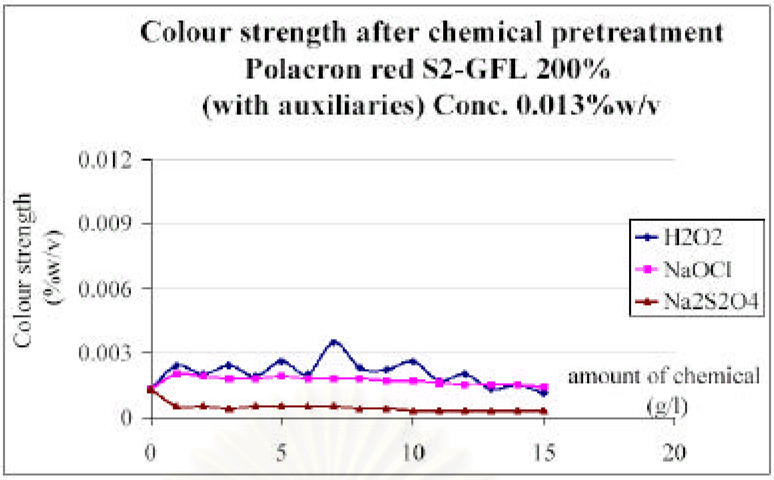


Figure 35 Colour strength after chemical pretreatment Polacron red S2-GFL 200% (with auxiliaries) Conc.0.0013%w/v

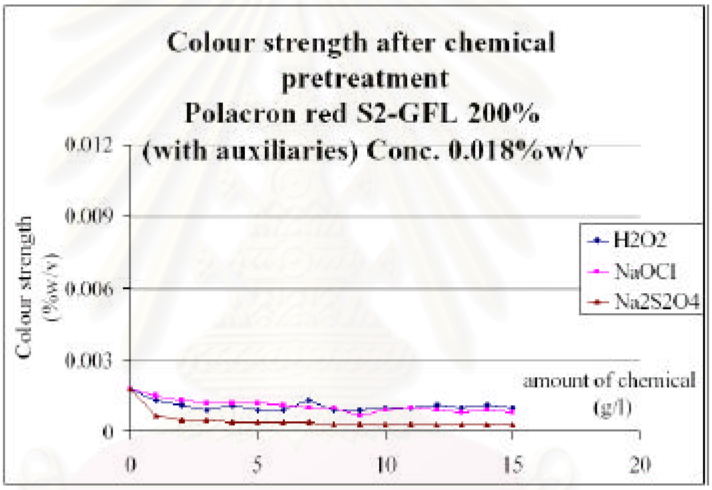


Figure 36 Colour strength after chemical pretreatment Polacron red S2-GFL 200% (with auxiliaries) Conc.0.0018%w/v

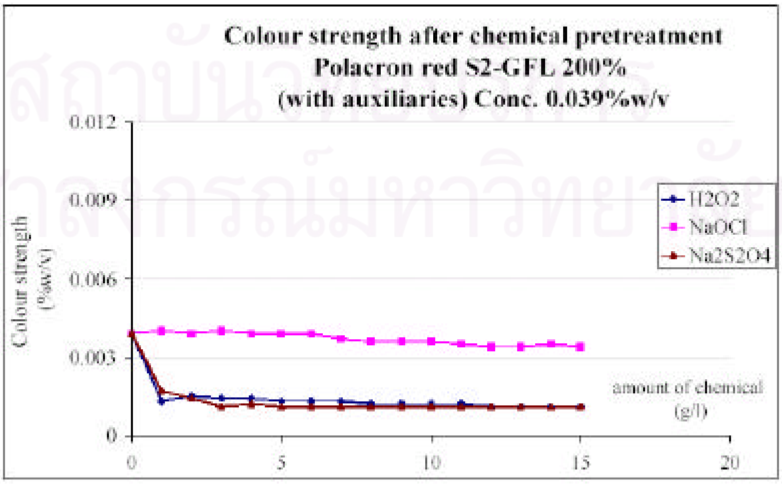


Figure 37 Colour strength after chemical pretreatment Polacron red S2-GFL 200% (with auxiliaries) Conc.0.0039%w/v

Table 16 Oxidation –Reduction (without auxiliaries)

Amount of Chemical (g/l)	Colour strength (%w/v)								
	0.0025			0.0029			0.0097		
	H_2O_2	NaOCl	$Na_2S_2O_4$	H_2O_2	NaOCl	$Na_2S_2O_4$	H_2O_2	NaOCl	$Na_2S_2O_4$
0	0.0025	0.0025	0.0025	0.0029	0.0029	0.0029	0.0097	0.0097	0.0097
1	0.0032	0.0026	0.0006	0.0038	0.0024	0.0008	0.0034	0.0102	0.0009
2	0.0032	0.0025	0.0006	0.0036	0.0023	0.0008	0.0017	0.0103	0.0004
3	0.0032	0.0025	0.0006	0.0033	0.0023	0.0007	0.0016	0.0102	0.0004
4	0.0031	0.0025	0.0005	0.0036	0.0022	0.0007	0.0015	0.0103	0.0003
5	0.0031	0.0024	0.0005	0.0033	0.0022	0.0007	0.0016	0.01	0.0003
6	0.0031	0.0023	0.0006	0.0033	0.0021	0.0006	0.0015	0.0099	0.0003
7	0.0033	0.0024	0.0004	0.0033	0.002	0.0006	0.0016	0.0096	0.0003
8	0.0031	0.0023	0.0004	0.0033	0.0019	0.0005	0.0013	0.0099	0.0004
9	0.0031	0.0025	0.0003	0.0033	0.0019	0.0004	0.0017	0.01	0.0004
10	0.0029	0.0025	0.0003	0.0033	0.0019	0.0004	0.0015	0.0096	0.0004
11	0.0031	0.0026	0.0003	0.0033	0.0017	0.0005	0.0014	0.0098	0.0003
12	0.0031	0.0025	0.0002	0.0033	0.0017	0.0004	0.0014	0.0096	0.0003
13	0.0031	0.0025	0.0002	0.0033	0.0016	0.0003	0.0014	0.0091	0.0003
14	0.0031	0.0025	0.0002	0.0033	0.0014	0.0003	0.0014	0.009	0.0003
15	0.0031	0.0023	0.0002	0.0033	0.0014	0.0004	0.0015	0.009	0.0003

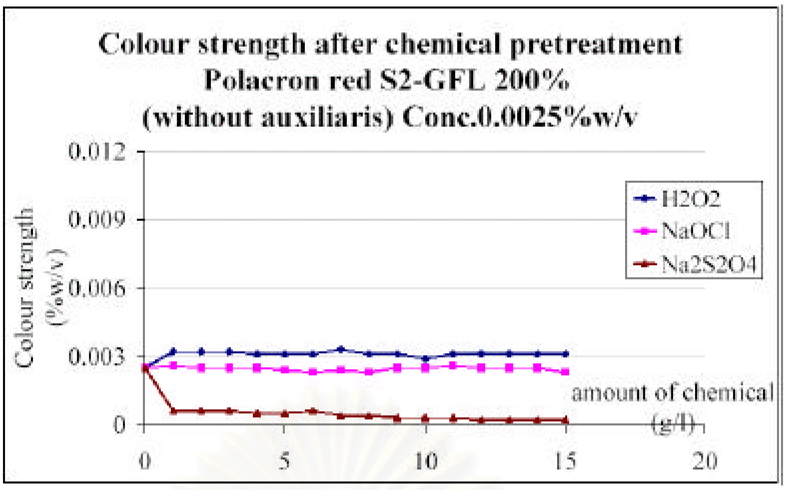


Figure 38 Colour strength after chemical pretreatment Polacron red S2-GFL 200% (without auxiliaries) Conc.0.0025%w/v

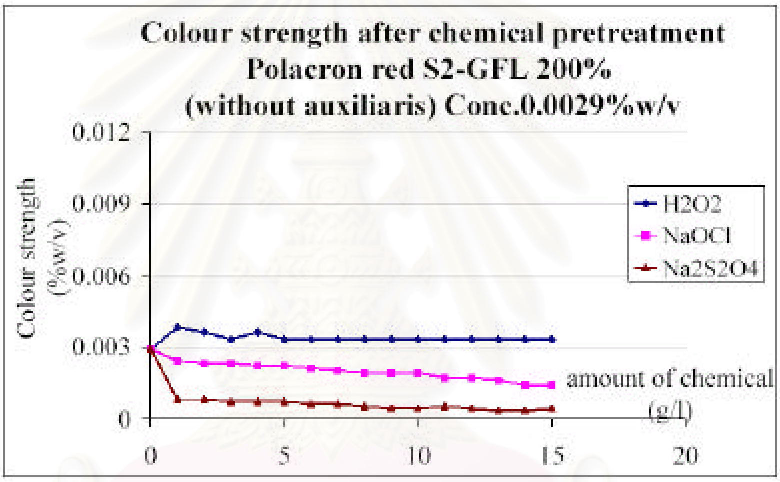


Figure 39 Colour strength after chemical pretreatment Polacron red S2-GFL 200% (without auxiliaries) Conc.0.0029%w/v

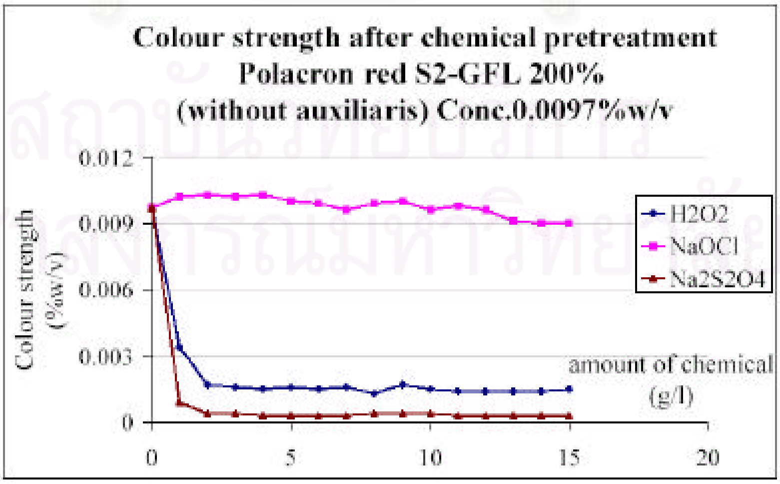


Figure 40 Colour strength after chemical pretreatment Polacron red S2-GFL 200% (without auxiliaries) Conc.0.0097%w/v

4. Acid dye

For acid dye at 0.5% and 1.0% shade all the colour was absorbed by the substrate, therefore chemical pretreatment was not on performed on the remaining dye solution.

Table 17 Oxidation –Reduction (with auxiliaries)

Amount of Chemical (g/l)	Colour strength (%w/v)								
	0.0000			0.0000			0.0031		
	H_2O_2	NaOCl	$Na_2S_2O_4$	H_2O_2	NaOCl	$Na_2S_2O_4$	H_2O_2	NaOCl	$Na_2S_2O_4$
0	N/A	N/A	N/A	N/A	N/A	N/A	0.0031	0.0031	0.0031
1	N/A	N/A	N/A	N/A	N/A	N/A	0.0025	0.0034	0.000
2	N/A	N/A	N/A	N/A	N/A	N/A	0.0022	0.0036	0.000
3	N/A	N/A	N/A	N/A	N/A	N/A	0.0018	0.0027	0.000
4	N/A	N/A	N/A	N/A	N/A	N/A	0.0018	0.0029	0.000
5	N/A	N/A	N/A	N/A	N/A	N/A	0.0019	0.0024	0.000
6	N/A	N/A	N/A	N/A	N/A	N/A	0.0018	0.0022	0.000
7	N/A	N/A	N/A	N/A	N/A	N/A	0.002	0.0023	0.000
8	N/A	N/A	N/A	N/A	N/A	N/A	0.0021	0.0022	0.000
9	N/A	N/A	N/A	N/A	N/A	N/A	0.002	0.0023	0.000
10	N/A	N/A	N/A	N/A	N/A	N/A	0.0019	0.0012	0.000
11	N/A	N/A	N/A	N/A	N/A	N/A	0.0021	0.0012	0.000
12	N/A	N/A	N/A	N/A	N/A	N/A	0.0021	0.0012	0.000
13	N/A	N/A	N/A	N/A	N/A	N/A	0.0021	0.0013	0.000
14	N/A	N/A	N/A	N/A	N/A	N/A	0.0021	0.0011	0.000
15	N/A	N/A	N/A	N/A	N/A	N/A	0.0021	0.0011	0.000

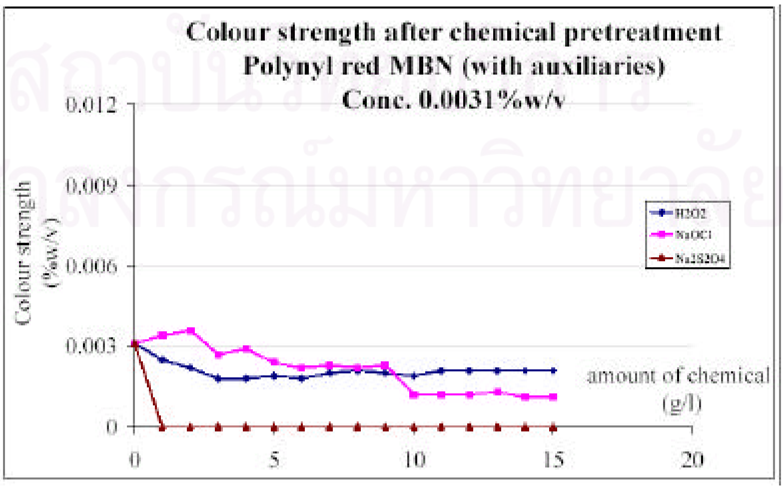


Figure 41 Colour strength after chemical pretreatment Polynyl red MBN (with auxiliaries) Conc.0.0031% w/v

Table 18 Oxidation –Reduction (without auxiliaries)

Amount of Chemical (g/l)	**Colour strength (%w/v)**								
	0.0037			**0.0080**			**0.1010**		
	H_2O_2	**NaOCl**	**$Na_2S_2O_4$**	**H_2O_2**	**NaOCl**	**$Na_2S_2O_4$**	**H_2O_2**	**NaOCl**	**$Na_2S_2O_4$**
0	0.0037	0.0037	0.0037	0.0080	0.0080	0.0080	0.1010	0.1010	0.1010
1	0.0025	0.0029	0.0036	0.0052	0.0072	0.0072	0.0101	0.0101	0.010
2	0.0026	0.0021	0.0033	0.0042	0.0061	0.0056	0.0101	0.0101	0.010
3	0.0025	0.0014	0.0031	0.0035	0.0054	0.000	0.0101	0.0101	0.007
4	0.0023	0.0007	0.0027	0.0031	0.0043	0.000	0.0101	0.0101	0.000
5	0.0023	0.0003	0.0006	0.0031	0.002	0.000	0.0101	0.0101	0.000
6	0.0025	0.000	0.000	0.0031	0.0026	0.000	0.0101	0.0101	0.000
7	0.0025	0.000	0.000	0.0029	0.0018	0.000	0.0101	0.0101	0.000
8	0.0023	0.000	0.000	0.0025	0.0011	0.000	0.0101	0.0101	0.000
9	0.0023	0.000	0.000	0.0025	0.0005	0.000	0.0101	0.0101	0.000
10	0.0023	0.000	0.000	0.0024	0.0002	0.000	0.0101	0.0101	0.000
11	0.0023	0.000	0.000	0.0023	0.000	0.000	0.0101	0.0101	0.000
12	0.0023	0.000	0.000	0.0023	0.000	0.000	0.0101	0.0101	0.000
13	0.0025	0.000	0.000	0.0021	0.000	0.000	0.0101	0.0101	0.000
14	0.0023	0.000	0.000	0.0021	0.000	0.000	0.0101	0.0101	0.000
15	0.0022	0.000	0.000	0.0022	0.000	0.000	0.0101	0.0101	0.000

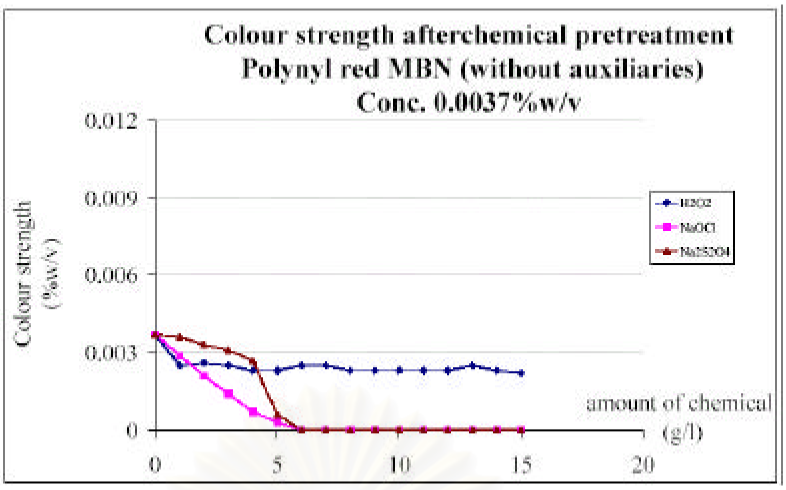


Figure 42 Colour strength after chemical pretreatment Polynyl red MBN (without auxiliaries) Conc.0.0037%w/v

