CHAPTER 2

REVIEW OF LITERATURE

2.1 TEXTILE HISTORY

The history of textile manufacturing is almost as old as mankind. The earliest ancient textile handicrafts were nets, produced from one thread and employing a single repeated movement to form loops, and basketry, the interlacing of flexible reeds, cane, or other suitable materials. The word textile is derived from the Latin word “texere” which meant knitting weaving, spinning. The production of knitting nets has been practiced by many people in different cultures. Examples of prehistoric textiles are extremely rare because of the perishability of fabrics. The earliest evidence of weaving, closely related to basketry, dates from Neolithic cultures of about 4500 BC. Weaving apparently preceded spinning of yarn; woven fabrics probably originated from basket weaving. Cotton, silk, wool, and flax fibres were used as textile materials in ancient Egypt; cotton was used in India by 3000 BC.

2.1.1 Textile Industry

The Textile industry, probably more than any other, gave its character to the British Industrial Revolution. The cotton-textile industry was supported or supplied mainly by the Indian market. Till the middle of the 18th century the spinning and weaving processes were using simple technologies. In Europe mainly wool was used as raw material, but with the rising availability of cotton in the European markets the scenario changed. Machines for processing the cotton in large scale were invented by James Hargraves in the year 1767, which he named spinning Jenny, like his daughter.
The inventor of the first mechanical loom was Dr. Edmund Cartwright, who issued his first patent in 1785. The traditional dates of the Industrial Revolution bracket this period in which the processes of cotton manufacture in Britain were transformed from those of a small-scale domestic industry into those of a large-scale, concentrated, power-driven, mechanized, factory-organized, urban industry. The transformation was undoubtedly dramatic both to contemporaries and to posterity, and there is no doubting its immense significance in the overall pattern of European and Asian industrialization. One of the important consequences of the rapid rise of the Cotton industry was the dynamic stimulus it gave to other processes and industries.

2.1.2 Textile trade worldwide

It is encouraging to note that world clothing trade has been growing over the past two decades at an overall rate twice as fast as the world merchandise trade, with Asia having achieved a progressively larger share. In spite of long term growth, the textile industry levelled out worldwide to almost zero in 1998, following high growth in 1997, when the textile demand rose up to 6% which was twice the 3% annual average. The main textile suppliers are shown in Table 2.1.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>INDIA</td>
<td>1.67*10^9</td>
<td>INDIA</td>
<td>1.66*10^9</td>
</tr>
<tr>
<td>2</td>
<td>TURKEY</td>
<td>1.44*10^9</td>
<td>TURKEY</td>
<td>1.66*10^9</td>
</tr>
<tr>
<td>3</td>
<td>U.S.A.</td>
<td>1.38*10^9</td>
<td>U.S.A.</td>
<td>1.48*10^9</td>
</tr>
<tr>
<td>4</td>
<td>CHINA P.R.</td>
<td>1.25*10^9</td>
<td>CHINA P.R.</td>
<td>1.37*10^9</td>
</tr>
<tr>
<td>5</td>
<td>SWITZERLAND</td>
<td>1.15*10^9</td>
<td>SWITZERLAND</td>
<td>1.20*10^9</td>
</tr>
</tbody>
</table>
This slow down in growth created an excess of capacity at every level of the industry, and prices for fabrics and yarns fell dramatically. In addition, the fluctuation of exchange rates created winners and losers; South Korea improved its competitive edge, as did Indonesia, making Chinese exports more expensive relative to other Asian suppliers. Textiles from Asia were priced low, which caused textile mill activity to remain flat in Western Europe and increase only slightly in North America. Although most parts of Asia experienced a rise in exports, local demand was weak, resulting in a reduction in overall textile activity; production also fell in the Middle East. China registered a slight increase in production, and India boosted its output. In such a volatile market, retailers tried initially to increase their profit margins by buying in volume, but competition rose for them, too, resulting in lower prices for the consumer. In 1998, 48,600,000 metric tons of textiles were produced, including 1,600,00 metric tons of wool, 19,200,000 metric tons of cotton, and 27,800,000 metric tons of manufactured fibres.

2.1.3 Textile trade and processing in India

The textile trade in India has a very old tradition reaching back even before the times of Alexander the Great who found great interest in Cotton from India. The textile industry contributes one fifth of the total value of industrial production. The growth rate over the last decades was encouraging. The economic liberalisation boosted the business and at the same time forced the industry to become more competitive. At present India has more than 1504 spinning units, over 278 composite mills and around 1.49 Million registered looms (Appasamy 2000). The textile exports from India increased substantially over a period of fifteen years as shown in Figure 2.1.
Chennai, has established itself as India’s leading knitwear centre producing 85-90% of India’s knitwear (hosiery) for exports in the so-called “Banian-City” (T-Shirt-City). 700 bleaching/dyeing units, processing 15,000 t/month cotton knitted material, dominate the city. They can be divided into small, middle and large-scale units according to their daily production:

- Small < 1,000 kg/d
- Middle 1,000-3,000 kg/d
- Large > 3,000 kg/d

This is to state that only 5 among them belong to the large-scale units.

Figure 2.1 Values of Textile Exports from India (in Mio. EURO)

Tirupur, situated in Tamil Nadu (South India), 450 km south-west of Chennai, has established itself as India’s leading knitwear centre producing 85-90% of India’s knitwear (hosiery) for exports in the so-called “Banian-City” (T-Shirt-City). 700 bleaching/dyeing units, processing 15,000 t/month cotton knitted material, dominate the city. They can be divided into small, middle and large-scale units according to their daily production:

- Small < 1,000 kg/d
- Middle 1,000-3,000 kg/d
- Large > 3,000 kg/d

This is to state that only 5 among them belong to the large-scale units.
This industrial progress brought economic benefits as depicted in Figure 2.2, but it also made its own demands on the environment.

2.2 THE TEXTILE PROCESS AND ITS ENVIRONMENTAL IMPACTS

A textile mill is generally defined as an industrial production plant which processes materials which can be spun, such as fibres, threads, yarns, twines, fabrics, knitted fabrics, fleeces, felts, and synthetic skins (dry processes). The clothing industry further processes the majority of products from the textile industry, but this environmental study considers only the Textile Processing Industry (TPI). The Textile processing industry's diverse operations have significant impacts on the local environment. In order to give an overview about the textile processing steps and their impact on the environment the Tirupur example is taken, and the textile chain is given in Figure 2.3.

Figure 2.2 Growth rates of Exports from Tirupur (Value in Mio. EURO)

Figure 2.3 The textile chain modified according to Schoenberger (1999)
This doctoral thesis takes a deeper look into the industrial textile processes and their environmental impacts and relates emissions (pollution) to the individual process providing the basis for waste segregation and integrated environmental management approaches.

Table 2.2 Emission benchmarks of the textile industry Schoenberger (1999)

<table>
<thead>
<tr>
<th>Consumption or Emission type</th>
<th>Factor</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water consumption</td>
<td>260.000</td>
<td>L/to</td>
</tr>
<tr>
<td>Wastewater flow</td>
<td>240.000</td>
<td>L/to</td>
</tr>
<tr>
<td>Total energy consumption</td>
<td>8000</td>
<td>kW/to</td>
</tr>
<tr>
<td>Consumption of electricity</td>
<td>1900</td>
<td>kW/to</td>
</tr>
<tr>
<td>Reactive dyestuff consumption</td>
<td>17.8</td>
<td>kg/to</td>
</tr>
<tr>
<td>Consumption of Textile Auxiliaries</td>
<td>184</td>
<td>kg/to</td>
</tr>
<tr>
<td>Consumption of basis chemical (without neutral salts)</td>
<td>105</td>
<td>kg/to</td>
</tr>
<tr>
<td>Consumption of neutral salts (NaCl and NaSO₄)</td>
<td>395</td>
<td>kg/to</td>
</tr>
</tbody>
</table>

In the thesis a own small scale pollution load assessment was done and compared with the benchmarks from other studies (see Table 2.2).

2.2.1 Textile Garments / Dry processes

2.2.1.1 Raw materials

The harvesting of raw material either by farmers who raise cotton, sheep, silkworms, or flax or produce synthetic fibres with chemical processes earmarks the initial stage of textile manufacturing. The cotton fibre must be processed to be made ready for the spinning plant. Raw cotton is put through the cotton gin, which removes seeds and other impurities, before the fibre is shipped in bales to the spinning mil
2.2.1.2 Cotton

Although cotton is the most common textile fibre now in use, it was the last natural fibre to attain commercial importance. In the 5th century BC the Greek historian Herodotus reported that among the valuable products in India there was the wild plant that bears fleece as its fruit. In the following century Alexander the Great introduced cotton from India into Greece. Although the early Greeks and Romans used cotton for awnings and sails as well as for clothing, it was not adopted for widespread use in Europe until centuries later (Fischbach 2000).

India has more than 9 Million hectares under cotton cultivation. Perennial cotton have a yield potential that is 10 to 20 times greater than the average yield of India’s cotton crop – which at present is about 250 kg per hectare. While India is the third largest producer of cotton in the world, it ranks 51st in per acre yield. However, per acre yields have remained stagnant for years. At present, cotton cultivation takes just five per cent of the agricultural area in India but accounts for almost 55 per cent of the annual pesticide usage in India, which causes groundwater pollution.

Cotton consists of Cellulose. Cellulose is one of the main cell wall constituents of all major plants. Cotton is almost pure cellulose, a linear polymer of D-glucose units (Cellulose) as in Figure 2.4.

![Figure 2.4 Empirical formula of cellulose (C₆H₁₀O₅)ₙ](image_url)
Cellulose is hygroscopic & absorbs under normal atmospheric conditions (20°C, 60% relative humidity) approx. 8-14% water. Cotton, being a natural fibre, contains amongst 88-96% of cellulose and 2-5% of Hemi cellulose also impurities such as 0.7-1.2% pectins, 0.4-1% waxes, 1.1-1.4% proteins, 0.7-1.6% ashes and 0.5-1.0% other organic compounds. These constituents can be removed if they interfere with the intended further processing, with procedures, causing water pollution in terms of pH, COD, BOD and TDS.

2.2.1.3 Fibre Processing Spinning

The fibre is spun into yarn, which is then processed into fabric in a weaving or knitting mill. Only twisting is required to process filament fibre into yarn, but staple fibres must be carded to combine the fibres into a continuous rope like form, combed to straighten the long fibres, and drawn out into continuous strands, which are then twisted to the desired degree, producing hosiery and crepes. The finished yarns are today supplied to the subsequent processing stages in the form of so-called cheeses, i.e. bobbins weighing between 0.8 and 3.5 kg.

Textiles, like shirts, skirts, shorts, suits, coats, capes, cloaks, pyjamas, dresses or trousers are made of woven fabrics, natural and synthetic filaments, yarns, and threads as well as woven, knitted, felted, tufted, braided, bonded, knotted, and embroidered. In Tirupur the focus lies on knitted cotton.

2.2.1.4 Weaving and knitting

Of these textile production techniques, weaving is by far the most important. It involves the production of a fabric from a set of threads aligned in one direction, called the “warp”, by interlacing “weft” threads at right angles to it. Considerable technical improvements have been made to the looms used for this purpose in the last twenty years, resulting in a marked increase in productivity.
Unlike woven goods, knitted products have only one thread system, i.e. the threads, which are made into a mesh, run diagonally or longitudinally. The items are produced on linear or circular knitting or hosiery machines or warp knitting machines.

Knitting, which originated with the knotting of fishnets and snares by ancient peoples, is the craft of forming a fabric by the interlocking of yarn in a series of connected loops by means of hand or mechanized needles. Modern machines are capable to shape the heels and toes of hosiery; Automatic-knitting machines were first introduced in 1889. The main threat to the workforces is the noise pollution and dust emission in the process of spinning, weaving and knitting.

