



Department of Textile Engineering

**STUDY OF ENVIRONMENTAL PARAMETERS OF WASTE
WATER GENERATED AFTER DYEING WITH REACTIVE DYES**

Course code: TH-517 Course title: Thesis

Submitted By

Sushama Saha Swati
ID: 122-32-185

Supervisor

Prof. Dr. S.M. Mahbub Ul Haque Majumder
Department of Textile Engineering
Faculty of Engineering
Daffodil International University (DIU)

Co-supervisor

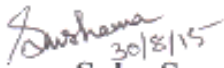
Sumon Mazumder
Assistant Professor
Department of Textile Engineering
Faculty of Engineering
Daffodil International University (DIU)

A thesis submitted in partial fulfillment of the requirements for the degree of
Master of Science in Textile Engineering

August 2015

DECLARATION

I hereby declare that, the research work of this thesis has been conducted by me under the supervision of **Prof. Dr. S.M. Mahbub Ul Haque Majumder & Mr. Sumon Mazumder**, Assistant Professor, Department of Textile Engineering, Faculty of Engineering, Daffodil international University (DIU). All belongings of this report are authentic according to my knowledge. I also declare that, neither this thesis report nor any part of it has been submitted elsewhere for award of any degree or diploma.


30/8/15
Sushama Saha Swati

ID: 122-32-185

Department of Textile Engineering
Daffodil International University

LETTER OF APPROVAL

Titled of the thesis “**STUDY OF ENVIRONMENTAL PARAMETERS OF WASTE WATER GENERATED AFTER DYEING WITH REACTIVE DYES**” is prepared by SUSHAMA SAHA SWATI of bearing ID: 122-32-185. This thesis report is submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE IN TEXTILE ENGINEERING. The whole report is prepared based on proper investigation and interpretation though critical analysis of data with required belongings.



Dr. S.M. Mahbub Ul Haque Majumder (Supervisor)

Professor and Founder Head,
Department of Textile Engineering
Faculty of Engineering
Daffodil International University



Sumon Mazumder (Co-supervisor)

Assistant Professor
Department of Textile Engineering
Faculty of Engineering
Daffodil International University

ACKNOWLEDGEMENT

First of all, I express my profound gratitude and submission to Almighty for making me capable to accomplish this thesis work successfully.

I also give my heartfelt thanks to honorable supervisor **Prof. Dr. S.M. Mahbub Ul Haque Majumder**, Department of Textile Engineering, Daffodil International University for his fruitful guidance, criticism, painstaking help, constant inspiration and for providing all necessary support for completing this project. I also like to thank my thesis co-supervisor **Mr. Sumon Mazumder**, Assistant Professor of the same department for his necessary advice, guidelines and cordial supervision to conduct the research work and to accomplish this thesis report.

Besides, I confer my heartiest gratitude to **Prof. Dr. Md. Mahbubul Haque**, Head of Textile Engineering Department, Daffodil International University, for giving me a great opportunity to carry out this research work in the University laboratory.

I would like to take this opportunity to thank all those people who helped me in this thesis and special thanks to **Dr. A. Nayeem Faruqui** who was related with the thesis at the beginning by boosting his guideline and suggestions which helped me a lot.

Finally, I like to thank all respected teachers of the Department of Textile Engineering, DIU for their insightful information, advice and suggestions.

*This thesis has been dedicated
to my beloved
Father & Mother*

ABSTRACT

Now-a-days, environmental consciousness is very imperative for all industries to maintain sustainability of lives and likewise other industries the major attention is also given to the arena of textile wet processing. In textile coloration industries, greater amount of cellulosic materials are now being colored with reactive dyes, contributing up to 36% of the overall dyestuff consumption. Cellulosic fibers of a specific shade (color) are produced by the chemical reaction of fibers with a mixture of reactive dyestuffs, salt, soda and auxiliary chemicals. Though this dye gives a superior quality in cellulosic fiber dyeing, but after dyeing a colossal amount of concentrated effluent liquor is generated due to immense hydrolysis of dyes. So, this textile effluent is considered as a major threat for the overall environment while discharged it in water bodies without further treatment. This research work is confined to the analysis of different parameters (DO, BOD, COD and pH) of waste water, generated from reactive dyeing of cotton at various conditions.

The study shows the assessment of effluent variables after dyeing of 100 % cotton fabric with three synthesized reactive dyes namely, homo bi-functional (VS) Reactive Black-5, hetero bi-functional (MCT/VS) Reactive Red-195 and mono functional (VS) Reactive Blue-19 under four concentrations 0.5%, 2.5%, 4.5% and 6.5% respectively. So, the effluent water contained mainly vinyl sulphone and mono chloro triazine functionality which comes from the hydrolyzed and unfixed dyes. Acidity or alkalinity of waste water was indicated by pH meter where comparatively lower values of pH are found for the after-treated solution than the solution of reactive dyes after the dyeing. In this analysis DO, BOD and COD values of solution after dyeing are found to be greater than that of solutions after dyeing-fixing. At the end of the study it is found that, homo bi-functional (VS) Reactive Black-5 provide maximum and vinyl sulphone (VS) Reactive Blue-19 give the minimum DO, BOD and COD values for all corresponding dye concentrations. Besides, waste water with 6.5 % and 0.5% dye concentration shows the greatest and least DO, BOD and COD values for each and every individual reactive dyestuff. So, it can be said that, waste water having least DO value has more BOD and COD values which must have more adverse effect on environment and vice-versa. Thus, this research work gives a comprehensive guideline for the industry people to understand effluent nature at different conditions and maintain sustainable environment by the selection of appropriate dye with the optimized energy, water and chemicals.

LIST OF CONTENTS

CONTENTS	PAGE
Declaration	ii
Letter of Approval	iii
Acknowledgement	iv
Dedication	v
Abstract	vi
List of Contents	vii-viii
List of Figures	ix
List of Tables	x
List of Abbreviations	xi
CHAPTER 01: INTRODUCTION	01-03
CHAPTER 02: LITERATURE REVIEW	04-32
2.1. About Cotton	05
2.2. Reactive Dyes	05-10
2.2.1. Simple representation of reactive dye	05-07
2.2.2. Nature of reactive dye	07
2.2.3. Classification of Reactive Dyes	07-08
2.2.4. Basic Principle of Reactive Dyeing with Cotton	08-09
2.2.5. Problems with Reactive Dyeing	09-10
2.3. Bi-functional reactive dyes	10-13
2.3.1. Types bi-functional dyes	11
2.3.2. Why bi-functional reactive dyes?	11-12
2.4. Vinyl Sulphone and Aspects of Bi-functional Vinyl Sulphone Dyes	13-14
2.5. Washing Off of Unfixed Reactive Dyes	14-16
2.5.1. Role of washing off agents in reactive dyeing	14-15
2.5.2. Mechanism of washing-off agents	15-16
2.6. Cationic Fixing of Reactive Dye After Washing	16-18
2.6.1. Why is cationic fixing necessary?	17
2.6.2. Role of fixing agents	17
2.6.3. The mechanism of cationic dye fixing agent	17-18
2.7. Water Quality Parameters	18-20
2.8. Waste Water/Effluent Generation and Characteristics	20-22
2.9. Effluent Treatment Plant (ETP)	22-32
2.9.1. Chemical Wastewater Treatment	24-25
2.9.2. Biological Wastewater Treatment	26-32
2.10. Effective Effluent Management Steps	32

CHAPTER 03:	EXPERIMENTAL DETAILS	33-48
3.1.	Sample Pattern	34
3.2.	Specification of Dyes	34
3.3.	Chemicals Specification	34-36
3.4.	Dye Structure and Related Properties	36-38
3.5.	Apparatus and Machines	39-40
3.6.	Method of Dyeing	41-42
3.6.1.	Dyeing parameters:(bi-functional reactive dyes)	41
3.6.2.	Dyeing curve:(bi-functional reactive dyes)	41
3.6.3.	Dyeing parameters :(vinyl sulphone reactive dyes)	42
3.6.4.	Dyeing curve: (vinyl sulphone reactive dyes)	42
3.7.	After-treatment	43
3.8.	Determination of DO and BOD	44-46
3.9.	Determination of COD	47-48
CHAPTER 04:	DISCUSSION OF RESULTS	49-59
4.1	DO values of waste water under light and dark condition after dyeing and dyeing-fixing with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes	50-53
4.1.1	DO values of waste water under light and dark condition after dyeing with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes	50-51
4.1.2	DO values of waste water under light and dark condition after dyeing-fixing with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes	52-53
4.2.	BOD values of waste water generated after dyeing and dyeing-fixing stages with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes	54-55
4.3.	COD values of waste water generated after dyeing and dyeing-fixing stages with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes	56-57
4.4.	pH values of waste water generated after dyeing and dyeing-fixing stages with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes	58-59
CHAPTER 05:	CONCLUSION	60-61
	REFERENCES	62-64
APPENDICES	A DO and BOD values of solutions treated under different conditions	65
	B COD and pH values of solutions treated under different conditions	66

LIST OF FIGURES

Figure No.	Title of the Figure	Page No.
Figure 2.1:	Chemical structure of cellulose	05
Figure 2.2:	Simple structure of reactive dye	06
Figure 2.3:	Structure of bi-functional Monochlorotriazine dyes	11
Figure 2.4:	Structure of CI Reactive Black 5	13
Figure 2.5:	Removal of hydrolyzed dye from textile fiber	15
Figure 2.6:	Chemical ETP Flow Chart	24
Figure 2.7:	Biological ETP Flow Chart	31
Figure 3.1:	Reactive Red 195	36
Figure 3.2:	Reactive Black 5	37
Figure 3.3:	Reactive Blue 19	38
Figure 3.4:	Apparatus and Machines	39-40
Figure 3.5:	Bi-functional reactive dyes dyeing diagram	41
Figure 3.6:	Vinyl sulphone reactive dyes dyeing diagram	42
Figure 3.7:	Procedure Chart for determination of DO and BOD	46
Figure 3.8:	Procedure Chart for determination of COD	48
Figure 4.1:	Bar diagrams represent DO values of waste water under light and dark condition after dyeing with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes.	50
Figure 4.2:	Bar diagrams represent DO values of waste water under light and dark condition after dyeing-fixing with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes.	52
Figure 4.3:	Line diagrams represent BOD values of waste water generated after dyeing and dyeing-fixing stages with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes.	54
Figure 4.4:	Line diagrams represent COD values of waste water generated after dyeing and dyeing-fixing stages with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes.	56
Figure 4.5:	Bar diagrams represent pH values of waste water generated after dyeing and dyeing-fixing stages with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes.	58

LIST OF TABLES

Table No.	Title of the Table	Page No.
Table 2.1:	Types of reactive dye on the basis of reactivity and temperature applied.	07
Table 2.2:	Characteristics of waste water to be discharged into the environment.	21
Table 2.3:	Characteristics of waste water of a typical textile wet processing industry.	21
Table 2.4:	List of name and functions of used chemicals in textile ETP	25
Table 3.1:	Specification of sample used in this investigation.	34
Table 3.2:	List of Dyes used in this research work.	34
Table 3.3:	List of chemicals used in this work.	34-36
Table 3.4:	Bi-functional dyes structure, feature and application.	36
Table 3.5:	Bi-functional vinyl sulphone dyes structure, feature and application	37
Table 3.6:	Vinyl sulphone dyes structure, feature and application	38
Table 3.7:	Dyeing recipe for bi-functional reactive dyes at different shade percentage	41
Table 3.8:	Dyeing recipe for vinyl sulphone reactive dyes at different shade percentage	42
Table 3.9:	Neutralization recipe	43
Table 3.10:	Soaping parameters	43
Table 3.11:	Fixing parameters	43
Table A1:	DO and BOD values of solutions after dyeing and after dyeing-fixing with 0.5%, 2.5%, 4.5% and 6.5% shade of Reactive dyes.	65
Table B1:	Table B1: COD and pH values of solutions after dyeing and after dyeing-fixing with 0.5%, 2.5%, 4.5% and 6.5% shade of Reactive dyes.	66

LIST OF ABBREVIATIONS

ICI	: Imperial Chemical Industries
pH	: Potential of Hydrogen
DO	: Dissolve Oxygen
BOD	: Biological Oxygen Demand
COD	: Chemical Oxygen Demand
MCT	: Monochlorotriazine
DCT	: Dichlorotriazine
MFT	: Monofluorotriazine
DCQ	: Dichloroquinoxaline
TCP	: Trichloropyrimidine
NT	: Nicotinyltriazine
VS	: Vinly Sulphone
MCT-VS	: Monochlorotriazine- Vinly Sulphone
MFT-VS	: Monofluorotriazine- Vinly Sulphone
TS	: Total Solid
TSS	: Total Suspended Solid
TDS	: Total Dissolve Solid
TOC	: Total Organic Carbon
ETP	: Effluent Treatment Plant
DAP	: Di-ammonium Phosphate
PAC	: Poly Aluminum Chloride
CI	: Color Index
DO _i	: Dissolve Oxygen Initial (in light)
DO _f	: Dissolve Oxygen Final (in dark)
IS	: International Standard

CHAPTER 01
INTRODUCTION

CHAPTER 01

INTRODUCTION

Reactive dyes are the recent and most important dye-class suitable for cellulosic materials. In 1955, Rattee and Stephen, who were working for ICI in Manchester, England, invented and patented a procedure for dyeing cotton with fiber-reactive dyes containing dichlorotriazine groups. They established that dyeing cotton with these dyes under mild alkaline conditions would create a covalent bond between cellulose and dye. In 1956, ICI introduced the first commercial range of reactive dyes. Following that first introduction, there were many more developments in the coloration industry, with almost 60% of the cellulosic material now being colored with reactive dyes, contributing up to 36% of the overall dye consumption. The tremendous and continuous demand of reactive dyes is due to the fact that the dye can be applied by the various process routes. They are easy to apply, have a wide shade gamut-from dull to bright and from yellow to black- and they have excellent fastness properties [1].

Reactive dyes have better property in terms of color fastness. Reactive dyeing of cellulosic substrate takes place under alkaline conditions. But this alkaline condition also facilitates the reaction of reactive group with the dye liquor (water), resulting in deactivation or hydrolysis of the dye. Approximately 3/4th of the dye gets fixed while remaining 1/4th gets hydrolyzed. So besides taking steps to reduce the hydrolysis as much as possible, this hydrolyzed dye must be removed by rinsing and using an appropriate washing-off agent in order to retain the fastness properties. Effective washing after reactive dyeing is crucially important. After dyeing the substrate contains unfixed hydrolyzed dyes and usually some residual active dyes. This hydrolyzed dye adheres onto the substrate and keep on getting removed during washing treatments causing poor wash fastness and harmful effect on the environment by the effluent [2]. Unlike other dye classes, as much as 50% of the total cost of a reactive dyeing process must be attributed to the washing of agents to remove unfixed or hydrolyzed dye and treatment of resulting effluent [3].

As vast amount of effluent produced from the reactive dyeing to after treatment stage so natural resources grow scarce, pollution increases and costs rises, and sustainability becomes a key priority. Efforts towards enhancing sustainability in the textile industry, as

in many other fields, are largely focused on: minimizing pollution and wastes, optimizing the use of energy, water and chemicals. Textile mills, brands and retailers need to deliver solutions that reduce impact on the environment and meet consumer requirements. Moreover sustainability requires innovation- the two go hand in hand [4].

Very less work in this field was conducted before and by considering that current situation it is decided to work with the effluent produced after dyeing of textile with reactive dye and from the after-treated solutions. It is expected that, this work will not only be helpful for the minimization of environment pollution and wastes but also for the optimization of energy, water and chemicals. The main objects of this research work can be stipulated in below:

- To evaluate and analyze the individual DO, BOD, COD and pH value of the effluent generated at dyeing and dyeing-fixing stages where 100% cotton fabric is dyed with reactive dye at light, medium and deep shades. Subsequently, dyed fabric is treated with dye fixing agent.
- To determine and make a comparison among the values of DO, BOD, COD and pH of the textile effluent containing bi-functional and mono functional reactive dyes at various conditions.
- To find out the effect of light, medium and dark shades on DO, BOD, COD and pH values of effluent containing bi-functional and mono functional reactive dyes.
- To select suitable dyes among the mono functional, homo bi-functional and hetero bi-functional reactive dyes in terms of environmental aspect.

CHAPTER 02
LITERATURE REVIEW

CHAPTER 02

LITERATURE REVIEW

2.1 About Cotton:

Cotton is a cellulosic fiber which actually represents the most pure natural form of cellulose. It is a soft fiber that grows around the seeds of the cotton plant, most often spun into thread and used to make a soft breathable textile. Cellulose content of the raw cotton fiber ranges from 88 to 96%. Cellulose is a polymer of β -D-glucose and the repeating unit of cellulose consists of two β -D-glucose molecules linked together at the 1:4 carbon atoms. The cellulose is arranged in a way that gives cotton exclusive properties of durability, absorbency, strength under water and stability against high temperatures. It's also comfortable and retains colors and dyes well [5].

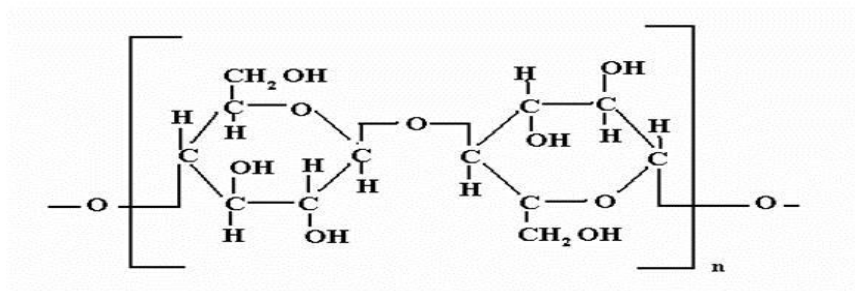


Figure 2.1: Chemical structure of cellulose

2.2 Reactive Dyes

Reactive dye is so called because their molecules react chemically with the fiber polymers of some fiber to form a covalent bond between the dye molecules and fiber polymer. Reactive dye is a class of highly colored organic substances, primarily utilized for tinting Textiles that attach themselves to their substrates by a chemical reaction that forms a covalent bond between the molecule of dye and that of the fiber. The dyestuff thus becomes a part of the fiber and is much less likely to be removed by washing than are dyestuffs that adhere by adsorption. The very first fiber-reactive dyes were designed for cellulose fibers, and are still used mostly in this way.