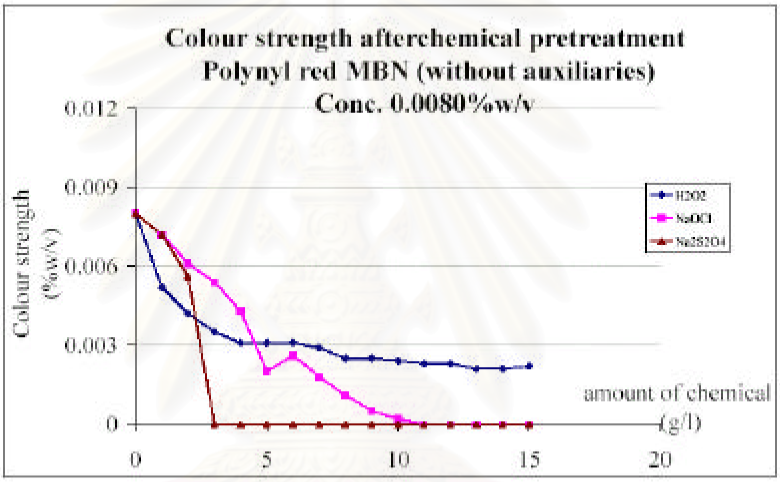


Figure 43 Colour strength after chemical pretreatment Polynyl red MBN (without auxiliaries) Conc.0.0080%w/v

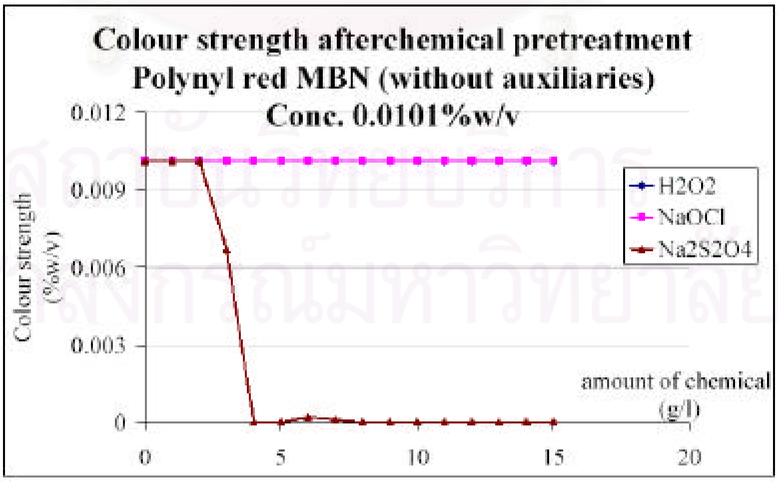


Figure 44 Colour strength after chemical pretreatment Polynyl red MB (without auxiliaries) Conc.0.1010%w/v

5. Basic dye

Table 19 Oxidation –Reduction (with auxiliaries)

Amount of chemical (g/l)	Colour Strength (%w/v)								
	0.0002			0.0021			0.0026		
	H_2O_2	NaOCl	$Na_2S_2O_4$	H_2O_2	NaOCl	$Na_2S_2O_4$	H_2O_2	NaOCl	$Na_2S_2O_4$
0	0.0002	0.0002	0.0002	0.0021	0.0021	0.0021	0.0026	0.0026	0.0026
1	0.0000	0.0001	0.0003	0.0001	0.0019	0.0001	0.0000	0.0026	0.0004
2	0.0000	0.0000	0.0002	0.0001	0.0017	0.0001	0.0000	0.0026	0.0005
3	0.0000	0.0000	0.0001	0.0001	0.0014	0.0001	0.0000	0.0026	0.0002
4	0.0000	0.0000	0.0000	0.0001	0.0012	0.0000	0.0000	0.0025	0.0001
5	0.0000	0.0000	0.0000	0.0001	0.0009	0.0000	0.0000	0.0021	0.0001
6	0.0000	0.0000	0.0000	0.0000	0.0007	0.0000	0.0000	0.0023	0.0001
7	0.0000	0.0000	0.0000	0.0000	0.0005	0.0000	0.0000	0.0016	0.0000
8	0.0000	0.0000	0.0000	0.0000	0.0003	0.0000	0.0000	0.0016	0.0000
9	0.0000	0.0000	0.0000	0.0000	0.0002	0.0000	0.0000	0.0016	0.0000
10	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0013	0.0000
11	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0001	0.0000
12	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
13	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
14	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
15	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

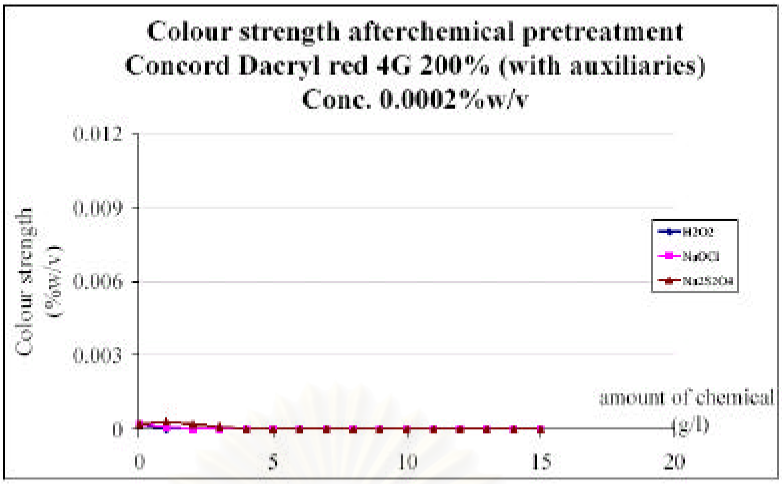


Figure 45 Colour strength after chemical pretreatment Concord Dacryl red 4G 200% (with auxiliaries) Conc. 0.0002%w/v

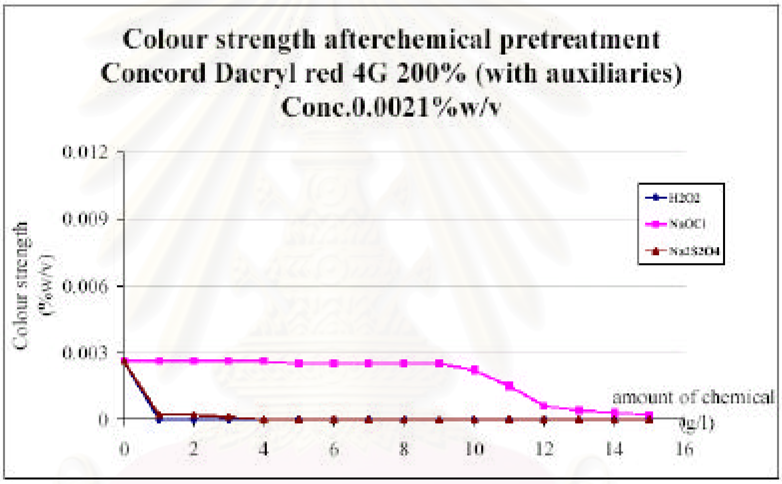


Figure 46 Colour strength after chemical pretreatment Concord Dacryl red 4G 200% (with auxiliaries) Conc.0.0021%w/v

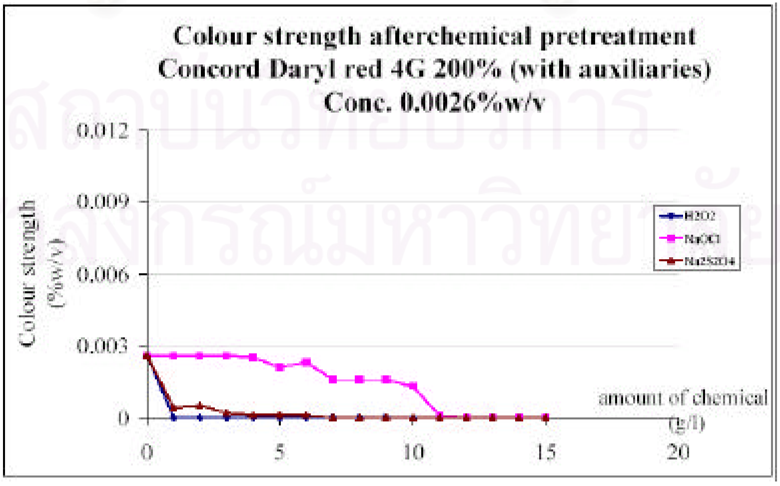


Figure 47 Colour strength after chemical pretreatment Concord Dacryl red 4G 200% (with auxiliaries) Conc. 0.0026%w/v

Table 20 Oxidation –Reduction (without auxiliaries)

Amount of chemical (g/l)	**Colour strength (%w/v)**								
	0.0004			**0.0030**			**0.0036**		
	H_2O_2	**NaOCl**	**$Na_2S_2O_4$**	**H_2O_2**	**NaOCl**	**$Na_2S_2O_4$**	**H_2O_2**	**NaOCl**	**$Na_2S_2O_4$**
0	0.0004	0.0004	0.0004	0.0030	0.0030	0.0030	0.0036	0.0036	0.0036
1	0.0001	0.0001	0.0000	0.0001	0.0032	0.0001	0.0002	0.0034	0.0003
2	0.0001	0.0000	0.0000	0.0001	0.0032	0.0001	0.0000	0.0026	0.0002
3	0.0001	0.0000	0.0000	0.0001	0.0032	0.0001	0.0000	0.0026	0.0002
4	0.0001	0.0000	0.0000	0.0001	0.0028	0.0001	0.0000	0.0026	0.0001
5	0.0001	0.0000	0.0000	0.0001	0.0019	0.0001	0.0000	0.0026	0.0000
6	0.0001	0.0000	0.0000	0.0000	0.0007	0.0001	0.0000	0.0025	0.0000
7	0.0000	0.0000	0.0000	0.0000	0.0002	0.0000	0.0000	0.0025	0.0000
8	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0025	0.0000
9	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0025	0.0000
10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0025	0.0000
11	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0022	0.0000
12	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0015	0.0000
13	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0006	0.0000
14	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0004	0.0000
15	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0003	0.0000

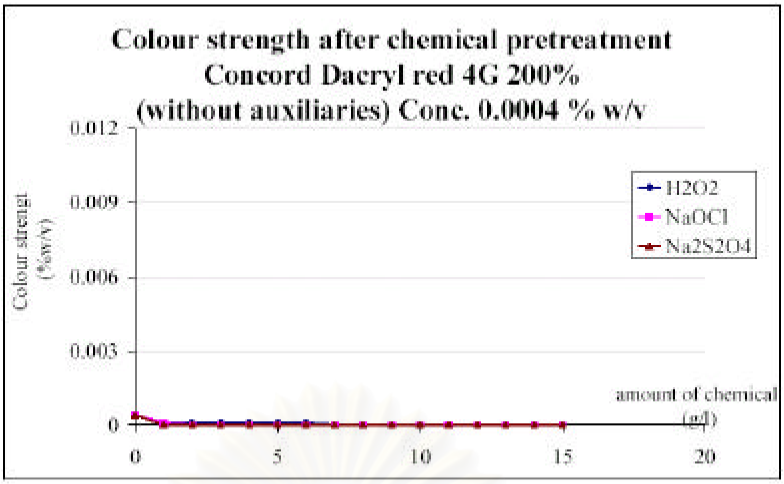


Figure 48 Colour strength after chemical pretreatment
Concord Dacryl red 4G 200% (without auxiliaries) Conc. 0.0004%w/v

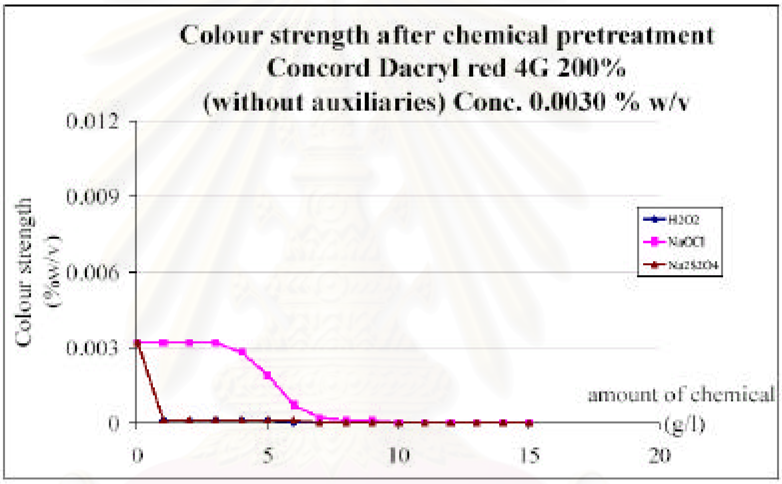


Figure 49 Colour strength after chemical pretreatment
Concord Dacryl red 4G 200% (without auxiliaries) Conc. 0.0030%w/v

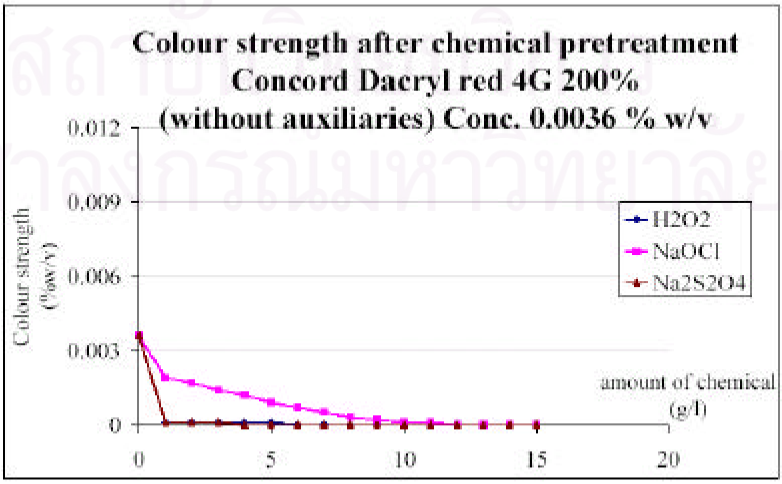


Figure 50 Colour strength after chemical pretreatment
Concord Dacryl red 4G 200% (without auxiliaries) Conc. 0.0036%w/v

3.5 Physical pretreatment

Physical pretreatment was performed in the batch apparatus shown in Figure 8, activated carbon was used as the absorbate. For a fixed effluent volume of 1 liter, the amount of activated carbon were varied. Mass 1, Mass 2, Mass 3 and Mass 4 are for 100 gm, 200 gm, 300 gm and 400 gm of activated carbon per 1 liter dye effluent respectively.

1. Direct dye

Table 21 Adsorption (with auxiliaries)

Time (hr)	**Colour strength (%w/v)**											
	0.0004				**0.0026**				**0.0049**			
	Mass 1	Mass 2	Mass 3	Mass 4	Mass 1	Mass 2	Mass 3	Mass 4	Mass 1	Mass 2	Mass 3	Mass 4
0	0.0004	0.0004	0.0004	0.0004	0.0026	0.0026	0.0026	0.0026	0.0049	0.0049	0.0049	0.0049
1	**0.0000**	0.0000	0.0000	0.0000	0.0022	0.0026	0.0001	0.0000	0.0036	0.0028	0.0032	0.0036
2	0.0000	0.0000	0.0000	0.0000	0.0012	0.0004	0.0000	0.0000	0.0026	0.0016	0.0024	0.0030
3	0.0000	0.0000	0.0000	0.0000	0.0004	**0.0000**	0.0000	0.0000	0.0022	0.0008	0.0018	0.0026
4	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0016	0.0007	0.0010	0.0018
5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0016	0.0007	0.0006	0.0004
6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0016	0.0007	0.0005	**0.0000**
7	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0016	0.0007	0.0002	0.0000
8	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0016	0.0006	0.0000	0.0000

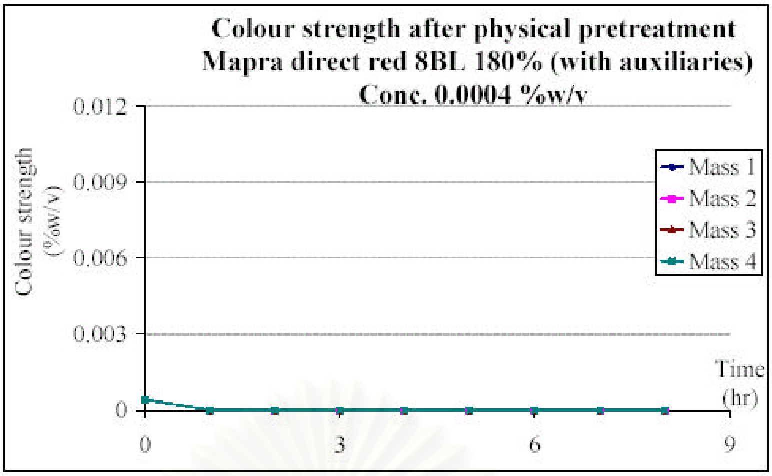


Figure 51 Colour strength after physical pretreatment
Mapradirect red 8BL 180% (with auxiliaries) Conc.0.0004%w/v

