# TECHNO-ECONOMIC ASSESSMENT OF PHYSIO-CHEMICAL AND ANAEROBIC TREATMENT OF TEXTILE WASTEWATER FROM THE TEXTILE INDUSTRIAL CLUSTERS IN TIRUPPUR

*Thesis Submitted to*

**BHARATHIAR UNIVERSITY, COIMBATORE**

*for the award of*

**DEGREE OF DOCTOR OF PHILOSOPHY**

**In Environmental Sciences**



**Submitted by**

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# CERTIFICATE

This is to certify that the thesis, entitled **"Techno-economic Assessment of Physio-chemical and Anaerobic Treatment of Textile Wastewater from the Textile Industrial Clusters in Tiruppur"** submitted to the Bharathiar University, in partial fulfillment of the requirements for the award of the **Degree of Doctor of Philosophy** in **Environmental Sciences,** is a record of original research work done by **Mr. M. BALADHANDAPANI** during the period of **2002-2007** of his research in the Department of **Environmental Impact Assessment** at **Salim Ali Centre for Ornithology and Natural History, Anaikatty, Coimbatore** under my supervision and guidance and the thesis has not formed the basis for the award of any Degree / Diploma / Associateship / Fellowship or other similar title of any candidate of any University.

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# DECLARATION

I, **M. BALADHANDAPANI** hereby declare that the thesis, entitled **"Techno-economic Assessment of Physio-chemical and Anaerobic Treatment of Textile Wastewater from the Textile Industrial Clusters in Tiruppur"** submitted to the Bharathiar University, in partial fulfillment of the requirements for the award of the **Degree of Doctor of Philosophy** in **Environmental Sciences,** is a record of original and independent research work done by me during **2002-2007** under the Supervision and Guidance of **Dr. PA. AZEEZ,** Department of **Environmental Impact Assessment, Salim Ali Centre for Ornithology and Natural History, Anaikatty, Coimbatore** and it has not formed the basis for the award of any Degree / Diploma / Associateship / Fellowship or other similar title of any candidate of any University.

(M. BALADHANDAPANI)

**Signature of the Candidate**

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**M BALADHANDAPANI**

## TABLE OF CONTENTS

## TABLE OF TABLES

## TABLE OF FIGURES

## TABLE OF PLATES

## GLOSSARY

| | |
|---|---|
| BDL | - Below Detectable Limit |
| BOD | - Biochemical Oxygen Demand |
| CAS Number | - Chemical Abstracts Service Registry Number |
| CETP | - Common Effluent Treatment Plant |
| $Cl^-$ | - Chloride |
| C:N | - Carbon : Nitrogen |
| C:N:P | - Carbon : Nitrogen : Phosphorus |
| COD | - Chemical Oxygen Demand |
| DNA | - Deoxy Ribonucleic Acid |
| EDTA | - Ethylene Diamine Tetraacetic Acid |
| G | - Gram |
| HC | - High Court |
| HUASB | - Hybrid Upward Anaerobic Sludge Blanket |
| IETP | - Individual Effluent Treatment Plant |
| Rs | - Rupees (Indian) |
| Kg | - Kilo gram |
| kL | - Kilo Litre |
| KLD | - Kilo Litres Per Day |
| Km | - Kilo Metre |
| L | - Litres |
| M'alkalinity | - Methyl Orange Alkalinity |
| M/H | - Metre Per Hour |
| ML | - Milli Litre |
| MLD | - Million Litres Per Day |
| MLR | - Material Liquor Ratio |
| MT | - Metric Tonnes |
| NGO | - Non Governmental Organizations |
| OLR | - Organic Loading Rate |
| P'alkalinity | - Phenolphthalein Alkalinity |

| | |
|---|---|
| PIL | - Public Interest Litigation |
| PVC | - Poly Vinyl Chloride |
| PWD | - Public Works Department |
| RO | - Reverse Osmosis |
| SBR | - Sequential Batch Reactor |
| SC | - Supreme Court Of India |
| SMBS | - Sodium Metabisulphite |
| Sq.Km | - Square Kilo Meter |
| SRT | - Sludge Retention Time |
| STP | - Standard Temperature And Pressure |
| TDS | - Total Dissolved Solids |
| TKN | - Total Kjeldahl Nitrogen |
| TLPA | - Tiruppur Local Planning Authority |
| TNPCB | - Tamil Nadu Pollution Control Board |
| TSS | - Total Suspended Solids |
| UASB | - Upward Anaerobic Sludge Blanket |
| USD | - United States Dollar |
| USEPA | - United States Environmental Protection Agency |
| VFA | - Volatile Fatty Acid |
| VSS | - Volatile Suspended Solids |
| ZED | - Zero Effluent Discharge |
| ZLD | - Zero Liquid Discharge |

## 1. INTRODUCTION

Tiruppur is known worldwide for hosiery and cotton textile garments. It is an undisputed fact that the ground water and surface water is contaminated from the discharge of treated /untreated effluents from the textile wet processing units of the town (Senthilnathan and Azeez, 1999). The Tiruppur town located on the banks of river Noyyal about 50 Km east of Coimbatore city is spread over 27.20 Sq.Km. The population of the town in 2001 was 5.43 lakhs showing the highest growth rate of urban agglomeration (77.24%) in Tamil Nadu, India. The so-called 'T Shirt city' or '*Baniyan* city' or 'Knit city' is frequent in the media regarding its poor environmental conditions and the consequences of the pollution of the textile industries.

The inception of the present day imposing banyan structure of the textile industry in the city dates back to 1935 when a manually operated hosiery unit came into being, accompanied by a consistent growth for 30 years to produce white and grey *baniyans*. The staggered growth of the industry from 1960 diversifying the range of products to inner wears and under garments catered the local markets of Tamil Nadu. In the early 80's Tiruppur entered the arena of exports of 'T' shirts. In the late 80s, knitwear industries further quickly diversified and took up manufacture and export of outer garments such as cardigan, jersey, pullover, ladies blouse, dress and skirt, trouser, nightwear, sportswear and even industrial wear. At present the units are involved in knitting and stitching, bleaching and dyeing, printing, embroidery works and allied activities such compacting, raising and calendaring. Besides, the industrial units directly involved in hosiery manufacture, various associate units producing elastic tapes, cartons, labels, polythene bags and other packing materials are also in operation in Tiruppur.

This blooming of industries was accelerated by Government policies favouring export of garments, with the availability of cheap labours and raw materials and flexible entrepreneurial environment. The high labour cost and movements against environmental pollution in the European countries and United States resulted in disbanding of similar industries in those countries. Consequently many of those countries have to depend on

the South Asian countries for garments. The lenient pollution control authorities weighing the socio-economic benefits of the industries encouraged the blooming industries further. The erratic rainfall and loss of agriculture offering insufficient returns in Tiruppur and neighbouring areas made people, who were basically agriculturists to search for an alternative source of livelihood. All these factors fostered the dramatic growth of textile industries in Tiruppur.

The textile policy framed in the year 1985 supported the compounded annual growth rate of 7.13% in cloth production. It raised the share of textiles export to 13% of value added domestic manufacturing of the country, and to one third of the export earnings of the country. Tiruppur started export with modest quantity in the range of about Rs 19/- crores, exporting 172 lakhs pieces in the year 1985. By 1996 the exports increased 100 fold by value, exporting 2574 lakhs pieces earning Rs 1897/- crores contributing 21.73% of national export of garments. During 2002 and 2003 the export was 349 million pieces earning US$ 667/- million and 370 million pieces earning US$ 793/- million respectively. In the year 2004, Tiruppur exporters earned Rs 4685/- crores by selling 4098 lakhs pieces which accounted for 31.98% of all India exports earnings. Woven garments mainly catering the domestic market was about Rs 5/- crores in 1996 which increased to Rs 132/- crores in 2004 selling 94 lakh pieces.

The industries in Tiruppur are providing enormous employment, mostly to erstwhile agricultural workers. Currently, former agricultural labours mostly from southern and eastern districts of Tamil Nadu are actively engaged in knitwear production. Two lakhs people are directly employed in Tiruppur and around five lakhs are indirectly employed.

Wet processing is an important step in the production of textile and hosiery. The wet processing units require fresh water and a variety of chemicals that include dyes, common salt or Glabour's salt, acids (hydrochloric acid, sulphuric acid and acetic acid), alkalis (sodium hydroxide and sodium carbonate), hydrogen peroxide or hypochlorite, wetting agents, detergents, softening agents and dye fixing agents. During the process of

dyeing only a portion of the dye gets fixed on the cloth while the rest along with the natural wax and gum from the fabric are released in the effluent.

In Tiruppur the fresh water intake by existing industries was around 100 Million Litters Per Day (MLD). Almost the same volume of wastewater is generated. Until 1998 the wastewater was disposed off without any treatment into the river Noyyal. The wastewater containing unused dyestuffs is deeply coloured. Generally, the effluent is alkaline, the electrical conductivity ranges from 10 to 15 mhos/cm and total dissolved salts (TDS) are more than 6000 mg/l with high chloride content and traces of heavy metals. Most of the parameters are higher than the discharge standards stipulated by the Tamil Nadu Pollution Control Board (TNPCB). The discharged wastewater flowing in the river Noyyal is stored at Orathupalayam dam constructed in the year 1992 across the river Noyyal about 30 Km downstream of Tiruppur.

The storage at Orathupalayam has caused severe ground water pollution in the Noyyal river basin and spoiled the potable water, agriculture and fisheries. For their role in polluting downstream areas these industries face severe protest from the public, NGOs and downstream farmers. On behalf of the Karur Taluk Noyyal Canal Agriculturist Associations, Mr.P.R.Kuppusamy, the then president, filed a writ petition in the Madras High Court against the industries during mid 90's. Consequently, as per the directions of the Court, TNPCB closed 166 industries that failed to comply with the directions to treat the wastewater. To handle the issue of pollution about 292 units occupied in dyeing and bleaching established 8 Common Effluent Treatment Plants (CETPs) in 1999; further, 437 units formed Individual Effluent Treatment Plants (IETPs) investing around Rs 70/- crores. The Government promoted the CETP scheme providing financial subsidy to the extent of 50% of the capital cost. However, these effluent treatment facilities employed only primary treatment techniques, where-in partly the colour, suspended solids, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) are removed. Since it is ineffectual in removing the dissolved solids, the treated wastewater with high TDS of about 7000 ppm is discharged into the river Noyyal.

Rapid growth of the industries has also led to high industrial demand of water and many farmers used their wells for selling water to industries rather than for irrigation. The depletion of ground water encouraged percolation of the polluted water to the aquifer spoiling its quality.

Loss of Ecology Authority (Tamil Nadu) examined the situation and identified the affected areas (Table 1.1) by the discharge of industrial effluents in the basins of the rivers Noyyal and Amaravathy (CES, 2003). The authority awarded Rs 108/- crores as compensation to the farmers for the losses incurred upto the year 2003 by the discharge of textile wastewater to the Noyyal river basin from Tiruppur industrial cluster. On appeal from industries, the authority reduced the compensation to Rs 24/- crores. The Public Works Department (PWD) also assessed Rs 12.5/- crores as the cost of desilting and cleaning the Orathupalayam dam where the textile effluent from Tiruppur industrial cluster was stored.

Because of the continued discharge of partly treated effluents from the Tiruppur industries the affected farmers again filed a writ petition in the honourable High Court of Madras (HC) in 2003. TNPCB and HC issued various directions to install Zero Liquid Discharge (ZLD) System to arrest the disposal of effluents to the river. The various events that took place regarding the control of textile wastewater and setting up the ZLD system are summarised below (Table 1.2) in chronological order.

| River basin/industrial cluster | Affected area (Hectares) | Number of villages |
|---|---|---|
| Noyyal river basin | 159022 | 121 |
| Amaravathy river basin | 141415 | 76 |
| Telungapalayam and Kumarapalayam industrial cluster | 32368 | 21 |
| Tiruppur industrial cluster | 85946 | 71 |
| Karur industrial cluster | 50651 | 40 |

**Table 1.1. Affected area by the discharge of industrial effluents**

**Table 1.2 The events related to textile wastewater discharge and setting up ZLD systems in Tiruppur**

| Date | Activity | Remarks |
|---|---|---|
| 2002 | TNPCB issued directions to install the (ZLD) system to first 10 large and medium scale processing units and later 28 units. | The industries that were not taken steps to install ZLD system were shut down. Later they were allowed to operate as they took measures to install ZLD system. |
| 2003 | The farmers' representative Mr. Pappavalasu Govindasamy filed a writ petition in the HC against the discharge of wastewater to the river. | |
| 2004 | HC issued directions to the processing units to take necessary steps to stop the discharge of wastewater. | |
| May-2005 | HC constituted an Expert Committee to advice on the technical aspects of textile wastewater management. | |
| 2005 | 11 more CETPs were initiated in Tiruppur apart from existing 8 CETPs to deal with the textile effluent treatment and reuse. | |
| June-2005 | The CETPs filed affidavits in the HC stating their willingness to install ZLD system within a year. | |
| Aug-2005 | HC appointed a Monitoring Committee, comprising of advocates, to intimate the court on the development of the ZLD systems. | |
| 10.6.2005 | The industries were directed to run their units for 5 days per week to reduce effluent generation. | |
| Jan-2006 | HC ordered the industries to deposit 50% of capital cost of ZLD system to show their bonafide in implementing the ZLD systems. | Most of CETPs deposited 50% of capital cost and complied with the directions of the HC. Few of the CETPs who had not complied with the directions were closed or slapped fine. |

| | | |
|---|---|---|
| July-2006 | CETPs did not complete the ZLD system before July 2006. Instead, they filed affidavits in HC praying for allowing time extension upto Dec-2006 to complete ZLD system and running their processing units. | |
| Sep-2006 | The HC permitted time extension upto December 2006 to complete and run the ZLD systems. | Nevertheless, all the CETPs failed to complete the ZLD project on or before December 2006. |
| Dec.2006 | The CETPs filed affidavits requesting further time extension upto July 2007 for completion of ZLD project. | |
| Dec.2006 | HC allowed the processing units to run their units with the condition of fine for not completing the project before Dec-2006. The fine amount would be in proportion to the quantum of wastewater generation at the rate of 6 paise/litre for three months from January 2007 onwards, 8 paise/litre for subsequent two months and 10 paise/litre for further two months upto July 2007. Further, the HC issued the directions to pay the dues for Loss of Ecology and desilting and cleaning the Orathupalayam Dam. | The CETPs paid the penalty as per the direction of the HC for three months. The dues for Loss of Ecology, and desilting and cleaning of Orathupalayam dam were paid partly. |
| Apr.2007 | The CETPs filed an affidavit in the Supreme Court of India (SC) stating their inability to pay penalty for discharge of wastewater and prayed for further time extension to complete the projects. | |
| Sep.2007 | SC directed the CETPs to deposit Rs 25/- crores meant to pay loss of ecology and other related consequences. | The CETPs deposited Rs 25/- crores as directed by SC. The case is still pending with SC. |

Presently, the industries operating in Tiruppur to sustain their operation have to solve the major disadvantages of physio-chemical treatment, generation of the hazardous sludge and the cost involved. The claims of the affected farmers and cost of desilting and cleaning the river and the dam increased the burden on the industries further. However

the industrialists are now on the look out for ways and means to reduce the cost of production and cost of the wastewater treatment. It is a need of the hour to search for alternative treatment system that is technically viable and cost effective.

In that context, the present study was undertaken aiming to address the following.

a) Characterisation and assessment of pollution load in the wastewater generated from the clusters of textile wet processing industries in Tiruppur.

b) Evaluation of the performance of established physio-chemical treatment systems in a CETP treating textile wastewater.

c) Explore any alternative treatment techniques applicable in Tiruppur.

# 2. TEXTILE WET PROCESSING INDUSTRIES IN TIRUPPUR AND ENVIRONMENTAL CONSEQUENCES OF WASTEWATER.

## 2.1 Introduction

Tiruppur is one of the major textile industrial clusters in India. It shows 52.4% decadal growth rate producing garments to cater local and international markets. The industrial units in Tirupur produce garments worth more than US$ 1 billion annually. The tremendous growth of industries was attributed by the favourable textile policy, available cheap labours and raw materials, and other such factors. The major occupation that was traditionally agriculture in this region shifted to industrial manufacture from the last three to four decades. The agriculture in the year 1971 was 78.52% in this region which reduced to 35.40% in 1991. This chapter discusses about the industrial units in Tiruppur, details of wastewater generation and effluent treatment facilities, environmental impact of the textile wastewater, and the environmental consequences of dyes and other chemicals used in the textile wet processing.

## 2.2 The industries in Tiruppur

The different industries functioning in Tiruppur industrial cluster are given in the table 2.2.1. The industries engaged in knitwear manufacturing and allied activities are predominant in Tiruppur. Of the total industrial units about 1987 are located within the Tiruppur Municipality and 661 in Tiruppur Local Planning Area. In addition, around 2500 garment stitching units, 200 embroidery units and about 200 allied industries involved in compacting, raising and calendering are operating in Tiruppur.

| S.No. | Type of industry | Number of industries |
|---|---|---|
| 1 | Bleaching / dyeing / printing | 1056 |
| 2 | Cotton ginning, cleaning and billing | 81 |
| 3 | Knitting industries | 1352 |
| 4 | Food processing | 48 |
| 5 | Weaving of cotton Textile/ Power Loom | 31 |
| 6 | Textile mills | 42 |
| 7 | Others | 38 |
| **Total** | | **2648** |

**Table 2.2.1 Number of industries functioning in Tiruppur**

## 2.3 Polluting industries

Among the various industries operating at Tiruppur, the wet processing units like dyeing, bleaching, mercerizing and printing are the major sources of water pollution. The Environmental (Protection) Act, (1986), classifies severely polluting industries such as dyeing units under the 'red' category, moderately polluting units like bleaching and printing industries under 'orange' category and non polluting industries under 'green' category. Textile wet processing industries such as dyeing, bleaching and mercerizing. are considered the backbone for garment manufacturing. In the 1980s, only 68 such industries were in operation in Tiruppur. During the eighties and nineties the scenario underwent a phenomenal change due to export demand and several other factors. The number of industries rose from 450 units in 1991 to 866 units in 1997. Meanwhile in 1999 enforcement by TNPCB of the directives from HC led to closure of certain industries that were not complying with the pollution control regulation. Currently 685 wet processing industries comprising of 593 dyeing and 92 bleaching units, are in operation in Tiruppur.

## 2.4 Textile wet processing

The textile wet processes such as scouring, neutralizing, desizing, mercerizing, carbonizing, bleaching, dyeing and printing require use of large quantity of water and are thus called 'wet processing'. The dyeing operations carried out in Tiruppur could be grouped into scouring and dyeing operations. Scouring operation involves removal of

non-cellulosic materials in the cloth to enable dyestuffs to react and bond with the fibers effectively. From the aqueous solution, the large molecules of the dye are transferred to the solid phase, such as cloth which can be explained by the second law of thermodynamics where in a fall in entropy occurs. The two processes of dyeing is followed by washing, soaping and other sequences to obtain the desired depth of shade.

### 2.4.1 Scouring

The raw cloth contains non-cellulosic natural impurities such as waxes, pectines, proteins, grease, fats and miscellaneous substances such as pigments, hemicelluloses and reducing sugars. Raw cotton contains 4 to 12% by weight of these items (Karapinar and Sariisik, 2004). These impurities must be removed before dyeing to ensure the dye molecules react with cloth effectively, as the hydrophobic nature of the impurities affect fabric wettability and absorbency (Etters, 1999; Hartzell and Durrant, 2000). Scouring (Kier boiling), the process in which the cloth is boiled for about 3-4 hours with steam in an alkaline solution containing caustic soda, soda ash, wetting agent and hydrogen peroxide or sodium hypochlorite removes the impurities. After the scouring operation the spent liquor is discarded. The spent liquor is highly alkaline, dark brown in colour, high in temperature and contains suspended cotton lint (Manivasakam, 1997). Traces of chemicals and impurities from the cloth are then washed off. Trace of hydrogen peroxide is removed by neutralizing with reducing agents commercially called 'peroxide killer'; if not the remaining trace of hydrogen peroxide will oxidize the dyes used in the subsequent process. After the neutralization of hydrogen peroxide the cloth goes though another step of washing.

### 2.4.2 Dyeing

Being an integral part of decorations since pre-historic stage of human development, various types of chemicals are in use for the purpose. In Tiruppur mostly azo reactive dyes are used for colouring the cloths. Of this class of dyes the first dye was made by Karl Alexander Von Martius (at Roberts, Dale and Co.) in France in 1862 and was known

as Bismarck Brown. Fibre reactive dyes were synthesized by Imperial Chemical Industries (ICI) in the year 1956 (Welham, 2000). A chromophore and a reactive group characterize the reactive dye molecules. The wide acceptability and popularity of this group of dyes was mainly due to its property of good wet fastness. The chemistry of coloring by reactive dye involves by a chromophore attached to a reactive group reacting with cotton imparting colour to the fiber. The reactive group is invariably electrophilic reacting with cellulose and thereby binding the chromophore to the fibers. The reaction is achieved by direct chemical covalent linkage, which is rapid and irreversible (Shenai, 1995). The chemical groups in the reactive group are typically pyrimidine, triazine and sulphones reacting with hydroxyl group of cellulose by either nucleophilic substitution or addition. This so called 'Exhaust Dyeing' is highly complex and advanced. Generally salts, usually either common salt or sodium sulphate are added to promote the dye binding onto the fiber. An alkali usually sodium carbonate and/or sodium hydroxide is added to induce the nucleophile-dye electrophile reaction. The heterogeneous mixture is heated using steam to augment the rate of reaction. However, portion of the dye that is hydrolyzed in the water is discharged in the wash-off and discarded to effluent. All reactive dyes are prone to hydrolysis and cause environmental consequences on discharge. Generally, the dyers use one or more dyes to produce the desired shade. Achieving the exact shade requires good quality of water and chemicals. If desired shade is not achieved in the first sequence of dyeing, the dyers carry out re-dyeing to match the required shade. This further increases the cost of the process and also the environmental impacts. Dyeing is followed by one or two washing sequence using fresh water to remove the unutilized dyes. This process requires large volume of water and the same is discarded as effluent.

The high pH raised during dyeing operation is neutralized by acid. Afterwards the cloth is subjected to soaping and washing at high temperature to remove loosely bound dye molecule. Based on the required depth of shade one or two washings are carried out. To enable dye molecule to fix to the fabric firmly, a fixing agent is added to the bath. Then the cloth normally is washed. However, this washing is not obligatory. The cloth is then dried in shade or in stream drier. In all sequences huge volume of water is discharged

along with the chemicals added for the purpose. Figure 2.4.1 shows the flow chart of dyeing process and the variety of chemicals used.

### 2.4.3 Bleaching

Natural fibers, due to the presence of colored bodies in the fiber, are off-white in colour. The organic molecules that colour the fibers contain conjugated double bond. Bleaching destroys these colors by breaking the conjugated double bond and thus rendering the cloth white. Chemicals that are used as bleaching agents are oxidizing agents. Usually sodium hypochlorite, hydrogen peroxide and sodium chlorite are used in bleaching applications.

Sodium hypochlorite and hydrogen peroxide are widely used in Tiruppur for bleaching the grey cloth. Sodium hypochlorite is a salt of moderately strong base and weak acid and forms alkaline solution in water. Upon ionization in water, it yields hyphochlorous acid which is an active bleaching agent. The optimum pH for bleaching operation of hypochlorous acid is 9–10. Nowadays, hydrogen peroxide is preferred for bleaching application, as it does not generate organochlorine compounds which are suspected carcinogens. $H_2O_2$, a weak acid, ionizes in water to form hydrogen ion and perhydroxyl ion. The perhydroxyl ion is the active agent in bleaching operation at optimum pH of 10.2 - 10.7. The figures 2.4.2 and 2.4.3 show the process flow chart of peroxide bleaching and hypochlorite bleaching respectively.

To achieve the required alkaline pH in both the cases sodium hydroxide is added. Wetting agent and chelating agent either EDTA salts or sodium silicate is added to the bleaching process for stabilization. After completion of bleaching process, the cloth is treated with acid to neutralize pH. The optimum temperature for sodium hypochlorite bleaching is 40°C and peroxide bleaching 95–100°C. Peroxide bleaching is carried out in modern softflow machines. Washing is done to remove the residue of chemicals and other impurities from the cloth. In the final bath optical brighteners are added to give an intensively brilliant white. Optical brighteners possess the property of fluorescence; that they absorb shorter wavelength radiations and emit longer wavelengths.

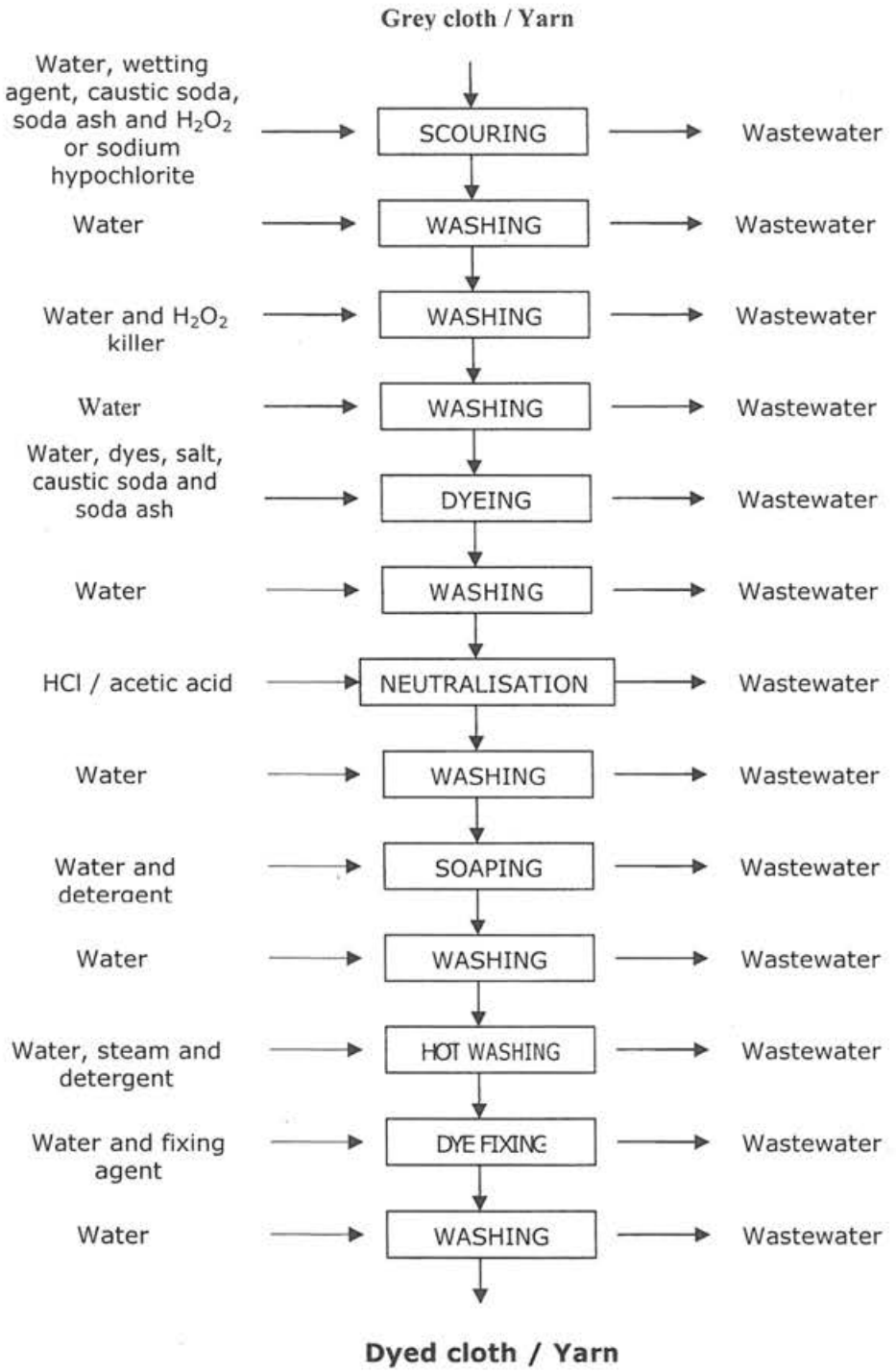



**Figure 2.4.1 Dyeing process**

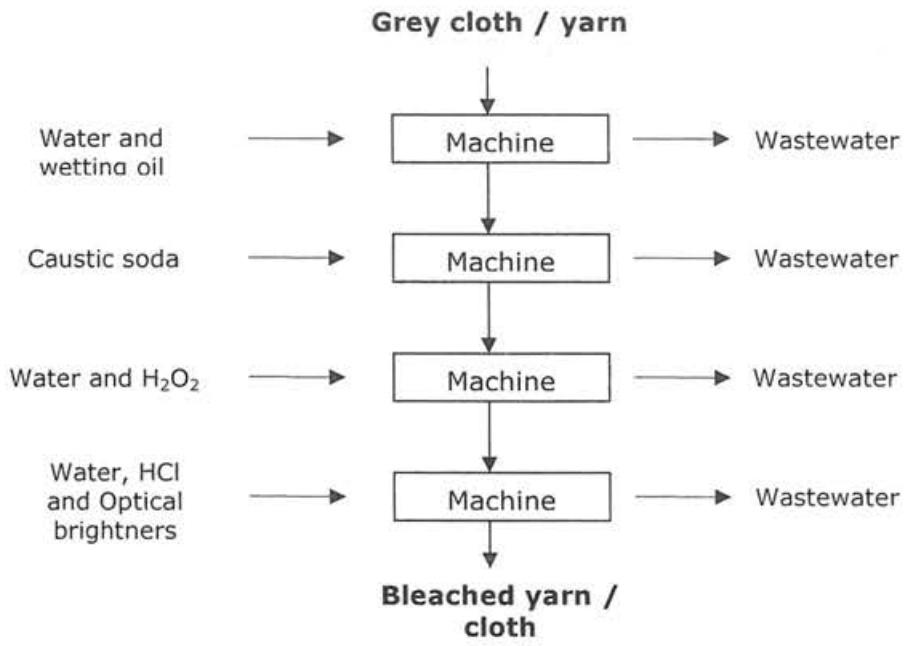



**Figure 2.4.2 Peroxide bleaching process**

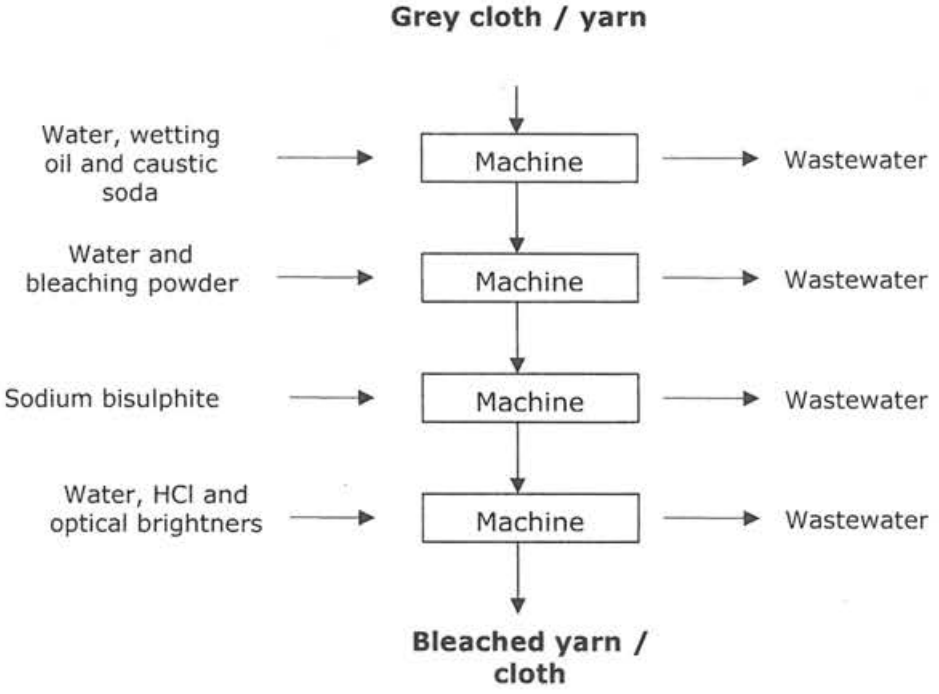



**Figure 2.4.3 Hypochlorite bleaching process**

## 2.5 Water and chemicals used in the textile wet processing units

Textile industries consume huge volume of water and a variety of chemicals. Textile industries are complex in terms of raw materials used, chemicals applied, and techniques employed and products manufactured (Germirli *et al.*, 1990). The chemical reagents used are very diverse in nature ranging from inorganic compounds to polymers and organic products (Mishra and Tripathy, 1993). The huge consumption of water and chemicals eventually results in generation of huge volume of wastewater (Ghoreishi and Haghighi, 2003) and hence, textile industries are the largest water users and polluters (Nemerow, 1978). Depending on the type of fabric processed water requirement varies from 60 - 400 l/Kg (PRG, 1998; AEPA, 1998). Germirli *et al.* (1999) opined that the volume of water consumption for textile processing varies from 20 to 100 $m^3$ per tonne of fabric, while Senthilnathan and Azeez (1999) reported that 175 to 200 litres of fresh water usage for processing of one Kg of fabric in Tiruppur. They further state that an average of 80 to 95% of the water flows out as effluent.

Quantum of water used for fabric processing depends on the type of machine used, material liquor ratio (MLR) and strength of the dyes applied. The MLR is ratio of weight of the fabric to the weight of the liquor. Shenai (1995) has pointed out that the MLR for conventional winch dyeing machine ranged from 1:14 to 1:20. The advanced softflow dyeing machines are designed to dye under low MLR. The dye exhaustion is more in high concentration of dye solution in the low MLR employing machine resulting in reduced generation of wastewater and wastages of dyes. Joseph (2000) reported the water requirement for dyeing of one Kg of cloth in the softflow machine as 70-100 liters while the conventional winch consumes 150-200 litres, where in the MLR applied was 1:6 to 1:10 and 1:14 to 1:20 respectively.

Various activities under wet-processing such as scouring, desizing, bleaching, mercerizing and dyeing generate huge volume of wastewater and face serious concerns globally (Yusuff and Sonibare, 2005; Germirli *et al.*, 1990). The huge volume of

effluents are dark coloured because of poor exhaustion of reactive dyestuffs (Shaw, 1998) from the medium. A comparison of water usage in Tiruppur in major activities such as bleaching and dyeing using the winch and softflow machine is given in the table 2.5.1. The approximate quantum of dyes and various chemicals used in the textile wet processing units in Tiruppur are given in the table 2.5.2.

| S.No. | Process | Water Usage L/Kg of cloth | |
|---|---|---|---|
| | | Winch machine | Softflow machine |
| 1 | Bleaching | 60 | 30 |
| 2 | Light shade dyeing | 130 | 70 |
| 3 | Medium shade dyeing | 140 | 90 |
| 4 | Dark shade dyeing | 160 | 110 |

**Table 2.5.1 Water usage for bleaching and dyeing of hosiery cloth**

| Dyes and chemicals | Usage (MT/Year) |
|---|---|
| Dyes | 3000 |
| Salts | 120000 |
| Caustic soda | 7500 |
| Soda ash | 40000 |
| Acid | 6000 |
| Wetting agents | 1500 |
| Hypochlorite | 3000 |
| Hydrogen peroxide | 6000 |
| Hydrogen peroxide killer | 1000 |
| Detergents | 3000 |
| Fixing agents | 3000 |
| Softening agents | 3000 |

**Table 2.5.2 Quantity of dyes and chemicals used in wet processing units in Tiruppur**

## 2.6 Water pollution of the Noyyal River

The river Noyyal, a tributary of river Cauvery, is originating in the Vellingiri hills of Western Ghats. It flows through Coimbatore, Tiruppur joining the river Cauvery at Noyyal village after flowing about 175 Km through Coimbatore, Erode and Karur

districts (Figure 2.6.1). The catchments in the river basin are around 3.49 lakhs hectares spread over in more than 100 villages. The river was once the source for drinking and irrigation activities for people living on its banks. In the year 1991 across the river Noyyal at Orathupalayam a dam was constructed with the water-spread area of 1049 acres with an estimate of Rs 1646/- Lakhs, The water storage at Orathupalayam was envisaged to irrigate 500 acres in Erode district and 9875 acres in Karur district.

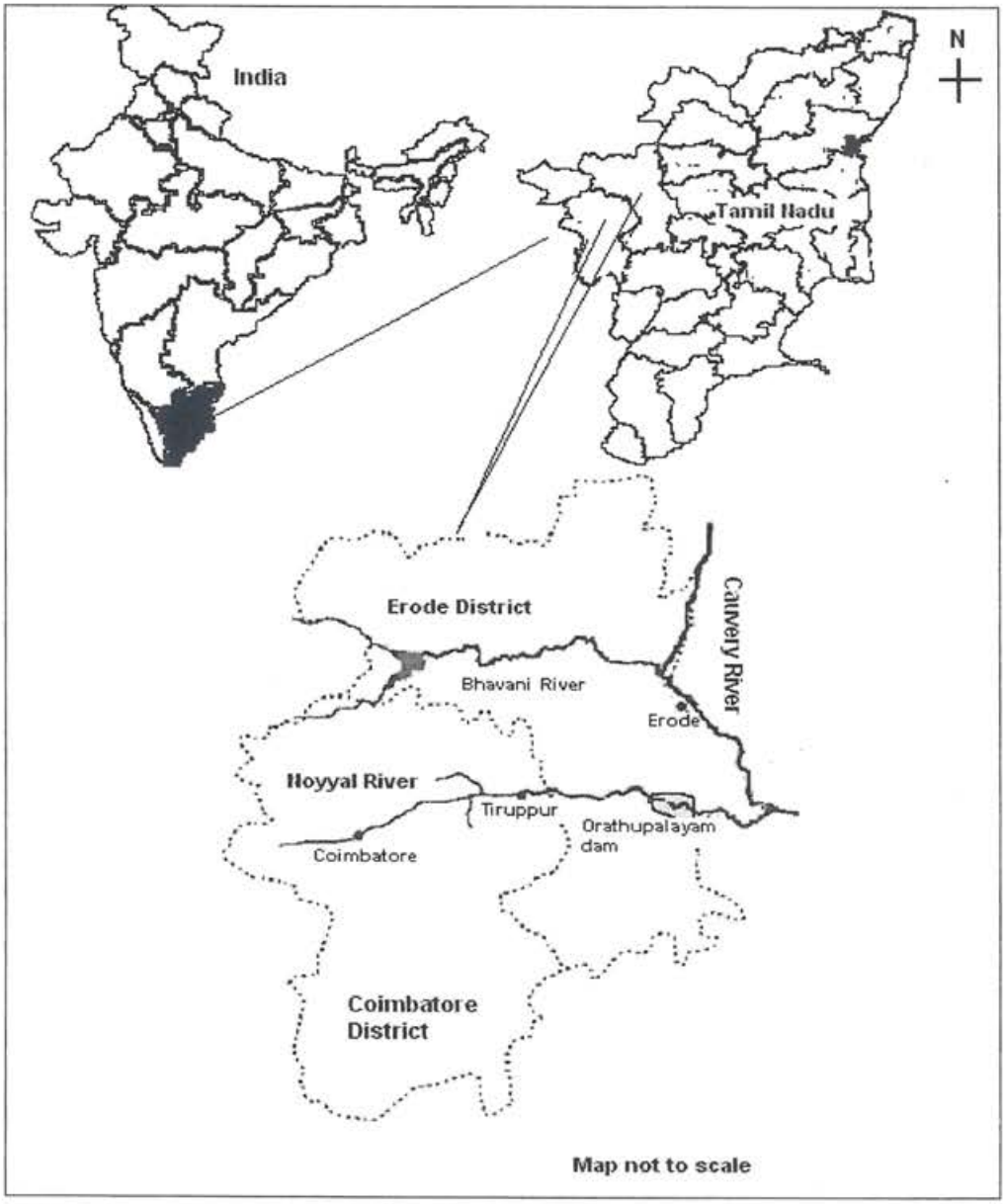



**Figure 2.6.1 Location of river Noyyal, Tiruppur and Orathupalayam dam**

Continuous discharge of untreated textile wastewater before 1999 and partially treated wastewater later from the Tiruppur textile industries has polluted the river Noyyal and ground water of the river basin considerably. In the past the river Noyyal was perennial one. The erratic rainfall, the untreated sewage from Coimbatore, Tiruppur and other human settlements located on the banks of the river, and unauthorized diversion and use of water at upper reaches of the river worsened the problems in the river and the downstream agricultural lands. Round the year, whatever flows in the river is wastewater. During monsoon, when the rainfall is heavy it dilutes the effluent. In general the water in the river looks so dark coloured, alkaline and highly brackish in nature. Rajaguru and Subbhuram (2000) had reported that wells located proximal to the river are highly polluted. They also observed high porosity and low levels of sorption capacity in the affected soil. The continuous release of effluents resulted in accumulation of pollutants in the ground water. The TDS levels in the open and bore wells ranged from 3000 to 11000 mg/l and chloride level ranged from 2000 to 5000 mg/l, which clearly indicate the effect of pollution, by the industries. Jayashree and Jothimani (1999) while examining the water qualities of river Noyyal reported it to be is severely polluted by industrial effluents.

## 2.7 Environmental consequences of textile wastewater, dyes and chemicals used in the textile wet processing

Various pollutants present in the textile wastewater find their way upon disposal finally to the aquatic systems. The textile wastewater chiefly contains unused reactive azo dyes. Among different types of dyes, azo dyes account for more than 50% in terms of worldwide use and about 2000 of such dyes are used in textile, leather, plastics, paper, cosmetics and food industries (Stolz, 2001; Carliell *et al.,* 1995). Some statistics regarding the azo dye usage world over in textile dyeing is as follows (Hutchings and Ebenezer, 2001): i) $4.0 \times 10^6$ MT/annum of cotton is dyed with reactive dye, ii) $4.0 \times 10^8$ MT/annum of fresh water is used for the processing, iii) $2.8 \times 10^6$ MT/annum of salt is used, iv) $8.0 \times 10^4$ MT/annum of reactive dye is used with fixation yield of 70% and v) $2.4 \times 10^4$ MT/annum of reactive dye is discharged in the wastewater.

As noted earlier, part of azo dyes remains unutilized during the production and processing. The dye loss from the processing varies according to the class of dyes used. Around 2% of the disperse dye and 50% of reactive dye is lost during the processing (McMullan *et al.,* 2001). The study by Reife and Freeman (1996) indicated that about 12% of synthetic dyes are lost during manufacturing and processing operations.

The effluent poses serious environmental problems on disposal. Severe contamination of the river and ground water is noticed in the places where large numbers of textile industries are operating (Stolz, 2001). Rajaguru *et al.* (2006) reported the presence of DNA damaging aromatic amines in ground water polluted by effluents discharged by the textile dyeing and bleaching industries functioning in Tiruppur.

Several of pollutants found in the textile wastewater such as dyes, insecticides, fungicides, oils and grease, detergents etc., showed recalcitrant and biotoxic property (Balanosky, 2000). The chemicals used in the textile wet processing cause varied effects on the receiving ecosystem. Sodium salt extensively used in dyeing process for fixation of the dyestuffs to the fabric, upon its discharge to ecosystems also functions as an electrolyte. It influences osmosis in the plants, and metabolism of microorganisms and animals. Bleaching agents such as sodium and calcium hypochlorite are known to cause irritation in eyes, skin, respiratory and gastrointestinal tract resulting in severe corrosive damage upon high-level exposure.

Some of the textile azo dyes, dye precursors and degradation products are carcinogenic in nature. The processes involved in synthesis of azo dyes are diazotization of aromatic amines followed by coupling to another aromatic compound (known as coupling component) resulting in formation of an azo bond (Shenai, 1995). The induction of cancer in human bladder by the azo dyes has been reported by Choudary (1996), Morgan *et al.* (1994) and Piolatto *et al.* (1991). Many aromatic amines are recognized as the human carcinogens (Stolz, 2001). Benzidine has been widely used in production azo dyes (Chung *et al.*, 2000). Benzidine and its analogues are known to damage DNA in human lymphocytes inducing genotoxicity (Chen *et al.*, 2003).