2.3 WET PROCESSES IN THE TEXTILE PROCESSING INDUSTRY (TPI)

The textile processing industry (TPI) is characterized by its fairly high specific water consumption and its large amount of wastewater discharges (see Table 2.3). The specific wastewater discharge, for example, varies, according to the production method between 40 m$^3$ and 300 m$^3$ per ton of substrate. Therefore the textile processing industry is rated among the highly water intensive industries. This industry is not only characterised by the vast quantity of water consumed, but also by the variety of organic and inorganic chemicals, which are involved in the finishing processes. Emissions of the TPI are rated among different industries as comparatively high. Among the emissions the wastewater residuals are dominating, containing about 80% of organic chemicals and 90% of the inorganic compounds. The remaining part of the organics is emitted as off gases (10%) and solid wastes (10% as mainly sludge from the effluent treatment). Within the solid waste about 10% of the inorganic compounds are included. Because the wastewater pollution dominates the overall emissions this study is focussed on the TPI effluents.
Table 2.3 Processwise water consumption in a typical industry (CPCB 1999)

<table>
<thead>
<tr>
<th>Process</th>
<th>Cloth processed (kg/day)</th>
<th>Water consumption m³/day</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desizing</td>
<td>4400</td>
<td>25</td>
<td>4.5</td>
</tr>
<tr>
<td>Kiering</td>
<td>6,640</td>
<td>95</td>
<td>17.0</td>
</tr>
<tr>
<td>Bleaching</td>
<td>2,640</td>
<td>110</td>
<td>19.6</td>
</tr>
<tr>
<td>Scouring</td>
<td>4,400</td>
<td>125</td>
<td>22.3</td>
</tr>
<tr>
<td>Mercerising</td>
<td>1,760</td>
<td>15</td>
<td>2.7</td>
</tr>
<tr>
<td>Printing</td>
<td>2,420</td>
<td>80</td>
<td>14.3</td>
</tr>
<tr>
<td>Dyeing</td>
<td>1,760</td>
<td>25</td>
<td>4.5</td>
</tr>
<tr>
<td>Soaping</td>
<td>1,760</td>
<td>30</td>
<td>5.3</td>
</tr>
<tr>
<td>Others</td>
<td>-</td>
<td>15</td>
<td>27</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>-</strong></td>
<td><strong>560</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

The main steps of the unit processing are a combination of treatment processes, which are shown in Figure 2.5 with the respective flow-streams of water and effluents.

Figure 2.5 Wet processing steps with in and outflow of water and chemicals
Tirupur’s natural resources like water bodies and soil are mainly endangered by the effluents of local dyeing industries. Therefore the research carried out focuses more on the wet processes, with the input of salt, dyes, chemicals and on the related wastewater amounts and characteristics.

2.3.1 Sizing (slashing) and Desizing

One particular feature of the production of woven fabrics is sizing. For certain articles one of the two thread systems, the warp, must be protected by a kind of glue coating, which involves “sizing” (soaking, coating) with starch, cellulose derivatives or other seizing agents such as polyvinylalcohol (PVA) in order to give the required tensile strength and smooth for the weaving process. Cotton yarns woven on high-speed looms or yarn blends with a high proportion of synthetic fibre must be sized with sizing formulations that contain carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA), or polymeth-acrylates to improve the sizing effect. The water required for sizing varies from 0.5-8.5 Litre per kg of yarn. The effluent has a pH of 7.0-9.5 and a TDS of 8,500-22,500 mg/L contributing 650-2,500 mg/L of BOD to the effluent, which is in fact a major source of the BOD load. Its wastewater would provide an ideal carbon source but the different unit processes are often found to be in different locations done by separate companies. In Tirupur the readymade knitwear/hosiery is used as raw material for the bleaching and dyeing process. The unit investigated in this study used non-biodegradable paraffin coatings for their threads.

2.3.2 Desizing

Acids or enzymes are used for the removal of starch, cellulose derivatives or other sizing agents such as polyvinylalcohol PVA that is called desizing. The process itself is usually carried out by acid or enzymatic desizing. Enzymatic deseizing is most economical and safe, the CPCB does not recommend enzymes, for unspecified reasons (Central Pollution Control Board 1990). Enzymes are biocatalysts
and there are three types of enzymes: bacterial, malt and pancreatic. The enzyme activity is influenced by the presence of salt - for full activity, sodium chloride must be present. Malt bacterial enzymes require the presence of calcium for full activation. Acid de-sizing means that the fabric is padded with diluted hydrochloric acid or sulphuric acid and stored for an hour. It subsequently undergoes several hot and cold washes and final neutralization. 2.50 –21.0 L/kg of water per kilogram of textile are required for this unit process with an average of 12.0 L. The entire water consumed during this process is discharged as effluent and contains 16,000-32,000 mg/L of Total solids and contributes 1,700-5,200 mg/L of BOD to the effluent. Modern plants in Europe recover the PVA by using ultra filtration (UF) membrane technologies. Apart from PVA, which is costly, in India still starch- or cellulose-derivates are common. In the case of knitwear the paraffin is removed with detergents separately or within the scouring process.

2.3.3 Scouring, Kiering

Scouring, Kiering is the process of removing impurities such as greases, waxes and/or fats from the fibre. This can either be done through conventional methods (kier boiling) or through modern continuous processes known as scouring. Souring and Kiering liquor is an alkaline solution containing caustic soda, soda ash, sodium silicate and sodium peroxide with small quantities of detergents viz. organic tensides. When applied to raw/grey textile goods, scouring removes substances that have adhered to the fibres during production of the yarn or fabric, such as oils, grease, dirt and any sizing or lint applied to warp yarns to facilitate weaving. The water required for the unit process is varying from 20-45 L/kg of knitted fabric. The effluent amounts almost to the same quantity and contains 2,200- 17,400 mg/L of TS as well as 100-2,900 mg/L of BOD at a high pH of 10-13.
2.3.4 Mercerising

Mercerising is a process to increase the lustre (enhancing appearance). It involves the immersion of the textile under tension in caustic soda (sodium hydroxide) mostly applied for cotton fabrics. The process, which may be applied at the yarn or fabric stage, involves immersion under tension in a caustic soda (sodium hydroxide) solution, which is later neutralized in acid. The treatment produces permanent swelling of the fibre. The water required by this process varies between 15-30 L/kg. The effluents have a pH of 12-13 and a TDS of 11,000-32,000 mg/L as well as a low BOD contribution of 100-300 mg/L. Modern mercerisation plants recover the caustic soda either by evaporation or membrane technology, which is a very vital cleaner production step reducing the TDS considerably. Mercerising is optional and does not take place in any process cycle.

2.3.5 Bleaching

For removing the natural colour and render the textile white, a unit process called bleaching, which chemically means oxidising the tan of linen, is applied. Chemical bleaching is usually accomplished by oxidation, destroying colour by the application of auxiliary chemicals, according to the chemical composition of the fibre. Cotton and other cellulose fibres are usually treated with heated alkaline hydrogen peroxide or hypochlorite. Cottons are frequently scoured and bleached by a continuous system. For bleaching yarn through either hydrogen peroxide or hypochlorite the same amount of water of 24-32 L/kg is required. For cloth bleaching the water required fluctuates between 40-48 L/kg of textile. The effluent amounts to almost the same volume of wastewater and contains Total dissolved solids up to 22,000 mg/L and SS of up to 6,500 mg/L at a pH of 6 in the case of hypochlorite bleaching. In hydrogen peroxide bleaching on one hand the pH has to brought up to 10.5 to enhance the reactivity, but on the other the TDS is considerable lower compared to the hypochlorite unit process with values of approximately 450 mg/L SS and 2,500 mg/L TDS.
2.3.6 The Dyeing Process

The dyeing and printing processes are to be found in the middle of wet processing. Textiles may be dyed in a number of ways: Dyeing is a process or combination of processes which is performed to give a reasonably permanent change in the appearance of textile raw materials like fibres, yarn or cloth and to receive special care qualities and wearing comforts. The fabrics can be dyed after knitting is completed (piece-dyed), the loose fibres can be dyed in a vat (stock-dyed), or the yarn or filament can be dyed before knitting is begun (yarn-dyed). The process of dyeing cellulose requires the presence of a base (e.g., sodium carbonate or sodium hydroxide) together with an electrolyte, usually sodium chloride or sodium sulphate, which increases the fixation yield. The optimal dyeing temperature and pH is a function of the dye’s anchor system. Thus, the optimal temperature for a “cold dye” is approximately 30–50°C, whereas that for a “hot dye” is approximately 70–98°C. Reactive dyes were developed for industrial application in 1956.

2.3.7 Dyes

Technically the chemical dye production was initiated after Runge isolated aniline from coal tar and observed the formation of aniline black on oxidation in 1834. The first synthetic dye of technical significance, called Mauveine after its mauve colour, was obtained in 1856 by Perkin in an attempt to synthesize quinine. In 1862 Griess created the azo dye chemistry with the discovery of diazo compounds (Cliffe 1958). Among the earliest azine dyes were indulines in 1863 and nigrosine in 1867. The first synthesis of an anthraquinone dye was that of alizarin in 1868. Progress became very rapid with the advent of structural organic chemistry; many thousands of dyes were synthesized within a few decades. Large chemical plants in operation in Germany and Switzerland today were built as dye factories in the second half of the 19th century. The manufacture of dyes has spread from Europe throughout the world; Western Europe still accounts for approx. 40% of the worldwide total.
Dyeing processes of different materials require various dyes. They can be classified by their chemical structure and application in the following groups as shown in Table 2.4.

<table>
<thead>
<tr>
<th>Class</th>
<th>Properties</th>
<th>Chemical Structure</th>
<th>Application</th>
<th>Substantivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Dyes</td>
<td>Water-soluble, anionic</td>
<td>Azo (incl. premetallized chromium complexes), anthraquinone</td>
<td>WO, PA, SE</td>
<td>85-98</td>
</tr>
<tr>
<td>Basic Dyes</td>
<td>Water-soluble, cationic</td>
<td>Triphenylmethane, methine, modified azo, anthraquinone</td>
<td>PAN, modified synthetics</td>
<td>97-98</td>
</tr>
<tr>
<td>Direct Dyes</td>
<td>Water-soluble, anionic</td>
<td>Azo, stilbene, phthalocyanine</td>
<td>CO, CV, LI</td>
<td>64-96</td>
</tr>
<tr>
<td>Pigments</td>
<td>Water-insoluble, non-ionic</td>
<td>Azo, anthraquinone, phthalocyanine, quinacridone</td>
<td>all</td>
<td>100</td>
</tr>
<tr>
<td>Disperse Dyes</td>
<td>Water-insoluble, non-ionic</td>
<td>Azo, anthraquinone, nitro</td>
<td>PES, CA, CTA, PA</td>
<td>88-99</td>
</tr>
<tr>
<td>Reactive Dyes</td>
<td>Water-soluble, anionic, forms covalent bonds with substrate</td>
<td>Azo (incl. premetallized), anthraquinone, phthalocyanine</td>
<td>CO, CV, LI, WO, SE</td>
<td>55-95</td>
</tr>
<tr>
<td>Sulphur Dyes</td>
<td>Temporarily solubilized with alkali sulphide</td>
<td>Sulphur</td>
<td>CO, CV</td>
<td>60-70</td>
</tr>
<tr>
<td>Vat Dyes</td>
<td>Temporarily solubilized as leuco ester with alkaline sodium hydrosulphate</td>
<td>Anthraquinone, indigoid</td>
<td>CO, CV, LI, (SE)</td>
<td>75-95</td>
</tr>
</tbody>
</table>

CA = Celluloseacetate    PA = Polyamide
CO = Cotton             PAN = Polyacrylnitri
CTA = Cellulosetriacetate PES = Polyester
CV = Viscose             SE = Silk
LI = Linen               WO = Wool
The substantivity is a mean to measure the exploitation of the applied dye. It is expressed by the ratio of dye concentration in the fibre \( c_{F,L} \) to dye concentration in the watery solution \( c_{F,L} \) as per the following Equation 2.1.

\[
S = \frac{c_{F,L}}{c_{F,L}}
\]

(2.1)

In Tirupur mainly reactive dyes are applied to dye cotton material.

