

**REMOVAL OF COD AND COLOUR FROM  
TEXTILE WASTEWATER USING LIMESTONE  
AND ACTIVATED CARBON**

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**REMOVAL OF COD AND COLOUR FROM TEXTILE WASTEWATER USING  
LIMESTONE AND ACTIVATED CARBON**

**by**

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## TABLE OF CONTENTS

	Page
<b>ACKNOWLEDGEMENTS</b>	ii
<b>TABLE OF CONTENTS</b>	iii
<b>LIST OF TABLES</b>	vii
<b>LIST OF FIGURES</b>	viii
<b>LIST OF PLATES</b>	xi
<b>LIST OF ABBREVIATION</b>	xi
<b>LIST OF APPENDICES</b>	xii
<b>ABSTRAK</b>	xv
<b>ABSTRACT</b>	xvii

### CHAPTER ONE : INTRODUCTION

1.1	Background	1
1.2	Problem Statement	2
1.3	Objectives of Research	5
1.4	Scope of Research	6

### CHAPTER TWO : PROCESS DESCRIPTION AND SOURCES

2.1	Process description	8
	2.1.1 Manufacturing of Polyester Fiber	8
	2.1.2 Spinning	9
	2.1.3 Weaving	9
	2.1.4 Pretreatment of Fabric for Dyeing and Finishing	10
	2.1.5 Dyeing	11
	2.1.6 Printing	12
	2.1.7 Finishing	13
2.2	Sources of Pollution	14

## **CHAPTER THREE : LITERATURE REVIEW**

3.1	Wastewater from Textile Industry	17
3.2	Textile Wastewater, Characteristics and Environmental Impact	18
3.3	Treatment of Textile Wastewater	21
	3.3.1 Biological Method	22
	3.3.2 Chemical Method	23
	3.3.3 Physical Method	24
3.4	Adsorption Process	25
	3.4.1 Equilibriums of Adsorption Process	27
	3.4.2 Factors Affecting Adsorption	29
	3.4.2.1 Effect of Contact Time	29
	3.4.2.2 Effect of pH	29
	3.4.2.3 Effect of Adsorbent Dosage	31
	3.4.2.4 Effect of Initial Concentration	33
	3.4.2.5 Effect of Different Adsorbents	33
3.5	Kinetics of Adsorption Process	34
	3.5.1 Pseudo-First-Order Kinetic Model	35
	3.5.2 Pseudo-Second-Order Kinetic Model	35
	3.5.3 Intra Particle Diffusion	36
3.6	Activated Carbon	37
3.7	Limestone	40

## **CHAPTER FOUR : MATERIALS AND METHODS**

4.1	Introduction	44
4.2	Characterization of Adsorbents	44
	4.2.1 Limestone	44
	4.2.1.1 Bulk Density	45
	4.2.1.2 Chemical Composition	45
	4.2.2 Activated Carbon	46
4.3	Wastewater Sampling	46

4.3.1	Wastewater Analysis	49
4.3.1.1	pH	50
4.3.2.1	COD, Colour and SS	51
4.4	Experimental Work	51
4.4.1	Batch Study	52
4.4.1.1	Optimum Mixture Ratio LS:AC	53
4.4.1.2	Effect of Shaking Time	55
4.4.1.3	Effect of Settling Time	56
4.4.1.4	Effect of Shaking Speed	56
4.4.1.5	Effect of Adsorbent Dosage	57
4.4.1.6	Effect of Initial Wastewater Concentration	58
4.4.1.7	Effect of Particle Size	59
4.4.1.8	Effect of pH	59
4.4.1.9	Adsorption Isotherms Study	60
4.4.1.10	Adsorption Kinetics	62
4.4.1.10 (a)	Pseudo-First-order Kinetic	62
4.4.1.10 (b)	Pseudo-Second-order Kinetic	63
4.4.1.10 (c)	Intra Particle Diffusion	64
4.4.2	Column Study	64

## **CHAPTER FIVE: RESULTS AND DISCUSSION**

5.0	Introduction	68
5.1	Properties of Media	68
5.2	Characteristics of Wastewater	69
5.3	Optimum Mixture Ratio (LS:AC)	70
5.4	Effect of Shaking Time	72
5.5	Effect of Settling Time	73
5.6	Effect of Shaking Speed	74
5.7	Effect of Adsorbent Dosage	76
5.8	Effect of Initial pH	77
5.9	Effect of Initial Concentration	79
5.10	Effect of Particle Size	80

5.11	Adsorption Isotherm	82
5.12	Kinetic Study	89
5.12.1	Comparison of Pseudo-First-order, Pseudo-Second-order and Intra-particle Diffusion Models	89
5.13	Column Study	94
 <b>CHAPTER SIX: CONCLUSIONS AND RECOMENDATIONS</b>		
6.1	Conclusions	101
6.2	Recommendation for future research	103
 <b>REFERENCES</b>		104

## LIST OF TABLES

		Page
Table 4.1	Composition of limestone	45
Table 4.2	Properties of activated carbon	46
Table 4.3	Amount of limestone and activated carbon at the respective ratios	54
Table 4.4	Volume and weight of media for the effect of adsorbent dosage	58
Table 4.5	Volume and mass of media for Isotherm experiments	61
Table 4.6	Operational parameters for the column experiments	67
Table 5.1	Physical properties of limestone and activated carbon	69
Table 5.2	Physical properties of limestone and activated carbon	69
Table 5.3	Characteristics of wastewater sampled at effluent (March 2004-April 2006)	70
Table 5.4	COD removal at different pH	78
Table 5.5	Freundlich and Langmuir constants and correlation coefficient	88
Table 5.6	Adsorption kinetics: Pseudo-first-order & second-order and Intra-particle diffusion data for COD removal	94
Table 5.7	Result of bed capacity for the mixture of limestone and activated carbon at the mixing ratio of 35:5	100



## LIST OF FIGURES

		Page
Figure 2.1	Results of bed capacity for the mixture of limestone and activated carbon at the mixing ratio of 35:5	16
Figure 4.1	Mill manufacturing process flow	47
Figure 4.2	Mill wastewater treatment flow	48
Figure 4.3	Schematic diagram of column study	66
Figure 5.1	COD removal efficiency Vs. different ratios of LS:AC Conditions: Shaking time, 120 min; settling time, 90 min; shaking speed, 350 rpm (40:0 means 40 mL of limestone and 0 mL of activated carbon)	71
Figure 5.2	The effect of shaking time on COD removal Conditions: LS:AC, 35:5; settling time, 90 min; shaking speed, 350 rpm	73
Figure 5.3	The effect of settling time Vs. COD removal (%) Conditions: Ratio of LS:AC (35:5); shaking time, 60 min; shaking speed, 350 rpm	74
Figure 5.4	The effect of shaking speed on COD removal Conditions: Ratio of LS:AC (35:5); shaking time, 60 min; settling time, 60 min	75
Figure 5.5	The effect of adsorbent dosage Vs COD removal in percentage Conditions: Ratio of LS:AC, 35:5; shaking time, 60 min; settling time, 60 min; shaking speed, 250 rpm (35:5 means 35 mL limestone and 5 mL activated carbon)	76