The dyes contain a reactive group that, when applied to a fiber in a weakly alkaline dye bath, form a chemical bond with the fiber. Reactive dyes can also be used to dye wool

and nylon, in the latter case they are applied under weakly acidic conditions. A fiber-reactive dye will form a covalent bond with the appropriate textile functionality is of great interest, since, once attached, they are very difficult to remove. The first fiber-reactive dyes were designed for cellulose fibers, and they are still used mostly in this way [6].

2.2.1. Simple representation of reactive dye

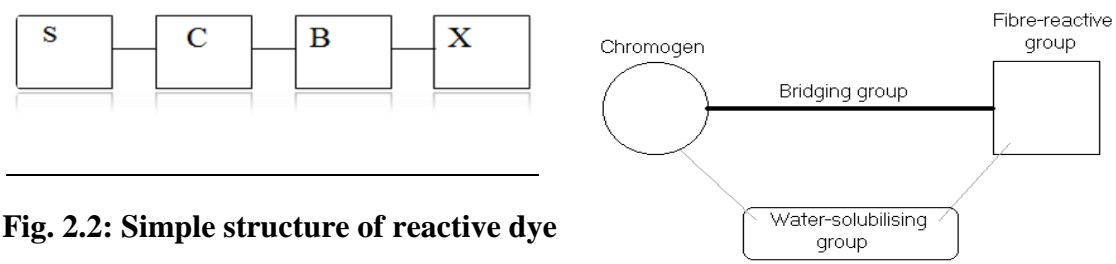


Fig. 2.2: Simple structure of reactive dye

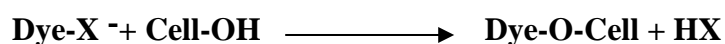
Where,

- S is the water solubilising group, which has the expected effect of improving the solubility of reactive dye in water. Reactive dye bearing solubilising groups are mainly ionic groups, often sulphonate salts etc.
- C is the Chromophoric group or the color bearing part..The chromogen is azo, carbonyl or phthalocyanine class.
- B is the bridging group. The bridging group links the chromogen and the fiber-reactive group. Frequently the bridging group is an amino, -NH-, group. This is usually for convenience rather than for any specific purpose.
- X is the halogen containing reactive group. The fiber-reactive group is the only part of the molecule able to react with the fiber. [7, 8] The different types of fiber-reactive group are discussed below.

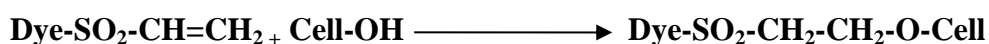
Reactive groups

Reactive groups are of two main types:

- i. those reacting with cellulose by nucleophilic substitution of a labile chlorine, fluorine, methyl sulphone or nicotinyl leaving group activated by an adjacent nitrogen atom in a heterocyclic ring ;

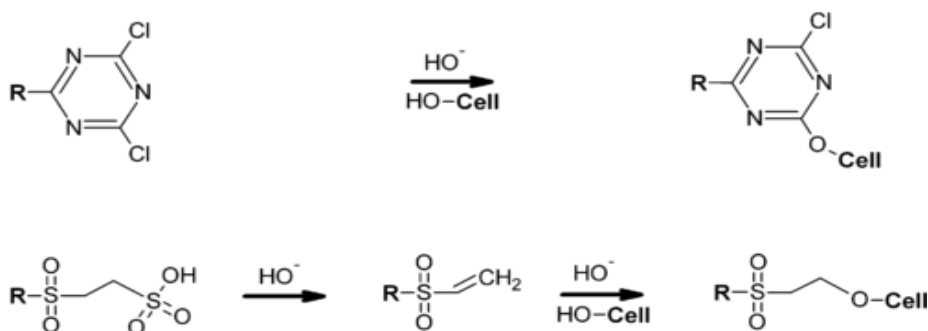


- ii. those reacting with cellulose by nucleophilic addition to a carbon–carbon double bond, usually activated by an adjacent electron-attracting sulphone group;[8,9]



2.2.2. Nature of reactive dyes

Reactive dyes are anionic soluble dyes which is capable to react with fiber. They possess in their dye molecule, a reactive group, either a haloheterocycle or an activated double bond, which under alkaline condition reacts with the hydroxyl groups of the cellulose to form a stable chemical linkage named co-valent bond. The molecules of reactive dyes are smaller and their smaller size is accompanied by a correspondingly lower substantivity.[10]



R = Chromophore Cell = Cellulose

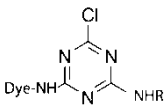
2.2.3. Classification of Reactive Dyes

➤ **According to reactivity and temperature applied:**

Three types which are shown below with required information in a table–

Table-2.1: Types of reactive dye on the basis of reactivity and temperature applied.

Sl. No	Reactivity	Brand	Exhaust Dyeing Temp. (°C)	Alkali Type	Reactive group	Structure
1.	High	Cold	20°-40°	Weak	DCT	
2.	Medium	Medium	40°-60°	Mild	MFT	

3.	Low	Hot	60°-80°	Strong	MCT	
----	-----	-----	---------	--------	-----	---

➤ **Recent classification of reactive dyes:**

1. **Alkali-controllable reactive dyes:** They exhibit low neutral exhaustion and high reactivity; due to the high reactivity alkali is to be carefully added to achieve level dyeing. Their optimum temperatures of fixation are between 40°C and 60°C. DCT, dichlorofluoropyrimidine, DCQ or VS reactive systems belong to this group.
2. **Salt-controllable reactive dyes:** These are characterized by low-reactivity but high neutral exhaustion; due to high exhaustion salt addition is to be made very carefully to achieve level dyeing. The dyes in this group show optimal fixation at a temperature between 80°C and boil. TCP, MCT dyes belong to this group.
3. **Temperature- controllable reactive dyes:** The dyes are self leveling and no auxiliary products are required to facilitate leveling. These dyes react with cellulose at temperatures above boil in the absence of alkali, although they can be applied as salt controllable dyes under alkaline conditions between 80°C and boil. Good results can be obtained by controlling the rate of temperature rise. At present only NT dyes belong to this group. [11,12]

2.2.4. **Basic Principle of Reactive Dyeing with Cotton**

Three basic steps are for dyeing of cellulose fibers with reactive dyes are as follows:-

- **Exhaustion** of the dye from an aqueous bath containing common salts or Glauber's salt in neutral condition. Dyeing is started in neutral solution and during this stage of dyeing, some reactive dye will be absorbed by the fibers, the amount depending upon its substantivity.
- **Fixation** of dye with fibre under alkaline condition. The pH of the dye bath is increased by complete or gradual addition of the appropriate type and amount of alkali. This causes dissociation of some of the hydroxyl groups in the cellulose and the nucleophilic cellulosate ions begin to react with the dye.

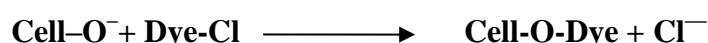
- **After-treatment** with soap or detergent including the post- dyeing washing. The rinsed water contains absorbed but unreacted hydrolyzed dye. There will also be residual alkali and salt, which are relatively easy to remove by successive rinsing in cold and then warm water. As much unfixed dye as possible must be washed out of the dyeing.[13,14]

➤ **Role of salt in the dye bath**

When a fiber is immersed in water, a negative electrostatic charge develops on its surface. This charge repels any dye anions present in the solution, so that the fiber cannot be dyed satisfactorily. If, however, the dye bath also contains an electrolyte such as sodium chloride or sodium sulphate, a diffuse layer of positive sodium ions forms at the fiber surface, neutralizing its charge. The dye ions are then able to approach sufficiently closely to the fiber for the inherent attractive forces between the dye and the fiber to operate. [15]

➤ **Role of alkali in the dye bath**

The role of the alkali is to cause acidic dissociation of some of the hydroxyl groups in the cellulose, and it is the cellulosate ion (Cell-O⁻) that reacts with the dye. [16]



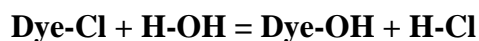
2.2.5. Problems with Reactive Dyeing

i. Hydrolysis of reactive dyes:

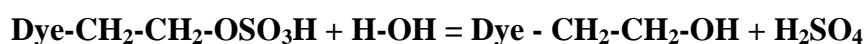
The reactive dyes have ability to react with fiber polymer as well as with water molecules. Under alkaline conditions, reactive dyes react with the terminal hydroxyl group of cellulose but if the solution of the dye is kept for long time, its concentration drops. Then hydrolysis take place and the dyes react with the hydroxyl group of water. The reaction of dye with water is called Hydrolysis of Reactive dyes. The

major problem of hydrolysis results in lower fixation rate (less than 70%) as well as incomplete utilization of dye [17].

Hydrolysis of halogen containing reactive dye,



Hydrolysis of activated vinyl compound containing dye,



Some problems of dye hydrolysis-

- Less color yield
 - Uneven surface after washing
 - The color become light after washing
 - The staining takes place during the washing with light and bright textile materials.
- ii. Relatively large amounts of electrolyte are required for exhaust and pad steam applications.
 - iii. Laborious removal of unreacted and hydrolyzed dye is required.
 - iv. Hydrolyzed dye is discharged as colored effluent and not easily removed by effluent treatment processes.
 - v. Unhydrolyzed, unfixed haloheterocyclic reactive dyes may pose an environmental hazard. To minimize above problems reactive dyes contains more than one reactive system is introduced in the market which shows higher fixation rate than conventional reactive dyes.

2.3. Bi-functional Reactive Dyes

Many of the new reactive dyes are bi-functional with similar or different reactive groupings in the dye molecule. Bi-functional dyes carry two reactive groups. They are known for their outstanding dyeing efficiency and overall fastness properties. Bi-functional dyes with good dyeing properties are created by the careful selection of the precise reactive groups and right choice of chromophores. [18]

2.3.1. Types bi-functional dyes

It can easily be assessed that dyes with two identical reactive groups and dyes with two different reactive groups exhibit a higher fixation yield than dyes with one group. There are two types of bi-functional reactive dyes-

- **Homo bi-functional dyes:**

Bi-functional dyes having two similar or identical functional groups are known as homo bi-functional group dyes. Example-

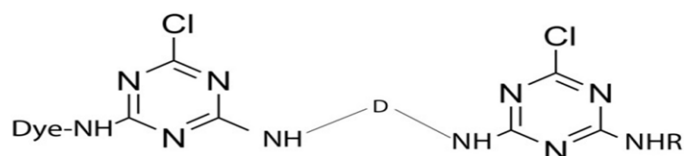


Figure: Bi functional Reactive dyes

Fig. 2.3: Structure of bi-functional Monochlorotriazine dyes

Here, two MCT reactive groups are present

- **Hetero bi-functional dyes:**

Bi-functional dyes having two different functional groups are known as hetero bi-functional dyes. The dyes were conventional Dichlorotriazine type, with the end condensation of β -sulphatoethylsulphone to have different type of reactive group in a single molecule. They offer enhanced reproducibility especially for medium to pale shades.

Important types of Bi functional reactive dyes include-

- MFT-VS,
- MCT-VS etc.[19]

2.3.2. Why bi-functional reactive dyes?

The main problem with conventional reactive dyes lies in the fact that their dyeing efficiency always stands below 100% because of incomplete fixation on the fiber. Usually the efficiency is not more than 70% even in printing application, the remainder undergoes hydrolysis instead of reaction with the fiber. The removal of 30% or more unfixed dye

during soaping is troublesome and time consuming, whereas the application procedures of reactive dyes are quite simple.[20]

It would be possible to achieve high fixation by using dyes having more than one reactive group. A dye molecule with only one reactive group may react either with fiber cellulose polymer or with water; but once it has reacted with the later its reactivity is completely gone it is then unable of reacting with the former. In case of dye having more than one reactive group, the part of the dye which has reacted with water is still capable of further reaction with cellulose. Although the presence of two or more reactive groups in a dye usually favors high fixation properties only carefully selected dyes of this type are technologically suitable in spite of higher probability of reaction with the fiber, a small amount of dye will always be completely hydrolyzed and has to be removed by washing off. [21]

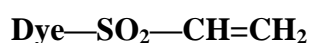
➤ **Variables in dyeing with bi-functional dyes**

- Pretreatment of the material
- Water
- pH
- Quality of Electrolyte
- Alkali system
- Dyeing temperature and dyeing duration [22]

Bi-functional dyes with two reactive groups of different reactivity towards the cotton, which have different optimal fixation conditions, give a more uniform degree of fixation over a wider range of dyeing temperature and fixation pH than dyes containing two identical groups. Therefore, process control does not need to be so stringent. These types of reactive dyes give quite high fixation yields. [23]

2.4. Vinyl Sulphone and Aspects of Bi-functional Vinyl Sulphone Dyes

- The vinyl sulphone group shows strong polarization caused by the sulphonyl (SO₂) group.

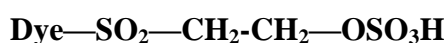


Vinyl sulphone dyes have vinyl sulphone as the reactive group. In presence of alkali, these dyes chemically react with the hydroxyl group of cellulose and form strong

covalent linkage. These dyes are versatile enough to suit different dyeing methods. Results are excellent and shade comes clean and brilliant with no variation in the dyeing and printing. These dyes are the sulphates ester of hydroxyethylsulphonyl dyes which on treatment with mild alkali, generates the vinyl sulphone group, which in turn reacts with ionized cellulose to form the dye fiber bond. [24]

- The vinyl sulphone group is not normally present in commercial dyes since it is more convenient to use a less reactive precursor such as the β -sulphatoethylsulphonyl group obtained from the corresponding β -hydroxyethylsulphonyl compounds.[25]

These dyes are marketed in the form of sulphatoethylsulphone dye:



- VS bi-functional reactive dye mainly consists of two vinyl sulphone groups in a dye molecule, because of having two potential vinyl sulphone reactive groups there is an increased probability of reaction with the fiber. An example of it is CI Reactive black 5.[26]

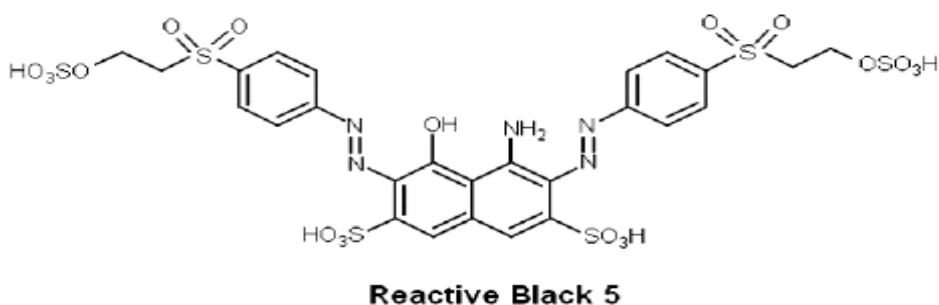


Fig. 2.4: Structure of CI Reactive black 5

➤ **Main features of bi-functional vinyl sulphone dyes:**

- The stability that exists in the dye-fiber bond between the vinyl sulphone group and cellulose against acid hydrolysis gives extra stability to these dyes in the acidic environment of the industry and makes the dyeing effect more lasting.
- The portion of bi-functional dyes that doesn't fix during the dyeing process can be removed easily due to the low substantivity of the hydrolyzed dye. This reduces the risk of staining of the adjacent whites.

- Better reproducibility in dyeing.
- High exhaustion and high fixation efficiency.
- Good leveling properties.
- Good all round fastness properties.
- Provide excellent brightness and good wet fastness.
- They are applicable at a range of 40°C -60°C.[27]

2.5 Washing Off of Unfixed Reactive Dyes

Removal of hydrolyzed dye from the goods is a vital step after dyeing.[28] Unlike other dye classes as much as 50% of the total cost of a reactive dyeing process must be attributed to the washing off stages to remove unfixed or hydrolyzed dye and treatment of the resulting effluent.[29] To achieve superior fastness in washing it is more than important to ensure all hydrolyzed or unfixed dye to be removed during washing off in reactive dyeing.

In general, reactive dyes on cellulosic fibers give dyeing with good to very good fastness to washing and other wet processes. Apparent inferior fastness to washing is usually because of incomplete removal of hydrolyzed dye from the material by washing after dyeing. [30] It is more likely to be a problem for deep dyeing. These hydrolyzed dyes possess some extent of affinity to cotton fiber and loosely held with the fabrics which in course of end use cause poor wash and rubbing fastness. To gain satisfactory result in end use this hydrolyzed dyes should be removed as much as possible. So an effective and efficient wash off is essential after dyeing cotton with reactive dyes.

2.5.1. Role of washing off agents in reactive dyeing

Washing off agents are necessary to remove the unfixed hydrolyzed dye from the dyed material. Soaping agents disperse hydrolyzed dyestuff and keep them in the water bath, preventing their re-deposition on the substrate. The washing-off efficiency of dyes would depend upon the amount of unfixed dye and ease of removal of unfixed dye. The washing-off agent should facilitate the diffusion of unfixed dye molecules from the fiber

into the water. It must eliminate the negative effect of hard forming ions on the solubility of unfixed hydrolyzed dye.

2.5.2. Mechanism of washing-off agents

Normally, washing off includes a first rinse step, a soaping step, a second rinse step, and a drying step. Typically, soaps, such as phosphate-based detergents, are added during the soaping step to assist in removal of unreacted, unfixed, hydrolysed reactive dyes. However, the liquid alkalis used during fixing have not been considered for use during soaping since they would not be expected to assist in excess dye removal. In addition, if the reaction mixture is too "hot" or alkaline, such as is seen with pure sodium hydroxide, the sensitive-type reactive dyes will hydrolyze with the water in the rinse bath and form a nonreactive pigment that has no effect on the fabric color. Furthermore, phosphate & silicate based soaping agents are not accepted by European countries due to their biodegradability issues.