**Acid dyes** are water soluble anionic dyes mainly applied for Wool (WO) and Polyamide (PA), but can be found in the leather and silk processing as well. **Basic dyes** are water-soluble cationic dyes mainly applied on acrylic fibres (such as PAN).

**Direct dyes** are substantive to cellulose without a mordant; historically they replaced naturally occurring mordant dyes. Direct dyes are the most important single class, and are simple to use. Optimum conditions vary, but dyeing is usually carried out at or near the boiling point in the presence of common salt or Glauber’s salt; the ratio of liquor to goods is fairly high (typically 20:1 in fabric-dyeing machinery).

Dyes are colouring agents that are soluble in the application medium. **Pigments** and dispersed dyes are defined as inorganic or organic, chromatic or achromatic colouring agents (that are practically insoluble in the application medium) employed in a medium such as a paint or polymer (Patton 1973). Physical properties such as crystal form, tinctorial strength, transparency, and rheology are much more important than with water-soluble dyes. As with textile dyes, the azo chromophore predominates, supplemented by phthalocyanine blues and greens and quinacridone reds where the highest fastness is required. Although azo pigments can, in principle, be produced in all colours, yellow, orange, red, and brown shades are the most important in practice.
Disperse dyes are colourants with low water solubility that, in their disperse colloidal form, are suitable for dyeing and printing hydrophobic fibres and fabrics. Disperse dyes give positive results on cellulose acetate, but not on wool or cotton. Since 1950, the production of disperse dyes has increased sharply, closely following the growth in worldwide production of synthetic fibres, especially polyester.

Reactive Dyes offer brighter shades of higher wet fastness than direct dyes. Batch wise application resembles dyeing with direct dyes ("salting" onto the fibre from hot aqueous solution) but is followed by alkaline treatment to fix the dye on the fibre by a chemical reaction with the hydroxyl groups of the cellulose.

Vat dyes are more expensive than direct or reactive dyes, but are used when the highest light fastness is required, for example, for home-furnishing fabrics. They are applied from an aqueous solution of the leuco dye (vatting stage) obtained by alkaline reduction with sodium hydrosulphite (dithionite). Oxidation reforms the insoluble dye within the substrate. Subsequent treatment in a boiling detergent solution gives maximal fastness. Vat dyes are also used in pigment form.

Sulphur dyes are applied similarly to vat dyes, with the dye being dissolved by sodium sulphide reduction; sodium carbonate may also be present. Dichromate is commonly used as an oxidant. This process obtains dull brown to black shades cheaply but fastness properties are modest. However the use of sulphide creates environmental problems. In Tirupur mainly reactive dyes are applied to dye cotton material. As a consequence this study just deals with the function and application of reactive dyes.

2.3.8 Reactive dyes

Most reactive dyes have azo groups as part of their chromophore group. The dye molecule contains furthermore specific reactive groups, which commonly consist
of fluorine (F), chlorine (Cl) or sulpho-groups (SO$_3^2$), that can undergo addition or substitution reactions with the –OH, –SH, and –NH$_2$ groups present in textile fibres. Reactive structures possess a bridge group B (most commonly consisting of NH-bonds), connecting the structure with the chromophoric part. Sulpho-groups (SO$_3^2$) make the dye water-soluble (Rouette 1995).

Reactive dyes are often classified according to the number of reactive systems they contain, leading to the terms mono-, double-, and multiple-anchor dyes. On the world market, the first two categories are of greatest importance; multiple-anchor dyes (those with three or more reactive groups) play a more minor role. (Heslop et al 1957).

The basic chemical structures of most mono-anchor dyes are derivatives of cyanuric chloride (2,4,6-trichloro-1,3,5-triazine), a molecule of wide synthetic potential because the three chlorine atoms on the triazine ring differ in their reactivities. These very reactive dyes are sensitive to hydrolysis, and a suitable buffer is usually added to the powdered dye to increase its stability. In addition to the 1,3,5-triazines, other classes of heterocycles having economic potential are dichloroquinoxalines (Levafix E) and dichlorophthalazines (Elisian), both shown with their chemical structure in Figure 2.6.

![Figure 2.6 Examples of heterocyclic reactive dyes](image-url)
A reactive group that has had the greatest impact on the market is the 2-sulfooxyethylsulfonyl (Remazol) group (Heslop 1962), (Sommer 1958). Treatment with alkali of dyes containing this reactive group causes the elimination of sulphuric acid to form a vinylsulfonyl moiety that reacts with cotton to give a dye–fibre bond (Zimmermann 1958). Describing this as an elimination–addition reaction is not meant to rule out the possibility that the nucleophile attacks the β-carbon directly, without intervention of a vinyl intermediate (Rath 1972).

Double-anchor dyes can be divided into two categories: those containing two equivalent reactive groups, and those with mixed-anchor systems (see Figures 2.7 and Figure 2.8). The synthetic approach to these compounds makes it possible to combine two different chromophores in a single system, opening the way to certain colour shades that are not easily accessible via a single chromophore (Tappe et al 1999).

![Figure 2.7 Example of dyestuff with two chromophores](image)

Other significant developments included the introduction of multiple-anchor dyes fluorotriazine-containing reactive dyes and fluorotriazine-containing multiple-anchor dyes (Waring 1990), (Venkataraman 1972).

Multiple-anchor systems in reactive dyes were first described by ICI in 1959 (Renfrew 1990). An example is Remazol Black B, which not only displays a high degree of fixation but is also accessible by a synthetic route that is both simple and economical.
The development of reactive dyes has continued to be rapid, and the world demand reached approx. 97,000 tonnes in 1990, valued at approx. $4 \times 10^9$ DM (1 DM = 1.96 EURO). Reactive dyes thus constitute the largest of the textile dye classes on a monetary basis, accounting for approx. 17% of the textile dye market by volume. The most important distinguishing characteristic of reactive dyes is that they form covalent bonds with the substrate that is to be coloured during the application process (see Figure 2.9). Two different reaction mechanisms between fibre and dye exist for the dyeing of cellulose. In alkaline environment the reactive groups react with the hydroxyl group of the substrate to form an ester- or ether-bond by substitution or addition reactions.

- **Substitution reaction (ester bond):**

  ![Substitution Reaction](image)

- **Addition reaction (ether bond):**

  a) \( R\text{-SO}_2\text{-CH}_2\text{-CH}_2\text{-OSO}_3^- + \text{NaOH} \rightarrow R\text{-SO}_2\text{-CH}_2\text{-CH}_2\text{-OH} + \text{HSO}_4^- \)

  b) \( R\text{-SO}_2\text{-CH} = \text{CH}_2 + \text{HO} \rightarrow R\text{-SO}_2\text{-CH} = \text{CH}_2\text{-O} \)

  ![Addition Reaction](image)

**Figure 2.8 Examples of two anchor system reactive dyes**

**Figure 2.9 Reaction mechanisms of reactive dyes**
A concurrent reaction occurs between water and dye. In alkaline dye baths near the reactive groups of the dye there are found not just fibre-hydroxyl-groups but also dissolved hydroxyl-groups. The latter also react with the dye. The thus inhibited hydrolysed dye cannot migrate into the fibre. Consequently it has to be removed by rinsing procedures so as not to fade out later. This hydrolysis causes a loss of 5-45% of dye, which is discharged, with the effluent of a dyeing unit (Schulze-Rettmer et al 1999).

2.3.9 Neutral Salts

The main salt used in the dyeing process is Sodium Chloride (NaCl), a crystalline compound, found abundantly in nature, that has widespread use as a food seasoning or preservative. It is sometimes called common, or table, salt to distinguish it from a class of chemical compounds called salts. Common salt is one of the most basic substances used by humans. It’s constituents sodium and chloride ions are essential nutrients. In addition, saltiness constitutes one of the four fundamental taste sensations. Because of its properties as a preservative and seasoning, salt has always been one of the most highly prized minerals. In the leather industry animal skins and hides are pickled in salt before being processed. It is indispensable in the manufacture of chemicals as hydrochloric acid, sodium hydroxide (caustic soda), sodium bicarbonate (baking soda), chlorine, and many other chemicals. Water-softening equipment uses salt, which exchanges sodium ions for those of calcium and magnesium in the water being treated. The economic importance of salt is indicated by the existence, even in the present day, of taxes on salt and of government salt monopolies. In fact the world salary is derived from the Latin salarium, which originally referred to the payments made to Roman soldiers for the purchase of salt. In the dyeing process salt is added in order to enhance the fixation of the dyestuff to the fibre and according to the shade desired, the colour yield varies with the salt concentration as shown in Figure 2.10.
Small (~10% w/w) amounts of Sodium Sulphate, also called Glauber Salt (Sodium sulphate decahydrate Na$_2$SO$_4$·10 H$_2$O) are added to the total salt dosage. In such cases, treatment of the wastewater by a membrane process (Gatea 1986) may involve an additional precipitation process (Walhalla-Kalk 1990).

### 2.3.10 Textile Auxiliaries (TA)

In addition to the dyes and salts other textile chemicals are used for dyeing. Several other organic and inorganic chemicals are used as textile auxiliaries in order to support the wet-processes. The dyeing auxiliaries form a very heterogeneous group of chemicals. Though many of them are surfactants, there are many other types, including inorganic compounds, water-soluble polymers and oligomers, polymer dispersions, and solubilizing agents. Most commercial dyeing auxiliaries are preparations containing several components. Consumption of dyeing auxiliaries is estimated at 60–70% of the consumption of the dyes themselves. Textile auxiliaries enhance the fixation processes. Different dyeing auxiliaries are added for dye solubilizing, or as carriers to accelerate the migration of the dye into the fibre or post-
treatment agents for fastness improvement (Rouette 1995). Prior to the dyeing caustic soda (NaOH) is added to liberate the reactive group by hydrolysis (Schulze-Rettmer 1999). Neutral salts are added as electrolytes to enhance the dye uptake and to increase the substantivity (Sosath 1999). After approximately 3 rinsing processes acetic acid is added to bring the pH-value from 13 to neutral. Further rinsing and washing procedures including fixation follow.

Table 2.5 gives an overview of usually applied chemicals in the textile process. (Central Pollution Control Board 1999).

**Table 2.5 Usually applied chemicals (TAs) in the textile process**

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalis, mineral acids, natural salts and oxidising agents</td>
<td>Relatively harmless inorganic pollutants</td>
</tr>
<tr>
<td>Starch sizes, vegetable oils, fats and waxes, biodegradable surfactants, organic acids and reducing agents</td>
<td>Readily biodegradable, moderate to high BOD</td>
</tr>
<tr>
<td>Dyes and fluorescent brighteners, fibres and polymeric impurities, polyacrylate sizes, synthetic polymer finishes and silicones</td>
<td>Dyes and polymers difficult to biodegrade</td>
</tr>
<tr>
<td>Wool grease, PVA sizes, starch ethers and esters, mineral oil, surfactant resistant to biodegradation, anionic and non-ionic softeners</td>
<td>Difficult to biodegrade, moderate BOD</td>
</tr>
<tr>
<td>Formaldehyde and N-methylol reactants, chlorinated solvents and carriers, cationic retarders and softeners, bio-tensides, sequestering agents, heavy metal, salts</td>
<td>Unsuitable for conventional biological treatment, negligible BOD</td>
</tr>
</tbody>
</table>

There are thousands of textile auxiliaries available in India and each company uses different Textile auxiliaries (TA). Finally unfixed dyes end up in the effluents of the dyeing units together with these TAs.
2.3.11 Dyeing technology

There are three major variants of the dyeing procedure for reactive dyes. The dominant method is still the *discontinuous exhaust dyeing*, but the *semi continuous pad-batch*, and the *continuous procedure* gaining in importance.

