

## I-INTRODUCTION

Industrialization in the third world countries has become a necessity, especially because of the low prices associated with raw materials and labor. Ecological concepts of clean technologies are usually difficult to meet and generation of wastes or losses of raw materials and products in the effluents represents a common problem associated with most industrial branches. If this problem can be solved with a cheap form of waste treatment and water reuse, it would further improve the benefits to industry.

Industrial pollution is one of the vital problem presently facing all over the world. The careless disposal of industrial effluents and other wastes may contribute greatly to the poor quality of the water (**Chindah *et al.*, 2004**). Textile industries are major sources of these effluents (**Ghoreishi and Haghighi, 2003**) due to the nature of their operations which requires large volume of water that eventually results in high waste water generation. They are one of the largest water users and polluters (**Nemerow, 1978**).

The extent of color and metals contamination of the water environment has raised much concern because of potential hazards associated with the entry of these substances into the food chain of humans and animals. Textile industry uses a large quantity of water in its production processes and highly polluted and toxic waste waters are discharged into sewers and drains without any kind of treatment (**Chindah *et al.*, 2004**).

Colour is a threat to water quality because it deteriorates the aesthetic value and purity of water due to the presence of organic matter like dyes (sulphur, reactive, azoic, and direct dyes) and pigments that were used on the cotton. Most fabrics are hydrocarbon derivatives having keto or carbonyl groups and insoluble in water. Others contains amino and nitro groups,

sodium sulphonate groups (reactive dyes) which are also insoluble but could be made soluble by treating with alkali. In some cases colour is due to the presence of phenols and some inorganic matter like suspended solids or precipitated metallic compounds, which enhance the colour changes (**Nikoladze *et al.*, 1989**).

Textile dyeing industries generated large amount of effluents, sewage sludge and solid waste materials everyday which are being directly discharged into the surrounding channel, agricultural fields, irrigation channels, surface water and finally enter into the River. Textile and dyeing industrial effluents offer the alteration of physical, chemical, and biological properties of aquatic environment by continuous changing in temperature, odor, noise, turbidity, and to the original properties that is harmful to public health, livestock, wildlife, fish, and other biodiversity (**Haque *et al.*, 2002**).

Considering both volume and effluent composition, the textile industry wastewater is rated as the most polluting among all industrial sectors. In addition, COD, BOD, TDS, and settable and filterable material contained in the produced waste waters. Important pollutants are present in textile effluents; they are mainly recalcitrant organics, colours, toxicants and inhibitory compounds (**Khelifi *et al.*, 2008**). It has been proven that some of these dyes and/or products are carcinogens and mutagens (**Manu and Chaudhari, 2003**). A part from the aesthetic deterioration of the natural water bodies, dyes also cause harm to the flora and fauna in the natural environment (**Kornaros and Lyberatos, 2006**). So, textile wastewater containing dyes must be treated before their discharge into the environment (**Forgas *et al.*, 2004**).

Numerous processes have been proposed for the treatment of colored wastewater e.g., precipitation, flocculation, coagulation, adsorption and wet

oxidation (**Hongman et al., 2004; Thomas et al., 2006**). All these methods have different colour removal capabilities, capital costs and operating speed. Among these methods coagulation and adsorption are the commonly used; however, they create huge amounts of sludge which become a pollutant on its own creating disposal problems (**Nyanhongo et al., 2002**).

Aerobic processes have been recently used for the treatment of textile wastewater as standalone processes (**Khelifi et al., 2008**) and they were conformed to be efficient, and cost-effective for smaller molecules. So that the aerobic reactor is an effective technique to treat industrial wastewater (**Coughlin et al., 2002 and 2003; Buitron et al., 2004; Yigong et al., 2004; Sandhaya et al., 2005; Steffan et al., 2005; Sudarjanto et al., 2006**). The aerobic reactor has the advantage of being a closed and comparatively homogeneous and stable ecosystem. Since little was known about this ecosystem, a molecular inventory is the first step to describe this dynamic bacterial community without cultivation (**Godon et al., 1997**). In order to better understand the functions of the bacterial community, a full description of the bacterial ecosystem was required (**Bouallagui et al., 2004**).