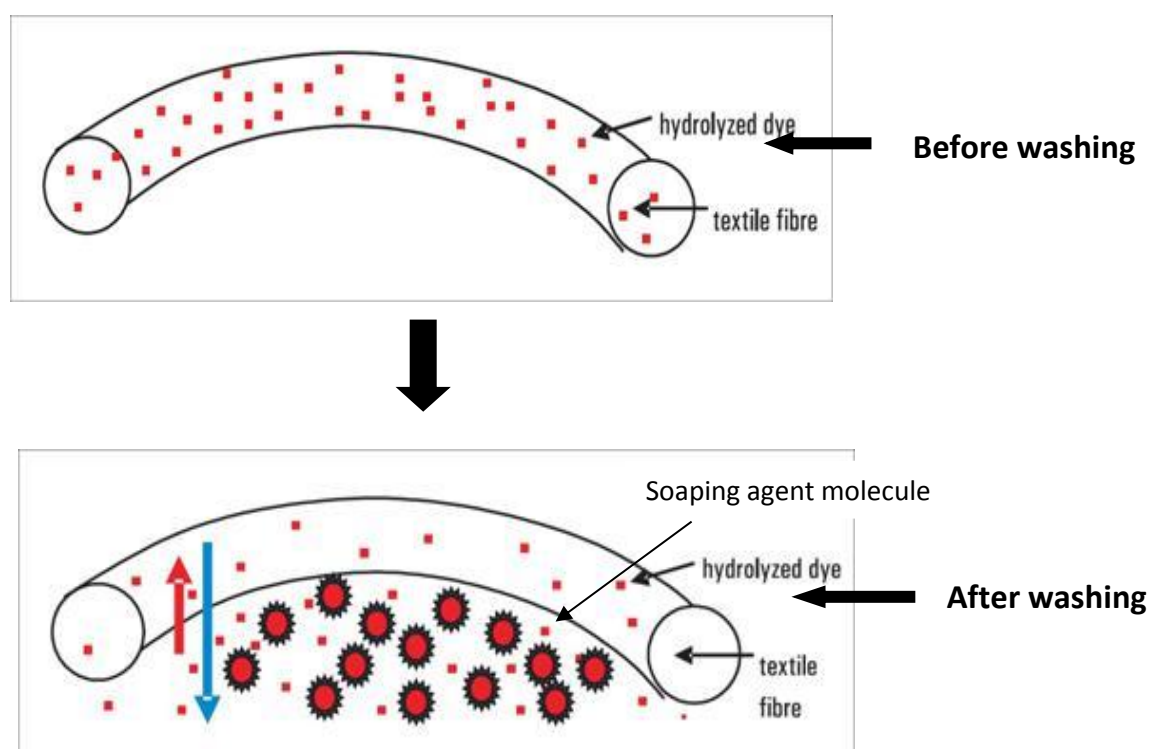


Fig. 2.5: Removal of hydrolyzed dye from textile fiber

Soaps have been replaced by surfactants but surfactants lack chelating properties. Thus surfactants have been replaced by polymeric washing-off agents or detergents. Together with low foaming surfactants, they exhibit excellent washing-off properties. The

dispersing properties in the washing-off agent helps to keep the dyes, particularly, disperse, naphthols in the disperse condition, thus not allowing it to re-deposit on the fabric. [31]

➤ **The factors governing the washing-off process are:**

- Time
- Temperature
- Type of washing-off agent
- Concentration of washing-off agent

➤ **Reasons for poor washing-off**

- i) Too high substantivity of dyes.
- ii) Low diffusion co-efficient dyes.
- iii) Short liquor ratio of washing bath.
- iv) High electrolyte concentration.
- v) Inadequate washing time.
- vi) Inadequate chemicals.

Washing of reactive dyed fabrics is more complex. It is very difficult to remove the unfixed dye from the fabric due to the presence of electrolytes. Thus it is advisable to rinse cold before treating with washing-off agents.

2.6. Cationic Fixing of Reactive Dye after Washing

After washing a reactive dyed fabric, cationic fixing is carried out to promote its dye fixation as well as to increase its fastness properties in terms of consumer's end use.

Chemical group

The earlier day fixing agents are based on alkyl pyridinium halides. Many amines, quarternary ammonium, phosphonium and tertiary sulphonium compound are used as dye-fixing agent. A number of synthetic resin compounds can also be used.

2.6.1. Why is cationic fixing necessary?

It is possible to eliminate color bleeding and staining of adjacent material when a fabric is first washed during use by after treating the dyeing with a cationic fixative. This cationic fixative reacts with any residual unfixed anionic dye, forming an organic salt of greatly increased molecular size and of lower water solubility and diffusion rate. Such cationic fixatives lack permanence on repeated washing but this is not a problem since the unfixed dye will have gradually been removed by that point. They may, however, reduce the light fastness of the dyeing and are therefore more suitable for treatment of deep shades. Such an after treatment is not a remedy for inefficient washing-off of unfixed dye. If the amount of unfixed dye remaining in the goods is significant there is a risk of the precipitated dye–auxiliary complex rubbing off, particularly on wet abrasion.

2.6.2. Role of fixing agents

Most of these are cationic surfactants, which unite with the dye anion producing a new substance of greater molecular complexity and less water-solubility with better wash fastness. The complexes may also be broken down by surface- active anions which compete with the dye anions for the cationic sites of the agent. The agent may thus be removed and wash fastness is lowered down to the original.

2.6.3. The mechanism of cationic dye fixing agent

The dye-fixing agents are cationic with long cations and short anions. The hydrolyzed reactive dyes have long anions and short cations. Wherever the unfixed dye is exhausted into the fibers the long anions of the dyestuff react with the long cations of the fixing agent and would precipitate inside the fibers getting trapped in situ. Since the complex is insoluble they cannot be removed by washing. Therefore the wash fastness will be improved.

The insoluble complex formed outside the fabric in the bath will also precipitate and they need to be kept in suspension with suitable dispersing agents during soaping and removed; otherwise rubbing fastness may be affected. This situation would arise if the dyeing parameters were not properly monitored and controlled or by the use of dyestuffs whose exhaustion characteristic is very high and the reactivity (fixation) is relatively very low. The chances are that the exhausted, but unfixed hydrolyzed dyestuff will leach out

during washing and hence the need to resort to dye fixing agents. As reacting with any residual unfixed anionic dye, cationic fixing agent form an organic salt of greatly increased molecular size and of lower molecular size and of lower water solubility and diffusion rate, they may reduce the light fastness of the dyeing and therefore more suitable for treatment of deep shades.

➤ **The factors governing the fixing process are:**

- Type of fixing agent
- Concentration of fixing agent
- Time & Temperature
- pH of the bath [32]

2.7. Water Quality Parameters

Some of the main parameters listed in the water quality discharge standards are briefly discussed under to give a working knowledge of what they are and why they are important.

Color

Although color is not included in the Environment Conservation Rules (1997), it is an issue in dye house effluent because unlike other pollutants it is so visible. Reducing color is therefore important for the public perception of a factory. Consequently, international textile buyers are increasingly setting discharge standards for color. However, as a health and environmental issue color is less of a concern than many of the other parameters.

BOD and COD

Measurement of the oxidizable organic matter in wastewater is usually achieved through determining the 5-day biological oxygen demand (BOD), the chemical oxygen demand (COD) and total organic carbon (TOC).

BOD₅ is a measure of the quantity of dissolved oxygen used by microorganisms in the biochemical oxidation of the organic matter in the wastewater over a 5-day period at 20°C. The test has its limitations but it still used extensively and is useful for determining approximately how much oxygen will be removed from water by an effluent or how

much may be required for treatment and is therefore important when estimating the size of the ETP needed.

COD is often used as a substitute for BOD as it only takes a few hours not five days to determine. COD is a measure of the oxygen equivalent of the organic material chemically oxidized in the reaction and is determined by adding dichromate in an acid solution of the wastewater.

TDS and TSS

Wastewater can be analyzed for total suspended solids (TSS) and total dissolved solids (TDS) after removal of coarse solids such as rags and grit. A sample of wastewater is filtered through a standard filter and the mass of the residue is used to calculate TSS. Total solids (TS) are found by evaporating the water at a specified temperature. TDS is then calculated by subtracting TSS from TS.

Metals

A number of metals are listed in the national environmental quality standards for industrial wastewater, including cadmium, chromium, copper, iron, lead, mercury, nickel and zinc. Many metals, which are usually only available naturally in trace quantities in the environment, can be toxic to humans, plants, fish and other aquatic life.

Phosphorus, Total Nitrogen, Nitrate and Ammonia

These parameters are all used as a measure of the nutrients present in the wastewater, as a high nutrient content can result in excessive plant growth in receiving water bodies, subsequent oxygen removal and the death of aquatic life.

pH

pH is a measure of the concentration of hydrogen ions in the wastewater and gives an indication of how acid or alkaline the wastewater is. This parameter is important because aquatic life such as most fish can only survive in a narrow pH range between roughly pH 6-9.

Sulphur and Sulphide

Textile dyeing uses large quantities of sodium sulphate and some other sulphur containing chemicals. Textile wastewaters will therefore contain various sulphur compounds and once in the environment sulphate is easily converted to sulphide when oxygen has been removed by the BOD of the effluents. This is a problem because hydrogen sulphide can be formed which is a very poisonous gas, it also has an unpleasant smell of rotten eggs. The presence of sulphides in effluents can interfere with biological treatment processes.

Temperature

Temperature of water is a very important factor for aquatic life. It controls the rate of metabolic and reproductive activities, and determines which aquatic species can survive. Different aquatic species require different quantity of DO to survive in the water. Temperature inversely affects the rate of transfer of gaseous oxygen into dissolved oxygen. On the other hand at higher temperature the metabolic rate of aquatic plants and animals increases producing an increase in oxygen demand.

International regulations related to water temperature and aquatic life classifies water, as "Class 1 Cold Water Aquatic Life" should never have temperatures exceeding 20°C, while waters classified, as "Class 1 Warm Water Aquatic Life" should never have temperatures exceeding 30°C.

Oil and Grease

This includes all oils, fats and waxes, such as kerosene and lubricating oils. Oil and grease causes unpleasant films on open water bodies and negatively affect aquatic life. They can also interfere with biological treatment processes and cause maintenance problems as they coat the surfaces of components of ETPs.

2.8. Waste Water/Effluent Generation and Characteristics

Wet processing of textiles involves, in addition to extensive amounts of water and dyes, a number of inorganic and organic chemicals, detergents, soaps and finishing chemicals to aid in the dyeing process to impart the desired properties to dyed textile products. Residual chemicals often remain in the effluent from these processes. In addition, natural impurities such as waxes, proteins and pigment, and other impurities used in processing

such as spinning oils, sizing chemicals and oil stains present in cotton textiles, are removed during desizing, scouring and bleaching operations. This results in an effluent of poor quality, which is high in BOD and COD load. Table 2.2 lists typical values of various water quality parameters in untreated effluent from the processing of fabric using reactive, sulfur and vat dyes and compares these to the Department of Environment of Bangladesh effluent standards for discharge into an inland surface water body (e.g. river, lake, etc.). As demonstrated, the effluent from textile industries is heavily polluted.

Table-2.2: Characteristics of wastewater to be discharged into the environment (Recommended by the Dept. of Environment of Bangladesh)

SL. No.	Effluent quality Parameters	Concentration Present
01	pH	7-8
02	BOD	<50 PPM
03	COD	<200 PPM
04	TSS	<100 PPM
05	TDS	<2500 PPM
06	Oil & Greases	< 10 PPM
07	Color	Clean
08	Temperature	< 30 °C

Table 2.3: Characteristics of wastewater of a typical textile wet processing industry.

SL. No.	Effluent quality Parameters	Concentration Present
01	pH	8-14
02	BOD	400-600 PPM
03	COD	800-1200 PPM
04	TSS	200-500 PPM
05	TDS	3000-6000 PPM
06	Oil & Greases	30-60 PPM
07	Color	Dark Mixed
08	Temperature	Up to 60°C

As mentioned textile wastewater may contain various types of contaminants but in most case the toxicity of the above eight parameters are considered important before discharging them into the environment

2.9. Effluent Treatment Plant (ETP)

Effluent treatment plant is used for treating the management of waste water after disposal. Satisfactory disposal of wastewater, whether by surface, subsurface methods or dilution, is dependent on its treatment prior to disposal. Adequate treatment is necessary to prevent contamination of receiving waters to a degree which might be interfere with their best or intended use, whether it be for water supply, recreation, or any other required purpose.

Wastewater treatment consists of applying known technology to improve or upgrade the quality of a wastewater. Usually wastewater treatment will involve collecting the wastewater in a central, segregated location (the Wastewater Treatment Plant) and subjecting the wastewater to various treatment processes. Most often, since large volumes of wastewater are involved, treatment processes are carried out on continuously flowing wastewaters (continuous flow or "open" systems) rather than as "batch" or a series of periodic treatment processes in which treatment is carried out on parcels or "batches" of wastewaters. While most wastewater treatment processes are continuous flow, certain operations, such as vacuum filtration, involving as it does storage of sludge, the addition of chemicals, filtration and removal or disposal of the treated sludge, are routinely handled as periodic batch operations.

Wastewater treatment, however, can also be organized or categorized by the nature of the treatment process operation being used; for example, physical, chemical or biological. Examples of these treatment steps are shown below. A complete treatment system may consist of the application of a number of physical, chemical and biological processes to the waste water.

There are basically three types of Effluent Treatment Plant. Like-

- Chemical ETP Plant
- Biological ETP Plant

- Chemical-Biological ETP Plant
- Electrical ETP Plant

➤ **Description of effluent treatment plant process sequence in textile industry**

Cooling & Mixing

After primary filtration, the liquor passes to cooling and mixing tank in which uniform mixing of effluents from various process takes place. A paddle mixer is provided for mixing. Cooling of the effluent may be done with the help of cooling tower or fan.

Neutralization

Effluent is pumped to a tank in which it is neutralized by acid or alkali dosing. The tank has an automatic dosing controller which automatically control the dose of acid or alkali to maintain the required pH.

Coagulation

Then the effluent is pumped to the coagulation tank. Chemical coagulation very effective for removal of color and suspended materials, aluminum, ferrous sulphates, ferric chloride, chlorinate copper etc. to increase the efficiency of coagulation, coagulation gain may be added for example polyacrylate.

Setting and separation of sludge

Some of the soluble organic matter and light suspended solids will form a blanket of flocculent matter with the coagulants. The blanket is skimmed off to another tank and the remaining solution is moved to pressure filter.

Pressure Filter

For pressure filtration vacuum pumps may be used to force through the filter and suspended flocks are collected in the pressure fine filter. Discharging to drain, after filtration the purified water sent to drain which eventually reach to the river or anywhere else.

2.9.1. Chemical Wastewater Treatment

Chemical Wastewater Treatment Methods consists of using some chemical reaction or reactions to improve the water quality. Probably the most commonly used chemical process is chlorination. Chlorine, a strong oxidizing chemical, is used to kill bacteria and to slow down the rate of decomposition of the wastewater. Bacterial kill is achieved when vital biological processes are affected by the chlorine. Another strong oxidizing agent that has also been used as an oxidizing disinfectant is ozone.

Coagulation consists of the addition of a chemical that, through a chemical reaction, forms an insoluble end product that serves to remove substances from the wastewater. Polyvalent metals are commonly used as coagulating chemicals in wastewater treatment and typical coagulants would include lime (that can also be used in neutralization), certain iron containing compounds (such as ferric chloride or ferric sulfate) and alum (aluminum sulfate).

Certain processes may actually be physical and chemical in nature. The use of activated carbon to "adsorb" or remove organics, for example, involves both chemical and physical processes. Processes such as ion exchange, which involves exchanging certain ions for others, are not used to any great extent in wastewater treatment.

➤ Chemical ETP Flow Chart

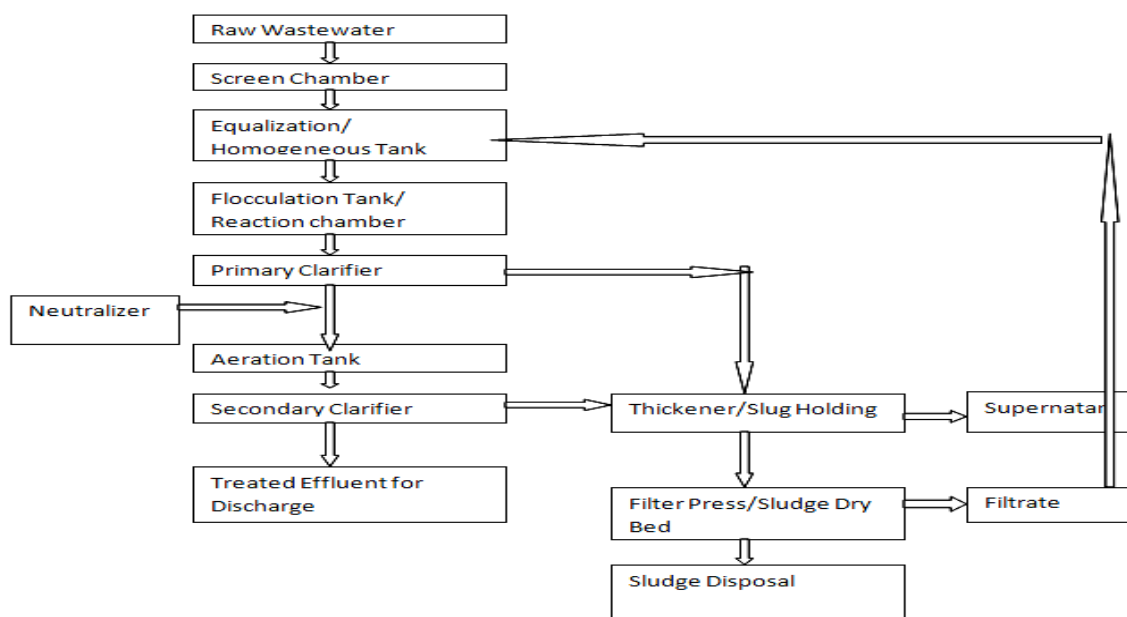
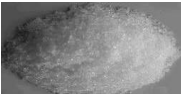










Figure 2.6: Chemical ETP Flow Chart

➤ **Chemicals used in textile ETP**

Table-2.4: List of name and functions of used chemicals in textile ETP

Sl. No.	Name of the chemicals	Purpose of Use	Price in BDT/Kg	Figure
1.	Di-ammonium phosphate (DAP)	It is used as food for bacterial growth.	30-40	
2.	Sodium Hypochlorite (NaOCl)	It is used to destroy the harmful bacteria.	12-15	
3.	Poly electrolyte	It is used to clean the water by the sedimentation.	350-450	
4.	Poly Aluminum Chloride (PAC)	It is used to clean the water.	50-60	
5.	Urea	It is used as food for bacterial growth.	20-30	
6.	Decolorant	It is used to make the textile effluent colorless.	130-150	
7.	Sulphuric Acid- (H ₂ SO ₄)	It maintains the pH of the discharged water.	30-40	
8.	Green Vitriol- (FeSO ₄ .7 H ₂ O)	It helps to separate colored bodies from the effluent water.	18-20	
9.	Lime-Ca(OH) ₂	It mainly remove the turbidity of colored effluent to make it transparent.	14-18	

2.9.2. Biological Wastewater Treatment

Biological treatment methods use microorganisms, mostly bacteria, in the biochemical decomposition of wastewaters to stable end products. More microorganisms, or sludges, are formed and a portion of the waste is converted to carbon dioxide, water and other end products. Generally, biological treatment methods can be divided into aerobic and anaerobic methods, based on availability of dissolved oxygen.