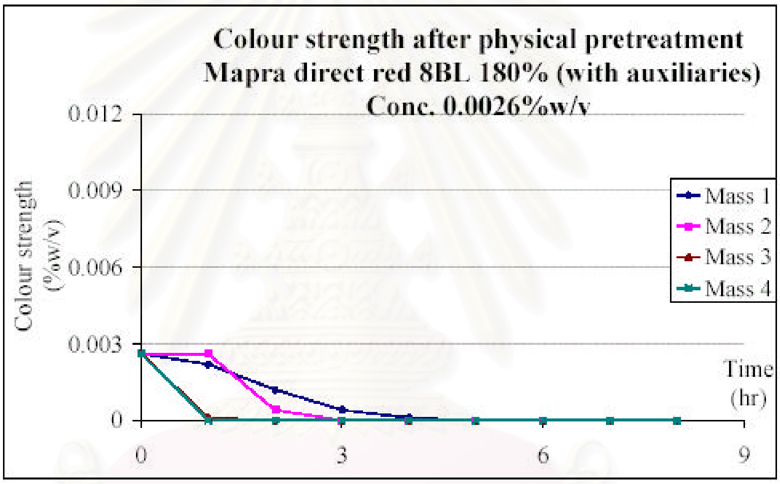


Figure 52 Colour strength after physical pretreatment
Mapradirect red 8BL 180% (with auxiliaries) Conc.0.0026%w/v

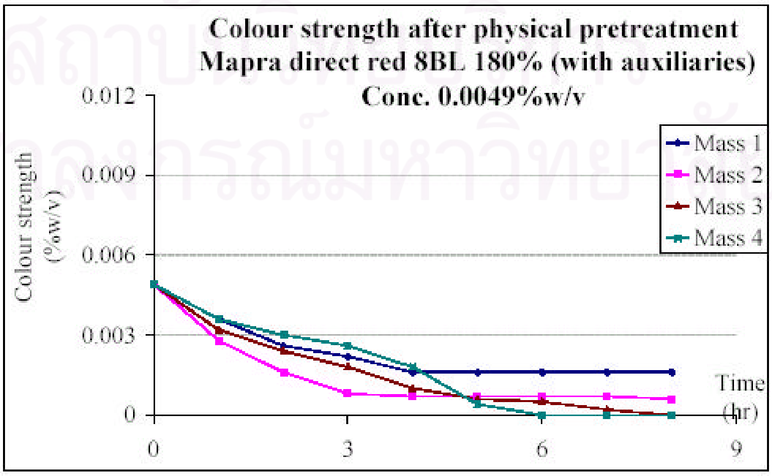


Figure 53 Colour strength after physical pretreatment
Mapradirect red 8BL 180% (with auxiliaries) Conc.0.0049%w/v

Table 22 Adsorption (without auxiliaries)

Time (hr)	**Colour strength (%w/v)**											
	0.0023				**0.0050**				**0.0072**			
	Mass 1	Mass 2	Mass 3	Mass 4	Mass 1	Mass 2	Mass 3	Mass 4	Mass 1	Mass 2	Mass 3	Mass 4
0	0.0023	0.0023	0.0023	0.0023	0.0050	0.0050	0.0050	0.0050	0.0072	0.0072	0.0072	0.0072
1	0.0014	0.0010	0.0006	**0.0000**	0.0038	0.0029	0.0020	0.0018	0.0062	0.0054	0.0046	0.0040
2	0.0008	0.0008	0.0002	0.000	0.0026	0.0018	0.0016	0.0012	0.0051	0.0044	0.0032	0.0026
3	0.0006	0.0006	0.000	0.000	0.0017	0.0009	0.0005	0.0002	0.0042	0.0031	0.0020	0.0018
4	0.0005	0.0004	0.000	0.000	0.0012	0.0007	0.0003	0.0001	0.0027	0.0022	0.0016	0.0007
5	0.0003	0.0001	0.000	0.000	0.0008	0.0004	0.0002	0.0001	0.0016	0.0014	0.0012	0.0004
6	0.0003	0.000	0.000	0.000	0.0007	0.0004	0.0001	**0.0000**	0.0016	0.0007	0.0005	**0.0000**
7	0.0002	0.000	0.000	0.000	0.0006	0.0002	0.0001	0.0000	0.0016	0.0005	0.0002	0.000
8	0.0002	0.000	0.000	0.000	0.0004	0.0001	0.0001	0.0000	0.0016	0.0004	0.0000	0.000

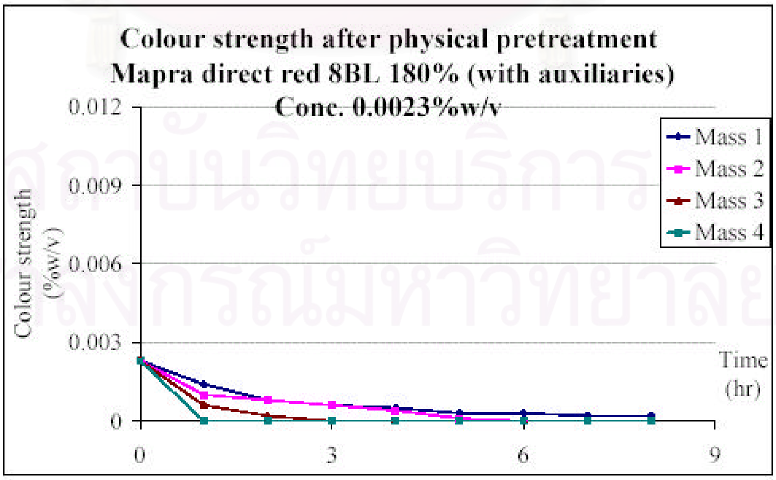


Figure 54 Colour strength after physical pretreatment Mapradirect 8BL 180% (without auxiliaries) Conc.0.0023%w/v

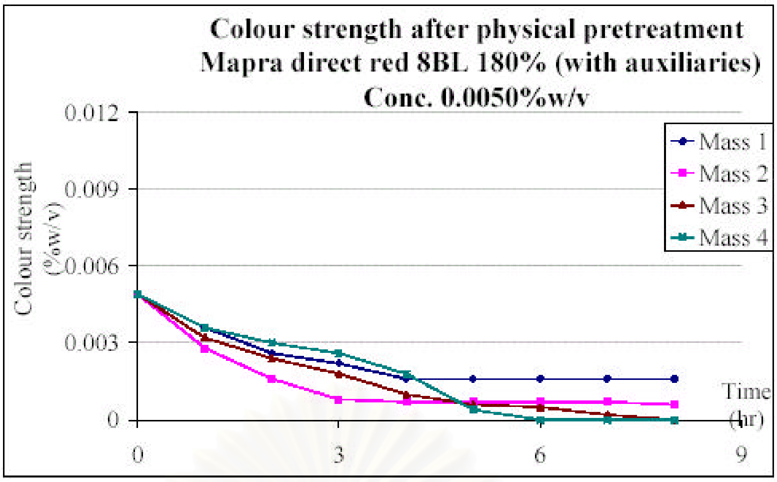


Figure 55 Colour strength after physical pretreatment Mapradirect 8BL 180% (without auxiliaries) Conc.0.0050%w/v

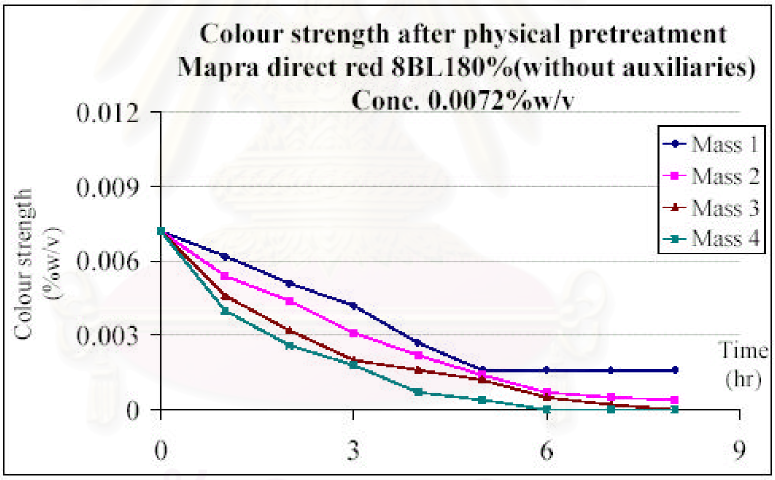


Figure 56 Colour strength after physical pretreatment Mapradirect 8BL 180% (without auxiliaries) Conc.0.0072%w/v

2. Reactive dye

Table 23 Adsorption (with auxiliaries)

Time (hr)	**Colour strength (%w/v)**											
	0.0017				**0.0040**				**0.0074**			
	Mass 1	Mass 2	Mass 3	Mass 4	Mass 1	Mass 2	Mass 3	Mass 4	Mass 1	Mass 2	Mass 3	Mass 4
0	0.0017	0.0017	0.0017	0.0017	0.0040	0.0040	0.0040	0.0040	0.0074	0.0074	0.0074	0.0074
1	0.0016	0.0015	0.0002	**0.0000**	0.0038	0.0034	0.0028	0.0008	0.0070	0.0061	0.0052	0.0054
2	0.0013	0.0010	**0.0000**	0.0000	0.0032	0.0028	0.0013	**0.0000**	0.0066	0.0052	0.0043	0.0038
3	0.0010	0.0006	0.0000	0.0000	0.0029	0.0024	0.0007	0.0000	0.0063	0.0046	0.0034	0.0014
4	0.0008	0.0004	0.0000	0.0000	0.0025	0.0019	0.0004	0.0000	0.0062	0.0040	0.0030	**0.0000**
5	0.0005	**0.0000**	0.0000	0.0000	0.0023	0.0015	0.0001	0.0000	0.0061	0.0040	0.0026	0.0000
6	0.0004	0.0000	0.0000	0.0000	0.0021	0.0011	**0.0000**	0.0000	0.0060	0.0039	0.0020	0.0000
7	0.0002	0.0000	0.0000	0.0000	0.0020	0.0008	0.0000	0.0000	0.0060	0.0039	0.0017	0.0000
8	0.0002	0.0000	0.0000	0.0000	0.0020	0.0003	0.0000	0.0000	0.0059	0.0038	0.0016	0.0000

Table 24 Adsorption (without auxiliaries)

Time (hr)	**Color strength (%w/v)**											
	0.0023				**0.0048**				**0.0081**			
	Ratio 1	**Ratio 2**	**Ratio 3**	**Ratio 4**	**Ratio 1**	**Ratio 2**	**Ratio 3**	**Ratio 4**	**Ratio 1**	**Ratio 2**	**Ratio 3**	**Ratio 4**
0	0.0023	0.0023	0.0023	0.0023	0.0048	0.0048	0.0048	0.0048	0.0081	0.0081	0.0081	0.0081
1	0.0016	0.0011	0.0009	**0.0000**	0.0032	0.0026	0.0020	0.0016	0.0073	0.0060	0.0054	0.0039
2	0.0011	0.0009	0.0006	0.0000	0.0028	0.0019	0.0014	0.0008	0.0064	0.0056	0.0046	0.0026
3	0.0009	0.0007	0.0004	0.0000	0.0024	0.0014	0.0008	0.0002	0.0052	0.0043	0.0038	0.0012
4	0.0006	0.0005	0.0002	0.0000	0.0018	0.0009	0.0006	0.0001	0.0048	0.0038	0.0026	0.0006
5	0.0006	0.0005	0.0000	0.0000	0.0012	0.0006	0.0004	**0.0000**	0.0048	0.0037	0.0023	0.0002
6	0.0005	0.0004	0.0000	0.0000	0.0012	0.0006	0.0001	0.0000	0.0048	0.0037	0.0019	0.0001
7	0.0004	0.0002	0.0000	0.0000	0.0012	0.0005	0.0001	0.0000	0.0048	0.0036	0.0012	**0.0000**
8	0.0004	0.0000	0.0000	0.0000	0.0012	0.0005	0.0000	0.0000	0.0048	0.0034	0.0009	0.0000

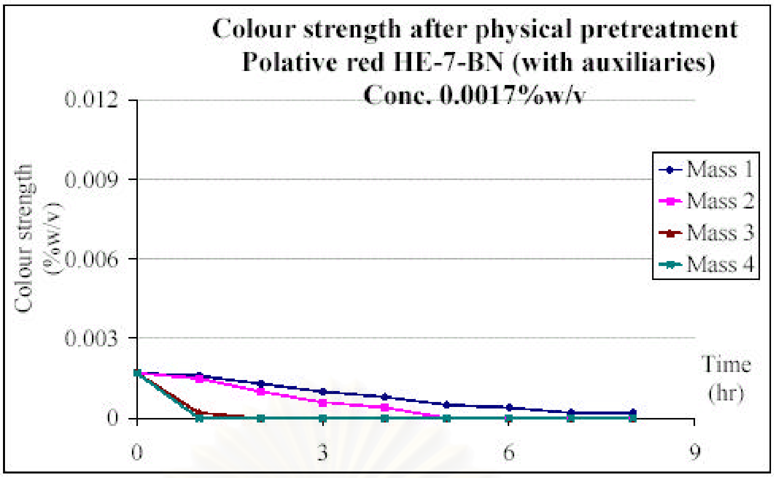


Figure 57 Colour strength after physical pretreatment Polative red HE-7-BN (with auxiliaries) Conc.0.0017%w/v

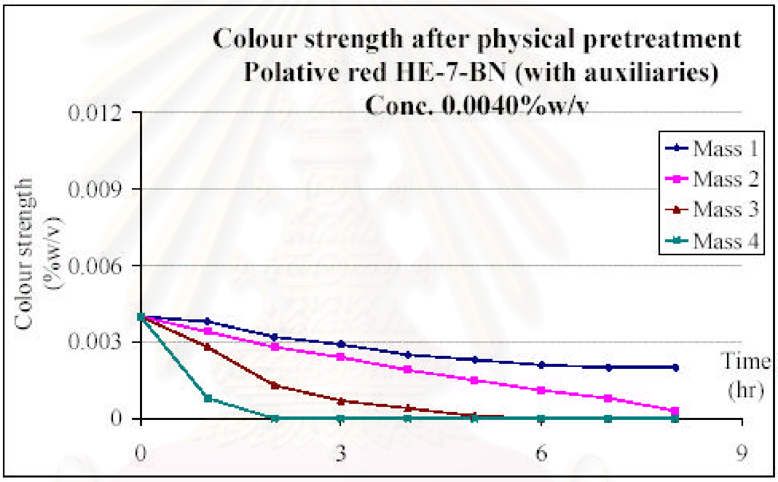


Figure 58 Colour strength after physical pretreatment Polative red HE-7-BN (with auxiliaries) Conc.0.0040%w/v

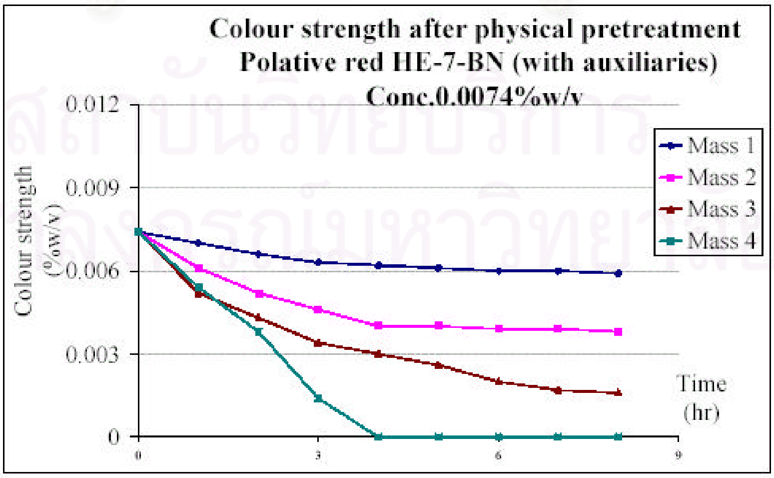


Figure 59 Colour strength after physical pretreatment Polative red HE-7-BN (with auxiliaries) Conc.0.0074%w/v

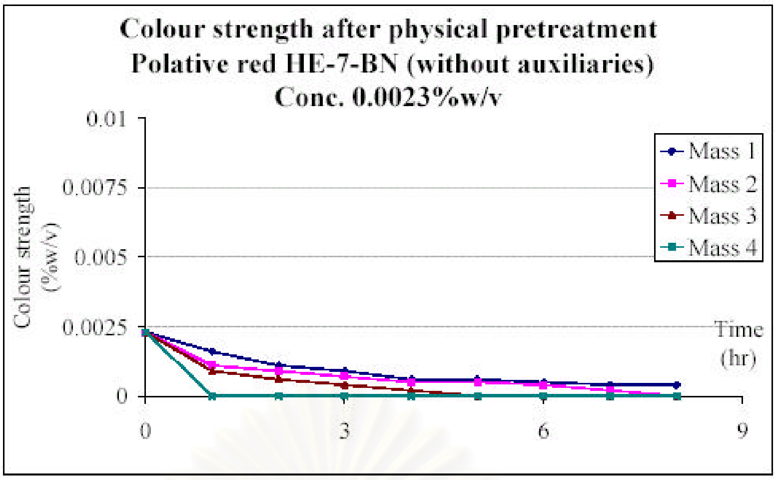


Figure 60 Colour strength after physical pretreatment Polative red HE-7-BN (without auxiliaries) Conc.0.0023%w/v