Textile dyeing plants, particularly those involving finishing processes are among the major sources of water industries consume large volumes of water pollution. These are more than 100,000 commercially and chemicals. There  $7 \times 10^5$  tons of dyestuff produced available dyes with over annually worldwide and used extensively in textile, dyeing and printing industries (**Spadero et al., 1994; Robinson et al., 2001; Zollinger, 2003**).

Wastewater streams from the textile dyeing operations contain unused dyes (about 8–20% of the total pollution load due to incomplete exhaustion of the dye) and auxiliary chemicals (**Mukherjee et al., 1999**) which would find their way into the environment. Dyes are designed to

remain stable and long-lasting colorants; they are usually not easily biodegradable. Azo dyes generally resist aerobic microbial degradation, only organisms with specialized azo dye reducing enzymes were found to degrade azo dyes under fully aerobic conditions (**Ganesh *et al.*, 1994**). Often, dyes are recalcitrant organic molecules that impart strong color to the wastewater, also contributing to the organic load and toxicity of the wastewater. Dye colors are visible in water at concentration as low as 1 mg/l, whereas textile processing wastewater, normally contain more than 10-200 mg/l dye concentration, resulting in aesthetic problems (**O'Neil *et al.*, 1999**). Apart from the aesthetic problem, the greatest environmental concern with dyes is the absorption and reflection of sunlight entering the water, which interferes with the growth of algae, limiting it to levels insufficient to biologically degrade impurities in the water. It is evident; therefore, that removal of such colored agents from aqueous effluents is of significant environmental, technical and commercial importance (**Vandevivere *et al.*, 1998**, **Pearce *et al.*, 2003**, **Forgas *et al.*, 2004**).

Textile industries consume the large volumes of water and chemicals for wet processing of textiles. The chemical reagents used are very diverse in chemical composition. The effluents thus generated contain a wide range of contaminants, such as salts, dyes, enzymes, surfactants, scouring agents, oil, oxidizing and reducing agents. Different methods are used for the purification and discoloration of textile colored wastewater: mechanical, chemical, physical-chemical and biological or their combination ( **Rettmer, 1998**; **Ferrero, 2000**; **Osterman *et al.*, 2002**).

The treatment of such dye-containing effluents is mostly based on physical and chemical procedures , e.g . adsorption, flotation, Fenton oxidation, reduction, ion exchange, chlorination / ozonation and incineration. These methods are rather costly and sometimes produce hazardous by products (**Shaul *et al.* , 1991**). The loss of dyes to effluent can be estimated

to be 10% for deep shades, 2% for medium shades and minimal for light shades (Laing, 1991). Dyes are present in the effluent at concentration of 10-50 mg/1, being visible to the naked eye . They are complex organic compounds which are refractory in aerobic treatment systems. Some contain metals such as Cr, Cu and Zn. Only 50 % is dye, the remainder is non-hazardous filler and surfactant.

- **Description of industry ;**
- **Chemicals and raw materials;**

The textile industry deals with fibrous materials in a form depending on the type of process, chemicals and other inputs, shown in Tables (1-1). (Sultan, 2002)

**Table (1-1): Raw materials for textile sub sectors**

|                        |                                                                                                                                                          |
|------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Cotton Spinning</b> | Raw cotton fibers, man-made fibers with specifications similar to cotton, or blends of cotton and man-made fibers. The raw fibers are supplied in bales. |
| <b>Wool Spinning</b>   | Raw wool fibers, man-made fibers with specifications of wool, or blends of wool and man-made fibers. The raw fiber material is supplied in bales.        |
| <b>Weaving</b>         | Cotton yarns, woolen yarns, man-made yarns, blended yarns, textured yarns, stretch yarns, ...etc.                                                        |
| <b>Knitting</b>        | Cotton yarns, woolen yarns, man-made yarns, blended yarns, textured yarns, stretch yarns, ...etc.                                                        |
| <b>Nonwoven</b>        | Man-made fibers, wool fibers, or blends                                                                                                                  |
| <b>Tufting</b>         | Acrylic yarns, polypropylene yarns, blended yarns with the wool-type.                                                                                    |
| <b>Garment</b>         | Woven or knitted fabrics, from cotton, wool, man-made fibers, blends of natural and man-made fibers, interlining fabric and lining fabric, buttons,      |