The purpose of wastewater treatment is generally to remove from the wastewater enough solids to permit the remainder to be discharged to receiving water without interfering with its best or proper use. The solids which are removed are primarily organic but may also include inorganic solids. Treatment must also be provided for the solids and liquids which are removed as sludge. Finally, treatment to control odors, to retard biological activity, or destroy pathogenic organisms may also be needed.

While the devices used in wastewater treatment are numerous and will probably combine physical, chemical and biological methods, they may all be generally grouped under six methods:

1. Preliminary Treatment.
2. Primary Treatment.
3. Secondary Treatment.
4. Disinfection.
5. Sludge Treatment.
6. Tertiary Treatment.

Degrees of treatment are sometimes indicated by use of the terms primary, secondary and tertiary treatment. Tertiary treatment, properly, would be any treatment added onto or following secondary treatment.

Preliminary Treatment

At most plants preliminary treatment is used to protect pumping equipment and facilitate subsequent treatment processes. Preliminary devices are designed to remove or cut up the larger suspended and floating solids, to remove the heavy inorganic solids, and to remove excessive amounts of oils or greases.

To affect the objectives of preliminary treatment, the following devices are commonly used:

1. Screens -rack, bar or fine
2. Comminuting devices - grinders, cutters, shredders
3. Grit chambers
4. Pre-aeration tanks

In addition to the above, chlorination may be used in preliminary treatment. Since chlorination may be used at all stages in treatment, it is considered to be a method by itself. Preliminary treatment devices require careful design and operation.

In this treatment, most of the settle able solids are separated or removed from the wastewater by the physical process of sedimentation. When certain chemicals are used with primary sedimentation tanks, some of the colloidal solids are also removed. Biological activity of the wastewater in primary treatment is of negligible importance.

The purpose of primary treatment is to reduce the velocity of the wastewater sufficiently to permit solids to settle and floatable material to surface. Therefore, primary devices may consist of settling tanks, clarifiers or sedimentation tanks. Because of variations in design, operation, and application, settling tanks can be divided into four general groups:

1. Septic tanks
2. Two story tanks – Inhofe and several proprietary or patented units
3. Plain sedimentation tank with mechanical sludge removal
4. Upward flow clarifiers with mechanical sludge removal

When chemicals are used, other auxiliary units are employed. These are:

1. Chemical feed units
2. Mixing devices
3. Flocculators

The results obtained by primary treatment, together with anaerobic sludge digestion as described later, are such that they can be compared with the zone of degradation in stream

self-purification. The use of chlorine with primary treatment is discussed under the section on Preliminary Treatment.

Secondary Treatment

Secondary treatment depends primarily upon aerobic organisms which biochemically decompose the organic solids to inorganic or stable organic solids. It is comparable to the zone of recovery in the self-purification of a stream.

The devices used in secondary treatment may be divided into four groups:

1. Trickling filters with secondary settling tanks
2. Activated sludge and modifications with final settling tanks
3. Intermittent sand filters
4. Stabilization ponds

The use of chlorine with secondary treatment is discussed under the section on Secondary Treatment

Chlorination

This is a method of treatment which has been employed for many purposes in all stages in wastewater treatment, and even prior to preliminary treatment. It involves the application of chlorine to the wastewater for the following purposes:

1. Disinfection or destruction of pathogenic organisms
2. Prevention of wastewater decomposition --
 - (a) Odor control and
 - (b) Protection of plant structures
3. Aid in plant operation -
 - (a) sedimentation,
 - (b) trickling filters,
 - (c) activated sludge bulking
4. Reduction or delay of biochemical oxygen demand (BOD)

While chlorination has been commonly used over the years, especially for disinfection, other methods to achieve disinfection as well as to achieve similar treatment ends are also used. Among the most common is the use of ozone. In view of the toxicity of chlorine and chlorinated compounds for fish as well as other living forms, ozonation may be more commonly used in the future. This process will be more fully discussed in the section on disinfection.

Sludge Treatment

The solids removed from wastewater in both primary and secondary treatment units, together with the water removed with them, constitute wastewater sludge. It is generally necessary to subject sludge to some treatment to prepare or condition it for ultimate disposal. Such treatment has two objectives - the removal of part or all of the water in the sludge to reduce its volume, and the decomposition of the organic solids to mineral solids or to relatively stable organic solids. This is accomplished by a combination of two or more of the following methods:

1. Thickening
2. Digestion with or without heat
3. Drying on sand bed -- open or covered
4. Conditioning with chemicals
5. Elutriation
6. Vacuum filtration
7. Heat drying
8. Incineration
9. Wet oxidation
10. Centrifuging

➤ **Required chemicals and their functions in biological effluent treatment plant (ETP):**

The effluent generated from different sections of a textile industry must be treated before they are discharged to the environment. Various chemicals and physical means are introduced for this purpose. Some chemicals are used to treatment those wastage polluted water. Here chemicals name are given which are used in effluent treatment plant.

H₂SO₄:

Function- Neutralize the waste water controlling the pH. It is auto dispensed in the neutralization tank.

Polyelectrolyte:

Function- Used for sedimentation / sludge coagulation and also killing bacteria.

Antifoaming Agent:

Function- Used for reduction / controlling foam. It is used auto / manually in the distribution tank.

De-colorant:

Function- Used for removing color. It is used auto / manually in the sedimentation feeding tank.

Sodium Hypochlorite:

Function- It is used to kill the harmful bacteria. It is used in the biological oxidation tank.

Product quality checked:

1. Biological Oxygen Demand (BOD)
2. Chemical Oxygen Demand (COD)
3. Total suspended solids
4. Total dissolved solids
5. Color
6. pH etc.

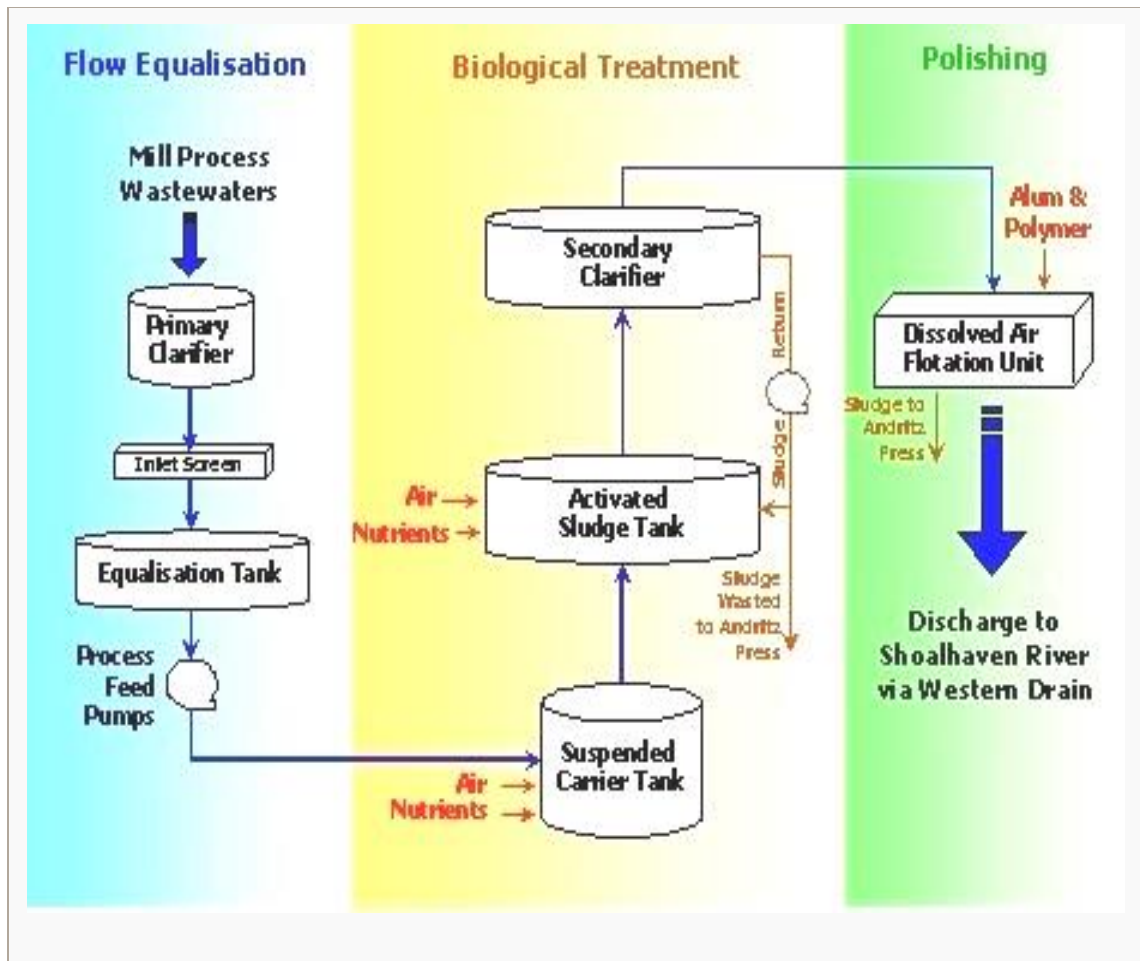


Figure 2.7: Biological ETP Flow Chart

➤ **Process description**

1. Inlet launder

The purpose of launder is to flow the effluent of gas scrubber to distribution chamber. Inlet channel is designed for a surge flow of $1950\text{m}^3/\text{hr}$ at the rate of slope of 2%. So water flows at 1.5m/s (self cleaning velocity). Self cleaning velocity is that velocity at which if the sludge flows it will not get accumulated in the launder.

2. Distribution on chamber

Purpose of distribution chamber is to divide the flow (design flow of $1140\text{m}^3/\text{hr}$) into two equal flows. In case if one of the thickeners is closed then there would be no distribution so selection of pipes is done on these criteria. The size of gates is designed such that there is equal distribution always.

3. Flash mixer

There are two flash mixers designed for a flow of 1140 m³/hr with a retention time of 60 sec. So its volume must lie around 19 m³. In flash mixer alum (coagulant) acts upon sludge so that suspended solids settle down. In addition pH of sludge is also raised by lime as it is required to have a pH of 7-9. Polyelectrolyte (flocculants) also acts upon to fasten the process of coagulation.

2.10. Effective Effluent Management Steps

The five steps to effective effluent management are:

1. Characterize all effluents produced on-site;
2. Implement a waste minimization program to reduce the volume and strengths of effluents;
3. Incorporate in-process conditioning and treatment, where appropriate;
4. Determine and install segregation facilities to tailor treatment options;
5. Optimize performance of ETP. [33]

CHAPTER 03
EXPERIMENTAL DETAILS

CHAPTER 03

EXPERIMENTAL DETAILS

3.1. Sample Specification:

Table-3.1: Specification of sample used in this investigation.

Sample Name	: Single jersey fabric
Fiber Composition	: 100% cotton
Fabric Type	: Knitted fabric
Fabric Condition	: Pre-treated (scoured, bleached and bio-polished)
Course/inch	: 52
Wales/inch	: 38
Fabric GSM	: 150
Yarn Count	: 37

3.2. Specification of Dyes:

Table-3.2: List of Dyes used in this research work.

<i>Dyes</i>		<i>Brand Name</i>	<i>Origin</i>
Hetero Bi-functional (MCT/VS)	Reactive Red 195	Nuva Red-3BS 150%	Dycin-Bnagladesh
Homo Bi-functional Vinyl Sulphone	Reactive Black 5	Nuvacron Black-B 150%	Dycin-Bnagladesh
Vinyl Sulphone	Reactive Blue 19	Nuva Brilliant Blue 140%	Dycin-Bnagladesh

3.3. Chemicals Specification

Table-3.3: List of chemicals used in this work.

<i>Chemicals used for dyeing of 100% cotton fabric</i>			
<i>Chemicals</i>	<i>Brand Name</i>	<i>Origin</i>	<i>Purpose</i>
Salt	Glauber's Salt	Germany	Dye exhaustion.
Alkali	Soda Ash	Germany	Dye fixation and pH control.
	Caustic Soda	Germany	

Sequestering agent	Complexant-P-H/C	Dycin-Bnagladesh	Water hardness elimination.
Wetting agent	Dynotex-MH ₁ D	Dycin-Bnagladesh	Reduce surface tension of and help to wet the fabric by increasing its absorbency.
<i>Chemicals used for after-treatment</i>			
Chemicals	Brand Name	Origin	Purpose
Acid	Acetic Acid	Germany	Neutralization of alkaline condition.
Soaping agent	Dekol SN	Germany	Remove hydrolyzed dyes and dust-darts.
Fixing agent	Aliba Fix	India	Fixation of unfixed dyes.
<i>Chemical used for determination of DO, BOD</i>			
Chemicals		Origin	Purpose
Calcium Chloride	:	Germany	Determination of DO, BOD
Manganous Sulfate	:	Germany	
Ferric Chloride	:	China	
Di Potassium Hydrogen Phosphate	:	China	
Potassium Di Hydrogen Phosphate	:	China	
Di Sodium Hydrogen Phosphate	:	China	
Ammonium Chloride	:	China	
Manganous Sulphate	:	China	
Potassium Hydroxide	:	China	
Potassium Iodide	:	China	
Sodium Azide	:	Germany	
Sulphuric Acid (Conc.)	:	Germany	
Starch Indicator	:	Germany	
Sodium Thiosulfate	:	China	
Distilled or deionized water	:	Bangladesh	
<i>Chemical used for determination of COD</i>			
Potassium Dichromate	:	China	Determination of COD
Sulphuric Acid	:	China	

Ferrous Ammonium Sulphate	: China	Determination of COD
Silver Sulphate	: China	
Mercury Sulphate	: China	
Ferroun Indicator	: China	
Organic free distilled water	: China	

3.4. Dye Structure and Related Properties

Table-3.4: Bi-functional dyes structure, feature and application.