Figure 5.6	The effect of initial pH Vs. COD removal (%) Conditions: Ratio of LS:AC, 35:5; shaking time, 60 min; settling time, 60 min; shaking speed, 250 rpm; (40:0 means 40 mL limestone and 0 mL activated carbon)	78
Figure 5.7	The effect of initial COD concentration Vs. COD removal (%) Conditions: Ratio of LS:AC, 35:5, shaking time, 60 min, settling time, 60 min; shaking speed, 250 rpm (40:0 means 40 mL limestone and 0 mL activated carbon)	79
Figure 5.8	The effect of particle size Vs. COD removal (%) Conditions: Shaking time, 60 min; Settling time, 60 min; Shaking speed, 250 rpm (40:0 means 40% limestone and 0% activated carbon)	81
Figure 5.9 (a)	Freundlich Isotherm for wastewater using the mixing ratio LS:AC (35:5)	83
Figure 5.9 (b)	Freundlich Isotherm for reactive yellow dye solution using mixing ratio of LS:AC (35:5)	84
Figure 5.9 (c)	Freundlich Isotherm for reactive red dye solution using mixing ratio of LS:AC (35:5)	84
Figure 5.9 (d)	Freundlich Isotherm for reactive black dye solution using mixing ratio of LS:AC (35:5)	85
Figure 5.10(a)	Langmuir Isotherm for wastewater using the mixing ratio of LS:AC (35:5)	86
Figure 5.10(b)	Langmuir Isotherm for reactive yellow dye solution using mixing ratio of LS:AC (35:5)	86
Figure 5.10(c)	Langmuir Isotherm for reactive red dye solution using mixing ratio of LS:AC (35:5)	87
Figure 5.10(d)	Langmuir Isotherm for reactive red dye solution using mixing ratio of LS:AC (35:5)	87

Figure 5.11(a)	Pseudo-first-order kinetic for wastewater (adsorption of COD at the mixing ratio of 35:5)	91
Figure 5.11(b)	Pseudo-first-order kinetic for reactive dyes (adsorption of COD at the mixing ratio of 35:5)	91
Figure 5.12(a)	Pseudo-second-order kinetic for wastewater (adsorption of COD at the mixing ratio of 35:5)	92
Figure 5.12(b)	Pseudo-second-order kinetic for wastewater (adsorption of COD at the mixing ratio of 35:5)	92
Figure 5.13(a)	Intra-particulate diffusion for wastewater (adsorption of COD at the mixing ratio of 35:5)	93
Figure 5.13(b)	Intra particulate diffusion for reactive dyes (adsorption of COD at the mixing ratio of 35:5)	93
Figure 5.14(a)	Breakthrough curves for COD removal using mixture ratio of limestone and activated carbon (35:5)	96
Figure 5.14(b)	Breakthrough curves for colour removal using mixture ratio of limestone and activated carbon (35:5)	96
Figure 5.15	Breakthrough curves for COD and Colour removal using limestone (40:0)	97
Figure 5.16	Breakthrough curves for COD and Colour removal using activated carbon (0:40)	98

## **LIST OF PLATES**

Plate 4.1	Sampling point	49
Plate 4.2	HACH pH meter (Sens ion1, USA)	50
Plate 4.3	HACH DR/2010 Spectrophotometer	51
Plate 4.4	Set up for column study	65

## **LIST OF ABBREVIATION**

1	NH <sub>4</sub> -N (Ammoniacal Nitrogen)
2	LS (Limestone)
3	AC (Activated Carbon)
4	COD (chemical Oxygen Demand)
5	BOD (Biological Oxygen Demand)
6	SS (Suspended Solids)

## LIST OF APPENDICES

### Appendix A

Table 1      Third Schedule Environmental Quality Act, 1974.      Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979

Table 2      Properties of activated carbon

Table 3      Mixture ratio of LS:GAC

### Appendix B

Table 4      Optimum mixture ratio for COD removal

Table 5      Effect of shaking time on COD removal.

Table 6      Effect of settling time on COD removal

Table 7      Effect of shaking speed on COD removal

### Appendix C

Table 8      Effect of particle size on COD removal

1. Particle Size 70-600 $\mu$ m
2. Particle Size 1.14-2.36mm
3. Particle Size 2.36-4.75mm

### Appendix D

Table 9      Effect of pH on COD removal at different ratios LS: AC

1. Effect of pH on COD removal at pH 2
2. Effect of pH on COD removal at pH 3
3. Effect of pH on COD removal at pH 4
4. Effect of pH on COD removal at pH 5
5. Effect of pH on COD removal at pH 6
6. Effect of pH on COD removal at pH 7
7. Effect of pH on COD removal at pH 8
8. Effect of pH on COD removal at pH 9

## Appendix E

Table 10	Effect of initial concentration on COD removal at different ratios of LS: AC
----------	--

1. Initial COD - 130 mg/L
2. Initial COD - 260 mg/L
3. Initial COD - 660 mg/L
4. Initial COD - 1260 mg/L

## Appendix F

Table 11	Effect of adsorbent dosage on COD removal
----------	---

## Appendix G

Table 12	Freundlich isotherm for COD removal
----------	-------------------------------------

1. Freundlich isotherm wastewater
2. Freundlich isotherm for reactive yellow 145
3. Freundlich isotherm for reactive red 195
4. Freundlich isotherm for reactive black 5

Table 13	Langmuir isotherm for COD removal
----------	-----------------------------------

1. Langmuir isotherm for wastewater
2. Langmuir isotherm for reactive yellow 145
3. Langmuir isotherm for reactive red 195
4. Langmuir isotherm for reactive black 5

## Appendix H

Table 14	Pseudo-first, second-orders and Intra particle diffusion for COD at LS:AC 35:5
----------	--

1. Pseudo-first, second-orders and Intra particle diffusion for wastewater
2. Pseudo-first, second-orders and Intra particle diffusion for reactive yellow 145
3. Pseudo-first, second-orders and Intra particle diffusion for reactive red 195
4. Pseudo-first, second-orders and Intra particle diffusion for reactive black 5