**Table (1-2): Chemicals for the wet processes**

|                           |                                                                                                     |
|---------------------------|-----------------------------------------------------------------------------------------------------|
| <b>Sizing</b>             | Polyvinyl alcohol, carboxymethyl Cellulose, oils, waxes, adhesives, urea, diethylene glycol, ..etc. |
| <b>Desizing</b>           | Enzymes, sulphric acid, detergents and alkali                                                       |
| <b>Scouring</b>           | Sodium hydroxide, sodium carbonate, surfactants, chlorinated solvents                               |
| <b>Bleaching</b>          | Hypochlorite, hydrogen peroxide, acetic acid.                                                       |
| <b>Mercerization</b>      | Sodium hydroxide, surfactants, acid, liquid ammonium                                                |
| <b>Dyeing</b>             | Dyestuffs, auxiliaries, reductants, oxidants                                                        |
| <b>Printing</b>           | Dyes (acids or alkalis), pigments, kerosene, binders, ammonia, xylenes.                             |
| <b>Chemical finishing</b> | Formaldehyde, phosphorus, ammonia, silicone, fluorocarbon resins, toluene, zircon salts,...etc.     |

## II- Review of Literature

### Textile Manufacturing Processes

Broadly defined, the textile industry includes the spinning, knitting and weaving of natural and man-made fibers, the finishing of textiles and the production of ready-made garments. The most common sectors in the Egyptian textile industry are: cotton fabrics, wool fabrics, man-made fabrics, synthetic fabrics and blended fabrics. (SEAM Project, 1999)

#### \*Wet Processing

The stages of wet processing of cotton textiles, both woven and knitted, are shown in Fig (2-1) and (2-2) as follows:

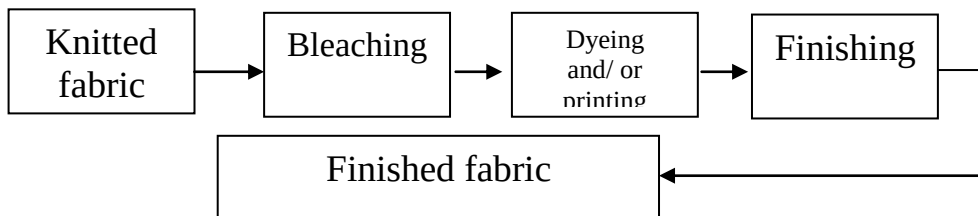


Fig (2-1): Wet Processing of Knitted Cotton Fabrics

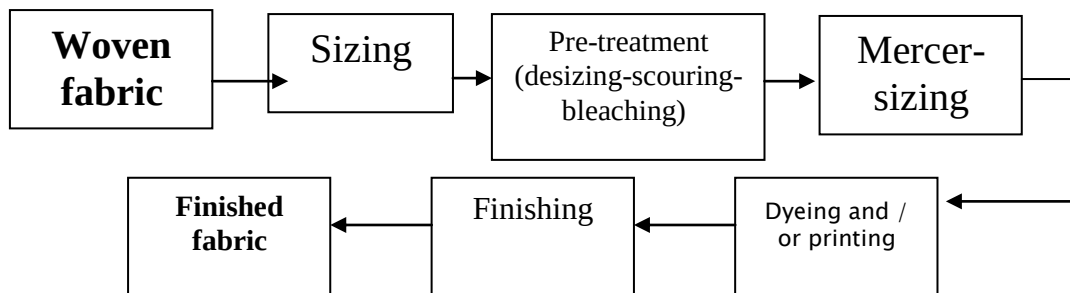


Fig (2-2): Wet processing of woven cotton fabrics

#### Pretreatment Processes

**Sizing and Desizing:** Sizing is carried out before the weaving process to increase the strength and smoothness of the yarn, as well as to reduce yarn breakages. Desizing, either with acid or enzymes then removes size from the fabric, so that chemical penetration of the fabric in later stages is not

inhibited. Desizing effluents have very high organic concentrations, contributing 40-50% of the total organic load from the preparatory sequences. Gums and PVA (polyvinyle acetates) may be removed by a simple hot wash but starch and its derivatives have to be made soluble by soaking with acids, enzymes or oxidants before being removed by a hot wash.