Dyeing technology can be divided into three different processes:

I Stagnating material and moving dye bath
II Moving material stagnating dye bath
III Moving material moving dye bath

Dyeing is done in watery media, which has dissolving and carrying functions for the dye (Fries 1990). The first principle is generally applied for yarn and synthetic fibre/textile dyeing. The second principle one of moving material stagnating dye bath is applied in jiggers (used for mixed textile which tend to wrinkle) and open winches which is normally a batch procedure.

2.3.11.1 Open Winches

Dyeing methods are characterised by the liquor ratio (LR). The liquor ratio describes the ratio between the textile substrate and the liquid phase. A liquor ratio of 1:10 signifies that 1 kg textile is dyed within 10 L of water. The higher the liquor ratio, the higher the specific effluent volume (referring to the amount of substrate). The liquor ratio in winches is typically high ranging from 1:15 up to 1:40. The concentration of dye in these non-continuous processes is in the range of 0.1-10 g/L.
2.3.11.2 Over/soft-flow machines

Material moving and dye bath moving techniques belong to the group of overflow, soft-flow, roto- or soft-stream processes. In these machines the textile fabric is transported through the pumped dye bath with speeds from 300 up to 600 m/min. They are often fully automated, providing temperature, time, flow rate and other process control, which enhances the reproducibility and increases the quality of the dyeing process. The liquor ratio is generally lower than in winches ranging from 1:3 up to 1:15. One over/soft-flow machine with 100% Addition Tank/Self Cleaning Filter is shown in Figure 2.11 (compliment copy from the Thies Company).

![Diagram of Eco Soft Plus 140°C machine, liquor ratio 1:5 to 1:6](image)

**Figure 2.11 Eco Soft Plus 140°C machine, liquor ratio 1:5 to 1:6**

The machine is suitable for most knit and woven fabric producers and commonly used in Tirupur.
The list of technologies pointing out only the most common machine in Tirupur cannot be complete because there are a variety of technologies available which all can be found in the other areas/fields in the practice.

2.3.12 Finishing

2.3.12.1 Drying

Water, used in various phases of textile processing, accumulates in fabrics, and the excess moisture must eventually be removed. Because evaporative heating is costly, the first stage of drying uses mechanical methods to remove as much moisture as possible by hydro extraction using centrifuges or a continuous method employing vacuum suction rolls. Any remaining moisture is then removed by evaporation in heated dryers. Various types of dryers operate by conveying the relaxed fabric through the chamber while festooned in loops, using a frame to hold the selvages taut while the fabric travels through the chamber, and passing the fabric over a series of hot cylinders. Because over drying may waste energy and produce a harsh hand, temperature, humidity, and drying time require careful control.

2.3.12.2 Finishing

The finishing process imparts the final aesthetic, chemical and mechanical properties to the fabric as per the end use requirements. Several finishing methods have been developed to improve the feel, drape, anti-static, anti-shrinking, anti-crease, water repelling and flame retarding properties of the fabric.

The finishing can be broadly classified into two categories

- mechanical finishing
- chemical finishing

The finished can be further classified as

- permanent finish
- non-durable finish
In addition to the major pollutants textile processing operations typically include the use of several non-process chemicals such as machine cleaners, shop chemicals, biocides, insecticides and boiler treatments are washed into effluents. Such constituents are rarely controlled. If any of these non-process chemicals enters the waste stream it increases the pollution load of the total effluent. In addition, process chemicals such as dyes, oils, surfactants and other substances can enter the effluent stream through spillage, leakage; clean up (drums, tanks), out of batch chemical dumping and poor housekeeping.

2.3.13 Product

2.3.13.1 From the manufacturer to the retailer to the Customer.

After dyeing, finishing and drying the knitted material is ready for delivery to a manufacturer who is designing and stitching the clothes and from there to a retailer, who sells it to the customer, who receives the manufactured finished textile for approx. 300-1,000,- Rs/kg. The share of the different stages of the production rises the closer it comes to the consumer. The farmer gets the smallest amount. While India is the third largest producer of cotton in the world, it ranks 51st in per hectare yield. This is despite steeply rising input costs, which have meant higher risks in case of crop failure. The Textile finishing units especially the wet processes carry also many risks of process and product quality and do have environmental constrains, but for the wet processing only approximately 45-65 Rs/kg can be earned. This figures indicates that the wet processing is not providing large profit margins. It is known that wet processing is very labour intensive and bears many risk as well. Exporters and retailers dominating the trade, controlling the prices in the market, make the main profit. The burden to make these processes environmental friendly lies with the processing units, but unless the environmental measures are later on paid to the retailers from exporters (ultimately by the customers) environmental protection will not be promoted in a broader sense.
2.4 CLEANER PRODUCTION

The Textile industry is a high water consuming industry and in most of the cases there is scope for further improvements in the field of cleaner production. Pollution prevention measures are used to explore the possibilities of cleaner production processes so as to generate only the smallest possible amount of waste. If pollution avoidance, recycling and treatment are carefully chosen, then there should be a little residue requiring treatment and disposal. In order to manage even this small waste generated, it becomes necessary to select the treatment strategy. Nevertheless, treatment and disposal must be carried out keeping in mind the possible environmental impacts as well as safety to the workers and the neighbouring community.

The Indian textile industries are often facing though competition in the world market and more and more the International Standardisation Organisation ISO certification becomes mandatory for them, so many units started to introduce cleaner production measures.

2.4.1 CP-Principle

The CP – principle shown in Figure 2.12 is simple but its application/implementation continues to be a challenge.

![Figure 2.12 Cleaner production principle](image)
CP processes are applicable in all industries where energy is consumed and wastes are produced. For its practical application it means to conduct an environmental audit including a waste stream/flow survey. This is done in three steps: First a process flow diagram indicating sample points is drafted, which is followed by a sampling and analysis plan and consequently a flow and material balance diagram is drawn up. Evaluating the statistical variation of waste characteristics and explore recycle or reuse options (cooling water reuse, wash etc.) is the final task.

2.4.2 Environmental benefits and Economic benefits

With the CP – procedures pollutants are reduced or even removed. This reduction ultimately leads to the protection of the environment and the implementation of cleaner production measures is often easier than the introduction of end of pipe treatment and disposal technology, which are considered as cost factors. Cleaner production can start with cost reduction in the production, instead.

Many of the activities within the CP –production audit lead to cost reduction and savings with reasonable return on investment periods. Recycling of materials reduces the amount of raw material necessary and saves money.

There are several pollution prevention (source reduction) strategies that have successfully been used. These include process modification, use of alternative methods and chemicals, water conservation, raw material screening and chemical substitution:

- Good housekeeping practices
- Process modification/retrofitting
- Raw material substitution
- By-product recovery
- Recycling/Reuse of Water and/or wastes
- Equipment modifications
2.4.3 Dye bath segregation

The segregation of dye bath is the precondition for all the work done in this study and is therefore regarded as a vital step. The segregation of the exhausted dye bath from the wash waters reduces the TDS levels of these remaining fractions considerably. Segregation of the dye bath would also reduce the colour of the remaining effluent. The exhausted dye bath contains a high concentration of pollutants and has a small volume. The wash water contains lower amounts of pollutants and large amount of water. Therefore it becomes subject for recycling/reuse of wash water or even disposal of the effluent with TDS levels below the regulatory requirements of 2,100 mg/L.

2.4.4 Solar heating systems

A solar collector is simply a thermal solar absorber installed on a sun-exposed area like a roof. This system often comprises a solar collector, storage tank, pump, controller, plumbing and may also include one or more heat exchangers. Solar collectors help to minimize green house gas emissions by reducing reliance on gas and electricity for heat production. In order to reduce landfill, collectors are primarily made from recyclable material such as stainless steel, glass, copper, rock wool, recyclable plastics and rubber.

2.4.4.1 Types of Solar Water Heating Systems

Solar water heating systems (SWHS) can be either active or passive. An active system uses an electric pump to circulate the fluid through the collector; a passive system has no pump and relies on thermo-siphoning to circulate water. The amount of hot water a solar water heater produces depends on the type and size of the system, the intensity of natural radiation, proper installation, and the tilt angle and orientation of the collectors. SWHS are also characterized as open loop (also called
“direct”) or closed loop (also called “indirect”). An open-loop system circulates household (potable) water through the collector. A closed-loop system uses a heat-transfer fluid (water) to collect heat and a heat exchanger to transfer the heat to the household water.

2.5 BIOLOGICAL TREATMENT METHODS FOR TEXTILE EFFLUENT

Treatment methods used for the treatment of liquid effluents from textile industry can be classified into primary or mechanical, secondary or biological and tertiary or advanced physico-chemical processes. Primary treatment includes processes such as screening, neutralization and equalization and gravity sedimentation. The purpose of primary treatment is to remove the suspended matter (including oil and grease) and to achieve uniform flows and concentrations. Biological or secondary treatment is targeted to achieve a major reduction in the effluent load in terms of BOD/COD present largely in the soluble form, so as to meet the effluent limitations. For tertiary treatment advanced physico-chemical processes are used for removal of colour, and toxic substances such as phenols. Colour in natural waters is aesthetically unacceptable and retards UV light penetration into the water hampering the photosynthetic activities of algae and water plants. Residual aromatic organic compounds like phenols cause damages to the whole aquatic system.

Examples of state-of-the-art tertiary treatment are chemical assisted sedimentation (floculation), mixed media filtration, adsorption, and advanced oxidation processes. These physico-chemical processes may be preceded by biological treatment for the latter’s proper functioning shown in Table 2.6 to meet specific discharge limits, which is so far not practiced in Tirupur. Another weak point in the existing treatment scheme is that in this conventional methods (CETP or ETPs) the TDS problem is not tackled. In India our major aim in the treatment of effluent from textile dyeing units should be the minimisation/removal of the high TDS
concentration. The high salt concentrations, as already described, cause severe problems in and around Tirupur by contamination of soil, superficial- and groundwater. With a negative water balance, as in Tirupur, nature has no means to compensate the inorganic salt-pollutants.

**Table 2.6 Available unit processes applicable in TPI (Rott 1995)**

<table>
<thead>
<tr>
<th>Biodegradation: aerobic, anoxic and anaerobic</th>
<th>Physico – Chemical Processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Destructive processes</td>
<td></td>
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<tr>
<td>Activated Sludge Process</td>
<td></td>
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<tr>
<td>anoxic</td>
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<td>aerobic</td>
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<td>fixed film</td>
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<tr>
<td>fixed bed</td>
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<tr>
<td>rotating biological contactors</td>
<td></td>
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<tr>
<td>filters</td>
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<tr>
<td>trickling</td>
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<tr>
<td>fluidized bed</td>
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<tr>
<td>Chemical oxidation</td>
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<tr>
<td>Electrochemical process</td>
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<tr>
<td>Reductive transformation</td>
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<tr>
<td>Separation Processes</td>
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<tr>
<td>Filtration</td>
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<tr>
<td>Membrane filtration</td>
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<tr>
<td>Precipitation / flocculation</td>
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<tr>
<td>Evaporation</td>
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<tr>
<td>Adsorption</td>
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<tr>
<td>Ion exchange</td>
<td></td>
</tr>
<tr>
<td>Complex formation</td>
<td></td>
</tr>
</tbody>
</table>

**2.5.1 Treatment with screened halophile microorganisms (MO)**

**2.5.1.1 Aerobic halophile**

Textile wastewater treatment is carried out by various means such as aerobic processes, anaerobic digestion as well as physical/chemical treatment
(Schoenberger 1997). Synthetic dyestuffs are designed to have excellent properties such as the fastness, the persistence of the colour and resistance against bleaching. They are designed to be stable against biological degradation, which is proofed by the fact that our T-Shirts do not decolourise easily. The dyestuff can be hardly removed from effluents by conventional biological treatment (Schoenberger 1996) The colour removal only by the biological process is reported only for selected dyes with limiting success. Many processes are combined either with flocculation/precipitation processes or with adsorption methods (Schoenberger 1996) Aerobic treatment of mixed effluents from the dying process with conventional processes is practised in a view companies in Europe making use of the possibility to mix the effluent with sewage in a ratio of 50/50 or 40/60 (Geis 1992) In this processes enough biomass is generated to adsorb the dyes on the cell wall of the MO. Consequently it can be said, that the biological treatment is only successful in the case of a combined adsorption and degradation process (Braun et al 1997).