## Appendix I

### Table 15 Upflow Column using LS:AC 35:5

Effect of flowrate on COD and Colour removal at 20 mL/min

1. COD
2. Colour

## Appendix J

### Table 16 Upflow Column using LS:AC 35:5

Effect of flowrate on COD and Colour removal at 40 mL/min

1. COD
2. Colour

## Appendix K

### Table 17 Upflow Column using LS:AC 40:0

Effect of flowrate on COD and Colour removal at 20 mL/min

1. COD
2. Colour

## Appendix L

### Table 18 Upflow Column using LS:AC 0:40

Effect of flowrate on COD and Colour removal at 20 mL/min

1. COD
2. Colour

## **PENYINGKIRAN COD DAN WARNA DARIPADA AIR SISA TEKSTIL MENGUNAKAN BATU KAPUR DAN KARBON TERAKTIF**

### **ABSTRAK**

Pengolahan air sisa adalah salah satu daripada masalah terbesar yang dihadapi oleh pengilang-pengilang tekstil. Salah satu daripada industri tekstil di Pulau Pinang, Malaysia, mengalami masalah COD dan warna yang tinggi dan melebihi tahap standard pelepasan effluen walaupun setelah diolah secara biologi. Tujuan utama kajian ini adalah untuk mengkaji kesesuaian penggunaan batukapur, karbon teraktif dan campuran kedua-dua bahan sebagai media berkos rendah untuk mengolah effluen yang dinyatakan. Kaedah fizikal-kimia yang digunakan dalam kajian ini lebih biasa digunakan berbanding kaedah lain kerana ianya lebih ringkas, mudah dikendali dan dikawal dari segi kualitinya. Empat sampel telah dikaji iaitu air sisa sebenar dan tiga jenis air sisa sintetik yang terhasil daripada tiga jenis dye yang lazim diguna dalam industri tekstil. Kepekatan COD dan warna awal dalam air sisa industri dan sintetik ialah masing-masing antara 200-400 mg/L dan 500-700 PtCo. Saiz partikel bagi batukapur dan karbon teraktif ialah antara masing-masing 2.36-4.75 mm dan 1.14-2.36 mm. Kajian kelompok telah dilakukan untuk menilai nisbah campuran bagi batu kapur dan karbon teraktif pada keadaan optimum bagi penyingkiran COD. Keputusan mendapati campuran batu kapur dan karbon teraktif dalam nisbah 35:5 dapat menyingkirkan 92% kandungan COD. Keputusan juga menunjukkan media yang mempunyai saiz partikel yang halus (75-600  $\mu\text{m}$ )



lebih efektif berbanding dengan partikel yang kasar (2.36-4.75 mm) disebabkan oleh saiz partikel yang halus mempunyai luas permukaan yang tinggi. Data keseimbangan penyerapan lebih mematuhi isoterma Freundlich jika dibandingkan dengan isoterma Langmuir. Data bagi kajian kinetik menepati korelasi pemalar untuk pseudo kinetic peringkat kedua ( $R^2 > 0.96$ ). Ujikaji turus dengan menggunakan campuran batu kapur dan karbon teraktif pada nisbah 35:5 berjaya menyingkirkan COD dan warna melebihi 80% dan mengesahkan keputusan ujikaji keseimbangan kelompok. Penyingkiran yang lebih baik diperolehi pada kadar alir yang lebih rendah iaitu 20 mL/min. Campuran karbon teraktif dan batu kapur merupakan media alternatif bagi penyingkiran COD dan warna pada kos yang jauh lebih murah jika dibandingkan dengan karbon teraktif sahaja.

## **REMOVAL OF COD AND COLOUR FROM TEXTILE WASTEWATER USING LIMESTONE AND ACTIVATED CARBON**

### **ABSTRACT**

Treatment of wastewater is one of the biggest problems faced by textile manufacturers. One of the textile industries in Penang, Malaysia is experiencing high concentration of COD and colour in the final effluent after biological treatment exceeding the standard discharge limit. The purpose of the present study was to investigate the suitability of using activated carbon (AC), limestone (LS) and mixture of both (LS:AC) as low cost media for the post-treatment of treated effluent. The physico-chemical treatment adopted in this study is preferred over the other methods because of its simplicity, easy maintenance and quality control. Four samples were studied i.e. an actual wastewater (final effluent), and synthetic wastewater made from three different types of most commonly used reactive dyes used in the production. The ranges of initial concentrations of COD and colour in industrial and synthetic wastewaters were 200-400 mg/L and 500-700 PtCo, respectively. The particle sizes of LS and AC used in studies were 2.36-4.75 mm and 1.14-2.36 mm, respectively. The batch experiments were conducted to evaluate the combined mixture ratio of LS:AC at optimum conditions for the removal of COD industrial and synthetic wastewater. The LS:AC mixture ratio of 35:5 removed about 92% of COD. Results indicated that smaller particle size of media (75-600  $\mu$ m) was more effective than larger particle size (2.36-4.75 mm) because small size particle causes a higher

adsorption capacity due to more available surface area. The equilibrium adsorption data fitted better to Freundlich isotherm when compared to Langmuir isotherm. The experimental data agreed with the pseudo-second-order kinetic model ( $R^2 > 0.96$ ). In upflow column, the experimental data showed that higher flowrate resulted in shorter column saturation time. Column studies conducted using mixture of limestone and activated carbon of 35:5 indicated over 80% removals of the COD and colour as proven in the batch studies. Lower flow rate resulted higher saturation time. The limestone and activated carbon mixture provides alternative medium for removing COD and colour at a much lower cost as compared with activated carbon.

## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Background**

The textile industry is one of the most complicated industries among manufacturing industry. Wastewater treatment is one of the major problems faced by textile manufacturers. A detailed study of the textile processes will reveal that there are many complicated processes and chemicals used throughout the production. In the case of manufacturing of woven polyester and cotton blended fabric, the textile main processes starts from fiber production in the case of synthetic fiber followed by spinning to convert the fiber to yarns. Yarns are then strengthened with sizing chemicals like starch, polyvinyl alcohol and wax so that they can withstand vigorous movements when the yarns are weaved into fabric in high speed weaving looms. After weaving, weaved fabric must be pretreated before they can be dyed, printed and finished. During pretreatment there are various chemicals being used. Fabric is desized either with enzyme or oxidative chemicals and scoured using sodium hydroxide and detergents. Bleaching is done normally by using hydrogen peroxide to remove the natural color of the fabric white. Fabric is then mercerized using high concentration sodium hydroxide to stabilize the fabric. During dyeing and printing, many types of dyes are used e.g. disperse, reactive, vat etc. together with dyeing auxiliaries and chemicals. Fabric is finally finished to give the last touch and intended properties by using resins, softeners and other finishing agents e.g. fluorocarbon, silicones etc.