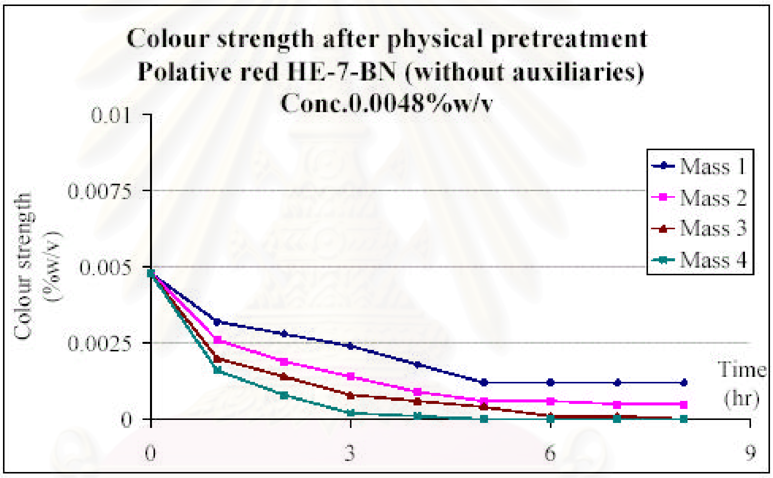


Figure 61 Colour strength after physical pretreatment Polative red HE-7-BN (without auxiliaries) Conc.0.0048%w/v

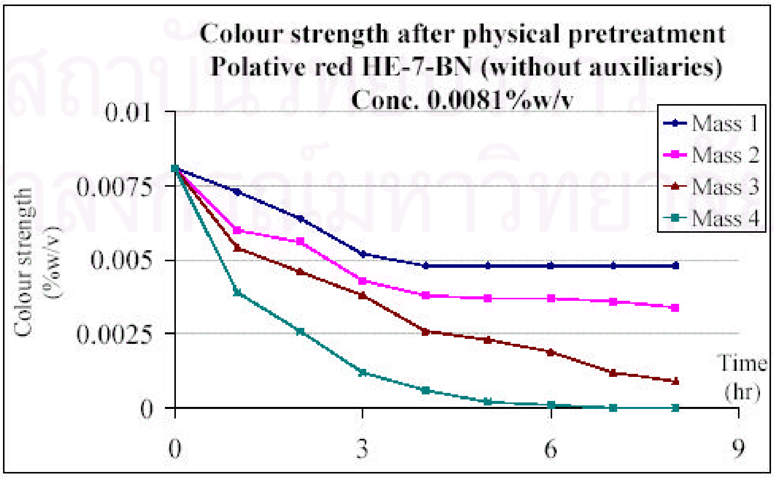


Figure 62 Colour strength after physical pretreatment Polative red HE-7-BN (without auxiliaries) Conc. 0.0081%w/v

3. Disperse dye

Table 25 Adsorption (with auxiliaries)

Time (hr)	Color Strength (%w/v)											
	0.0013				0.0018				0.0039			
	Mass 1	Mass 2	Mass 3	Mass 4	Mass 1	Mass 2	Mass 3	Mass 4	Mass 1	Mass 2	Mass 3	Mass 4
0	0.0013	0.0013	0.0013	0.0013	0.0018	0.0018	0.0018	0.0018	0.0039	0.0039	0.0039	0.0039
1	0.0008	0.0002	0.0000	0.0000	0.0018	0.0012	0.0002	0.0000	0.0032	0.0028	0.0024	0.0016
2	0.0001	0.0000	0.0000	0.0000	0.0013	0.0005	0.0000	0.0000	0.0025	0.0019	0.0019	0.0008
3	**0.0000**	0.0000	0.0000	0.0000	0.0010	0.0002	0.0000	0.0000	0.0016	0.0009	0.0008	0.0000
4	0.0000	0.0000	0.0000	0.0000	0.0008	**0.0000**	0.0000	0.0000	0.0009	0.0005	0.0002	0.0000
5	0.0000	0.0000	0.0000	0.0000	0.0008	0.0000	0.0000	0.0000	0.0005	0.0003	**0.0000**	0.0000
6	0.0000	0.0000	0.0000	0.0000	0.0003	0.0000	0.0000	0.0000	0.0005	0.0002	0.0000	0.0000
7	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0004	0.0001	0.0000	0.0000
8	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0004	0.0001	0.0000	0.0000

Table 26 Adsorption (without auxiliaries)

Time (hr)	Colour strength (%w/v)											
	0.5 % shade				1.0 % shade				2.0 % shade			
	Mass 1	Mass 2	Mass 3	Mass 4	Mass 1	Mass 2	Mass 3	Mass 4	Mass 1	Mass 2	Mass 3	Mass 4
0	0.0025	0.0025	0.0025	0.0025	0.0029	0.0029	0.0029	0.0029	0.0097	0.0097	0.0097	0.0097
1	0.0016	0.0010	0.0006	**0.0000**	0.0018	0.0014	0.0007	0.0002	0.0082	0.0076	0.0072	0.0063
2	0.0012	0.0005	0.0001	0.0000	0.0012	0.0008	0.0002	0.0000	0.0063	0.0068	0.0059	0.0050
3	0.0008	0.0003	0.0000	0.0000	0.0008	0.0001	**0.0000**	0.0000	0.0045	0.0049	0.0046	0.0043
4	0.0004	0.0001	0.0000	0.0000	0.0004	0.0000	0.0000	0.0000	0.0036	0.0035	0.0035	0.0038
5	0.0002	0.0000	0.0000	0.0000	0.0003	0.0000	0.0000	0.0000	0.0024	0.0028	0.0028	0.0021
6	0.0002	0.0000	0.0000	0.0000	0.0003	0.0000	0.0000	0.0000	0.0018	0.0026	0.0019	0.0010
7	0.0002	0.0000	0.0000	0.0000	0.0003	0.0000	0.0000	0.0000	0.0016	0.0024	0.0013	**0.0000**
8	0.0002	0.0000	0.0000	0.0000	0.0003	0.0000	0.0000	0.0000	0.0016	0.0022	0.0005	0.0000

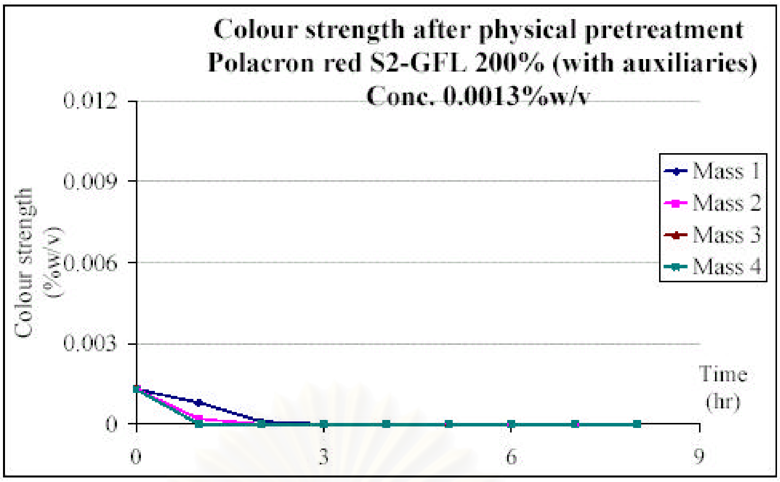


Figure 63 Colour strength after physical pretreatment
Polacron red S2-GFL 200% (with auxiliaries) Conc.0.0013%w/v

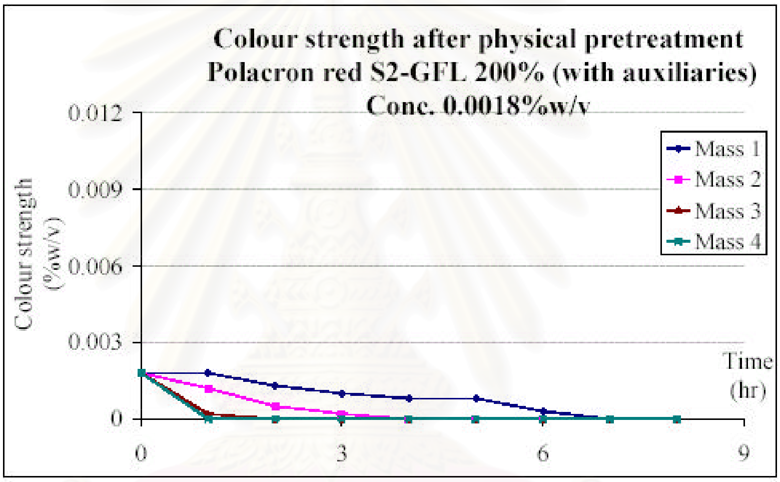


Figure 64 Colour strength after physical pretreatment
Polacron red S2-GFL 200% (with auxiliaries) Conc.0.0018%w/v

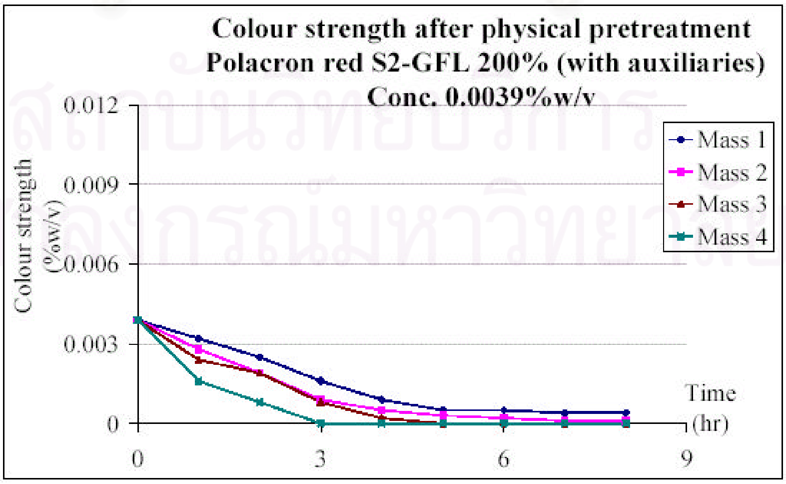


Figure 65 Colour strength after physical pretreatment
Polacron red S2-GFL 200% (with auxiliaries) Conc.0.0039%w/v

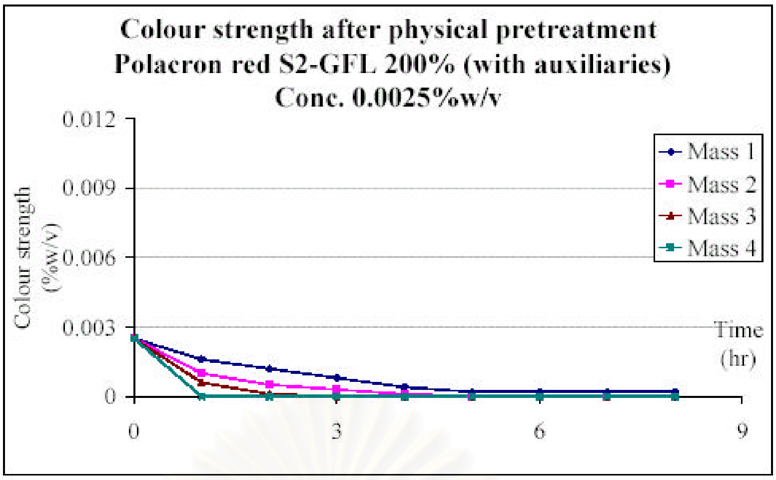


Figure 66 Colour strength after physical pretreatment Polacron red S2-GFL 200% (without auxiliaries) Conc.0.0025%w/v

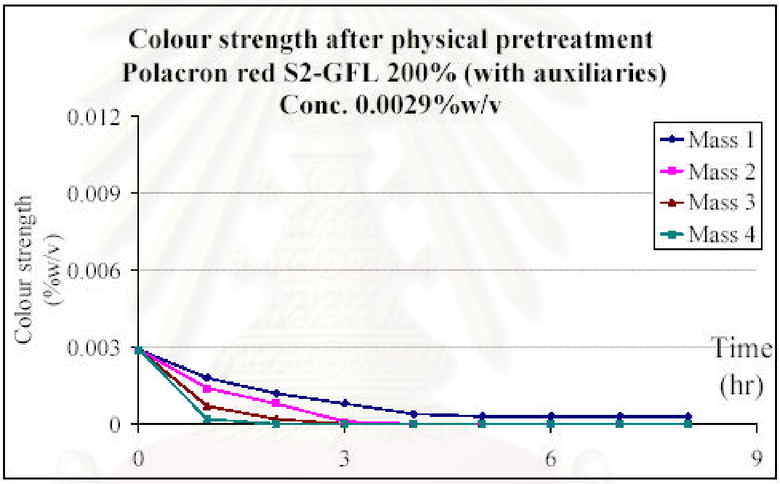


Figure 67 Colour strength after physical pretreatment Polacron red S2-GFL 200% (without auxiliaries) Conc.0.0029%w/v

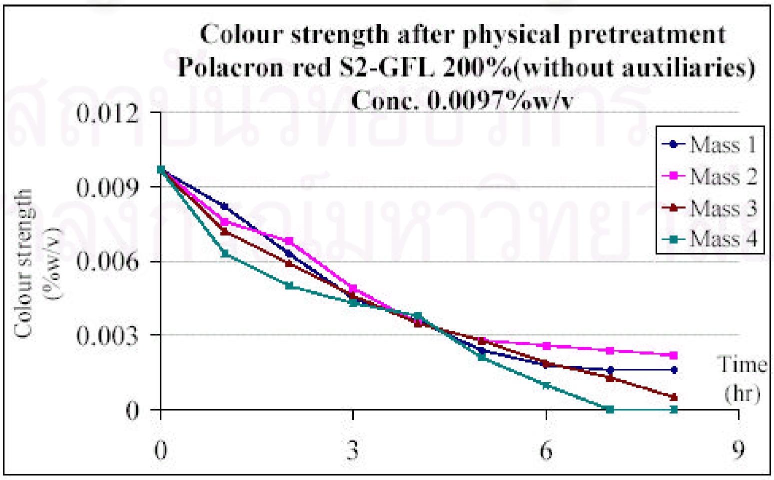


Figure 68 Colour strength after physical pretreatment Polacron red S2-GFL 200% (without auxiliaries) Conc.0.0097%w/v

4. Acid dye

Table 27 Adsorption (with auxiliaries)

Time (hr)	Colour strength (%w/v)											
	0.0000				**0.0000**				**0.0031**			
	Mass 1	Mass 2	Mass 3	Mass 4	Mass 1	Mass 2	Mass 3	Mass 4	Mass 1	Mass 2	Mass 3	Mass 4
0	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.0031	0.0031	0.0031	0.0031
1	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.0026	0.0016	0.0016	**0.0000**
2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.0013	0.0006	0.0001	0.0000
3	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.0008	0.0004	0.0000	0.0000
4	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.0003	0.0001	0.0000	0.0000
5	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.0001	0.0000	0.0000	0.0000
6	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.0000	0.0000	0.0000	0.0000
7	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.0000	0.0000	0.0000	0.0000
8	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.0000	0.0000	0.0000	0.0000

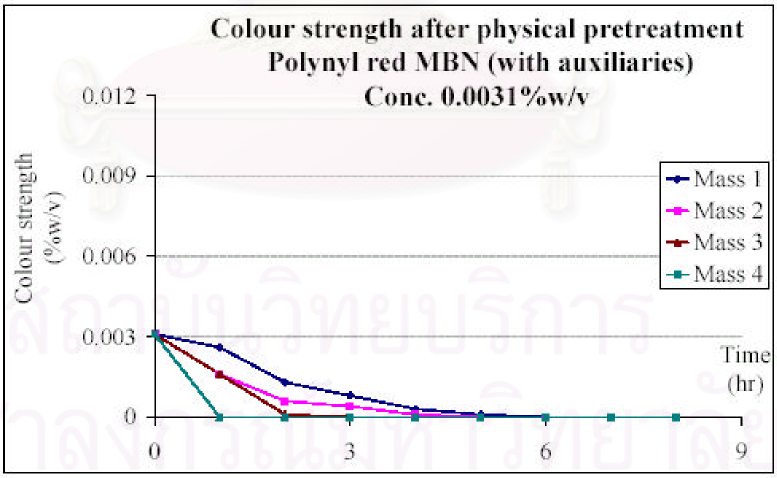


Figure 69 Colour strength after physical pretreatment Polynyl red MBN (with auxiliaries) Conc.0.0031%w/v

Table 28 Adsorption (without auxiliaries)

Time (hr)	**Colour strength (%w/v)**											
	0.0037				**0.0080**				**0.0101**			
	Mass 1	Mass 2	Mass 3	Mass 4	Mass 1	Mass 2	Mass 3	Mass 4	Mass 1	Mass 2	Mass 3	Mass 4
0	0.0037	0.0037	0.0037	0.0037	0.0080	0.0080	0.0080	0.0080	0.0101	0.0101	0.0101	0.0101
1	0.0030	0.0024	0.0016	**0.0000**	0.0070	0.0066	0.0062	0.0051	0.0096	0.0093	0.0091	0.0083
2	0.0026	0.0011	0.0003	0.0000	0.0066	0.0053	0.0043	0.0028	0.0087	0.0086	0.0081	0.0069
3	0.0012	0.0004	0.0000	0.0000	0.0054	0.0049	0.0029	0.0006	0.0072	0.0070	0.0069	0.0043
4	0.0002	0.0001	0.0000	0.0000	0.0042	0.0036	0.0020	**0.0000**	0.0063	0.0056	0.0051	0.0025
5	0.0000	0.0000	0.0000	0.0000	0.0036	0.0024	0.0011	0.0000	0.0049	0.0043	0.0042	0.0010
6	0.0000	0.0000	0.0000	0.0000	0.0024	0.0019	0.0006	0.0000	0.0032	0.0026	0.0020	0.0003
7	0.0000	0.0000	0.0000	0.0000	0.0012	0.0009	0.0000	0.0000	0.0026	0.0016	0.0012	**0.0000**
8	0.0000	0.0000	0.0000	0.0000	0.0008	0.0003	0.0000	0.0000	0.0013	0.0006	0.0002	0.0000