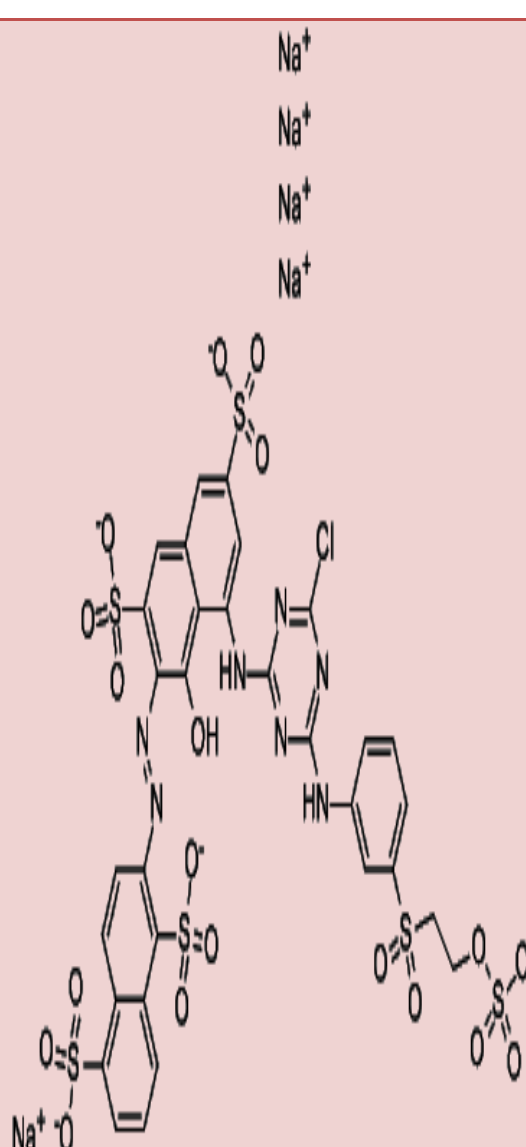
Bi-functional Dye	Related features and application
 <p>Figure 3.1: Reactive Red 195</p>	<p>Reactive Red 195</p> <p>Synonyms : Red F3B; Reactive red 195; C.I. Reactive red 195; Reactive Brilliant Red M-3BE; Cino.red.195</p> <p>Molecular Formula : $C_{31}H_{19}ClN_7O_{19}S_6 \cdot 5Na$</p> <p>Molecular Weight : 1136.32</p> <p>Mol File : 93050-79-4.mol</p> <p>Raw materials : Cyanuric chloride --> 2-Aminonaphthalene-1-sulfonic acid</p> <p>Nature : Anionic</p> <p>Appearance : Red powder</p> <p>Solubility : Soluble in water</p> <p>Application : This chemical can be used for dyeing and printing of cotton cloth. [34]</p>

Table 3.5: Bi-functional vinyl sulphone dye structure, feature and application

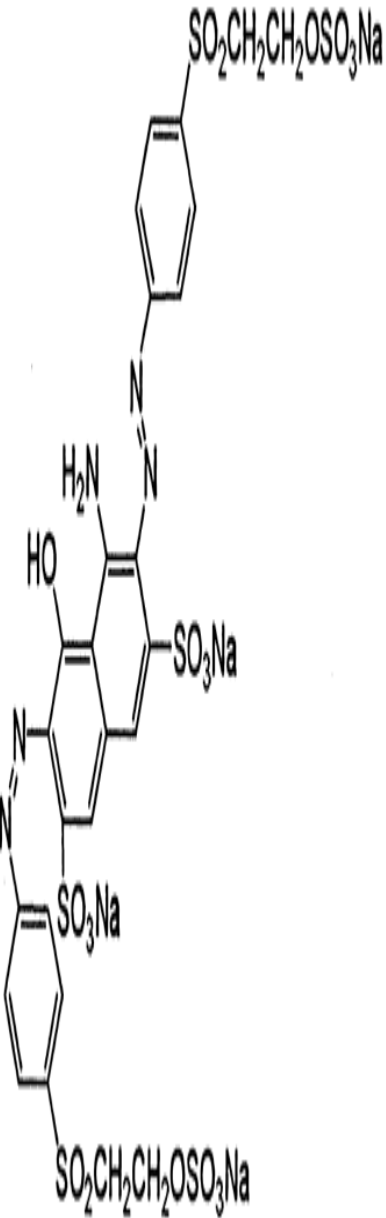
Bi-functional Vinyl Sulphone Dye	Related features and application
	<p>Reactive Black 5</p>
	<p>Synonyms :</p> <ul style="list-style-type: none"> • C.I. Reactive Black 5, • Black-B 150% • Reactive Black KN-B, • Black B
	<p>Molecular Formula : C₂₆H₂₁N₅Na₄O₁₉S₆</p>
	<p>Molecular Weight : 991.82</p>
	<p>Appearance : Black powder</p>
	<p>Nature : Anionic, organic</p>
	<p>Manufacturing Methods : 2-(4Aminophenylsulfonyl) ethyl hydrogen sulfate (2 Moore) diazo, and 4-Amino-5-hydroxynaphthalene-2, 7-disulfonic acid coupling.</p>
<p>Application : Used for cotton, viscose, wool and polyamide fiber disseminated, roll the dye, knot dyeing piled up and dyeing of continuous. Can also be used for cotton or viscose fabric printing and dyeing, direct printing and discharge printing. [36]</p>	

Figure 3.2: Reactive Black 5 [35]

Table-3.6: Vinyl sulphone dye structure, feature and application

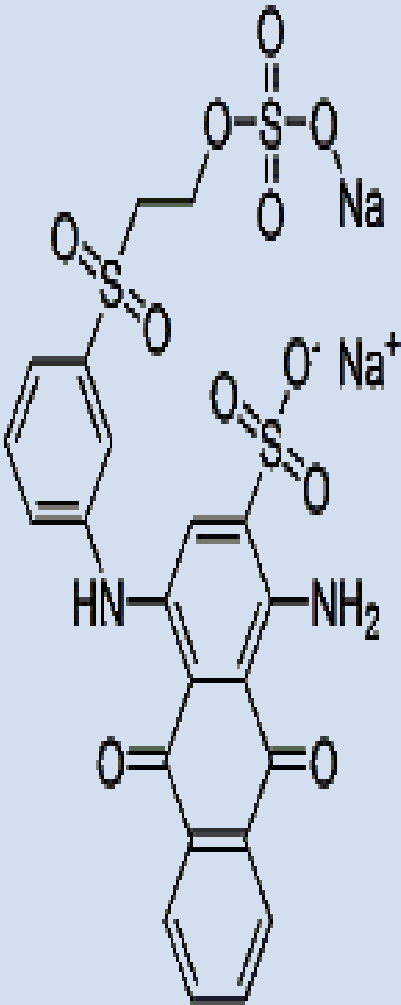
Vinyl Sulphone Dye	Related features and application
	<p>Reactive Blue 19</p> <p>Synonyms :</p> <ul style="list-style-type: none"> • 2-anthracenesulfonicacid, 1-amino-9,10-dihydro-4-(m-((2-hydroxyethyl)sulfonyl)); • 2-anthracenesulfonicacid, 1-amino-9,10-dihydro-9,10-dioxo-4-((3-((2-(sulfooxy))); • 2-anthracenesulfonicacid, 1-amino-9,10-dihydro-9,10-dioxo-4-[[3-[[2-(sulfooxy);anilino]-9,10-dioxo- hydrogensulfate(ester), disodiumsalt;anilino-9,10-dioxo- , hydrogensulfate(ester),disodium salt; • C.I.Reactiveblue19; • C.I.ReactiveBlue19(61200) • C.I.Reactiveblue19, disodiumsalt <p>Molecular Formula : $C_{22}H_{16}N_2Na_2O_{11}S_3$</p> <p>Molecular Weight : 626.54</p> <p>Mol File : 2580-78-1.mol</p> <p>Application : Can be used for dyeing and printing of cotton cloth.</p> <p>Nature : Anionic, organic [37]</p>

Figure 3.3: Reactive Blue 19

Reactive Blue 19 Usage And Synthesis

Chemical Properties	Dark blue crystalline powder
General Description	Fine blue-black powder.
Air & Water Reactions	Water soluble.
Health Hazard	Acute/chronic hazards: When heated to decomposition Reactive Blue 19 emits very toxic fumes of sodium oxide, nitrogen oxides and sulfur oxides.
Fire Hazard	Flash point data for Reactive Blue 19 are not available; however, Reactive Blue 19 is probably combustible.
Raw materials	Sodium bicarbonate-->Cuprous chloride-->Sulfate standard-->Bromaminic acid-->Dihydroxyethylsulfone [38]

3.5. Machines and Apparatus Used

List of Apparatus and Machines used for dyeing and after-treatment

- Beaker
- Stirrer
- Spoon
- Glass rod
- Thermometer
- Measuring Cylinder
- Conical Flask
- Burette
- Burette Stand
- Pipette
- Pipette Pillar
- Glass bottle with stopper
- Boiling water bath

Electric Dryer

It is an electric equipment used to dry fabrics.

Brand Name: Miyako

Model No: MHD-800D

Rated Voltage: 230V-50H

Rated Power: 800W

Origin: China



Electric Balance

It is an electric balance used to measure powder dyes and chemicals.

Brand Name: G&G

Model: JJ200B

Capacity: 600 gm

Origin: China

pH Meter/ pH Tester

A **pH meter** is an electronic device used for measuring the pH (acidity or alkalinity) of a liquid (though special probes are sometimes used to measure the pH of semi-solid substances). A typical pH meter consists of a special measuring probe (a glass electrode) connected to an electronic meter that measures and displays the pH reading.

Brand Name: HANNA Instruments

Model: M-26505

Origin: Italy



Electric Heater

It is an electric apparatus used to dye fabrics.

Brand Name: Miyako

Origin: China

Boiling water bath

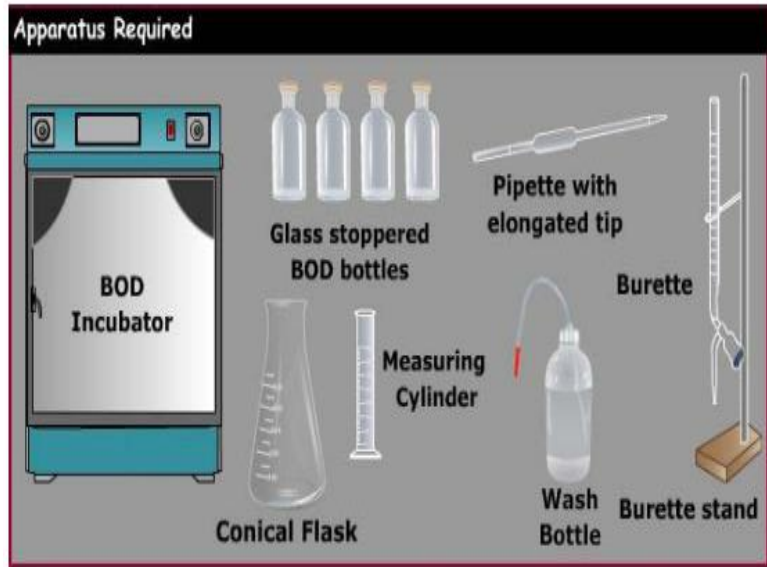
A boiling water bath is a machine mainly used for the purpose of heating several bath by maintaining same temperature at same time.

Origin: China



List of Apparatus and Machines used for determination of DO and BOD

- BOD Incubator
- Burette and burette stand
- 300 ml glass stopper BOD bottles
- 500 ml Conical flask
- Pipettes with elongated tips
- Pipette bulb
- 250 ml graduated cylinders
- Wash Bottle



List of Apparatus and Machines used for determination of COD

- COD Digester
- Burette and burette stand
- COD vials with stand
- 250 ml conical flask
- Pipette
- Pipette bulb
- Tissue papers
- Wash Bottles



COD Digester:

It is an electric machine used for the purpose of heating COD vials at high temperatures.

Origin: China

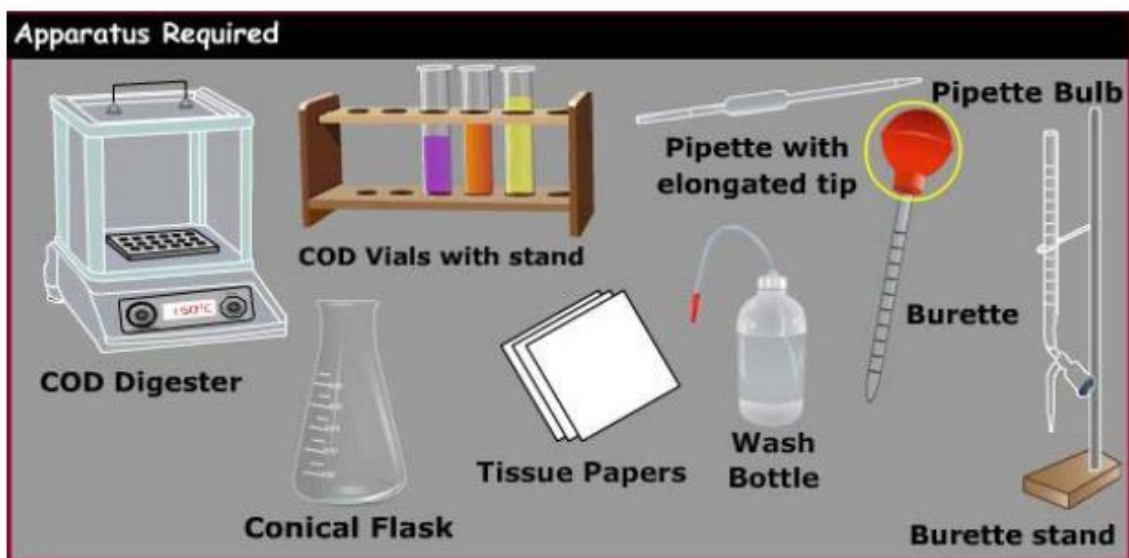


Figure 3.4 - Apparatus and Machines

3.6. Method of Dyeing

- **Fabrics:** Scoured-bleached single jersey plain knitted cotton fabrics are collected from laboratory.

3.6.1. Dyeing parameters: (bi-functional reactive dyes)

Table-3.7: Dyeing recipe for bi-functional reactive dyes at different shade percentage

Dye (o.w.f)	0.5%	2.5%	4.5%	6.5%
Fabric weight (gm)	X	X	X	X
Glauber's Salt (g/l)	12	40	60	80
Soda ash (g/l)	5	5	5	5
Caustic soda 50% (ml/l)	0.7	1.2	1.6	2
1 st Alkali addition	Soda ash	Soda ash+1/3 Caustic soda		
2 nd Alkali addition	Caustic soda	2/3 Caustic soda		
*Sequestering agent(g/l)	1	1	1	1
**Wetting agent(g/l)	1	1	1	1
Temperature °C	60	60	60	60
Fixing Time, min	15	30	30	30
Liquor Ratio	1:30	1:30	1:30	1:30

*Complexant-P-H/C, ** Dynotex-MH₁D

3.6.2. Dyeing curve: (bi-functional reactive dyes)

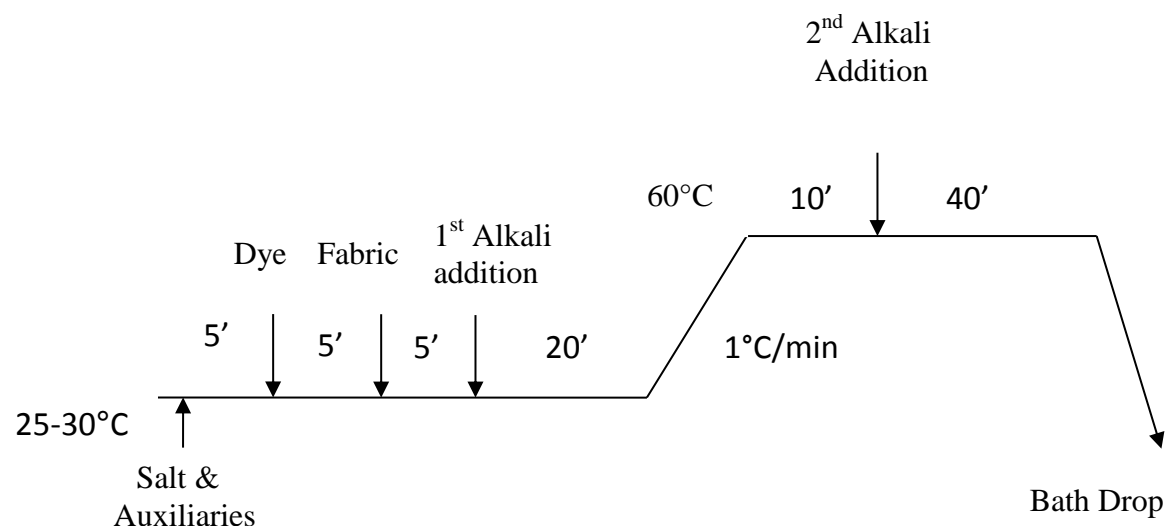


Figure 3.5: Bi-functional reactive dyes dyeing curve.

3.6.3. Dyeing parameters: (vinyl sulphone reactive dyes)

Table-3.8: Dyeing recipe for vinyl sulphone reactive dyes at different shade percentage

Dye (o.w.f)	0.5%	2.5%	4.5%	6.5%
Fabric weight (gm)	X	X	X	X
Glauber's Salt (g/l)	15	45	65	85
Soda ash (g/l)	7	14	17	20
1 st Alkali addition	½ Soda ash			
2 nd Alkali addition	½ Soda ash			
*Sequestering agent(g/l)	1	1	1	1
**Wetting agent(g/l)	1	1	1	1
Temperature °C	60	60	60	60
Fixing Time, min	15	30	30	30
Liquor Ratio	1:30	1:30	1:30	1:30

*Complexant-P-H/C, ** Dynotex-MH₁D

3.6.4. Dyeing curve: (vinyl sulphone reactive dyes)

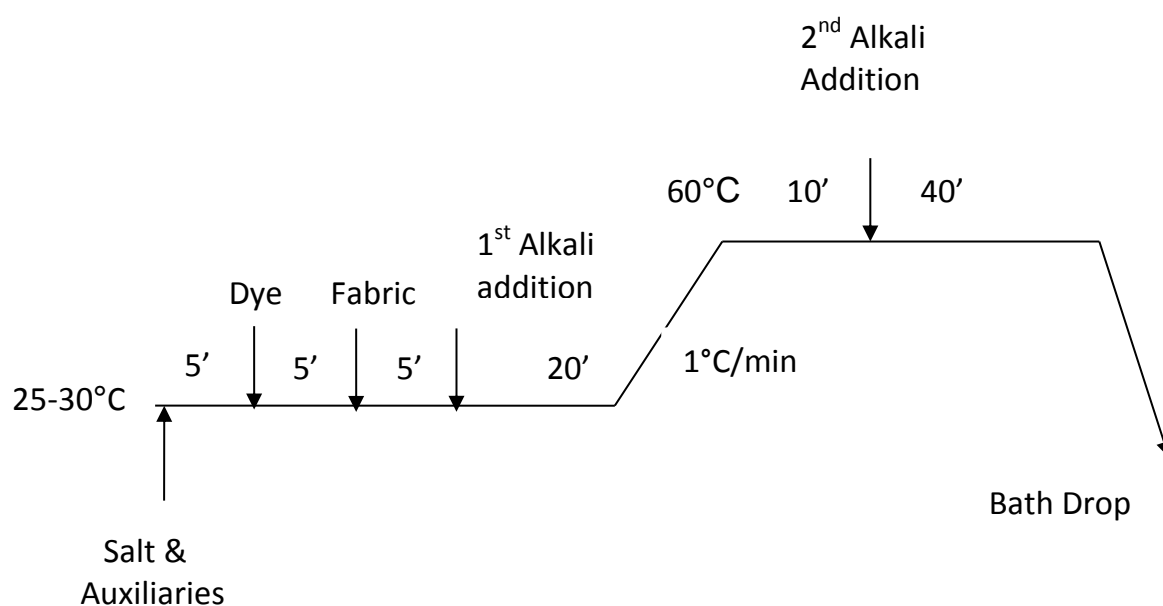


Figure 3.6: Vinyl Sulphone reactive dyes dyeing curve.

3.7. After-treatment

Cold Rinsing: After dyeing every shade, the dyed fabrics are first cold rinsed.