The combination of the processes and products make the wastewater from textile plant contains many type of pollutants. The dyeing and finishing operations are such that the dyestuffs, chemicals and textile auxiliaries used can vary from day to day and sometimes even within several times a day (Lin and Chen, 1997). It contains various waste chemical pollutants such as sizing agents, wetting agents, complexing agents, dyes, pigments, softening agents, stiffening agents, fluorocarbon, surfactants, oils, wax and many other additives which are used throughout the processes. These pollutants contributes to high suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), heat, color, acidity, basicity and other soluble substances (Ahn *et al.*, 1999).

Price competition, demand in high quality products, new and innovative products that are highly durable put further pressure to the industry as they have to use more dosage of chemicals and continually change to new chemicals to suit the market demand. This will finally result in the complication in the wastewater that is being discharged. Stringent legislation on discharge as per the requirement of Environmental Quality Act of Malaysia and other developed countries give further challenges to the industry. Thus there is a need for continues study and research on the waste water treatment to find new methods of treatment in order to sustain this industry.

## **1.2 Problem Statement**

Textile processes produce multi component wastewater which can be difficult to treat (O'Neill *et al.*, 2000). This wastewater can cause serious

environmental problems due to their high colour, large amount of suspended solids, and high chemical oxygen demand (Kim *et al.*, 2004). Standard discharge limits of textile effluent are becoming more stringent in recent days creating continuous problems for industries to comply with. The conventional treatment of wastewater containing dyestuffs includes biological oxidation, chemical oxidation and adsorption. Biological methods are generally cheap and simple to apply and are currently used to remove organics and color from dyeing and textile wastewater. However this wastewater cannot be readily degraded by conventional biological processes e.g. activated sludge process because the structure of most commercial dye compounds are generally complex and many dyes are non biodegradable due to the chemical nature and molecular size (Kim *et al.*, 2004).

At present, several methods have been developed to treat textile wastewater but they cannot be used individually because this wastewater has high salinity, color and non biodegradable organics. In coagulation process, large amount of sludge is created which may become a pollutant itself and increase the treatment cost. Oxidation process such as ozonation effectively decolorizes almost all dyes except disperse dyes but does not remove COD effectively (Ahn *et al.*, 1999). Electrochemical oxidation produce pollutants which increases the treatment cost (Kim *et al.*, 2003).

There is no single process capable of adequate treatment mainly due to the complex nature of these effluents. The use of combined processes has been suggested recently to overcome the disadvantage of individual unit

processes (Kim *et al.*, 2003). Most of the existing processes include an initial step of activated sludge treatment to remove the organic matter followed by oxidation, UV radiation, membrane separation, or adsorption (Pereira *et al.*, 2003).

Adsorption is an effective method of lowering the concentration of dissolved dyes in the effluent resulting in color removal. Other means of dye removal such as chemical oxidation, coagulation and reverse osmosis are generally not feasible due to economic considerations (Tsai *et al.*, 2001). The adsorption process is one of the most efficient methods to remove dyes from effluent. The process of adsorption has an edge over the other methods due to its sludge free clean operation and complete removal of dyes even from dilute solution (Malik, 2003).

Activated carbon is the most widely used adsorbent because of its extended surface area, microporous structure, high adsorption capacity and high degree of reactivity. However, commercially available activated carbons are very expensive (Malik, 2003). There is a growing interest in using low cost commercially available materials for the adsorption of color. A wide variety of low cost materials such as agricultural by product (Kadirvelu *et al.*, 2000), waste coir pith (Namasivayam *et al.*, 2001), Indian rosewood sawdust (Garg *et al.*, 2004), pine sawdust (Ozacar *et al.*, 2005), banana pith (Namasivayam *et al.*, 1998), rice husk (Low and Lee, 1997), orange peel (Namasivayam *et al.*, 1996), industrial solid waste such as Fe(III)/Cr(III) hydroxide (Namasivayam *et al.*,

2005) and silica (Andrzejewska *et al.*, 2007) are used as low cost alternatives to activated carbon.

The case study is on wastewater from one of a textile mill in Penang. The mill is manufacturing cotton and polyester/cotton blend woven fabric. The production consists of desizing, scouring, bleaching, mercerization, dyeing and finishing. Wastewaters from all these processes are mixed together in a buffer tank. The wastewater is then neutralized and treated in anaerobic pond with retention of 10-15 days. The wastewater is then treated in activated sludge treatment plant. The wastewater sample for this study was taken after the activated sludge treatment plant. The range of COD and colour concentrations of wastewater are 200-260 mg/L and 500-700 Pt/Co, respectively.

It has been reported that mixture of activated carbon and limestone can effectively remove COD and color of domestic waste landfill leachate. Hence this research was undertaken to investigate the suitability of activated carbon, limestone and mixture as alternative and cheaper filtering medium capable of removing COD and color from textile plant waste water.

### **1.3 Objectives of Research**

The main objective of this study is to examine the COD and colour reduction in a selected textile wastewater by a combination of activated carbon and limestone, which will minimize the treatment cost. Specific objectives include:



1. To determine the preliminary conditions viz. optimum mixture ratio of limestone: activated carbon (LS: AC), optimum shaking time, settling time and shaking speed that will give maximum reduction of COD.
2. To determine the removal performance at different experimental conditions i.e. optimum pH, effect of particle size, effect of adsorbent dosage and initial concentration.
3. To establish the adsorption isotherm and the kinetics models for widely used single reactive dyestuffs in comparison with an actual wastewater from a textile mill.
4. To determine the saturation times using different flow rates for optimum mixture ratio (35:5) and for limestone and activated carbon alone at optimum flowrate in removing COD and colour.