The aromatic amines are released by cleavage of azo bond by a reducing agent or azo reductase enzyme present in the anaerobic microflora. Benzidine and analogues are produced by certain intestinal and environmental microbes via reduction of azo dyes catalysed by the azo reductase enzyme (Chung and Cerniglia, 1992; Chung *et al.*, 1993). *Staphylococcus aureus* a skin bacterium capable of metabolizing the azo dye *Direct blue 14* to o-tolidine aromatic amine was reported by Platzek *et al.* (1999).

Due to malignant property of the azo dyes and aromatic amines, several countries have banned their manufacture and use. The German Government in 1994 banned use of dyes which release one or more aromatic amines listed in the table 2.7.1 (German Consumer Goods Ordinance, 1997). In India the manufacture, processing, storage, consumption and sale of 42 benzidine based dyestuffs and its congeners were banned from 30.1.1993. 70 other dyestuffs that release carcinogenic arylamines were also banned by law on 26.06.1997. Dyestuffs causing carcinogenicity are regulated from use, production and import in Turkey since March 1995. European Union initiated similar actions on the azo dyes that release carcinogenic amines on reductive cleavage by reducing agents and microbes.

Apart from carcinogenicity many azo dyes are known to cause genotoxic and mutagenic effects. Four textile dyes namely *Astrazon Yellow*, *Red*, *Blue* and *Black* were tested for the genotoxic effects in *Drosophila melanogaster* by Dogan *et al.* (2005) and was found that these dyes decreased survival rate proportionate to the concentration of dyes used. Mutagenicity of different textile dyes available in the European market were tested by Jager *et al.* (2004) using the bacterium *Salmonella typhimurium* and mouse lymphoma cells. The results indicated that out of 53 dyes, 15 were positive to Ames test and 15 showed positive results with TA98 and TA100 strains of the bacterium. Using the mouse lymphoma assay 6 out of 9 dyes showed genotoxic effects. Similar effects was observed in *Salmonella typhimurium* strains like TA100, TA98, TA1535, TA1537 and TA1538 for six concentrations 2.5, 4.5, 9.0, 18 and 22.5 μg/mL of the dye solution (Moawad *et al.*, 2003). The same dyestuffs were toxic to seed germination and changed shoot and root length of the plants such as clover, wheat, tomato and lettuce. Bakshi and Sharma (2003) have demonstrated that structural groups such as phenylenediamaine, amino and nitro-

groups, methylation, CH=CH and chloro groups are genotoxic to *Salmonella typhimurium.* Mathur *et al.* (2005) had shown that six dyes among Cremazoles dyes (*Orange 3R, Brown GR,* and *Blue S1* and direct dyes viz *Congo red, Royal blue* and *Bordeaus*) were mutagenic to *Salmonella typhimurium.* They indicated that the dyes *Congo red, Royal Blue, Orange 3R* and *Brown GR* dyes were moderately mutagenic whereas *Bordeaux dye* was extremely mutagenic to 100 µL of dye dose. Cremazole dyes inhibited growth of bacteria at higher dose levels.

| S.No | Substances | CAS No |
|---|---|---|
| 1 | 4-aminodiphenyl | 92-67-1 |
| 2 | benzidine | 92-87-5 |
| 3 | 4-chloro-o-toluidine | 95-69-2 |
| 4 | 2-naphthylamine | 91-59-8 |
| 5 | 4-amino-2',3-dimethylazobenzene | 97-56-3 |
| 6 | 2-amino-4-nitrotoluene | 99-55-8 |
| 7 | 4-chloroaniline | 106-47-8 |
| 8 | 2,4-diaminoanisole | 615-05-4 |
| 9 | 4,4'-diaminodiphenylmethane | 101-77-9 |
| 10 | 3,3'-dichlorobenzidine | 91-94-1 |
| 11 | 3,3'-dimethoxybenzidine | 119-90-4 |
| 12 | 3,3'-dimethylbenzidine | 119-93-7 |
| 13 | 3,3'-dimethyl-4,4'diaminodiphenylmethane | 838-88-0 |
| 14 | 4-cresidine | 120-71-8 |
| 15 | 4,4'-methylene-bis-(2-chloroaniline) | 101-14-4 |
| 16 | 4,4'-oxydianiline | 101-80-4 |
| 17 | 4,4'-thiodianiline | 139-65-1 |
| 18 | 2-aminotoluene | 95-53-4 |
| 19 | 2,4-diaminotoluene | 95-80-7 |
| 20 | 2,4,5-trimethylaniline | 137-17-7 |
| 21 | 2-methoxyaniline | 90-04-0 |
| 22 | 4-aminoazobenzene | 60-09-3 |

**Table 2.7.1 Aromatic amines banned by Germany**

Rajaguru *et al.* (2001) had studied genotoxic effects of four sulphur dyes used in the textile wet processing namely *Sandopel Basic Black BHLN, Negrosine, Demapel Black FNI* and *Turquoise Blue* on *Rana hexadactyla* tadpoles. They observed all four dyes caused DNA damage. Birhani and Ozmen (2005) evaluated the potential toxicity of six commercial textile dyes such as *Astrazon red FBL, Astrazon blue FGRL, Ramazol red RR, Ramazol turquoise blue G-A, Cibacron red FN-3G* and *Cibacron blue FN-R* dyes. They used frog embryo teratogenesis assay-Xenopus (FETAX) and found varying degrees of teratogenicity in the order of *astrazon blue FGRL > Ramazol turquoise blue G-A > Astrazon red FBL > Cibacron blue FN-R > Cibacron red FN-3G > Ramazol red RR.*

The azo dye $RP_2B$ is reported to have effects on growth of nitrogen fixing cyanobacteria, *Anabaena* sp (Hu and Wu, 1995). The toxicity of 17 selected process effluents, 11 reactive dyestuffs and 8 auxiliaries collected from a textile dyeing and finishing mill in Turkey was evaluated by bioluminescence test using bacteria *Vibrio fischeri.* It was found that one among them exhibited high toxicity, 7 showed moderate toxicity and 9 indicated a low or no toxicity (Wang *et al.,* 2001). Synthetic textile wastewater prepared by Ledakowicz and Gonera (1999) using the anthraquinone dyestuff *Acid Blue 40 C.I. 2115* and other constituents showed inhibitory action to the level of 47% on growth of bacteria isolated from activated sludge employed for biodegradation. Azo dyes are known to effect in three ways, (a) azo dyes exhibit toxicity when reduced to aromatic amine, (b) azo dye containing aromatic amine structure that can be oxidized without azo reduction and (c) direct activation of azo linkage in the azo dye to highly reactive electrophilic diazonium salt (Brown and DeVito., 1993).

Some of the reactive azo dyes are known to contain heavy metal moiety and are known as metal complex dyes. The azo dyes like *Reactive Red 171, Reactive Blue 209* and *Reactive violet 5* contain copper, and *reactive blue 38* contains nickel (Shenai, 1995). The presence of heavy metals such as copper, zinc, chromium and cadmium in the textile wastewater collected from Tiruppur was reported by Senthilnathan and Azeez (1999). The harmful effects of the heavy metals are widely reported and well recognised.

## 2.8 Summary

The textile wet processing industries pose serious threat to the aquatic ecosystems in several developing nations. Rapid growth of textile industries in Tiruppur has resulted in notable environmental consequences locally. The wet processing of cotton cloth is a highly water intensive operation requires so many chemicals. About 70-120 litres of water is used to dye one Kg of cloth. The dyes are not fully utilized during the colouring process and a notable portion is lost to the waste. Consequently enormous volume of deeply colored wastewater is generated and discharged by the dyeing and bleaching industries polluting the Noyyal river and its basin. This has also deteriorated ground water quality, which has turned hazardous and unfit for any purposes. The release of effluents in the river Noyyal has affected agricultural activities in the downstream areas severely. Many azo dyes are reported to have mutagenic and carcinogenic properties. Several other chemicals used in the processing units also cause harmful effects on the environment. The wet processing units face severe pressure from public, NGOs, Courts and Pollution control authorities for safe disposal of effluents. The effective management of such wastewater is a concern that requires serious attention.

# 3. CHARACTERISATION OF WASTEWATER FROM DYEING AND BLEACHING UNITS IN TIRUPPUR

## 3.1 Introduction

The textile wet processing industries in Tiruppur consume about 100 MLD of water, and almost the same volume of wastewater is generated. Large quantum of dyes, salts, alkalis, acids and other chemicals are used to process the hosiery cloth, a notable portion of which flows down the drain. Effluents characterisation and quantification helps in assessment of the gravity of pollution caused by the industries and thereby initiating preventive and control measures which in-turn will help sustain the growth and continued operation of the industries. The present chapter aims to characterize the textile wastewater received in a CETP in Tiruppur. The quantification of the wastewater and assessment of pollution load are also discussed in this chapter.

## 3.2 Variable composition of the textile wastewater

There are varieties of dyestuffs and many chemicals, as intimated earlier, are used in textile wet processing. In the course of time they are being upgraded and replaced by the superior products. The characteristics of the textile wastewater are variable in nature depending upon the fabric processed, dyestuffs, and ancillary chemicals used (Correia *et al.*, 1994) and type of process machinery. As noted earlier, textile effluents contain many types of chemical substances added at various stages of operations like desizing, dyeing, bleaching, printing and finishing processes. Therefore, the wastewater contains different types of dyes, detergents, sulphide compounds, solvents, heavy metals and inorganic salts and the concentrations of these compounds depend on the kind of process adopted (Marcucci *et al.*, 2002). Usage of dyes vary from day to day because of batch wise operation of dyeing that adds on to variation in the wastewater characteristics especially the pH, colour and COD (Gurnham, 1965; Chu, 1999). The type of processing equipments is also linked with the quantum as well as the quality of wastewater. It is often not possible to predict the characteristics of the textile wastewater by the available literature because every textile industry is unique regarding the type of production, the technology and chemicals used.

## 3.3 Colour – the major issue in the textile wastewater

Colour is the most infamous part of the textile wastewater. The reactive dyes impart colour by covalent reaction with the fiber. However, some portions of the reactive group in the dyes are hydrolyzed and remain in the dyebath, and are released with the spent dyebath and washing baths. Disposal of dark colored effluents into water bodies exerts various impacts such as fall in aesthetic value and change in light penetration leading to damage of the structure and function of aquatic ecosystems. The colour due to reactive dyes even in very low concentration is visible and undesirable (Nigam *et al.*, 2000). Slokar and Marechat (1998) pointed out that the aniline dye in concentration even of 0.05 $g/m^3$ gives visible colour in the water. O'Neill *et al.* (1999) while reviewing problems of colour in the textile effluents pointed out objections to be more due to aesthetic and industrial reasons rather than toxicity to the mammals and aquatic organisms as the dyes exhibit low toxicity to organisms.

## 3.4 The pollutants of the textile wastewater and assessment of pollutants load

Textile processing releases alkaline as well as acidic waste. In dyeing sequence high pH wastewater is caused due to the usage of alkali where such alkali is neutralized using the acid in the subsequent process. The detergents are common in the textile wastewater. Pollutants such as polyvinyl alcohol, carboxymethyl cellulose and starch used for the sizing of man-made fibers contribute high COD values more than 10000 mg/L. The organic pollution of the textile wastewater is contributed by the dyes and other organics such as acetic acid and wetting agent. Natural impurities such as waxes, pectines, proteins, grease, fats and miscellaneous substances like pigments, hemicelluloses and reducing sugars. removed by the scouring operation also contribute to the organic load of the textile wastewater. The major inorganic pollutant is sodium chloride or sodium sulphate salt. Presence of calcium, magnesium, carbonates and bicarbonates ions in the textile wastewater are also reported by many researchers (Wells *et al.*, 1994). Several heavy metals such as cadmium, copper, zinc, nickel, lead, chromium, and mercury are known to be present in the textile wastewater (Senthilnathan and Azeez 1999). Phenols

and oil and grease compounds are also known to be present in the textile wastewater. Chlorinated organic compounds formed by the reaction of chlorine with the lignin present in the cloth were reported by Balcioglu (1999). The adsorbable organic halogens (AOX) levels of wastewater discharge from kraft bleaching using hypochlorite was reported by Yetis *et al.* (1996). Yusuff and Sonibare (2004) characterized the textile effluent for a proposed Central Effluent Treatment Plant in Nigeria and found that colour intensity is 350 folds of prescribed parameters; while COD, TSS, $NH_3$, $BOD_5$, $S^{2-}$ were by 24, 13, 8, 7, 3 folds higher to the prescribed standards respectively. Assessment of pollutant loads attains prime importance for the textile clusters like Tiruppur where very large number of processing units are functioning, polluting the river Noyyal and damaging thousands of hectares of agricultural lands in the river basin. The whole volume of generated wastewater is discharged to the river Noyyal which was earlier a perennial river. The sewage from the urban centres located on the banks of the river worsened the troubles. Most of the studies on the textile wastewater mainly concentrated on the characterisation and treatment, and assessment of the pollutants load is scanty. The variable composition of the textile effluents heightens the significance for characterization and assessment of pollutants load.

## 3.5 Methods

### 3.5.1 Wastewater sampling

The wastewater samples from two locations in a CETP, namely i) Inlet to the equalisation tank and ii) Outlet of equalization tank were collected to characterize the textile effluent.

500 mL of sample at each sampling location was collected at an interval of 4 hours in a wide mouthed bottle, put into the polythene containers, and stored in the refrigerator at 4°C for 24 hours. The samples were then mixed together and 2 litres of sample taken for physio-chemical analyses. 1000 mL of sample was preserved at 4°C after adding 4 mL concentrated nitric acid in glass bottles for heavy metal analysis. Two samples in a month for a period of 5 years were collected.

### 3.5.2 Analytical methods

The analyses were carried out following standard methods. The table 3.6.1 shows the methods adopted for each of the parameters used in this study.

**Table 3.5.1 Standard procedures and methods used in this study**

| Parameter | Method | References |
|---|---|---|
| pH | Potentiometry | APHA-1998, 4500-H+ B |
| Total Suspended Solids (mg/L) | Ignition | APHA-1998, 2540-D |
| Volatile Suspended Solids (mg/L) | Ignition | APHA-1998, 2540-E |
| Total Dissolved Solids (mg/L) | Ignition | APHA-1998, 2540-C |
| $BOD_5$ (mg/L) | 5 day BOD test | APHA-1998, 5210-B |
| COD (mg/L) | Open reflex | APHA-1998, 5220-B |
| Chloride (mg/L) | Argentometry | APHA-1998, 4500-$Cl^-$ B |
| Residual chlorine (mg/L) | Iodometry | APHA-1998, 4500-Cl B |
| Sulphate (mg/L) | Turbidimetry | APHA-1998, 4500-$SO^{4-}$ E |
| Alkalinity (mg/L) | Titrimetry | APHA-1998, 2320-B |
| Total hardness (mg/L) | EDTA titrimetry | APHA-1998, 2340-C |
| Calcium hardness (mg/L) | EDTA titrimetry | APHA-1998, 3500-Ca D |
| Magnesium hardness (mg/L) | By Calculation | APHA-1998, 3500-Mg E |
| Oil and grease (mg/L) | Partition gravimetric | APHA-1998, 5520-B |
| Phenolic compounds (mg/L) | Direct photometric | APHA-1998, 5530-D |
| Copper (mg/L) | Neocuproine | APHA-1998, 3500-B |
| Total chromium (mg/L) | Colorimetric | APHA-1998, 3500-B |
| Lead (mg/L) | Dithizone | APHA-1998, 3500-Pb B |
| Zinc (mg/L) | Zincon | APHA-1998, 3500-Zn B |
| Nickel (mg/L) | Zincon | APHA-1998, 3500-Ni- |
| Mercury (mg/L) | Zincon | APHA-1998, 3500-Hg |
| Cadmium (mg/L) | Zincon | APHA-1998, 3500-Cd |
| Volatile fatty acid | Distillation | APHA-1998, 5560-C |
| Total Kjeldahl Nitrogen | Macro Kjeldahl | APHA-1998,4500-$N_{org}$ B |
| Nitrate | Ultra Violet Spectrophotometric Screening | APHA-1998,4500-$NO^{3-}$ B |
| Phosphate | Stannous chloride | APHA-1998,4500 - PD |
| Potassium | Flame Photometric | 3500-K B |
| TCLP | 1311 | US-EPA, SW-846 |

### 3.5.3 Estimation of pollutants load

Actual loads of water pollutants discharged over a period of time can be estimated as the product of volume of the wastewater and the concentration of pollutants (The Environment Protection Authority, 2005). The annual mean value of the parameter was taken and multiplied with the cumulative volume of the wastewater received in the CETP in a year.

### 3.5.4 Quantification of wastewater

The cumulative and instant flow of the wastewater was measured using the electromagnetic flow meter (Make: Krohne Marshall, Model K300) installed in the CETP.

### 3.5.5 Estimation of pollutants load from all processing industries in Tiruppur

Collection of wastewater samples and data from all CETPs and IETPs operating in Tiruppur is unfeasible considering that large numbers of industries functioning in scattered locations. The industries might also provide incorrect information in terms of quantity of wastewater generation. The processing units would be cautious to record only the volume of wastewater consented by the concerned authorities apprehending a possible pro-rata based liability towards loss of ecology, cleaning of the river, and Orathupalayam dam and other consequences related to the industrial operation.

During the present study the Veerapandi CETP was closely studied. This CETP received wastewater from 75 individual (member) units; 60 (80%) dyeing units and 15 (20%) bleaching units. The CETP under study was designed to treat 10 million litres per day (MLD), which was about 10% volume of wastewater generated in Tiruppur (total volume of wastewater generation from all processing units in Tiruppur was 100 MLD). Hence the estimation of pollutants load from all the processing units in Tiruppur was done by interpolating the data collected in the CETP to the total volume of wastewater produced in Tiruppur.

## 3.6 Results and discussions

The physio-chemical characteristics of the raw and equalized effluent are discussed below.

### 3.6.1 pH

The wastewater collected from the receiving sump and the equalisation tank outlet of the CETP through out the study period was alkaline. The pH of the raw effluent ranged between 7.52 to 9.32 and that in the equalized effluent ranged from 7.61 to 9.31. The table 3.6.1 shows the mean values of pH (with the standard deviation) for each year during the study period. It is found that the pH values in the raw effluent and equalized effluent fluctuated only narrowly. pH values of most samples were less than 9.0. (the norm stipulated by TNPCB for disposal into inland surface water for pH is 5.5 to 9.0). However, in the raw effluent 2 samples in 2002 and 2004, and 3 samples in 2003 had more than 9.0 pH. Similarly, after equalization 2 samples in 2002, 1 sample in 2003 and 6 samples in 2006 showed pH beyond 9.0.

| Year | Raw effluent | Equalized effluent |
|---|---|---|
| 2002 | 8.36 ± 0.43 | 8.50 ± 0.34 |
| 2003 | 8.50 ± 0.43 | 8.47 ± 0.35 |
| 2004 | 8.50 ± 0.35 | 8.63 ± 0.38 |
| 2005 | 8.31 ± 0.34 | 8.30 ± 0.30 |
| 2006 | 8.37 ± 0.28 | 8.45 ± 0.19 |

**Table 3.6.1 pH values in the raw effluent and equalized effluent**

Textile wastewater is generally alkaline in nature because of addition of alkalis such as calcium carbonate or sodium hydroxide to raise the pH to about 12 in dye bath. Bringing up the pH in this range, enable the dye - fibre bond formation (Shenai, 1995). The spent dye bath having alkaline pH is discharged as wastewater. The composite wastewater from textile processing is also of alkaline pH. Senthilnathan and Azeez (1999) also have

reported that the wastewater generated from hypochlorite and peroxide bleaching operations and subsequent washing operation was alkaline pH. Similar observations were made by Pia *et al.* (2002), Abdessemed *et al.* (2000), Aslam *et al.* (2005), and Yusuff and Sonibare (2004).

### 3.6.2 Total suspended solids (TSS)

The TSS in the raw effluent and equalized effluent is given in the table 3.6.2. The TSS showed wide variations during the period of study; the variation was from 231 mg/L to 452 mg/L in the raw effluent. Similarly, 187–372 mg/L was the range of TSS in equalized wastewater of the CETP.

| Year | Raw effluent (mg/L) | Equalized effluent (mg/L) |
|---|---|---|
| 2002 | 310.37 ± 41.20 | 261.92 ± 46.71 |
| 2003 | 323.17 ± 45.26 | 270.57 ± 39.64 |
| 2004 | 339.39 ± 59.31 | 289.50 ± 45.25 |
| 2005 | 366.57 ± 34.57 | 315.01 ± 28.42 |
| 2006 | 337.31 ± 39.76 | 318.64 ± 23.94 |

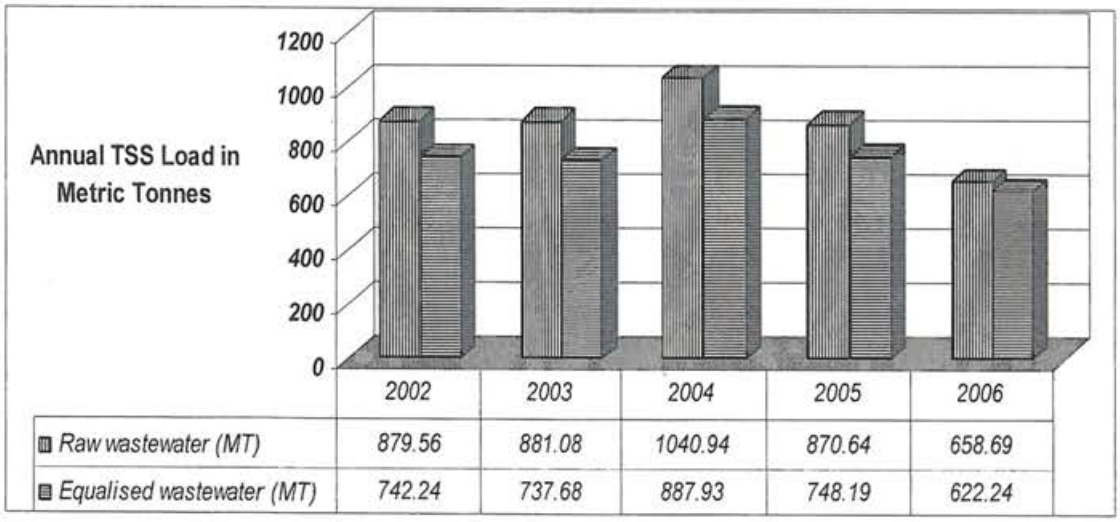
**Table 3.6.2 Yearly average of TSS in the raw effluent and equalized effluent**

During the study period it was noted, the yearly average of TSS in the raw effluent and in homogenised effluent increased gradually. The TSS of raw effluent increased about 26.5% from 2002 to 2005. Similarly in the equalized effluent 21.7% of increase was noted. The TSS in equalized effluent was considerably low in all the years than the raw effluent of the respective year. The TSS of equalized effluent was 18.7 to 52.6 mg/L lesser than the raw effluent during 2002 to 2006.

The TSS in the textile wastewater originates from fibers detached from the cloth during the scouring operation of dyeing and bleaching processes. TSS of the textile wastewater has moderately low TSS values compared to other industrial wastes. Orhon *et al.* (2000)

reported 2229 and 2988 mg/L of suspended solids in the raw and homogenized wastewater collected at Istanbul Organised Tanning Industries, Turkey. The tannery wastewater from CETPs in Kanpur, India contained 1645 mg/L TSS (Tare *et al.,* 2003). Borja *et al.* (1996) reported that 2000 to 3000 mg/L TSS in wash water from purification of virgin Olive oil.

**TSS load**: The TSS load estimated from the raw effluent and equalized effluent is shown in the figure 3.6.1. The TSS load was highest in 2004. The total TSS load estimated for the whole study period was 4331MT in the raw effluent and 3738 MT in the equalized effluent. There was a net fall of 593 MT in the equalized effluent than the raw effluent. Though the TSS concentrations increased gradually from 2002 to 2006, the TSS load decreased after 2004, since the volume of wastewater generation decreased after 2004.




| | 2002 | 2003 | 2004 | 2005 | 2006 |
|---|---|---|---|---|---|
| Raw wastewater (MT) | 879.56 | 881.08 | 1040.94 | 870.64 | 658.69 |
| Equalised wastewater (MT) | 742.24 | 737.68 | 887.93 | 748.19 | 622.24 |

**Figure 3.6.1 Annual TSS load received to the CETP**

The rise of TSS content and TSS load in the wastewater during the early years of the study is attributed to the industries modernizing dyeing machineries by deploying low MLR softflow machines which discharge more concentrated wastewater. The fall in TSS since 2004 was due to the fall in quantum of wastewater. During the study period, the CETP experienced frequent breakdown and stoppage of equalisation tank aerators. This resulted in sedimentation of solids due to poor mixing of the effluent. In the equalized

effluent about 593 MT of TSS load was less through out the study period compared to the raw effluent which perhaps the settled solids.

### 3.6.3 Total dissolved solids (TDS)

The TDS is the major issue in the textile effluents generated in Tiruppur. The mean value of TDS content in the effluents is given in the table 3.6.3. The annual minimum values of TDS in the raw effluent varied between 5544 and 6607 mg/L during 2002 to 2006 where as during the same period the annual maximum values were in the range of 7433 to 8199 mg/L. Similarly, minimum annual TDS in the equalized effluent ranged from 5547 and 6271 mg/L, and the maximum annual values fell between 7477 and 8419 mg/L. The table 3.6.3 depicts the changes in the TDS in the course of time during the study. The net increase of TDS concentration from to 2002 to 2006 was 941 mg/L in the raw effluent and 1063 mg/L in the equalized effluent.

| Year | Raw effluent (mg/L) | Equalized effluent (mg/L) |
|---|---|---|
| 2002 | 6495 ± 578 | 6416 ± 481 |
| 2003 | 6784 ± 689 | 6677 ± 751 |
| 2004 | 6877 ± 605 | 6857 ± 565 |
| 2005 | 7384 ± 698 | 7479 ± 663 |
| 2006 | 7436 ± 573 | 7470 ± 707 |

**Table 3.6.3 TDS in raw effluent and equalized effluent**

Both the raw effluent and equalized wastewater showed seasonal variations (Figures 3.6.2 and 3.6.3). The low TDS were found in January and February and it increased progressively upto September. The values were on the decline for the rest of the months of the year. Thus mostly the mean TDS values during January, February and October to December months of year were low compared to rest of the months of the year (Table 3.6.4).

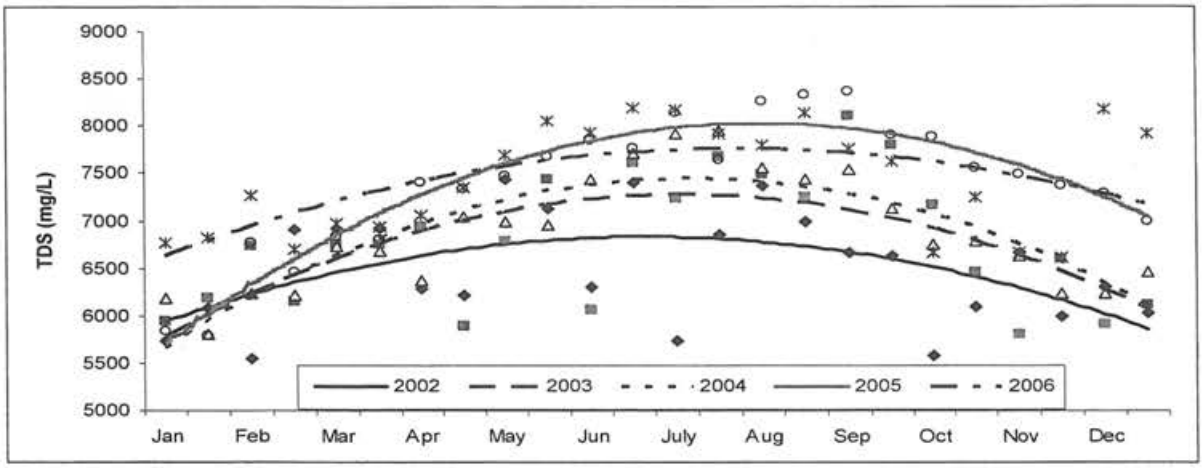



**Figure 3.6.2 Seasonal variations in TDS in raw effluent**

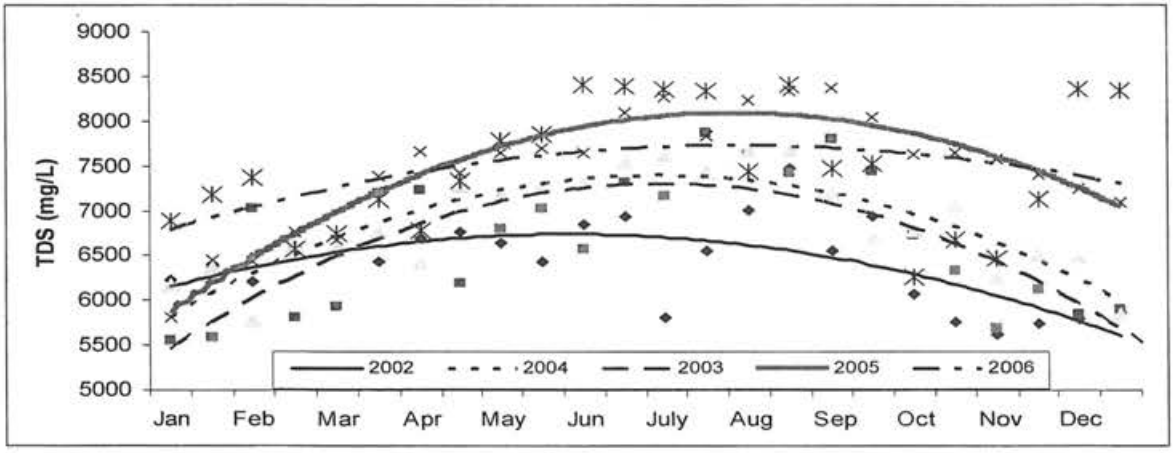



**Figure 3.6.3 Seasonal variations in TDS in equalized effluent**

| Month/year | 2002 | 2003 | 2004 | 2005 | 2006 |
|---|---|---|---|---|---|
| January | 6303 | 5571 | 6274 | 6133 | 7038 |
| February | 6406 | 6414 | 6200 | 6601 | 6973 |
| March | 6500 | 6573 | 6690 | 7038 | 6944 |
| April | 6733 | 6716 | 6854 | 7548 | 7062 |
| May | 6542 | 6909 | 7226 | 7670 | 7816 |
| June | 6897 | 6946 | 7424 | 7877 | 8407 |
| July | 6181 | 7526 | 7528 | 8063 | 8349 |
| August | 7244 | 7532 | 7659 | 8294 | 7928 |
| September | 6751 | 7622 | 6955 | 8213 | 7505 |
| October | 5917 | 6532 | 6935 | 7643 | 6473 |
| November | 5689 | 5907 | 6385 | 7496 | 6801 |
| December | 5831 | 5874 | 6159 | 7171 | 8349 |

**Table 3.6.4 Monthly mean values of TDS (mg/L) in the equalized effluent**

**TDS load:** The TDS load estimated in the equalized effluent is given in the table 3.6.5. The load showed increase up to 2004, followed by a steady decline. Load amounting to 3269 MT in 2005 and 6445 MT in 2006 was lower compared to that of 2004.

| Year | TDS load in equalized effluent (MT) |
|---|---|
| 2002 | 18183 |
| 2003 | 18204 |
| 2004 | 21032 |
| 2005 | 17763 |
| 2006 | 14587 |

**Table 3.6.5 TDS load in the untreated textile wastewater**

Addition of salts (sodium chloride or sodium sulphate), to act as the electrolyte in dye reaction with the cotton fibre, and products of reactants like acids and alkalis, dissolved and unexhausted dyes and bleaching agents contribute to the TDS load of the wastewater. In addition the quality of water used for the processing also affects TDS. Joseph (2000) had pointed out that the salt usage for dyeing 100 Kg of cloth is 48 to 80 Kg in the softflow dyeing machine and 112 to 160 Kg in the winch dyeing machine. The industries functioning in Tiruppur are modernizing the equipments from conventional (winch) to modern (softflow) dyeing machine. The later is characterized with low MLR and generation of less volume of highly concentrated effluents. This change in the machinery leading to production of concentrated effluents would be the cause for the rise in the TDS concentration during the study period. However the TDS load falling after 2004 was due to less volume generation of wastewater. This may be a result of the execution of the statutory orders issued to the industries to minimize the volume of wastewater generation.

The seasonal variation in TDS values is perhaps due to the quality variation of ground water that is sourced by the industrial units from various locations in the outskirts of Tiruppur. The ground water shows variations in TDS from monsoon. During the monsoon better dilutions in ground water by rainwater recharge result in low TDS in the raw water.

### 3.6.4 Chloride

Chloride contents in the raw effluents and equalized effluents estimated during the study period is given in the table 3.6.6. The values at the receiving sump and outlet of the equalisation tank did not differ much for each sampling day. The chloride content apparently increased gradually towards later years of the study. The increase was 10.6 to 12.5% for the raw and equalized effluent from the year 2002 to 2006.

| Year | Raw effluent (mg/L) | Equalized effluent (mg/L) | Annual chloride load in equalized effluent (MT) |
|---|---|---|---|
| 2002 | 3584 ±261 | 3552 ± 233 | 10065 |
| 2003 | 3619 ± 346 | 3610 ± 353 | 9841 |
| 2004 | 3751 ± 325 | 3745 ± 338 | 11487 |
| 2005 | 3954 ± 347 | 3995 ± 351 | 9488 |
| 2006 | 3965 ± 291 | 3911 ± 186 | 7637 |

**Table 3.6.6 Chloride concentration and load in the untreated textile effluent**

Seasonal variations as seen in the TDS content of the wastewater was also noticed in the case of chloride contents (Figure 3.6.4). The chloride contents were low during January and February, and October to December of the year. The values during March to September were comparatively high in most cases. The calculated chloride load for each year is given in table 3.6.6. The chloride load increased upto 2004 and then decreased. The chloride loads amounts for 54.2% of TDS load.

Chloride content of the textile wastewater is contributed mainly by the sodium chloride used in the dyeing process. Products formed by the chemicals used in the processing units and use of the ground water also contribute to the chloride content. The increase of chloride in the wastewater is caused by the modernization, use of low MLR softflow dyeing machines which generate less volume of wastewater with high concentration of pollutants. The chloride load was highest during 2004 (11487 MT). Afterwards it is decreasing because of generation of lesser volume of wastewater. The ground water diluted by fresh recharge during monsoonal seasons resulted in low chloride content in

the raw water used in the processing units and subsequently this is reflected in the wastewater. From March to September the water used for dyeing and bleaching purpose contained more chloride content that would have supplemented increase in the chloride content in the wastewater.

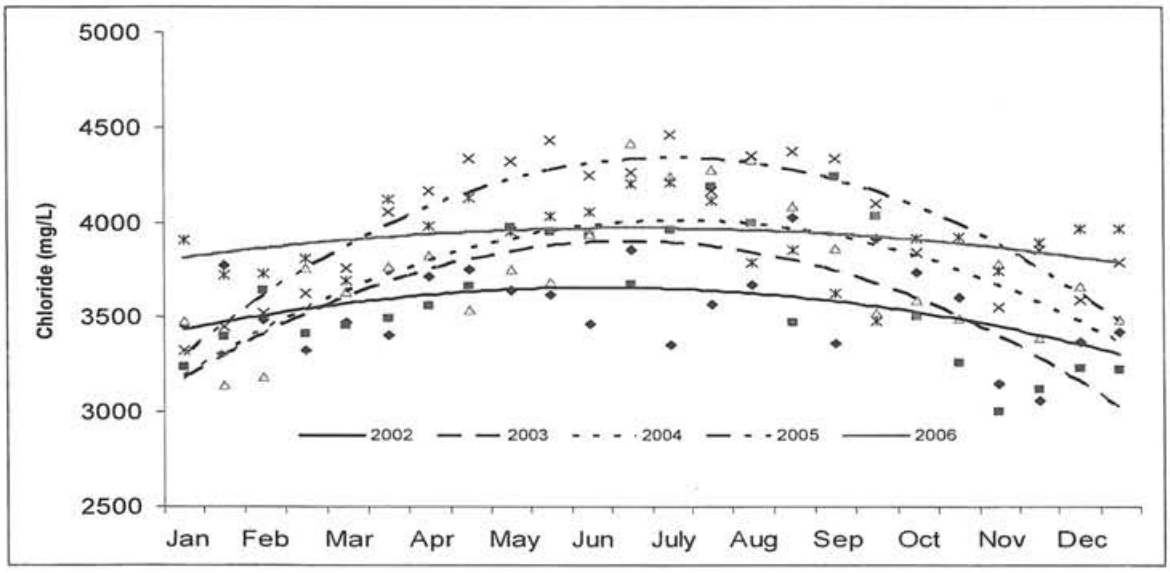



**Figure 3.6.4 Seasonal variations in chloride content of the equalized effluent**

### 3.6.5 Residual chlorine

Residual chlorine was not found during the study period, perhaps for any free chlorine released to the wastewater getting reduced to chloride immediately by the organic matters present in the wastewater. However chlorinated organics to level of 17.2 - 18.3 mg/L was found in the textile wastewater where chlorine based bleaching agents were used (Ranganathan *et al.* 2007a).

### 3.6.6 Sulphate

The sulphate contents of the textile wastewater during the study period are shown in the table 3.6.7. The values in the raw effluent and equalized effluent did not differ much in between. The sulphate concentrations showed an increasing trend according to the years from 2002 to 2006. The increase in the equalized effluent was about 10.0%. The seasonal variations as in the case of TDS and chloride, was also seen in the case of sulphate. The

sulphate contents during January, February and October to December was less in most of the samples compared to the rest of the months of the same year.

| Year | Raw effluent (mg/L) | Equalized effluent (mg/L) | Annual sulphate load in equalized effluent (MT) |
|---|---|---|---|
| 2002 | 515.7 ± 62.8 | 524.8 ± 62.4 | 1487 |
| 2003 | 535.7 ± 88.3 | 530.6 ± 88.3 | 1425 |
| 2004 | 530.4 ± 54.8 | 539.1 ± 54.0 | 1653 |
| 2005 | 542.0 ± 51.1 | 544.0 ± 61.6 | 1292 |
| 2006 | 558.0 ± 35.1 | 577.4 ± 34.2 | 1127 |

**Table 3.6.7 Sulphate concentration and load in the untreated textile effluent**

**Sulphate load:** Total sulphate load received by the CETP was 6985 MT during the study period. Annual sulphate load is given in the table 3.6.7. Total sulphate load accounts to 7.8% of TDS load. The sulphate load also showed increasing trend upto 2004, afterwhich it decreased.

Sulphate is originated in the textile wastewater by the addition of sodium sulphate instead of sodium chloride to the dyeing process. Further, the products of chemicals like sulphuric acid used in the textile wet processing also contribute to the sulphate content. Though the sulphate concentration showed steady increase during the study period, the sulphate load decreased after the year 2004. During the year 2005 and 2006 the volume of wastewater received in the CETP was lower compared to 2004.

### 3.6.7 Chemical oxygen demand (COD)

COD is an important parameter for assessing pollution due to wastewaters. During the period of study the COD values in the raw effluent ranged from 408 to 774 mg/L while after equalisation it ranged from 384 to 738 mg/L. The year wise mean values in the raw effluent and equalized effluent are given in the table 3.6.8. The COD values in both the sampling locations did not deviate much during any sampling day. Gradual increase of COD value year by year was observed in both types of samples collected. The increase in

COD in the raw effluent was from 561.5 to 643.4 mg/L while in the equalized effluent the increase was from 565.3 to 598.7 mg/L.

**COD load:** The COD load in the equalized effluent is shown in table 3.6.8. During the study period the total COD load received to the CETP was 7463 MT. The maximum COD load was noticed in 2004 (1761 MT). Though the COD concentration increased from 2002 to 2004, the COD load decreased thereafter; because of generation of lesser of volume effluent during 2005 and 2006 compared to 2004.

| Year | COD concentration (mg/L) | | COD load (MT) | |
|---|---|---|---|---|
| | Raw effluent | Equalized effluent | Raw effluent | Equalized effluent |
| 2002 | 561.5 ± 74.5 | 565.3 ± 65.7 | 1591 | 1602 |
| 2003 | 581.9 ± 74.1 | 570.9 ± 98.2 | 1586 | 1557 |
| 2004 | 586.3 ± 64.2 | 574.2 ± 74.5 | 1798 | 1761 |
| 2005 | 579.9 ± 70.2 | 578.7 ± 66.6 | 1377 | 1374 |
| 2006 | 643.4 ± 63.8 | 598.7 ± 72.8 | 1256 | 1169 |

**Table 3.6.8 COD concentration and load in the textile effluent**

Similar range of COD were reported by Pathe *et al.* (2005) who reported that the textile wastewater received at the CETP in India having COD values of 790 mg/L. Lin and Lin (1992) categorized the textile wastewater into high, medium and low strength based on COD and colour intensity. The high strength wastewater have COD levels exceeding 1600 mg/L and the strong colour with very low transparency; the medium strength wastewater have COD between 800 and 1600 mg/L while the low strength wastewater is characterized with COD values lesser than 800 mg/L. In the present study it was observed that the COD values in the textile wastewater generated in Tiruppur was lower than 800 mg/L and hence falling in the category of low strength.

As noted above, the COD values during the study period showed an increasing trend. The replacement of conventional dyeing machine (winch) by the mordern dyeing machine (softflow) would be a reason for the same. The MLR is relatively low in the softflow

dyeing machine compared to the winch dyeing machine. Baladhandapani and Azeez (2004b) documented that the water usage in the winch dyeing machine as about 60% more than the softflow dyeing machine. The use of softflow machine eventually resulted in generation of concentrated waste stream.

### 3.6.8 Biochemical oxygen demand (BOD)

The BOD values in the raw effluent varied from 81.6 to 296.1 mg/L and that of the equalized effluent from 92.4 to 257.9 mg/L. The BOD values in the textile wastewater are shown in the table 3.6.9. The mean BOD values gradually increased in both samples i.e. raw effluent and equalized effluent annually starting from 2002 to 2006. The values of BOD in the raw effluent and the equalized effluent fluctuated narrowly in the same sampling day.

| Year | Raw effluent (mg/L) | Equalized effluent (mg/L) | BOD load (MT) | |
|---|---|---|---|---|
| | | | Raw effluent | Equalized effluent |
| 2002 | 156.6 ± 30.8 | 152.1 ± 31.5 | 444 | 431 |
| 2003 | 164.3 ± 46.8 | 156.2 ± 35.8 | 448 | 426 |
| 2004 | 166.4 ± 28.9 | 163.6 ± 27.7 | 510 | 502 |
| 2005 | 174.0 ± 32.7 | 166.3 ± 20.7 | 413 | 395 |
| 2006 | 176.8 ± 24.7 | 170.6 ± 25.1 | 345 | 333 |

**Table 3.6.9 BOD values and load in the untreated textile wastewater**

**BOD load:** The BOD load in the equalized effluent is given in the table 3.6.9. The total BOD load generated through out the study period was 2087 MT. Upto 2004 the BOD load increased and after that it declined considerably. Compared to 2004, a fall of 21% of BOD load was seen during the year 2005 and 34% in the year 2006.

**BOD and COD ratio:** The BOD and COD ratio of raw effluent varied from 1:3.3 to 1:3.6. In the case of equalized effluent the ratio varied from 1:3.5 to 1:3.7. The mean BOD and COD ratio in the equalized effluent was 1:3.6 that indicates that the textile wastewater is moderately vulnerable to biological oxidation. The organic contents of the

wastewater were contributed by the dyes and other organics such as acetic acid and wetting agent added to the processing. Natural impurities such as waxes, pectines, proteins, grease, fats and miscellaneous pigments, hemicelluloses and reducing sugars removed by the scouring and bleaching operations also contribute to the BOD load of the textile wastewater.