2.5.1.2 Microbial Growth Kinetics

To determine the suitability of a medium for bacteria, it is important to observe their growth kinetics. The microbial growth of a batch culture follows a growth curve, which is divided into four different phases.

In the lag phase, inoculated cells adjust to the new environment and conditions. The second phase is characterised by the exponential growth of cells. It differs with the type of microorganisms and their growth conditions like temperature, oxygen availability or medium composition. In the stationary phase cell growth is in balance with cell death because of lack of nutrients and electron acceptors and also because they produce inhibitory and/or toxic metabolites. The death phase begins when the decay (death) rate of microorganisms exceeds the growth rate. The viable count of cells decreases.
2.5.1.3 Halophile Microorganisms

Waste minimisation and cleaner technologies, which involve the segregation of the waste streams become more and more popular. Highly concentrated wastewaters are the consequence. Textile effluents often contain considerably amounts of salts including sulphates. In many cases the salinity of these concentrated waste waters inhibits a common biological treatment. The first dye bath liquor out of the dyeing process contains the highest salt load in the waste stream. These saline conditions resemble to the conditions in marine or salt lake ecosystems. If such concentrated effluents are treatable at all, they require salt tolerant (resistant) organisms for their treatment. In order to investigate if the application of halophile microorganisms for biological textile effluent treatment is a viable option, this research was carried out.

The growth of some bacteria and fungi is not inhibited by high concentration of sodium chloride salt. Some microorganisms as a matter of fact require high osmotic pressures for growth. Halophile bacteria are MOs, which adapt one to the special environmental conditions of saline locations. Halophile MO grow in high concentrations of salt and need this environment to retain their cell integrity. Depending on their salt need, the organisms are described as “halo-tolerant“, “halophile“ and “extreme halophile“. Extreme halophilie microorganisms need salt concentrations of 2.0-5.2 mol NaCl or 10-35% w/w NaCl like the Halobacterium for example, it needs at least a TDS of 150,000 mg/L as displayed in Figure 2.13 (Bitton 1999).
Figure 2.13 Required salt concentration for different halophile microorganisms

The conformity of halophile bacteria to a saline system requires an osmotic balance between cytoplasm and surrounded medium. The cells have different strategies to achieve that balance. For the treatment purpose it is important to note that extracellular microbial products of halotolerant MOs, which work outside the cell, also need salt for their optimal activities – i.e. they are also halophile (extracellular enzymes for example) as shown in Figure 2.13. Because of the excellent adjustment of the halophile products to the saline environments, it would be possible to use them as biotechnological tools for applications under extremely saline conditions. A lot of industrial effluents show apart from organic foreign substances high salt concentrations and therefore provide conditions that are much alike their natural halosaline habitats. The classification of microorganisms was done in cooperation with the Institute Nationale de Recherche Argonomique (INRA) in Montpellier. The microbes showed characteristics of halophile archaea. Phylogenetic (from a common ancestor) relationships according to Carl R. Woese's “Three-Kingdom System” are depicted in Figure 2.14 (Tortora et al 1992).
Figure 2.14 The three kingdom system

The Chart differentiates between three cell groups: Eucaryote and two different types of Procaryotes. These two procaryotic cell groups are the Eubacteria (commonly called "true bacteria") and Archaebacteria (archaios=ancient). The Archaebacteria differ from Eubacteria in many ways. For example they often live in extreme environments (extremophiles), carry out unusual metabolic processes and their cell walls vary in composition and colour (Tortora et al 1992).

They can be divided into three groups:

- The methanogens, strict anaerobes producing methane (CH₄) from hydrocarbons
- Thermoacidophiles living in hot, acidic environments
- (Extreme) halophiles (= salt-lover), they require high concentrations of salt to survive (Tortora et al 1992)
The halophile archae (halobacteria) dominate the microbial population of hypersaline waters and are found when they reach saturation. At least nine taxa of halophile archaea diverged from a common ancestor. For example neutral hypersaline brines harbour a wide range of "neutrophile" halophile taxa (pH around 7.2), whereas soda lakes just offer appropriate environment to a restricted amount of alkaliphile halophile taxa (pH around 9.5). Because of high sulphate concentrations in hypersaline ecosystems methanogens seem to be out-competed by sulphate reducing bacteria (Horikoshi et al 1998).

Apart from the halophile microorganisms there are only few higher organisms like e.g. the brine shrimp (Artemia salina) and the brine fly (Ephydra) that can live in saline environments. Artemia salina eggs were brought from Germany by the author and it was tested in the Centre for Environmental Studies and found to grow in leather industry effluents. Textile effluent did not provide enough proteins. Halophile microorganisms have special mechanisms to adapt to the hypersaline environment. Two basic strategies are known to avoid water loss by osmosis and to maintain the shape:

• Osmoregulation due to accumulation of up to 5 mol potassium chloride (KCl)

• Production or accumulation of low-molecular-weight compounds which have osmotic potential (Horikoshi et al 1998).

Usually halobacteria can live well without light sources (Tortora et al 1992), (Horikoshi et al 1998), but some halobacteria species have pigmented plasma membranes serving as a light-mediated proton pump for energy conservation. In the presence of light these pigments translocate ions across the cell membrane. Some Halobacteria species can use this additional energy source when the oxygen concentration in saline environment is not sufficient for oxidative phosphorylation.
Halobacteria already showed organic-degrading capacity in relation to the treatment of oil fields degrading complex organic molecules. In the experiments conducted in this study it is attempted to determine their potential for the treatment of exhausted dye baths because for the fixation of reactive dyes the addition of salts such as Sodium chloride and Sodium sulphate is quite common. For dark shades up to 80 g/L of salt are added to the dye bath liquor. Therefore the wastewater is characterised by a high salt concentration, which might be a suitable environment for halophile microorganisms.

2.5.2 Root zone treatment plant (RZTP) systems

Root zone treatment plant (RZTP) systems are complex ecological systems called constructed wetlands (CWL) with characteristics of both, dry land and water. Natural wetlands are located in areas that receive fresh water at the edges of lakes, ponds, streams and rivers as well as salt water from tides in coastal areas. The natural treatment systems have a unique attraction as they do not involve use of chemical and synthetic materials. Further, they are capable of removing at least to some degree, almost all of the major and minor constituents of wastewater that are considered pollutants – suspended solids, organic matter, nitrogen, phosphorous, trace elements, trace organic compounds and microorganisms. In systems such as subsurface flow wetlands, suspended solids are removed primarily by filtration through the soil or subsurface media. A wide range of constructed wetland systems for wastewater treatment is available. CWL Constructed wetlands include aquatic systems, wetland systems and land treatment systems. Among these Root Zone Treatment System (RZTS), a variation of constructed wetland has been attracting the attention of environmental engineers and scientists in many parts of the world. In comparison with technical treatment processes the CWL systems do not rely on microbial degradation as the major process, but include also the reactive/adsorptive potential of soil and to some extent the uptake by plants. This complexity causes a stable treatment process. Natural systems consume lesser amounts of energy. There
are various treatment options including the horizontal and vertical flow root zone treatment plant (RZTP) systems. In the vertical RTZP the effluent is passed vertically through the sand matrix, and in the horizontal RZTP perpendicular to the gravity flow. According to the aerobic, anoxic zones and their microbial colonizing potential of the different systems show different performances per given treatment area. The design parameters are 5 m$^2$/inhabitant or 16 g BOD$_5$/m$^2$ per day for horizontal flow and 2.5 m$^2$/inhabitant or 24 g BOD$_5$/m$^2$ per day for vertical flow.

Under temperate conditions with vertical treatment of household water following treatment efficiencies can be achieved on 5 m$^2$/inhabitant:

- COD $>$ 90%
- BOD$_5$ $>$ 95%
- PO$_4$ $>$ 95%
- NH$_4$ $>$ 95%
- $N_{nit}$ $>$ 69% removal.

Pathogens are also effectively reduced (Niklas 1998)

Major cost factors are the land requirement, sealing of the treatment plant to prevent infiltration of untreated water into the ground water and the filter material. Like in technical treatment plants the major limiting factors influencing the performance are:

- soil or plant root surface area to be colonized by the microorganisms
- reactive/adsorptive potential
- oxygen supply to allow microbial degradation
- evapo-/transpiration (water loss especially under arid tropical conditions)
- plant growth viz. resistance to organic pollutants and TDS
Industrial applications of natural treatment plants were used to treat dairy effluents, waste water of starch industry, steel works and even landfill leachate, partly as post treatment. Major concern should be, in case of industrial application, the possible accumulation of persistent organics pollutant POP and heavy metals in the soil matrix.

Natural treatment systems have a unique attraction as they do not involve the use of chemicals and synthetic materials. Further, they are capable of removing at least to some degree, almost all of the major and minor constitutes of wastewater that are considered pollutants — suspended solids, organic matter, nitrogen, phosphorous, trace elements, trace organic compounds and microorganisms.

2.5.3 Anaerobic methods

Decolourization of azo-dyes under anaerobic conditions has been observed before. Azo-bonds are cleaved and reduced to their corresponding amines by biologically induced reactions. (Bluemel et al 1997). However, it is not expected that a significant removal of organic compounds takes place (Sosath 1999).

Many classes of dyes, as reactive or direct dyes, contain azo-groups as chromophoric part. They are cleaved when treated reductively.

Anaerobic treatment has been chosen as pre-treatment because of its low costs and easy maintenance. Energy costs, which represent a high cost-factor in India (see Appendix 6), are kept on a minimal level. In subtropical regions suitable temperatures for anaerobic treatment are given and no heating system needs to be installed. Additionally, anaerobic reduction of azo-dyes does not require any chemicals to be added, apart from a possible pH-adjustment. Biogas, produced in the process, can be used within the other production processes as energy source. In anaerobic processes (see Figure 2.15), just a small quantity of excess sludge is
expected. Consequently, this treatment step does not cause solid waste problems as the reductive treatment with metal salts.

Generally, the anaerobic biological degradation of organic matter occurs in three stages. Divided into hydrolysis, acidification and methane formation. The conversion is carried out by a multitude of anaerobic organisms (Helmig et al. 1995). These microbes consist of a large group of complex and differently acting microbe species, notable the methane-producing bacteria. A minimum of three types of bacteria are involved (Maerkl 1997).

Figure 2.15 Anaerobic processes chart

2.5.3.1 Hydrolysis

In the first step (hydrolysis), the organic matter is enzymolyzed externally by extracellular enzymes (cellulase, amylase, protease and lipase) of microorganisms. Bacteria decompose the long chains of the complex carbohydrates, proteins and lipids into shorter parts. For example, polysaccharides are converted into monosaccharides. Proteins are split into peptides and amino acids.
2.5.3.2 Acidification

Acid-producing bacteria, involved in the second step, convert intermediates of fermenting bacteria into acetic acid (CH₃COOH), hydrogen (H₂) and carbon dioxide (CO₂). These bacteria are facultative anaerobic and grow under acid conditions. To produce acetic acid, they need oxygen and carbon. For this, they use the oxygen dissolved in the solution or bounded-oxygen. Hereby, the acid-producing bacteria create an anaerobic condition that is essential for the methane producing microorganisms. Moreover, they reduce the compounds with a low molecular weight into alcohols, organic acids, amino acids, carbon dioxide, hydrogen sulphide and traces of methane. From a chemical standpoint, this process is partially endergonic (i.e. only possible with energy input), since bacteria alone are not capable of sustaining that type of reaction.