#### **1.4 Scope of Research**

The scope of this study is limited to the following,

1. Industrial wastewater was collected from the effluent outlet point of a textile wastewater treatment plant. Synthetic wastewaters were also used in this study i.e. aqueous solution of reactive yellow 145, reactive red 195 and reactive black 5. Limestone (LS) and activated carbon (AC) were used as adsorbents in the present research.
2. The behavior of COD reduction from textile wastewater with different LS: AC ratios were tested to determine the optimum mixture ratio of adsorbents, optimum shaking and settling time and shaking speed. Several other effects such as effect of particle size, initial concentrations,

adsorbent dosage and pH were also examined. The ranges of initial COD concentrations of industrial wastewaters throughout batch study experiments were 130-1260 mg/L. During batch study, different range of selected mixture ratios of LS and AC were used i.e. 40:0, 35:5, 30:10, 25:15, 20:20, 15:25, 10:30, 5:35 and 0:40

3. Batch adsorption isotherm studies were conducted on real textile wastewater and synthetic wastewater for COD reduction to obtain the equilibrium isotherm data and from this equilibrium data, adsorption isotherms models, Freundlich and Langmuir isotherms were studied. The adsorption kinetic studies were conducted to determine the type of adsorption, whether physical or chemical.
4. The particle sizes of LS and AC used in batch study were 2.36-4.75 mm and 1.14-2.36 mm, respectively
5. In column study, three columns were set up such that first column with mixture ratio of LS:AC (35:5), second column with LS and third column with AC. The COD and colour were analyzed for column study.
6. In upflow column study, the effect of flowrates (20 mL/min & 40 mL/min), filtration of  $0.0013 \text{ m}^3/\text{m}^2\cdot\text{min}$  at flowrate of 20 mL/min and  $0.0026 \text{ m}^3/\text{m}^2\cdot\text{min}$  at flowrate of 40 mL/min, respectively were studied. Regeneration of media was not examined in present study.

## **CHAPTER 2**

### **PROCESS DESCRIPTION AND SOURCES**

#### **2.1 Process Description**

There are many types of textile materials used all over the world. Textile materials are made of fibers. Textile fibers are divided into two major groups i.e. natural fibers and synthetic fibers. The type of textiles materials used varies from place to place. It depends on many factors such as country, place, climate, customs, tradition society etc. A process description of woven cotton and polyester blended fabric manufacturing is discussed in this chapter as this is one of the major textile material commonly used all over the world and furthermore the process covers almost a huge area of the textile manufacturing which contributes to the source of pollution.

##### **2.1.1 Manufacturing of Polyester Fiber**

The manufacture of polyester fibre is part of organic chemical industry. Polyester fiber has remarkable resistance to heat, low flammability, heat resistance and readily processible. Polyester fibre is a polymeric ester formed by reacting terephthalic acid or dimethyl terephthalate and mono ethylene glycol. Polyester is made in the melt by driving off the ethylene glycol. When the appropriate viscosity is achieved, the product is extruded and then cut into polymer chips. The polymer chips are then made into fibre in the spinning process (Noyes, 1993; NIIR Board, 2003a).

### **2.1.2 Spinning**

The polymer chips are dried to remove the residual moisture and are then put into hopper reservoirs ready for melting. The fiber is spun from the molten polymer through spinneret with circular holes. The individual filaments solidify and wound on to circular cylinders as undrawn yarn. This yarn is hot stretched to about five times its original length. This yarn is supplied to customers as filament yarn. During this process additional numbers of yarns are brought together to form a thick tow. This tow is drawn and crimped mechanically and cut into specific length of a few inches according to the textile processes for which it is intended. This fiber is blended with other fibers and spun into yarns (NIIR Board, 2003a).

### **2.1.3 Weaving**

Weaving is a process to convert textile yarns to textile fabrics. Fabrics are formed by interlacing length-wise yarns called warp and cross-wise yarns called weft. During weaving the warp yarns undergo strain while the weft yarns undergo less strain as compared to the warp yarns. The yarns need to withstand this strain during weaving. Before weaving the warp yarns first wound on cones placed on rack called creel. The warp yarns are then unwound and passed through a size solution before wound onto a warp beam. A typical size solution normally contains starch, polyvinyl alcohol, acrylic size and wax. Starch is the most common size component for natural fibers. Polyvinyl alcohol is the most common size component for synthetic fibers. Acrylic sizes oil and waxes are used in conjunction to increase the softness and yarn pliability. The yarns are dipped once or more times in the size solution and dried on hot drums. The

size solution forms a layer of coating and prevents the yarn against abrasion and snapping. Once sizing is completed, the size beam is mounted on a looms where weaving is performed to form fabric (NIIR Board, 2003a).

#### **2.1.4 Pretreatment of Fabric for Dyeing and Finishing**

Pretreatment is a series of processes mainly comprised of singeing, desizing, scouring, bleaching and mercerizing to prepare fabric for subsequent processes i.e. dyeing, printing and finishing. Singeing is a dry process to remove the protruding fibers, which normally termed as hairs from yarns or fabrics. These hairs are burned off by passing through the fabric over flame. Singeing provides the fabric with smooth surface improves the appearance and reduces pilling. Desizing is a process to remove the sizing chemicals used during weaving. Manmade fibers are normally sized with water-soluble sizes that can be easily washed out by hot water. Natural fibers are often sized with water in soluble size starches or mixture of starch with other materials.

There are two types of desizing employed i.e. enzymatic and oxidative method. In enzymatic desizing, starches are broken down into water-soluble sugars, which are then removed by washing. In oxidative desizing, starch is oxidized at high temperature by the usage of chemical oxidizing agent such as sodium persulphate. Scouring is a cleaning process to remove the oils and waxes contained on the fabric. Scouring uses strong alkali typically sodium hydroxide and surfactants to breakdown and emulsifies natural oils. Normally desizing and scouring are often combined to simplify the process. Bleaching whitens the fabric and removes the natural colour impurities, impurities and

foreign matters in the fabric. Bleaching decolorizes the coloured impurities that are not removed by scouring and prepares a white material for subsequent dyeing and printing.

There are many types of chemicals used depending on the type of fabric and fiber and requirement. The most commonly used bleaching agents are hydrogen peroxide, sodium hypochlorite, sodium chlorite etc. Hydrogen peroxide is the most common among all as it can be easily used. Sodium hypochlorite and sodium chlorite is not preferred due to environmental reasons. In bleaching, fabric is saturated with bleaching agents, activator, stabilizer and other chemicals and steamed for a certain period followed by a washing process to remove the residue. Mercerizing is a process to increase the strength and stability of cotton fiber. It will also increase the fiber's affinity to dyestuffs and improves the luster of the fabric. This process makes the flat and twisted cotton fiber to swell into round shape and contract in length. During mercerizing, fabric is passed through caustic soda solution at the concentration of 15-25% and then stretched on both length-wise and width-wise direction on a stenter frame with caustic shower to ensure good penetration and treatment. After treatment the fabric is washed to remove the caustic under tension. Remaining caustic is neutralized with a weak acid followed with series of hot and cold rinsing. After these pretreatment processes the fabric is ready for dyeing, printing and finishing (Noyes, 1993; NIIR Board, 2003a).