### 3.6.9 Hardness

Total hardness measured in the raw effluent varied from 479 to 985 mg/L while in the equalized effluent it varied from 530 to 927 mg/L (Average values are given in table 3.6.10). The average values of total hardness in the raw effluent and the equalized effluent increased gradually to a considerable extent. The net increase in the raw effluent was 81.0 mg/L; similarly the equalized effluent showed increase of 72.7 mg/L, about 10.2%.

| Year | Raw effluent (mg/L) | Equalized Effluent (mg/L) |
|---|---|---|
| 2002 | 724.7 ± 87.1 | 714.6 ±102.0 |
| 2003 | 737.9 ± 76.1 | 722.4 ± 108.2 |
| 2004 | 746.1 ± 118.5 | 742.1 ± 91.8 |
| 2005 | 755.0 ± 89.1 | 749.1 ± 75.5 |
| 2006 | 805.8 ± 89.8 | 787.2 ± 67.7 |

**Table 3.6.10 Total hardness measured in raw effluent and equalized effluent**

The calcium hardness and the magnesium hardness in the CETP are given in the table 3.6.11. They showed gradual increase. Since 2002, the average calcium hardness increased to 363.1 from 326.1 mg/L in the raw effluent; whereas in the equalized effluent it increased from 322.0 to 353.1 mg/L. The average magnesium hardness increased to 442.6 from 398.6 mg/L in the raw effluent and 434.1 from 392.6 mg/L in the equalized effluent. The increase was about 11.0% in the raw wastewater and equalized wastewater. Magnesium hardness contributed to 46.6% to 64.3% of total hardness.

| Year | Raw effluent | | Equalized effluent | |
|---|---|---|---|---|
| | Calcium hardness (mg/L) | Magnesium hardness(mg/L) | Calcium hardness (mg/L) | Magnesium hardness (mg/L) |
| 2002 | 326.1 ± 53.8 | 398.6 ± 63.1 | 322.0 ± 66.2 | 392.6± 53.2 |
| 2003 | 329.0 ± 44.1 | 404.8 ± 56.3 | 328.4 ± 60.6 | 394.0 ± 67.9 |
| 2004 | 330.8 ± 59.1 | 415.3 ± 77.0 | 334.8 ± 56.5 | 407.2 ± 51.5 |
| 2005 | 341.2 ± 54.0 | 413.8 ± 47.7 | 338.3 ± 45.2 | 410.8 ± 47.3 |
| 2006 | 363.1 ± 52.2 | 442.6 ± 73.0 | 353.1 ± 35.6 | 434.1 ± 53.9 |

**Table 3.6.11 Calcium and magnesium hardness in the untreated effluent**

Seasonal variation was also noted in the hardness of the textile wastewater. The values were higher during March to September compared to January, February and October to December. Higher values of total hardness ranging from 869.3 to 985.1 mg/L were found in March to September months of the study period in the raw effluent (Figure 3.6.5). Values ranging from 865 to 927 mg/L were found in the equalized effluent during these months.

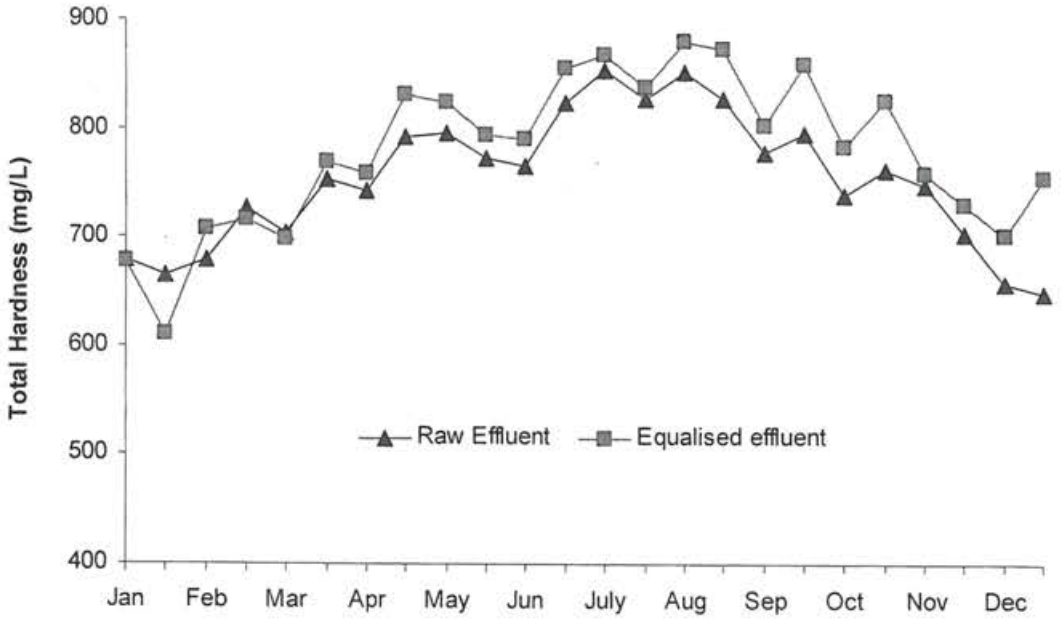



**Figure 3.6.5 Seasonal variations in total hardness**

**Hardness load:** Total hardness and calcium hardness load generated by the member units of industries discharging to the CETP is shown in the table 3.6.12. The difference between total hardness and calcium hardness is the magnesium hardness load. The overall hardness load for the whole study period was 9587 MT, the sum of calcium (4328 MT, 45% of total hardness load) and magnesium (5259 MT) load. It is found that hardness load decreased after the year 2004 though the concentration of the hardness has shown a trend of annual increase.

The hardness content of the wastewater was contributed by the water used in the processing, impurities found in the salt and other chemicals used. Replacement of conventional winch dyeing machine by the modern softflow dyeing machine and subsequent generation of concentrated wastewater from the softflow dyeing machine resulted in the trend of hike in hardness during the study period. However calcium and magnesium hardness loads show a fall after 2004 due to lesser wastewater generation. Seasonal variation of ground water in concentrations of calcium and magnesium hardness is also reflected in the variation of the same in the wastewater.

| Year | Hardness load (MT) | |
|---|---|---|
| | Calcium hardness | Magnesium hardness |
| 2002 | 913 | 1112 |
| 2003 | 895 | 1075 |
| 2004 | 1027 | 1249 |
| 2005 | 803 | 976 |
| 2006 | 690 | 847 |

**Table: 3.6.12 Calcium and magnesium hardness load before the treatment of wastewater**

### 3.6.10 Alkalinity

The range of total alkalinity in the raw effluent was from 664.5 to 1172.9 mg/L. In the equalized effluent the range was from 678.9 to 1119.6 mg/L. The methyl orange

alkalinity varied from 648.3 to 1130.4 mg/L in the raw effluent. In the equalized wastewater the range was from 653.3 to 1119.6 mg/L. The phenolphthalein alkalinity was not found in 54 samples of the raw effluent and 47 samples of the equalized effluent out of 120 samples analysed through out the study period. The maximum level of P'alkalinity measured was 157.2 mg/L in the raw effluent and 184.1 mg/L in the equalized effluent. The mean values with standard deviations of total alkalinity, P'alkalinity and M'alkalinity are tabulated separately for the raw and the equalized effluent in the table 3.6.13.

**Alkalinity load:** The estimated load of total alkalinity, M'alkalinity and P'alkalinity are shown in the table 3.6.14. The maximum alkalinity load was found in the year 2004. Total alkalinity load was lesser in the year 2006 than 2004. Similarly, the M'alkalinity load (about 946 MT) in the year 2006 was lesser than that in 2004.

| Year | Raw effluent (mg/L) | | | Equalized effluent (mg/L) | | |
|---|---|---|---|---|---|---|
| | M'alkalinity | P'alkalinity | Total alkalinity | M'alkalinity | P'alkalinity | Total alkalinity |
| 2002 | 849.5±96.1 | 28.8±39.2 | 878.3±95.1 | 808.7±89.0 | 43.3±46.0 | 852.0±79.4 |
| 2003 | 842.7±107.3 | 49.8±51.7 | 890.6±90.1 | 836.1±94.0 | 39.2±41.9 | 873.0±93.5 |
| 2004 | 887.4±102.2 | 36.6±40.7 | 920.5±106.1 | 879.2±66.0 | 49.8±41.6 | 924.3±77.1 |
| 2005 | 886.6±114.1 | 22.5±28.1 | 909.0±118.9 | 876.5±98.4 | 21.8±26.9 | 898.4±93.6 |
| 2006 | 881.3±78.1 | 16.8±16.1 | 898.1±77.5 | 896.6±67.4 | 20.1±18.8 | 917.0±65.2 |

**Table 3.6.13 Concentration of alkalinity in the untreated wastewater**

The alkalinity of the textile wastewater originates from alkaline chemicals such as sodium hydroxide and calcium carbonate added during dyeing as well as bleaching. The M'alkalinity in the textile wastewater is predominantly more than the P'alkalinity. This clearly indicates that the carbonate and bicarbonate ions were predominant in the wastewater. Seasonal variation as seen in several other parameters discussed earlier was not recorded in the case of alkalinity.

| Year | Alkalinity load (MT) | | |
|---|---|---|---|
| | M'alkalinity | P'alkalinity | Total alkalinity |
| 2002 | 2291.9 | 122.6 | 2414.5 |
| 2003 | 2279.5 | 106.9 | 2380.0 |
| 2004 | 2696.7 | 152.7 | 2835.0 |
| 2005 | 2081.9 | 51.8 | 2133.7 |
| 2006 | 1751.0 | 39.2 | 1790.6 |
| **Total** | **11100.9** | **473.2** | **11553.8** |

**Table 3.6.14 Alkalinity load in the equalized effluent**

### 3.6.11 Oil and grease

Oil and grease content of the raw effluent varied from 2.16 to 13.56 mg/L, while after the equalization its concentration varied from 1.95 to 10.77 mg/L. The mean values and standard deviations of oil and grease content in CETP wastewater are shown in table 3.6.15. The values in the raw effluent and equalized effluent did not differ much on the same sampling day. Unlike other parameters, the oil and grease content of the wastewater did not show seasonal variations or annual hike. On the other hand, decrease of oil and grease load was noticed in the wastewater; it decreased to 11.5 from 21.2 MT in the raw effluent and to 11.7 from 19.7 MT in the equalized effluent. The total oil and grease load was 32.0 MT in the equalized effluent through out the study period.

Oil and grease content in the wastewater is contributed by the lubricants used in the processing machineries and also in the treatment facility. The levels of oils and grease in the wastewater are always lesser than the norm stipulated by the statutory body. The load after 2004 was found declining due to lesser volume of wastewater generated in the later years compared to the year 2004. Seasonal variations as well as the trend of increase in concentration noticed in many parameters are not found in the oil and grease content.

| Year | Raw effluent (mg/L) | Equalized effluent (mg/L) | Oil and Grease load (MT) |
|---|---|---|---|
| 2002 | 7.49 ± 2.83 | 6.95 ± 1.77 | 19.70 |
| 2003 | 7.09 ± 2.49 | 7.08 ± 2.23 | 19.32 |
| 2004 | 6.05 ± 1.88 | 5.84 ± 1.39 | 17.92 |
| 2005 | 6.04 ± 2.41 | 6.13 ± 2.29 | 14.56 |
| 2006 | 5.89 ± 1.90 | 5.98 ± 1.57 | 11.68 |

**Table 3.6.15 Oil and grease content and load in the untreated effluent**

### 3.6.12 Phenolic Compounds

Phenolic compounds ranged from 0.08 to 0.70 mg/L in the raw effluent and 0.06 to 0.79 mg/L in the equalized effluent. In 38 samples of the raw effluent and 40 samples of the equalized effluent, the phenolic compounds were found below detectable level (BDL). The mean levels of phenolics in each year of the study period are shown in the table 3.6.16. The total phenol load generated during the whole study period was 2000 Kg.

| Year | Phenolic compounds concentration (mg/L) | | Phenolic compounds load (Kg) |
|---|---|---|---|
| | Raw effluent | Equalized effluent | |
| 2002 | 0.20 | 0.19 | 526.6 |
| 2003 | 0.17 | 0.14 | 394.3 |
| 2004 | 0.17 | 0.10 | 314.4 |
| 2005 | 0.26 | 0.19 | 439.4 |
| 2006 | 0.19 | 0.17 | 325.2 |

**Table 3.6.16 Concentration and load of phenolic compounds in the untreated effluent**

Phenolic compounds collectively referred as phenols are hydroxyl derivatives of benzene or its condensed nuclei. Many reactive dyes used in the textile processing contain a phenol ring in their structure (Stolz, 2001; Abadulla et al., 2000). Phenolic compounds impart a characteristic objectionable odor to the receiving water bodies.

### 3.6.13 Heavy metals

Heavy metals such as total chromium, copper, zinc, nickel and cadmium were analysed in the raw effluent and equalized effluent for the years 2002 to 2006. The total heavy metals load was also calculated accordingly and the results are given in table 3.6.17. The chromium concentration ranged from 0.08 to 0.72 mg/L. Total chromium contents were BDL in 36 samples of the raw effluents and 43 samples of the equalized effluents. The copper content was BDL in 41 samples of raw effluent and 47 samples of equalized effluent. In the case of the rest of the samples the copper ranged from 0.015 to 0.767 mg/L. Zinc content varied from 0.023 to 0.85 mg/L. In the case of Zn as well of the total 120 samples 42 samples of the raw effluent and 48 samples of equalized effluent were BDL. Nickel content in the samples varied from 0.06 to 0.78 mg/L. Ni was in BDL range in 40 raw effluent and 47 equalized effluent respectively. Regarding Cd, about 87 and 82 samples in the raw effluent and equalized effluent respectively were BDL. In the rest of the samples, the cadmium content varied from 0.018 to 0.26 mg/L.

| Year | Raw effluent | | | | | Equalized effluent | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cr | Cu | Zn | Ni | Cd | Cr | Cu | Zn | Ni | Cd |
| | Concentration (mg/L) | | | | | | | | | |
| 2002 | 0.24 | 0.22 | 0.33 | 0.21 | 0.04 | 0.37 | 0.18 | 0.31 | 0.17 | 0.04 |
| 2003 | 0.28 | 0.14 | 0.29 | 0.19 | 0.05 | 0.18 | 0.13 | 0.25 | 0.15 | 0.03 |
| 2004 | 0.19 | 0.18 | 0.29 | 0.19 | 0.02 | 0.21 | 0.15 | 0.31 | 0.19 | 0.03 |
| 2005 | 0.35 | 0.12 | 0.31 | 0.17 | 0.03 | 0.38 | 0.09 | 0.29 | 0.18 | 0.03 |
| 2006 | 0.31 | 0.11 | 0.28 | 0.15 | 0.04 | 0.26 | 0.10 | 0.26 | 0.13 | 0.05 |
| | Load (Kg) | | | | | | | | | |
| 2002 | 691.47 | 634.87 | 923.84 | 597.95 | 107.69 | 1042.87 | 519.94 | 881.34 | 467.59 | 124.69 |
| 2003 | 749.76 | 374.88 | 779.75 | 507.11 | 125.41 | 485.30 | 342.32 | 673.42 | 419.87 | 92.70 |
| 2004 | 579.68 | 564.43 | 901.73 | 595.02 | 73.61 | 647.16 | 452.95 | 953.87 | 576.61 | 104.28 |
| 2005 | 840.78 | 287.39 | 738.65 | 408.52 | 73.63 | 900.16 | 202.64 | 681.65 | 437.02 | 66.50 |
| 2006 | 613.18 | 221.37 | 554.60 | 300.73 | 82.02 | 497.97 | 199.02 | 515.54 | 259.72 | 89.83 |

**Table 3.6.17 Heavy metals concentration and their loads**

It is observed that the heavy metals concentration in the textile wastewater generated in Tiruppur are found only in trace levels. The metals in terms of their respective concentration in the textile effluent was in the order Zn>Cr>Cu>Ni>Cd. The findings of the present study are in conformity to the levels reported almost a decade back by Senthilnathan and Azeez (1999). Although the individual concentration of heavy metals in the effluent is very low, their annual load is considerable.

### 3.7 Volume of wastewater

The table 3.7.1 shows the month wise volume of wastewater received in the CETP from the processing industries during 2002 to 2006. The total yearly flows during 2002 to 2004 did not differ much. Since 2005 the wastewater generated from the processing units declined; the volumes were 2375.1 million liters for 2005 and 1952.8 million litres for 2006. It showed a fall of 692 and 1114.3 million litres in the year 2005 and 2006 respectively with reference to the volume of wastewater received in 2004.

The CETP, under study was designed to handle 10 MLD of the textile wastewater collected from 75 member units. During the years 2002 to 2004 on all working days the CETP received wastewater almost equal to the designed capacity. During the middle of the year 2005 a reduction of wastewater volume was seen. The major reason attributed for reduction was the orders from the honorable Madras High Court to restrict the release of wastewater. The industries were directed to operate only 5 days per week and quantum of wastewater was to be limited to what was consented by TNPCB. Also, some of the member units of the CETP installed reverse osmosis (RO) system to recover and recycle water. The decrease of wastewater volume subsequently resulted in lesser load of pollutants in 2005 and 2006.

| Month/ Year | Quantity of wastewater generation (million litres) | | | | |
|---|---|---|---|---|---|
| | 2002 | 2003 | 2004 | 2005 | 2006 |
| January | 215.3 | 243.3 | 251.1 | 212.3 | 77.4 |
| February | 232.9 | 230.7 | 275.5 | 247.0 | 160.4 |
| March | 239.4 | 223.9 | 260.7 | 263.1 | 180.3 |
| April | 245.3 | 220.3 | 244.8 | 259.3 | 155.3 |
| May | 253.6 | 224.3 | 258.0 | 266.7 | 174.1 |
| June | 242.9 | 245.2 | 266.2 | 236.0 | 174.1 |
| July | 210.4 | 239.5 | 284.3 | 117.7 | 164.0 |
| August | 209.7 | 202.9 | 221.8 | 155.9 | 185.9 |
| September | 202.5 | 202.2 | 255.7 | 161.7 | 170.7 |
| October | 265.7 | 205.3 | 272.1 | 146.8 | 137.8 |
| November | 219.4 | 268.9 | 201.2 | 146.0 | 181.2 |
| December | 296.9 | 220.0 | 275.6 | 162.7 | 191.8 |
| **Total** | **2833.9** | **2726.4** | **3067.1** | **2375.1** | **1952.8** |

**Table 3.7.1 Volume of wastewater received in the treatment facility**

## 3.8 Pollutants load generated by all the processing industries in Tiruppur

The volume of wastewater and calculated load of each pollutant is shown in the table 3.8.1 and 3.8.2. It is apparent that the load for certain parameters, especially the annual TDS, generated by the processing industries are enormous. Although phenolic compounds and heavy metals in concentrations were in traces in the wastewater, their load was high due to the huge volume of wastewater generated by industries. During the year 2006 some of the large and medium scale processing units operating in Tiruppur installed RO system. This has reduced the total wastewater from the processing units in Tiruppur.

| Year | Wastewater Generation (Million Litres) |
|---|---|
| 2002 | 28339 |
| 2003 | 27264 |
| 2004 | 30671 |
| 2005 | 23751 |
| 2006 | 19528 |

**Table: 3.8.1 Volume of effluent generation by all textile processing units in Tiruppur**

| Parameter | Year wise pollution load in the untreated wastewater (MT) | | | | |
|---|---|---|---|---|---|
| | 2002 | 2003 | 2004 | 2005 | 2006 |
| Total Suspended Solids | 8796 | 8811 | 10409 | 8706 | 6587 |
| Total Dissolved Solids | 181830 | 182040 | 210318 | 177630 | 145874 |
| $BOD_5$ | 4309 | 4259 | 5018 | 3950 | 3331 |
| COD | 16018 | 15565 | 17613 | 13744 | 11691 |
| Chloride | 100654 | 98414 | 114866 | 94878 | 77430 |
| Sulphate | 14871 | 14252 | 16534 | 12920 | 11275 |
| Total Hardness | 20250 | 19695 | 22760 | 17793 | 15373 |
| Calcium Hardness | 9126 | 8954 | 10270 | 8035 | 6896 |
| Magnesium Hardness | 11124 | 10741 | 12490 | 9758 | 8477 |
| Total Alkalinity | 24145 | 23800 | 28350 | 21337 | 17906 |
| P'alkalinity | 1226 | 1069 | 1527 | 518 | 392 |
| M'alkalinity | 22919 | 22795 | 26967 | 20819 | 17510 |
| Oil and Grease | 197.02 | 193.15 | 179.19 | 145.56 | 116.77 |
| Phenols | 5.27 | 3.94 | 3.14 | 4.39. | 3.25 |
| Total Chromium | 10.43 | 4.85 | 6.47 | 9.00 | 4.98 |
| Copper | 5.20 | 3.42 | 4.53 | 2.03 | 1.99 |
| Zinc | 8.81 | 6.73 | 9.54 | 6.82 | 5.16 |
| Nickel | 4.68 | 4.20 | 5.77 | 4.37 | 2.60 |
| Cadmium | 1.25 | 0.93 | 1.04 | 0.67 | 0.90 |

**Table: 3.8.2 Pollutants load generation by all dyeing and bleaching units in Tiruppur**

The effects caused by the discharge of the wastewater to the river Noyyal and subsequent ground water pollution and damage to the agricultural crops in the river basin are perhaps due to the massive load of pollutants. The Noyyal river being a seasonal one received storm water only during the rainy seasons. During the rest of the months it received only incessant flow of industrial and domestic wastewater. Although several researchers have documented the quality of textile wastewater; estimation of the load of pollutants from the Tiruppur processing units was not attempted.

## 3.9 Summary

The textile processing units operating in Tiruppur are generating large volume of wastewater. Although the levels of the parameters, other than the total dissolved solids, are moderate; their loadings are very high. The composite textile wastewater was of alkaline pH. The TSS ranged from 231 to 425 mg/L during the study period. The level of dissolved solids present in the wastewater ranged from 5547 to 8419 mg/L. Chloride and sulphate contents of the homogenised effluent ranged from 3003 to 4461 mg/L and 428 to 778 mg/L respectively. COD and BOD ranges were 396 to 738 mg/L and 92 to 258 mg/L respectively. The total hardness of the untreated wastewater was 530 to 927 mg/L. Total alkalinity was found in the range of 714 to 1119 mg/L. Heavy metals and phenolic compounds levels were in traces but their annual loads considerably high. Oil and grease content of the equalized effluent was from 1.95 to 12.25 mg/L. The residual chlorine was not found in any of the samples collected during the study period. The parameters such as TSS, COD, BOD, TDS, $Cl^-$, $SO_4^-$, and hardness increased progressively since 2002. Seasonal variations were seen in the case of the dissolved constituents of the wastewater. The volume of wastewater and pollutants load decreased after 2004 due to the execution of various statutory orders to minimize wastewater generation.

# 4. PHYSIO-CHEMICAL TREATMENT OF THE TEXTILE WASTEWATER

## 4.1 Introduction

The wastewater arising from textile fabric wet processing units consists of several pollutants such as salts, dyes, enzymes, surfactants, scouring agents, oil, oxidizing agents and reducing agents. The environmental impacts of the textile wastewater are widely reported from several places where such industries are located. In Tamil Nadu, Coimbatore, Karur and Erode districts face severe surface water and ground water pollution from discharge of industrial wastewater (CES, 2003), as it spoils agriculture, fisheries and make ground water unfit for use. Colour and salt are the major issues in the areas affected by such pollutants. Despite stringent laws in force in the country environmental problems are rampant. As a measure to combat such problems, Tiruppur industries have been employing physio-chemical treatment since 1999. The adopted technology in the treatment facilities is to remove colour and other organics primarily by coagulation and flocculation techniques. However, the dissolved pollutants not being controlled by the physio-chemical treatment, the large volume of wastewater with high levels of TDS and other pollutants is discharged in the river Noyyal flowing close by. Moreover, requirement of massive quantity of chemicals in the physio-chemical treatment result in generation of massive volume of sludge. This chapter aims to evaluate the efficiency of adopted physio-chemical treatment in Tiruppur.

## 4.2 Treatment of textile wastewater

The treatment of the textile wastewater is challenging due to the variable quality of the wastewater, the types of dyes used, fabric, types of dyeing machines and nature of other raw materials used in the dyeing process. The places where the textile industries functioning are facing severe constraints from the generation and disposal of the effluents. Textile wastewater has difficulty in meeting the standards for parameters such as dissolved solids, ionic salts, pH, colour, COD and some times heavy metals (Lin and Peng, 1996; Vlyssides *et al.*, 1999). Colour, the major issue in the textile wastewater, is caused by numerous complicated compounds, making decolourisation a difficult and

challenging task. There are several methods to treat the textile wastewater. A combination physical, chemical, and biological process is often used to treat the textile wastewater. Various researchers had explored and reported different techniques depending on the nature of wastewater. A brief on some such reports / findings are given in the table 4.2.1.

**Table 4.2.1 Various techniques used for the textile wastewater treatment**

| Techniques | Findings | Authors |
|---|---|---|
| Biological Treatment | Effectiveness of batch activated sludge process and powdered activated carbon adsorption for organic and colour removal from textile wastewaters containing starch and *Disperse-red-60* dyes was experimented under different ratios. The results show that starch containing wastewater undergoes higher bio-oxidation than wastewater containing equal amount of dyes. | Yeh, 2002. |
| | Aerobic and anaerobic experiments were carried out on dye *Disperse Blue 79* and real effluent using batch reactor. The dyes are biotransformed into amines by anaerobic systems and amines are mineralized by subsequent aerobic systems. | Melgoza *et al.*, 2004. |
| | Study of colour removal in the sequential batch reactor (SBR) having anaerobic and aerobic phases showed maximum and optimum colour removal of the azo dye *Remazol Brilliant Violet 5R* after 40-45 days of the sludge retention time. | Lourenco *et al.*, 2000. |
| | The sulfonated azo dye *Mordant Yellow 3* reduced under anaerobic conditions where biomass was grown aerobically with 6-aminonaphthalene-2-sulfonic acid. The amines generated during the anaerobic degradation were mineralized by the aerobic cultures. | Haug *et al.*, 1991. |

| | | |
|---|---|---|
| | The enzyme peroxidase from *Pleurotus ostreatus* was capable of decolourising triphenyl methane and azo dyes effectively. However, heterocyclic dyes, *Methylene Blue* and *Toluidine Blue O* were decolourised upto 10 %. The *Bromophenol Blue* was decolourised upto 98%. | Shin and Kim, 1998. |
| | Pre-grown mycelium and the spores of the fungus, *Phanerochaete chrysosporium* was found to decolourise the reactive dye *Procion Red MX-5B.* | Jacob *et al.*, 1998. |
| Ozonisation | Destruction of dyestuffs and alteration of surfactant molecular structure of the dyeing wastewater by ozone oxidation was found. | Perkowski *et al.*, 1996. |
| | Using ozone, reduction of foaming ability and deocolourisation of dyes were achieved. However COD and TOC were not completely removed. | Narkis and Rotel, 1980. |
| | Synthetic wastewater containing dye *Bomaplex Red CR-L* was ozonised and colour removal achieved. The COD removal increased with increasing pH. However, rate of ozone generation decreased with increasing temperature and no change was found with increasing ozone–air flow rate and initial dye concentration. The pre-ozonation of the wastewater enhanced coagulation process. | Oguz *et al.*, 2005. |
| | Even the high dose of ozone did not bring the change of organic matter to carbon dioxide and water completely; ozonation can be applied along with biological or advanced oxidation methods. | Ledakowicz, 1998. |
| | After ozonation the color absorbance (523 nm) was reduced by 80.9 % and the pH decreased from 10.9 to approximately 7.5 while COD reduction reached nearly 87 %. | Radetski *et al.*, 2002. |

| | | |
|---|---|---|
| Electrocoagul-ation / Electrochemi-cal oxidation | 100% removal of colour and 84% removal of COD within 3 minutes at electric potential of 600 mV using an iron electrode in a batch reactor were demonstrated. | Zaroual, 2005. |
| | Investigation of nonylphenol polythoxylate and textile wastewater degradation by electro-coagulation using iron and aluminum electrodes and electro-chemical Fenton's reaction. | Martins *et al.*, 2006. |
| | Addition of poly aluminum chloride in the electro-chemical reaction enhanced the COD removal rate. Efficiency depended upon the total aluminum supplied by initial addition and electro-chemical generation. | Can *et al*, 2006. |
| | Using the multi-cathode electrolyser with high cathode area, the decolourisation of the dyes such as *CI Acid Red 27* and *CI Acid Yellow 9* as model azo dyes and *CI Reactive Red 4*, *CI Reactive Orange 4* and *CI Reactive Black 5* was demonstrated. The required energy was 6 $KWHm^{-3}$ for 50% reduction of colour. | Bechtold *et al.*, 2001. |
| | Electro-chemically generated hypochlorite in the electro-chemical cell was found to remove COD upto 87% and 100% colour in 50 minutes from textile effluents containing high concentration of sodium chloride; while direct electro-chemical oxidation removed COD by 47% and color by 50% in 5 hours. | Zhan *et al.*, 2001. |
| | Electro-chemical oxidation of textile effluents using $Ti/RuO_2$, Ti/Pt and Ti/Pt/Ir electrodes showed 85–92% reduction of COD and about 85% reduction of DOC after 60 minutes at 6 $A/dm^2$; the efficiency of organics removal was in the order of $Ti/RuO_2$>Ti/Pt>Ti/Pt/Ir. However the electro-chemical oxidation of textile wastewater resulted in formation of chlorinated organics. | Naumczyk *et al.*, 1996. |

| | | |
|---|---|---|
| Pulse radiolysis | The anthraquinone dye, *Acid Blue+962* was decolourised using radiation in presence of nitrous oxide and combined use of hydrogen peroxide and UV radiation. | Perkowski *et al.*, 2003. |
| Ultra sound | Application of ultra sound in decolourisation and mineralization of the textile dyes was reviewed and opined as an effective tool in managing the textile dyeing wastewater. | Vajnhandl *et al.*, 2005 |
| Photo-catalysis | The photo-catalytic reaction in the presence of $TiO_2$ was experimented where UV-A was used to induce the reaction. It resulted in reduction of COD to the extent of 40-90% at the optimum concentration of 0.5g $TiO_2$/l. Further, elimination of ecotoxicity to the marine luminescent bacteria *Vibrio fischeri* was achieved. | Pekakis *et al.*, 2006. |
| Adsorption | Direct dyes such as *Direct Red 23* and *Direct Red 80* were adsorbed from aqueous solution using orange peel as the adsorbent. | Ardejani *et al.*, 2007. |
| | The biosorption of the textile reactive dyes by bacterial biomass of the activated sludge process rather than biodegradation was evaluated. | Alinsafi *et al.*, 2006 |
| | Coconut husk modified by N-(3-chloro-2-hydroxypropyl)-trimethylammonium chloride was able to adsorb the dyes such as *Reactive Blue 2*, *Reactive Yellow 2*, *Reactive Orange 16* and *Reactive Blue 4* to the extent of 128.9, 182.2, 254.5 and 423.7 mg/g respectively under low pH values. | Low *et al.*, 1998. |

| | | |
|---|---|---|
| Chemical coagulation & flocculation | Coagulation using the aluminum sulphate and a cationic organic flocculent resulted in complete decolourisation and removal of TOC, COD, AOX, BOD and anionic surfactants. Further the biodegradability was increased. | Golob *et al.*, 2005. |
| | The food grade polysaccharide mucilage from *Plantago psyllium* was found to remove dyes such as golden yellow (*C.I. Vat Yellow 4*) and reactive black (*C.I. Reactive Black 5*). This was more effective in removing vat dyes than reactive dyes. | Mishra and Bajpai, 2005. |
| | The coagulation/flocculation and precipitation of mixed textile wastewater using a combination of ferrous sulphate, lime and polyelectrolyte removed colour successfully. | Pala, 2001. |
| Fenton's reaction | Comparative study of Fenton's oxidation and coagulation–flocculation and ozone processes revealed that Fenton's oxidation and coagulation – flocculation removed 59% of COD and 89% of colour while ozone removed only 33% of COD and 91% of colour. | Meric *et al.*, 2005. |
| | Using coagulation technique by organic coagulant, Fenton's reaction, coagulation by iron hydroxide followed by sand filtration the wastewater containing the reactive, disperse and direct dyes were decolourised more than 99% and COD removed upto 96%. | Elkiadri *et al.*, 2002. |
| Membrane techniques | The ultrafiltration technique is proven for 87.5% of water recovery and 80% of COD removal from textile wastewater. Combination of the membrane bioreactor and nanofiltration is costlier than ultrafiltration. | Schoeberl *et al.*, 2005. |

homogenize the influent to enable easy operation of downstream processes at a constant flow rate with less variation in loading. Equalization tank provided for the purpose is of 16 hours hydraulic retention time (HRT). Equalization is accompanied by homogenizing the wastewater by floating aerators. Equalization is also useful in addition of chemicals required for the treatment at constant flow rate that enables their optimum usage ensuring maximum removal of pollutants. The plate 4.3.1 gives a view of the equalization tank of the CETP.

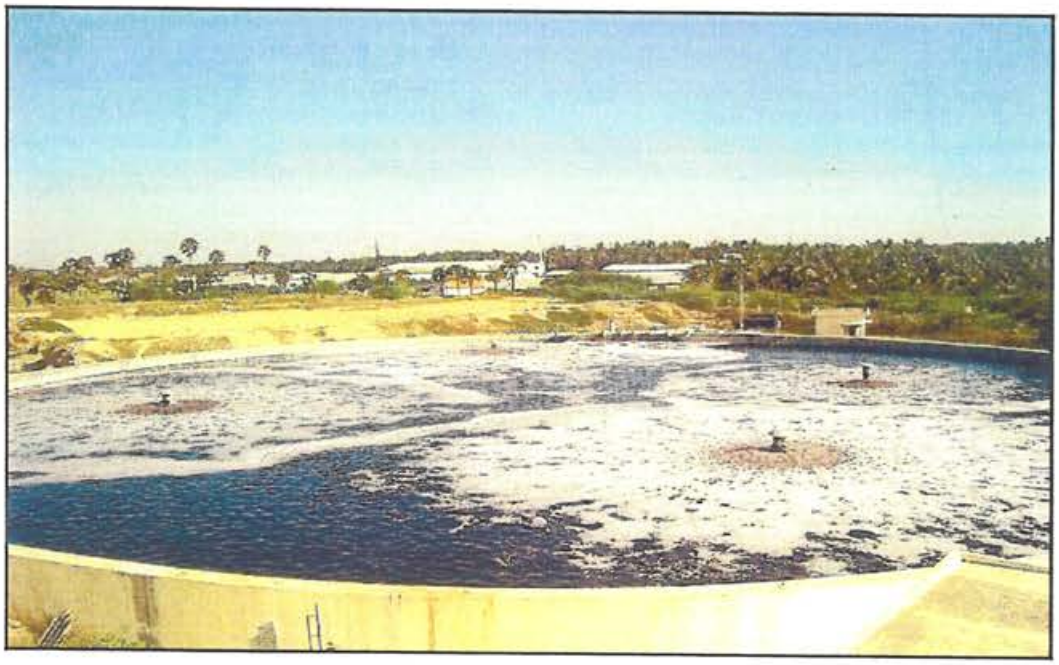


**Plate 4.3.1 Equalisation tank of the CETP treating textile effluent**

The physio-chemical treatment process is the sequence of the three steps namely coagulation, flocculation and clarification (liquid-solids separation). By the physio-chemical process the solids are separated from the wastewater by both chemical (coagulation) and physical process (mixing and agglomeration). Coagulation is carried out by addition of solutions of hydrated lime and ferrous sulphate in a flash mixer. Flash mixing process involves rapid mixing of a coagulant and hydrated lime in the wastewater, achieving a homogenous distribution. As a result of this process small particles (floccules) called 'pin point floc' are formed. Flocculation process ensures satisfactory separation of coagulated solids in the wastewater. During this process the colloidal

particles or floccules aggregate together and form denser and larger flocs. Slow stirring during flocculation is effected by a stirrer in the clariflocculator unit with an intention of maximizing contact of solids and thereby forming large, gelatinous and insoluble floc mass. These denser flocs settle down rapidly by gravitational force. While settling the denser flocs collect other suspended solids alongwith. Flocculation can be further enhanced by addition of synthetic polyelectrolytes. The overflow of the clarifier is filtered through a sand filter that removes other suspended solids. The filter continuously removes the suspended solids. The trapped solids in the sand filters are removed periodically by backwashing. The plates 4.3.2 and 4.3.3 show the clariflocculator units and discharge of the treated wastewater. The schematic flow diagram of the physio-chemical treatment employed in a CETP in Tiruppur is shown in the figure 4.3.1

**Plate 4.3.2 Clariflocculator unit of the CETP**

**Plate 4.3.3 Discharge point of treated effluent from the CETP**

### 4.3.2 Sludge management

The settled sludge from the clariflocculator is transferred to the sludge thickener. In the sludge thickener the sludge settles at the bottom by gravity and is compacted by the weight of the overlying loads, thus reducing the volume of the sludge considerably. However, to remove the remaining water from the sludge it is sent to the filter press (Plate 4.3.4) or solar sludge drying beds (Plate 4.3.5). The compacted and dried sludge is stored in polythene bags or sludge pits developed inside the CETP premise. The CETPs association is also developing a Common Landfill facility to dispose the sludge safely.

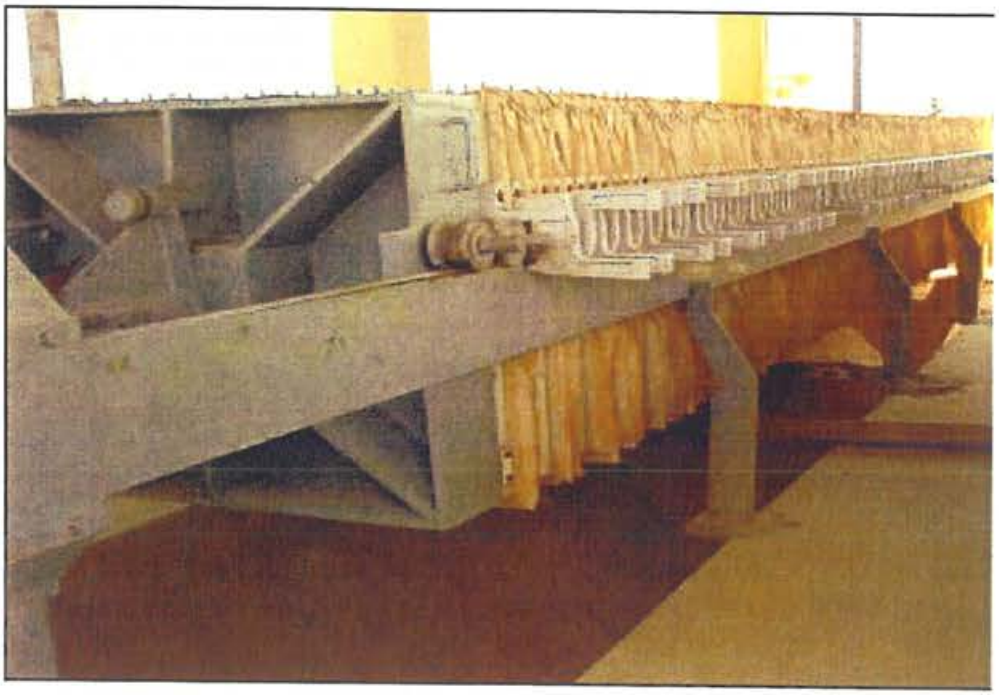


Plate 4.3.4 Filter press unit to dewater the sludge.

Plate 4.3.5 Solar Sludge drying beds.

| | | |
|---|---|---|
| | Membrane techniques such as microfiltration, ultra filtration and nanofiltration were evaluated for permeate flux and their suitability in separating COD, colour, conductivity, TDS and turbidity. These techniques are proven to have promising applications in management of textile wastewater. | Fersi *et al.*, 2005. |
| | The pilot scale system of microfiltration, nanofiltration and ultrafiltration were examined and found that the outlet from the ultrafiltration was of reusable standard. | Marcucci *et al.*, 2002. |
| | Demonstration of ultrafiltration and reverse osmosis in treating the textile printing wastewater generated from Slovenian factory containing reactive dyes, urea, and sodium alginate and oxidation agents carried out. The permeate from the RO system was of reusable standard for washing printed textiles. | Turk *et al.*, 2005. |

## 4.3 Physio-chemical treatment of textile wastewater employed in a CETP

Collection and conveying system and the treatment plant are the two main components in all Common Effluent Treatment schemes in Tiruppur. The wastewater generated by the member units is collected in a storage tank and pumped into the conveyance pipe line. Electromagnetic flow meter is established by each members of the CETP to measure instantaneous and cumulative flow of wastewater generated by them.

### 4.3.1. Treatment scheme

The coarse materials such as fibers, piece of cloth, plastics and such items, which are likely to disturb downstream operations and chock the pipelines and pumps, in the raw effluent are captured by screening by the Steel bars are placed vertically in the screen chamber. Screening is followed by equalisation. Since the textile wastewater discharged from the processing industries varies in qualities and flow rate, it is necessary to

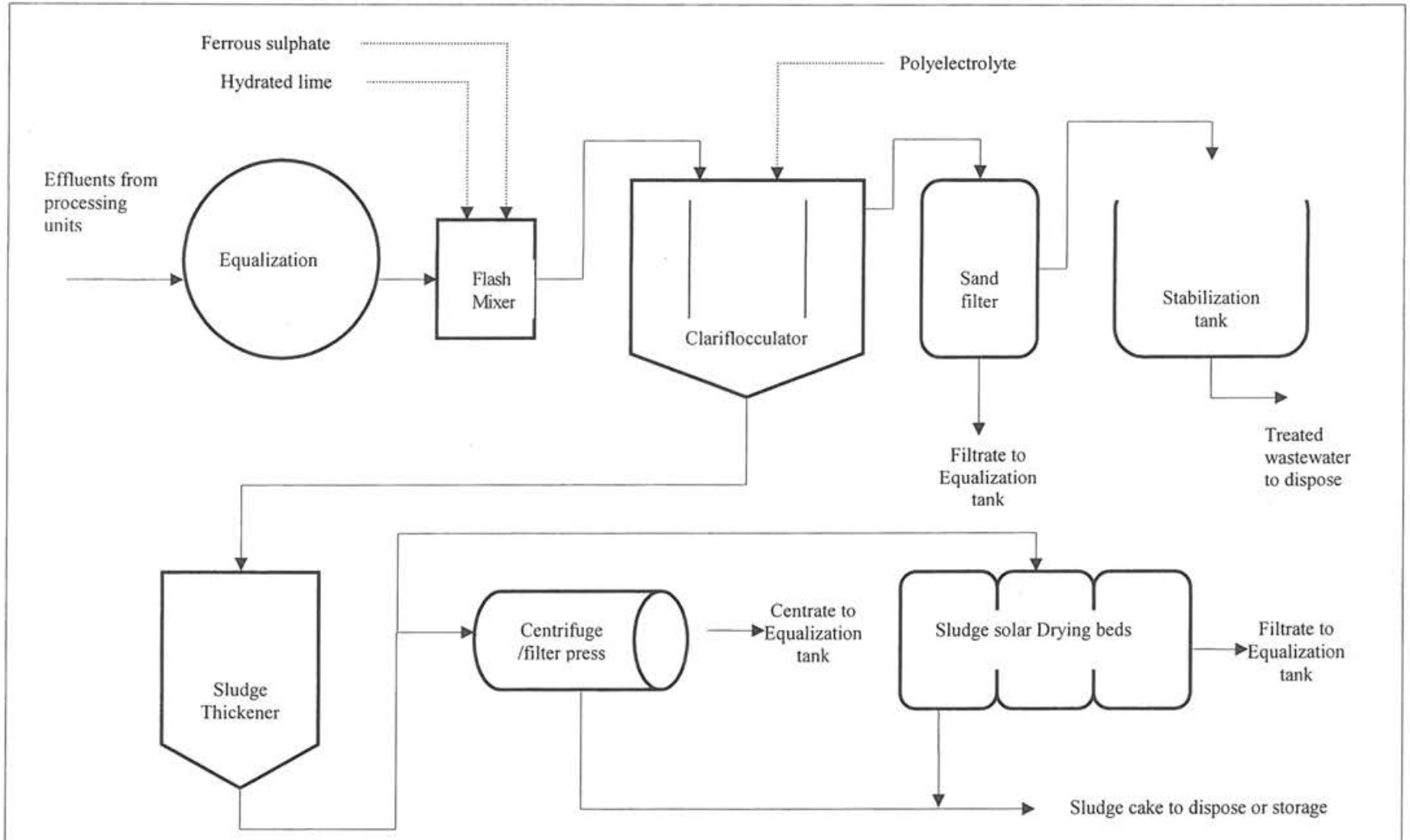



**Figure 4.3.1 Schematic diagram of physio-chemical treatment employed in CETPs in Tiruppur**

## 4.4 Methods

### 4.4.1 Wastewater sampling

Samples from two sampling locations, namely i) outlet of clari-flocculator, and ii) final discharge point to the river, in the CETP was collected to characterize the treated textile wastewater. The sample preservation and processing was the same as mentioned earlier in the previous chapter. 500 mL of sample at each sampling location was collected at an interval of 4 hours in a wide mouthed bottle, transferred to polythene containers and kept at 4°C for a period of 24 hours. The samples were then mixed together and 2 litres of sample were taken for physio-chemical analyses. 1000 mL of sample was preserved at 4°C after adding 4 mL concentrated nitric acid in glass bottles for heavy metal analysis. Two composite samples in a month for a period of 5 years were collected.