2.5.3.3 Methane formation

Methane-producing bacteria, involved in the third step, decompose compounds with a low molecular weight. For example, they utilize hydrogen, carbon dioxide and acetic acid to form methane and carbon dioxide. Under natural conditions, methane producing microorganisms occur to the extent that anaerobic conditions are provided, e.g. under water (for example in marine sediments), in ruminant stomachs and in marshes. They are obligatory anaerobic and very sensitive to environmental changes. In contrast to the acidogenic and acetogenic bacteria, the methanogenic bacteria belong to the archaeabacter genus, i.e. to a group of bacteria with a very heterogeneous morphology and a number of common biochemical and molecular-biological properties that distinguish them from all other bacteria in general. The main difference lies in the bacteria's cell walls composition.
2.5.3.4 Symbiosis of bacteria

Methane- and acid-producing bacteria act in a symbiotic way. On the one hand, acid-producing bacteria create an atmosphere with ideal parameters for methane-producing bacteria (anaerobic conditions, compounds with a low molecular weight). On the other hand, methane-producing microorganisms use the intermediates of the acid-producing bacteria. Without consuming them, toxic conditions for the acid-producing microorganisms would develop.

In practical fermentation processes, the metabolic actions of various bacteria all act in concert. No single bacterium is able to produce fermentation products alone.

There are different approaches to explain the anaerobic degradation of textile effluents. In this context just two of them are presented. Libra et al (1997) claims that the following reaction in Figure 2.16 takes place in the first and second step of digestion by acidogenic and acetogenic bacteria.

\[
\begin{align*}
R - N = N - R' & \quad \text{azoreductase (produced by bacteria)} \\
2 \text{NADH} + 2 H^+ & \rightarrow R - NH_2 = R' - NH_2 \\
2 \text{NAD}^+ &
\end{align*}
\]

Figure 2.16 Scheme for the anaerobic decolourization of azo-dyes

Coenzymes (NAD\(^+\), NADP\(^+\)) receive hydrogen previously split by enzymes. While transporting hydrogen to other hydrogen acceptors they gain energy. In this hypothesis, azo-dyes serve as artificial hydrogen acceptors. When receiving the hydrogen-ion the azo-bonds are cleaved (Figure 2.17). Aromatic amines are generated in this reduction (Sosath 1999).
A general scheme for the reductive cleavage of reactive dyes is displayed in Figure 2.17 (Grund 1986).

![Figure 2.17 Reductive cleavage of azo-bonds (Grund 1986)](image)

The approach is based on a bio mediated chemical reduction with sulphide ($SO_3^{2-}$). Textile effluent contains sulphate, because of the addition of salts like sodium sulphate Glaubersalt ($Na_2SO_4$). The dye itself contains sulphate as well. Sulphides are generated by sulphate reducing bacteria. Libra (1997) used inhibitors for methane producing bacteria and sulphate reducing bacteria to receive information about their contribution to the decolourization of synthetic dye baths. They propose that methanogens do not contribute significantly to decolourization whereas sulphate reducing bacteria succeed in decolourization. This takes place by a biomediated chemical reduction with sulphide according to the reactions shown.

In all approaches to explain the unspecific decolourization under anaerobic conditions chemical reduction and biological processes go hand in hand.

About 5 % of the total number of Azo-dyes can release carcinogenic aromatic amines by cleavage of the azo group. This is normally possible under reductive conditions only. In order to protect the consumers coming into contact with such azo - dyestuffs their use was banned. The Azo - dyes falling under the German Consumer Goods Ordinance forming carcinogenic aromatic amines are listed under the Appendix 5.
2.6 ADVANCED OXIDATION PROCESSES (AOP)

The term advanced oxidation processes (AOPs) is used for water treatment processes that involve the formation of highly reactive, short-lived chemical intermediates. These intermediates (e.g., the hydroxyl radical) are powerful oxidants and are used to oxidize wastewater contaminants that resist other forms of treatment.

Oxidation processes are used in water treatment for disinfection and removal of obnoxious or potentially toxic contaminants and for some industrial purposes such as bleaching and purification of wastewater before discharge into the environment. The most familiar chemical oxidants used in water treatment are chlorine, chloroamines, ozone, chlorine dioxide, hydrogen peroxide, and potassium permanganate. Sometimes these oxidants are used in combination with each other (e.g., ozone with hydrogen peroxide) or with photons from irradiation lamps. The power of a chemical oxidant to cause a chemical oxidation reaction is determined by two properties: the thermodynamic driving force and the rate constant of oxidation. The thermodynamic driving force of the oxidation process for one oxidant compared to another is determined by its relative oxidation potential (see Table 2.7).

<table>
<thead>
<tr>
<th>Species</th>
<th>Oxidation potential, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>3.06</td>
</tr>
<tr>
<td>Hydroxyl radical</td>
<td>2.80</td>
</tr>
<tr>
<td>Nascent oxygen</td>
<td>2.42</td>
</tr>
<tr>
<td>Ozone</td>
<td>2.07</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>1.77</td>
</tr>
<tr>
<td>Perhydroxyl radical</td>
<td>1.70</td>
</tr>
<tr>
<td>Hypochlorous acid</td>
<td>1.49</td>
</tr>
<tr>
<td>Chlorine</td>
<td>1.36</td>
</tr>
</tbody>
</table>

Table 2.7 List of the standard potentials $E^\theta$ for common chemical oxidants in aqueous solution at 298 K (Latimer 1952)
The oxidation potential is a measure of a chemical's oxidizing (or reducing) power; the more positive the value of $E^\circ$, the more likely is the chemical reaction to take place. All common chemical oxidants shown in the table are relatively powerful and should oxidize most organic compounds to carbon dioxide and water, but in fact, in very few cases the oxidants listed in the table oxidize environmental contaminants as completely as would be expected from thermodynamic considerations. This is due to the fact that when the rate constant for the process is low, these chemical reactions occur, as indicated by the thermodynamic driving force, but only very slowly.

For example, the reaction of formate with ozone is a very slow reaction, whereas that of another common pollutant, phenol, is very fast (Hoigne et al 1983). Another example is the rate of oxidation of two important natural products that contribute to bad taste and odour in water supplies: geosmin and methylisoborneol. The rates of chemical oxidation of geosmin and methylisoborneol by chemical oxidants vary substantially, making some impractical for use in water treatment.

Ozone is always produced when oxygen is decomposed in air, e.g., in an electric discharge or when short wave (<190 nm) UV radiation is absorbed by oxygen. This decomposition occurs naturally in the atmosphere, but it may also be used to generate ozone for water treatment by the reaction of air, oxygen-enriched air, or pure oxygen. Ozone is a powerful oxidant but reacts with different chemicals at various rates that range over several orders of magnitude. For example, the half-lives of ozone's reactions with phenol and formate under similar conditions differ by a factor of about 100,000. Of the common oxidants, ozone is more effective than others for the control of obnoxious taste and odour.

Chlorine dioxide is a clear, colourless gas that dissolves readily in water without dissociation. It is a powerful disinfectant and oxidant and has been used extensively for water treatment. Chlorine dioxide is becoming an increasingly important alternative to chlorine as a bleaching agent in pulp and paper production.
**Potassium permanganate** has been used in water treatment for many years, primarily for oxidation of manganese (II) and iron (II) to the corresponding insoluble oxides or hydroxides, for colour removal, and for taste and odour control.

**Hydrogen peroxide** is a milder oxidant than chlorine or ozone. It is used in many industrial and medical applications as a mild disinfectant or oxidant, but worldwide its principal application is in wood pulping.

Several AOPs using these oxidants in combination with UV light, catalysts or specially designed reactors have been developed and commercialised including the following:

1) **Ozone** in combination with hydrogen peroxide (sometimes called Peroxone process) with UV radiation, or with both hydrogen peroxide and UV.

2) **Hydrogen peroxide** in combination with iron(II) salts (known as Photo-Fenton process), with UV radiation, and other modifiers such as iodine ion produces OH radicals by an oxidation-reduction reaction.

3) **Oxygen** in combination with high-energy, high-frequency sound waves (sonication), electron-beam irradiation, or gamma radiation.

Oxidation with AOPs is used worldwide for the drinking water treatment, for oxidation of herbicides such as atrazine and simazine, and for oxidation of taste and odor compounds that are formed in rivers, lakes, and reservoirs. AOPs are also used in groundwater treatment to oxidize contaminants such as halogenated solvents (trichloroethylene and tetrachloroethylene). In addition, AOPs are being investigated for treatment of industrial wastewater, but they appear to be substantially more expensive than conventional biological treatment. Thus, **AOPs may be most useful for treating streams containing compounds that are not easily biodegraded.** In this case, oxidizing the target compounds only partially (i.e., not completely to carbon...
dioxide) may be most economical. Partially oxidized compounds are likely to be more easily biodegradable than their precursors, and the stream may then be given to a biological treatment unit process for final polishing before discharge into the environment.

2.6.1 UV induced photocatalysis

Advanced oxidation processes that involve UV radiation utilize lamps such as mercury arc lamps that produce radiation of various wavelengths, depending on the power density of the current in the lamp. Low-pressure mercury arc lamps produce UV radiation primarily at 254-nm wavelength, whereas high-pressure lamps (operated at higher current densities and therefore at higher internal pressure and temperature) produce UV radiation with variable intensity at several different wavelengths from the visible region down to less than 200 nm.

Three different types of photooxidative water treatment are known. They are introduced in Figure 2.18. (Bolton et al 2002).

**Figure 2.18** Photooxidative treatment methods (Oppenlaender et al 2000)
Each induction of light is applied in different wavelength ranges (see Figure 2.19). UV-radiation, is performed at wavelengths in UV-C-spectrum below 270 nm sometimes even in combination with hydrogen peroxide (H₂O₂) or ozone (O₃). Photocatalysis studies, performed in pilot-projects, were done with UV-A radiation as natural energy source at wavelengths below 400 nm. Finally, water photolysis, still in research, uses vacuum-UV-radiation with wavelengths below 200 nm. However, the UV-lamps are usually housed in quartz tubes that cut off all radiation below 200 nm or, in the case of highly purified quartz, below 185 nm.

**Photodegradation of Pollutants**

<table>
<thead>
<tr>
<th>Photolysis of O₂, H₂O</th>
<th>Photooxidation UV + O₃, H₂O₂</th>
<th>Photocatalysis UV + TiO₂</th>
</tr>
</thead>
</table>

**Direct Photocleavage of Pollutant**

<table>
<thead>
<tr>
<th>VUV</th>
<th>UV-C</th>
<th>UV-B</th>
<th>UV-A</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>200</td>
<td>300</td>
<td>400</td>
</tr>
</tbody>
</table>

Wavelength (nm)

Figure 2.19 Photooxidative treatment methods and their wavelength ranges

### 2.6.1.1 The UV-Oxidation Process

The photolysis of added oxidants hydrogen peroxide (H₂O₂) (Equation 2.2) or/and ozone (O₃) (Equation 2.3) occurs in the UV-C-range according to following simplified equations:

\[
\text{Photolysis of } H₂O₂ \xrightarrow{\text{UV } \text{C} < 250 \text{ nm}} 2(OH^-)
\]  \hspace{1cm} (2.2)

\[
\text{Photolysis of } O₃ \xrightarrow{\text{UV } \text{C} < 250 \text{ nm}} H₂O₂ + O₂
\]  \hspace{1cm} (2.3)
The hydroxyl radicals induce the oxidative decomposition of organic bonds. They have a high oxidation potential of $E^0=2.80$ V. The organic bonds are cleaved due to hydrogen abstraction and electrophile addition to C-C-multiple bonds or direct reaction with the photon (Oppenlaender et al 1996).