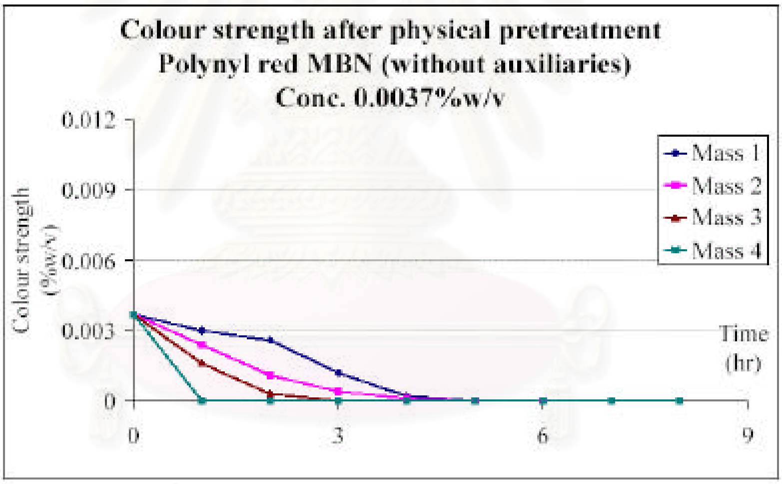


Figure 70 Colour strength after physical pretreatment Polynyl red MBN (without auxiliaries) Conc.0.0037%w/v

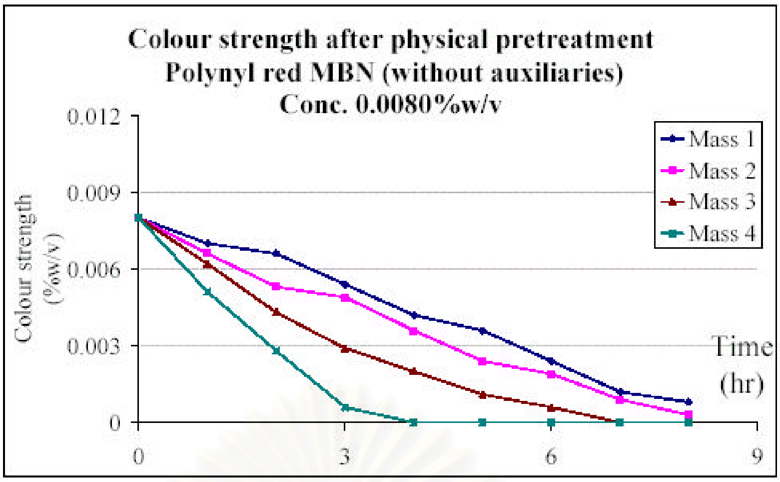


Figure 71 Colour strength after physical pretreatment Polynyl red MBN (without auxiliaries) Conc.0.0080%w/v

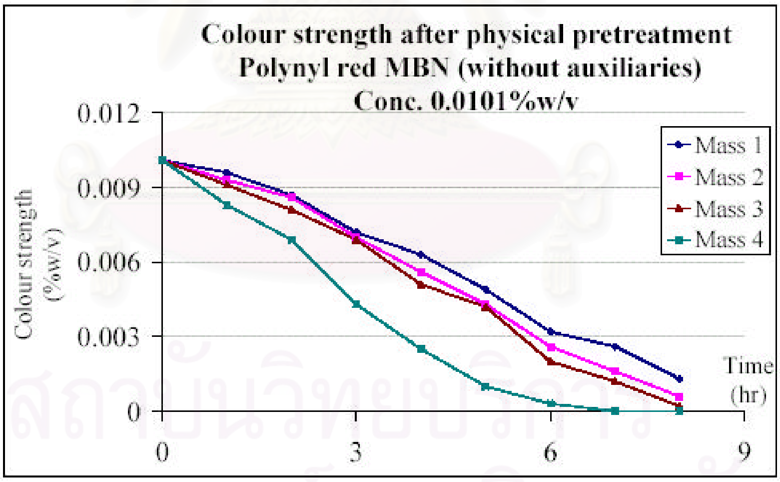


Figure 72 Colour strength after physical pretreatment Polynyl red MBN (without auxiliaries) Conc.0.0101%w/v

5. Basic dye

Table 29 Adsorption (with auxiliaries)

Time (hr)	Colour Strength (%w/v)											
	0.0002				**0.0021**				**0.0026**			
	Mass 1	Mass 2	Mass 3	Mass 4	Mass 1	Mass 2	Mass 3	Mass 4	Mass 1	Mass 2	Mass 3	Mass 4
0	0.0002	0.0002	0.0002	0.0002	0.0021	0.0021	0.0021	0.0021	0.0026	0.0026	0.0026	0.0026
1	**0.0000**	0.0000	0.0000	0.0000	**0.0000**	0.0000	0.0000	0.0000	0.0000	**0.0000**	0.0000	0.0000
2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
3	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
7	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
8	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 30 Adsorption (without auxiliaries)

Time (hr)	Colour Strength (%w/v)											
	0.0004				**0.0030**				**0.0036**			
	Mass 1	Mass 2	Mass 3	Mass 4	Mass 1	Mass 2	Mass 3	Mass 4	Mass 1	Mass 2	Mass 3	Mass 4
0	0.0004	0.0004	0.0004	0.0004	0.0030	0.0030	0.0030	0.0030	0.0036	0.0036	0.0036	0.0036
1	**0.0000**	0.0000	0.0000	0.0000	0.0006	**0.0000**	0.0000	0.0000	0.0006	0.0002	0.0000	0.0000
2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	**0.0000**	0.0000	0.0000
3	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
7	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
8	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

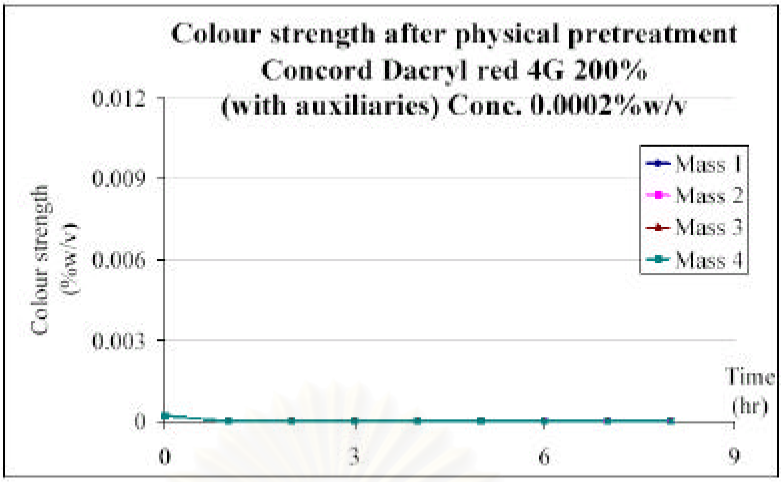


Figure 73 Colour strength after physical pretreatment Concord Dacryl red 4G 200% (with auxiliaries) Conc. 0.0002%w/v

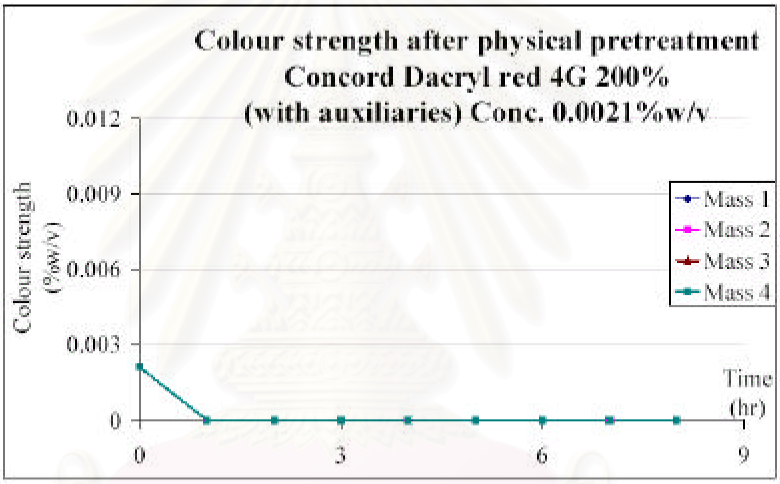


Figure 74 Colour strength after physical pretreatment Concord Dacryl red 4G 200% (with auxiliaries) Conc. 0.0021%w/v

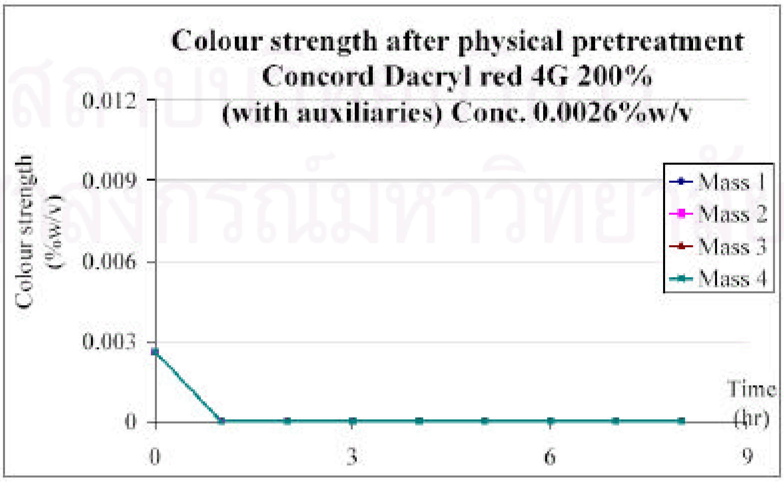


Figure 75 Colour strength after physical pretreatment Concord Dacryl red 4G 200% (with auxiliaries) Conc. 0.0026%w/v

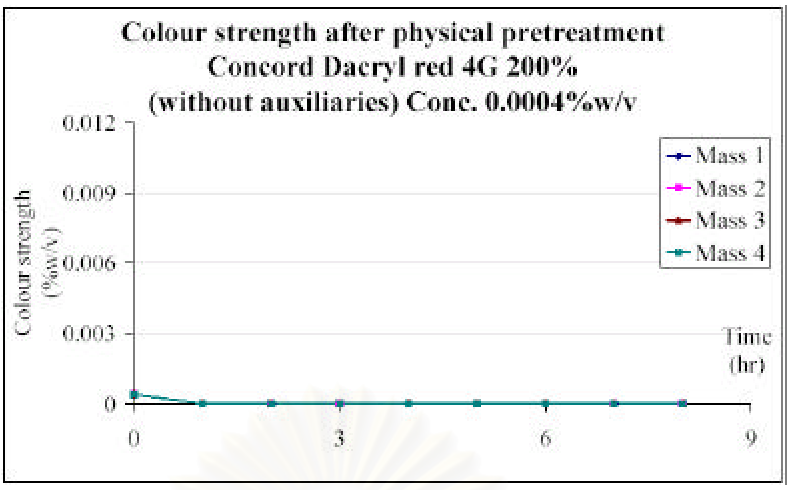


Figure 76 Colour strength after physical pretreatment
Concord Dacryl red 4G 200% (with auxiliaries) Conc. 0.0004%w/v

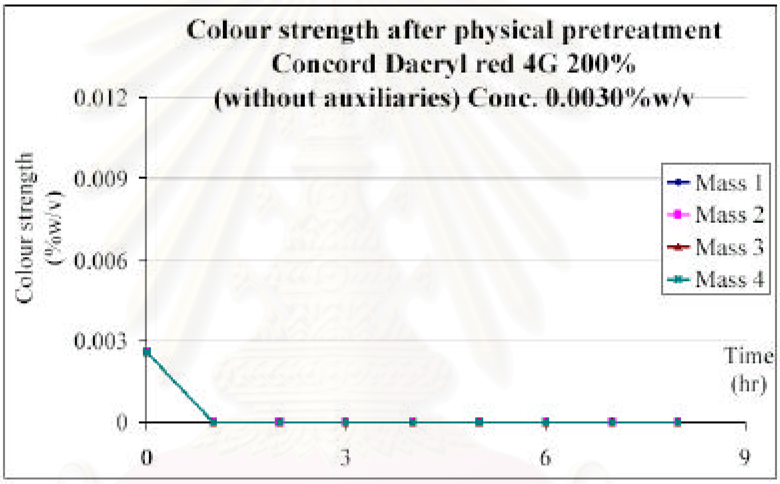


Figure 77 Colour strength after physical pretreatment
Concord Dacryl red 4G 200% (with auxiliaries) Conc. 0.0030%w/v

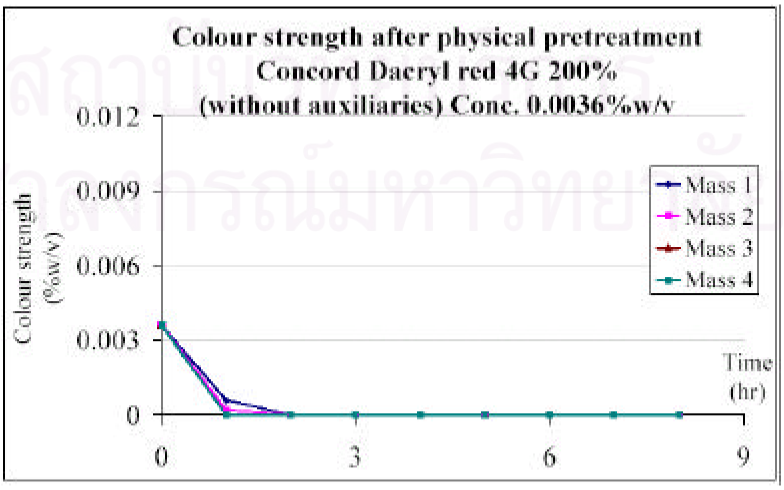


Figure 78 Colour strength after physical pretreatment
Concord Dacryl red 4G 200% (with auxiliaries) Conc. 0.0036%w/v

Result of chemical and physical pretreatment experiments can be summarized below:

1. Direct dye : Results showed that both chemical and physical pretreatment are efficient in reducing the dye colour strength.

2. Reactive dye : For chemical pretreatment only a small amount of reducing agent was used because this type of dye is self-reaction. Reactions occurred very quickly. The colour of the effluent turned to yellowish. The auxiliaries did not have any effect on chemical pretreatment. Oxidation processes could not reduce the dye colour strength. For physical pretreatment when no auxiliaries are added, the dye effluent had high colour strength therefore the time used for physical pretreatment is longer than in case when auxiliaries are present.

3. Disperse dye : Experemental results showed that both chemical and physical pretreatment are efficient in reducing the colour strength. Oxidation reaction could not reduce the dye colour strength. Since this type of dye is not soluble in water and is acidic in nature, therefore physical pretreatment of this dye type gave good results.

4. Acid dye : This dye has the little residual dye colour. For 0.5 and 1.0 % shade with auxiliaries added, the fibre can absorb all of the dyed. Chemical and physical pretreatment can reduced the dye colour strength. For physical pretreatment the favoured condition in the dyeing process is acidic.

5. Basic dye : Overall this dye has the little residual dye colour after dyeing. Experiments showed that both chemical and physical pretreatment gave very satisfactory results, dye colour strength could be reduced drastically. For physical pretreatment, acidic condition enhanced adsorption.

6. All of dye : Addition of chemical auxiliaries to the dye solution promotes the adsorption of dye onto the fibre, they do not have direct effect on the methods of treatment. If no auxiliaries are present, adsorption of dye onto the fibre would be less than having auxiliaries present, therefore colour strength of the dye effluent would be high. For chemical pretreatment more chemical are needed and for physical pretreatment longer time of treatment necessary. The effect of auxiliaries in all of dyes has the little effect in chemical pretreatment. But they make the residual dyed

has high colour strength only. So that in physical pretreatment must the long time for pretreatment.

CHAPTER IV
DISCUSSION OF RESULTS

This research work is aimed to determine the effect of chemical auxiliaries on colour strength of various dyes and conditions of dyeing processes that effect the physical and chemical pretreatment.

4.1 Effect the physical and chemical pretreatment.

4.1.1 Effect of Chemical Auxiliaries

The results of effect of chemical auxiliaries on colour strength of various dyes used were compared and tabulated in Table 31 below.

Table 31 Comparison of colour strength

Dyestuff	Concentration (% shade)	Colour strength (%w/v)	
		with auxiliaries	without auxiliaries
Direct dye	0.5	0.0004	0.0023
	1.0	0.0026	0.0050
	2.0	0.0049	0.0072
Reactive dye	0.5	0.0017	0.0023
	1.0	0.0040	0.0048
	2.0	0.0074	0.0081
Disperse dye	0.5	0.0013	0.0025
	1.0	0.0018	0.0029
	2.0	0.0039	0.0097
Acid dye	0.5	0.0000	0.0037
	1.0	0.0000	0.0080
	2.0	0.0031	0.101
Basic dye	0.5	0.0002	0.0004
	1.0	0.0021	0.0030
	2.0	0.0026	0.0036

As can be seen from Table 31 that the colour strength of all dye type with auxiliaries have higher value than those without auxiliaries. This is because auxiliaries enhanced the absorption of dye onto the fibre.