### 4.4.2 Analytical methods

Standard procedures and methods used for the sample analysis are shown in the table 3.6.1 of chapter 3. The estimation of pollution load removed by the physio-chemical treatment and disposed to the river along the treated effluent was done by interpolating the data collected in the CETP to the total volume of wastewater produced in Tiruppur since all the CETPs and most IETPs in Tiruppur employ only more or less same physio-chemical treatment techniques.

### 4.4.3 Quantification of treated wastewater discharge

Since there was no separate electromagnetic flow meter installed in the CETP to measure the discharge of treated wastewater, the data on inflow of the raw effluent was taken as equivalent to the discharge. The inflow data was reasonably appropriate as a measure of outflow as well since no loss of wastewater occurs during its physio-chemical treatment in the CETP except evaporation losses which seems very negligible.

### 4.4.4 Sludge quantification and analysis

#### a. Quantification

The CETP was not equipped to quantify the sludge accurately. Hence, the following formula was used to quantify the sludge.

Sludge quantity (dry form, Kg) = Volume of wastewater treated (kL) X 1.05

The factor 1.05 was the mean value of sludge generated to the optimized dose of the chemicals determined using the Jar Test apparatus.

**b. Collection of sludge samples and characterisation**

The sludge stored in the sludge pits of the CETP was collected randomly four times in a year. Characterisation of sludge was carried out as per the methods shown in the table 3.6.1.

## 4.5 Results and discussions

The following physio-chemical parameters were analysed and used to evaluate the efficiency of physio-chemical treatment of textile wastewater.

### 4.5.1 pH

The pH value in the clariflocculator outlet was always alkaline in nature. The values during the study period ranged from 8.41 to 9.81. The pH values in the final treated wastewater were in the range of 8.35 to 9.79. The norm for pH of wastewater to be disposed into inland surface water is 5.5 to 9.0 as per The Environmental (Protection) Act, (1986). During 2002 to 2006, 7 to 15 samples exceeded the norm (Figure 4.5.1).

It was observed that the clariflocculator outlet and final treated outlet showed higher pH than that of the equalized effluent. The net increase of pH was from 8.50 to 9.22 during 2002 in the clariflocculator outlet compared to the equalized effluent. Similarly, the pH increased to 9.12 from 8.47 in 2003, to 9.28 from 8.63 in 2004, to 8.90 from 8.30 in 2005 and to 9.12 from 8.45 in 2006. Only a minor reduction of pH was observed after the sand filtration. The figure 4.5.2 shows the increase of pH after the physio-chemical treatment.

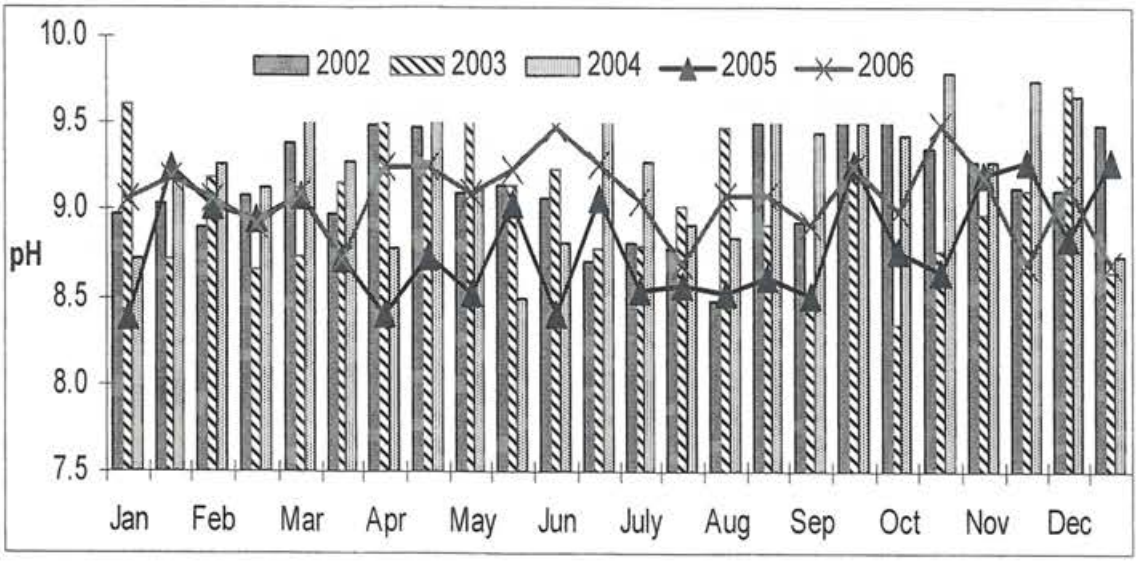



**Figure 4.5.1 pH values in treated textile wastewater**

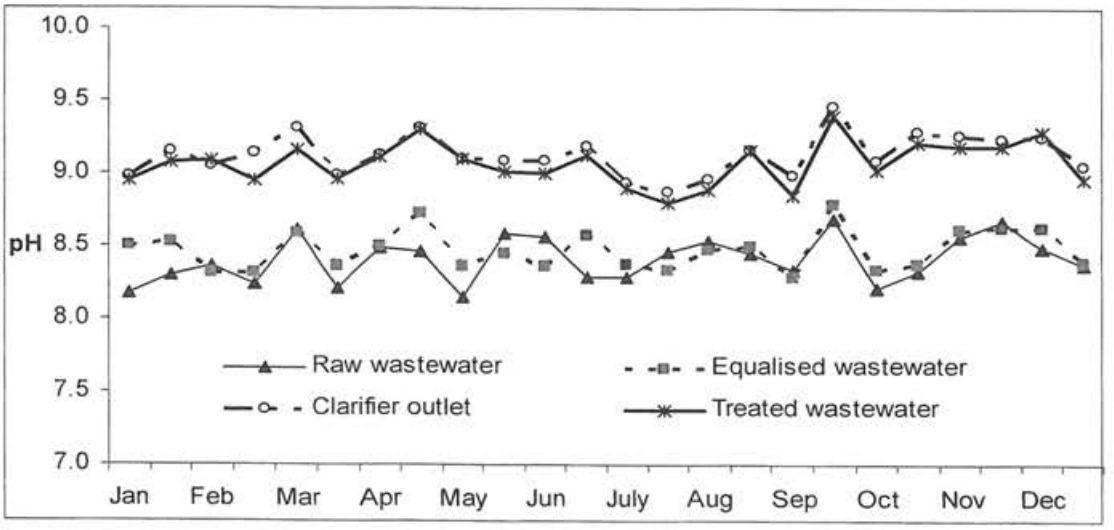



**Figure 4.5.2 Increase of pH after the physio-chemical treatment**

The coagulation mechanism requires sufficient alkalinity to enhance the coagulation. Dovletoglou *et al.* (2002) examined the effective range of pH for the coagulants such as ferrous and aluminum sulphate and found that about 9.7 pH is essential for an effective coagulation. The hydrated lime is added for the purpose. Ferrous sulphate is added to act as the coagulant and also to lower the pH mildly. However, in many samples measured, the pH values were slightly exceeding the norms stipulated by TNPCB.

### 4.5.2 Total suspended solids

The TSS in the clariflocculator outlet and final outlet from the CETP is given in the table 4.5.1. The TSS ranged from 95.0 to 116.0 mg/L for the clariflocculator outlet and 72.5 to 84.8 mg/L in the final outlet. Both the values were the minimum in the year 2002 and maximum in the year 2005. The removal of TSS by coagulation and flocculation, and sand filtration was measured and the percent removals are tabulated in the table 4.5.2. Coagulation and flocculation mechanisms had a major role in the removal of TSS. The TSS carried over from the clariflocculator was filtered by the sand filter. This mechanism removed 14.2 to 31.3 mg/L (4.5 to 10.0%) of TSS from the equalized effluent. The total removal of TSS by both of the mechanisms was 72.3% to 74.5%.

**TSS load removal:** The table 4.5.3 shows the TSS load removed by the coagulation - flocculation and filtration mechanisms in the CETP. The total TSS load removal was 3327 MT during the study period. The coagulation - flocculation mechanism in the clariflocculator unit removed 2435 MT and the remaining load was removed by the filtration mechanism. The TSS content carried over to the outlet of the CETP was 205.3 MT, 201.9 MT, 237.0 MT, 201.3 MT and 158.6 MT during 2002 to 2006 respectively. The norm fixed by the statutory body for TSS is 100 mg/L. The treated wastewater satisfied the requirement specified by TNPCB in most of the samples. Only 2 samples in 2006 and one sample in 2005 slightly overshot the stipulated norm. The figure 4.5.3 illustrates TSS levels in various stages of physio-chemical treatment.

| Year | Clariflocculator outlet (mg/L) | Treated effluent (mg/L) |
|---|---|---|
| 2002 | 95.0 ± 13.3 | 72.45 ± 9.3 |
| 2003 | 98.1 ± 15.7 | 74.04 ± 10.9 |
| 2004 | 99.3 ± 15.5 | 77.26 ± 8.6 |
| 2005 | 116.0 ± 19.8 | 84.76 ± 11.0 |
| 2006 | 95.4 ± 12.8 | 81.2 ± 11.2 |

**Table 4.5.1 TSS content in the clariflocculator outlet and final treated effluent**

| Year | Clariflocculator | | Sand filter | | Total removal of TSS (%) |
|---|---|---|---|---|---|
| | Quantity of removal (mg/L) | Percentage of removal (%) | Quantity of removal (mg/L) | Percentage of removal (%) | |
| 2002 | 166.9 | 63.7 | 22.6 | 8.6 | 72.3 |
| 2003 | 172.5 | 63.8 | 24.1 | 8.9 | 72.6 |
| 2004 | 190.2 | 65.7 | 22.1 | 7.6 | 73.3 |
| 2005 | 199.0 | 63.2 | 31.3 | 9.9 | 73.1 |
| 2006 | 223.2 | 70.1 | 14.2 | 4.5 | 74.5 |

**Table 4.5.2 TSS removal by clariflocculator and sand filter**

The chemical precipitation mechanism to a great extent is effective in controlling the TSS and other organics of wastewater. Metcalf and Eddy (1995) recorded that coagulation and flocculation mechanism is capable of removing TSS to the extent of 80-90%. The established physio-chemical treatment system in the CETP removed about 73% of TSS. However the work of Bidhendi (2007) showed about 90% removal of TSS from textile effluents using ferrous sulphate as the coagulant.

| Year | Coagulation cum flocculation (MT) | Filtration (MT) | Total (MT) |
|---|---|---|---|
| 2002 | 473.0 | 64.0 | 674.2 |
| 2003 | 470.3 | 65.6 | 679.2 |
| 2004 | 583.2 | 67.7 | 804.0 |
| 2005 | 472.7 | 74.2 | 669.3 |
| 2006 | 435.9 | 27.8 | 500.1 |

**Table 4.5.3 TSS load removed by the physio-chemical treatment**

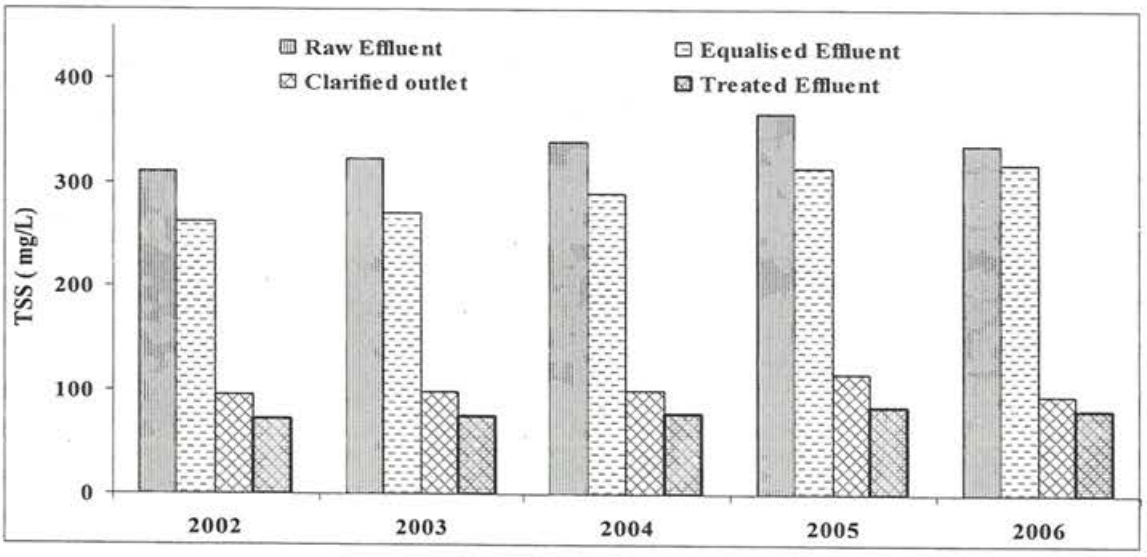



**Figure 4.5.3 TSS levels in each of the sampling locations of the CETP**

### 4.5.3 Total dissolved solids

The textile industries face severe restraints in recent years due to the discharge of either treated or untreated wastewater containing high level of TDS. The yearly mean values of TDS measured in the clariflocculator outlet and final outlet is shown in the table 4.5.4. The lowest values measured were 5539, 5556, 5752, 5715, and 6343 mg/L in the clariflocculator outlet and 5632, 5388, 5735, 5513 and 6381 mg/L in the final outlet during the study period from 2002 to 2006 respectively. Similarly, the highest values were 6853, 7770, 7810, 8353 and 8318 mg/L found in the clariflocculator outlet and 6751, 7878, 7694, 8364 and 8349 mg/L in the treated wastewater.

| Year | Clariflocculator Outlet (mg/L) | Treated Effluent (mg/L) |
|---|---|---|
| 2002 | 6274 ± 407 | 6349 ± 313 |
| 2003 | 6521 ± 718 | 6483 ± 734 |
| 2004 | 6782 ± 540 | 6796 ± 567 |
| 2005 | 7345 ± 722 | 7348 ± 769 |
| 2006 | 7374 ± 675 | 7367 ± 632 |

**Table 4.5.4 TDS levels in clariflocculator outlet and final treated effluent**

The progressive increase of TDS content in the treated wastewater discharged from the CETP was noticed from the year 2002 to 2006. In the clariflocculator outlet the increase was about 17.5% while in the final outlet the increase was about 16.0%. The seasonal variations in TDS as seen in the case of equalized wastewater were also found in the clariflocculator outlet and final outlet (Figure 4.5.4). The TDS values were lowest during January, February and October to December than the period from March to September.

No reduction in TDS could be observed in any stages of the treatment system. During 2002 to 2006, the annual average TDS found in the discharges were 6349 ± 313, 6483 ± 734, 6796 ± 567, 7348 ± 769 and 7367 ± 632 mg/L respectively, which were similar to the values found in the wastewater before the treatment (Figure 4.5.5). The norms stipulated for TDS for discharge of wastewater into the inland surface water is less than 2100 mg/L. However, the treated wastewater never met this requirement. The TDS content in the treated wastewater almost always exceeded stipulated norm by 3 to 3.5 times.

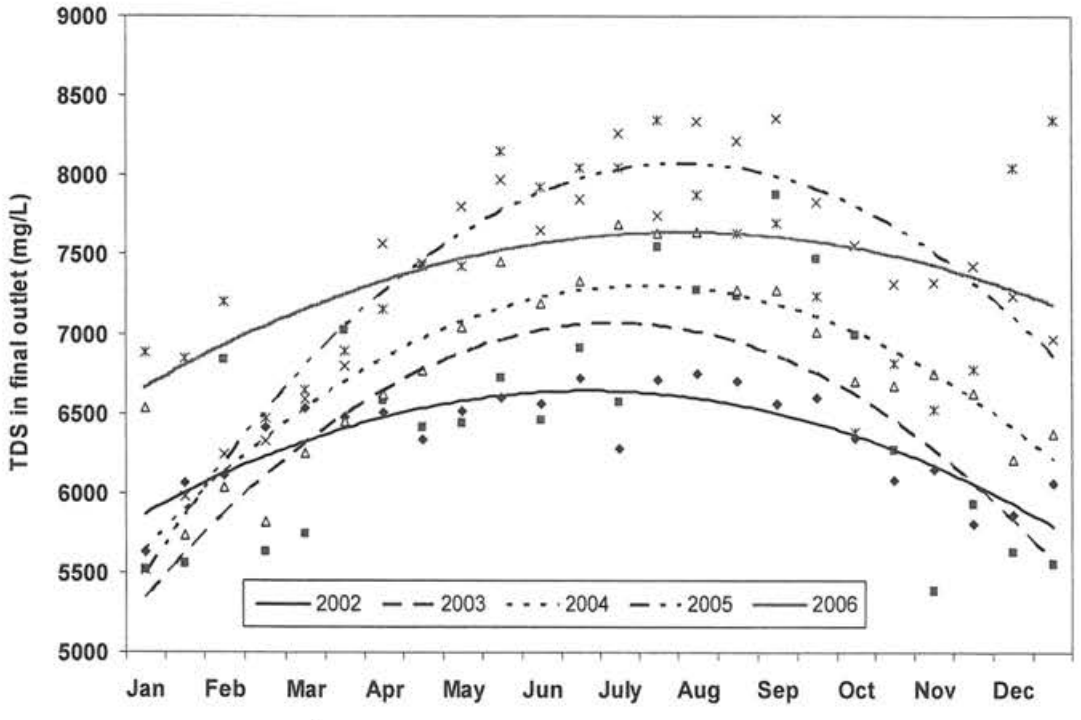



**Figure 4.5.4 Seasonal variations of TDS in treated textile effluent**

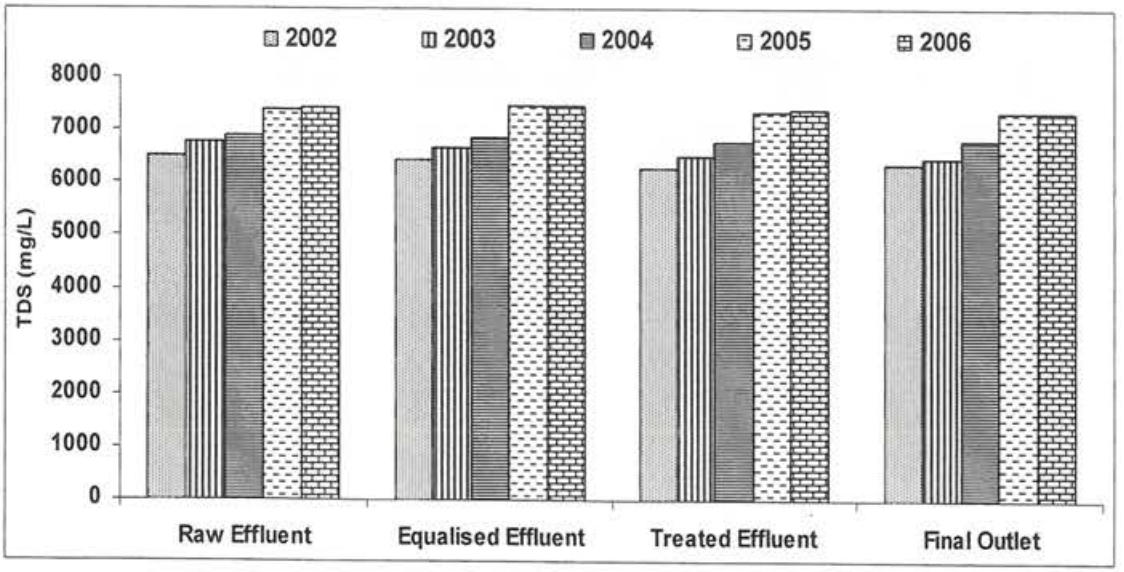



**Figure 4.5.5 TDS contents of wastewater in each sampling locations of the CETP**

**TDS load discharged to the river Noyyal:** As noted above the physio-chemical treatment was not capable to control the TDS content of wastewater. The cumulative volume of TDS load disposed to the river during the study period was 88350 MT which was very close to the TDS load estimated in the untreated wastewater of 89769 MT. The year wise discharge of TDS load from the CETP is shown in the figure 4.5.6. Maximum TDS load discharged was in the year 2004 (20845 MT). During 2005 to 2006 though the TDS concentration in the effluent increased the TDS load showed a fall.

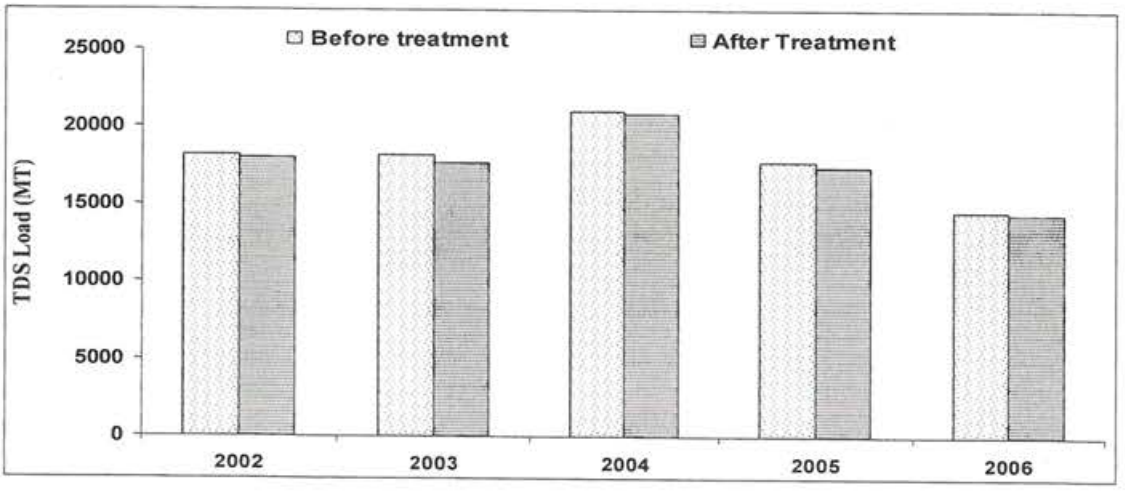



**Figure 4.5.6 TDS load before and after the physio-chemical treatment of textile wastewater**

The physio-chemical treatment system using chemical coagulation and flocculation mechanisms was established aiming at removing the colour and other organics. It was known that the technology engaged did not control the TDS. Therefore, massive quantity of TDS load was discharged to the river Noyyal which damaged the water and ground water quality in the river and immediate portions of its basin. It is found that the Tiruppur textile industries generally have failed in meeting wastewater discharge limits, particularly with regard to TDS, as observed by Senthilnathan and Azeez (1999).

### 4.5.4 Chloride

The values of chloride contents estimated each year of the study period are presented in the figure 4.5.7. The values were closer in the clariflocculator outlet and final outlet which indicates that the chloride was not controlled by the physio-chemical treatment. Further the chloride showed increase in concentration as seen in the TDS content of the wastewater. The rise of chloride values was about 15% in the final treated wastewater.

Seasonal variation was found in the case of chloride contents in the clariflocculator outlet and treated wastewater outlet. The lower values were seen during January, February and October to December months than the period from March to September (Figure 4.5.8). Chloride contents did not deviate much before and after the physio-chemical treatment. Higher chloride content than the equalized effluent was noticed during March to August in 2005. The chloride load disposed during the study period is given in the table 4.5.5.

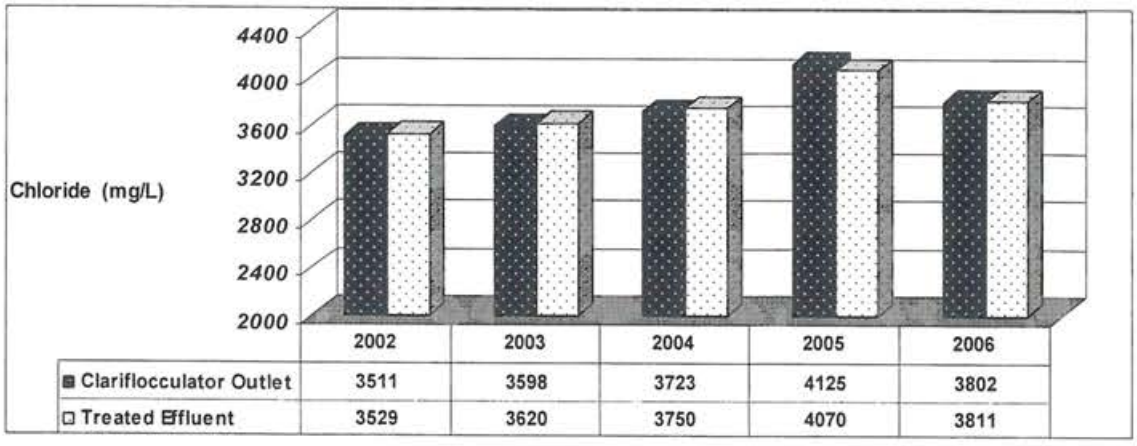



**Figure 4.5.7 Chloride contents in the clariflocculator outlet and final treated effluent**

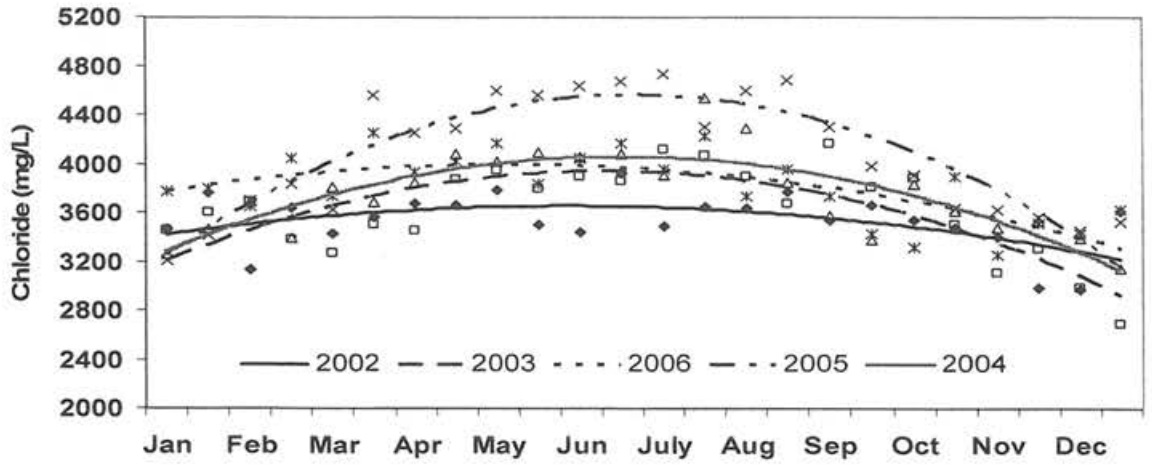



**Figure 4.5.8 Seasonal variations in chloride in the treated effluent**

| Year | Chloride annual load (MT) |
|---|---|
| 2002 | 10001 |
| 2003 | 9870 |
| 2004 | 11502 |
| 2005 | 9667 |
| 2006 | 7442 |

**Table 4.5.5 Chloride load in the treated textile effluent**

The stipulated norm for chloride content in treated wastewater for disposal into the inland surface water is less than 1000 mg/L. The treated wastewater in Tiruppur never met this requirement. The chloride content in the treated wastewater was 3.5 to 4.0 times higher than the stipulated norm. During March to August 2005 the CETP used ferric chloride instead of ferrous sulphate. Ferric chloride in wastewater in reaction with the hydrated lime resulted in the increase of chloride content in those months.

### 4.5.5 Sulphate

The sulphate contents in the clariflocculator outlet varied from 520 mg/L to 840 mg/L; in the final treated effluent it varied from 445 mg/L to 819 mg/L. The mean values of sulphate during the study period are given in the table 4.5.6. The values measured in both

the sampling locations were not much different. The concentration of sulphate content in the discharges from the CETP increased with year. The net increase was 64.3 mg/L, to the tune of 9.9%.

| Year | Clariflocculator Outlet (mg/L) | Treated effluent (mg/L) |
|---|---|---|
| 2002 | 645.69 ± 61.04 | 651.31 ± 63.90 |
| 2003 | 656.79 ± 42.13 | 652.14 ± 51.03 |
| 2004 | 678.29 ± 48.05 | 677.96 ± 50.03 |
| 2005 | 618.29 ± 78.16 | 620.55 ± 81.09 |
| 2006 | 712.95 ± 34.58 | 715.65 ± 29.93 |

**Table 4.5.6 Sulphate concentrations in the clariflocculator outlet and final treated effluent**

The seasonal variations of sulphate were noticed both in the case of clariflocculator outlet and final outlet. The figure 4.5.9 displays the average of sulphate against the respective months measured in the clariflocculator outlet and final outlet, showing the seasonal variations.

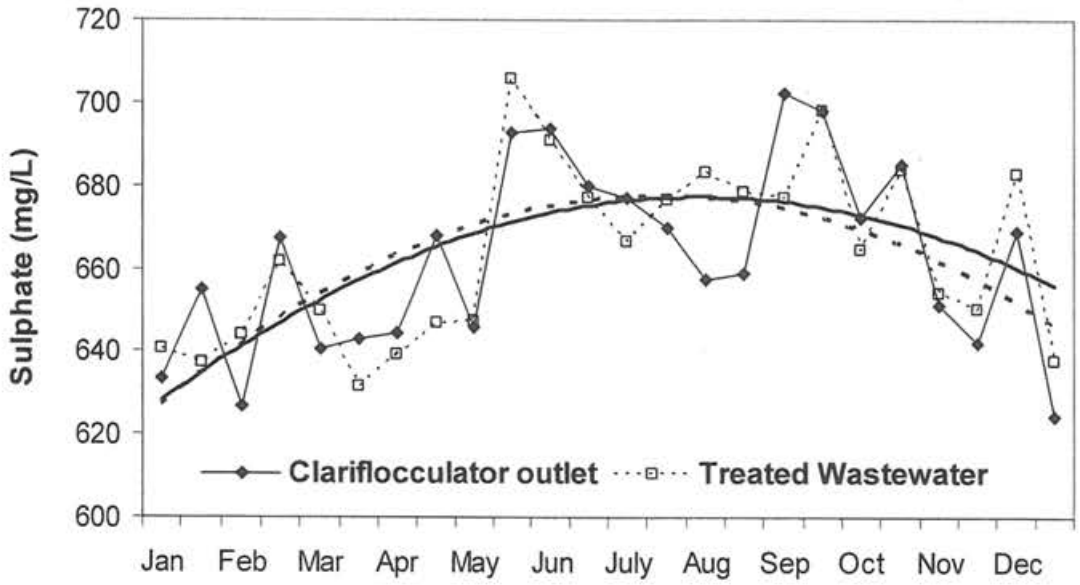



**Figure 4.5.9 Seasonal variations in sulphate contents in the clariflocculator outlet and final treated effluent**

It was noticed that the physio-chemical treatment could not reduce sulphate content in the textile wastewater. Instead, sulphate was found increasing considerably after the treatment. The year wise increase of sulphate added by the physio-chemical treatment was 126.6, 129.4, 138.9, 76.6 and 138.28 mg/L during 2002 to 2006 respectively. The mean increase in concentration of sulphate was around 130 m/L after the physio-chemical treatment. The figure 4.5.10 illustrates increase in sulphate in the clariflocculator outlet and final discharge of the wastewater compared to the raw effluent and equalized effluent. The sulphate content was found to be lower than the limits (less than 1000 mg/L) specified for disposal of wastewater into open surface water bodies.

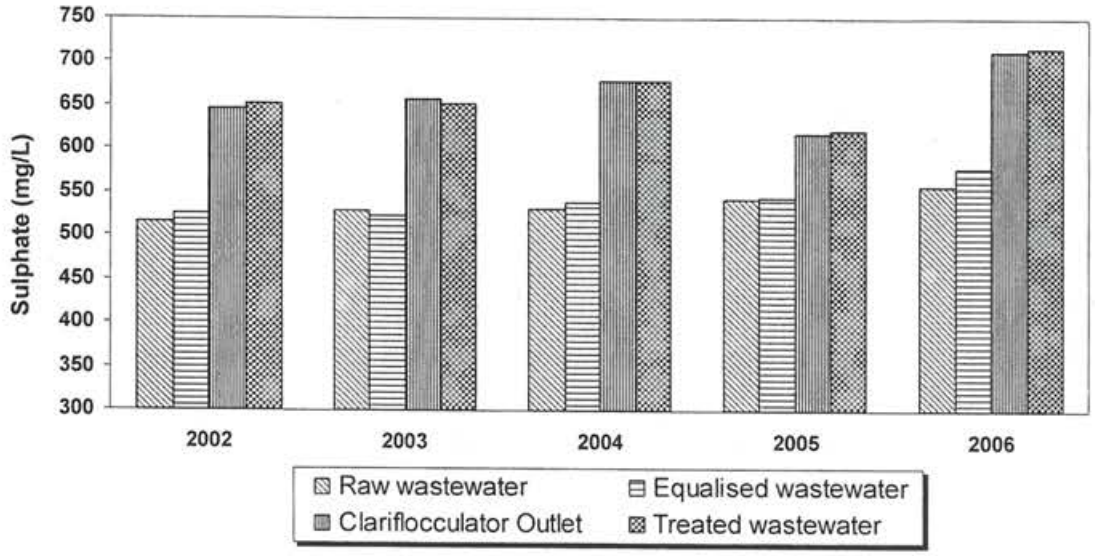



**Figure 4.5.10 Increase of sulphate after physio-chemical treatment**

| Year | Final outlet (MT) | Increase during physio-chemical treatment (MT) |
|---|---|---|
| 2002 | 1846 | 359 |
| 2003 | 1778 | 353 |
| 2004 | 2079 | 426 |
| 2005 | 1474 | 182 |
| 2006 | 1398 | 270 |

**Table 4.5.7 Sulphate load in the final treated effluent and added by the physio-chemical treatment**

**The increase of sulphate load in the physio-chemical treatment:** The sulphate load calculated in the treated wastewater is listed in the table 4.5.7. The sulphate load disposed into the river from the CETP decreased after the year 2004. The increase of sulphate load by the addition of ferrous sulphate as the coagulant was calculated and shown in the same table. During the year 2005, sulphate load in the treated effluent was lower than other years. The CETP discharged 8575 MT of the sulphate load to the river during the period of study including 1589 MT added by the physio-chemical treatment.

The increase of sulphate after the physio-chemical treatment was due to the use of ferrous sulphate as the coagulant. The ferrous sulphate on reaction with the hydrated lime result in formation of soluble calcium sulphate which would have increased the sulphate concentration and sulphate load. As mentioned earlier during the year 2005, from March to August, the CETP used ferric chloride instead of ferrous sulphate as the coagulant which might have increased the chloride content in the wastewater. However after 2004 the discharge of sulphate load to the river from the CETP was decreasing because of reduction of volume of wastewater.

### 4.5.6 Chemical oxygen demand

The COD values measured in clariflocculator outlet and final outlets of the CETP are shown in the table 4.5.8. The COD values ranged from 217.9 to 261.6 mg/L in the clariflocculator outlet and 189.8 to 231.1 mg/L in the final outlet during the study period. The coagulation and flocculation process played major role in the removal of COD from the textile wastewater. The clariflocculator mechanism reduced 56% to 62% of COD while the sand filtration removed 4% to 5%. The net removal by both of the systems together was around 63%.

| Year | **Clariflocculator outlet** (mg/L) | **Final treated effluent** (mg/L) |
|---|---|---|
| 2002 | 233.7 ± 32.5 | 208.9 ± 29.9 |
| 2003 | 239.7 ± 49.2 | 210.7 ± 39.5 |
| 2004 | 241.9 ± 37.2 | 211.1 ± 33.7 |
| 2005 | 217.9 ± 36.7 | 189.8 ± 29.8 |
| 2006 | 261.6 ± 40.6 | 231.1 ± 31.5 |

**Table 4.5.8 COD values reduced by clariflocculator and sand filter**

The stipulated norm for the COD of treated wastewater for disposal into the inland surface water is less than 250 mg/L. The treated wastewater met the standard in most of the cases; however some samples (1 sample in 2002, 5 samples in 2003 and 2006, and 3 samples in 2004) exceeded the limit. The figure 4.5.11 shows the levels of COD in the treated wastewater of the CETP.

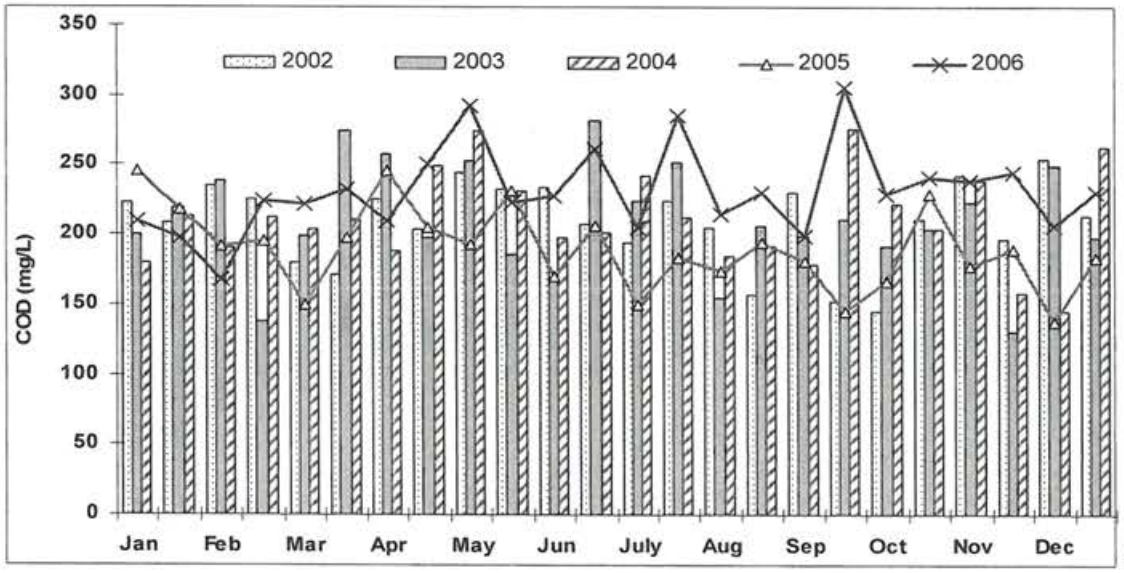



**Figure 4.5.11 COD levels in the treated wastewater**

**COD load removal**: The COD load removed by the clariflocculator and sand filter systems is given in the table 4.5.9. During the study period the total load removed by the physio-chemical treatment was 4747 MT. The clariflocculator played major role in removal of COD. However, The COD load in the treated wastewater was considerably high. The portion of the COD load carried over with the discharge of the treated wastewater is shown in the table 4.5.10. Nevertheless, there was a trend of decrease in COD load in the treated wastewater. After 2004 the COD load discharged by the CETP is decreasing due to the generation of less volume of wastewater.

As it is already evident, the effluent treatment facilities established in Tiruppur during 1999 were designed primarily to remove organics and colour. The established primary treatment system removed COD to an extent of 63%. Metcalf and Eddy (1995) reported that chemical precipitation possibly removes COD to the tune of 30-60% from

wastewater. Georgiou *et al.* (2003) reported the removal of COD to the extent of 50 to 60% from textile wastewater by coagulation and flocculation using hydrated lime and ferrous sulphate. Ferrous sulphate (at 1000 mg/L dose) removed about 60% COD from textile wastewater (Selcuk, 2005). The conventional physio-chemical treatments were reported to remove only about 50% of colour and around 60% of COD from textile wastewater (Azbar, 2004).

| Year | COD load removal (MT) | | |
|---|---|---|---|
| | Clariflocculator | Sand filter | Total |
| 2002 | 940 | 70 | 1010 |
| 2003 | 903 | 79 | 982 |
| 2004 | 1019 | 95 | 1114 |
| 2005 | 857 | 67 | 924 |
| 2006 | 658 | 60 | 718 |

**Table 4.5.9 COD load removed by the physio-chemical treatment**

| Year | COD load in the treated effluent (MT) |
|---|---|
| 2002 | 592 |
| 2003 | 575 |
| 2004 | 647 |
| 2005 | 451 |
| 2006 | 451 |

**Table 4.5.10 COD load in the treated effluent**

However other chemical treatment techniques based on Fenton's reactions and electro-chemical oxidation were proven more efficient in removing organic pollutants from textile wastewaters. Chen *et al.* (2005) reported about 90% reduction of COD from the textile wastewater by electro-chemical oxidation process. $TiO_2$-mediated photocatalytic and photo induced and dark Fenton/Fenton-like reactions removed 77–98% of COD and 51–86% TOC from the wastewater containing reactive dyes such as *Remazol Black B* and *Remazol Turquoise Blue G 133* (Arslan and Balcioglu, 1999). The study by Solmaz *et al.* (2006) showed that COD removal by Fenton process and Fenton-like process ($Fe^{3+}/H_2O_2$)

was 78% and 64% respectively, while ozonation of the wastewater removed only 43% COD. It is apparent that complete COD removal from the textile effluents was possible by a combination of appropriate processes rather than a single one. Kim *et al.* (2003a) showed that the combined process comprising biological treatment, chemical coagulation and electro-chemical oxidation removed 95.4% of COD and 98.5% colour from the textile wastewater.

### 4.5.7 Biochemical oxygen demand

The BOD in the clariflocculator outlet was in the range of 55.7 to 126.5 mg/L and the final outlet 44.0 to 107.1 mg/L. The average BOD measurements are given in the table 4.5.11. It was observed that the physio-chemical treatment removed 51 to 60% BOD from the textile wastewater.

| Year | BOD levels (mg/L) | |
|---|---|---|
| | Clariflocculator Outlet | Final outlet |
| 2002 | 80.0 ± 11.7 | 71.07 ± 12.4 |
| 2003 | 85.1 ± 12.2 | 74.31 ± 13.7 |
| 2004 | 86.2 ± 16.1 | 75.94 ± 12.7 |
| 2005 | 82.7 ± 13.2 | 67.12 ± 11.4 |
| 2006 | 85.4 ± 16.7 | 73.12 ± 16.8 |

**Table 4.5.11 BOD levels in the clariflocculator and final treated effluent**

The coagulation and flocculation mechanisms played major role in removal of BOD. It removed about 47% of BOD, while the sand filtration mechanism removed only about 7% only. Nearly half of the BOD in the untreated wastewater was not removed by the physio-chemical treatment.