### **2.1.5 Dyeing**

Dyeing is a process in which yarns and fabric acquire color. Textiles are dyed using a wide range of dyestuffs, techniques and machines. Different fiber

requires different types of dyestuffs and processes in order to produce goods having good colour and the required properties. Dyes used are mainly synthetic and derived from coal tar and petroleum intermediates. The main group of dyestuff that is normally used for polyester is known as “disperse” and the main groups of dyestuffs used for cotton are known as “reactive, vat or sulphur dyes”. There are two types of dyeing methods i.e. continuous and batch. In a continuous dyeing process, fabric is fed into a dye bath containing dyestuff solution and squeezed through a set of padder. The fabric which is padded with dyes passes through dye fixation with either heat or chemicals depending on the dye selection. For the fixation of disperse dyes, fabric is passed through high temperature chamber to diffuse the disperse dyes into the polyester fiber. Reactive, vat and sulphur dyes are fixed to the cotton fiber through chemical and steaming. The unfixed dyes for both processes are then washed out with the use of detergents and hot water in order to clean the fabric. In a batch dyeing, a known quantity of fabric is loaded into a dyeing machine with a solution containing dyes and chemicals. The dye molecules leave the solution and enter the fabric due its affinity to the fibers. The dye is fixed in the fiber by either heat or chemicals. The unfixed dyes are removed by washing (Preston, 1986; Noyes, 1993).

#### **2.1.6 Printing**

Printing is a process which colours and design are printed on fabric. The most common printing technique is rotary screen-printing, roller printing and others. Pigments and dyestuffs are mainly used for printing. Pigments prints are normally preferred as it does not require washing and generate little wastewater

as compared to dyestuff print. In pigment printing, pigments are mixed in a paste system together with binder to form a pigment paste. This paste is applied to the fabric through a screen or roller with designs. The fabric is then passed through a baking process to fix the pigment to the fabric. In dyestuff printing, dyes are mixed in a paste system a dyestuff paste. This paste is similarly applied to the fabric through a screen or roller with designs. The fabric is then passed through a chemical steaming followed by washing with detergents and hot water to remove the unfixed dyes (Noyes, 1993).

#### **2.1.7 Finishing**

Finishing is divided into two main categories i.e. mechanical and chemical treatments performed to the fiber, yarn or fabric in order to impart the final touch and also the special properties to the fabric. Mechanical processes, involves brushing or raising to make the surface hairy, physical treatment to improve the luster, sanforize to minimize the wash shrinkage and others. In the mechanical processes, the water consumption is almost negligible except for the washing to remove the loose fibers after the mechanical treatment to raise the fabric or yarn surface. In the chemical process, chemicals like resins, softeners, stiffeners and other auxiliaries to impart special function to the fabric are applied to the fabric (NIIR Board, 2003a).

Resin and catalyst are used to improve the dimensional stability and the wash and wear properties of the fabric. Softeners and stiffeners are used to give the handle and touch to the fabric. Apart from these main chemicals, there are also special auxiliaries chemicals to give certain properties like fluorocarbon



(to give good oil repellency), antibacterial chemicals (to give good anti bacteria properties), hydrophilic softeners (to give good absorbency to the fabric) etc. Depending on the final requirements and also the usage, a series of chemicals are normally selected to form a finishing chemical mixture. This mixture is padded to the fabric and cured at high temperature chambers. After finishing the fabric is ready to be made into garments. However there are also some post treatments for certain type of fabric such as washing to attain faded look, treatment with enzyme, softeners or some abrasive materials to achieve superior handfeel. Chemical treatment and post finishing treatment processes also produces considerable amount of wastewater (Noyes, 1993; Schindler and Hauser, 2004).

## **2.2 Sources of Pollution**

The water consumption varies widely in the industry depending on the mill, processes, equipment used and type of materials produced. Each of textile process utilizes large amount of water, which will finally become wastewater. The most significant sources of pollution among various process stages are pretreatment, dyeing, printing, and finishing of textile materials.

At the pretreatment stage, desizing is the industry's largest source of pollution. During desizing, all the sizes used during weaving are removed from the fabric and discarded into the wastewater. In scouring, dirt, oil, waxes from natural fibers are removed from the fabric and washed into wastewater stream. Normally desizing and scouring are combined and these two processes may

contribute to 50% of BOD in the wastewater in the wet processing. Pollution from the peroxide bleaching is not a major problem (NIIR Board, 2003b).

Dyeing wastewater generate the largest portion of the total wastewater. The source of wastewater is from the dye preparation, spent dye bath and washing processes. Dyeing wastewater contains high salt, alkalinity and colour. Finishing processes generate organic pollutants such as residue of resins, softeners and other auxiliaries. A composite wastewater from an integrated textile plant consist of following materials: starches, dextrin, gums, glucose, waxes, pectin, alcohol, fatty acids, acetic acid, soap, detergents, sodium hydroxide, carbonates, sulfides, sulfites, chlorides, dyes, pigments, carboxymethyl cellulose, gelatin, peroxides, silicones, flourcarbons, resins and others (Noyes, 1993; NIIR Board, 2003b). Pollutants at various stages of manufacturing of polyester and cotton blended woven fabric are presented in Figure 2.1.