Light-sources for the above mentioned reactions are powerful medium-pressure (industrial purpose) or low-pressure (preferably water disinfection) mercury lamps.

### 2.6.1.2 Water photolysis with a high-pressure Incoherent Excimer Lamp

The Vacuum Ultraviolet (VUV) Process is limited to the strong UV absorption bands of oxygen, e.g., in air at 190 nm. Excitation in the VUV spectral region leads in most cases to a homolysis of chemical single bonds and became feasible with the availability of excimer light sources, which emit in this UV range. The principles of conventional H$_2$O$_2$- and O$_3$-UV treatment are combined in the VUV-technology without addition of any chemicals. (Oppenlaender et al 1996) Water photolysis just takes place, because water has a high linear absorption coefficient ($k=\varepsilon c$) at low wavelengths (Figure 2.20) (Oppenlaender et al 1995).

![Figure 2.20 Emitted spectrum by a xenon-excimer lamp, linear absorption coefficient of water, transmission of suprasil quartz](image-url)
Besides photohomolysis of the target substance, VUV photolysis of H$_2$O generates hydroxyl radicals very efficiently which then oxidises dissolved or dispersed substrates. Water photolysis is the homolytic cleavage of water under high potential vacuum-UV (VUV) radiation (λ=30-200 nm) (Oppenlaender 1996).

$$\text{Water photolysis } H_2O \xrightarrow{\text{VUV } \lambda = 172 \text{ nm}} H \cdot + OH \cdot \quad (2.4)$$

Products of this photoreaction are H-atoms and high concentrations of OH-radicals (Equation 2.4). Oxygen photolysis at a wavelength of $\lambda=172$ nm generates these two compounds, but in addition to that in air-saturated water intrinsic formation of ozone (O$_3$) and hydrogen peroxide (H$_2$O$_2$) can be observed. The Xe excimer lamps currently available can be used for water photolysis on a preparative scale. Suitable reactors were developed for the VUV production of ultrapure water for pharmaceutical and microelectronic industries. Colour removal or TOC-degradation in textile effluent was not yet tried, but the disadvantages could be the short penetration depth of the VUV (several μm) and the maximum electrical power input of 1.5 kW. These factors make xenon excimer lamps less suitable for effluent treatment ground and wastewater decontamination. The reaction zone is confined by the penetration depth according to Lambert-Beer-Law (Equation 2.5) (Kuester et al 1982).

$$E = \varepsilon \cdot c \cdot d \quad (2.5)$$

With:  
- $E$: Extinction at wavelength $\lambda$  [-]  
- $\varepsilon$: Molar absorption coefficient [1/(mol*μm)]  
- $c$: Molar concentration [mol]  
- $d$: Penetration depth [μm]  

For water photolysis, the penetration depth is $5 \leq d \leq 300$ nm. However, many contaminants have even a higher absorption coefficient in the low wavelength ranges. They absorb the photons before water molecules can do this. In a concurrent reaction,
direct photocleavage of contaminants is carried out. The reaction zone is even more
restricted due to the high linear absorption coefficient k. A scheme of the complex
reactions taking place in a photoreactor with VUV-radiation is given in Figure 2.21
(Oppenlaender et al 2000), (Oppenlaender et al 1995).

![Diagram of VUV-induced oxidation and mineralisation of organic water contaminants](image)

Figure 2.21 Mechanisms of the VUV-induced oxidation and mineralisation of
organic water contaminants

An incoherent xenon-excimer lamp provides high-intensity narrow-band
radiation. Excimer (means “excited dimers”) are “excited molecular complexes
without stable ground states”. Electrons collide with a rare-gas atom, e.g. Xe and
transfer their energy on the atom (Figure 2.22, steps 1 and 2). As a result the atom
reaches an excited state (Xe*). The excited rare-gas atom Xe* now collides with an
atom in the ground state to form an excimer Xe*₂ (Figure 2.22, step3). The unstable
complex Xe*₂ disintegrates within a few nanoseconds. Its excitation energy is
transformed into optical radiation in the form of a UV-photon with a wavelength of
\( \lambda = 172 \) nm (Figure 2.22, step 4).
Figure 2.22 Generation of VUV-radiation with xenon-excimer lamps

The spectral range of the emitted optical radiation is confined to a few nm. Thus, wavelength-selective photochemistry is getting possible with incoherent excimer sources.

The simple and efficient excitation of electrons is called “silent” or “dielectric-barrier discharge” with an insulator positioned between the electrodes. This insulator consists of the quartz walls of the UV source (Figure 2.23). The extremely short acceleration of electrons takes place in the electrical field between outer and inner electrode both not in contact with the discharge plasma (Kogelschatz 1993).

Figure 2.23 Possible cross-section of an excimer lamp reactor (Kogelschatz 1992)
The annular discharge gap, sealed by the quartz barrier, contains the excimer forming gases under high pressure. UV-radiation is directed outside by means of a reflecting inner electrode. The outer electrode is designed to transfer UV radiation, e.g. a wire mesh electrode. The cooling system is established in the inner tube.

2.7 MEMBRANE TECHNOLOGY AND ITS APPLICATIONS

In many areas, membrane processes have gone through developmental stages in the past ten years but now many of them have transformed to fully commercial products. In addition to that, most industrial countries face economic pressure due to rising prices for fresh water and charges for wastewater treatment and disposal. Innovative companies are looking for means of recycling their own process water and thus reducing the costs. In fact, strict legal regulations for wastewater discharge quality also forces the industries to find solutions for their wastewater problems.

Ultrafiltration (UF), microfiltration (MF), and reverse osmosis (RO) are the most important pressure-driven membrane separation processes. A mixture of components of different sizes is brought to the surface of a semipermeable membrane. Under the driving force of a hydrostatic pressure gradient, some components permeate the membrane, whereas others are retained (retentate). A feed solution is separated into a filtrate that is depleted of particles or molecules and a retentate in which these components are concentrated. In membrane based cross-flow technology (dynamic filtration) in addition to hydrostatic filtration pressure a flow on the membrane surface is produced. This flow, working crosswise to the direction of filtration, keeps solids, microorganisms and colloids floating and counteracts the build-up of a scaling on the surface layer. After a few minutes an equilibrium is produced. At continuous operation the filtrate output is almost constant with a merely asymptotic decrease. Cross-flow filtration differs from the classical dead end filtration with depth filters or membrane
cartridges. During the dead end filtration the continuously increasing filter cake thickness is responsible for the rising inlet pressure. When the required flow rate can no longer be maintained, blocking occurs and the filtration has to be stopped. After filtration the filter has to be cleaned and, in most cases, the filter material has to be discarded. The service life of dead end filter materials is comparatively short.

In order to increase the service life of membrane filters, dynamic filtration was developed. The performance of a membrane in a pressure-driven separation process is determined by its filtration rate (i.e., the transmembrane flux $L/m^2*h$ at a certain hydrostatic pressure) and its mass separation properties (i.e., retention capability).

Membrane filtration systems using the cross-flow principle have some typical properties that distinguish them from conventional treatment and filtration systems. Advantages and disadvantages typical for almost all kinds of membrane systems are listed below.

The advantages include:

Continuous operation enclosed system (toxic products), operation can be automated, long membrane life, reduced labour, simplified filtration, sometimes only one step, filter aid saving (small waste volumes), easy Cleaning In Place (CIP), standardized filtrate quality due to defined particle retention (no particle breakthrough), reliable microbiological stabilisation in conjunction with a final membrane filter in one step and in comparison to depth filtration lower product losses due to adsorption/absorption.
Whereas the disadvantages are:

High investment costs, further processing of the concentrate rest is necessary, very low specific output per unit area, high energy consumption, the products are subjected to high mechanical stress due to continuous circulation, possible loss of effective substances or components due to adsorption onto the membrane, chemical cleaning of the membrane is required and new technologies always require skilled personnel for the operation.

The degree of freedom for optimising the filtration processes is confined to the suitable choice of system-specific parameters. The Table 2.8 shows product specific parameters that have an effect on the dynamic layer and thus the filtration process and its costs.

**Table 2.8 Product-specific parameters and system-specific cost factors of membrane technology**

<table>
<thead>
<tr>
<th>Product-specific parameter</th>
<th>System-specific cost factors</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. Composition and nature of the solids</strong></td>
<td>1. Design of membrane and module</td>
</tr>
<tr>
<td>• particle size</td>
<td>• membrane material</td>
</tr>
<tr>
<td>• particle size distribution</td>
<td>• membrane thickness</td>
</tr>
<tr>
<td>• concentration of the particles</td>
<td>• pore size and pore geometry</td>
</tr>
<tr>
<td>• charge of the particles</td>
<td>• surface characteristics</td>
</tr>
<tr>
<td>• nature of the particles</td>
<td>• module type (capillary or other)</td>
</tr>
<tr>
<td><strong>2. Additives</strong></td>
<td><strong>2. Process technology</strong></td>
</tr>
<tr>
<td>• anti-foam agents</td>
<td>• tangential flow conditions</td>
</tr>
<tr>
<td>• diatom earth</td>
<td>(module geometry, spacers etc)</td>
</tr>
<tr>
<td>• organic solvents</td>
<td>• pressure levels in kPa</td>
</tr>
<tr>
<td>• activated carbon</td>
<td>• filtrate flow L/min</td>
</tr>
<tr>
<td><strong>3. Properties of the medium</strong></td>
<td><strong>3. Regeneration of the membrane</strong></td>
</tr>
<tr>
<td>• viscosity</td>
<td>• cleaning method (duration, temperature, agent, etc.)</td>
</tr>
<tr>
<td>• pH</td>
<td>• back flushing during filtration</td>
</tr>
<tr>
<td>• gas content</td>
<td>(mode, duration, sequence, etc.)</td>
</tr>
<tr>
<td>• corrosive</td>
<td>• preservation, method and agent</td>
</tr>
</tbody>
</table>
Due to complex interactions, optimisation of membrane based plants practically always rely on test runs, whereby the process-technological parameters are adapted to the process.

2.8 MEMBRANE PROCESSES IN THE TEXTILE INDUSTRY

2.8.1 Nanofiltration

In principle, nanofiltration membranes are nonporous solution - diffusion membranes like reverse osmosis membranes (Schneider 1993). However, they have a low rejection for low molar mass substances. Nanofiltration is characterized by two extremely interesting properties:

The first is the ability to fractionate organic components of varying molar mass and/or structure in aqueous solutions (e.g., mixtures of mono- and polyhydric alcohols). This selectivity of nanofiltration for organic components in the molar mass range 100 g/mol < M < 300 g/mol is shown in Figure 2.24.

![Figure 2.24 Separation characteristics of nanofiltration in organic aqueous systems](image)

1=Methanol; 2=Ethanol; 3=α-Butanol; 4=Ethylene glycol; 5=Triethylene glycol; 6=Glucose; 7=Sucrose; 8=Lactose

**Figure 2.24 Separation characteristics of nanofiltration in organic aqueous systems** (operating conditions: Δp=10 bar; T=25°C; osmotic concentration x_p=200 mOsmol per kilogram H_2O)
For example, the rejection capacity of the membrane "Desal 5" is only approx. 30% for ethylene glycol, but more than 80% for glucose. These results were obtained from experiments with binary solutions of the same osmolarity i.e., the same driving force (Groeschel 1991).

The second is the possibility of utilizing the Donnan effect. Through the addition of one ionic species (e.g., $SO_4^{2-}$ ions), the rejection capacity for another ionic species (e.g., $NO_3^-$) is drastically decreased. The addition of $SO_4^{2-}$ ions, in the form of $Na_2SO_4$, reduces the rejection capacity for $Cl^-$ ions significantly, even to negative values, while the rejection capacity for $Na^+$ ions increases slightly.