As per the pollution control norms, the BOD of treated wastewater for disposal into the inland surface water is to be less than 30 mg/L. The treated wastewater by the physio-chemical treatment never met the requirement (Figure 4.5.12). In the figure the mean BOD values of raw effluent, equalized effluent, clariflocculator outlet and final treated

outlet are plotted year wise. It was found that 24 samples exceeded the norm by 1.5 to 2.0 times and 84 samples exceeded by 2 to 3 times. 10 samples had BOD 3 to 4 times higher than the stipulated norm. About ¾ of samples exceeded the norm 2 to 3 times.

| Year | Clariflocculator | | Sand Filter | | Total | |
|---|---|---|---|---|---|---|
| | Values (mg/L) | Percentage | Values (mg/L) | Percentage | Values (mg/L) | Percentage |
| 2002 | 72.1 | 46.3 | 8.9 | 5.9 | 81.0 | 52.2 |
| 2003 | 71.1 | 43.7 | 10.8 | 7.5 | 81.9 | 51.2 |
| 2004 | 77.4 | 46.4 | 10.3 | 6.3 | 87.7 | 52.6 |
| 2005 | 83.6 | 50.0 | 15.6 | 9.4 | 99.2 | 59.4 |
| 2006 | 85.2 | 49.8 | 12.3 | 7.1 | 97.5 | 56.8 |
| Mean | 77.9 | 47.2 | 11.6 | 7.2 | 89.4 | 54.4 |

**Table 4.5.12 BOD values removed by the physio-chemical treatment**

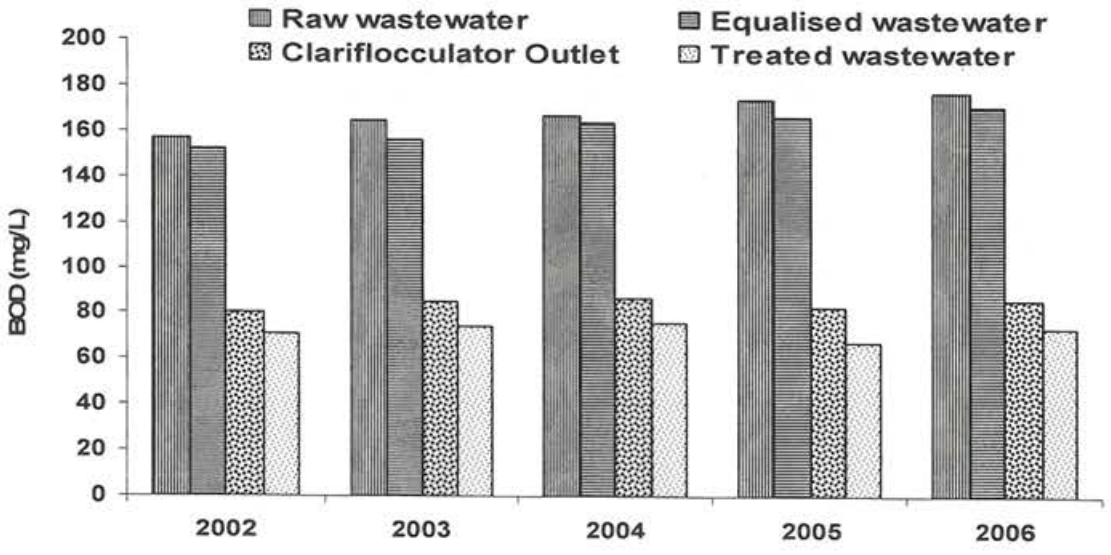



**Figure 4.5.12 BOD levels in each of the sampling locations of the CETP**

**BOD load removal:** Removal of the BOD load by the physio-chemical treatment is shown in the table 4.5.13. The total removal through out the study period was 1148 MT, of which the coagulation and flocculation process removed 1000 MT while the rest was removed by the filtration mechanism. It is unfortunate that after treatment, nearly half of the BOD load in the wastewater flows down to the river (Table 4.5.13). The total BOD

load disposed into the river Noyyal is 939.1 MT through out the study period. After the year 2004 the BOD load in the disposed effluent has come down to 159.42 MT from 232.92 MT found in the year 2004 and further reduction was noticed in subsequent years.

| Year | BOD load Removed (MT) | BOD load disposed (MT) |
|---|---|---|
| 2002 | 229.5 | 201.4 |
| 2003 | 223.3 | 202.6 |
| 2004 | 268.9 | 232.9 |
| 2005 | 235.6 | 159.4 |
| 2006 | 190.3 | 142.8 |

**Table 4.5.13 BOD load removed by the treatment and found in disposed treated effluent**

**BOD and COD ratio:** The calculated COD and BOD ratio in each sampling locations of the CETP is given in the table 4.5.14. In the case of raw effluent before treatment the ratio was from 1:3.33 to 1:3.64. In the equalized effluent the ratio varied from 1:3.48 to 1:3.72. After the physio-chemical treatment the ratio ranged from 1:2.64 to 1:3.06 in the clariflocculator outlet while in the final outlet it ranged from 1:2.84 to 1:3.16. The BOD and COD ratio has decreased from 1: 3.6 to 1:2.9 after the physio-chemical treatment, suggesting that after the physio-chemical treatment the wastewater is more vulnerable to the biological oxidation.

| Year | Raw effluent | Equalized effluent | Clariflocculator Outlet | Final Treated effluent |
|---|---|---|---|---|
| 2002 | 1:3.58 | 1:3.72 | 1:2.92 | 1:2.94 |
| 2003 | 1:3.54 | 1:3.65 | 1:2.82 | 1:2.84 |
| 2004 | 1:3.52 | 1:3.51 | 1:2.81 | 1:2.78 |
| 2005 | 1:3.33 | 1:3.48 | 1:2.64 | 1:2.83 |
| 2006 | 1:3.64 | 1:3.51 | 1:3.06 | 1:3.16 |

**Table 4.5.14 BOD, COD ratio in each of the sampling locations in the CETP**

Coagulation and flocculation mechanisms employed in the CETP removed only about half of the BOD from the textile wastewater. The report of Pathie *et al.* (2005) showed much higher reduction in BOD and COD in a CETP treating the textile wastewater. However the CETP under their study was additionally equipped with dual media filter, activated carbon filter and chemical oxidation which would have enhanved removal of organics. The toxicity reduction of textile wastewater after the chemical precipitation has been reported by many researchers. Selcuk (2005) found that the ferrous sulphate at the dose of 1000 mg/L to the textile wastewater has removed toxicity to an extent of 70-80% to *Daphnia magna.*

### 4.5.8 Hardness

The total hardness of the clariflocculator outlet varied from 239 to 492 mg/L. In the final treated outlet hardness was a bit lower (209.3 to 454.8 mg/L). The calcium hardness ranged from 70.2 to 240.9 mg/L and 71.8 to 232.9 mg/L in the clariflocculator outlet and final outlet respectively. The magnesium hardness varied from 101.0 to 369.0 mg/L and 110.8 to 319.3 mg/L in the clariflocculator outlet and final treated effluent respectively. The mean values of hardness during wastewater treatment are shown in the table 4.5.15.

| Year | Clariflocculator Outlet | | | Treated Wastewater | | |
|---|---|---|---|---|---|---|
| | Calcium hardness (mg/L) | Magnesium hardness (mg/L) | Total hardness (mg/L) | Calcium hardness (mg/L) | Magnesium hardness (mg/L) | Total hardness (mg/L) |
| 2002 | 157.9 ± 30.6 | 194.7 ± 27.7 | 352.6 ± 49.6 | 151.5 ± 32.1 | 183.8 ± 27.6 | 335.3 ± 48.4 |
| 2003 | 153.4 ± 25.4 | 206.0 ± 35.4 | 359.3± 50.3 | 144.3 ± 25.9 | 195.3 ± 34.8 | 339.6 ± 48.8 |
| 2004 | 157.5 ± 38.6 | 232.4 ± 46.5 | 389.8 ± 55.5 | 149.1 ± 31.9 | 217.9 ± 35.0 | 367.1 ± 46.9 |
| 2005 | 178.3 ± 35.8 | 180.2 ± 25.9 | 358.5 ± 50.1 | 163.8 ± 31.3 | 169.8 ± 28.3 | 333.7 ± 49.0 |
| 2006 | 190.7 ± 19.3 | 196.7 ± 37.9 | 387.3 ± 42.0 | 177.6 ± 21.7 | 202.9 ± 29.7 | 380.5 ± 38.0 |

**Table 4.5.15 Total, calcium and magnesium hardness found in the clariflocculator outlet and final treated effluent**

From the table a gradual increase of total hardness values from 2002 could be seen. The calcium and magnesium hardness also increased accordingly. The increase was about 13% in total hardness, 17% in calcium hardness and 10% in magnesium hardness. This

observation conforms to the observation on the raw and equalized effluents where in the hardness in untreated wastewater also showed a gradual increase with the years.

The figures 4.5.13 and 4.5.14 shows the seasonal variations exhibited by the total hardness and calcium hardness respectively. Hardness values in the clariflocculator outlet and treated wastewater were found higher during March to September of every year while lower values were found in January, February, and October to December months of year. The peak values of total hardness were found during May to September and lower values in the months of October, November and January of the study period. Similar observations were made in the case of calcium and magnesium hardness also.

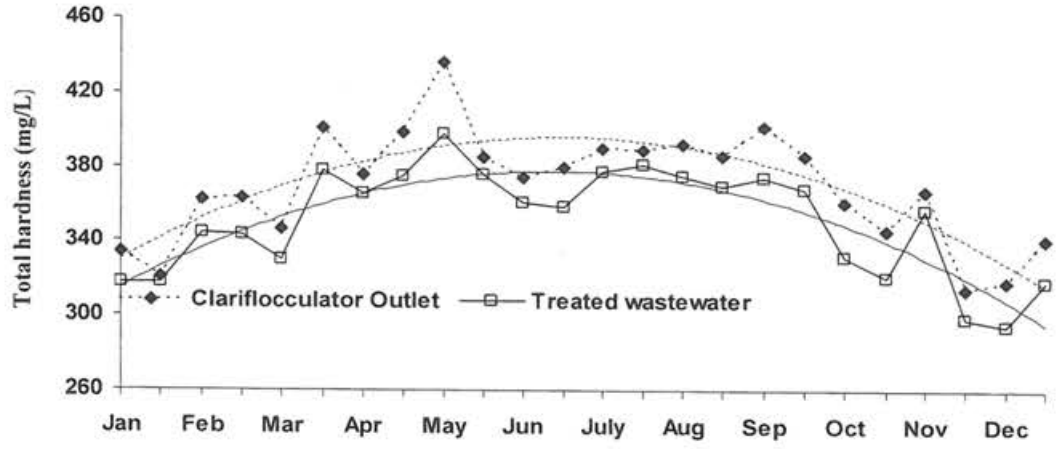



**Figure 4.5.13 Seasonal variations in total hardness in the clariflocculator outlet and treated wastewater samples**

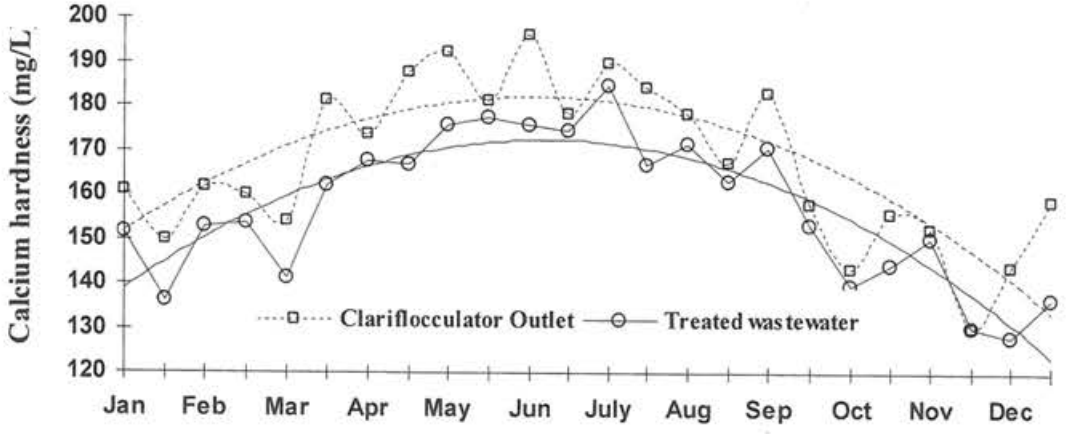



**Figure 4.5.14 Seasonal variations in calcium hardness in the clariflocculator outlet and treated wastewater samples**

**Hardness removal by the physio-chemical treatment:** Physio-chemical treatment is found very effective in removing the hardness. By the coagulation and flocculation mechanisms, total hardness was removed to an extent of about 50%. Removal of hardness by filtration was as low as 2.5%. The removal of calcium and magnesium hardness removed by the clariflocculator was about 53%, while removal by the filtration mechanism was about 52%. The mean values of total hardness, calcium hardness and magnesium hardness removed by the clariflocculator and sand filter mechanisms for each year of the study period is shown in the table 4.5.16.

**Hardness load removal:** The load of total hardness, calcium hardness and magnesium hardness removed by the coagulation cum flocculation and filtration mechanisms is given in the table 4.5.17. Highest removal was noticed in the year 2004. In the subsequent years the removal by the physio-chemical treatment reduced significantly. The physio-chemical treatment removed hardness by about 53%. About 4537 MT of total hardness load comprising of 2043 MT of calcium hardness load and 2494 MT of magnesium hardness load that could not be removed by the treatment, is disposed to the river. The figures 4.5.15 and 4.5.16 depict the hardness load before and after treatment. After the year 2004, there was a significant reduction of hardness load in the equalized effluent and subsequently there was reduction in the treated wastewater also. Total hardness load in the treated effluent came down to 792 MT during the year 2005 and 743 MT in the year 2006 compared to 2004 (1126 MT). As per 'The Environmental (Protection) Act, 1986' no norms are set for hardness for disposal of the wastewater.

Chemical precipitation is a conventional method to remove hardness from wastewater. The chemicals normally used for the purpose are calcium hydroxide and soda ash. Calcium hydroxide is used to remove the chemicals that contribute carbonate hardness, while soda ash is used to remove the chemicals that contribute non-carbonate hardness. Since the treatment facility used only calcium hydroxide the chemicals contributing the carbonate hardness is likely to be removed.

| | Year | Removal by Coagulation and flocculation | | Removal by Filtration | | Total removal | |
|---|---|---|---|---|---|---|---|
| | | Reduction (mg/L) | % | Reduction (mg/L) | % | Reduction (mg/L) | % |
| Total Hardness | 2002 | 361.99 | 50.66 | 17.26 | 2.42 | 379.25 | 53.07 |
| | 2003 | 363.04 | 50.26 | 19.79 | 2.74 | 382.83 | 52.99 |
| | 2004 | 352.22 | 47.46 | 22.77 | 3.07 | 374.98 | 50.53 |
| | 2005 | 390.62 | 52.14 | 24.87 | 3.32 | 415.49 | 55.46 |
| | 2006 | 399.88 | 50.80 | 6.85 | 0.87 | 406.74 | 51.67 |
| | **Mean** | **373.55** | **50.26** | **18.31** | **2.48** | **391.86** | **52.75** |
| Calcium hardness | 2002 | 164.09 | 50.96 | 6.41 | 1.99 | 170.50 | 52.95 |
| | 2003 | 175.03 | 53.29 | 9.14 | 2.78 | 184.17 | 56.08 |
| | 2004 | 177.34 | 52.96 | 8.36 | 2.50 | 185.70 | 55.46 |
| | 2005 | 159.99 | 47.29 | 14.50 | 4.29 | 174.49 | 51.58 |
| | 2006 | 162.46 | 46.00 | 13.09 | 3.71 | 175.55 | 49.71 |
| | **Mean** | **167.78** | **50.10** | **10.30** | **3.05** | **178.08** | **53.16** |
| Magnesium hardness | 2002 | 197.90 | 50.41 | 10.85 | 2.76 | 208.75 | 53.18 |
| | 2003 | 188.01 | 47.72 | 10.65 | 2.70 | 198.67 | 50.43 |
| | 2004 | 174.87 | 42.94 | 14.41 | 3.54 | 189.28 | 46.48 |
| | 2005 | 230.63 | 56.14 | 10.36 | 2.52 | 240.99 | 58.66 |
| | 2006 | 237.42 | 54.70 | -6.24 | -1.44 | 231.18 | 53.26 |
| | **Mean** | **205.77** | **50.38** | **8.01** | **2.02** | **213.77** | **52.40** |

**Table 4.5.16 Reduction of total, calcium and magnesium hardness**

| Year | Calcium hardness load (MT) | | | Magnesium hardness load (MT) | | | Total hardness load (MT) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Clariflocc-ulator | Filtration | Total | Clariflocc-ulator | Filtration | Total | Clariflocc-ulator | Filtration | Total |
| 2002 | 465 | 18 | 483 | 561 | 31 | 592 | 1026 | 49 | 1075 |
| 2003 | 477 | 25 | 502 | 513 | 29 | 542 | 990 | 54 | 1044 |
| 2004 | 544 | 26 | 570 | 536 | 44 | 580 | 1080 | 70 | 1150 |
| 2005 | 380 | 34 | 414 | 548 | 25 | 573 | 928 | 59 | 987 |
| 2006 | 317 | 26 | 343 | 464 | -12 | 452 | 781 | 13 | 794 |
| **Total** | **2183** | **129** | **2312** | **2622** | **116** | **2738** | **4805** | **245** | **5050** |

**Table 4.5.17 Reduction of total, calcium and magnesium hardness load by the physio-chemical treatment**

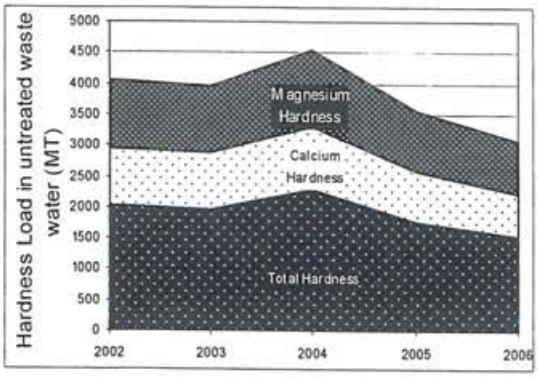



**Figure 4.5.15 Hardness load before the physio-chemical treatment of the textile effluent**

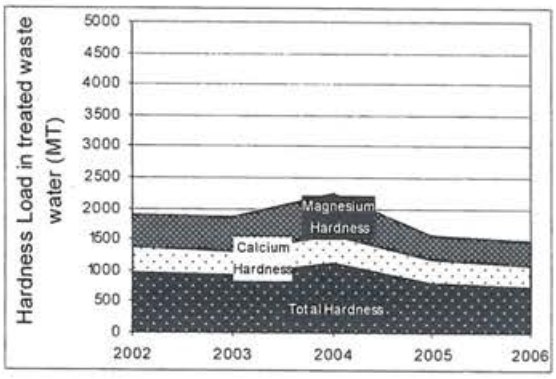



**Figure 4.5.16 Hardness load after the physio-chemical treatment of textile effluent**

### 4.5.9 Alkalinity

The total alkalinity varied from 283.0 to 709.9 mg/L found in the clariflocculator outlet and from 292.1 to 653.2 mg/L found in the final outlet. The M'alkalinity of the clariflocculator outlet ranged from 248.0 to 649.1 mg/L while in the outlet after final treatment it ranged from 253.8 to 586.7 mg/L. The highest level of P'alkalinity measured was 121.6 mg/L in the clariflocculator outlet and 138.2 mg/L in the final outlet. There was only one sample in the year 2005 which lacked P'alkalinity in both of sampling locations of clariflocculator outlet and final outlet. The alkalinity values in the clariflocculator outlet and final outlet are shown in the table 4.5.18.

| Year | Clariflocculator Outlet | | | Treated wastewater | | |
|---|---|---|---|---|---|---|
| | P'alkalinity (mg/L) | M'alkalinity (mg/L) | Total alkalinity (mg/L) | P'alkalinity (mg/L | M'alkalinity (mg/L | Total alkalinity (mg/L |
| 2002 | 54.1 ± 14.4 | 405.4 ± 44.5 | 459.5 ± 45.2 | 53.4 ± 14.7 | 385.9 ± 46.2 | 439.3 ± 48.8 |
| 2003 | 66.4 ± 24.2 | 428.7 ± 85.4 | 491.3 ± 96.1 | 63.9 ± 26.8 | 405.0 ± 79.1 | 465.0 ± 94.3 |
| 2004 | 61.0 ± 19.1 | 454.7 ± 69.7 | 511.5 ± 71.0 | 54.5 ± 16.2 | 439.7 ± 60.4 | 490.9 ± 62.5 |
| 2005 | 57.3 ± 23.9 | 440.6 ± 82.7 | 497.9 ± 88.0 | 52.6 ± 22.7 | 413.3 ± 75.0 | 465.9 ± 80.6 |
| 2006 | 54.2 ± 12.8 | 437.8 ± 55.7 | 492.7 ± 56.4 | 49.8 ± 10.1 | 419.3 ± 42.0 | 470.0 ± 43.1 |

**Table 4.5.18 Alkalinity concentration in the clariflocculator outlet and final treated effluent**

**Alkalinity removal by the physio-chemical treatment:** The efficiency of physio-chemical treatment in removing the total alkalinity and M'alkalinity for each of year is shown in the table 4.5.19. Chemical precipitation was found considerably more effective in removing the total alkalinity than filtration. Both methods in total removed about 48% of hardness. Similarly the M'alkalinity removal was also high in the clariflocculator than by the filtration. The total removal of M'alkalinity by both the mechanisms was about 52.0%. The coagulation cum flocculation mechanisms in the clariflocculator removes nearly half of the total alkalinity and M'alkalinity. Only the remaining portion flows out in the treated wastewater to the river.

After the physio-chemical treatment an increase in P'alkalinity was noticed. In the clariflocculator outlet the P'alkalinity was high by about 77% than the equalized effluent. However, the filtration reduces the P'alkalinity to the range of 0.67 to 6.51 mg/L.

| Year | M'alkalinity (mg/L) | | | Total alkalinity (mg/L) | | |
|---|---|---|---|---|---|---|
| | Clariflocculator | Sand filter | Total | Clariflocculator | Sand filter | Total |
| 2002 | 403.33 | 19.53 | 422.87 | 392.56 | 20.20 | 412.76 |
| 2003 | 407.37 | 23.75 | 431.11 | 381.67 | 26.26 | 407.92 |
| 2004 | 424.57 | 15.00 | 439.56 | 412.83 | 20.55 | 433.39 |
| 2005 | 435.91 | 27.34 | 463.25 | 400.45 | 32.01 | 432.46 |
| 2006 | 458.85 | 18.51 | 477.35 | 424.24 | 22.70 | 446.94 |

**Table 4.5.19 Concentration of total and M'alkalinity removal by the physio-chemical treatment**

**Alkalinity load removal:** The coagulation cum flocculation process removed 5199 MT of the total alkalinity load while filtration removed 312 MT through out the study period. The M'alkalinity load removed by the coagulation and flocculation process was 5487 MT while by the filtration the removal was 267 MT. However the alkalinity load that could not be removed by the physio-chemical treatment was about 6043 MT (52.7%) of total alkalinity load and 5347 MT (48%) of M'alkalinity load. Total alkalinity and

M'alkalinity load disposed to the river along the treated wastewater has decreased during 2005 and 2006. The disposal of total alkalinity load was lesser about 302.1 MT in 2005 and 456.5 MT in 2006 compared to 2004. Similarly the disposal of M'alkalinity load was lesser about 247.9 MT in 2005 and 416 MT in 2006 compared to 2004. The table 4.5.20 shows the total alkalinity and M'alkalinity load removed by the physio-chemical treatment system.

| Year | M'alkalinity (MT) | | | Total alkalinity (MT) | | |
|---|---|---|---|---|---|---|
| | Clariflocculator | Sand filter | Total | Clariflocculator | Sand filter | Total |
| 2002 | 1143.00 | 55.35 | 1198.35 | 1112.47 | 57.24 | 1169.71 |
| 2003 | 1110.64 | 64.74 | 1175.39 | 1040.58 | 71.58 | 1112.16 |
| 2004 | 1302.19 | 45.99 | 1348.18 | 1266.20 | 63.04 | 1329.24 |
| 2005 | 1035.32 | 64.94 | 1100.26 | 951.10 | 76.03 | 1027.13 |
| 2006 | 896.04 | 36.14 | 932.18 | 828.46 | 44.33 | 872.79 |
| **Sum** | **5487.19** | **267.17** | **5754.36** | **5198.82** | **312.22** | **5511.04** |

**Table 4.5.20 Total and M'alkalinity load removed by the clariflocculator and filtration mechanisms**

Contrary to total alkalinity and M'alkalinity, by the physio-chemical treatment the P'alkalinity load increased. The physio-chemical treatment added in total about 242 MT of P'alkalinity load through out the study period. Thus the P'alkalinity load disposed to the river by the treatment facility was 715.0 MT. During the year 2002 and 2003 the disposal of P'alkalinity load was 151.3 and 174.2 MT respectively. Then the discharge of P'alkalinity load decreased annually.

Seasonal variation noticed in the case of several dissolved constituents of textile wastewater could not be found in alkalinity. Load of total alkalinity and M'alkalinity were removed by the physio-chemical treatment. In contrast after the treatment P'alkalinity increased. Addition of hydrated lime to raise the alkalinity necessary to enhance coagulation process increases the pH and subsequently P'alkalinity. As per 'The Environmental Protection Rules (1986) there is no norm fixed for the alkalinity of the textile wastewater.

### 4.5.10 Oil and grease

Oils and grease contents in the clariflocculator outlet and treated wastewater is shown in the table 4.5.21. Though the CETP was not equipped with specific mechanism to remove oil and grease content, the oil and grease content was lower after the coagulation cum flocculation process. About an average of 4.8 mg/L oil and grease content was found in the treated effluent disposed to the river. The norm fixed for oil and grease content of the treated effluent to be disposed into the inland surface water bodies is to be less than 10 mg/L. The highest value noted in the treated effluent was 9.4 mg/L during (July) 2005.

The total oil and grease load found in the treated effluent was 11.8 and 13.1 MT in the year 2002 and 2003 respectively. The load disposed in 2004 was 15.1 MT; while during 2005 and 2006 the oil and grease load was only 13.1 and 9.3 MT respectively. The treated wastewater met the standard in all samples collected during the study period although the CETP did not employ specific treatments to remove these pollutants from the raw effluent.

| Year | Clariflocculator outlet (mg/L) | Final outlet (mg/L) |
|---|---|---|
| 2002 | 4.84 ± 1.40 | 4.18 ± 1.19 |
| 2003 | 5.43 ± 1.41 | 4.80 ± 1.55 |
| 2004 | 4.77 ± 1.35 | 4.93 ± 1.13 |
| 2005 | 5.69 ± 1.97 | 5.53 ± 2.24 |
| 2006 | 5.32 ± 1.65 | 4.77 ± 1.10 |

**Table 4.5.21 Oil and grease contents measured in the clariflocculator outlet and final treated effluent**

### 4.5.11 Phenolic compounds

The phenolic compounds in traces were found in the clariflocculator outlet and treated wastewater. In 59 samples from the clariflocculator outlet phenolics were seen BDL. In the final outlet only in 48 samples phenolic compounds were detected and remaining 72 samples had BDL. The phenolic compounds (Table 4.5.22) ranged from 0.07 mg/L to 0.16 mg/L in the clariflocculator outlet and 0.05 mg/L to 0.11 mg/L in the final treated

wastewater. The norm fixed for phenolic compounds is 1 mg/L. The treated textile wastewater met the standard in all the samples.

The phenol load found in the final outlet was less compared with the equalized effluent. The total phenol load removed by the physio-chemical treatment through out the study period was 1202 Kg. The coagulation cum flocculation mechanism is known to remove the phenolic compounds from the wastewater. Ozbelge *et al.* (2001) have reported upto 94% removal of phenols from rubber textile wastewater using lime and coagulants like iron and aluminum through coagulation and flocculation mechanisms.

| Year | Phenols concentration (mg/L) | | Phenols load (Kg) | |
|---|---|---|---|---|
| | Clariflocculator Outlet | Final outlet | Removal | Discharged |
| 2002 | 0.16 | 0.11 | 211.4 | 315.3 |
| 2003 | 0.07 | 0.05 | 255.1 | 139.3 |
| 2004 | 0.06 | 0.03 | 92.01 | 222.36 |
| 2005 | 0.09 | 0.05 | 327.1 | 112.3 |
| 2006 | 0.09 | 0.07 | 186.5 | 138.7 |

**Table 4.5.22 Phenolic compounds concentrations and load in the treated textile effluent**

### 4.5.12 Heavy metals

The total chromium content after the physio-chemical treatment in the clariflocculator outlet and final outlet fluctuated from 0.02 to 0.66 mg/L during the study period. 51 samples in the clariflocculator outlet and 59 samples from final outlet had heavy metals in the BDL range. The copper content of the both the sampling locations varied from 0.021 to 0.640 mg/L. 57 samples in the clariflocculator outlet and 58 samples in final outlet had copper below BDL. Zinc content of the wastewater varied from 0.017 to 0.721 mg/L. In the case of Zn 58 samples in the clariflocculator outlet and 60 samples in the final outlet were BDL. Nickel content ranged from 0.110 to 0.720 mg/L. 68 samples were BDL for Ni in the clariflocculator outlet while 70 samples in the final outlet were BDL. The cadmium content of the textile wastewater ranged from 0.011 to 0.24 mg/L. 93 samples in the clariflocculator outlet and 95 samples in the final had Cd BDL. The number of samples found BDL in clariflocculator outlet and final outlet exceeded the

number of samples found in the raw effluent and equalized effluent. Among the heavy metals cadmium was found lowest in both the sampling locations. It is found that after the physio-chemical treatment more than half of the samples were BDL for heavy metals. The levels of each heavy metal with the corresponding estimates of the loads during 2002 to 2006 is tabulated in 4.5.23. The table 4.5.24 showed the removal of heavy metals in terms of concentration and load by the physio-chemical treatment.

Even though the heavy metal concentrations in the wastewater were only in traces, their concentrations get reduced by the physio-chemical treatment. This can be attributed to the soluble heavy metals present in the wastewater getting converted to insoluble metal hydroxides by the higher pH caused by the addition of hydrated lime and thereby making them settled in the clarifier. All most all heavy metals start settling in alkaline pH. However, each metal have specific pH at which it will precipitate highest. The specific pH for zinc precipitation is 10.1, cadmium 11.0, copper 8.1, chromium 7.5 and nickel 10.8 (Metcalf and Eddy, 1995).

| Year | Clariflocculator Outlet | | | | | Treated wastewater | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cr | Cu | Zn | Ni | Cd | Cr | Cu | Zn | Ni | Cd |
| | Concentration (mg/L) | | | | | | | | | |
| 2002 | 0.184 | 0.085 | 0.161 | 0.096 | 0.021 | 0.144 | 0.072 | 0.152 | 0.085 | 0.020 |
| 2003 | 0.105 | 0.048 | 0.178 | 0.087 | 0.024 | 0.104 | 0.047 | 0.146 | 0.082 | 0.018 |
| 2004 | 0.145 | 0.077 | 0.162 | 0.105 | 0.029 | 0.136 | 0.048 | 0.166 | 0.079 | 0.021 |
| 2005 | 0.201 | 0.045 | 0.151 | 0.121 | 0.019 | 0.214 | 0.051 | 0.135 | 0.105 | 0.015 |
| 2006 | 0.164 | 0.045 | 0.187 | 0.096 | 0.025 | 0.182 | 0.029 | 0.172 | 0.088 | 0.017 |
| **Norm for heavy metals of the wastewater to be disposed into the inland surface water (mg/L).** | | | | | | **2.0** | **3.0** | **5.0** | **3.0** | **2.0** |
| | Load (Kg) | | | | | | | | | |
| 2002 | 521.43 | 240.64 | 456.25 | 272.05 | 59.51 | 408.08 | 204.04 | 430.75 | 240.88 | 56.68 |
| 2003 | 286.27 | 130.26 | 485.30 | 237.20 | 65.43 | 283.55 | 127.23 | 398.05 | 223.56 | 49.08 |
| 2004 | 444.73 | 237.23 | 496.87 | 322.05 | 88.95 | 417.13 | 147.01 | 509.14 | 242.30 | 64.41 |
| 2005 | 477.39 | 106.48 | 358.64 | 287.39 | 45.13 | 508.27 | 120.54 | 320.64 | 249.39 | 35.63 |
| 2006 | 320.26 | 87.25 | 365.17 | 187.47 | 48.82 | 355.41 | 55.82 | 335.88 | 171.85 | 33.20 |

**Table 4.5.23 Heavy metals levels and load in the clariflocculator outlet and final treated effluent**

All the heavy metals in the effluent are within the norms fixed by the TNPCB. About 50% of heavy metals were removed by the physio-chemical treatment. The higher pH from the addition of hydrated lime favored the precipitation of the heavy metals. The coagulation and flocculation mechanism using the hydrated lime is effective in removal of the heavy metals from the wastewater. Cecen and Gursoy (2000) reported removal of heavy metals from the leachate at high alkaline pH using the hydrated lime.

| Year | Heavy metals concentration removal and their percentage of removal | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Total Chromium | | Copper | | Zinc | | Nickel | | Cadmium | |
| | (mg/L) | (%) | (mg/L) | (%) | (mg/L) | (%) | (mg/L) | (%) | (mg/L) | (%) |
| 2002 | 0.224 | 60.87 | 0.111 | 60.76 | 0.159 | 51.13 | 0.08 | 48.48 | 0.024 | 54.55 |
| 2003 | 0.074 | 41.57 | 0.079 | 62.83 | 0.101 | 40.89 | 0.072 | 46.75 | 0.016 | 47.06 |
| 2004 | 0.075 | 35.55 | 0.100 | 67.54 | 0.145 | 46.62 | 0.109 | 57.98 | 0.013 | 38.24 |
| 2005 | 0.165 | 43.54 | 0.035 | 40.52 | 0.152 | 52.96 | 0.079 | 42.93 | 0.013 | 46.43 |
| 2006 | 0.073 | 28.63 | 0.073 | 71.95 | 0.092 | 34.85 | 0.045 | 33.83 | 0.029 | 63.04 |
| Heavy metals load removal | | | | | | | | | | |
| | (Kg) | | (Kg) | | (Kg) | | (Kg) | | (Kg) | |
| 2002 | 634.79 | | 315.9 | | 450.59 | | 226.71 | | 68.01 | |
| 2003 | 201.75 | | 215.08 | | 275.37 | | 196.3 | | 43.62 | |
| 2004 | 230.03 | | 305.94 | | 444.73 | | 334.31 | | 39.87 | |
| 2005 | 391.89 | | 82.11 | | 361.01 | | 187.63 | | 30.88 | |
| 2006 | 142.55 | | 143.21 | | 179.66 | | 87.88 | | 56.63 | |

**Table 4.5.24 Concentration and load of heavy metals removed by the physio-chemical treatment**

## 4.6 Quantification of treated wastewater discharge

The treated wastewater discharge from the CETP is equal to that of the raw effluent. Since, there was no separate flow meter to measure the treated wastewater; the measurement of incoming was taken to further analysis. No water is lost during the physio-chemical treatment except the negligible evaporative loss. Therefore, for all practical reasons, the treated wastewater discharged from the treatment facility can be considered equal to the volume of received which is shown in the table 3.7.1 of chapter 3.

## 4.7 Quantity of sludge generation and characterisation

The sludge generated during the physio-chemical treatment of the textile wastewater is categorized as 'Hazardous Waste' as per the Hazardous Waste (Management and Handling) Rules, 1989 and the Amended Rules in January 2000 and May 2003. The waste is listed in the Schedule–1 of Hazardous Waste (Management and Handling) amended rules 2003 under the Process of 'Production or industrial use of synthetic dyes, dye intermediates and pigments' and the sub category of 'chemical sludge from wastewater treatment'.

The quantum of sludge generated from the treatment facility during the physio-chemical treatment is shown in the table 4.7.1. The treatment facility generated about 3057 MT of dry sludge every year. The peak generation was in 2004 (3374 MT). The ETPs or CETPs operating in Tiruppur face problems in handling and management of the so-called 'Hazardous Waste' lacking required area for storage. So far no landfill is developed in Tiruppur for proper disposal of the sludge. Currently the CETPs store the sludge in its own premises either in an open manner or in polythene bags. The plates 4.7.1 and 4.7.2 show the sludge generated in the CETP stored on the open ground.

| Year | Quantity (MT, Dwt) |
|---|---|
| From 1999 - 2001 | 10201 |
| 2002 | 3117 |
| 2003 | 2999 |
| 2004 | 3374 |
| 2005 | 2613 |
| 2006 | 2148 |
| **Total** | **24452** |

**Table 4.7.1. Quantum of sludge generation**

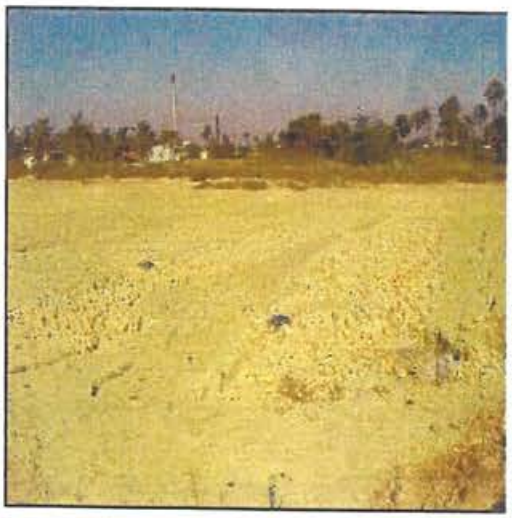


**Plate 4.7.1 Sludge pit where the sludge stored on open ground (view -1)**

**Plate 4.7.2 Sludge pit where the sludge stored on open ground (view -2)**

**Sludge Characterization:** The characteristics of the sludge collected during the study period from the CETP are shown in the table 4.7.2. The sludge was alkaline in nature and its pH ranged from 9.05 to 9.58. The pH range of more than 12 and less than 2 is considered as highly corrosive and the sludge from Tirupur is very lightly corrosive. The moisture content in the sludge varied from 6.29 to 9.34 %. The volatile solids were always less than the fixed solids in all the samples analyzed, which indicates that the sludge is predominantly consisting of inorganic materials. The solubility of the sludge is always less than 3.33 %. The heavy metals estimated in the sludge never exceeded the hazardous concentration.

Further, the toxicity characteristics leachate procedure (TCLP) test conducted for the sludge showed that heavy metals in leachate were below the regulatory limits. The table 4.7.3 shows results of TCLP analysis. The table also gives the limits prescribed by US-EPA for TCLP results. Among the 5 samples analysed chromium was not found in any of the samples, lead and nickel were not found in 2 samples and copper in 1 sample. Phenol was not found in 2 samples. The study by Palanivelu and Kumar (2001) also supports the above findings.

## 4.8. Pollutants load removal and disposal from all effluent treatment plants

The estimated pollution load for each of the parameters in the discharged treated wastewater and the load removed by the physio-chemical treatment is shown in the table 4.8.1. The physio-chemical treatment was partially effective in removal of the load for the parameters such as TSS, BOD, COD, hardness, total alkalinity, M'alkalinity, oil and grease, phenols and the heavy metals. The treatment did not alter the TDS. The TDS load in the discharged wastewater was equal to the load found in untreated wastewater. The chloride and sulphate increased by the physio-chemical treatment when ferric chloride and ferrous sulphate was used for the treatment. The phenolphthalein alkalinity always increased after the treatment.

The enormous loads for each of the parameters such as TDS, chloride and sulphate in the discharged wastewater are problematic. The release of the wastewater with these loads altered the ecology of the river, which received the wastewater. The total heavy metals load present in the discharged wastewater computed for 2002 to 2006 varied from 9.5 to 13.8 MT. Such quantities of heavy metal being released to the natural system is alarming even though the individual metal concentrations in the wastewater were in traces.

| Parameter | 2002 | 2003 | 2004 | 2005 | 2006 | Hazardous Level (mg/Kg) |
|---|---|---|---|---|---|---|
| pH | 9.26 ± 0.03 | 9.58 ± 0.06 | 9.05 ± 0.05 | 9.39 ± 0.06 | 9.58 ± 0.04 | -- |
| Moisture Content (%) | 6.29 ± 0.17 | 8.11 ± 0.14 | 9.34 ± 0.35 | 6.44 ± 0.10 | 7.70 ± 0.13 | -- |
| Solubility (g/100 mL) | 1.83 ± 0.10 | 1.01 ± 0.09 | 2.03 ± 0.08 | 1.16 ± 0.05 | 3.33 ± 4.27 | -- |
| Volatile Solids (%) | 31.42 ± 1.05 | 24.22 ± 0.97 | 28.50 ± 0.99 | 32.43 ± 1.01 | 25.66 ± 1.15 | -- |
| Fixed Solids (%) | 68.58 ± 1.05 | 75.78 ± 0.97 | 71.50 ± 0.99 | 67.57 ± 1.01 | 74.34 ± 1.15 | -- |
| Cadmium (mg/KG) | 1.59 ± 0.09 | 0.89 ± 0.09 | 1.86 ± 0.08 | 1.17 ± 0.06 | 1.64 ± 0.07 | 50 |
| Copper (mg/KG) | 18.40 ± 0.79 | 32.35 ± 2.19 | 22.05 ± 1.14 | 43.96 ± 1.51 | 27.36 ± 1.89 | 5000 |
| Total Chromium (mg/KG) | 52.22 ± 2.61 | 30.25 ± 1.59 | 21.15 ± 1.55 | 33.60 ± 2.11 | 28.11 ± 1.76 | 5000 |
| Lead (mg/KG) | 17.61 ± 0.84 | 24.03 ± 1.77 | 14.23 ± 1.03 | 18.52 ± 0.61 | 22.54 ± 0.96 | 5000 |
| Zinc (mg/KG) | 66.84 ± 3.14 | 85.86 ± 2.57 | 54.58 ± 3.43 | 74.35 ± 3.63 | 66.85 ± 2.28 | 20000 |
| Nickel (mg/KG) | 13.78 ± 1.42 | 22.13 ± 1.86 | 11.52 ± 0.95 | 18.63 ± 1.80 | 24.70 ± 3.17 | 5000 |
| Mercury (mg/KG) | 4.81 ± 0.34 | 3.05 ± 0.14 | 1.61 ± 0.26 | 3.51 ± 0.15 | 2.99 ± 0.11 | 50 |

**Table 4.7.2 Characteristics of textile CETP sludge**

| Parameters | 2002 | 2003 | 2004 | 2005 | 2006 | Regulatory level (mg/L) |
|---|---|---|---|---|---|---|
| Cadmium (mg/l) | 0.037 ± 0.006 | 0.080 ± 0.010 | 0.057 ± 0.006 | 0.127 ± 0.015 | 0.050 ± 0.010 | 1.0 |
| Copper (mg/l) | 0.026 ± 0.002 | 0.021 ± 0.003 | 0.037 ± 0.003 | 0.030 ± 0.003 | BDL | -- |
| Total Chromium (mg/l) | BDL | BDL | BDL | BDL | BDL | 5.0 |
| Lead (mg/l) | 0.015 ± 0.005 | BDL | BDL | 0.007 ± 0.003 | 0.028 ± 0.003 | 5.0 |
| Zinc (mg/l) | 0.080 ± 0.010 | 0.053 ± 0.006 | 0.113 ± 0.015 | 0.107 ± 0.015 | 0.160 ± 0.010 | -- |
| Nickel (mg/l) | 0.013 ± 0.006 | BDL | BDL | 0.037 ± 0.006 | 0.034 ± 0.002 | -- |
| Mercury (mg/l) | 0.043 ± 0.002 | 0.030 ± 0.002 | 0.021 ± 0.004 | 0.015 ± 0.001 | 0.036 ± 0.002 | 0.2 |
| Phenol (mg/L) | 1.333 ± 0.289 | 2.333 ± 0.289 | BDL | BDL | 1.167 ± .289 | 200 |

**Table 4.7.3 TCLP analysis of textile CETP sludge**

| Parameter | Year wise pollution load removal by the physio-chemical treatment (MT). | | | | | Year wise pollution load discharged in treated water (MT). | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 2002 | 2003 | 2004 | 2005 | 2006 | 2002 | 2003 | 2004 | 2005 | 2006 |
| Total Suspended Solids | 6742 | 6792 | 8040 | 6693 | 5001 | 2053 | 2019 | 2370 | 2013 | 1586 |
| Total Dissolved Solids | 1902 | 5285 | 1873 | 3114 | 2011 | 179930 | 176750 | 208445 | 174516 | 143863 |
| Biochemical Oxygen Demand | 2295 | 2233 | 2689 | 2356 | 1903 | 2014 | 2026 | 2329 | 1594 | 1428 |
| Chemical Oxygen Demand | 10098 | 9820 | 11138 | 9235 | 7179 | 5921 | 5745 | 6475 | 4509 | 4512 |
| Chloride | 649 | -283 | -156 | -1790 | 3009 | 100005 | 98697 | 115022 | 96668 | 74421 |
| Sulphate | -3587 | -3528 | -4259 | -1819 | -2700 | 18457 | 17780 | 20794 | 14739 | 13975 |
| Total Hardness | 9502 | 9258 | 11259 | 7924 | 7430 | 9502 | 9258 | 11259 | 7924 | 7430 |
| Calcium Hardness | 4832 | 5021 | 5696 | 4144 | 3428 | 4294 | 3933 | 4574 | 3890 | 3468 |
| Magnesium Hardness | 5916 | 5416 | 5806 | 5724 | 4515 | 5209 | 5325 | 6684 | 4034 | 3962 |
| Total Alkalinity | 11697 | 11122 | 13292 | 10271 | 8728 | 12448 | 12679 | 15058 | 11065 | 9178 |
| Phenolphthalein Alkalinity | -286 | -673 | -145 | -731 | -582 | 1513 | 1742 | 1672 | 1250 | 973 |
| Methyl Orange Alkalinity | 11984 | 11754 | 13482 | 11003 | 9322 | 10935 | 11041 | 13485 | 9816 | 8188 |
| Oil and Grease | 78.68 | 62.29 | 28.04 | 14.23 | 23.71 | 118.34 | 130.86 | 151.15 | 131.33 | 93.06 |
| Phenols | 2.11 | 2.55 | -3.95 | 3.27 | 1.86 | 3.15 | 1.39 | 7.09 | 1.12 | 1.39 |
| Total Chromium | 6.35 | 2.02 | 2.30 | 3.92 | 1.43 | 4.08 | 2.84 | 4.17 | 5.08 | 3.55 |
| Copper | 3.16 | 2.15 | 3.06 | 0.82 | 1.43 | 2.04 | 1.27 | 1.47 | 1.21 | 0.56 |
| Zinc | 4.51 | 2.75 | 4.45 | 3.61 | 1.80 | 4.31 | 3.98 | 5.09 | 3.21 | 3.36 |
| Nickel | 2.27 | 1.96 | 3.34 | 1.88 | 0.88 | 2.41 | 2.24 | 2.42 | 2.49 | 1.72 |
| Cadmium | 0.68 | 0.44 | 0.40 | 0.31 | 0.57 | 0.57 | 0.49 | 0.64 | 0.36 | 0.33 |

**Table 4.8.1 Pollutants load removal and disposal to the river from all the treatment facilities of Tiruppur**

### 4.9 Volume of treated effluent discharge and sludge generation from Tiruppur

The estimated wastewater discharge and quantity of sludge generated from the effluent treatment facilities in Tiruppur for each of the year is shown in the table 4.9.1. The wastewater discharge and quantity of the sludge generation in the year 2006 could be more due to installation of the reverse osmosis plant in some of the units to recover and recycle the wastewater. The accumulated quantity of the sludge arising out of the physio-chemical treatment is estimated to be 244520 MT upto 2006.

| Year | Wastewater discharge (Million Litres) | Sludge generation (MT) |
|---|---|---|
| 2002 | 28339 | 31170 |
| 2003 | 27264 | 29990 |
| 2004 | 30671 | 33740 |
| 2005 | 23751 | 26130 |
| 2006 | 19528 | 21480 |

**Table 4.9.1 Volume of the treated wastewater disposal and quantity of sludge generation from all effluent treatment facilities in Tiruppur**

### 4.10 Summary

The physio-chemical treatment employed to treat the textile effluents generated in Tiruppur increased the pH in the treated effluent. About 40 samples of treated wastewater collected during the study period exceeded the pollution control norms specified for pH. TSS was removed to an extent of 73%. Most of the samples fell within the levels specified for TSS. The reduction in BOD and COD was 54% and 63% respectively. BOD in the treated effluent never met the norm while COD values were within the norm in 88% of the samples. The TDS and chloride contents of the wastewater were not controlled by the physio-chemical treatment. The level of TDS and chloride contents in the treated wastewater was manifold than the norms. Sulphate content increased after the physio-chemical treatment due to ferrous sulphate used as the coagulant. About half of hardness and alkalinity were removed from the wastewater. Traces of phenolics, heavy metals and oil and grease contents were found in the treated effluent. The physio-chemical treatment facilities employed in Tiruppur generated about 142510 MT of sludge during the total study period. The sludge is stored inside the treatment facilities either on the open ground or in polythene bags without any safety measures. Enormous volume of wastewater with massive loadings of pollutants is disposed to the river.