4.1.2 Effect on pH of dye solution

Suitable conditions are required to enhance dyeing processes and conditions vary for different types of dyes. Suitable pH values for various dyes are shown in the table below.

Table 32 Comparison of pH values

Dyestuff	**Concentration (% shade)**	**pH value**	
		with auxiliaries	**without auxiliaries**
Direct dye	0.5	7.65	8.28
	1.0	7.82	8.06
	2.0	7.56	8.06
Reactive dye	0.5	11.59	8.14
	1.0	11.59	7.85
	2.0	11.63	7.97
Disperse dye	0.5	7.65	8.1
	1.0	6.92	8.51
	2.0	6.64	8.35
Acid dye	0.5	4.17	8.57
	1.0	4.23	8.67
	2.0	4.59	8.79
Basic dye	0.5	3.75	8.72
	1.0	4.81	7.68
	2.0	4.75	8.21

It can be seen that the pH value with no auxiliaries added was between 7.85 – 8.79, this range is considered to be neutral condition. In dyeing processes salt should be added to the dye solution to improve the solubility of the solution. In addition, when the dyestuff is used in industrial processes, conditions for dyeing have to be adjusted thus:

Direct dye	Neutralize	pH	7-9	adjust with Na_2SO_4
Reactive	Base condition	pH	11-12	adjust with Na_2CO_3
Acid	Acid condition	pH	4-5	adjust with CH_3COOH
Basic	Acid condition	pH	2-6	adjust with CH_3COOH
Disperse	Acid condition	pH	6-7.5	adjust with CH_3COOH

For disperse dye, when no auxiliaries are present the true shade of the dye will not be obtained. To obtain the true shade dyeing process should be performed in an acidic condition.

4.2 Chemical Pretreatment

The amount of oxidizing or reducing agents needed for chemical pretreatment operations are summarized in Table 33. In this study, the decolouration was determined by monitoring the change in concentration using a UV Spectrophotometer (Shimadzu UV 160A)

Results showed that the chemical pretreatment was able to reduce the concentration of the effluent dye solution. However, chemical auxiliaries have little or no effect on the treatment but they effect the concentration of the dye, as a result the amount of chemicals needed for the pretreatment process is higher.

Reactive dye composed of reactive groups in its structure making it self-reacted. Thus, when only a small amount of reducing agent is added the reduction reaction occurred very quickly and the solution obtained has a yellowish colour.

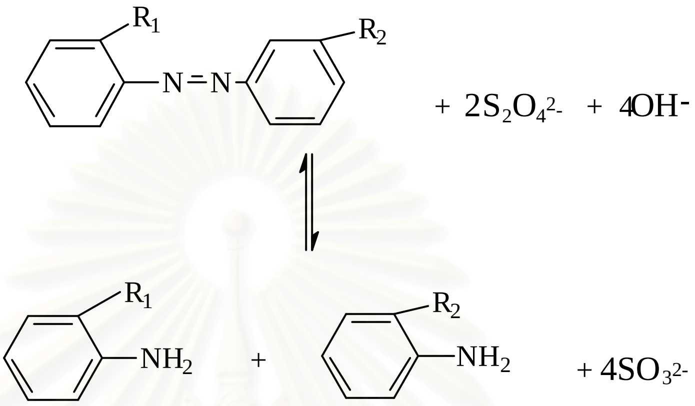
Table 33 Chemical Pretreatment

Dyestuff	Chemicals	With auxiliaries		Without auxiliaries	
		Conc. %(w/v)	Amount of chemical (g/l)	Conc. %(w/v)	Amount of chemical (g/l)
Direct Dye	H_2O_2	0.0004	10	0.0023	22
		0.0026	X	0.0050	X
		0.0049	X	0.0072	X
	NaOCl	0.0004	6	0.0023	6
		0.0026	7	0.0050	7
		0.0049	>15	0.0072	>15
	$Na_2S_2O_4$	0.0004	1	0.0023	1
		0.0026	1	0.0050	1
		0.0049	1	0.0072	1
Reactive Dye	H_2O_2	0.0017	X	0.0023	X
		0.0040	X	0.0048	X
		0.0074	X	0.0081	X
	NaOCl	0.0017	X	0.0023	X
		0.0040	X	0.0048	X
		0.0074	X	0.0081	X
	$Na_2S_2O_4$	0.0017	3.75	0.0023	0.25
		0.0040	3.75	0.0048	0.25
		0.0074	3.75	0.0081	0.25
Disperse Dye	H_2O_2	0.0013	X	0.0025	X
		0.0018	X	0.0029	X
		0.0039	X	0.0097	X
	NaOCl	0.0013	X	0.0025	X
		0.0018	X	0.0029	X
		0.0039	X	0.0097	X
	$Na_2S_2O_4$	0.0013	>15	0.0025	>15
		0.0018	>15	0.0029	>15
		0.0039	>15	0.0097	>15
Acid Dye	H_2O_2	0.0000	N/A	0.0037	22
		0.0000	N/A	0.0080	X
		0.0031	X	0.1010	X
	NaOCl	0.0000	N/A	0.0037	X
		0.0000	N/A	0.0080	6
		0.0031	X	0.1010	11
	$Na_2S_2O_4$	0.0000	N/A	0.0037	>15
		0.0000	N/A	0.0080	3
		0.0031	1	0.1010	4
Basic Dye	H_2O_2	0.0002	1	0.0004	6
		0.0021	1	0.0030	6
		0.0026	1	0.0036	7
	NaOCl	0.0002	2	0.0004	2
		0.0021	12	0.0030	11
		0.0026	15	0.0036	12
	$Na_2S_2O_4$	0.0002	4	0.0004	1
		0.0021	4	0.0030	4
		0.0026	7	0.0036	7

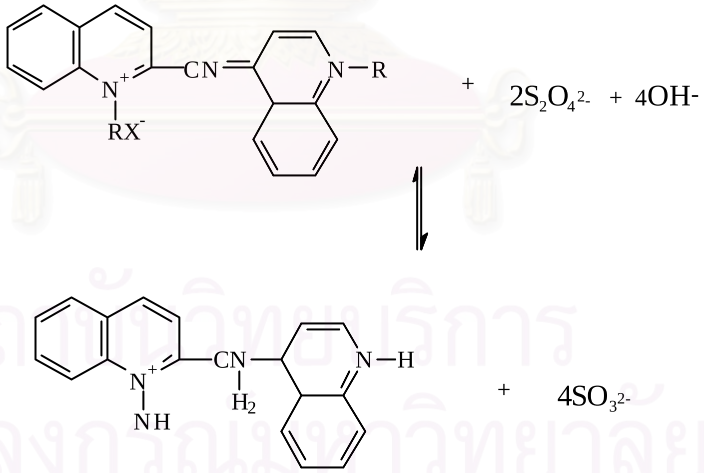
Remark: Sulphur gas evolved when treated with $Na_2S_2O_4$.

For chemical pretreatment with various dyes the type of reaction that gave the best results in reducing the colour strength was reduction reaction using Sodium dithionite (hydro). Removal of colour strength occurred by destroying the conjugate double bonding system of the chromophore structure forming non chromophore structure.

Direct, reactive, disperse and acid dye have azo structure (N=N), the reduction reaction that occurred is

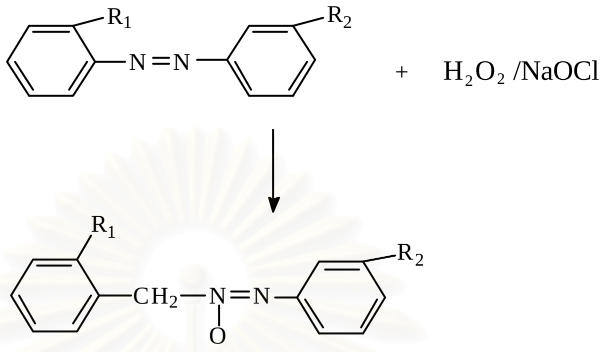


Reduction reaction for basic dye that has Cynanine structure (-CN=) is

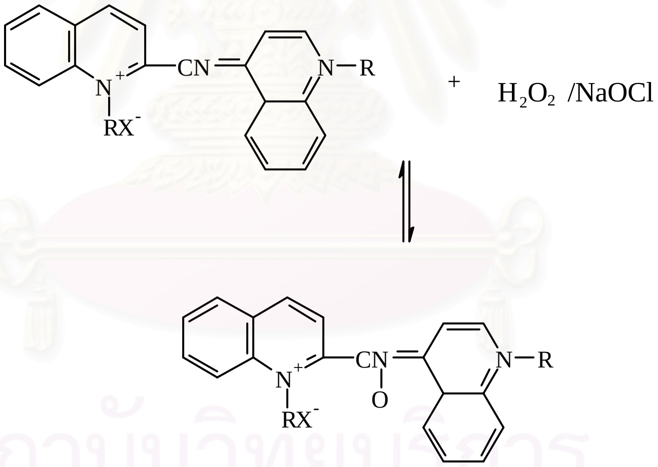


Oxidation reaction do not destroy the conjugate double bonding system of the chromophore structure, but only changes the structure, therefore the colour still remain.

For direct, reactive, disperse and acid dye that have azo structure (N=N), we have



For basic dye that has Cynanine structure (-CN=), the reaction occurred as follow



4.3 Physical Pretreatment

Physical pretreatment was the other method employed to reduce the colour strength of the effluent from dyeing processes. This was achieved by using activated carbon to adsorb the colour.

Table 34 Physical Pretreatment

Dyestuff	**With auxiliaries**			**Without auxiliaries**		
	Conc. (%w/v)	**Mass (gm)**	**Time (hr)**	**Conc. (%w/v)**	**Mass (gm)**	**Time (hr)**
Direct Dye	0.0004	100	1	0.0023	400	1
	0.0026	200	3	0.0050	400	6
	0.0049	400	6	0.0072	400	6
Reactive Dye	0.0017	200	5	0.0023	400	1
	0.0040	400	2	0.0048	400	5
	0.0074	400	4	0.0081	400	7
Disperse Dye	0.0013	300	3	0.0025	400	1
	0.0018	200	4	0.0029	300	3
	0.0039	300	5	0.0097	400	7
Acid Dye	0.0000	N/A	N/A	0.0080	400	1
	0.0000	N/A	N/A	0.1010	400	4
	0.0031	400	1		400	7
Basic Dye	0.0002	100	1	0.0004	100	1
	0.0021	100	1	0.0030	200	1
	0.0026	100	1	0.0036	200	2

As can be seen from the table above, height of activated carbon vary on colour strength of dye (table 31). The factors of adsorbtion on activated carbon can summarize below.

a. Colour strength of dye (from Table31)

Table 35 Range of Colour Strength

Concentration (%w/v)	**Mass (gm)**	**Time (hr)**
0.0002-0.0004	100	1
0.0013	100	3
0.0017	200	5
0.0023-0.0032	300	3
0.0032-0.0040	400	2
0.0041-0.0072	400	6
0.0074-0.0101	400	7

b. pH value (from Table 32)

Table 32 showed that the dye for good adsorption are basic > acid > disperse >direct > reactive respectively

4.4 Adjusted pH value after pretreatment

After pretreatment of the effluent the pH had to be adjusted to meet the standard requirement (pH 5.5-9). This is done by adding acid (CH_3COOH) or base (NaOH).

Table 36 Amount of chemical auxiliaries needed to adjust the pH value

Method	Dyestuff	With Auxiliaries (g/l)	Without Auxiliaries (g/l)
Chemical	Direct dye	0.01	0.01
		0.01	0.01
		0.01	0.01
	Reactive dye	0.42	0.01
		0.42	0.01
		0.42	0.01
	Disperse dye	0.02	0.01
		0.02	0.01
		0.02	0.01
	Acid dye	0.24	0.01
		0.24	0.01
		0.24	0.01
	Basic dye	0.38	0.02
		0.38	0.02
		0.38	0.02
Physical	Direct dye	0.01	0.00
		0.01	0.00
		0.01	0.00
	Reactive dye	0.42	0.01
		0.42	0.01
		0.42	0.01
	Disperse dye	0.02	0.00
		0.02	0.00
		0.02	0.00
	Acid dye	0.26	0.00
		0.26	0.00
		0.26	0.00
	Basic dye	0.43	0.00
		0.43	0.00
		0.43	0.00

Note: For direct, reactive and disperse dye CH_3COOH was used.

For acid and basic dye, NaOH was used.

4.5 Cost of chemicals

In Table 37, the cost of chemicals used in chemical and physical pretreatment are summarized.

$Na_2S_2O_4$	80	Baht/kg
Activated carbon	48	Baht/kg
CH_3COOH	184	Baht/l
NaOH	300	Baht/kg

Table 37 Comparing the costs of chemical used in chemical pretreatment and in physical pretreatment

Dyestuff	Condition	Cost (Baht/l)	
		Method	
		Chemical	Physical
Direct dye	With Auxiliaries	0.08	0.07
		0.08	0.14
		0.08	0.28
	Without Auxiliaries	0.08	0.28
		0.08	0.28
		0.08	0.28
Reactive dye	With Auxiliaries	0.38	0.14
		0.38	0.28
		0.38	0.28
	Without Auxiliaries	0.02	0.28
		0.02	0.28
		0.02	0.28
Disperse dye	With Auxiliaries	1.20	0.21
		1.20	0.14
		1.20	0.21
	Without Auxiliaries	1.20	0.28
		1.20	0.21
		1.20	0.28
Acid dye	With Auxiliaries	0.00	0.00
		0.00	0.00
		0.15	0.28
	Without Auxiliaries	0.24	0.28
		0.24	0.28
		0.32	0.28
Basic dye	With Auxiliaries	0.48	0.07
		0.32	0.07
		0.32	0.07
	Without Auxiliaries	0.56	0.07
		0.09	0.14
		0.33	0.14

Normally activated carbon can be used about 45-60 times/l of effluent. For this study the activated carbon used was about 50 times/1.

Results of experiments showed that for chemical pretreatment the method of reduction using $Na_2S_2O_4$ gave better result than oxidation method using NaOCl and H_2O_2. In addition, oxidizing agent NaOCl is more efficient than H_2O_2.

In physical pretreatment, it was found that activated carbon can adsorb all types of dye, but the degree of adsorption depended on the characteristics of individual dye effluent. The pH value is the essential factor for adsorption of activated carbon according Zogerski’s theory “ If pH value of contaminate solution is higher than the power of dissociation constant (P_{ka}) , the adsorption ability will decrease because of the interaction between the anions and the surface area of the activated carbon or between the anions themselves”

CHAPTER V
CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The main objective of this study is to remove residual dyestuff in effluents from dyeing processes by physical and chemical methods. Removal of colour strength is obtained by destroying the conjugate double bonding system of the chromophore structure of the dye. From the experiments, it can be concluded as follows.

5.1.1 Chemical pretreatment

1. Oxidation reaction can destroy the chromophore structure of only one type of dye, i.e. basic dye, which has cyanine structure. Oxidation of azo compounds changes them to azoxy compounds but the chromophore structures are not destroyed.
2. Reduction reaction gives better result than oxidation because it can destroy the chromophore structure of all types of dye. Azo compounds and cynanine compounds are converted to aromatic amines upon reaction.

Therefore for many types of dyes, particularly azo dyes, chemical reduction is an effective decolourization technique.

5.1.2 Physical pretreatment

Most dyes can be adsorbed with activated carbon. The degree of adsorption depends on the height of activated carbon bed in the column. Results of adsorption of various dyes on activated carbon can be summarized below as follows.

- Direct dyes – high degree of adsorption, apparently unrelated to the number of sulphonic acid groups in its structure.
- Reactive dyes – very low degree of adsorption, apparently unaffected by the degree of sulphonation or ease of hydrolysis.
- Disperse dyes – adsorption in the high-to-medium range.

- Acid dyes – high solubility leads to low adsorption, which appears to depend on the degree of sulphonation.
- Basic dyes – high levels of adsorption.

Classification of dye for good adsorption are basic > acid > disperse> direct > reactive respectively

Chemical pretreatment using reduction method gave good results for effluents with low colour strength and moderate result for high colour strength. In the case of reactive dye the results was not so good because of its characteristic that it is self-reacted, so it is difficult to destroy the conjugate double bond of the chromophore molecule.

Physical pretreatment is suitable for all types of effluent. At low colour strength good results are obtained. However, to be effective in the removal of colour strength from highly coloured effluent, large amount of activated carbon is needed. The cost of activated carbon would be high. Although treatment of high colour strength effluent by physical method is expensive but the treated effluent obtained has better clarity than treated by chemical method.

Finally, the process chosen to remove the colour strength must match the dye waste of a factory. It must be recognized that the smaller the discharge, the higher the unit cost. Most industries in Thailand are small or medium-size enterprises.

5.2 Recommendation

1. Synthetic dyes with other chromophore structures, such anthraquinone, indigoid should be studied.
2. Similar studies should also be carried out on natural dye.
3. Treatment of effluents from fabric printing processes that use the same type of dyes should also be investigated.
4. Perform similar experiments as a continuous process.