**Scouring:** Scouring is carried out to remove impurities that are present in cotton, both natural (e.g. waxes, fatty acids, proteins, etc.) and acquired (such as size, dirt and oil picked up during processing). This is usually done at high temperatures (above 100°C) with sodium hydroxide and produces strongly alkaline effluents (around pH 12.5) with high organic loads. They tend to be dark in color and have high concentrations of total dissolved solids (TDS), oil and grease. The scouring is normally done either on a Kier, a J Box, or an open width pad roll system, or on open width continuous plant. Common scouring agents include detergents, soaps, alkalis, antistatic agents, wetting agents, foamers, defoamers and lubricants.

**Bleaching:** Bleaching is used to whiten fabrics and yarns, using sodium hypochlorite or hydrogen peroxide. Many cotton processing factories in Egypt use sodium hypochlorite as it is cheaper than hydrogen peroxide. However, this is highly toxic and is now strictly limited or banned in many countries. It can also break down to form adorable organo-halogen compounds, which are both toxic and carcinogenic. Bleaching generates effluents with a low organic content, high TDS levels and strong alkalinity (pH 9-12). Once bleaching is complete, the bleaching agent must be completely removed, either by a thorough washing or using enzymes.

**Mercerizing** In this process, the cotton yarn or fabric is treated with an alkali (sodium hydroxide, NaOH) to improve luster, strength and dye uptake. It also removes immature fibers. The process is normally carried out on dry fabric; wet mercerization reduces the steam consumption, but requires stringent control of the operational parameters, such sodium hydroxide



concentration. Excess sodium hydroxide is normally recovered for reuse in either the scouring or other mercerization stages. The rinse wastes are alkaline, high in inorganic solids, caustic alkalinity and low in BOD. With the increasing trend toward cotton-polyester blends, much less mercerizing is being carried out.

Combined mercerizing, where scouring is carried out simultaneously with the mercerization in hot conditions, is now becoming popular, as the mercerization increases the rate of scouring. This combined process reduces capital cost, space requirements, energy costs, labour requirement and chemical costs.

### ***Dyeing***

The major classes of dyestuffs used in the textile industry are as follows:

- **Acid Dyes.** Mainly used on wool, silk and polyamide fibers. They give very bright colors, whose fastness ranges from very poor (allowing colors to run) to very good.
- **Basic Dyes.** Usually applied to acrylics and polyesters to produce very bright colors.
- **Direct Dyes.** Commonly applied to rayon and cotton.
- **Disperse Dyes.** Applied to cellulose acetate, polyamide and polyester fibers.
- **Reactive Dyes.** this group produces a range of bright shades, and commonly used for cellulose textiles.
- **Sulphur Dyes.** Most commonly used for dyeing cotton, rayon and cotton-synthetic blends and produce strong, deep colors in the final fabric.
- **Vat Dyes.** These cover an almost full range of shades and are particularly important in the dyeing of cellulose fibers (such as cotton).
- **Azoic Dyes.** Produce deep shades of blue, violet, yellow, orange and scarlet. More detail on the characteristics of these dyes is given in Table 2-1