# 5. ANAEROBIC TREATMENT OF TEXTILE WASTEWATER

## 5.1 Introduction

From the previous chapter it is apparent that the physio-chemical treatment employed in the textile effluent treatment generates enormous volume of sludge. The handling, storage and disposal of the sludge (a hazardous waste as per the HW (M & H) Rules, 1989) in a scientific and ecologically benign manner is a major challenge faced by the industries. The cost of disposal of the sludge increases the financial burdens to industry. So far no properly designed common disposal site is operating in Tiruppur, although a location was identified way back in 2002, to dispose the sludge generated for a decade. Further, the physio-chemical treatment employed in Tirupur is incapable of controlling several parameters. The best way to avoid these ills is finding an alternative technology replacing the current physio-chemical treatment technology which would be generating less sludge, have low operating cost and other operating benefits. Biological systems of treatment for the textile wastewater are widely advocated by various researchers. It has many promising merits over the conventional one. It is claimed that it requires less chemicals and energy, generates less of biodegradable sludge, reduces operating cost and is more environment friendly.

## 5.2 Objective of the study

Various researchers had examined the methods of treatment of textile wastewater and shown interest for an alternative technology. Robinson *et al.* (2001) reviewed the methods of treatment of textile effluent and opined that although physio-chemical method of treatment removes colour and various parameters, generates sludge, the disposal of which is an issue, and suggested alternatives that remove the dyes effectively. Biological systems for textile wastewater treatment are extensively reported and are in operation in many places. Willetts and Ashbolt (2000) assumed that aerobic treatment of textile dyes has poor degradation ability than anaerobic system in splitting the dye molecule resulting in decolouration. In the aerobic system, removal of dyes is assisted by physical adsorption on biomass rather than splitting the dye biochemically. In textile wastewater management the anaerobic system has advantages over the aerobic systems like absence

of an energy-intensive oxygen transfer, low generation of sludge, production of biogas, and space saving (Gavrilescu, 2002). Delee *et al.* (1998) while reporting that the reductive conditions in anaerobic treatment lead to decolourisation of the dye stuffs; suggest anaerobic systems as the right option for the high strength wastewater from textile wet processings such as desizing and scouring. Haandel and Lettinga (1994) reported the operating benefits of anaerobic system compared to aerobic system as briefed in the table 5.2.1. By the anaerobic treatment, the biodegradable organic matters can be converted into valuable methane gas, besides reducing sulphate and heavy metals, removing nitrates and breaking down toxic pollutants to harmless products.

| Parameter | Aerobic | Anaerobic |
|---|---|---|
| Energy required (W/kg COD/d) | 20-30 | 35 |
| Sludge production (kg VSS/ kg COD) | 0.2-0.3 | 0.05-0.15 |
| Nature of excess sludge | Unstable | Stable |

**Table: 5.2.1 Operating benefits of aerobic and anaerobic systems of effluent treatment**

Inspite of so many researchers suggesting anaerobic system for effective treatment of textile wastewater, so far no specific microbe or enzyme is known to be identified to carryout the decolourisation of textile wastewater which contains different types of dye molecules. Therefore, it becomes obligatory to choose an anaerobic granular sludge technology that makes use of a variety of highly dense active microbes. Accordingly, the aims of the study were as follows.

1. Develop a Hybrid Upward Anaerobic Sludge Blanket (HUASB) reactor with polyurethane foam cubes as the media for attached growth of the anaerobic consortium.
2. Study the start-up of the HUASB reactor using real textile wastewater.
3. Conduct treatability studies of textile wastewater using the HUASB reactor.
4. Compare the anaerobic treatment of textile wastewater with existing physio-chemical treatment system technically and economically.

## 5.3 The UASB system

The Upward Anaerobic Sludge Blanket (UASB) technology was developed by Dr. Gatze Lettinga and his colleagues in late 1970s at Wageningen University, The Netherlands, while investigating the anaerobic filter concept. Subsequently a pilot UASB reactor was developed at a beet sugar refinery unit in The Netherlands. Thereafter a large number of full-scale plants were installed throughout The Netherlands at sugar refineries, potato starch processing plants and other food industries as well as paper recycle plants. Initially the UASB technology was confined to treatment of high strength wastewater and digestion of sludge. Recently attempts are made to apply this novel method to low strength wastewater like textile wastewater.

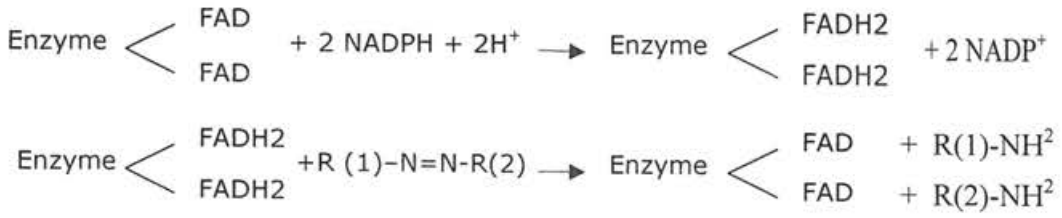
### 5.3.1 The mechanism of azo dye reduction in anaerobic system

Azo dyes are the largest and most versatile class of dyes and more than half of the annual production of dyes belongs to this group. The azo dyes are characterized with the azo bond (-N=N-). More than 2000 different azo dyes are being used in textiles, leather, plastics, cosmetics and food (Stolz, 2001). The basic mechanism involved in the decolourisation of azo dyes in anaerobic system, by the anaerobic microflora, is the reduction of azo bond and subsequent destruction of chromophore yielding aromatic amines. Azo bond cleavage in the azo dye is catalyzed by azo reductase enzyme. Azo reduction reaction generally is considered as a specific reaction under aerobic conditions (Bin *et al.*, 2004; Chen *et al.*, 2004; Nakanishi *et al.*, 2001). There are specifically adapted aerobic microorganisms synthesizing the true azo reductase enzyme that cleave the azo bond under presence of molecular oxygen. However, azo reduction in anaerobic system is a non-specific reductive reaction mediated by redox mediators shuttling electrons from the bacteria to the azo dyes (Kudlichjm *et al.*, 1997; Rau and Stolz, 2003).

The anaerobic azo reduction mechanism is rather low specific process. The azo bond cleavage involves transfer of four electrons proceeding through two stages at the azo linkages. The azo reduction occurs via the enzymatically generated reduced flavins and the final step is the non-enzymatic steps where transfer of electrons takes place. This

process involves the generation of reduced flavins, either flavinmononucleotide (FMN) or Flavinadeninenucleotide (FAD), by the re-oxidation of reduced nicotinamide adenine dinucleotide (NADH) or Nicotinamide adenine dinucleotide phosphate (NADPH). Finally the reduced flavins transfer the electrons to the azo dye. The flavins are re-oxidized subsequently. Since the azo dyes are sole terminal electron acceptor better decolourisation is obtained.

The proposed mechanism of azo reduction by anaerobic reduction systems is as follows (Huang *et al.*, (1968) cited by Kremer (1989) cited by Carliell (1995).




Nevertheless, the exact location of azo reduction, whether intracellularly or extracellularly, is not fully understood. Stolz (2001) and Kudlich *et al.* (1999) stated that the intracellular azo reduction could not be possible for the sulphonated azo dyes because of the low membrane permeability. The current hypothesis proposes the reduction of azo bond by the extracellular or membrane bond enzymes (Stolz, 2001).

### 5.3.2 Anaerobic treatment of textile wastewater

The azo dyes in the textile wastewater, due to their recalcitrant nature, can not be biodegraded readily under conventional sewage treatment plants. Hence specialized systems, either specific enzyme or anaerobic system, is required to remove the dyes present in the wastewater.

Breaking down the azo bond is the major concern in removing the colour. Several microorganisms are able to cleave the azo bond under the anaerobic conditions to yield

the aromatic amines as products. Most of amines are suspected carcinogens and are mineralized under aerobic microorganisms. Many enzymes are isolated from bacteria that are capable of decolourisation. Chen *et al.* (2002) characterised the azo reductase enzyme separated from the skin bacterium *Staphylococcus aureus* and reported colour reduction of the azo dyes *Methyl red, Orange II, Amaranth* and *Orange G* enzymatically. Moosvi *et al.* (2005) isolated a bacterium RVM 11.1 at a textile wastewater contaminated site in Vatva, Gujarat, India with ability to degrade 10 different dyestuffs and achieved 94% decolourisation of *Reactive Violet 5* within 37 hours under a pH range of 5 to 8.5 and temperature range of 25 to 40°C. Textile dyes such as *Drimaren Orange K-GL, Everzol Red RBN* and *Everdirect Supra Yellow PG* were completely decolourised at the concentration of 200 mg/L within 24 hours by mixed consortia of anaerobic microorganisms (Kapdan *et al.*, 2000).

Donlon *et al.* (1997) proved that the UASB reactor had detoxified the azo dyes, and the cleavage products 1, 4-phenylenediamine and 5-aminosalicylic acid was less toxic than parent dye *Mordant orange 1*. However this process requires a co-substrate such as glucose or a volatile fatty acid. A textile dye decolourising bacterium was isolated from activated sludge of textile printing effluent treatment plant by Xu *et al.* (2005). This bacterium was similar to the species *Shewanella baltica* and *Shewanella putrefaciens*, and was proposed to be called *Shewanella decolorationis* sp.

Apart from the enzyme and bacterial experiments on removal of the colour of azo dyes or textile wastewater, studies on fungal decolourisation are also reported. Lignolytic fungi are capable of decolourising azo dyes using the ligninases, manganese peroxidases and laccases. McMullan *et al.* (2001) reviewed the microbial decolourisation of textile wastewaters bearing the azo dyes and opined that the colour removal was achieved by the active role of white rot fungi. Ramsay and Nguyen (2002) reported that the textile dyes such as *Amarnath, Tropaeolin, O, Reative Blue 15, Congo Red and Reactive Black 5* were completely decolourised by *Trametes versicolor* where dye sorption to the biomass did not take place. Cripps *et al.* (1990) reported that nitrogen limited cultures of

*Phanerochaete chrysosporium* decolourised the dyes such as *Acid Orange 7 (Orange II) Acid Orange 6 (Tropaeolin O) or direct Red 28 (Congo Red).* Other fungal strains *Geotrichum candidum, Trametes versicolor, Bjerkandera adusta, Penicillium sp., Pleurotus ostreatus, Pycnoporus cinnabarinus and Pyricularia oryzae* are also capable of decolourising the azo dyes. The exo-enzymes from the fungal strains such as lignin peroxidases, manganese peroxidases and laccases degrade azo dyes, although they showed the different substrate specificity.

Anaerobic reactors for textile wastewater treatment were examined by several Researchers. Sen and Demirer (2003) used the anaerobic fluidized bed reactor with pumice as the support material for treatment of real cotton wastewater and found that with carbon supplement of 2 g/L, 82%, 94% and 59% removal of COD, BOD and colour at HRT of 24 hours and OLR of 3 kg COD/$m^3$/day. Simulated textile wastewater containing the reactive dye *Procion Red H-E7B* and other ingredients giving a mean COD 3480 mg /L was fed to an inclined tubular anaerobic digester and UASB. The outlet from both the systems was fed to the aerobic system and found the inclined anaerobic reactor to be more efficient than UASB (O'Neill, 1999). Liao *et al.* (2006) reported application of membrane bioreactors for anaerobic system where anaerobic membrane technology was used for treatment of wastewater from food processing, industrial and municipal solids. 56 - 99% removal of COD under membrane fluxes ranging from 10 to 40 L/$m^2$/h was reported. Isık and Sponza (2004) evaluated degradation of synthetic wastewater containing azo dyes such as *Reactive Black 5 and Congo Red (CR)* under batch anaerobic and sequential UASB/aerobic continuous stirred tank reactor system with glucose as the carbon source. The textile reactive dye *Remazol Black-5* containing N=N, -$SO_3$, S=O linkages were subjected to treatability study by anaerobic/aerobic sequential process using laboratory scale reactor by Sponza and Isik (2002) with different OLRs and HRTs. They report that the increased OLR from 5 kg COD/ $m^3$/day to 25 kg COD/$m^3$/day reduced COD removal from 56 to 27% and colour removal from 92 to 87%. Further the methane production was 50% and 76% at OLR of 2.49 and 14.8 kg COD/$m^3$/day. The optimum sludge age was 11 days.

While various researchers experimented textile wastewater treatment or azo dyes removal under different factors governing the anaerobic system. Yu *et al.* (2000) evaluated the thermophillic UASB reactor and mesophillic aerobic fluidized bed (AFB) reactor and achieved 75% COD removal from medium strength textile wastewater having 2700 mg/L of COD. Under anoxic and anaerobic conditions the transformation of the azo dye *Schwarz GRS* in batch reactor was investigated by Nikolova and Nenov (2004). They found that the dye transformation related with the utilization of carbon source and the degradation rates were much higher in the anaerobic conditions than anoxic conditions.

### 5.3.3 Operational conditions of UASB

#### a. Inoculation

The rapid start-up and establishment of biofilm of bacteria in the anaerobic reactor can be easily achieved by proper selection of inoculum. Hickey *et al.* (1991) reported that the inoculum would be the microbial consortium that posses ability to degrade organic pollutants and induce granulation; further they had shown that the inoculum collected from the same type of anaerobic reactors has no problems in start-up and establishment but regarding inoculum from different wastewater they were uncertain.

Various non-granular materials such as anaerobic digested sludge (Pol and Lettinga, 1986), waste activated sludge (Wu *et al.*, 1987) and cow manure (Wiegant and Man, 1986) have been successfully used as inoculum for the start-up of UASB reactors and to cultivate granular sludge. Digested sewage sludge is commonly used as the inoculum. Amount of inoculum required during the start-up of the reactor is a crucial factor. About 10% of inoculum is known to be stimulative during start-up phase and granuation process. Hajji *et al.* (2000) showed that encapsulated microbial consortium with the calcium alginate showed better performance at the inoculum concentration of 10%. However, Young and McCarty (1969) showed the inoculum could be increased to 30-50% when there was no toxic material.

**b. Organic loading rate (OLR)**

Various authors have reported treatment of low strength wastewater in UASB reactor. Manariotis and Grigoropoulos (2003) examined treatment of municipal wastewater with the OLR of 0.02 to 0.91 kg COD/$m^3$/day and achieved 72-80 % COD removal and 80-92% TSS removel. During the start-up period care should be taken about characteristics of the wastewater. Campos and Anderson (1992) postulated that dilution is required if COD exceeds 5000 mg/L in the wastewater. When granulation is observed during the start-up phase, influent feed rate can be increased stepwise. Sandhya and Swaminathan (2006) used the upflow anaerobic fixed bed reactor to treat textile wastewater and evaluated the efficiency of the system using operational parameters like Hydraulic Rentention Time (HRT) ranging from 9.6–23.76 hours and OLR ranging from 1.038–8.21 g COD/$m^3$/day.

**c. Hydraulic Retention Time (HRT)**

A favourable HRT helps growth of granules and maintain anaerobic system. Li and Xi (2004) opined that OLR and HRT are two important parameters influencing greatly the decolourisation of dye wastewater by facultative aerobic bacteria. Very long HRT is known to result in dispersed bacterial growth and is less favorable for granulation (Ghangrekar *et al.*, 2003). A short HRT, especially if combined with a high upflow velocity, could cause washout of dispersed bacterial matter and will not promote granulation (Alphennar *et al.*, 1993).

**d. Upflow Velocity**

Upflow velocity of the wastewater in the UASB reactors has great influence in maintenance of the granules in the reactor. Many researchers evaluated the optimum upflow velocity required for normal operation of the reactor. Ghangrekar *et al.* (2003) showed upflow velocities in the range of 0.25-0.8 m/h to be favorable for granule growth and accumulation. Viera and Garcia (1992) reported disintegration and washout of the granules at the higher upflow velocity. Low upflow velocity will lead to the development

of a hollow core within the granules that lead to the accumulation of biogas inside the granules resulting in floatation of the granule (Kosaric *et al.,* 1990). Shayegan *et al.* (2005) studied the effects of upward velocity and effects of COD concentrations on behaviour of sulphate reducing bacteria in the UASB reactor and found that in low-strength wastewaters (500 mg/L of COD) where COD to sulphate ratio was 2, an upward velocity in the range of 1.5–2.5 m/h could be appropriate.

**e. Packing Material**

In the UASB system maintenance of high solid retention is an important criteria to be attended to achieve higher performance of the reactor. Non- biodegradable packing media is used to provide more surface area for the anaerobes attachment to enhance high solid retention. The roughness of surface area, porosity and pore size affect the rate of colonization of the bacteria. Rough surface and large porosity of the media enhanced the COD removal efficiency due to higher growth of suspended biomass (Show and Tay, 1999). Presence of pores and crevices in the surface of the packing media provide adequate conditions for microbial attachment thereby protected from the shear forces. Various types of packing media have been used in UASB system such as PVC cut rings, corrugated plastic rings, Polyurethane foam (Hysman *et al.* 1985), rasching rings and berl saddles (Mosey 1978, Khagesan 1998).

### 5.3.4. Factors affecting anaerobic system

The operational parameters in the anaerobic system such as specific growth rate, decay rate, gas production, substrate utilization and start-up are susceptible to changing environmental factors like temperature, pH, nutrients, organic loading rate, presence of toxic substances and the nature of wastewater to be treated.

The microbial consortia involved in the anaerobic system are prone to varying degree of inhibition or stimulation to the substances or constituents of the wastewater or by the

metabolic intermediates generated. Hence, it is appropriate that an optimum concentration of the substances is to be maintained at the anaerobic reactor.

Temperature is a major environmental factor limiting anaerobic digestion. The temperature in tropical country like India favours anaerobic digestion of wastewater. The optimum range of temperature for the mesophilic organisms is 30-40°C (Hennzen and Harremoes, 1983). Eugenio *et al.* (2002) showed a strict anaerobe *Clostridium thiosulfatireducens* sps, a sulphur reducing bacterium grows at the optimum temperature of 37°C and pH of 7.4. The digestion rate decreases by decrease in temperature. pH is also an important critical factor for the anaerobic digestion. Sandberg and Ahring (1992) reported disintegration of granules beyond the 8.3 pH in anaerobic digestion of fish process wastewater. Miranda *et al.* (2005) maintained pH of the wastewater generated from pig and cattle slaughter house and meat packing plant between 6.8 to 7.3 to feed the UASB reactor.

Apart from the carbon source, anaerobic bacteria require nutrients like nitrogen, phosphorus, magnesium, sodium, manganese, calcium, and cobalt (Speece and McCarty, 1964). Nutrients play the crucial role in optimizing microbial activity in the anaerobic reactor. Jennet and Dennis (1975) had reported the net growth of the microorganisms being directly related with the available concentration of the elements such as carbon, nitrogen, phosphorus and sulphur. The carbon nitrogen ratio is a critical factor for the anaerobic system. Hills (1979) had reported the C:N ratio between 20 to 30:1 was necessary for biogas production. Somayaji (1994) investigated the requirement of C:N ratio for the maximum methanogenic activity and found that a C:N ratio of 16 to 19:1 is sufficient. Apart from the C:N ratio the phosphorus is an another important nutrient for the anaerobic bacteria. The optimum C:N:P ratio to optimize the biogas yield is 100-128:4:1 as reported by Kivaisi and Mtila (1998).

Inorganic cations such as $Ca^{++}$, $Mg^{++}$, $Na^{+}$, $K^{+}$, $Fe^{++}$ and $NH_4^{+}$ have a stimulatory effect at normal concentration to the methanisation; but exhibit inhibitory effect at higher concentrations. Sodium, potassium and magnesium ions are necessary for proper growth

of microbes (Perski *et al.* (1981). Schonheit *et al.* (1980) showed cations such as nickel, cobalt and molybdenum facilitating the microbial growth. Patidar *et al.* (2004) had studied the impacts of the elements iron, nickel, zinc, cobalt and molybdenum on biomass evaluation in the UASB and found that the nickel and cobalt limitation appears to affect the activity of hydrogen-utilizing methane producing bacteria (HMPB) significantly without having an appreciable effect on the activity of acetate utilizing methane producing bacteria (AMPB). The stimulatory effects of the elements iron and nickel was reported by Murray and Berg (1981). Calcium ions are known to increase granulation under optimum concentration (Tiwari *et al.*, 2006).

### 5.3.5 Toxic substances to anaerobic digestion

#### a. Azo dye toxicity to the anaerobic system

The aromatic amines released on cleavage of azo dyes by anaerobic microorganisms are often reported to have toxic effects on the microorganisms and human beings. Release of carcinogenic amine from the azo dye by the extracellular fluid protein isolated from *Streptomyces* species SS07 was reported by Bhaskar *et al.* (2003). Brown and DeVito (1993) reviewed the mechanisms of azo dyes toxicity. They reported either by the aromatic amines which are metabolically oxidized to reactive electrophilic species that covalently bind DNA or azo dyes with structures containing free aromatic amine groups that can be metabolically oxidized without azo reduction or azo dyes that may be activated via direct oxidation of the azo linkage to highly reactive electrophilic diazonium salts. Isik and Sponza (2007) studied the anaerobic biodegradability of five azo dyes like *Reactive Black 5, Direct Red 28, Direct Black 38, Direct Brown 2, Direct Yellow 12* and found that the *Direct Black 38 and Direct Brown 2* yielded partially persistent toxic amines, which have low toxicity under long-term incubations.

#### b. Volatile Fatty Acids (VFA)

Volatile fatty acids are important metabolic intermediates generated during anaerobic digestion. It is often taken as indicating the health of the anaerobic reactor by the various

researchers. Ahring *et al.* (1992) and Pind *et al.* (1999) reported VFA as the central control parameter though the acetate and propionate are dominating metabolic intermediates. The VFA will increase drastically during the shock loading, nutrient depletion and infiltration.

**c. Sulphide toxicity**

Sulphide content in anaerobic system is derived from reduction of sulphate and sulphur containing inorganics. Sulphide generation in anaerobic wastewater treatment produces several difficulties like reduction of the methane production, odour, corrosion and increase of effluent COD. Stronach *et al.* (1986) recorded inhibitory effects of the sulphide that lead to severe imbalance condition even cessation of biogas generation beyond the concentration of 200 mg/L.

**d. Ammonia – Nitrogen**

Usually ammonia is formed in the anaerobic digestion from urea and proteins containing wastewater. It usually occurs in the form of ammonium ions or dissolved gas in equilibrium with respect to the pH of the wastewater. McCarty (1964) showed that the ammonia nitrogen had beneficial effects to anaerobic process in the range of 50-200 mg/L; had no adverse effects in the concentrations of 200-1000 mg/L; was inhibitory at the range of 1500-3000 mg/L and toxic beyond 3000 mg/L. The adverse effects are due to ammonium ions when the pH level is 7.2 or less and due to ammonium gas when the pH is higher; usually ammonium gas has more impacts at the lower concentrations compared to the ammonium ions. The non methanogenic bacteria are tolerant to ammonia concentration upto the level of 6000 mg/L at a pH 8 (Haandel and Lettinga, 1994).

**e. Heavy metals and cations**

The heavy metals toxicity has been widely reported in anaerobic system. Copper, zinc and nickel salts are quite toxic under the soluble and low concentrations. In addition,

oxidizing agents and organic compounds such as formaldehyde, chloroform, ethyl benzene, ethyl dichloride and detergents are known to impart toxicity to the anaerobic microbes (Henzen and Harremoes, 1983). However they are converted to the insoluble sulfide salts, which are quite inert to microorganisms, by reaction with available sulphide. Addition of sodium sulphide salt is often practiced to enable formation of sulphide salts to minimize the heavy metals toxicity in the anaerobic treatment (Lawrence and McCarty, 1965).

The alkali and alkaline earth metal salts sodium, potassium, calcium and magnesium are present in high concentration in the industrial wastewater. Their presence is either inhibitory or stimulatory based on their concentration. The cations of the salt, at higher concentration are inhibitory even leading to failure of anaerobic reaction. The following table 5.3.1 provides the impacts of the alkaline earth metals on the anaerobic systems (McCarty, 1964).

| Cations | Concentration (mg/L) | | |
|---|---|---|---|
| | Stimulatory | Moderately inhibitory | Strongly inhibitory |
| Sodium | 100-200 | 3500-5500 | 8000 |
| Potassium | 200-400 | 2500-4500 | 12000 |
| Calcium | 100-200 | 2500-4500 | 8000 |
| Magnesium | 75-150 | 1000-1500 | 3000 |

**Table: 5.3.1 Impacts of alkaline earth metals on the anaerobic systems**

## 5.4 Methods

### 5.4.1 Analytical methods for the various parameters

The analyses were carried out as per the standard methods. The analyses were triplicated and an average value was taken for each parameter. The table 3.6.1 lists out the methods adopted for the each of the parameters.

### 5.4.2 Biogas quantification

Inverted graduated tube water replacement method is used to quantify the biogas generated from the HUASB reactor.

### 5.4.3 Seed materials

Slurry from an active and well functioning biogas plant was collected in airtight plastic containers and used as seed materials. The sediments collected from the equalisation tank of the CETP were also used along with the slurry collected from the biogas plant in the ratio of 1:1. Since currently there was no UASB reactor treating the textile wastewater in this region, the inoculum was prepared accordingly assuming that the sediments of the equalisation tank, being void of oxygen, might have adapted microbes.

### 5.4.4 Experimental set-up

HUASB reactor with 20 L working volume was fabricated in PVC tubes for the treatability study of the effluent. The total height of the reactors was 140 cm with 150 mm internal diameter. The bottom and top of the reactor was fitted with airtight flanges. 20 cm height from the bottom in the reactor is used for sludge accumulation. A valve was fitted at the bottom to remove the sludge. At 20 cm from the bottom feed nozzle was fitted. 4 sampling ports at an interval of 30 cm from the feed nozzle were also fitted on the reactor. The volume equivalent for each 30 cm height in the reactor was 5 litres. 90 cm height from the feed nozzle was used as the sludge blanket with a cumulative volume of 15 L which constituted 75% working volume of the reactor. The top 30 cm height from 3$^{rd}$ sampling port to effluent outlet with the volume of 25% was used as the filter. Two perforated plates were fitted to keep the packing medium in the filtration area. The top 20 cm was used to collect the gas and a gas vent was fitted here which was connected to the gas quantification system. The 4$^{th}$ sampling port was provided with a 'U' tube for wastewater collection and to prevent entry of air inside the reactor. 'Schlauchpumpe' make peristaltic pump was used to feed wastewater to the reactors at the desired flow

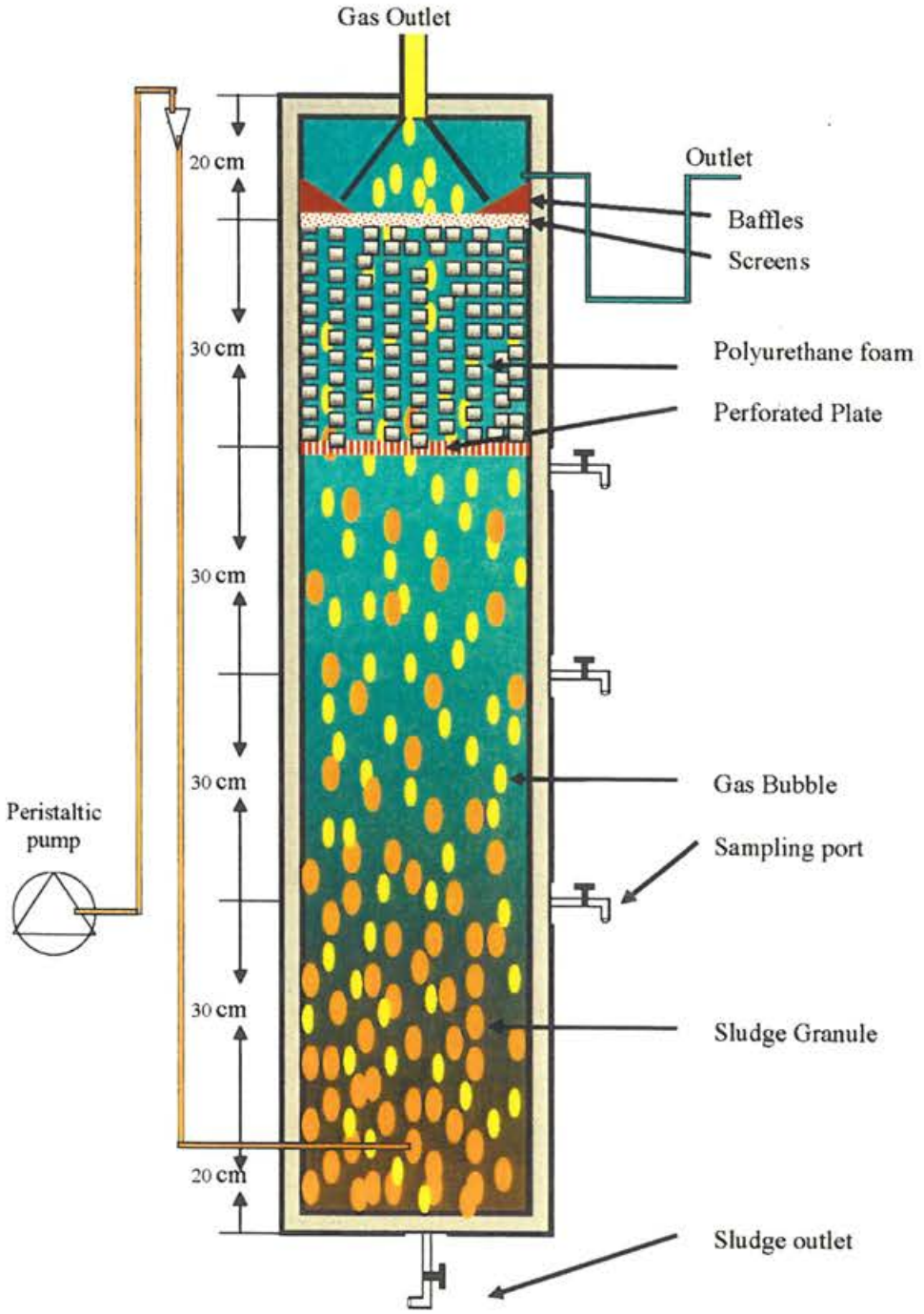



**Figure 5.4.1 Schematic diagram of Hybrid UASB reactor**

rate. The pump delivered wastewater at the feeding funnel with feeding tube maintained at the height slightly above the height of outlet of the reactor. The hydraulic retention time (HRT) and organic loading rate were calculated based on the volume of the reactor and flow rate of the wastewater.

Polyurethane foam cubes of 1 $cm^3$ size were used as the filter media. They were placed between two perforated plates to the height of 30 cm on the top of the reactor. Two perforated plates kept the media submersed in the reactor, which otherwise would float on the effluent.

### 5.4.5 Nature of wastewater used for the start-up of the reactor

Real textile wastewater collected from the equalisation tank of the CETP in Tiruppur is used for the experimental purpose including the start-up of the reactor.

## 5.5 Results and discussions

### 5.5.1 Characteristics of textile wastewater used for the studies

Real textile effluent collected from the CETP was adjusted to the pH of 6.8 using hydrochloric acid (10% concentration, v/v), since the equalized wastewater is always slightly alkaline. Ping and Bao-lan (2002) reported successful start-up of the UASB reactor with real pharmaceutical wastewater. Chinwetkitvanich *et al.* (2000) prepared the feed wastewater from real textile wastewater.

The characteristics of the wastewater used for the start-up and treatment phase of the Hybrid UASB reactor are shown below (Table 5.5.1). The physio-chemical parameters such as pH, total suspended solids, volatile suspended solids, volatile fatty acids, alkalinity, COD and biogas generation are used to evaluate the performance of the hybrid UASB reactor.

| Parameter | Values |
|---|---|
| pH | 6.8 |
| Total Suspended Solids (mg/L) | 328.9 ± 11.9 |
| Volatile solids (mg/L) | 236.1 ± 9.7 |
| COD (mg/L) | 776.6 ± 34.7 |
| BOD (mg/L) | 198.1 ± 10.1 |
| TKN (mg/L) | 15.7± 1.7 |
| Total Alkalinity (mg/L) | 775.2± 49.4 |
| Chloride (mg/L) | 3791.6± 204.8 |
| Sulphate (mg/L) | 569.2 ± 21.6 |
| Phosphate (mg/L) | 5.6 ± 1.5 |
| Nitrate (mg/L) | 4.8 ± 1.1 |

**Table 5.5.1 Characteristics of the wastewater used in the study of HUASB reactor**

### 5.5.2 Inoculation

The characteristics of the inoculum used in the HUASB system for the start-up are shown in the table 5.5.2. The inoculum was fed along with the textile wastewater in the ratio of 1:3 (v/v). The nature of inoculum was comparable with the inoculum used by Banu (2005) for treatment of sago wastewater where the inoculum showed total solids 58054 mg/L, total suspended solids 41984 mg/L and volatile suspended solids 10924 mg/L.

| | |
|---|---|
| Total Solids | 51211 (mg/L) |
| Total Suspended Solids | 38552 (mg/L) |
| Volatile Suspended Solids | 9851 (mg/L) |

**Table 5.5.2 Characteristics of the inoculum used for the start-up of the HUASB reactor**

### 5.5.3 Studies on the start-up period

#### a. Organic loading pattern and hydraulic retention time

The initial Organic Loading Rate (OLR) applied for the start-up of the reactor was 0.30 kg COD/$m^3$/day. Since the textile wastewater is known to contain many recalcitrant

materials, the preferred initial OLR was very low and maintained so upto 24 days. The OLR was increased by increasing the flow rate of wastewater since the real wastewater was used to start-up the reactor. The organic loading pattern and calculated hydraulic retention time maintained during the start-up of the HUASB system is shown in the table 5.5.3. The mean HRT was 61.63 hours on the first 24 days of start-up period and it gradually decreased with increasing OLR which was done by increasing flow rate of feed wastewater. On the 132$^{nd}$ day, the mean HRT was 32.23 hours.

The HRT during the start-up of the reactor is a crucial factor where it should be favourable to retain the sludge and thereby prevent the washout of biomass. Hickey *et al.* (1991) preferred such HRT during the start-up phase of the reactor. The OLR was then gradually increased (with an increment of 0.03 kg COD/m$^3$/day per 12 days) upto 135 days (OLR of 0.57 kg COD/m$^3$/day). Similar step of increase was carried out by Banu (2005) for start-up of the reactor treating the sago wastewater. The OLR applied during the current experiments was comparable to the literature available. Talarposhti *et al.* (2001) carried out the treatability studies on the simulated dye wastewater using a two-phase anaerobic packed bed reactor and reported that 90% colour removal applying similar OLR.

| Digestion period | OLR (kg COD/m$^3$/day ) | HRT (hours) |
|---|---|---|
| 0-24 | 0.30 | 67.63 |
| 25-36 | 0.33 | 56.51 |
| 37-48 | 0.36 | 53.06 |
| 49-60 | 0.39 | 47.65 |
| 61-72 | 0.42 | 42.53 |
| 73-84 | 0.45 | 41.04 |
| 85-96 | 0.48 | 38.21 |
| 97-108 | 0.51 | 34.84 |
| 109-120 | 0.54 | 32.29 |
| 121-132 | 0.57 | 32.23 |

**Table 5.5.3 OLR and HRT maintained during start-up phase**

**b. Biogas production**

Biogas generated in the hybrid UASB reactor during the start-up period for each of the OLR is shown in the figure 5.5.1. The mean biogas generation for the initial OLR (0.30 kg COD/$m^3$/day) was 64.8 mL and it increased gradually to reach 404.2 mL at the OLR of 0.57 kg COD/$m^3$/day.

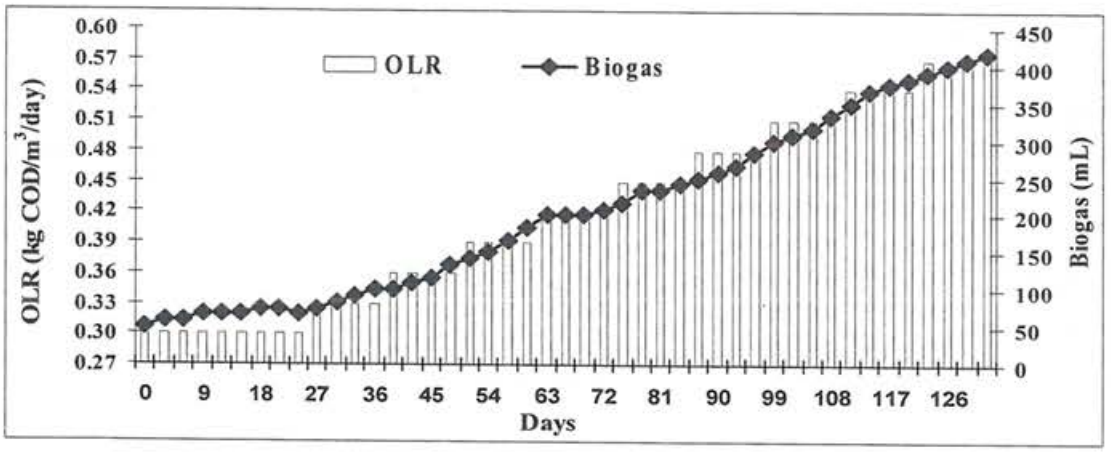



**Figure 5.5.1 Biogas generation during the start-up phase**

The low volume of biogas during the initial days of start-up period could be attributed to the process of acclimatization of the system. The figure 5.5.1 shows that after the acclimatization period which lasted upto 24 days the biogas generation steadily increased. It is emphasized that the inoculum fed to the system was capable of supporting the development of microbial consortium. Anderson *et al.* (1984) reported increasing biogas generation to the increased OLR applied in the anaerobic packed bed reactors. The study by Banu (2005) in treating the sago wastewater showed the gradual increase of biogas generation for the stepped increase of OLR from 0.81 to 8.10 kg COD/$m^3$/day and found 9.7 L/day of biogas for the OLR of 8.10 kg COD/$m^3$/day.

**c. BOD removal**

The efficiency of the HUASB system in removal of BOD from the textile wastewater is shown in the figure 5.5.2. During acclimatization period of start-up phase the mean BOD removal was 43.3% for the OLR of 0.30 kg COD/$m^3$/day and on increasing the digestion period and OLR, the BOD removal increased in a steady state manner upto the OLR of

0.57 kg COD/$m^3$/day applied. The corresponding percentage removal of BOD reached 82.8% at the OLR of 0.57 kg COD/$m^3$/day. Consequently, the levels of BOD values in outlet of the reactor came down gradually as the days of digestion and OLR increased. During the acclimatization period, the mean value of BOD in the outlet of the reactor was 114.7 mg/L. This level of BOD further reduced steadily upto 34.0 mg/L at the OLR of 0.57 kg COD/$m^3$/day towards the end of 132 day of digestion.

The anaerobic technology is widely applied to remove organics and decolourise textile wastewater under similar operating conditions. Complete decolourisation (greater than 95%) of the wastewater containing the azo dye Orange II was performed in an UASB system when working at 0.30 g COD/l/day of OLR and 24 hours of HRT (Ong *et al.*, 2005).