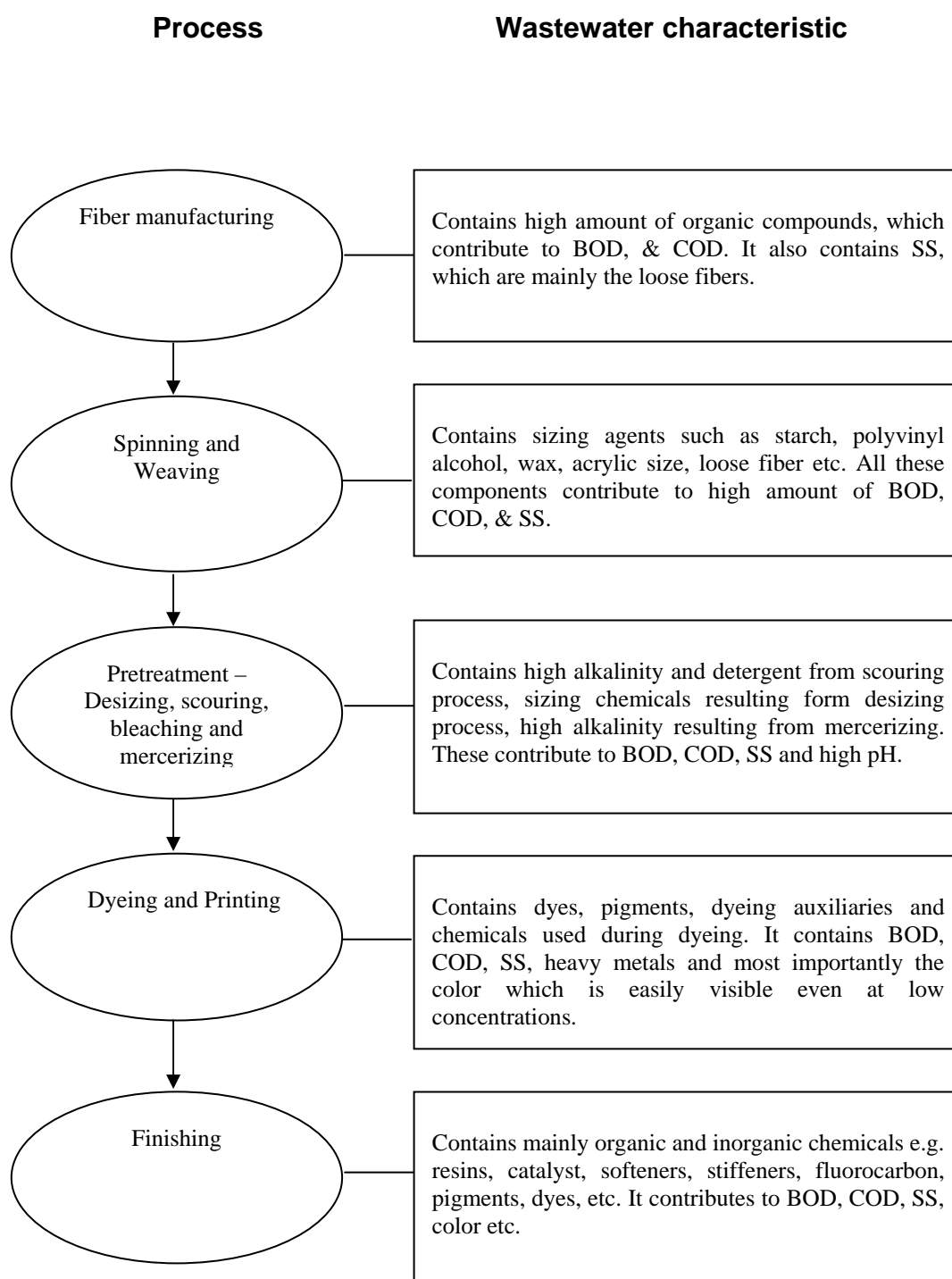


Figure 2.1: Sources of pollution in textile manufacturing (NIIR Board, 2003b)

## CHAPTER 3

### LITERATURE REVIEW

#### 3.1 Wastewater from Textile Industry

Textile industry is one of the most complicated industries among manufacturing industry (Selcuk, 2005). The main sources of wastewater normally come from cleaning water, pretreatment, dyeing and finishing process water non-contact cooling water and others (Kim *et al.*, 2003). The amount of wastewater varies widely depending on the type of process operated at the mill. Various toxic chemicals such as complexing agents, sizing, wetting, softening, anti-felting and finishing agents, wetting agents, biocides, carriers, halogenated benzene, surfactants, phenols, pesticides dyes and many other additive are used in wet processing, which are mainly called washing scouring, bleaching, mercerizing, dyeing, finishing (Selcuk, 2005).

The water employed in the process eventually ends up as wastewater (Lin and Chen, 1997). Main pollutants from dyeing and finishing units include high suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), heat, colour, acidity, basicity, and other organic pollutants (Ahn *et al.*, 1999; Karim *et al.*, 2006). Government legislation is becoming more stringent in most developed countries regarding the removal of dyes from industrial effluent. This creates problems for the textile industries to comply with. Environmental protection in Europe is promoting prevention of transferal of pollution problems from one part of the environment to another.

This means that most textile industry is developing on site or in-plant facilities to treat their own effluent before discharge (Banat *et al.*, 1996).

### **3.2 Textile Wastewater, Characteristics and Environmental Impact**

Normal textile dyeing and finishing operations are such that the dyestuffs used can vary from day to day and sometimes even several times a day because of the batch wise nature of the processes. Frequent changes of dyestuff employed in the dyeing process and finishing process cause considerable variation in the waste water characteristic particularly the pH, colour and COD. Strong colour is another important component of the textile wastewater which is very difficult to deal with (Lin and Chen, 1997). Colour is noticed in the wastewater effluent and the presence of small concentrations of dyes in water is highly visible, and may affect their transparency and aesthetics (Banat *et al.*, 1996).

Dye wastewater from textile mills is a serious pollution problem because it is high in both colour and organic content. A dye is a colored substance that can be applied in solution or dispersion to a substrate in textile manufacturing, thus giving a color appearance to textile materials. Discharging of dyes into water resources even in a small amount can affect the aquatic life and food web. Dyes can also cause allergic dermatitis and skin irritation (Ugurlu *et al.*, 2007). One of the main problem regarding textile waste-waters is the colored effluent. The colored effluent contains visible pollutants. The primary concern about effluent color is not only its toxicity but also its undesirable aesthetic impact on receiving waters. Non-biodegradable nature of most of the dyes

reducing aquatic diversity by blocking the passage of sunlight through the water represents serious problems to the environment. In some cases, dyes in low concentration are harmful to aquatic life. Since many dyes have adverse effect on human beings, the removal of color from the effluent or process has appeared of importance for ensuring healthy environment. Hence, it is imperative that a suitable treatment method should be applied. The colour of the effluent discharges into receiving waters affects the aquatic flora and fauna and causes many water borne diseases. Some of dyes are carcinogen and others after transformation or degradation yield compound such as aromatic amines, which may carcinogen or otherwise toxic. In addition, dyes accumulate in sediments at many sites, especially at location of wastewater discharge, which has an impact on the ecological balance in the aquatic system. These pollutants because of leaching from soil also affect ground water system (Namasivayam and Sumithra, 2005).

Textile finishing wastewater, especially dyehouse effluents contain different classes of organic dyes, chemicals and auxiliaries thus they are colored and have extreme pH, COD, BOD and AOX values and they contain different salts, surfactants, heavy metals, mineral oils and others (Golob *et al.*, 2005). A composite wastewater from an integrated textile plant consist of following materials: starches, dextrin, gums, glucose, waxes, pectin, alcohol, fatty acids, acetic acid, soap, detergents, sodium hydroxide, carbonates, sulfides, sulfites, chlorides, dyes, pigments, carboxymethyl cellulose, gelatin, peroxides, silicones, fluorocarbons, resins etc. Textile wastewater is known to

exhibit strong colour, a large amount of suspended solids, high fluctuating pH, high temperature and high COD concentration.