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APPENDICES

A. Wavelength and Absorbance of experiment dye.

1. Direct dyes

1.1 Mapra direct red 8BL 180% (with auxiliaries)

Wavelength (l)	Absorbance (%)
600	0.215
595	0.289
590	0.379
585	0.482
580	0.596
575	0.717
570	0.84
565	0.955
560	1.054
555	1.137
550	1.205
545	1.272
540	1.347
535	1.442
530	1.552
525	1.661
520	1.755
515	1.818
510	1.846
505	1.825
500	1.764
495	1.678
490	1.575
485	1.462
480	1.351
475	1.234
470	1.126
465	1.031
460	0.95
455	0.893
450	0.854
445	0.834
440	0.829
435	0.835
430	0.85
425	0.873
420	0.902
415	0.929
410	0.952
405	0.964
400	0.96

1.2 Mapra direct red 8BL 180% (without auxiliaries)

Wavelength (l)	Absorbance (%)
600	0.095
595	0.138
590	0.2
585	0.283
580	0.389
575	0.519
570	0.667
565	0.829
560	0.987
555	1.131
550	1.243
545	1.329
540	1.397
535	1.468
530	1.539
525	1.609
520	1.682
515	1.743
510	1.769
505	1.749
500	1.686
495	1.577
490	1.453
485	1.323
480	1.201
475	1.088
470	0.978
465	0.875
460	0.784
455	0.712
450	0.66
445	0.629
440	0.615
435	0.615
430	0.625
425	0.642
420	0.666
415	0.693
410	0.72
405	0.742
400	0.754

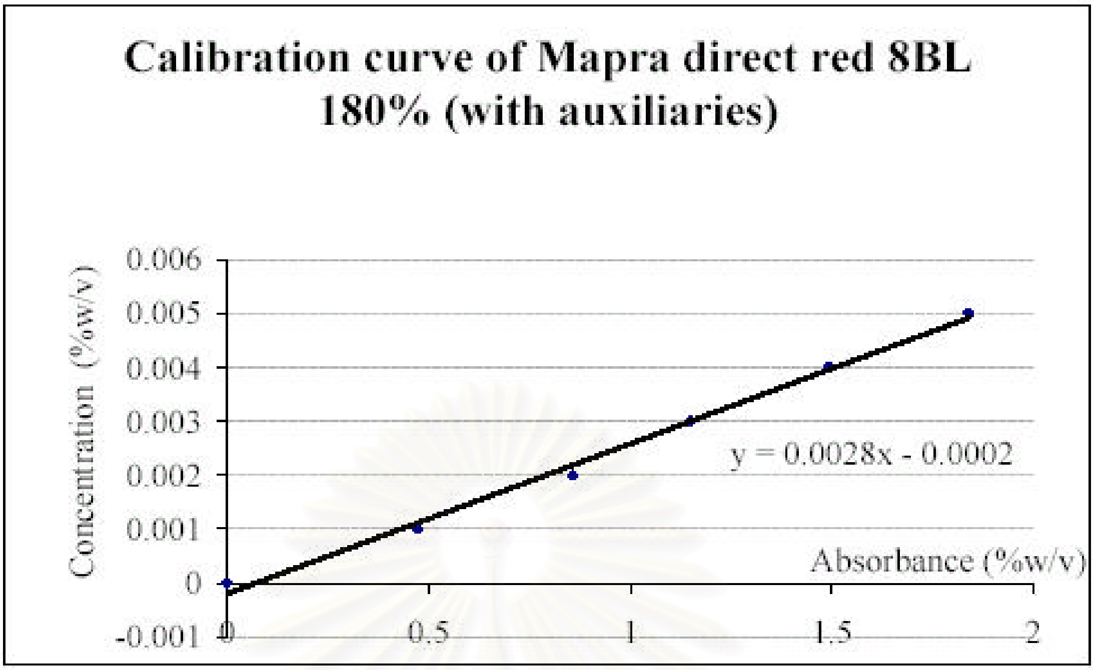

Figure 79 Wavelength VS Absorbance of Mapra direct red 8BL 180% (with auxiliaries)

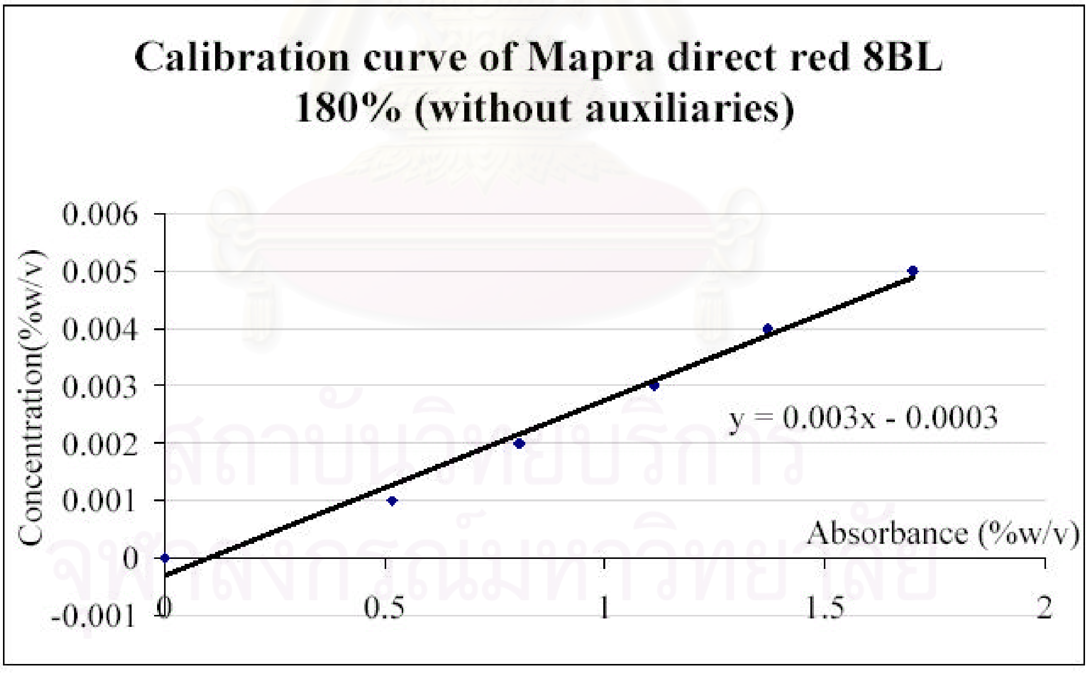

Figure 80 Wavelength VS Absorbance of Mapra direct red 8BL 180% (without auxiliaries)

2. Reactive dyes

2.1 Polative red HE-7-BN (with auxiliaries)

Wavelength (l)	Absorbance (%)
600	0.054
595	0.074
590	0.107
585	0.158
580	0.229
575	0.322
570	0.424
565	0.519
560	0.587
555	0.621
550	0.624
545	0.613
540	0.614
535	0.639
530	0.684
525	0.73
520	0.746
515	0.724
510	0.669
505	0.603
500	0.544
495	0.499
490	0.457
485	0.41
480	0.356
475	0.303
470	0.255
465	0.217
460	0.187
455	0.164
450	0.145
445	0.134
440	0.131
435	0.134
430	0.138
425	0.141
420	0.143
415	0.145
410	0.151
405	0.16
400	0.167

2.2 Polative red HE-7-BN (without auxiliaries)

Wavelength (l)	Absorbance (%)
600	0.03
595	0.046
590	0.073
585	0.116
580	0.181
575	0.273
570	0.399
565	0.551
560	0.71
555	0.842
550	0.925
545	0.959
540	0.953
535	0.935
530	0.917
525	0.912
520	0.914
515	0.903
510	0.87
505	0.808

Wavelength (l)	Absorbance (%)
500	0.731
495	0.651
490	0.582
485	0.521
480	0.466
475	0.41
470	0.353
465	0.299
460	0.252
455	0.215
450	0.188
445	0.169
440	0.159
435	0.154
430	0.155
425	0.158
420	0.162
415	0.166
410	0.17
405	0.179
400	0.188

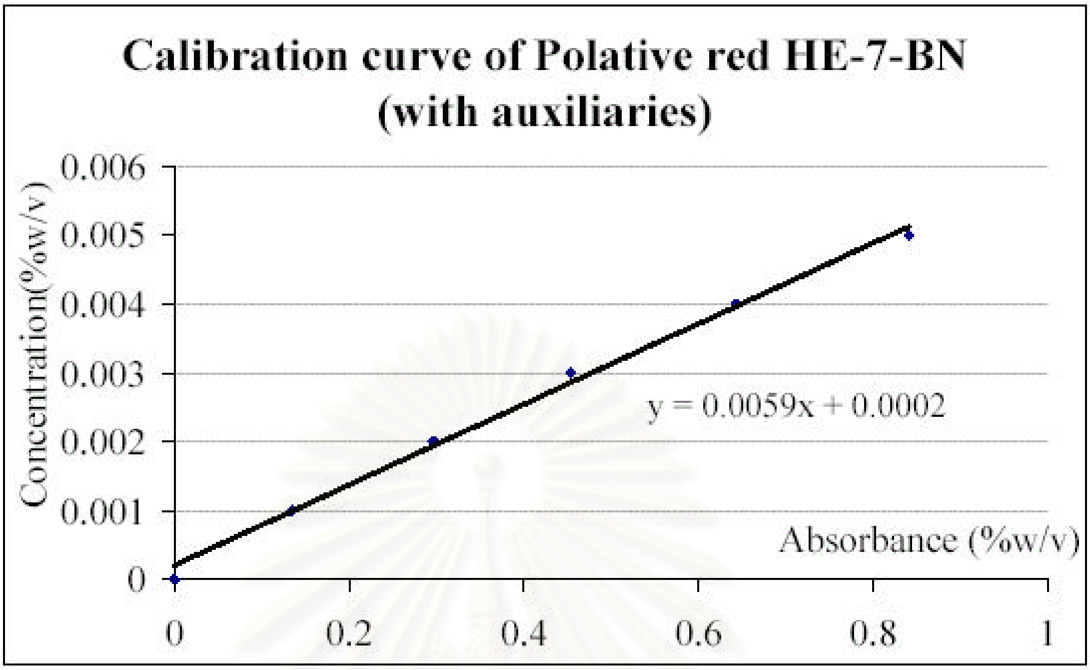

Figure 81 **Wavelength VS Absorbance of Polative red HE-7-BN (with auxiliaries)**

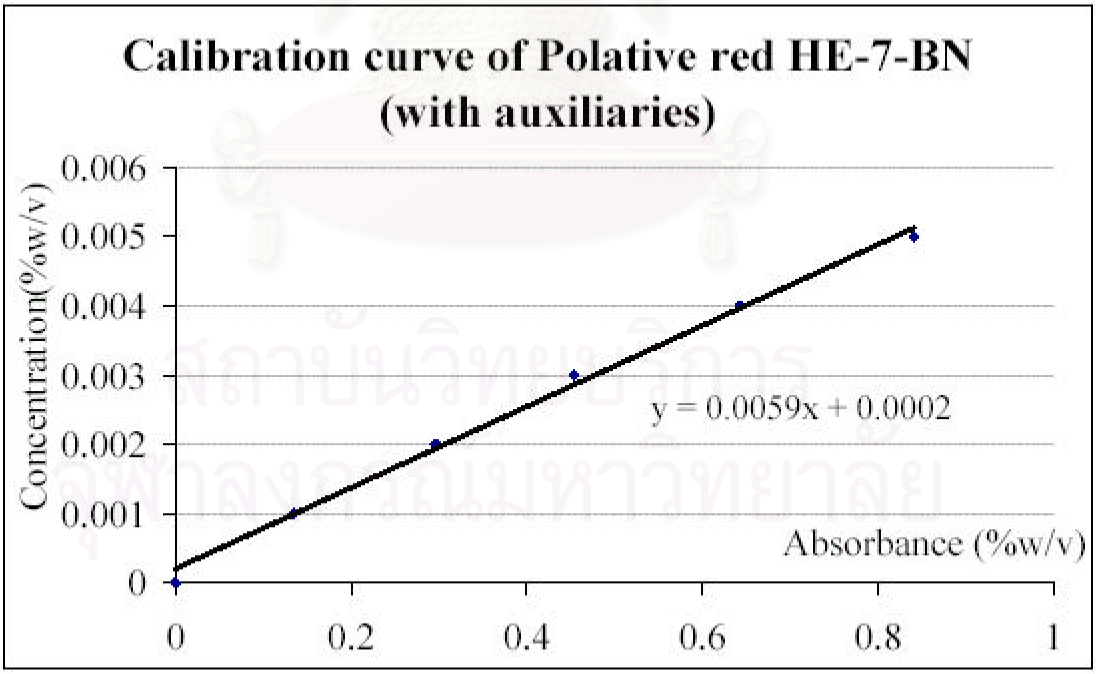

Figure 82 **Wavelength VS Absorbance of Polative red HE-7-BN (without auxiliaries)**

3. Disperse dyes

3.1 Polacron red S2-GFL 200% (with auxiliaries)

Wavelength (l)	Absorbance (%)
600	0.253
595	0.266
590	0.281
585	0.298
580	0.316
575	0.336
570	0.358
565	0.382
560	0.406
555	0.431
550	0.456
545	0.478
540	0.497
535	0.513
530	0.526
525	0.537
520	0.545
515	0.551
510	0.555
505	0.557

Wavelength (l)	Absorbance (%)
500	0.556
495	0.555
490	0.552
485	0.551
480	0.548
475	0.545
470	0.542
465	0.536
460	0.527
455	0.518
450	0.506
445	0.491
440	0.471
435	0.447
430	0.419
425	0.392
420	0.369
415	0.348
410	0.335
405	0.327
400	0.325

3.2 Polacron red S2-GFL 200% (without auxiliaries)

Wavelength (l)	Absorbance (%)
600	0.201
595	0.211
590	0.222
585	0.233
580	0.242
575	0.252
570	0.26
565	0.266
560	0.271
555	0.278
550	0.286
545	0.294
540	0.303
535	0.313
530	0.322
525	0.33
520	0.338
515	0.345
510	0.352
505	0.358

Wavelength (l)	Absorbance (%)
500	0.364
495	0.37
490	0.377
485	0.382
480	0.388
475	0.393
470	0.396
465	0.398
460	0.397
455	0.395
450	0.388
445	0.376
440	0.356
435	0.329
430	0.298
425	0.266
420	0.236
415	0.208
410	0.186
405	0.171
400	0.161

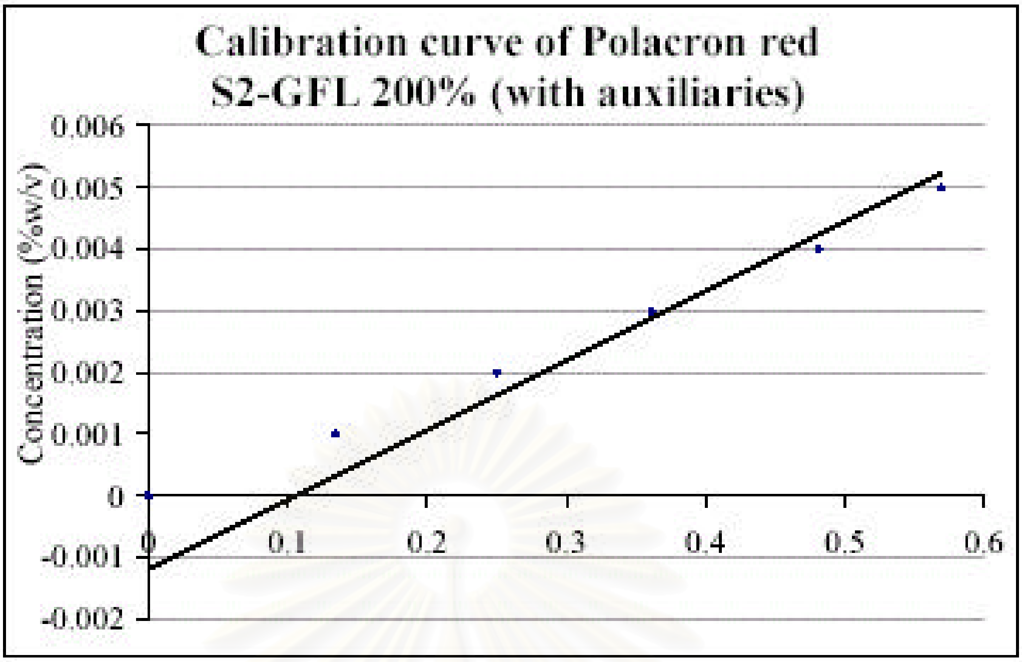

Figure 83 Wavelength VS Absorbance of Polacron red S2-GFL 200% (with auxiliaries)