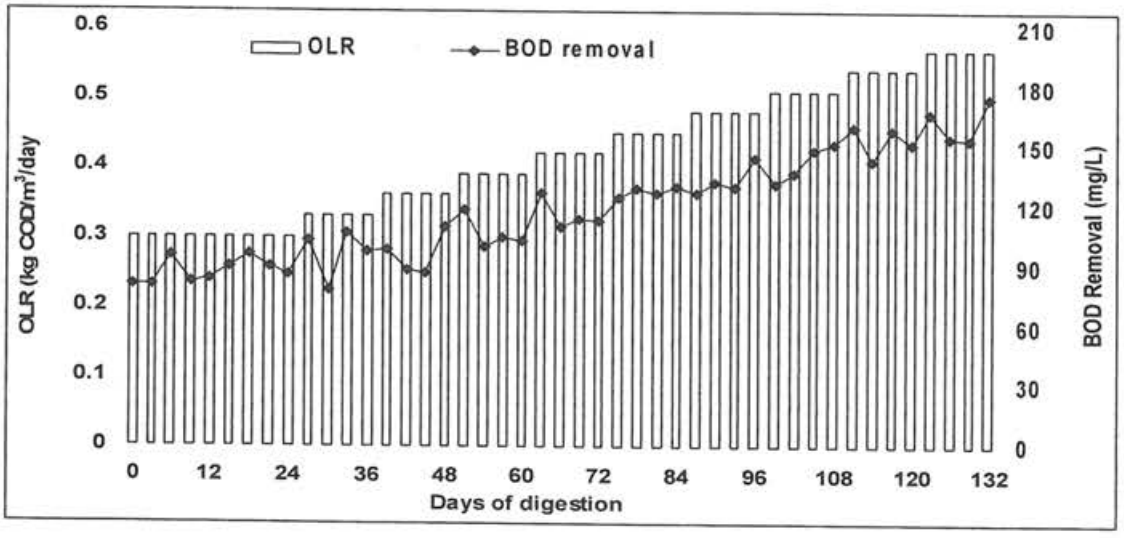



**Figure 5.5.2 Gradual increase of BOD removal against OLR during the start-up phase**

**d. COD removal**

The removal of COD increased with increase in OLR during the start-up period. On the first day, the concentration of COD removed was 273.1 mg/L and it constituted 34 % of the COD of the feed water. Gradually the COD removal increased to 49.2% by 51$^{st}$ day at the OLR of 0.39 kg COD/$m^3$/day, 67.9% on 99$^{th}$ day at the OLR of 0.51 kg COD/$m^3$/day

and 77.9% on 135 days of operation at the OLR of 0.60 kg COD/$m^3$/day. Table 5.5.4 shows the percent COD removal during the start-up period of HUASB reactor.

The increasing efficiency of the COD removal was due to gradual establishment of the microbial consortium in the HUASB system which utilized the organics. Further, it is presumed that the inoculation contained sufficient number of microbial consortium. The essential nutrients were also contained in the feed wastewater and the optimum environmental conditions favoured the development of biomass in the system. A similar trend of relationship in COD removal to the organic loading rate was reported by Backman *et al.* (1985).

**e. Volatile fatty acid accumulation**

VFA content estimated on the first day was 155.4 mg/L and it decreased with the increasing COD removal and OLR during the start-up period. The value of VFA measured against the OLR during the start-up period is presented in the table 5.5.4. The VFA showed non-linear relationship with the OLR. The figure 5.5.3 shows the influence of OLR on the COD removal and VFA during the start-up period where the increased OLR resulted in increase of COD removal and reduction of VFA content.

| Digestion period (days) | OLR (kg COD/$m^3$/day) | COD removal (%) | VFA (mg/L) |
|---|---|---|---|
| 0-24 | 0.30 | 40.0 | 150.6 |
| 25-36 | 0.33 | 45.5 | 136.0 |
| 37-48 | 0.36 | 46.4 | 121.5 |
| 49-60 | 0.39 | 54.4 | 115.2 |
| 61-72 | 0.42 | 60.5 | 110.5 |
| 73-84 | 0.45 | 62.7 | 105.8 |
| 85-96 | 0.48 | 65.9 | 102.6 |
| 97-108 | 0.51 | 72.6 | 98.4 |
| 109-120 | 0.54 | 77.9 | 98.7 |
| 121-132 | 0.57 | 78.0 | 96.6 |

**Table 5.5.4 Influence of the organic loading pattern on the COD removal and VFA accumulation during start-up of the reactor**

VFA is a biochemical intermediate in anaerobic process. It is a critical parameter and its status indicates the health of the system (Pind *et al.,* 1999). In the first phase of operation, acetogenesis would be prevalent and hence accumulation of VFA was noticed. Gradually VFA content gets reduced which indicates the dominance of methanogens than acetogens. Lettinga and Vinken (1980) showed the accumulation of the VFA during the initial phase and gradual reduction and subsequently development of methanogenic activity in the reactor. It is presumed that the inoculated seed material contained the necessary microorganisms to establish the required bacterial biomass.

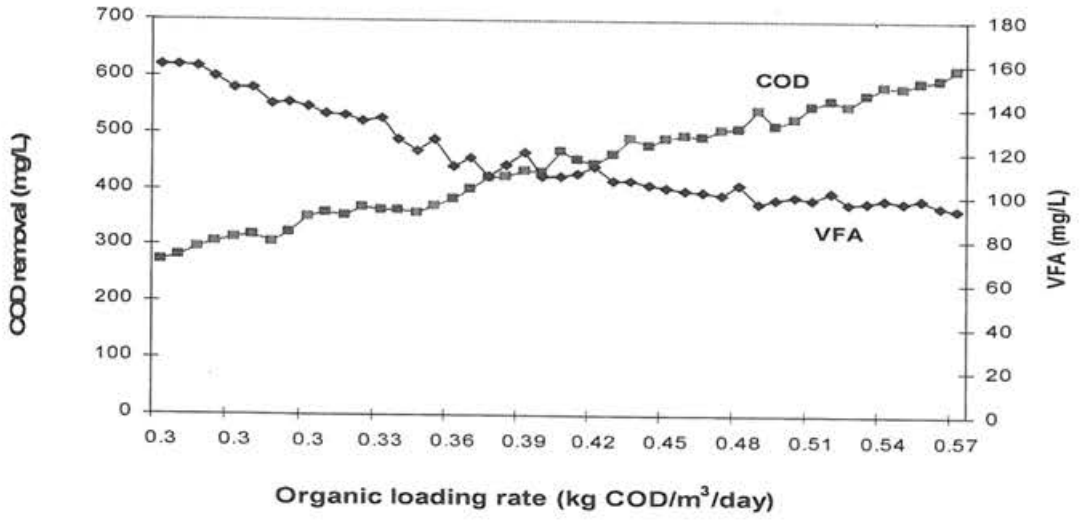



**Figure 5.5.3 COD and VFA during start-up phase**

**f. Solids removal**

The total suspended solids (TSS) removal during the start-up period for the OLR of 0.3 kg COD/$m^3$/day was 55.8% and the TSS removal increased with the increasing OLR. It reached 75.8% on 132$^{nd}$ day of operation. In terms of quantity the TSS removal was 184 mg/L at the OLR of 0.30 kg COD/$m^3$/day and 250 mg/L with the OLR of 0.57 kg COD/$m^3$/day. Table 5.5.5 shows the nature of TSS to the varying OLR. Similarly, removal of volatile suspended solids (VSS) showed progressive increase to the increasing OLR. The mean VSS removal was 151.0 mg/L at the OLR of 0.30 kg COD/$m^3$/day, which constituted 34.6%. At the OLR of 0.57 kg COD/$m^3$/day, the VSS removed was to the tune of 64.4%, 148.9 mg/l.

Removal of TSS and VSS was linear to the increase of OLR coinciding with the gradual establishment of anaerobic microbial consortia in the reactor. However, a non-linear relationship of TSS with OLR was reported by Chakradhar and Kaul (1993) in the experiments treating cotton digestion wastewater using the anaerobic fixed bed reactor. Shanta *et al.* (1988) reported increase of solids to the increased OLR applied in the attached fixed film fixed bed reactor treating dairy wastewater. It is presumed that the polyurethane foam acted as good media in trapping the TSS. Hence, removal of TSS in the very initial stage was very high to the level of 55.81%.

| **OLR** (kg COD/$m^3$) | **TSS removal (%)** | **VSS Removal (%)** |
|---|---|---|
| 0.30 | 55.8 | 34.6 |
| 0.33 | 59.0 | 37.5 |
| 0.36 | 58.2 | 41.0 |
| 0.39 | 65.2 | 43.6 |
| 0.42 | 63.4 | 45.9 |
| 0.45 | 65.0 | 52.7 |
| 0.48 | 70.2 | 57.2 |
| 0.51 | 69.3 | 59.4 |
| 0.54 | 69.6 | 61.0 |
| 0.57 | 75.8 | 64.4 |
| 0.60 | 76.4 | 64.5 |

**Table 5.5.5 Removal of TSS and VSS during start-up phase**

**g. pH**

The pH of the outlet of the reactor during the start-up period increased with days of the operation and increasing OLR.. The pH measured during the days of start-up of the reactor is shown in the table 5.5.6. During the initial stage of start-up period the pH was maintained at 6.6 to 6.9. It reached 7.4 to 7.5 on the 132$^{nd}$ days of operation.

The low pH values during initial stage of anaerobic system were due to formation of VFA. Slight drop of the pH within 24 hours of start-up and eventually continued drop resulting in acidification of the reactor was noticed in the case of UASB system by

Britz *et al.* (2002). Similar drop of the pH due to increase of VFA was reported by Kalogo *et al.*, (2001). In later stages the alkalinity of the system increased and subsequently the pH values increased. Such increase in pH value is an usual phenomenon in a healthy anaerobic system.

| Digestion period (Days) | pH |
|---|---|
| 0-24 | 6.6-6.9 |
| 25-36 | 6.8-7.0 |
| 37-48 | 6.9-7.1 |
| 49-60 | 7.0-7.1 |
| 61-72 | 7.1-7.2 |
| 73-84 | 7.1-7.3 |
| 85-96 | 7.2-7.3 |
| 97-108 | 7.2-7.4 |
| 109-120 | 7.3-7.5 |
| 121-132 | 7.4-7.5 |

**Table 5.5.6 pH measurements during the start-up of the HUASB reactor**

**h. Alkalinity**

The alkalinity in the UASB system is known to have buffering ability to neutralize the VFA generated during anaerobiosis and is considered as an important factor in the maintenance of the system. Total alkalinity, presented in the figure 5.5.4, showed a gradual increase from 2 to 9% compared to the feed water. In terms of quantity, the increase was 14.25 mg/L on the first day and 70 mg/L on the 135$^{th}$ day.

Increase of total alkalinity is a natural phenomenon in UASB system during start-up. Subramanyam and Sastry (1988) reported progressive increase of alkalinity in anaerobic filter treating the perfumery industrial effluent. Khageshan (1998) and Banu (2005) also noticed elevation of alkalinity values during the start-up of UASB reactor treating sago wastewater. Conversion of sulphate present in feed wastewater into the sulphide eventually increased the alkalinity (Kim *et al.*, 2003b). Certain materials such as protein on biodegradation release ammonia nitrogen which combines with carbon-di-oxide or

water to form ammonium bicarbonate alkalinity, as in the case of municipal wastewater treatment, thereby increasing of the alkalinity (McCarty, 1964).

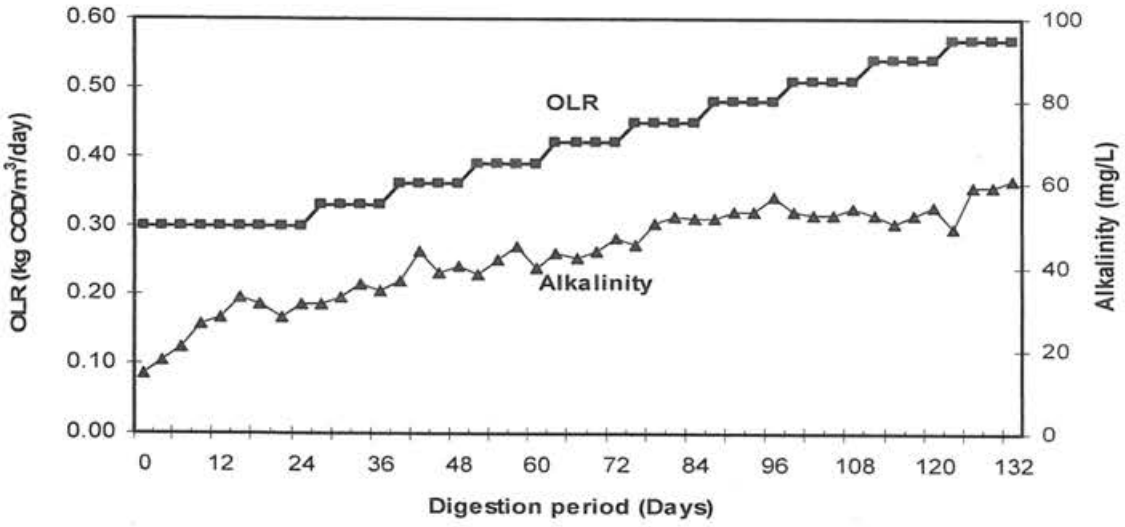



**Figure 5.5.4 Nature of alkalinity in the HUASB system during start-up phase**

**i. Sulphate reduction**

The sulphate content of the outlet of HUASB reactor showed gradual decline during start-up phase of the reactor. The mean reduction of sulphate for each of the OLR is given in the table 5.5.7. Sulphate reduction in the UASB system under the anaerobic condition is quite a normal phenomenon. The sulphate reducing bacteria are able to convert the sulphates into sulphide utilizing available organics or added substances. The organics are either partially oxidized to acetic acid or completely oxidized to carbon dioxide. Sulphate acts as secondary electron acceptor in the anaerobic system. The sulphides, in turn react with the soluble heavy metals to form insoluble metal sulphides that can get settled and separated from the wastewater. Lima *et al.* (2001) also reported sulphate reduction to sulphide by sulphate reducing bacteria utilizing the available organics in the supplied sewage.

| **OLR (kg COD/m$^3$/day** | 0.30 | 0.33 | 0.36 | 0.39 | 0.42 | 0.45 | 0.48 | 0.52 | 0.55 | 5.70 |
|---|---|---|---|---|---|---|---|---|---|---|
| **Sulphate removal (mg/L)** | 8.1 | 10.4 | 8.4 | 13.6 | 16.2 | 18.0 | 11.3 | 13.9 | 18.8 | 19.3 |

**Table 5.5.7 Sulphate removal during start-up phase**

**j. Chloride**

The chloride content of the outlet of HUASB reactor remained same as the feed.

**k. Nutrients utilization**

Utilization of the nutrients such as nitrogen, phosphate and potassium is given in the table 5.5.8. The Total Kjeldahl Nitrogen (TKN) in feed wastewater ranged from 14.2 to 16.4 mg/L. It was noticed that the TKN content increased in the outlet of the reactor. The outlet of the reactor showed TKN ranging from 15.0 to 18.8 mg/L. Gradual increase of TKN was observed to increasing OLRs. At the OLR of 0.57 kg COD/$m^3$/day, the increase of TKN was 16.5%.

Similarly, the phosphate content in the outlet of the reactor showed slight rise. The phosphate found in feed wastewater varied from 3.1 to 7.2 mg/L, while its concentration in the outlet of the reactor ranged from 3.8 to 8.0 mg/L. The increase of phosphate was 4.5% at the initial OLR (0.30 kg COD/$m^3$/day) and 22.6% at the OLR of 0.57 kg COD/$m^3$/day.

| OLR | TKN (mg/L) | | Phosphate (mg/L) | | Potassium (mg/L) | |
|---|---|---|---|---|---|---|
| | Feed | outlet | Feed | outlet | Feed | outlet |
| 0.30 | 15.3 | 15.9 | 5.8 | 6.0 | 27.7 | 30.0 |
| 0.33 | 14.2 | 15.0 | 7.2 | 7.8 | 27.6 | 30.9 |
| 0.36 | 16.2 | 16.9 | 6.8 | 7.3 | 28.9 | 32.4 |
| 0.39 | 15.6 | 16.6 | 6.1 | 6.9 | 28.6 | 32.2 |
| 0.42 | 15.2 | 16.9 | 5.0 | 5.8 | 25.4 | 29.2 |
| 0.45 | 16.2 | 17.7 | 5.0 | 5.6 | 25.8 | 29.2 |
| 0.48 | 16.1 | 18.1 | 3.1 | 3.8 | 27.0 | 31.1 |
| 0.51 | 14.8 | 16.8 | 3.9 | 4.7 | 25.8 | 30.8 |
| 0.54 | 15.4 | 16.8 | 3.9 | 4.9 | 28.4 | 33.1 |
| 0.57 | 16.2 | 18.8 | 6.5 | 8.0 | 28.5 | 33.7 |

**Table: 5.5.8 Nutrients utilisation during start-up phase of the HUASB reactor**

Potassium also showed similar increase after the treatment of the wastewater in the HUASB reactor. The range of potassium found in the feed wastewater was from 25.4 to 28.9 mg/L. The outlet of the reactor showed potassium values varying from 29.2 to 33.1 mg/L. The increase was 8.3% at the initial stage and 18.1% at the OLR of 0.57 kg COD/$m^3$/day. The mineralisation of organics contained in the wastewater resulted in increase of nutrients. Similar increase of nutrients during the start-up of the HUASB reactor with sewage was noticed by Banu (2005).

### 5.5.4 Attaining steady state condition in the reactor

Steady state condition was attained by the end of 135 day of operation at the OLR 0.60 kg COD/$M^3$/day. The maximum COD removal was noticed in the OLR of 0.60 kg COD/$M^3$/day which was around 75%. The COD removal did not increase with further increase in the OLR. Similar observations were made in the case of BOD, solids, and sulphate. On the contrary, the increase of alkalinity was highest at the OLR of 0.60 kg COD/$m^3$/day.

The end of start-up period was evaluated by Westhuizen and Pakkies (1992) and indicated that the measured parameters varied less than 10% after the four reactor volume changes. The results obtained from our study are comparable to the above findings. The steady state condition was attained for synthetic sago wastewater on 130 days at the OLR of 8.30 kg COD/$m^3$/day (Banu, 2005). However Khagesan (1998) achieved the steady state condition in the HUASB using the sago wastewater between 95 to 105 days. Sen and Demirer (2003) reported that the start-up period for the anaerobic fluidized bed reactor was 128 days using real textile.

### 5.5.5 Studies on the treatment phase of HUASB reactor

#### a. Organic loading pattern and hydraulic retention time

The OLR applied during the treatment phase of HUASB system and the corresponding mean HRTs calculated for each of OLR is given in the table 5.5.9. The OLR is raised in a stepped manner from 0.60 to 0.90 kg COD/$m^3$/day. On increasing the OLR from 0.60 kg

COD/$m^3$/day the system showed fluctuation in removing the organics but it adapted to the increase of OLR upto 0.81 kg COD/$m^3$/day. During this stage of operation, the performance of the system was stable. The stable operation period lasted from 135 to 228 day. Beyond the OLR 0.81 kg COD/$m^3$/day, there was sudden reduction in organics removal. The system was unable to recover upon further increase of OLR. It is assumed that the system could not tolerate high OLR beyond 0.81 kg COD/$m^3$/day. The experiment was carried out upto the OLR of 0.90 kg COD/$m^3$/day which lasted upto 264 days. The experiments beyond the OLR 0.90 kg COD/$m^3$/day were not carried out since the efficiency of the system dropped down to un-recoverable level.

The period between the OLR 0.60 to 0.81 kg COD/$m^3$/day considered as stable operational period since the system adapted to the increasing OLR applied and the parameters were controlled at the maximum level.

| Digestion period | OLR (kg COD/$m^3$/day) | HRT (Hours) |
|---|---|---|
| 133-144 | 0.60 | 31.1 |
| 145-156 | 0.63 | 30.7 |
| 157-168 | 0.66 | 29.6 |
| 169-180 | 0.69 | 27.4 |
| 181-192 | 0.72 | 25.8 |
| 193-204 | 0.75 | 24.3 |
| 205-216 | 0.78 | 23.9 |
| 217-228 | 0.81 | 23.1 |
| 229-240 | 0.84 | 22.9 |
| 241-252 | 0.87 | 22.0 |
| 253-264 | 0.90 | 21.7 |

**Table 5.5.9 Organic loading pattern and HRT during treatment period**

A stepped manner of increase in OLR was experimented by many researchers to evaluate the effectiveness of the UASB system during the treatment phase. Banu (2005) used similar manner of increasing OLR for treatment of sago wastewater, dairy wastewater and municipal wastewater in Hybrid UASB reactor. Manariotis and Grigoropoulos (2003) reported the operation of the anaerobic filter with the OLR ranging from 0.02 to

0.91 kg COD/$m^3$/day for the low strength wastewater such as textile wastewater bearing low COD values ranging 325-403 mg/L. Bras *et al.* (2005) investigated decolourisation of two azo textile dyes, a monoazo dye (*Acid Orange 7)* and a diazo dye (*Direct Red 254*) under methanogenic conditions in UASB reactor and achieved 88% of colour removal with HRT of 24 hours. Isik (2004) evaluated the performance of treating simulated textile wastewater in UASB at the HRT of 20 hours.

**b. Biogas production**

Biogas generation during the treatment period of the HUASB reactor is shown in the table 5.5.10. The Biogas generation at the OLR of 0.60 kg COD/$m^3$/day was 427.1 mL/day. On stepped increase in OLR there was gradual increase in biogas (table 5.5.10). Maximum volume of biogas measured at the OLR of 0.81 kg COD/$m^3$/day was 566.7 mL/day. With further increase of the OLR, the volume of biogas generation declined drastically. At the OLR of 0.84 kg COD/$m^3$/day, the volume was 475 mL/day. The decline of biogas generation was comparable to decline of COD removal at the OLR of 0.81 kg COD/$m^3$/day. The normalized generation of biogas lasted from the days 135 to 228 when the OLR applied from 0.60 to 0.81 kg COD/$m^3$/day.

| Digestion period (Days) | OLR (kg COD/$m^3$/day) | Biogas (mL) @ STP |
|---|---|---|
| 133-144 | 0.60 | 427.1 |
| 145-156 | 0.63 | 439.6 |
| 157-168 | 0.66 | 452.1 |
| 169-180 | 0.69 | 479.2 |
| 181-192 | 0.72 | 514.6 |
| 193-204 | 0.75 | 531.3 |
| 205-216 | 0.78 | 550.0 |
| 217-228 | 0.81 | 566.7 |
| 229-240 | 0.84 | 475.0 |
| 241-252 | 0.87 | 368.8 |
| 253-264 | 0.90 | 258.3 |

**Table 5.5.10 Biogas production during treatment period**

The decline of biogas generation at higher OLR was due to inability of the system to cope with the increased OLR. Similar, decline of biogas generation was noticed by Banu (2005) at the OLR of 22.2 Kg COD/$m^3$/day in hybrid reactors.

**b. BOD Removal**

The BOD removal observed during the stable operation period ranged from 75.1% to 82.6%. The quantum of BOD values reductions varied from 135.7 to 182.6 mg/L. However the BOD removal dropped down after 228 days of digestion at the OLR of 0.84 kg COD/$m^3$/day. The removal at this OLR was 51.7% of BOD only. The percent reduction further dropped down to 41.8% and 25.6% to further increase of OLR and days of digestion (Figure 5.5.5).

The BOD measured in the outlet of the reactor is given in the table 5.5.11. It is found that during the stable operation period the BOD in the outlet of the reactor fluctuated from 35.1 to 50.0 mg/L. These values are quite near to the norm stipulated by TNPCB for BOD. However, after OLR of 0.81 kg COD/$m^3$/day, the BOD in the outlet of the reactor suddenly increased to 98.5 from 50.0 mg/L and further increase in BOD for the subsequent OLRs was also noticed as shown in the table 5.5.11. O'Neill *et al.* (1999) have also seen the BOD removal to the level of 86% for the simulated textile effluent treated in combined anaerobic and aerobic process.

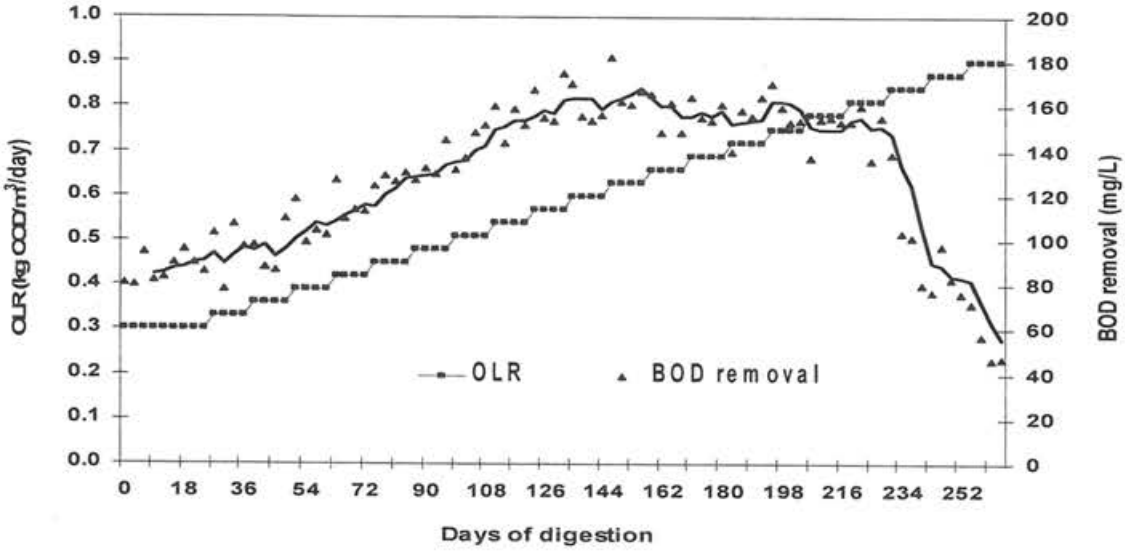



**Figure 5.5.5 BOD removal during the treatment period of HUASB reactor**

| Days | OLR (kg COD/$m^3$/day) | BOD in the Outlet (mg/L) |
|---|---|---|
| 133-144 | 0.60 | 35.1 |
| 145-156 | 0.63 | 35.3 |
| 157-168 | 0.66 | 41.5 |
| 169-180 | 0.69 | 34.4 |
| 181-192 | 0.72 | 37.4 |
| 193-204 | 0.75 | 40.3 |
| 205-216 | 0.78 | 42.9 |
| 217-228 | 0.81 | 50.0 |
| 229-240 | 0.84 | 98.5 |
| 241-252 | 0.87 | 115.6 |
| 253-264 | 0.90 | 160.7 |

**Table 5.5.11 BOD values in the outlet of HUASB reactor during treatment period**

**c. COD removal**

The quantum of COD removal during the treatment period of HUASB reactor ranged from 547 to 606 mg/L (71.6 to 78.0% of removal). During this period, the COD measured in the outlet varied from 140 to 229 mg/L. Drop in COD removal was noticed at the OLR of 0.84 kg COD/$m^3$/day. COD removal at this OLR was only 468 mg/L. To further increase of OLR, the removal of COD dropped to 310 mg/L at the OLR of 0.90 kg COD/$m^3$/day. The figure 5.5.6 illustrates the COD removal in the HUASB reactor.

The findings of the present study are comparable to the report of Manariotis and Grigoropoulos (2003) where they achieved 72-80% COD removal in the real textile wastewater at the OLR ranging from 0.27 to 0.91 kg COD/$m^3$/day. The hybrid UASB reactors are known to have more efficiency in controlling the organics from the wastewater. Willetts *et al.* (2000) showed that thermophillic bacteria in UASB was more efficient than mesophillic bacteria for azo dyes decolourisation tested under high salt condition to the level of 20 g/L in the synthetic textile dyeing wastewater. They observed toxic effect under higher dye concentration where in low COD removal and methane gas production was noticed. It was shown (Herbert *et al.*, 1994) that HUASB treating sewage removed 95% COD at the OLR of 20 g COD/l/Day while the fluidized and expanded bed reactors removed only 80% of COD at the same OLR. However, sewage contains highly

biodegradable organics which are easily degraded in the HUASB reactor than the textile effluents that contains recalcitrant organics.

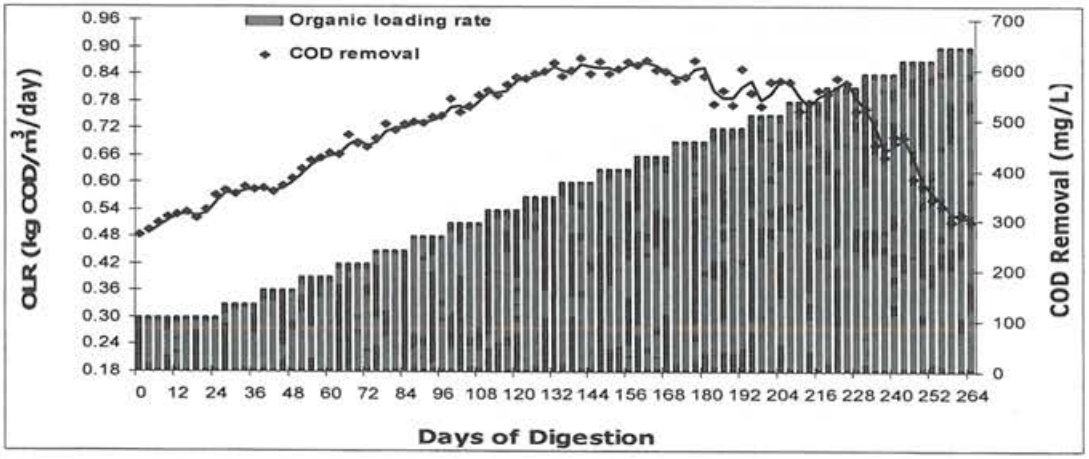



**Figure 5.5.6 COD removal in the HUASB reactor during treatment period**

**e. Volatile fatty acid**

During the stable operation period of the reactor the VFA ranged from 90.0 mg/L to 111.0 mg/L for the OLR starting from 0.60 to 0.81 kg COD/$m^3$/day. The VFA increased abruptly to 142.6, 151.7 and 176.7 mg/L for subsequent OLRs of 0.84, 0.87 and 0.90 kg COD/$m^3$/day. The accumulation of VFA indicates the intolerance of UASB system to high OLRs. The increase of VFA at the OLR of 0.84 kg COD/$m^3$/day was found coeval with the drop of COD, BOD removal and biogas generation at the same OLR. The figure 5.5.7 shows the VFA and COD values to the OLR applied in the HUASB system.

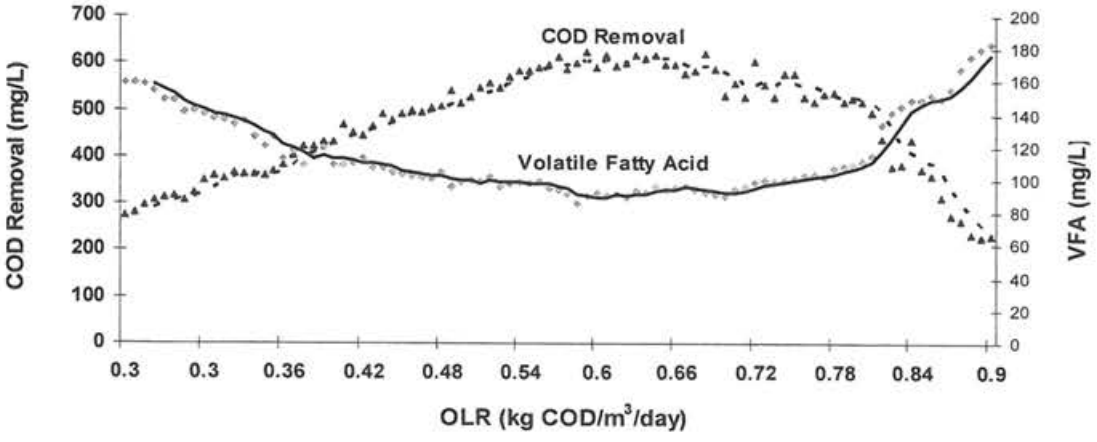



**Figure 5.5.7 Relationship of VFA and COD in the anaerobic system**

**f. Solids removal**

Removal of solids such as TSS and VSS is shown in the figures 5.5.9 (TSS) and 5.5.8 (VSS). The removal of VSS ranged from 56.9 to 64.5 % while TSS removal varied from 66.2% to 76.4 during the stable operation period of the reactor. The phenomenal decline of efficiency of the UASB at the OLR of 0.84 kg was also noticed in the case of solids removal The VSS removal was 37.0% when the OLR was 0.84 kg COD/$m^3$/day and further dropped to 23.0% when the OLR increased to 0.90 kg COD/$m^3$/day. Similarly, the TSS removal declined to 56.1, 48.2 and 40.8% when the OLR was 0.84, 0.87 and 0.90 kg COD/$m^3$/day respectively. During the stable operation period the TSS in the outlet of the reactor ranged from 74.0 to 136.6 mg/L and the VSS ranged from 77.4 to 117.7 mg/L. Most of the samples collected during the stable operation period showed TSS values within the limit set in the pollution control law.

The drastic reduction of solids was attributed to the inability of the system to adapt to the increased organic load. The VSS resembles the organic matter of the wastewater and its removal is a good indication of removal of organics. Vandenburgh and Ellis (2002) studied anaerobic process under varying total solids, volatile solids and organic loading rate; the total solids contents were removed upto 61.5% at the feed concentration 4.9% and dropped to 52.5% at the feed concentration of 7.9% with 20 days of holding time.

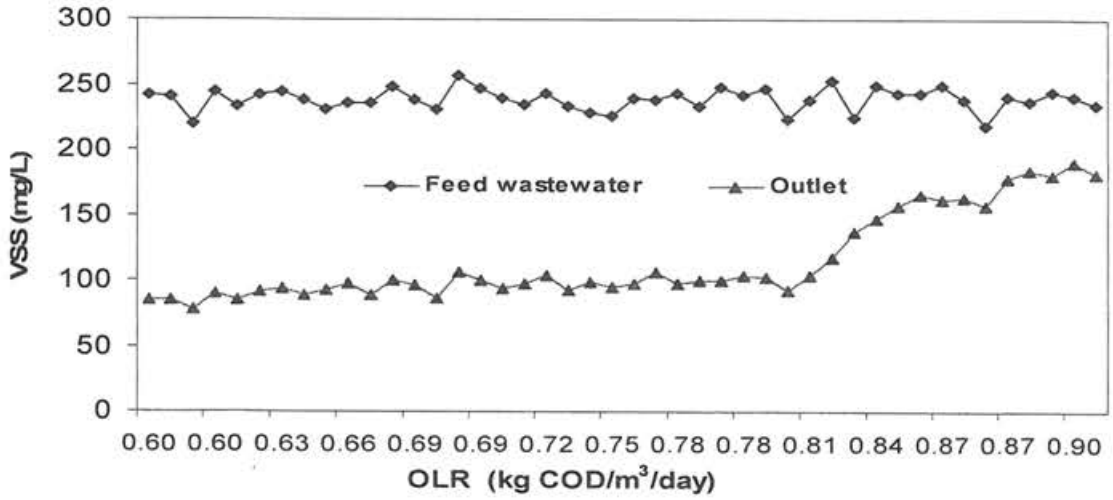



**Figure 5.5.8 VSS in the feed and outlet of the HUASB reactor during treatment period**

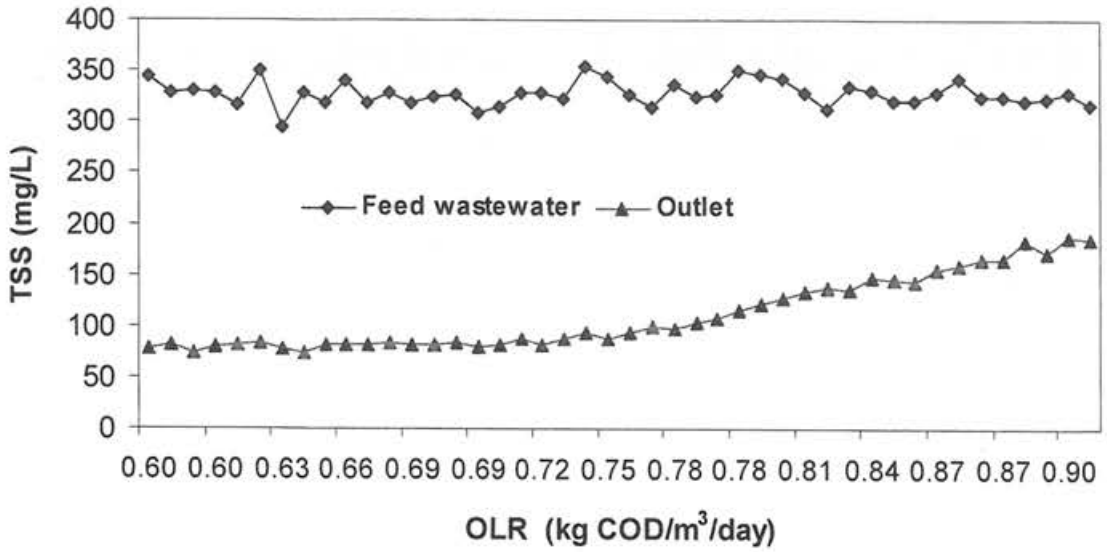



**Figure 5.5.9 TSS in the feed and outlet of the HUASB reactor during treatment period**

**g. pH**

The pH of outlet of the HUASB ranged from 7.4 to 7.6 during the stable operation period. The pH slightly increased during the stable operation period than the start-up period. At the OLR of 0.84 kg COD/$m^3$/day there was abrupt drop in pH to 6.6. It further dropped to subsequent increase of OLR. The abrupt drop in the pH was due to accumulation of VFA, since the UASB system failed to adapt the higher OLR. The readings can be correlated with the VFA content of the reactor where the VFA values were maintained at the minimum level during stable operation. It is presumed that the methanogenesis was affected during the OLR beyond 0.81 kg COD/$m^3$/day. During the stable operation period the range of pH in the reactor was at the optimum levels. Wheatly (1991) showed that the pH less than 6.8 and greater than 8.6 could cause souring of the reactor.

**h. Alkalinity**

The total alkalinity measured during the treatment phase of HUASB is presented in the figure 5.5.10. During the stable operation period, the increase of total alkalinity ranged from 51.2 to 71.2 mg/L. This range of alkalinity lasted for OLR of 0.60 to 0.81 kg

COD/$m^3$/day. Beyond the OLR 0.81 kg COD/$m^3$/day there was sudden drop of alkalinity (19.1 mg/L from 31.0 mg/L). This phenomenon is related to drop in pH and increase in VFA noticed beyond the OLR of 0.81 kg COD/$m^3$/day.

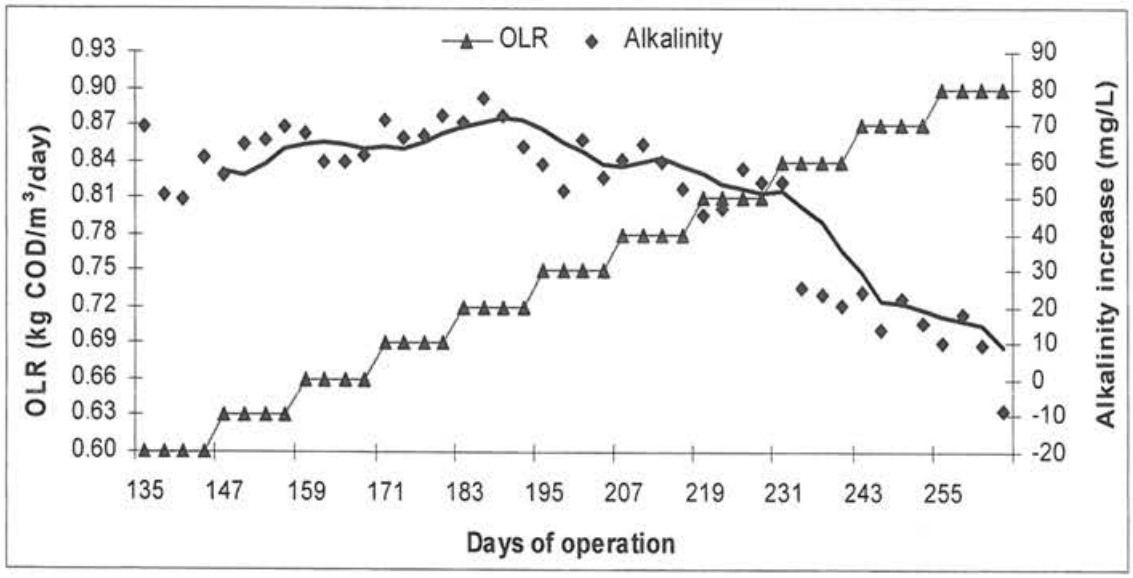



**Figure 5.5.10 Alkalinity in the HUASB reactor during the treatment phase**

Gerardi (2003) opined that the drop of alkalinity before the drop of the pH in the UASB system because of accumulation of VFA which indicates the failure of the reactor. During the operation phase of the UASB reactor treating paper wastewater, production of alkalinity by the reduction of sulphate to hydrogen sulphide by sulphate reduction bacteria was reported by Kim *et al.* (2003b).

**i. Sulphate reduction**

Reduction in sulphate during the stable operation period ranged from 3.1 to 4.4%. During this period the efficiency of the HUASB system was maximum. However beyond OLR 0.81 kg COD/$m^3$/day there was sudden decline in sulphate reduction. The sulphate reduction at the OLR of 0.84 kg COD/$m^3$/day was 1.5 % only. It further declined to 0.9 and 0.4 % in further increase in OLR. The reduction of sulphate content during the treatment phase of the reactor is presented in the figure 5.5.11.

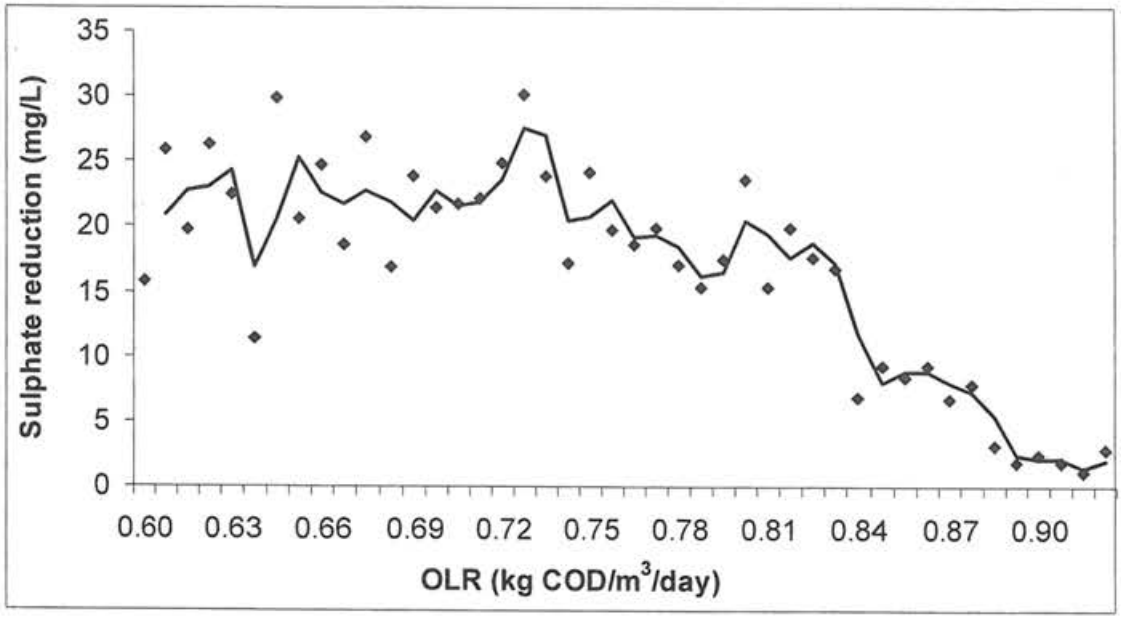



**Figure 5.5.11 Sulphate reduction during treatment phase of the HUASB reactor**

Anaerobic techniques are widely applied to remove sulphates and heavy metals from the wastewater by the sulphide precipitation process. Using the tannery wastewater as carbon source about 60-80% sulphate removal from the total feed level of 1800 mg/L was reported by Boshoff *et al.* (2004). Tuppurainen *et al.* (2002) examined sulphate and zinc removal using anaerobic techniques from mine wastewater. They achieved 23-72% removal of sulphate and almost complete removal of zinc. The presence of sulphate in the wastewater containing azo dyes was reported to enhance reduction of azo dyes (Cervantes *et al.*, 2006) where the sulphide ions acted as an electron donor.

### j. Chloride

The chloride of the wastewater remained unaltered during the treatment phase of the reactor.