Table (2-1): Typical characteristics of dyes used in textile Dyeing operation

| Dye Class                                                                                                                                                                                                                                                                                             | Description                                                                                                                         | Method                                     | Fibers Typically Applied to               | Typical Fixation (%) | Typical Pollutants Associated with Various Dyes                                                                          |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------|-------------------------------------------|----------------------|--------------------------------------------------------------------------------------------------------------------------|
| Acid                                                                                                                                                                                                                                                                                                  | Water-soluble anionic compounds                                                                                                     | Exhaust/Beck/Continuous (carpet)           | Wool Nylon                                | 80-93                | Color; organic acids; unfixed dyes                                                                                       |
| Basic                                                                                                                                                                                                                                                                                                 | Water-soluble, applied in weakly acidic                                                                                             | Exhaust/Beck                               | Acrylic<br>Some polyesters                | 97-98                | N/A                                                                                                                      |
| Direct                                                                                                                                                                                                                                                                                                | Water-soluble, anionic compounds; can be applied directly to cellulose fibers without mordents (or metals like chromium and copper) | Exhaust/Beck/Continuous                    | Cotton<br>Rayon<br>Other cellulose fibers | 70-95                | Color; salt; unfixed dye; cationic fixing agents; surfactant; defoamer; levelling and retarding agents; finish; diluents |
| Disperse                                                                                                                                                                                                                                                                                              | Not water-soluble                                                                                                                   | High temperature exhaust<br>Continuous     | Polyester<br>Acetate<br>Other synthetics  | 80-92                | Color; organic acids carriers; levelling agents; phosphates; defoamers; lubricants; dispersants; delustrants; diluents   |
| Reactive                                                                                                                                                                                                                                                                                              | Water-soluble, anionic compounds; largest dye Class                                                                                 | Exhaust/Beck/ Cold pad<br>Batch/Continuous | Cotton<br>Other cellulose fibers,<br>Wool | 60-90                | Color; salt; alkali; unfixed dye; surfactants; defoamer; diluents; finish                                                |
| Sulphur                                                                                                                                                                                                                                                                                               | Organic compounds containing sulphur or Sodium sulphide                                                                             | Continuous/<br>Exhaust                     | Cotton Other<br>cellulose fibers          | 60-70                | Color; alkali; oxidizing agent; reducing agent; unfixed dye                                                              |
| Vat                                                                                                                                                                                                                                                                                                   | Oldest dyes; more chemically complex; Water-insoluble                                                                               | Exhaust/Package/<br>Continuous             | Cotton<br>Other cellulose fibers          | 80-95                | Color; alkali; oxidizing agents; reducing agents                                                                         |
| Source: Best Management Practices for Pollution Prevention in the Textile Industry, EPA, Office of Research and Development, 1995; Nowden-Swan, L.J. Pollution Prevention in the Textile Industries, in "Industrial Pollution Prevention" Handbook, Freeman, H.M. (Ed.), McGraw-Hill, Inc., New York, |                                                                                                                                     |                                            |                                           |                      |                                                                                                                          |

**Printing:** Printing is a process that is used for applying color to a fabric. Unlike dyeing, it is usually only carried on prepared fabric where it is applied to specific areas to achieve a planned design. The color is applied to the fabric and then treated with steam, heat or chemicals to fix the color on the fabric. The most commonly used printing techniques are:

- Pigment printing, commonly used for all fabric types.
- Wet printing uses reactive dyes for cotton and generally has a softer feel than pigment-printed fabrics.
- Discharge printing creates patterns by first applying color to the fabric and then removing selected areas.
- Final washing of the fabric is carried out to remove excess paste and leave a uniform color.

### ***Finishing***

The finishing process imparts the final aesthetic, chemical and mechanical properties to the fabric as per the end use requirements.

Common finishing processes include:

- Wrinkle Resistant/Crease Retentive - using synthetic resins.
- Water/Oil Repellent - using silicones and other synthetic materials (e.g. fluorocarbon resins).
- Flame Retardant - most commonly carried out on synthetic fabrics, by co-polymerization of the flame retardant into the fabric itself; introduction of an additive during processing; application as a textile finish. Natural fibers such as cotton can only be made flame retardant by applying a chemical finish.
- Mildew Resistance - using hazardous substances such as mercury, copper, arsenic and chlorinated phenols (e.g. PCP).

## **2.2 Physical Characteristics of the dyeing wastewater**

The most important physical characteristic of wastewater is its total solids content, which is composed of floating matter, settleable matter, colloidal matter, and matter in solution. Other important physical characteristics include odor, temperature, color, and turbidity.

### **a) Total Solids**

Analytically the total solids content of a wastewater is defined as all the matter that remains as residue upon evaporation at 103 to 105 °C. Matter that has a significant vapor pressure at this temperature is lost during evaporation and is not defined as a solid. Settable solids are those solids that will settle to the bottom of a cone-shaped container (called an Imhoff cone) in a 60-minute period.

Settable solids, expressed as ml/L, are an approximate measure of the quantity of sludge that will be removed by primary sedimentation. Total solids, or residue upon evaporation, can be further classified as non-filterable (suspended) or filterable by passing a known volume of liquid through a filter.