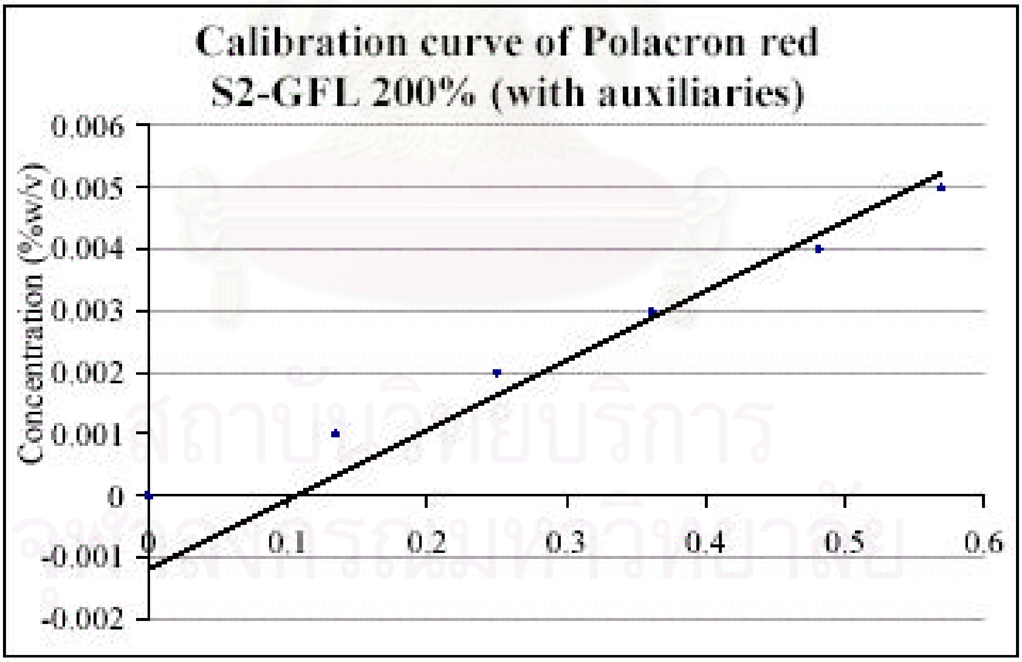

Figure 84 Wavelength VS Absorbance of Polacron red S2-GFL 200% (without auxiliaries)

4. Acid dyes

4.1 Polynyl Red MBN (with auxiliaries)

Wavelength (l)	Absorbance (%)
600	0.105
595	0.191
590	0.344
585	0.594
580	0.911
575	1.189
570	1.338
565	1.379
560	1.357
555	1.285
550	1.21
545	1.18
540	1.206
535	1.264
530	1.28
525	1.223
520	1.122
515	1.002
510	0.882
505	0.786

Wavelength (l)	Absorbance (%)
500	0.715
495	0.65
490	0.58
485	0.499
480	0.422
475	0.352
470	0.296
465	0.251
460	0.211
455	0.178
450	0.15
445	0.133
440	0.131
435	0.151
430	0.192
425	0.243
420	0.289
415	0.316
410	0.334
405	0.361
400	0.406

4.2 Polynyl red MBN (without auxiliaries)

Wavelength (l)	Absorbance (%)
600	0.051
595	0.099
590	0.174
585	0.281
580	0.423
575	0.595
570	0.785
565	0.962
560	1.1
555	1.178
550	1.199
545	1.188
540	1.17
535	1.17
530	1.181
525	1.189
520	1.181
515	1.137
510	1.058
505	0.956

Wavelength (l)	Absorbance (%)
500	0.854
495	0.758
490	0.678
485	0.602
480	0.528
475	0.453
470	0.379
465	0.312
460	0.257
455	0.213
450	0.177
445	0.149
440	0.134
435	0.133
430	0.143
425	0.158
420	0.174
415	0.192
410	0.21
405	0.229
400	0.252

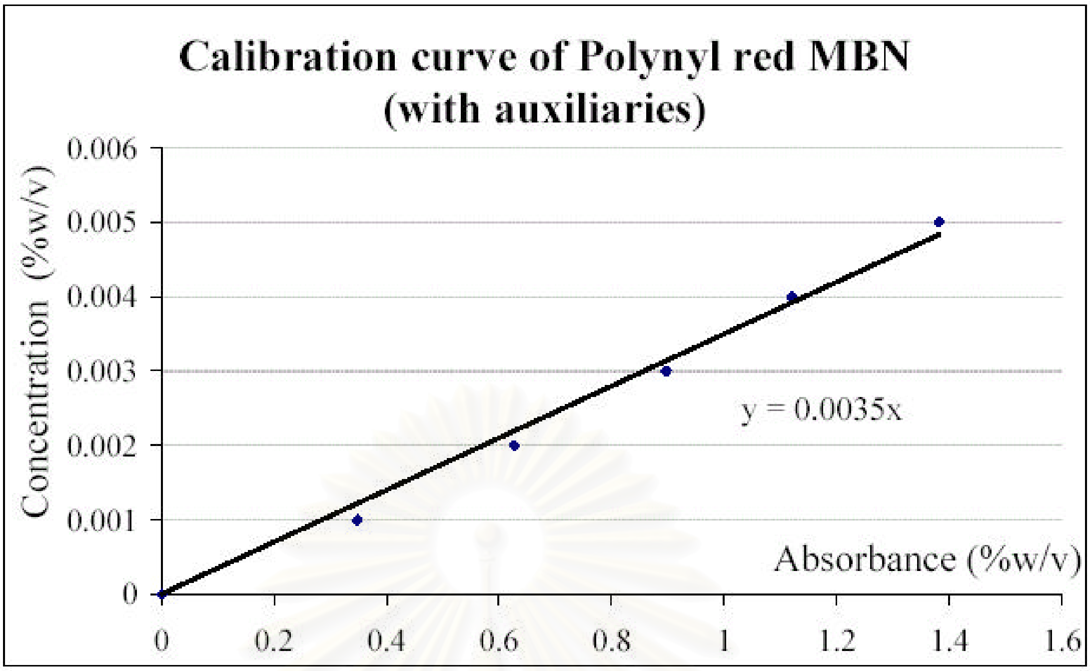

Figure 85 Wavelength VS Absorbance of Polynyl red MBN (with auxiliaries)

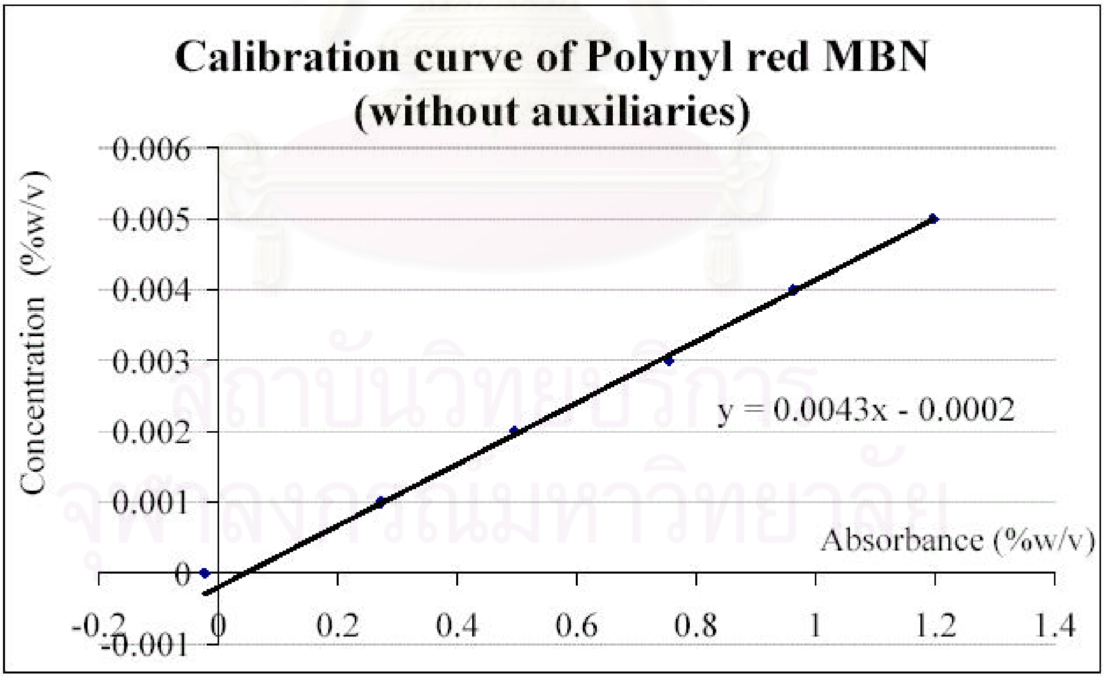

Figure 86 Wavelength VS Absorbance of Polynyl red MBN (without auxiliaries)

5. Basic dyes

5.1 Concord Dacryl red 4G 200% (with auxiliaries)

Wavelength (l)	Absorbance (%)
600	0
595	0
590	0.009
585	0.023
580	0.047
575	0.089
570	0.153
565	0.246
560	0.366
555	0.508
550	0.656
545	0.797
540	0.92
535	1.018
530	1.087
525	1.129
520	1.153
515	1.161
510	1.156
505	1.133
500	1.097
495	1.037
490	0.97
485	0.894
480	0.816
475	0.735
470	0.656
465	0.577
460	0.502
455	0.433
450	0.369
445	0.311
440	0.259
435	0.214
430	0.176
425	0.143
420	0.115
415	0.091
410	0.071
405	0.054
400	0.04

5.2 Concord Dacryl red 4G 200% (without auxiliaries)

Wavelength (l)	Absorbance (%)
600	0.005
595	0.009
590	0.019
585	0.039
580	0.074
575	0.134
570	0.231
565	0.37
560	0.553
555	0.773
550	1.002
545	1.223
540	1.414
535	1.575
530	1.688
525	1.759
520	1.799
515	1.819
510	1.812
505	1.785

Wavelength (l)	Absorbance (%)
500	1.725
495	1.645
490	1.543
485	1.428
480	1.311
475	1.188
470	1.065
465	0.944
460	0.828
455	0.721
450	0.623
445	0.533
440	0.453
435	0.380
430	0.321
425	0.267
420	0.222
415	0.183
410	0.151
405	0.124
400	0.101

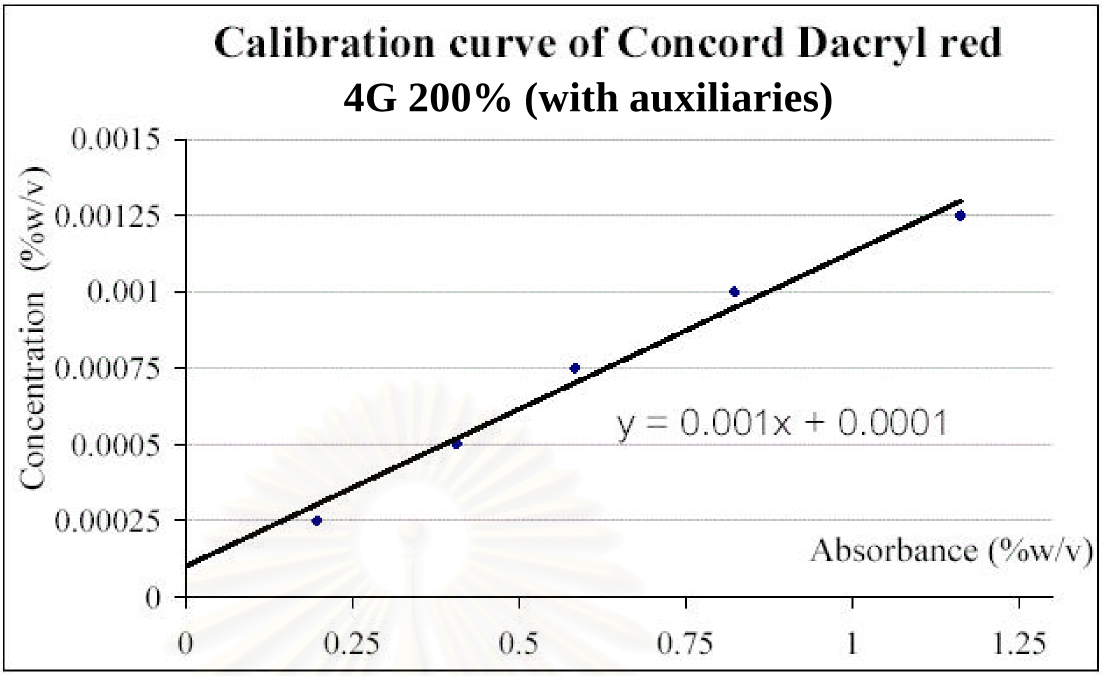

Figure 87 Wavelength VS Absorbance of Concord Dacryl red 4G 200% (with auxiliaries)

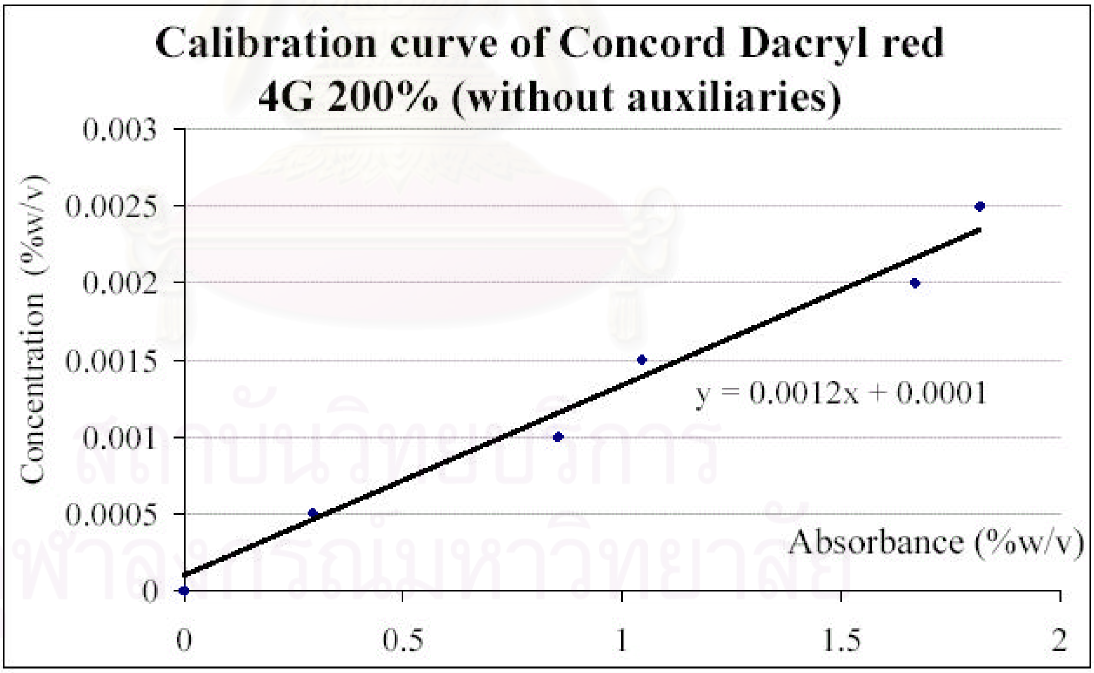

Figure 88 Wavelength VS Absorbance of Concord Dacryl red 4G 200% (without auxiliaries)

Appendix B : General data

Characteristic of activated carbon on this study

Properties	**Range**
Methylene Blue	120 ~ 210mg/g
CTC	30 ~ 80%
Iodine No	700 ~ 1500mg/g
Bulk Density	0.27 ~ 0.55g/ml
Moisture (as packed)	3% ~ 10%
Total Ash	1% ~ 6%MAX
pH	4 ~ 10
Particle Size	0.08mm ~ 6.5mm (dia.)
Hardness	90 ~ 99

Remark: 48 Bath/kg (Carbokarn Co.Ltd. , 1 Feb. 2003)

2. Cost calculation

For chemical pretreatment used $Na_2S_2O_4$ in reduction For physical pretreatment were used Activated carbon. The both of all methods were added CH_3COOH and NaOH to adjust pH value.

The cost of chemical shown below:

1. $Na_2S_2O_4$	80	Baht/kg
2. Activated carbon	48	Baht/kg
3. CH_3COOH	184	Baht/l
4. NaOH	300	Baht/kg

Classification of Dyestuff		Cost (Bath/l)					
		Chemical			Physical		
		$Na_2S_2O_4$	Adjust pH	Total	Activated carbon	Adjust pH	Total
Direct	With	0.08	0.00184	0.08	0.07	0.00184	0.07
		0.08	0.00184	0.08	0.14	0.00184	0.14
		0.08	0.00184	0.08	0.27	0.00184	0.28
	With out	0.08	0.00184	0.08	0.27	0.00184	0.28
		0.08	0.00184	0.08	0.27	0.00184	0.28
		0.08	0.00184	0.08	0.27	0.00184	0.28
Reactive	With	0.3	0.07728	0.38	0.14	0.00184	0.14
		0.3	0.07728	0.38	0.27	0.00184	0.28
		0.3	0.07728	0.38	0.27	0.00184	0.28
	With out	0.02	0.00184	0.02	0.27	0.00184	0.28
		0.02	0.00184	0.02	0.27	0.00184	0.28
		0.02	0.00184	0.02	0.27	0.00184	0.28
Dis - perse	With	1.2	0.00368	1.20	0.21	0.00184	0.21
		1.2	0.00368	1.20	0.14	0.00184	0.14
		1.2	0.00368	1.20	0.21	0.00184	0.21
	With out	1.2	0.00184	1.20	0.27	0.00184	0.28
		1.2	0.00184	1.20	0.21	0.00184	0.21
		1.2	0.00184	1.20	0.27	0.00184	0.28
Acid	With	0	0	0.00	0.00	0.00184	0.00
		0	0	0.00	0.00	0.00184	0.00
		0.08	0.072	0.15	0.27	0.00184	0.28
	With out	0.24	0.003	0.24	0.27	0.00184	0.28
		0.24	0.003	0.24	0.27	0.00184	0.28
		0.32	0.003	0.32	0.27	0.00184	0.28
Basic	With	0.48	0.003	0.48	0.07	0.00184	0.07
		0.32	0.003	0.32	0.07	0.00184	0.07
		0.32	0.003	0.32	0.07	0.00184	0.07
	With out	0.56	0.003	0.56	0.07	0.00184	0.07
		0.08	0.006	0.09	0.14	0.00184	0.14
		0.32	0.006	0.33	0.14	0.00184	0.14

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