After separation of the dye, the wastewater of the process contains the salt and, unavoidably, small amounts of dye. Treatment of this wastewater by reverse osmosis is not economical use of the high osmotic pressure and the resulting concentrate would contain both salts and organics. However, the ability of nanofiltration to fractionate low molar mass salts and higher molar mass dyes could be used here.

A plant installed in a Swiss chemical company with a total membrane area of 960 m$^2$ is equipped with tubular modules because of the high fouling potential of feed. It operates at a volumetric concentration factor $CF_V = 10$ and has an average capacity of approx. 16 m$^3$/h. Since the wastewater of several dye-production plants is treated simultaneously, the NF concentrate cannot be recycled, but must be disposed off. To this end, the concentrate is subjected to wet oxidation. The permeate, containing the major part of the salts, is discharged into the Rhine river (though it could even be reused).
Nanofiltration provides the user with two advantages:

1) The mass flow rate of the stream subjected to wet oxidation is significantly lower.
2) The corrosion potential of this stream is strongly reduced, because the major part of the salts is removed.

Obviously, nanofiltration offers a possibility of recovering the dyes and/or salt solution at least in principle. The dye reuse would be of economic interest only where large amounts of only one dye are present in the wastewater, which is not the case in the textile units in Tirupur.

If the concentrate from nanofiltration is recycled to the bioreactor, the hydraulic residence time and the residence time of the recalcitrants are decoupled, in contrast with classic biological treatment, e.g. small substrates are degraded immediately, bigger molecules that are non-biodegradable or poorly biodegradable are recycled back into the bioreactor. As a consequence the rate of degradation increases according to the Monod law, unless inhibition by toxic substances occurs. Low molar mass salts (main part of the textile effluent TDS) permeate the membrane and drain out with the filtered water.

2.8.2 Ultra and microfiltration

The term microfiltration is used when particles with a diameter of 0.1–10 μm are separated from a solvent. The separation mechanism is based on a sieving effect, and particles are separated solely according to their dimensions. The membranes used for microfiltration are symmetric microporous structures with pore sizes of 0.1–10 μm. The hydrostatic pressure differences used are in the range of 10–500 kPa (0.1–5 bar).
In ultrafiltration the components to be retained by the membrane are molecules or small particles ≤0.1 μm in diameter. This corresponds roughly to the resolution limit of an optical microscope. Generally, the osmotic pressure of the feed solution is negligibly small and hydrostatic pressures of 100 up to 1000 kPa (1-10 bar) are used. Ultrafiltration membranes are mostly asymmetrically structured, with pores in the skin layer having a diameter of 1–90 nm.

Both filtration techniques can be applied as a pre-treatment prior to the NF or RO in order to achieve the required quality of the feed water (expressed as Silt Density Index SDI). Further applications could be in the field of combining biological treatment and ultra/microfiltration with recirculation of the concentrate into the bioreactor.

In treating textile effluents, membrane bioreactors could replace traditional techniques (i.e., open-tank bioreactors combined with sedimentation). Instead of sedimentation, ultrafiltration in combination with an aerobic–anoxic biological treatment stage making use of the higher biomass has the following advantages (Mellis 1994) 100% retention of biomass, especially of the nitrifying bacteria that are difficult to settle and allowing the process operation at significantly increased biomass concentrations (solids up to 20–30 mg/L), resulting in significantly increased volume-specific capacities (space–time yield).

2.8.3 Reverse Osmosis

In reverse osmosis, particles, macromolecules and low molecular mass compounds (e.g., salts and sugars) are separated from a solvent, usually water. Feed solutions, therefore often have significant osmotic pressure, which must be overcome by the hydrostatic pressure applied as driving force and thus limit the practical application of this technique. The transmembrane flux is a function of hydrodynamic permeability and net pressure difference (the hydrostatic pressure difference between
feed and filtrate solutions minus the difference in osmotic pressure between these solutions). The osmotic pressure of a solution containing low molecular mass solutes can be rather high, even at relatively low solute concentrations. The osmotic pressure of seawater, for instance, is about 2–2.5 MPa, that of orange juice is 2.5–3 MPa.

The membranes used today in the desalination of seawater and brackish water are either composite membranes (Dow-Filmtec, Desalination Industries) or asymmetric phase inversion membranes made of polyamide (DuPont). The modules configurations used are spiral-wound, hollow-fibre, and disk modules.

In all RO desalination plants in operation, the great effort involved in the pre-treatment of water is conspicuous. The extent of treatment depends, first, on the composition of the raw water and, second, on the module concept employed. The required pre-treatment is directly proportional to the sensitivity to fouling and scaling of the module type employed. In disk modules with a relatively open feed channel, adjustment of the pH, chlorination, and separation of the suspended solids by sand filtration are sufficient. In spiral-wound or hollow-fibre modules, additional fine filtration by dead cartridge filters or cross-flow micro- or ultrafiltration is required. In general the pre-treatment includes the following steps viz.,

Chlorination to prevent growth of algae, Filtration (e.g., by a combination “sand filter and subsequent pre-coat filter”), adjustment of pH, addition of hexametaphosphate to prevent CaSO₄ precipitation in the modules and fine filtration with a 10-μm dead end cartridge filter (5-μm in the case of hollow-fibre modules)

All dynamic filtration processes create rejects (concentrates) corresponding to the concentration factor. These rejects cannot be neglected and have to be looked after in an environmental friendly manner.
2.9 REJECT MANAGEMENT

2.9.1 High rate brine concentrator (HRBC)

Ancient brine (aqueous solution of sodium chloride) concentrators were developed in Europe for the salt production. They were developed because of depleted resources in terms of firewood. The salt industry in Europe used Brine Concentrators (BC) in order to concentrate brine from concentrations below 15% Sodiumchloride NaCl up to concentrations close to the saturation point by using sustainable wind, water and solar energy. In 1716 the BC technology was brought to Germany by Joseph Todesco. In spite of their success over centuries there are not many publications existing about them. They were implemented in times when low concentrated salt solutions were used for the production of salt. From 1824 onwards their role was diminished by the success of exploring source of salt in mines, but still many of them are in operation for recreational purposes proving that it is a very robust and profitable technology.

The technology was transferred and adopted to for the concentration of RO rejects within the scope of this Ph.D. thesis. A High Rate Horizontal brine Concentrator HRBC was developed. This profitable and sustainable technology seems to have never been applied in Asia before, in spite of the fact that the conditions are ideal. The solar radiation in Chennai exceeds that in Europe by far. Other processes using thermal or electrical energy consume large amounts of natural resources such as firewood, diesel, and/or furnace oils. Low salt solutions are derived as reject from brackish water RO -systems. The reject concentration is often too high for disposal and too low for further processing. Only after the diluted salt solution is concentrated it can be utilised, reused again (recycled).
2.9.2 Chlorine-Alkali Electrolysis

The concentrated brine out of the HRBC will be used in the chlorine-alkali electrolysis process as raw material:

The concentrated aqueous solution of sodium chloride (brine) is decomposed electrolytically by direct current, producing chlorine, hydrogen gas and a sodium hydroxide solution (Equation 2.6). The overall reaction of the process

\[ 2 \text{NaCl} + 2 \text{H}_2\text{O} \rightarrow \text{Cl}_2 + \text{H}_2 + 2 \text{NaOH} \quad (2.6) \]

takes place in two parts, at the anode and at the cathode. The evolution of chlorine takes place at the anode (Equation 2.7):

\[ 2 \text{Cl}^- \rightarrow 2 \text{Cl} + 2 \text{e}^- \rightarrow \text{Cl}_2 + 2 \text{e}^- \quad (2.7) \]

There are 3 basic processes for the electrolytic production of chlorine:
- Diaphragm cell process
- Mercury cell process
- Membrane cell process

Each process represents a different method of keeping the chlorine produced at the anode separate from the caustic soda and hydrogen produced, directly or indirectly, at the cathode. In all three processes, nearly saturated, purified brine must be introduced into the electrolysis cell. In the mercury cell process, sodium amalgam is produced at the cathode. The amalgam reacts with water in a separate reactor, called the decomposer, to produce hydrogen gas and caustic soda solution. For economic (energy) and environmental reasons, mercury and diaphragm plants are increasingly being converted to membrane electrolysers. The products are extremely pure. The chlorine, along with a little oxygen, generally can be used without further
purification. The sodium hydroxide solution contains little chloride and leaves the decomposer with a 50% (w/w) concentration.

Out of the three processes, the mercury process uses the most electric energy; however, no steam is required to concentrate the caustic solution. The use of large quantities of mercury demands measures to prevent environmental contamination. In addition, the hydrogen gas and sodium solution must be freed from mercury. Generally, the operation of the cells is not simple.

In the diaphragm cell process, the anode area is separated from the cathode area by a permeable, generally asbestos-based diaphragm. The brine is introduced into the anode compartment and flows through the diaphragm into the cathode compartment. Asbestos is banned in many countries and the process is not very popular any more. Caustic brine leaves the cell, and this brine must be freed from salt in an elaborate evaporative process. Even so, the resultant 50% (w/w) sodium hydroxide solution contains up to 1% (w/w) NaCl. The salt separated from the caustic brine can be used to saturate dilute brine. The chlorine contains oxygen and must be purified by liquefaction and evaporation.

The consumption of electric energy with the diaphragm cell process is approximately 15% lower than for the mercury process, but the total energy consumption is higher because of the steam required to concentrate the caustic brine. Environmental contamination with asbestos must be avoided. Under constant operating conditions, cell operation is relatively simple.

In the membrane cell process, the anode and cathode are separated by a cation-permeable ion-exchange membrane. Only sodium ions and a little water pass through the membrane.
Because the brine is recirculated some amount of solid salt is required for resaturation. The brine, which must be quite pure, is first dechlorinated and then purified by a straightforward precipitation-filtration process.

The introduction of membrane technology into chlorine-alkali electrolysis has dramatically increased the demands on brine purity (Du Pont 1991). The lifetime of chlorine-alkali membrane cells is determined by the operating conditions and the quality and purity of the feed into the electrolysers. Good long-term performance of the cells may be obtained if brine impurities are kept within the limits recommended. A major source of performance decline is the accumulation of solid material in the membrane (Bayer AG 1995).

Specific impurity levels are dependent on membrane design, cell design, operating conditions, the impurity itself and other impurities present. The pre-equisite for long membrane life is to maintain low levels of, for example, Ca\(^{2+}\), Mg\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\), Al\(^{3+}\), SO\(_4^{2-}\) and SiO\(_2\) in the brine. Traces of these impurities damage the membrane and/or electrodes and result in irrecoverable decreases in current efficiency and/or increased cell voltage.

The caustic soda solution has a concentration of up to 32±1% (w/w) NaOH. If a NaOH concentration of 50% (w/w) is required, evaporation can be used. The typical NaCl content is 20 ppm in a 32% (w/w) caustic solution.

The hydrogen has almost synthesis quality with a concentration of about 99.9 vol% H\(_2\) (dry basis). The chlorine has an oxygen content of about 1.5 vol% (dry basis). Chlorine with an oxygen content below 0.6 vol% (dry basis) can be obtained by acidifying the brine with hydrochloric acid.

As in the mercury process, the brine is dechlorinated and recirculated, which requires solid salt to resaturate the brine. The life of the expensive membrane
depends on the purity of the brine. Therefore, after purification by precipitation–filtration, the brine is also purified with an ion exchanger.

The caustic solution leaves the cell with a concentration of 30–36% (w/w) and must be concentrated. The chloride content of the sodium hydroxide solution is almost as low as that from the mercury process. The chlorine gas contains some oxygen and must be purified by liquefaction and evaporation.

The consumption of electric energy with the membrane cell process is the lowest of the three processes, approx. 25% less than for the mercury process, and the amount of steam needed for concentration of the caustic is relatively small. The energy consumption should be even lower when oxygen-consuming electrodes become common. There are no special environmental problems. The cells are easy to operate and are relatively insensitive to current changes, allowing greater use of the cheaper off-peak-time electric power.