### k. Nutrients utilisation

The nutrients TKN, phosphate and potassium measured in the feed as well as outlet of the reactor during the treatment phase are shown in table 5.5.12. The TKN in the feed varied

from 12.9 to 17.6 mg/L while in the outlet it varied from 15.0 to 20.0 mg/L. During the stable operation period TKN was found to increase. The increase was from 13 to 20% at the normalised operation of the reactor where the OLRs applied varied from 0.60 to 0.81 kg COD/$m^3$/day; but after the OLR of 0.81 kg COD/$m^3$/day the increase in the TKN was found decreasing. The increases were 5.2, 2.5 and 1.8% only at the OLR 0.84, 0.87 and 0.90 kg COD/$m^3$/day respectively.

| OLR | TKN (mg/L) | | Phosphate (mg/L) | | Potassium (mg/L) | |
|---|---|---|---|---|---|---|
| | Feed | outlet | Feed | outlet | Feed | outlet |
| 0.60 | 14.5 | 16.9 | 4.3 | 5.3 | 28.7 | 33.2 |
| 0.63 | 17.6 | 19.9 | 5.6 | 6.8 | 26.9 | 32.5 |
| 0.66 | 14.5 | 17.5 | 5.2 | 6.4 | 25.3 | 30.7 |
| 0.69 | 12.9 | 15.0 | 5.8 | 6.8 | 29.9 | 34.0 |
| 0.72 | 17.2 | 19.4 | 4.8 | 5.9 | 27.4 | 32.2 |
| 0.75 | 17.0 | 19.6 | 5.5 | 6.6 | 25.0 | 29.7 |
| 0.78 | 16.9 | 19.5 | 5.9 | 7.1 | 26.2 | 30.0 |
| 0.81 | 16.5 | 18.9 | 6.2 | 7.3 | 24.7 | 28.4 |
| 0.84 | 16.1 | 17.0 | 7.2 | 7.7 | 28.1 | 29.4 |
| 0.87 | 17.3 | 17.7 | 6.0 | 6.1 | 26.3 | 27.7 |
| 0.90 | 15.9 | 16.2 | 5.4 | 5.5 | 26.4 | 27.5 |

**Table: 5.5.12 Nutrients utilisation during treatment phase of the HUASB reactor**

Phosphate contents in the feed wastewaters varied from 4.3 to 7.2 mg/L and in the outlet of the reactor it varied from 5.3 to 7.7 mg/L. Increase of phosphate in the range of 18.5 to 25.7% was observed at the normalised operation of the reactor. However, during the OLR 0.81 kg COD/$m^3$/day, the increase was only 8.3%; the increase was 2.7% and 2.1% for the subsequent OLRs applied. Potassium content in the wastewater showed similar trend of increase during normalised operation period as in the case of TKN and phosphate contents. The mean increase was in the range of 14.0 to 21.8%.

Since real textile wastewater was used for the study of HUASB reactor, the concentration of the nutrients differed in each batch of wastewater fed to the system. However, there

was steady and clear increase of the nutrients in the outlet of the reactor during the normalised operation. The increase of such nutrients is a usual phenomenon in any healthy anaerobic system. Mineralization of organic matters present in the wastewater by the anaerobic microbes releases such nutrients (Haandel and Lettinga, 1994). Higher increase of TKN than phosphate was also noticed. This indicates the healthy maintenance of anaerobic system.

## 5.6 Technical comparison of physio-chemical and anaerobic treatment

From the studies carried out on the physio-chemical and anaerobic treatment of textile effluent the efficiency of both of the systems is consolidated in the table 5.7.1. The pH of anaerobic treated textile effluent is near neutral, but the treated effluent from physio-chemical treatment is slightly alkaline. Removal of TSS is equally effective in both of the systems. The chloride content is not controlled by either of the systems. Sulphate increased in the physio-chemical treatment while the anaerobic system slightly reduced sulphate contents. The BOD and COD removal was high in the anaerobic system compared to the physio-chemical system. However, generation of low volume, biodegradable sludge is the major advantage in the anaerobic system.

| **Parameters** | **Physio-chemical treatment** | **Anaerobic treatment** |
|---|---|---|
| PH | Alkaline (around 9.0) | Around neutral |
| TSS | 73% removal | 73% removal |
| TDS | No removal | No removal |
| Chloride | Remains unaltered | Remains unaltered |
| Sulphate | Increased | Slightly reduced |
| BOD | 54% removal | 80% removal |
| COD | 63% removal | 75% removal |
| Alkalinity | 50% removal | Slightly increase |
| Hardness | 48% removal | No removal |
| Sludge generation | More (about 1.05 Kg/kL) | Very less (less than 10% compared to physio-chemical treatment) |

**Table 5.6.1 Comparison of physio-chemical and anaerobic systems of textile effluent treatment**

## 5.7 Summary

The HUASB reactor was started successfully using real textile effluent. The treatability study carried out for the textile effluent using the reactor revealed that such low strength textile wastewater could be treated by the system efficiently. The HUASB attained steady state condition on 135$^{th}$ day at an OLR of 0.60 kg COD/m$^3$/day. The normal operation of the HUASB reactor lasted from OLR of 0.60 to 0.81 kg COD/m$^3$/day. The VFA content varied from 90 to 111 mg/L during the stable operation period. The maximum VSS and TSS removal was 64.5 and 73% respectively. Biogas generation was maximum (566.7 mL/day) at 0.81 kg COD/m$^3$/day OLR. The HUASB system was more effective in organics removal than physio-chemical treatment in operation in the CETPs in Tiruppur. About 80% of BOD and 75% of COD were removed at OLR of 0.81 kg COD/m$^3$/day. Chloride was not removed by anaerobic treatment. Unlike the physio-chemical treatment the sulphate content was slightly reduced by the anaerobic system. The anaerobic system was ineffective in controlling the alkalinity of the wastewater. Nutrients such as TKN, phosphate and potassium increased due to mineralisation of organic matter present in the wastewater. Low generation of organic sludge is an added advantage of the anaerobic system of wastewater treatment.

# 6. ECONOMICS OF TEXTILE WASTEWATER TREATMENT

## 6.1 General

Small scale industries provide enormous employment, promote decentralized industrial development, are flexible to emerging demands and thus play a major role in Indian economy. However, they are also among the biggest polluters (Agarwal, 2002). Clusters of dyeing and bleaching units in Tiruppur have led to serious water and ground water pollution and environmental degradation. Several public interest litigations, public protests and verdicts from the courts of judicature in past few years resulted in severe enforcement of pollution control laws and more stringent norms. The primary effluent treatment facilities established in Tiruppur in 1999 and subsequent up-gradation of those facilities in later years are result of verdicts of the Courts on several PILs by the farmers of affected areas and NGOs. A large amount of money is also invested in Tiruppur. Nevertheless, the pollution problems in Tiruppur still remains challenging. This chapter revisits the economics of textile wastewater treatment in Tiruppur. The relevant data was collected directly from the operating facility or the association of the treatment facilities. Relevant data for anaerobic treatment of textile wastewater was collected from available literatures.

## 6.2 CETP concept

The concept of Common Effluent Treatment Plant in India was promoted by the Ministry of Environment and Forest to treat wastewater generated by a large number of small and medium scale industries by way of collective effort. It was expected to achieve an end of the pipe treatment with lower costs that could be afforded by individual small scale units engaging professionally trained personnel. The CETP concept also facilitates easy enforcement of pollution laws and monitoring by competent authorities. By the organized treatment disposal of treated wastewater and sludge in a scientific manner could be achieved and the reusability of wastewater could be encouraged. First time CETP in India was constructed in 1985 in Jeedimetla near Hyderabad in Andra Pradesh to treat wastewater from pharmaceuticals and chemical industries. This was followed by several CETPs in Gujarat, Madhya Pradesh, Maharastra and Tamil Nadu.

## 6.3 Capital investment of the CETPs in Tiruppur

Eight CETPs were established in Tiruppur in 1999 with an investment of about Rs 38.75/- crores (Table 6.3.1). These CETPs cater the need of 292 dyeing and bleaching units. Remaining 437 textile processing units established Individual Effluent Treatment Plants (IETPs) expending about Rs. 50/- crores. The IETPs were established using own funds from individual textile processing units. The CETPs were designed to treat 41 MLD of wastewater and the IETPs took care of around 60 MLD. The CETPs schemes were aided by the state and central governments by subsidies amounting to 50% of the project cost. Large number of industries who failed to comply with the directions of TNPCB and the honourable High Court of Madras in establishing the effluent treatment facilities were forced to shut operation.

| Name of the CETP | Designed capacity (MLD) | Capital investment (Rs in Lakhs) |
|---|---|---|
| Angeripalayam CETP | 8.50 | 850 |
| Veerapandi CETP | 10.00 | 720 |
| Chinnakarai CETP | 5.00 | 500 |
| Andipalayam CETP | 4.50 | 500 |
| Mannarai CETP | 4.20 | 400 |
| Kasipalayam CETP | 4.00 | 400 |
| Kunnangalpalayam CETP | 3.69 | 380 |
| Manickapuram pudur CETP | 1.60 | 125 |
| **Total** | **41.49** | **3875** |
| Individual ETPs | 60.00 | 5000 |
| **Total** | **101.49** | **8875** |

***Source: Dyers Association of Tiruppur***

**Table 6.3.1 CETPs with designed capacity and capital investment established in Tiruppur during 1999**

## 6.4 Operation and maintenance cost

The operating cost includes the cost of chemicals, power, manpower, maintenance and administration which was met by the industries. Since the primary treatment did not

eliminate the damage caused to the environment totally the industries are further liable to pay the damage cost.

### 6.4.1 Primary treatment

The primary treatment systems in all CETPs were based on technology of physio-chemical treatment methods. The processes adopted in general were coagulation and flocculation followed by filtration. Minor variations are seen in individual CETP operation. Some of the CETPs applied chemical oxidants to remove trace organics before disposal. Operation of the physio-chemical systems required tonnes of chemicals, mainly calcium hydroxide (for adjusting the pH), ferrous sulphate (for effective coagulation), polyelectrolyte (for enhancing flocculation) and oxidants (for removing trace organics). The table 6.4.1 shows the chemicals used for the primary treatment of wastewater in the studied CETP.

| Year | Quantum of effluent treated (Million litres) | Quantity of chemicals used (MT) | | |
|---|---|---|---|---|
| | | Calcium hydroxide | Ferrous sulphate | Ferric chloride |
| 2002 | 2834 | 1279 | 843 | -- |
| 2003 | 2726 | 1027 | 1027 | -- |
| 2004 | 3067 | 1724 | 1300 | -- |
| 2005 | 2375 | 1633 | 444 | 1139 |
| 2006 | 1953 | 1521 | 904 | -- |

**Table 6.4.1 Chemicals consumption for the primary treatment of the textile effluent in the CETP**

In the CETP that was closely examined during the present study, the energy consumption was about 250 KW for the operation of pumps and motors. About 35 people were employed to operate and maintain the plant. The operation and maintenance cost incurred during study period is shown in the table 6.4.2. Cost of the chemicals is the major expenditure in the physio-chemical treatment. The estimated cost for treating the entire effluent generated in Tiruppur is almost 10 times more than the values shown in the table 6.4.2, which is specific for the CETP under study.

| Year | Chemicals | Power | Repairs, maintenance & administration | Manpower | Total |
|---|---|---|---|---|---|
| 2002 | 97 | 47 | 26 | 12 | 182 |
| 2003 | 109 | 44 | 15 | 12 | 180 |
| 2004 | 113 | 42 | 39 | 12 | 206 |
| 2005 | 99 | 39 | 71 | 13 | 221 |
| 2006 | 92 | 42 | 79 | 17 | 229 |

**Table 6.4.2 Operation and maintenance cost (Rs in Lakhs, 10 MLD capacity) for the physio-chemical treatment employed in the CETP**

The operation and maintenance cost per kilolitre of effluent treated is given in the table 6.4.3. The average cost for the treatment of textile wastewater by the physio-chemical methods was around to Rs. 9.00/kL of wastewater. However, this treatment as discussed earlier does not satisfy the norms prescribed for disposal into the inland surface waters by the pollution control board.

| Chemicals (Rs/kL) | Power (Rs/kL) | Repairs, maintenance and administration (Rs/kL) | Man power (Rs/kL) | Hazardous waste disposal (Rs/kL) | Total (Rs/kL) |
|---|---|---|---|---|---|
| 4.00 | 1.70 | 1.95 | 0.50 | 0.81 | 9.00 |

**Table 6.4.3 Operation and maintenance cost of the textile wastewater treated in CETP by the physio-chemical method**

### 6.4.2 Cost of sludge disposal

As noted earlier elsewhere, the sludge from the textile effluent treatment facilities is classified as 'Hazardous Waste' as per the Hazardous Waste (M & H) Rules 1986, which makes it inevitable to find and adopt an appropriate method to dispose the sludge safely. Secured landfills are widely known to be a suitable method for the purpose. Sludge generated by and large by the physio-chemical method in Tiruppur is about 1.2 Kg/kL effluent (Baladhandapani and Azeez, 2004b). So far there is no central facility in Tiruppur for disposal of the sludge generated by the treatment facilities. To address such issues an association of the CETPs in Tiruppur was formed in 2001 named 'Federation of Common Effluent Treatment Plants–Tiruppur'. The association identified few potential sites for disposal of the sludge, such as abandoned quarries located in and around

Tiruppur. The association entered into an agreement with a consulting firm to safely dispose the sludge in the landfills developed in abandoned quarries. Rate for the disposal of sludge in the secured landfill developed in an abandoned quarry as per the agreement was Rs 720.00/MT of sludge. The disposal cost calculated for the sludge would be Rs 0.90/kL of effluent treated. Further Rs 2.90/- per tonne of sludge per kilometer will be charged towards transport. The money required for disposal of the entire volume of sludge generated from the date of commissioning of the effluent treatment facilities is shown in the table 6.4.4. The sludge generation by the entire effluent treatment facilities operating in Tiruppur is 10 times more than the quantum of sludge shown in the table 6.4.4, and the disposal cost would be 10 fold the cost shown in the table 6.4.4.

| Year | Qty. of sludge generated (MT) | Expected cost of sludge disposal (Rs in lakhs) |
|---|---|---|
| 1999-2001 | 10201 | 75.0 |
| 2002 | 3117 | 22.9 |
| 2003 | 2999 | 22.0 |
| 2004 | 3374 | 24.8 |
| 2005 | 2613 | 19.2 |
| 2006 | 2148 | 15.8 |

**Table 6.4.4 Expected cost for disposal of the sludge generated in the CETP**

## 6.5 Environmental damage cost

The Loss of Ecology Authority in 2003 examined the impacts of the industrial wastewater in the Noyyal river basin and Amaravathy river basin. The affected areas in these river basins are shown in the table 1.1. About 85946 hectares of land of 71 villages of Noyyal river basin are affected by the discharge of textile wastewater from the Tiruppur industrial cluster. The authority assessing loss of agriculture in the affected area of Noyyal river basin awarded Rs 108/- crores as compensation to the farmers. Upon appeal from the industries, the amount was reduced to Rs 24/- crores. This amount was to meet the loss upto the year 2004. The High Court upon hearing PILs directed the industries to pay another Rs 12/- crores for the loss incurred during 2005, 2006 and 2007.

Besides, the Supreme Court of India issued directions to the processing units to deposit Rs. 25/- crores meant to environmental damage caused by the industries.

As noted earlier the Orathupalayam Dam, located about 30 Km downstream of the river Noyyal from Tiruppur, receives continuous discharge of textile effluents and sewage from Tiruppur and upstream urban centres resulting in severe water pollution and siltation. In 2001 as a mitigation measure, the Public Works Department, Government of Tamil Nadu, proposed to clean and desilt the reservoir, at an estimated cost of Rs 12.5/- crores. This expenditure will have to be shared by the processing units based on their respective pollution load.

## 6.6 Upgradation of CETPs and IETPs to achieve Zero Liquid Discharge

From our study on the effectiveness of established physio-chemical treatment system it is found that the above mentioned technology of treatment fails miserably to control many parameters in the wastewater; the treated wastewater did not meet the standards fixed by pollution control authority. Upon hearing the PILs on regard of disposal of such wastewater, the honourable High Court of Madras issued directions to the dyeing and bleaching units to stop discharge of wastewater to the river. The processing units were prepared to establish the Zero Liquid Discharge (ZLD) system to stop release of wastewater from the CETPs and IETPs. Additional 12 CETPs were established in Tiruppur aiming to achieve ZLD. The table 6.6.1 provides the details on the CETPs, their designed capacity and capital investments (Source: Dyers Association of Tiruppur)

### 6.6.1 Treatment scheme and capital cost for ZLD systems in Tiruppur

The CETPs establishing ZLD system in Tiruppur selected different pre-treatment technologies. Nine of the CETPs in Tiruppur opted the activated sludge process, while four of the CETPs have chosen the oxidation and reduction technology by chlorine gas and sodium metabisulphite (SMBS) followed by chemical precipitation. The pre-treatment is followed by filtration. Reverse Osmosis (RO) system is used to desalinate the wastewater. The reject from the RO will be evaporated by mechanical evaporators. The

individual effluent treatment plants have chosen different pre-treatment systems such as physio-chemical system using hydrated lime and coagulants followed by activated sludge process and ozone treatment. The overall scheme is to treat and recover the water and salt in reusable quality to be used in the processing units. As noted earlier 8 CETPs were existing since 1999 and 12 new CETPs were initiated during 2005-2006 to take care of the effluent, totally 105 MLD generated from 553 processing units. Besides, 152 units established individual ZLD system to manage their own effluents. The capital cost in CETPs is met by bank loans upto 80% and the balance as contributing by the processing units.

| S.No | Name of the CETP | Old /New | No. of member units | | Designed Capacity (MLD) | Capital Investment (Rs in Crores) |
|---|---|---|---|---|---|---|
| | | | Dyeing | Bleaching | | |
| 1 | Murugampalayam CETP | New | 47 | 20 | 11.00 | 89.20 |
| 2 | Veerapandi CETP | Old | 70 | 3 | 12.00 | 74.80 |
| 3 | Eastern CETP | New | 23 | 4 | 6.00 | 63.00 |
| 4 | Chinnakarai CETP | Old | 31 | - | 8.00 | 56.00 |
| 5 | Sirupooluvapatti CETP | New | 20 | 4 | 5.00 | 51.70 |
| 6 | Rayapuram CETP | New | 24 | 1 | 5.50 | 46.50 |
| 7 | Arulpuram CETP | New | 15 | 2 | 5.50 | 46.10 |
| 8 | Angeripalayam CETP | Old | 58 | 19 | 10.00 | 43.00 |
| 9 | Mangalam CETP | New | 15 | 2 | 4.00 | 40.80 |
| 10 | Kunnangalpalayam CETP | Old | 15 | 4 | 5.50 | 40.30 |
| 11 | Kuppondampalayam CETP | New | 14 | 5 | 4.60 | 38.00 |
| 12 | Kasipalayam CETP | Old | 16 | 2 | 4.40 | 31.40 |
| 13 | Karaipudhur CETP | New | 19 | 6 | 4.50 | 27.50 |
| 14 | Mannarai CETP | Old | 19 | 10 | 4.20 | 24.50 |
| 15 | Manickapurampudhur CETP | Old | 9 | 1 | 2.50 | 23.60 |
| 16 | Andipalayam CETP | Old | 20 | - | 4.01 | 23.00 |
| 17 | Kallikadu CETP | New | 12 | - | 3.00 | 22.10 |
| 18 | S. Periapalayam CETP | New | 7 | - | 1.50 | 14.20 |
| 19 | Park CETP | New | 7 | - | 2.00 | 12.50 |
| 20 | Vettuvapalayam CETP | New | - | 9 | 1.50 | 6.00 |
| **Sub total** | | | **441** | **92** | **104.71** | **774.20** |
| 21 | Individual ETPs | Old | 152 | - | 25.00 | 200.0 |
| **Total** | | | **685** | | **129.71** | **974.20** |

**Table 6.6.1 The CETPs in Tiruppur establishing ZLD system**

The capital cost of different pre-treatment systems is discussed in the chapter 6.6.2. The capital cost RO system varies to Rs. 1 - 1.5/- crores for treatment of one MLD of textile wastewater. The capital investment for the mechanical evaporators is estimated around Rs. 10 - 13/- crores to handle one MLD of the RO rejects.

### 6.6.2 Cost analysis of anaerobic system and comparison between different pre-treatment options

The pre-treatment system has to facilitate the textile wastewater to meet the quality requirements to feed the RO system. As discussed earlier, the existing physio-chemical treatment could not meet the standards required to feed the RO system and would also generate tonnes of hazardous waste. That makes it essential to have an improved pre-treatment system in place before using the RO technology for treatment of the wastewater. The table 6.6.2 provides a comparison of the different pre-treatment options and their cost. The capital and running cost of anaerobic system greatly depends on volume of the plant, the nature of wastewater and the management skills. The capital cost for the 5 MLD HUASB plant treating textile wastewater is estimated Rs.70 millions with the scheme of treatment as shown in the figure 7.2.1.

| Pre-treatment options | Capital cost for 5 MLD pre-treatment plant (Rs) | Operation and maintenance cost (Rs/kL) | | | |
|---|---|---|---|---|---|
| | | Chemicals | Power | Man power & maintenance | Total |
| Enhanced physio-chemical treatment | 90 Million | 7.00 | 4.00 | 2.00. | 13.00 |
| Activated sludge process | 80 Million | 6.00 | 5.00 | 3.00 | 14.00 |
| Oxidation and Reduction | 100 Million | 15.00 | 10.00 | 5.00 | 30.00 |
| Anaerobic treatment | 70 Million | 2.50 | 3.50 | 2.00 | 8.00 |

**Table 6.6.2. Pre-treatment options and their costs for the textile wastewater treatment**

The operation and maintenance cost for the pre-treatment varies according to the type of system chosen. The operation and maintenance cost for the activated sludge process is Rs. 14.00/kL of wastewater. The oxidation and reduction by chlorine gas and SMBS

costs about Rs 30.00/kL. The estimated cost by the anaerobic system of treatment is Rs 8.00/kL. The anaerobic pre-treatment system is among the least cost intensive in terms of both capital and recurring cost. The CPCB (2007) has shown that the cost for the pre-treatment of coagulation and flocculation using hydrated lime, iron salts and polyelectrolyte followed by sand filtration and ozone treatment was Rs 13.00/kL. Scott and Ollis (1995) have shown that capital and operating cost for the biological process are much lower than the ozonation and advanced oxidation technologies and are 5 to 20 and 3 to 10 times lower respectively. The capital investment for 4000 KLD treatment plant for food processing wastewater was 1.3 million dollars where the combined biological treatment scheme comprising of anaerobic digestion and aerobic biological filters were employed (Defrawy and Shaalan, 2003).

## 6.7 Cost analysis of recovery and reuse of water and salt

The projected cost of operation and maintenance of reverse osmosis and RO reject treatment systems like mechanical evaporation and nanofiltration for recovery and reuse of textile effluent at the CETPs is given in the table 6.7.1. All the CETPs in Tiruppur had planned to install mechanical evaporator to manage the reject from RO from a single vendor whose system works in vacuum and is known to use lesser quantity of steam compared to the conventional thermal evaporators.

| Utilities | Reverse osmosis (Rs/kL) | Reverse osmosis reject management (Rs/kL) | |
|---|---|---|---|
| | | Mechanical evaporation | Nanofiltration |
| Chemicals | 2.00 | 2.00 | 0.5 |
| Power | 10.00 | 51.00 | 2.00 |
| Steam | --- | 53.00 | --- |
| Manpower and maintenance | 3.00 | 10.00 | 1.00 |
| **Total** | **15.00** | **116.00** | **3.50** |

**Table: 6.7.1 Operation and maintenance cost of RO and RO reject management systems**

The recurring cost for the treatment of textile effluent in the reverse osmosis system is Rs 15.00/kL. The reject from RO constitutes about 10 - 20% of feed wastewater that

contains high dissolved solids which is being managed by the mechanical evaporator and/or nanofiltration system. The recurring cost is estimated to Rs 116 /kL of RO rejects by the mechanical evaporator while using the nanofiltration system costs about Rs 3.50/kL. The brine solution recovery from the nanofiltration system is less than 50% whose reuse is uncertain because of impurities and inconsistent quality of brine solution; while the remaining portion has to be evaporated in the mechanical evaporator. The overall estimated recurring cost including the interest and principal for capital cost for the treatment of textile wastewater in ZLD system using the different pre-treatment options is given in the table 6.7.2.

| Pre-treatment methods | Operation and maintenance cost ZLD plant (Rs/kL) | Interest and principle for capital cost (Rs/kL) | Total cost of textile effluent recovery and reuse (Rs/kL) |
|---|---|---|---|
| Oxidation & Reduction | 60 | 30 | 90 |
| Activated sludge process | 40 | 35 | 75 |
| Anaerobic system | 30 | 20 | 50 |

**Table 6.7.2 Recurring cost of textile wastewater recovery and reuse adopting the different pre-treatment options**

On computing the above data the overall operation and maintenance cost for the entire textile wastewater ZLD plants to be established in Tiruppur is estimated to Rs 102 lakhs/day. Assuming that about 95% water and 80% of Glabour's salt could be recovered from the textile wastewater that contains about 8000 ppm of dissolved solids, the expected returns are as water about 62 lakhs/ day and as Glabour's salt about 100 lakhs/day totaling Rs. 162 lakhs/day indexing the present cost of water @ Rs 50/kL and Glabour's salt @ Rs 12/Kg. The net saving of about Rs 60 lakhs/day could be expected on recovery and reuse of water and salt from the textile effluents generated in Tiruppur.

The operating cost for recovery of textile effluents in Indian conditions is reported by many researchers. The recurring cost for the operation and maintenance of RO system will be around Rs 15.00–20.00/kL of wastewater using the ultrafiltration, RO I & II (CPCB, 2007) while the recurring cost for treatment of textile wastewater by the I$^{st}$ stage

and II$^{nd}$ stage RO systems alone was Rs 10.00/kL. Ranganathan *et al.* (2007b) reported recurring cost for the reusable water from the textile wastewater to be around Rs 60-80/kL and the cost for evaporation of RO reject was Rs 114.30/kL. The overall cost was Rs 41.53/kL when the pre-treatment is physio-chemical treatment (CPCB, 2007).

## 6.8 Cost of fresh water from river

Pure water is a major raw material for the processing units. During 90s when the industries started to bloom they used ground water from own bore or dug wells. The increase in water requirement and consequent discharge of effluent resulted in ground water contamination making it unfit for industrial usage. The processing units then started to buy water from neighbouring agricultural areas. More industrial demand of water considerably hiked the cost of water. The cost of water during 2003 was Rs 50/kL. The farmers preferred to sell water to the processing units rather than going for agriculture for the higher earnings. Uncontrolled exploitation resulted in ground water depletion, damage to seasonal and permanent crops and inadequate water availability for household uses. Frequent agitations especially in summer disrupted supply of water to the processing units. Along with other issues, accidents and damage to property / road became rampant by over speeding tankers carrying water.

In 2004 the New Tiruppur Area Development Corporation Limited was started to take care of water supply to the processing units from Cauvery river at a capital investment of around Rs 1000/- Crores. Presently, the cost of the river water in Tiruppur is around Rs 50/kL.

## 6.9 Cost analysis of textile processing using river water and recycled water and salt

Assuming a minimum of 95% of effluent and 80% of salt to be recovered by the ZLD plants, the cost analysis of dyeing one Kg of hosiery cloth is given in the table 6.9.1. Here the highest cost of recycling among the different pre-treatment systems is taken into consideration. The estimated cost of production in softflow dyeing machines using the recycled water and salt is about 3.8% less compared to the dyeing using the river water.

The cost of production is even less to about 9.8% when adopting the anaerobic system as the pre-treatment. Though cost of production in conventional dyeing machines using recycled water and salt is lesser than the river water, it is about 23% more compared to softflow dyeing machines. Hence, it is not economical to use conventional winch dyeing machines to carry out dyeing using either river water or recycled water. From the table 6.9.1 it is apparent to conclude that the implementation, and operation and maintenance of wastewater recovery and reuse system for the textile wastewater will not have any negative financial implication on the dyeing units.

| Utilities | Modern softflow machines | | | Conventional winch machines | | |
|---|---|---|---|---|---|---|
| | Usage | River water (Rs.) | Recycled water & salt (Rs.) | Usage | River water (Rs.) | Recycled water & salt (Rs.) |
| Water | 100 ltrs | 5.00 | 0.40 | 150 ltrs | 7.50 | 0.60 |
| Power | 0.3 KWH | 1.50 | 1.50 | 0.1 KWH | 0.50 | 0.50 |
| Steam | 5 Kg | 5.00 | 5.00 | 7.5 Kg | 7.50 | 7.50 |
| Dyes | 40 g | 20.00 | 20.00 | 40 g | 20.00 | 20.00 |
| Wetting agent | 5 mL | 1.40 | 1.40 | 7.5 mL | 2.10 | 2.10 |
| Lubricant | 10 mL | 0.60 | 0.60 | 15 mL | 0.90 | 0.90 |
| Caustic soda | 25 g | 0.80 | 0.80 | 37.5 g | 1.20 | 1.20 |
| Stabiliser | 5 mL | 0.30 | 0.30 | 7.5 mL | 0.45 | 0.45 |
| Hydrogen peroxide | 30 mL | 1.30 | 1.30 | 45 mL | 1.95 | 1.95 |
| Hydrogen peroxide Killer | 5 mL | 0.40 | 0.40 | 7.5 mL | 0.60 | 0.60 |
| Acetic acid | 20 mL | 1.00 | 1.00 | 30 mL | 1.50 | 1.50 |
| Glabour's salt | 600 g | 7.20 | 1.40 | 900 g | 10.80 | 2.16 |
| Soda ash | 200 g | 4.20 | 4.20 | 300 g | 6.30 | 6.30 |
| Soaping agent | 20 mL | 1.90 | 1.90 | 30 mL | 2.85 | 2.85 |
| Fixing agent | 10 mL | 1.30 | 1.30 | 15 mL | 1.95 | 1.95 |
| Softening agent | 10 mL | 0.70 | 0.70 | 15 mL | 1.05 | 1.05 |
| Others (Man power, transport, etc.,) | | 10.00 | 10.00 | | 10.00 | 10.00 |
| Effluent treatment charges | | 0.90 | 9.00 | | 1.35 | 13.50 |
| Environmental damage cost | | 1.00 | 1.00 | | 1.35 | 1.35 |
| **Total (Rs/ Kg of hosiery)** | | **64.50** | **62.05** | | **79.85** | **76.26** |

**Table 6.9.1 Cost analysis of dyeing of hosiery in softflow and winch dyeing machine using river water and recycled water and salt**

## 6.10 Discussions

The increased public awareness, laws and directives from judiciary and Pollution Control Board forced the processing units in Tiruppur to adopt ZLD system to abate the pollution arising during their operation. Further, the processing units were directed to compensate the damage due to pollution. The projected abatement cost by the ZLD system ranged from Rs 50 to 90/kL depending on type of pre-treatment system. The present cost for the primary treatment of textile wastewater is Rs 9.00/kL while the cost for raw water is Rs 50/kL. On accounting overall cost of recycling of water and salt the processing units are likely to be benefited by savings in cost of production. In addition the issues on water and groundwater pollution caused by the textile processing units will be prevented; the river water resources could be saved. Recycled water can satisfy most water qualities, as it is adequately treated to ensure water quality appropriate for the reuse in the dyeing units. However, the environmental damage caused by the prolonged discharge of wastewater from processing units will exist as long as the pollutants remain in the system and exhibit impacts. Many pollutants present in textile effluents are recalcitrant in nature and they exhibit stock characteristics. The environmental damage in any period will be a function of accumulated pollutants. The processing units have to pay the damage cost as long as the impacts of the pollutants occur. The industries can minimize the damage cost by earlier implementation and effective management of ZLD system by preventing the disposal of effluents.

## 6.11 Summary

The treatment cost by physio-chemical treatment employed in the effluent treatment facilities in Tiruppur was around Rs 9.00/kL of textile wastewater. However, the efficiency of this treatment has to be enhanced to meet the standard to feed to the RO setups. The projected operation and maintenance cost by the anaerobic pre-treatment is Rs 8.00/kL. The anaerobic treatment is more effective in removing the organics than the physio-chemical treatment which is pre-requisite for the RO systems. The abatement cost of ZLD system by the anaerobic system as the pre-treatment is of the least cost among the different pre-treatment options. The capital and operation and maintenance cost of ZLD system is economical to the textile processing units in view of getting water and salt. The cost of production is 3.8 % less using recycled water compared to use of river water.

# 7. RECOMMENDATIONS

The textile wet processing industries are required to recover water and salt from the wastewater in order to avoid water and ground water pollution and related consequences. The pre-treatment of textile effluent is important in meeting the requirement of the effluent to feed to RO systems and thereby achieving zero effluent discharge. The efficiency and life of reverse osmosis membranes are highly susceptible to the feed wastewater characteristics. So an enhanced pre-treatment of textile wastewater is required to enable operation of RO system efficiently. More over the dyeing and bleaching units are in a position to minimise cost of production to survive the international competition of textile trade. So, cost effective and technically efficient pre-treatment is necessary for the textile wastewater recovery and reuse.

## 7.1 Waste minimization

Waste minimization at the source is an effective approach offering several benefits to the industries that adds up in saving the resources and reduction of cost of production. The low MLR Softflow dyeing machines require relatively less water, salt and other chemicals compared to the conventional winch dyeing machines; the waste generation is low subsequently. The low salt dyes require relatively less salt addition in the dyeing operation. This will result in generation of lower pollution load.

## 7.2 Load based norms for the wastewater disposal

Wastewater from the various industries in India and through out the world is discharged to the nearby water bodies either treated or untreated. Water recovery from wastewater is a recent approach to minimize environmental impacts of industries. The norms fixed for disposal of such wastewater is based on the concentration of pollutants. In Tiruppur it is revealed that the surface water and ground water pollution caused by the textile industries is by massive loadings of pollutants. The wastewater is of low strength in terms of pollutants especially organics. Hence it is timely to frame appropriate norms for the disposal of wastewater based on pollutants load and not exclusively based on the

concentration of pollutants. The carrying capacity of receiving water bodies/land should be also considered while framing norms based on the pollutants load.

## 7.3 The scheme of zero effluent discharge system for textile wastewater

It appear anaerobic treatment of textile wastewater is an apparently appropriate option to treat textile wastewater to polish it and achieve the requirements to feed the RO systems in the most economical and environmentally friendly way. It is understood that the textile azo dyes are cleaved into aromatic amines resulting in reduction of colour by anaerobic system. However, the aromatic amines are suspected carcinogens. The amines are susceptible to mineralization under aerobic system of treatment (Tan *et al.*, 2003; Stolz, 2001).

From our study it is found that the BOD level after the anaerobic treatment was in the range of 35-50 mg/L and COD was 140-229 mg/L. Operation of aerobic system such as activated sludge process with this low organic load is not easy. However, such trace organics can be easily removed by ultrafiltration or activated carbon adsorption. An appropriate treatment scheme recommended for the textile wastewater and recover water and salt is as shown in the figure 7.2.1.

The recommended scheme of zero effluent discharge (ZED) consists of equalisation followed by neutralisation of wastewater before feeding to the HUASB reactor. The outlet of the reactor is filtered to remove any suspended impurities by dual media filter. The filtered wastewater is fed to an ultra-filtration system that removes most colloidal particles and organics. Two stage reverse osmosis system enables separation of salts and water. The permeate is reused in the processing house. The reject is evaporated by mechanical evaporator. The condensate from the evaporator could be reused by the processing units. The salt in the concentrate liquor from the evaporator is crystallized to salt of acceptable quality that also could be reused in the processing units. The biomass from the UASB can be used as manure in agriculture. Nevertheless, the suitability of the biomass for the purpose could be decided after ascertaining the absence of suspected carcinogenic amines formed during the anaerobic treatment and that they are unlikely to

contaminate natural systems after agricultural use. Appropriate land filling is also an acceptable option to dispose such biomass.

## 7.4 Advantages of proposed scheme

1. The recommended system solves the problem of hazardous waste by physio-chemical treatment where hydrated lime and iron salts are used to remove the organics. The sludge from the HUASB is organic in nature, the volume is less than 10% of physio-chemical treatment, and even less compared to the activated sludge process.

2. The operation and maintenance cost of pre-treatment, recovery and reused system is significantly low among several other pre-treatment systems.

3. This system needs significantly less number of electrical and mechanical components and require low degree of maintenance.

4. The energy requirement is low compared to other options available for textile wastewater treatment.

5. This system requires lesser space, which is a major advantage in the case of developing cities, such as Tirupur, where space is expensive.

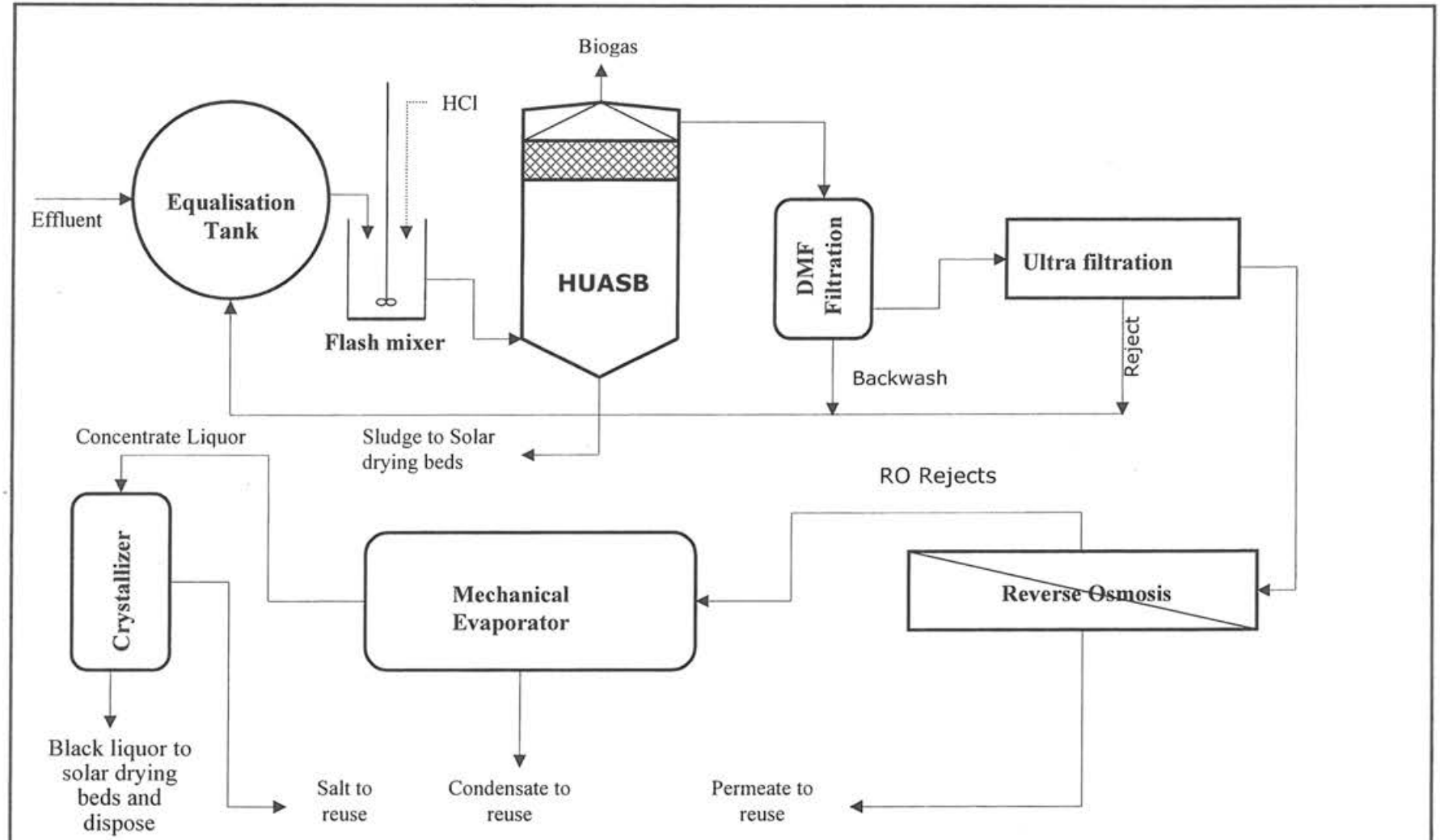



**Figure 7.2.1 Schematic diagram of recommended zero effluent discharge system for the textile wastewater**

## 8. SUMMARY AND CONCLUSIONS

The bulk of environmental damages in the river Noyyal and river basin are caused by incessant disposal of effluents from textile wet processing industries functioning in Tiruppur. The present study documents various issues concerning water pollution in Tirupur such as, wastewater generation and disposal, consequences of the disposal of the trade effluent to the river, the effects of azo dyes and other chemicals used in the processing, and various methods for treatment of the wastewater..

Characterization of the effluent received in a CETP treating the textile wastewater was carried out during 2002 to 2006. The study revealed that the alkaline wastewater could be classified as "low strength wastewater" in terms of organics. The COD values were in the range of 384 to 738 mg/L. BOD values were in the range of 92 to 258 mg/L. The TSS values varied from 187 to 372 mg/L. The total dissolved solids content of the wastewater is the burning issue in Tiruppur. The range of TDS varied from 5547 to 8419 mg/L. Chloride content varied from 3003 to 4461 mg/L while sulphate varied from 372 to 675 mg/L. The hardness of the textile wastewater ranged 530 to 927 mg/L. The total alkalinity was in the range of 679 to 1120 mg/L. Phenolic compounds were found in the range of 0.06 to 0.79 mg/L. 38 samples of raw effluent and 40 samples of equalized effluent showed BDL for phenolic compounds. Oil and grease contents found in the textile wastewater ranged from 1.95 to 13.56 mg/L. The heavy metals such as total chromium, copper, zinc, nickel and cadmium were in traces in some of the samples collected. The pollution load from the industries in Tiruppur is alarming. It is noticed that the pollutants concentration is increasing year by year.

The study also examined the effectiveness of treatment of textile wastewater by the physio-chemical treatment employed in a CETP. The physio-chemical treatment consuming tonnes of chemicals such as hydrated lime, ferrous sulphate and polyelectrolyte removed 74% of TSS, 54% of BOD and 63% of COD from the wastewater. The pH increased after the physio-chemical treatment. TDS and chloride constituents of the textile wastewater remained uncontrolled. Sulphate increased after the physio-chemical treatment due to the solubility of sulphate originating from the use of ferrous sulphate. About half of hardness and alkalinity were removed from the wastewater. The pH, TSS, COD values were within the norms fixed by TNPCB in most

of the samples. The BOD value in the treated wastewater exceeded the norm. TDS and chloride contents present in the treated wastewater were manifold higher than the norms stipulated by TNPCB. However, sulphate, oil and grease, phenolic compounds and heavy metals were within the norms since their presence in the untreated wastewater itself were low. The physio-chemical treatment produced massive volume of so called hazardous sludge.

As a potential alternative to the ineffective physio-chemical treatment, a lab scale Hybrid UASB reactor was constructed and the treatability study was carried out. The HUASB reactor was initiated successfully using real textile effluent. It attained the steady state condition on 135$^{th}$ day of operation at the OLR of 0.60 kg COD/m$^3$/day. The normalised operation of the reactor lasted from the OLR 0.60 to 0.81 kg COD/m$^3$/day. It was found that the anaerobic treatment was more effective in removing the organics than the physio-chemical treatment. The pH of the outlet of anaerobic reactor was neutral. The TSS removal was 73% while the VSS removal was 64.5%. The BOD and COD removals were upto 80 and 75% respectively. Highest biogas generation was 566.7 mL/day recorded at the OLR of 0.81 kg COD/m$^3$/day. The anaerobic system was unable to control TDS and chloride like the physio-chemical treatment system. However sulphate content could be removed slightly. The sludge generation from the anaerobic system is organic in nature and its volume is very low (less than 10%) compared to the physio-chemical treatment system.

An examination of the economics of the textile wastewater treatment was also done during the study. The operation and maintenance cost for the physio-chemical treatment was around Rs 9.00/kL. The projected cost by the anaerobic pre-treatment system is Rs 8.00/kL. The wet processing units in Tiruppur are forced to install reverse osmosis system to recover water from the textile wastewater. Anaerobic treatment as the pre-treatment to RO is found to be a techno-economically viable option than the activated sludge or other oxidation methods. The projected operation and maintenance cost was Rs 30.00/kL. Recovery and reuse of textile wastewater is economically viable to the textile processing units. The cost of production using the recovered water and salt is about 3.8% less compared to the cost of production using purchased river water. Wastewater recovery and reuse is a sustainable approach and will provide tremendous environmental benefits.

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