### **b) Odors**

Odors are usually caused by gases produced by the decomposition of organic matter or by substances added to the wastewater. Industrial wastewater may contain either odorous compounds or compounds that produce odor during the process of wastewater treatment.

### **c) Temperature**

The temperature of water is a very important parameter because of its effect on chemical reactions and reaction rates, aquatic

life, and the suitability of the water for beneficial uses. Increased temperature, for example, can cause a change in the species of fish that can exist in the receiving water body. Industrial establishments that use surface water for cooling-water purposes are particularly concerned with the temperature of the intake water.

It should also be realized that a sudden change in temperature can result in a high rate of mortality of aquatic life. Moreover, abnormally high temperatures can foster the growth of undesirable water plants and wastewater fungus.

#### **d) Color**

Color of industrial wastewater varies according to the type of industry. Knowledge of the character and measurement of color is essential. Since most colored matter is in a dissolved state, it is not altered by conventional primary devices, although secondary treatment units, such as activated sludge and trickling filters, remove a certain percentage of some types of colored matter. Sometimes color matters needs chemical oxidation procedures for removal.

#### **e) Turbidity**

Turbidity, a measure of the light-transmitting properties of water, is another test used to indicate the quality of wastewater discharges and natural waters with respect to colloidal and residual suspended matter. In general, there is no relationship between turbidity and the concentration of suspended solids in untreated wastewater. There is, however, a reasonable relationship between turbidity and suspended solids for the settled secondary effluent from the activated sludge process. (**Industrial Wastewater Treatment Plants Inspection Manual (May 2002).**

## 2.3 Chemical Characteristics of the dyeing wastewater

### a) Organic Matter

Organic compounds are normally composed of a combination of carbon, hydrogen, and oxygen, together with nitrogen in some cases. Other important elements, such as sulfur, phosphorus, and iron, may also be present. Also, industrial wastewater may contain small quantities of a large number of different synthetic organic molecules ranging from simple to extremely complex in structure.

- **Fats, Oils, and Grease.** Fats are among the more stable of organic compounds and are not easily decomposed by bacteria. If grease is not removed before discharge of the wastewater, it can interfere with the biological life in the surface waters and create unsightly floating matter and films. The oil and grease is a very important test used to determine the hydrocarbon content of industrial wastewaters. Free O and G can be removed by flotation and skimming using gravity oil separator (GOS). However, emulsified oil is removed by Dissolved Air Flotation system after chemical de-emulsification of oil. In any case, O and G have to be removed prior biological treatment as they will clog the flow distributing devices and air nozzles.
- **Surfactants.** Surfactants are large organic molecules that are slightly soluble in water and cause foaming in wastewater treatment plants and in surface waters into which the wastewater effluent is discharged. Surfactants tend to collect at the air-water interface. During aeration of wastewater, these compounds collect on the surface of the air bubbles and thus create very stable foam.

## **Parameters of Organic Content**

### **(i) Biochemical Oxygen Demand (BOD5)**

The most widely used parameter of organic pollution applied to wastewater is the 5-day BOD (BOD5). The BOD5 is usually exerted by dissolved and colloidal organic matter and imposes a load on the biological units of the treatment plant. Oxygen must be provided so that bacteria can grow and oxidize the organic matter. An added BOD5 load, caused by an increase in organic waste, requires more bacterial activity, more oxygen, and greater biological-unit capacity for its treatment.

The determination of the BOD5 involves the measurement of the dissolved oxygen used by microorganisms in the biochemical oxidation of organic matter. Several dilutions of the wastewater are put into standard BOD5 bottles with water that has been saturated with oxygen, and contains bacteria. A control bottle is also prepared with only water and bacteria. The bottles are put into a standard incubator for five days, hence this is called the “Five-Day BOD Test (BOD5).” The difference in oxygen levels between the control bottle and the bottles with oxygen remaining is used to calculate the BOD5 in mg/L. (**Industrial Wastewater Treatment Plants Inspection Manual, May 2002**).

The limitations of the BOD5 test are as follows:

- A high concentration of active, acclimated seed bacteria is required.
- Pretreatment is needed when dealing with toxic wastes, and the effects of nitrifying organisms must be reduced.
- Only the biodegradable organics are measured.