The colour of reactive dyes is due the presents of N=N azo bonds and chromophoric groups. The dyes are first absorbed on the cellulosic and then fiber. After fixation of the dyes on the fiber about 10-15% of initial loading is present in the dye bath effluent (Karim *et al.*, 2006). Reactive dyes in both ordinary and hydrolyzed form are not easily biodegradable and thus even after treatment; colour may be present in the effluent. The conventional processes such as coagulation, flocculation and biological methods adopted for decolouration of effluent containing reactive dyes are no longer able to achieve adequate colour removal (Santhy and Selvapathy, 2006).

The discharge of organic pollutant either BOD or COD to the receiving stream can lead to the depletion of dissolved oxygen and thus creates anaerobic condition (Al-Degs *et al.*, 2000). Under anaerobic condition foul smelling compound such as hydrogen sulfides may be produced. This will consequently upset the biological activity in the receiving stream.

Textiles effluent contains dyestuffs, which are visible, even at low concentration (Prado *et al.*, 2004). These coloured effluents are aesthetically displeasing as colours are normally related to untreated wastewater. Dyes even in low concentration can affect the aquatic life and food web. Since many of the organic dyes are harmful to human being, the removal of colour from processes on waste effluent becomes environmentally important (Malik, 2003). The

discharge of coloured wastewater is not only damaging the aesthetic nature of receiving streams but also it may be toxic to the aquatic life. In addition, colour interferes with the transmission of sunlight in a stream and therefore reduces photosynthetic action (Kadirvelu *et al.*, 2000). This disturbs the natural equilibrium by affecting the aquatic life and food chain.

### **3.3 Treatment of Textile Wastewater**

Generally, it is rather difficult to treat textile effluent because the industry produces multi-component wastewater. The dye contained in the effluent can vary daily and even hourly. The hot and strongly coloured wastewater contains large amount of suspended solids, high chemical oxygen demand concentration and greatly fluctuating pH which can be difficult to be treated. Hundreds of small scale dyeing industries is facing closure since they are not treating their effluent as it is not economical (Rao and Rao, 2006). In Malaysia, the discharge standard is stipulated in the Third Schedule Environmental Quality Act, 1974. Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979 is shown in Table 1 (Appendix A).

After every effort of reduce waste strength and volume by conservation and good housekeeping there are still problems of disposing the effluent without affecting the receiving stream. Governmental agencies, non governmental agencies and also the public are becoming more and more concern over environmental issues. There are many ways for treating the textile effluent. The best combination of methods differs from plant to plant depending on the size, type of waste and degree of treatment needed. Generally the treatment options



can be divided into three main categories namely biological, chemical and physical methods. Considerable amount of research has been undertaken on the treatment of industrial effluent to decrease the impacts of the environment (NIIR Board, 2003b).

### **3.3.1 Biological Method**

There are many types of biological treatment methods. Among them include trickling filters, activated sludge process, anaerobic process, oxidation ponding etc. To date the commonest treatment of textile wastewater has been based on mainly on aerobic biological process, consisting mainly conventional and extended activated sludge system. The trickling filters simulate stream flow by spraying wastewater over a broken, medium such as stone or plastic. The medium serves as a base for biological growth, which attacks the organic matter of wastewater, and uses it as food.

In activated sludge process, the wastewater flows into a tank after primary settling. The microorganism in activated sludge is suspended in the wastewater as aggregates. The sludge and wastewater is kept in suspension by compressed air, which also supplies the oxygen, necessary for biological activities. The aerated waste is continuously withdrawn and settled and a portion of the sludge is returned to the influent (Metcalf and Eddy, 1991).

Biological methods of removing pollutants from wastewater using natural process involving bacteria and other microorganism for oxidation of the organic waste. Biological methods are generally cheap and simple to apply and are

currently used to remove organic and color from dyeing and textile wastewater (Kim *et al.*, 2004). Most of existing process includes an initial step of activated sludge treatment to remove the organic matters, followed by oxidation, membrane, activated carbon etc (Pereira *et al.*, 2003).

Anaerobic and aerobic treatments have been used together or separately for the treatment of textile effluents. Hence aerobic treatment is not effective in colour removal from textile wastewater containing azo dyes (O'Neill *et al.*, 2000). Conventional biological process are not effective for treating dyestuff wastewater because many commercial dyestuff are toxic to organism being used and result in the problems of sludge bulking, rising sludge and pin flock (Ahn *et al.*, 1999). Because of low biodegradability of many textiles chemicals and dyes, biological treatment is not always effective for textile industry wastewater (Pala and Tokat, 2002).

### **3.3.2 Chemical Method**

Chemical method includes coagulation or flocculation and oxidation. The main advantage of the conventional coagulation and flocculation is removal of the waste stream due to the removal of dye molecules from the dyebath effluent and not due to partial decomposition of dyes which can lead to an even more potentially harmful and toxic aromatic compound (Golob *et al.*, 2005).

Physical and chemical treatment techniques are effective for colour removal but use more energy and chemicals than biological processes. They also concentrate the pollution into solid or liquid side streams requiring

additional treatment of disposal (Shaw *et al.*, 2002). The major disadvantage is the production of sludge (Golob *et al.*, 2005). In coagulation process large amount of sludge is created which may become a pollutant itself and increase the treatment cost (Ahn *et al.*, 1999).

Chemical oxidation uses strong oxidizing agents such as hydrogen peroxides, chlorine and others to force degradation of resistant organic pollutant. Chemical oxidation is the most commonly used method of decolourization by chemical owing to its simplicity and the main oxidizing agent is hydrogen peroxide (Robinson *et al.*, 2001).

Oxidation of by ozone is capable of degrading chlorinated hydrocarbons, phenol, pesticides and aromatic hydrocarbon. One of the major advantage of ozonation it does not increase the volume of wastewater and sludge. A major disadvantage of this process is its short-half life typically being 20 minutes (Robinson *et al.*, 2001).

### **3.3.3 Physical Method**

Physical method include membrane filtration such nano filtration, reverse osmosis and adsorption. Membrane filtration is an effective mean of removing pollutant from the wastewater. However the initial investment cost is very huge and the periodic replacement of membrane is remarkably high.

Adsorption is an effective method of lowering the concentration of dissolved dyes in the effluent resulting in colour removal. Other means of dye