Hot Rinsing: Hot rinsing at 60°C for 10 min

Neutralization (Acid wash): Then the fabric is neutralized by acid wash.

Table-3.9: Neutralization recipe

Liquor, ml	500
Acetic acid, ml/l	1
Temperature , °C	Room Temperature
Time, min	10

Soaping: After Neutralization, Hot wash is done with soaping agent.

Table-3.10: Soaping parameters

Soaping agent, g/l	1
Fabric wt, gm	X
Temperature , °C	95
Time, min	15

Rinsing: After every soaping, fabric is rinsed with fresh water and then dried with the help of dryer.

Fixing: Fixation is carried out with fixing agent after soaping for a single shade.

Table-3.11: Fixing parameters

Fixing agent, g/l	1
Acetic acid, g/l	0.5
pH	5-5.5
Temperature , °C	40
Time, min	10

Drying parameters:

Temperature: 110°C

Time: 10 minutes

3.8. Determination of DO and BOD

Test Method: IS: 3025 (Part-44) – Reaffirmed 2003

Principle:

The sample is filled in an airtight bottle and incubated at specific temperature for 5 days. The dissolved oxygen (DO) content of the sample is determined before and after five days of incubation at 20°C and the BOD is calculated from the difference between Initial and final DO.

The initial DO is determined shortly after the dilution is made; all oxygen uptake occurring after this measurement is included in the BOD measurement.

Test Procedure: (For determination of DO and BOD)

a. Preparation of dilution water:

High quality organic free water was used for dilution purposes.

The required volume of water (five litres of organic free distilled water) was aerated with a supply of clean compressed air for at least 12 hours. It was then allowed to stabilize by incubating at 20°C for at least 4 hours.

For the test we have taken five litres of organic free aerated distilled water. Then 5ml each of the nutrients was added.

- 5ml calcium chloride solution,
- 5ml magnesium sulphate solution,
- 5ml ferric chloride solution and
- 5ml phosphate buffer solution was added.

This is the standard dilution water. Preparation of dilution water before 3 to 5 days, initiating BOD test ensure that the BOD of the dilution water is less than 0.2 mg/L.

a. Titration procedure:

- Four 300 ml glass stoppered BOD bottles (two for the sample and two for the blank) were taken.
- 10 ml of the sample was added to each of the two BOD bottles and the remaining quantity was filled with the dilution water. i.e., sample was diluted 30 times.
- The remaining two BOD bottles were for blank, to those bottles only dilution water alone was added.

- After the addition the glass stopper was immediately placed over the BOD bottles and the numbers of the bottle was noted down for identification.
- Then one blank solution bottle was preserved and another bottle was kept in a BOD incubator at 20°C for five days.
- The other two bottles (one blank and one sample) were needed to be analyzed immediately.
- On that time any kind of bubbling and trapping of air bubbles was avoided.
- 2ml of manganese sulfate to the BOD bottle was added by inserting the calibrated pipette just below the surface of the liquid.
- 2 ml of alkali-iodide-azide reagent was added in the same manner.
- (The pipette should be dipped inside the sample while adding the above two reagents. If the reagent was added above the sample surface, then oxygen would be introduced into the sample.)
- It was allowed to settle for sufficient time in order to react completely with oxygen.
- When this floc has settled to the bottom, the contents were shaken thoroughly by turning it upside down.
- 2 ml of concentrated sulfuric acid was added via a pipette held just above the surface of the sample.
- Then carefully stoppered and inverted several times to dissolve the floc.
- Titration was needed to be started immediately after the transformation of contents to Erlenmeyer flask.
- The burette was rinsed with sodium thiosulphate and then filled with sodium thiosulphate. After that the burette was fixed to the stand with the help of clamp.
- 20 ml of the solution from the bottle was measured out and transferred to an Erlenmeyer flask.
- Titration of the solution was done with standard sodium thiosulphate solution until the yellow color of liberated iodine was almost faded out. (Pale yellow color).
- 1 ml of starch solution was added then and the titration was continued until the blue color disappears to colorless.
- The volume of sodium thiosulphate solution added was noted down, which gave the DO in mg/L. Titration was repeated for concordant values.
- After five days, the bottles from the BOD incubator were taken out and DO of the sample and the blank was analysed.
- 2ml of manganese sulfate was added to the BOD bottle by inserting the calibrated pipette just below the surface of the liquid.
- 2 ml of alkali-iodide-azide reagent was added in the same manner.
- If oxygen was present a brownish-orange cloud of precipitate or flock would appear.
- Then it was allowed to settle for sufficient time in order to react completely with oxygen.
- When this flock has been settled to the bottom, the contents were shaken thoroughly by turning it upside down.

- 2 ml of concentrated sulfuric acid was added via a pipette held just above the surface of the sample.
- Then carefully stoppered and inverted several times to dissolve the flock.
- Titration was needed to be started immediately after the transformation of contents to Erlenmeyer flask.
- The burette was rinsed and then filled with sodium thiosulphate.
- 203 ml of the solution from the bottle was measured out and transferred to an Erlenmeyer flask.
- Titration of the solution was done with standard sodium thiosulphate solution until the yellow color of liberated Iodine is almost faded out. (Pale yellow color)
- 1 ml of starch solution was added and the titration continued until the blue color disappears to colorless.
- The volume of sodium thiosulphate solution added for titration was noted down, which gave the DO in mg/L. Titration was repeated for concordant values.

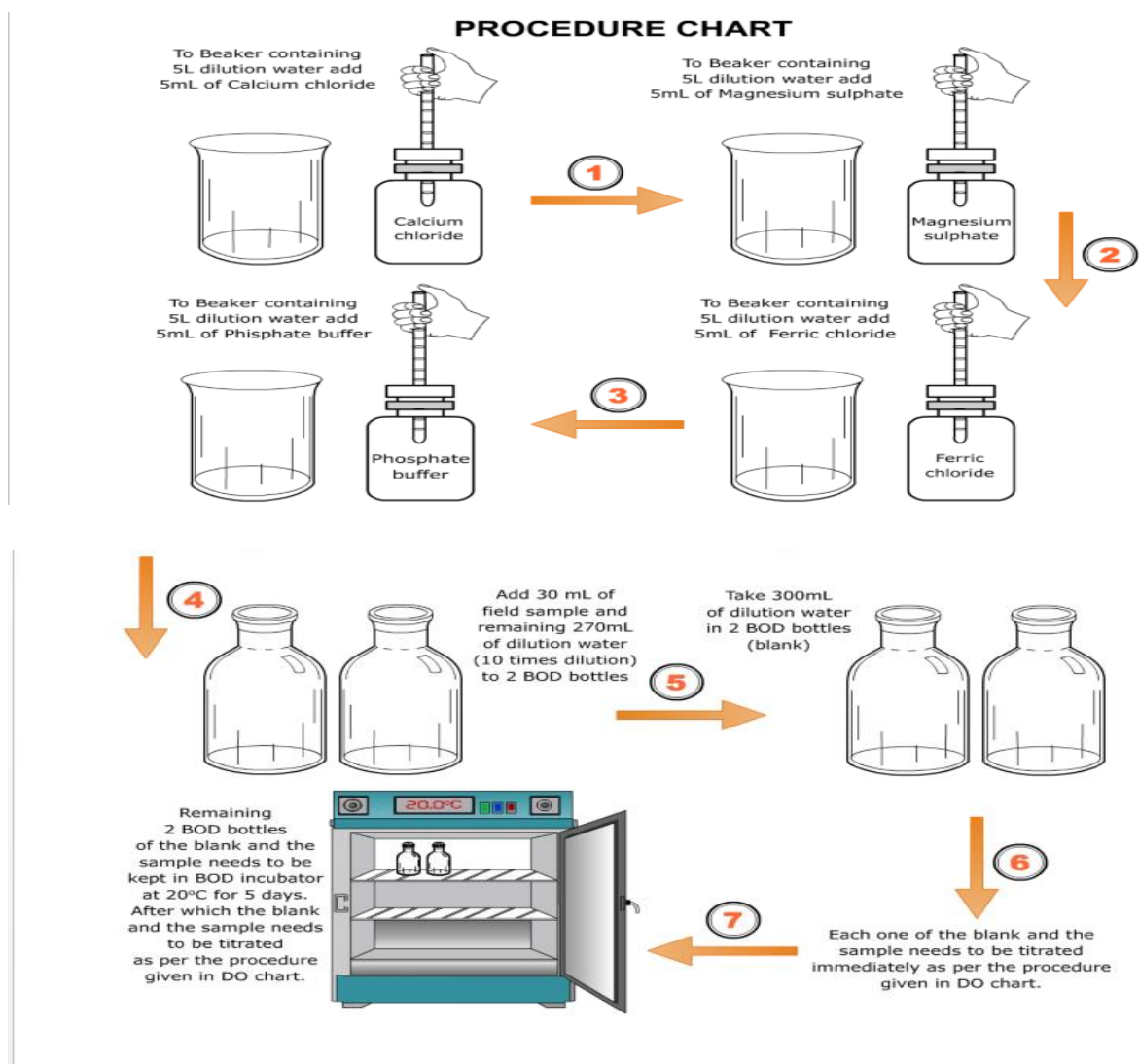


Figure 3.7: Procedure Chart for determination of DO and BOD

3.9. Determination of COD:

Test Method: IS: 3025 (Part-58) – Reaffirmed 2006

Principle:

The organic matter present in sample gets oxidized completely by potassium dichromate ($K_2Cr_2O_7$) in the presence of sulphuric acid (H_2SO_4), silver sulphate (Ag_2SO_4) and mercury sulphate ($HgSO_4$) to produce CO_2 and H_2O . The sample is refluxed with a known amount of potassium dichromate ($K_2Cr_2O_7$) in the sulphuric acid medium and the excess potassium dichromate ($K_2Cr_2O_7$) is determined by titration against ferrous ammonium sulphate, using ferroin as an indicator. The dichromate consumed by the sample is equivalent to the amount of O_2 required to oxidize the organic matter.

Test Procedure: (For determination of COD)

- Three COD vials with stopper (two for the sample and one for the blank) were taken.
- 2.5 ml of the sample was added to each of the two COD vials and the remaining COD vial was for blank; to this COD vial distilled water was added.
- 1.5 ml of potassium dichromate reagent was added for the digestion of solution to each of the three COD vials.
- 3.5 ml of sulphuric acid reagent was added and the solution was catalyzed in the same manner.
- CAUTION: COD vials were hot on that condition.
- Caps of the tubes were closed tightly. The COD Digester was switched on and the machine was set at $150^\circ C$ temperature for 2 hours.
- The COD vials were placed into a block digester at $150^\circ C$ and heated for two hours.
- When the digester automatically switched off, then the vials were removed and it was allowed to cool to the room temperature.
- Meanwhile, the burette was prepared by clamping it with the burette stand for the titration.
- The burette was filled with the ferrous ammonium sulphate solution, adjusted to zero.
- The contents of the blank vial were transferred to conical flask.
- Few drops of ferroin indicator were added and the solution became bluish green in color.
- Titration of the solution was started with the ferrous ammonium sulphate taken in the burette.
- End point of the titration was the appearance of the reddish brown color.
- The volume of ferrous ammonium sulphate solution added for the blank (A) was noted down.
- The contents of the sample vial were transferred to conical flask.
- Few drops of ferroin indicator were added and the solution became green in color.
- It was titrated with the ferrous ammonium sulphate taken in the burette.
- End point of the titration was the appearance of the reddish brown color.

- The volume of ferrous ammonium sulphate solution added for the sample (B) was noted down.

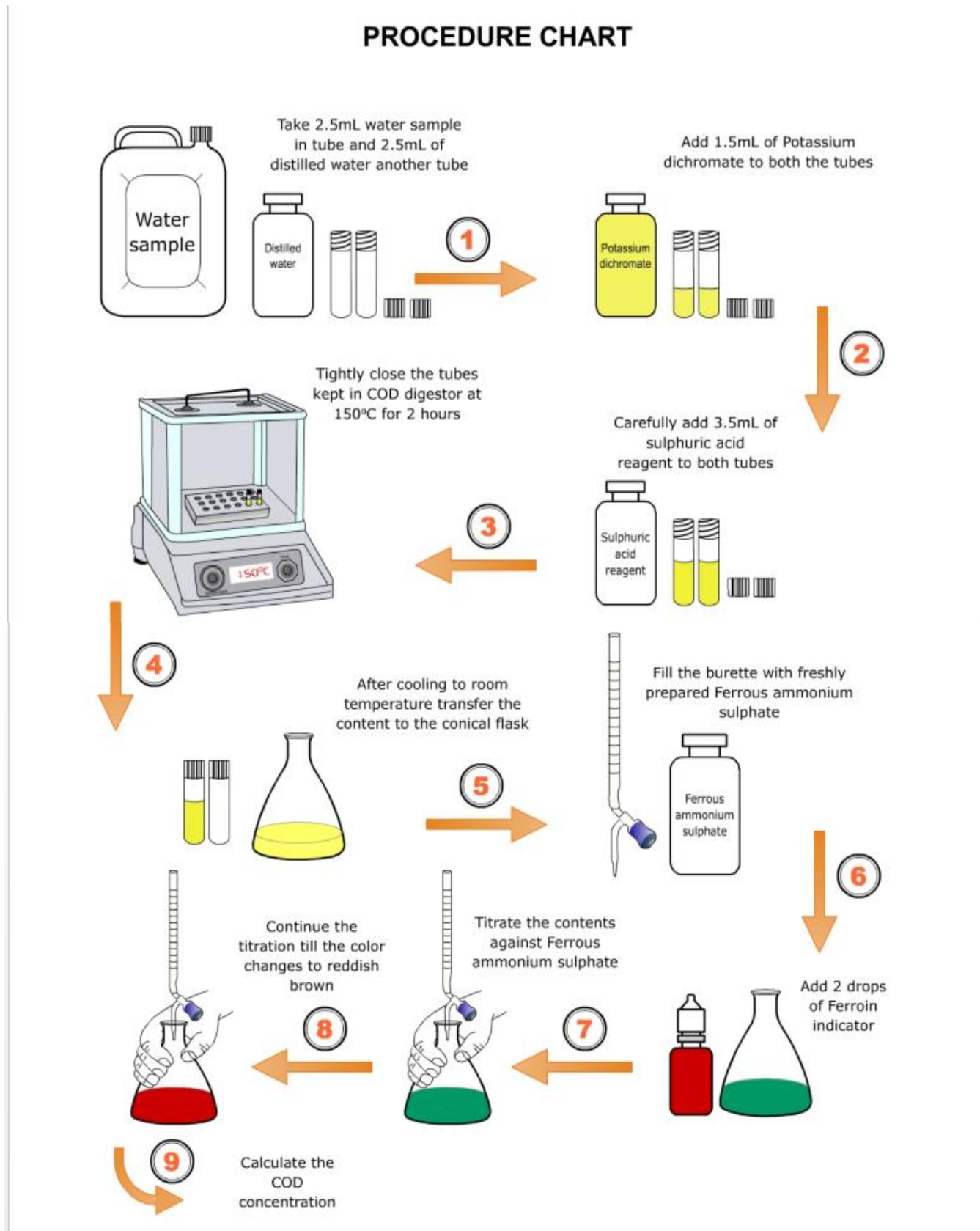


Figure 3.8: Procedure Chart for determination of COD

CHAPTER 04
DISCUSSION OF RESULTS

CHAPTER 04

DISCUSSION OF RESULTS

4.1 DO values of waste water under light and dark condition after dyeing and dyeing-fixing with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes

4.1.1 DO values of waste water under light and dark condition after dyeing with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes

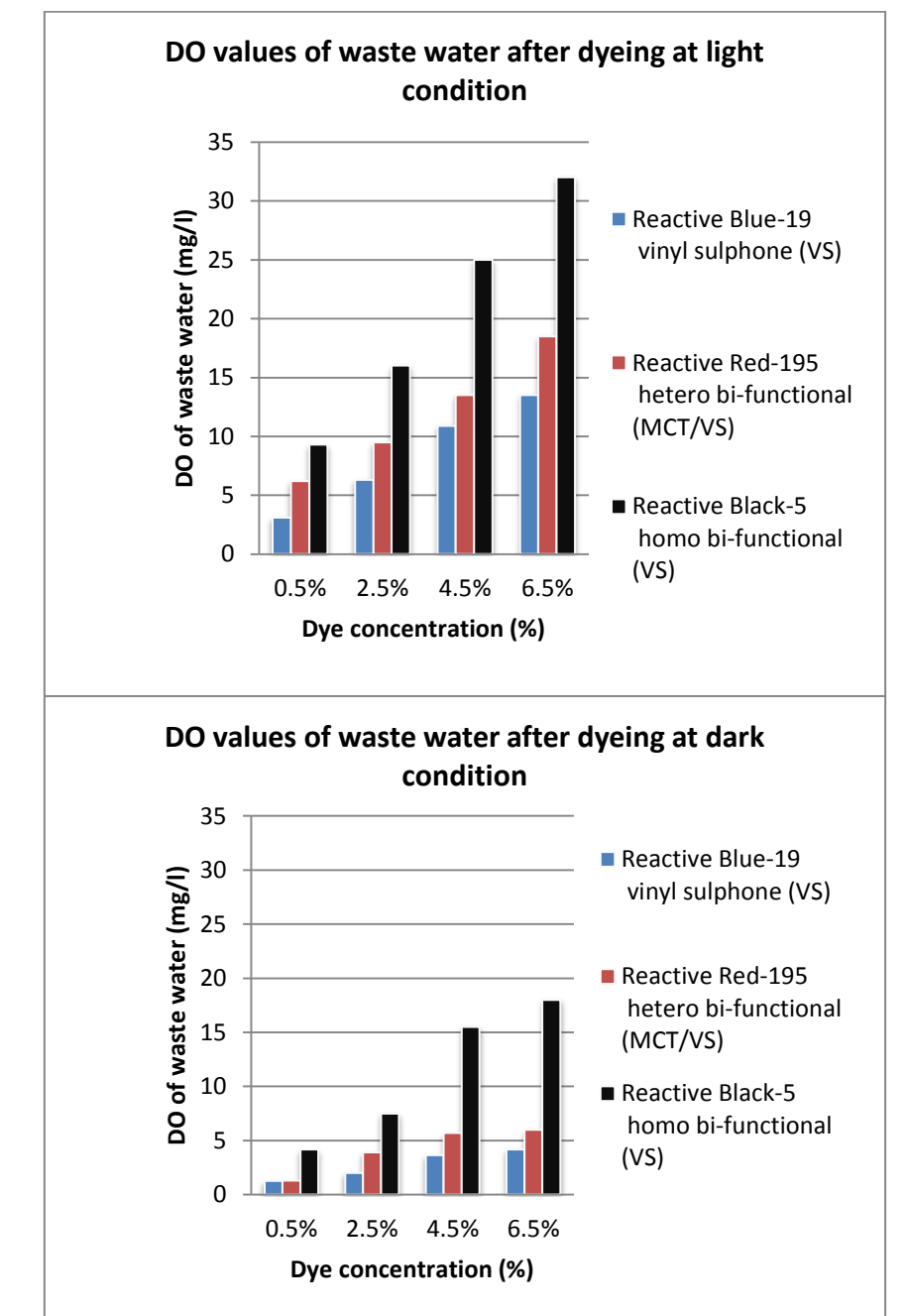


Figure 4.1: Bar diagrams represent DO values of waste water under light and dark condition after dyeing with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes.

Figure stipulated above represents DO values of waste water only after dyeing for 0.5%, 2.5%, 4.5% and 6.5% shade under two conditions, light and dark stage.

For all shade %, DO values of waste water at light are found to be greater than DO values in dark condition. This occurs due to the growth of micro-organisms in waste water on dark stage after preserving at 5 day time, which mainly soak up the oxygen in this long period of time and causes decrease in dissolve oxygen at dark.

For all conditions light and dark, DO values of solutions of deep shade and medium shade is found to be greater than DO values of light shade respectively. This occurs because after dyeing the concentrations of liquor of light, medium and deep shade remaining concentrated condition correspondingly. The main reason is the liquor of the deep shade solution became more concentrated than the medium or light shade solution for containing extremely large amount of salt, alkali, hydrolyzed and unfixed dye molecules and vice-versa.

In the figure, homo-bi functional (VS) Reactive Black-5 of 6.5% shade shows the highest DO values among all dyes in where vinyl sulphone (VS) Reactive Blue-19 of 0.5% shows the lowest values among all light, medium and deep conditions and values of hetero-bi functional (MCT/VS) Reactive Red-195 remain in between for all shade%. Reactive Blue-19 and Reactive Red-195 in the line diagram show close DO values in case of 0.5% shade at dark stage.

4.1.2 DO values of waste water under light and dark condition after dyeing-fixing with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes

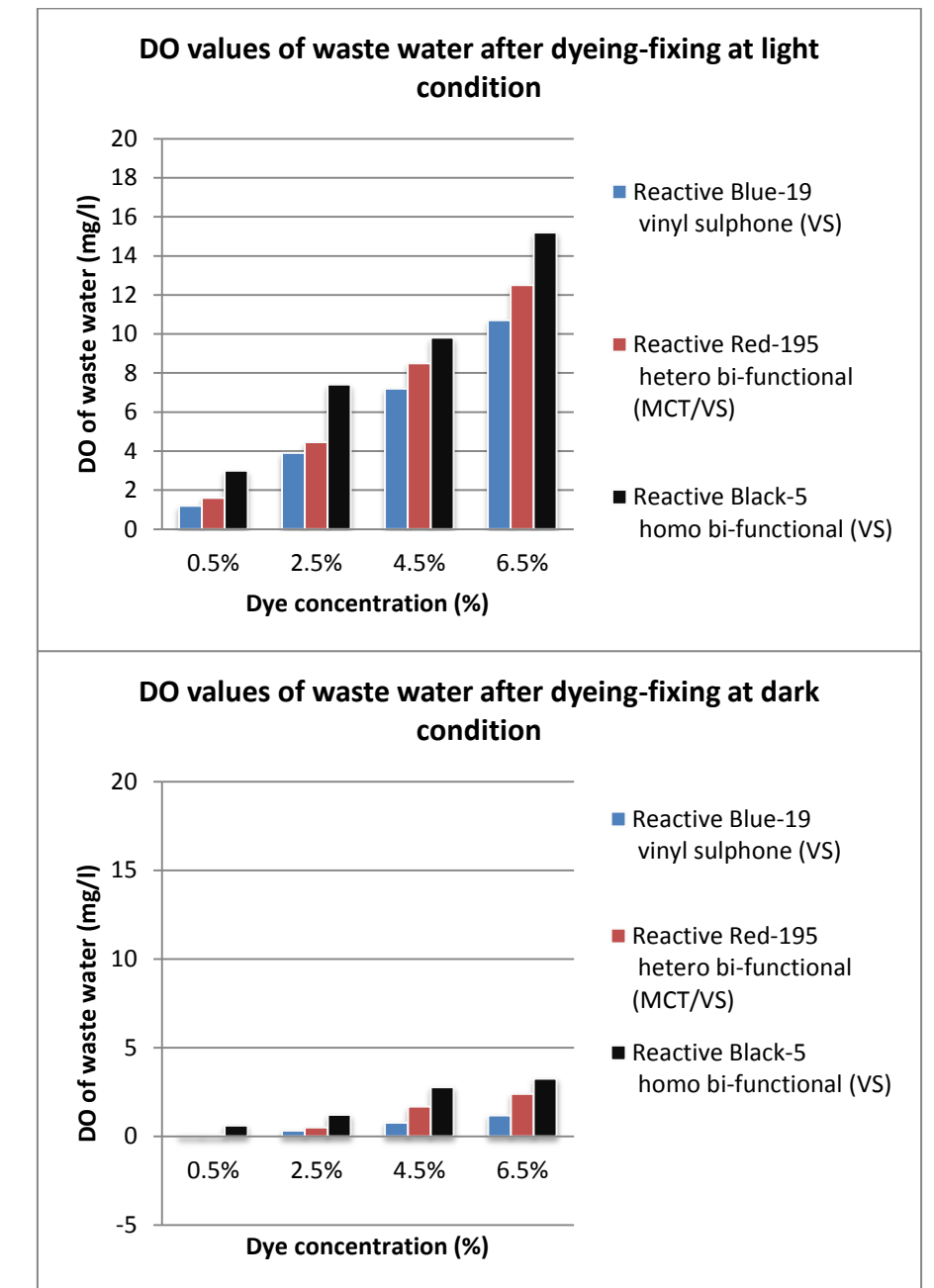


Figure 4.2: Bar diagrams represent DO values of waste water under light and dark condition after dyeing-fixing with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes.

The figure stipulated above represents DO values of solutions only after dyeing-fixing for the different range of shade percentage approximating light, medium and deep shade percentage under two conditions, light and dark stage.

For all shade %, DO values of waste water at light are found to be greater than DO values in dark condition. At dark stage, this occurs because after 5 day time present oxygen in waste water mainly soaks up by the growth of micro-organisms and causes decrease in dissolve oxygen in waste water.

Again for both conditions light and dark, DO values of solutions of deep shade and medium shade is found to be greater than DO values of light shade correspondingly. Though after fixing the liquor become more diluted than after dyeing but in terms of shade percentage, again the concentrations of liquor of light, medium and deep shade remaining respectively on concentrated condition. The main reason is the liquor of the deep shade solution became more concentrated than the medium or light shade solution for containing comparatively gigantic amount of hydrolyzed and unfixed dye molecules and vice-versa.

In the figure, homo-bi functional (VS) Reactive Black-5 of 6.5% shade shows the highest DO values among all dyes in where vinyl sulphone (VS) Reactive Blue-19 of 0.5% shows the lowest values among all light, medium and deep conditions. Reactive Blue-19 and Reactive Red-195 in the line diagram show close DO values in case of 0.5% and 2.5% shade at dark stage.

4.2. BOD values of waste water generated after dyeing and dyeing-fixing stages with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes

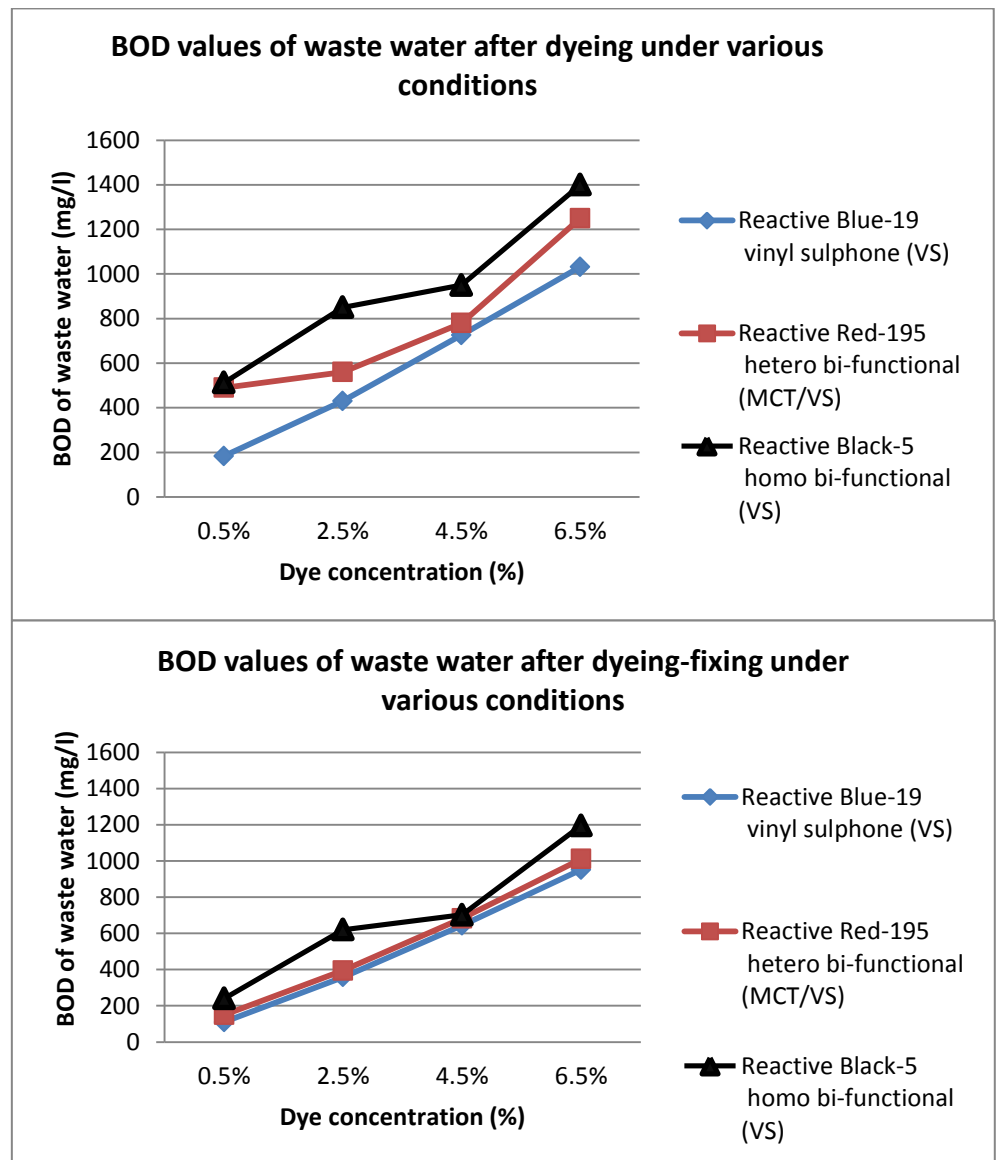


Figure 4.3: Line diagrams represent BOD values of waste water generated after dyeing and dyeing-fixing stages with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes.

The figure mounted above represents BOD values of waste water generated after dyeing and dyeing-fixing stages for the different range of shade percentage approximating light, medium and deep shade percentage under different conditions.

For both dyeing and dyeing-fixing conditions, BOD values of deep shade and medium shade is found to be greater than BOD values of light shade respectively.

For dyeing, BOD values of deep shade and medium shade is found to be greater than BOD values of light shade respectively. During dyeing the heavily concentrated waste water are produced by reacting the fibers with a mixture of reactive dyestuffs, salt and auxiliary chemicals. This occurs in case of dyeing, because after dyeing the concentrations of waste water of light, medium and deep shade remaining concentrated condition correspondingly for containing gigantic amount of chemicals including hydrolyzed dyes and vice-versa.

In the figure waste water after dyeing under various conditions, homo-bi functional (VS) Reactive Black-5 of 6.5% shade shows the highest BOD values among all dyes in where vinyl sulphone (VS) Reactive Blue-19 of 0.5% shows the lowest values among all light medium and deep conditions. In the line diagram, BOD values of hetero-bi functional (MCT/VS) Reactive Red-195 remain in between the values of Reactive Black-5 and Reactive Red-195 where Reactive Blue-19 and Reactive Red-195 shows closest values at 4.5% shade.

For dyeing-fixing, again BOD values of deep shade and medium shade is found to be greater than BOD values of light shade respectively. From dyeing to after-treatment stages the concentration of waste water decreases. So, the concentration of waste water after dyeing-fixing stage becomes comparatively diluted than the concentration of waste water after dyeing stage. Though after dyeing-fixing the liquor become more diluted than after dyeing but in terms of shade percentage, again concentrations of waste water of light, medium and deep shade remaining respectively on concentrated condition. The main reason is the liquor of the deep shade solution became more concentrated than the medium or light shade solution for containing extremely large amount of unfixed hydrolyzed dye molecules here and vice-versa.

In the figure waste water after dyeing-fixing under various conditions, homo-bi functional (VS) Reactive Black-5 of 6.5% shade shows the highest BOD values among all dyes in where vinyl sulphone (VS) Reactive Blue-19 of 0.5% shows the lowest values among all light , medium and deep conditions. Reactive Blue-19 and hetero-bi functional (MCT/VS) Reactive Red-195 in the line diagram show closer BOD values for all shade % only after dyeing-fixing state.

4.3. COD values of waste water generated after dyeing and dyeing-fixing stages with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes

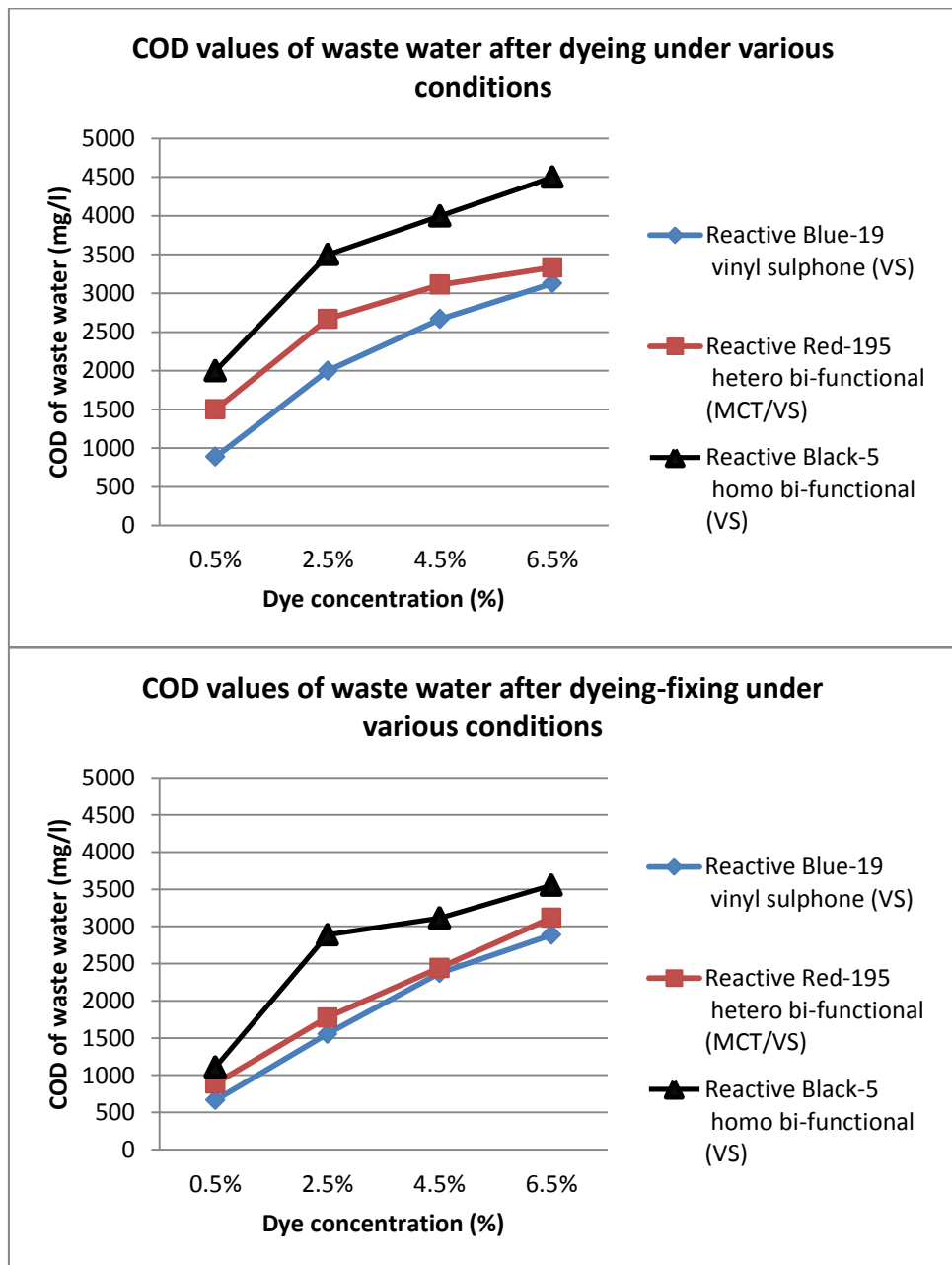


Figure 4.4: Line diagrams represent COD values of waste water generated after dyeing and dyeing-fixing stages with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes.

The figure above represents COD values of solutions after dyeing and dyeing-fixing for the different range of shade percentage like light, medium and deep shade percentage under different conditions.

For both dyeing and dyeing-fixing conditions, COD values of deep shade and medium shade is found to be greater than COD values of light shade respectively.

During dyeing the heavily concentrated waste water are produced by reacting the fibers with a mixture of reactive dyestuffs, salt and auxiliary chemicals. For dyeing, COD values of deep shade and medium shade is found to be greater than COD values of light shade respectively. This occurs in case of dyeing, because after dyeing the concentrations of waste water of light, medium and deep shade remaining concentrated condition correspondingly for containing gigantic amount of chemicals including hydrolyzed dyes and vice-versa.

In the figure waste water after dyeing under various conditions, homo-bi functional (VS) Reactive Black-5 of 6.5% shade shows the highest COD values among all dyes in where vinyl sulphone (VS) Reactive Blue-19 of 0.5% shows the lowest values among all light medium and deep conditions. In the line diagram, COD values of hetero-bi functional (MCT/VS) Reactive Red-195 remain in between the values of Reactive Black-5 and Reactive Red-195 where Reactive Blue-19 and Reactive Red-195 shows closest values at 6.5% shade.

From dyeing to after-treatment stages the concentration of waste water decreases. So, the concentration of waste water after dyeing-fixing stage becomes comparatively diluted than the concentration of waste water after dyeing stage. But for dyeing-fixing stages again, COD values of deep shade and medium shade is found to be greater than COD values of light shade respectively. Though after dyeing-fixing the liquor become more diluted than after dyeing but in terms of shade percentage, again concentrations of waste water of light, medium and deep shade remaining respectively on concentrated condition. The main reason is the liquor of the deep shade solution became more concentrated than the medium or light shade solution for containing extremely large amount of unfixed hydrolyzed dye molecules here and vice-versa.

In the figure waste water after dyeing-fixing under various conditions, homo-bi functional (VS) Reactive Black-5 of 6.5% shade shows the highest COD values among all dyes in where vinyl sulphone (VS) Reactive Blue-19 of 0.5% shows the lowest values among all light medium and deep conditions. Reactive Blue-19 and hetero-bi functional (MCT/VS) Reactive Red-195 in the line diagram show closer values for all shade % only after dyeing-fixing state.

4.4. pH values of waste water generated after dyeing and dyeing-fixing stages with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes

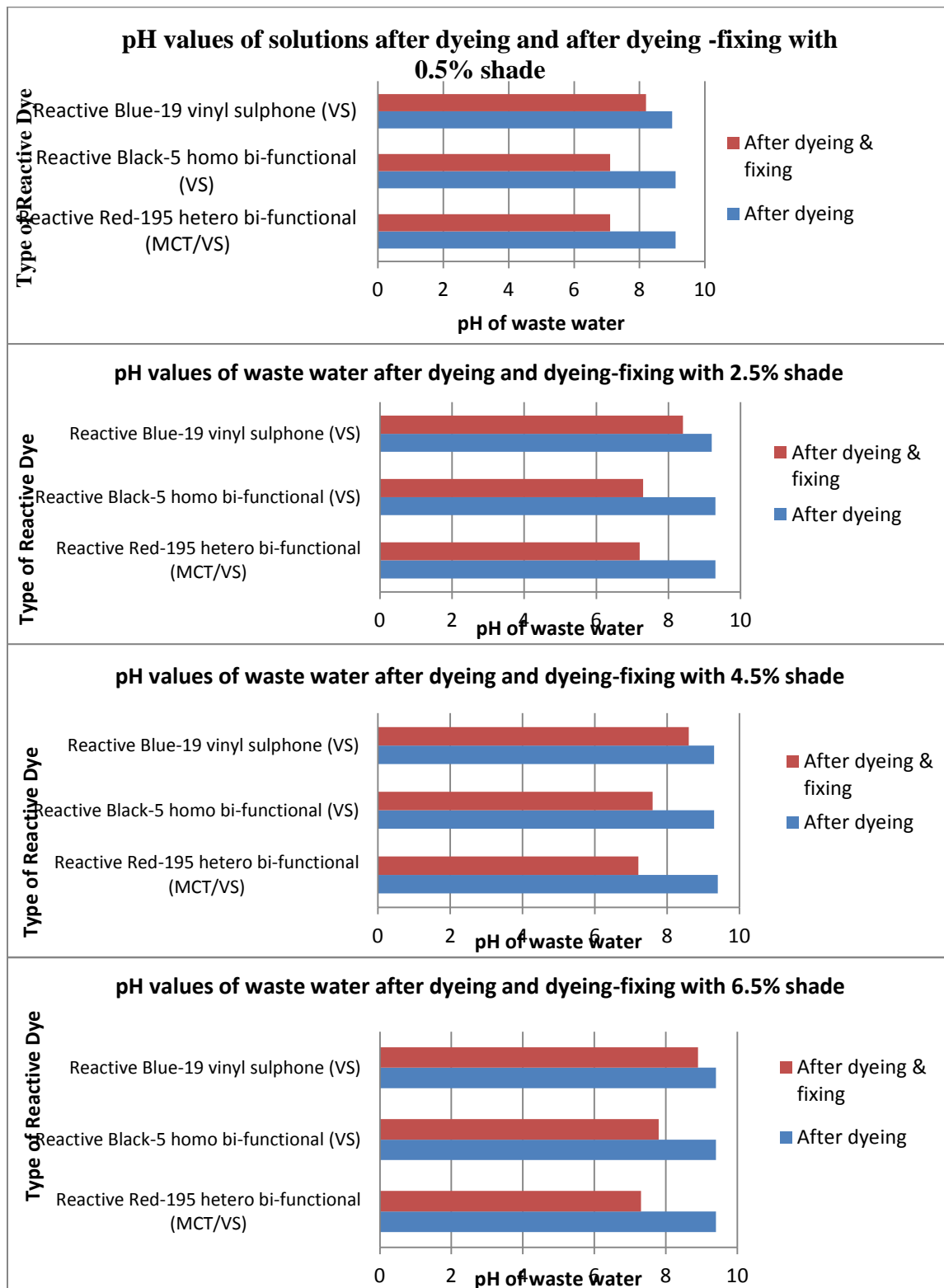


Figure 4.5: Bar diagrams represent pH values of waste water generated after dyeing and dyeing-fixing stages with 0.5%, 2.5%, 4.5% and 6.5% shades of reactive dyes.

Bar diagram represents pH values of solutions after dyeing and after dyeing- fixing with 0.5%, 2.5%, 4.5% and 6.5% shade of reactive dyes. For all type of shade% like light, medium and dark shade pH values of solution after dyeing (include basic alkali fixing) is found to be greater than pH values of the solutions after dyeing-fixing (include after-treatment with additional fixing with fixing agent). This mainly occurs because after dye bath fixation a huge amount of alkali is absorbed by the dye and fiber to make the strong dye-fiber co-valent bond in case of reactive dyeing. Moreover, after dyeing-fixing state the value of pH again decrease as the final solution contain the chemicals of acid neutralization, soaping and additional fixing with fixing agent.

CHAPTER 05
CONCLUSION

CHAPTER 05

CONCLUSION

This research work has been conducted to measure the environmental parameters (DO, BOD, COD and pH) of waste water after dyeing of cotton materials under various conditions with reactive dyes having three different chemical structures. Those environmental parameters of waste water are assessed after dyeing and after dyeing-fixing stage to observe any change in characteristics of textile effluent generated. Following observations are found after the investigation:

- ✚ DO, BOD and COD values of solutions after dyeing are found to be greater than the values of solutions after dyeing-fixing for three dye structures and four dye concentrations. Besides, pH values of solutions after the dyeing are found to be more than that of solutions after dyeing-fixing (after-treatment with cat-ionic dye fixing agent).
- ✚ Dyeing with hetero and homo bi-functional reactive dyes (MCT/VS and VS/VS) discharge the effluent with higher DO, BOD and COD values while compare to mono functional reactive dye (VS). Waste water with greatest and lowest DO, BOD and COD are found from the homo bi-functional (VS/VS) Reactive Black-5 and mono functional (VS) Reactive Blue-19 respectively for all dye concentrations. Besides, dyeing of cotton with hetero bi-functional (MCT/VS) Reactive Red-195 delivered effluent where DO, BOD and COD values remain on the values between Reactive Black-5 and Reactive Blue-19 for all conditions.
- ✚ Among four dye concentrations (0.5%, 2.5%, 4.5% and 6.5 %), 6.5% is found to be responsible for generating waste water having greatest DO, BOD and COD values. With the increase in dye concentration, corresponding values of DO, BOD and COD in waste water are also increased. So, dyeing of textiles with light shade % has little chances for environment pollution and vice-versa. Less DO indicates more oxygen demand (BOD and COD) of waste water which in combine with natural water bodies create hindrance for sustainable leaving of water leaving biological substances.

Those observations from the research work give a detailed indication to the readers about the impacts of textile coloration with different structures of reactive dyes and various dye concentrations on the sustainable environment. So, this research report will be essential for the dye house people to select suitable dyes in terms of environmental aspect and understand the characteristics of textile effluent at various conditions.

REFERENCES

- [1] Errol Fernandes, Navnath Pingale and V.R. Sai Ganesh, "Hot Dyeing Reactive Dyes", Dystar India, Page-27, April 2011.
- [2] Sushama Saha, Report on "Effect of soaping agent and fixing agent on the color fastness to wash of the reactive dyed cotton fabrics", Page-06, 2011.
- [3] Asim Kumar Roy Chowdhury, Textile Preparation and Dyeing, Oxford & IBH Publishing co. Pvt. Ltd. New Delhi, ISBN 81-204-1701-1, Page 514, 2006.
- [4] "Textile Effects Take Care", HUNTSMAN, The Dhaka Water Catastrophe 2020, SDC, Society of dyers and Colorists, Bangladesh, Page-01, April 2011.
- [5] <http://www.cotton.missouri.edu/Cellulose-Chemical-Composition.htm> (Retrieved on 04 March 2014, 11.00 am).
- [6] <http://textilebe-dyeing.blogspot.com/2011/01/effect-of-ph-on-cotton-dyeing-with.html> (Retrieved on 04 March 2014, 11.13 am).
- [7] Mohammad Mahbubul Alam, A Hand book of Dyeing Technology, Books Fair Publications, Page-35, October 2008.
- [8] [<http://www.chm.bris.ac.uk/webprojects2002/price/reactive.htm>] (Retrieved on 11 September, 07.18 pm).
- [9] Arthur D Broadbent, Basic principles of Textile Colorations, Society of Dyers and Colourists, ISBN 0901956767, Page-335, 2010.
- [10] http://en.wikipedia.org/wiki/Reactive_dye (Retrieved on 11 September, 07.18 pm).
- [11] Mohammad Mahbubul Alam, A Hand book of Dyeing Technology, Books Fair Publications, Page-42, October 2008.
- [12] Asim Kumar Roy Chowdhury, Textile Preparation and Dyeing, Oxford & IBH Publishing co. Pvt. Ltd. New Delhi, ISBN 81-204-1701-1, Page 533, Month 2006.
- [13] Mohammad Mahbubul Alam, A Hand book of Dyeing Technology, Books Fair Publications, Page-43, October 2008.
- [14] Arthur D Broadbent, Basic principles of Textile Colorations, Society of Dyers and Colourists, ISBN 0901956767, Page-340, 2010.
- [15] Mohammad Mahbubul Alam, A Hand book of Dyeing Technology, Books Fair Publications, Page-36, October 2008.
- [16] Mohammad Mahbubul Alam, A Hand book of Dyeing Technology, Books Fair Publications, Page-33, October 2008.

- [17] <http://textilefire.blogspot.com/2012/08/hydrolysis-of-reactive-dye-prevention.html>
(Retrieved on 6 December 2014, 2.00 am)
- [18] <http://www.scribd.com/doc/245991547/Bifunctional-Reactive-Dyes> (Retrieved on 06 December 2014, 02.26 am)
- [19] Mohammad Mahbubul Alam, A Hand book of Dyeing Technology, Books Fair Publications, Page-58, October 2008.
- [20] Asim Kumar Roy Chowdhury, Textile Preparation and Dyeing, Oxford & IBH Publishing co. Pvt. Ltd. New Delhi, ISBN 81-204-1701-1, Page 528, Month 2006.
- [21] Mohammad Mahbubul Alam, A Hand book of Dyeing Technology, Books Fair Publications, Page-57, October 2008.
- [22] <http://www.scribd.com/doc/245991547/Bifunctional-Reactive-Dyes> (Retrieved on 6 December 2014, 02.26 am)
- [23] Arthur D Broadbent, Basic principles of Textile Colorations, Society of Dyers and Colourists, ISBN 0901956767, Page-348, 2010.
- [24] Mohammad Mahbubul Alam, A Hand book of Dyeing Technology, Books Fair Publications, Page-55, October 2008.
- [25] Mohammad Mahbubul Alam, A Hand book of Dyeing Technology, Books Fair Publications, Page-54, October 2008.
- [26] Sushama Saha, Report on “Effect of soaping agent and fixing agent on the color fastness to wash of the reactive dyed cotton fabrics”, Page-16, 2011.
- [27] Mohammad Mahbubul Alam, A Hand book of Dyeing Technology, Books Fair Publications, Page-60, October 2008.
- [28] Mohammad Mahbubul Alam, A Hand book of Dyeing Technology, Books Fair Publications, Page-63, October 2008.
- [29] Asim Kumar Roy Chowdhury, Textile Preparation and Dyeing, Oxford & IBH Publishing co. Pvt. Ltd. New Delhi, ISBN 81-204-1701-1, Page 514, Month 2006.
- [30] Arthur D Broadbent, Basic principles of Textile Colorations, Society of Dyers and Colourists, ISBN 0 901956 76 7, Page-338, 2010.
- [31] Rajendra Sanap, "Role of washing-off agents in textile wet-processing", Bangladesh Textile Today, ISSN 1999-2076, Page-27, January-February 2011.
- [32] Sushama Saha, Report on “Effect of soaping agent and fixing agent on the color fastness to wash of the reactive dyed cotton fabrics”, Page 19-21, 2011.
- [33] Report on” Study on Chemicals Consumption and Operational Cost of Textile ETP Plants”

- [34] http://www.chemicalbook.com/ProductChemicalPropertiesCB4241898_EN.htm
(Retrieved on 06 July 2014, 11.45 pm).
- [35] Arthur D Broadbent, Basic principles of Textile Colorations, Society of Dyers and Colorists, ISBN 0901956767, Page-347, 2010.
- [36] <http://www.worlddyevariety.com/reactive-dyes/reactive-black-5.html> (Retrieved on 08 July 2014, 02.00 am).
- [37] http://www.chemicalbook.com/ProductChemicalPropertiesCB5413212_EN.htm
(Retrieved on 06 July 2014, 11.45 pm).
- [38] <http://www.chemicalbook.com/Search.aspx?keyword=reactive%20blue%2019>
(Retrieved on 06 July 2014, 11.45 pm).

APPENDIX-A

(DO and BOD values of solutions treated under different conditions)

Table A1: DO and BOD values of solutions after dyeing and after dyeing-fixing with 0.5%, 2.5%, 4.5% and 6.5% shade of Reactive dyes.

Reactive Dyes	Shade%	DO and BOD values of solutions after dyeing			DO and BOD values of solutions after dyeing-fixing		
		DO _i (mg/l)	DO _f (mg/l)	BOD (mg/l)	DO _i (mg/l)	DO _f (mg/l)	BOD (mg/l)
Reactive Red-195 hetero bi-functional (MCT/VS)	0.5%	6.2	1.3	490.0	1.6	0.1	150.0
	2.5%	9.5	3.9	560.0	4.45	0.5	395.0
	4.5%	13.5	5.7	780.0	8.5	1.67	683.0
	6.5%	18.5	6.0	1250.0	12.5	2.39	1011.0
Reactive Black-5 homo bi-functional (VS)	0.5%	9.3	4.17	513.0	3.0	0.6	240.0
	2.5%	16.0	7.5	850.0	7.4	1.2	620.0
	4.5%	25.0	15.5	950.0	9.8	2.77	703.0
	6.5%	32.0	18.0	1400.0	15.2	3.24	1196.0
Reactive Blue-19 vinyl sulphone (VS)	0.5%	3.1	1.27	183.0	1.2	0.1	110.0
	2.5%	6.3	2.0	430.0	3.9	0.31	359.0
	4.5%	10.9	3.64	726.0	7.2	0.76	644.0
	6.5%	14.5	4.18	1032.0	10.7	1.18	952.0

APPENDIX-B

(COD and pH values of solutions treated under different conditions)

Table B1: COD and pH values of solutions after dyeing and after dyeing-fixing with 0.5%, 2.5%, 4.5% and 6.5% shade of Reactive dyes.

Reactive Dyes	Shade %	COD Values of solution		pH Values of solution	
		After dyeing (mg/l)	After dyeing-fixing (mg/l)	After dyeing (mg/l)	After dyeing-fixing (mg/l)
Reactive Red-195 hetero bi-functional (MCT/VS)	0.5%	1499.0	0889.0	9.1	7.1
	2.5%	2669.0	1777.0	9.3	7.2
	4.5%	3111.0	2444.0	9.4	7.2
	6.5%	3333.0	3117.0	9.4	7.3
Reactive Black-5 homo bi-functional (VS)	0.5%	1999.0	1111.0	9.1	7.1
	2.5%	3499.0	2888.0	9.3	7.3
	4.5%	3999.0	3114.0	9.3	7.6
	6.5%	4498.0	3555.0	9.4	7.8
Reactive Blue-19 vinyl sulphone (VS)	0.5%	0889.0	0667.0	9.0	8.2
	2.5%	1999.0	1556.0	9.2	8.4
	4.5%	2666.0	2374.0	9.3	8.6
	6.5%	3127.0	2889.0	9.4	8.9