# CHAPTER TWO : LITERATURE REVIEW

## 2.1 Rubber Product Manufacturing Industries

### 2.1.1 Background of Rubber Product Manufacturing Industries

With Malaysia's economy expected to further diversify with greater emphasis on industrialisation and development in the service sector, there appears little doubt that in the future, the role of rubber will continue to be overshadowed by other economic sectors. However, this does not indicate that the rubber industries that once played a major role in our country's development are nearing their ends. On the contrary, with the current economic downturn that is affecting the IT manufacturing industries in particular and the shifting of government's emphasis back to agriculture, rubber is expected to play a significant role in Malaysia's economic development.

In the future, rubber's contribution in the export earning will be in the form of exports of rubber-based products, rubberwood-based furniture and new speciality rubber such as those used in the engineering, marine and construction applications. Indeed, Malaysia's rubber industry has succeeded in fulfilling our government's call to enhance the downstream activities of the country's raw material. Among the natural rubber producing countries, Malaysia has been one of the successful ones in converting almost half of its rubber output into value added products. Henceforth, apart from being a major natural rubber producer, Malaysia is one of the major exporters of rubber products.

The expansion of the rubber products industry in the early years was slow and gradual. The initial post-independence period saw a change in the national policies and commitment from agriculture-based to one of manufacturing, primarily to replace imports. The industrialisation policies under the First Malaysian Plan (1965-1970) provided various incentives to promote manufacturing activities. Manufacturing of rubber products manufacturing became one of the beneficiaries of the various industrial development programs but growth was relatively slow. This industry leapfrogged to new heights in the second half of the 1980s when the demand for medical gloves escalated due to foreign demand. The upsurge happened particularly as a result of AIDS scare, and the issuance of "Universal Precautions" by the Center for Disease Control and Prevention (CDC) providing for mandatory requirement for gloves to be worn when in contact with blood and other body fluid (Liew, 2001). The rubber gloves are used as a primary barrier against the transmission and infection of AIDS and other infectious diseases cause by blood-borne pathogens. From then on, the rubber-based manufacturing sector has achieved tremendous growth within a period of less than a decade. This is due to the increasing world demand for its products. Malaysia leads the world in the dipped goods industry in volume and also quality. There are over 300 companies making a wide range of rubber products that are exported to over 60 countries (Wong, 2001).

### 2.1.2 Types of Rubber Products

There are five main groups in this sector, namely latex goods, tyres and related products, industrial and general rubber goods (IRG / GRG), footwear and rubber wood products. Each of these groups comprises different kind of products, as shown in Table 2.1 (Third National Agricultural Policy (1998 – 2010), Ministry of Agriculture Malaysia, 1998). Currently there are six main rubber product group clusters in the rubber industries, namely 1) plantations, 2) latex goods, 3) tyres and related products, 4) industrial and general rubber goods (IRG/GRG), 5) footwear and 6) rubberwood products (Ministry of Primary Industries Malaysia, 1998). Each group consists of a wide variety of products. It is noted that while the current groups are more generalised, the products for the future structure of these group cluster focus more on the value-added and high technology rubber products. For example, in the latex group, the current products are examination household and surgical gloves, latex thread, catheters, foam products and condoms. In the future structure group, the products are the high value added gloves and medical devices. There is a certain element of changes in our country's focus. In the tyres and related product group, pneumatic tyres and solid tyres, inner tubes and natural rubber (NR) retreads are produced. However, more emphasis is placed on the expansion of off-the-road tyre and high performance tyre, precured NR /synthetic rubber (SR) thread and carbon black masterbatches. In the plantation group, currently the main focus is on the products such as latex concentrates, ribbed smoke sheet (RSS), standard malaysian rubber (SMR) and rubberwood. However, in future, focus will be on the latex timber clone (LTC), speciality rubber and also the management of the plantations itself (Wong, 1999).

Export earnings from rubber products by Product Group from 1994 till June 2000 are shown in Table 2.2 (Ministry of International Trade & Industry, 2001). The data

Table 2.1 : The Current and Future Structure of Rubber Product Group Cluster

| **CURRENT** | Plantations | **Latex Goods** | **Tyres & Related Products** | **Industrial & General Rubber Goods (IRG / GRG)** | **Footwear** | **Rubberwood Products** |
|---|---|---|---|---|---|---|
|  | • Mainly Peninsular Malaysia<br>• Latex concentrates<br>• RSS<br>• SMR<br>• Rubberwood<br>• Smallholders | • Examination household and surgical gloves<br>• Latex thread<br>• Catheters<br>• Foam products<br>• Condoms | • Pneumatic tyre, solid tyres<br>• Inner tubes<br>• NR tyre retreads | • Hoses<br>• Beltings<br>• Pipings<br>• Tubings<br>• Bridge bearings<br>• General fenders | • Boots<br>• Canvas shoes<br>• Rubber shoes<br>• Sandals / slippers<br>• Footwear components | • Sawntimber<br>• Furniture<br>• Joinery / panel products |
| FUTURE | • Latex Timber Clone (LTC)<br>• Specialty rubber<br>• Estate-type management<br>• New plating areas (Sabah & Sarawak)<br>• Reorganise and consolidation of smallholders<br>• Agroforestry<br>• Rubber forest | • High value-added gloves<br>• Medical devices | • Precured NR / SR threads for export<br>• Expansion in off-the-road tyre/high performance tyre<br>• Carbon black masterbatches | • Application in :<br>– Civil engineering<br>– Electronics / electrical<br>– Marine<br>– Petroleum/gas<br>– Transportation | • Customised and fashion footwear<br>• Industrial footwear | • ODM / OBM of high quality and office furniture<br>• Specialty joinery / panel products |

Source: Third National Agricultural Policy :1998-2010, Ministry of Agriculture Malaysia (1998).

indicates that the latex goods contributed the highest income for the export of rubber products as compared to tyres, footwear and IRG/GRG. Exports of rubber products came into prominence amongst Malaysia's resource-based exports within a short span of a decade. In the 1970s quantity of exports of all types of rubber goods was rather insignificant. However, in the 1990s, it has posted a phenomenal growth to peak at RM6.49 billion in 1998, though a slight decline was recorded in 2000 (see Table 2.2).

Table 2.2 : Export of Rubber Product by Product Group, 1994 –2000

| **Year** | **Rubber Product** (Value in RM million) | | | | | | **Total** |
|---|---|---|---|---|---|---|---|
| | Latex goods | Tyres | Inner Tubes | Footwear | Industrial Rubber Goods | General Rubber Goods | |
| 1994 | 2,645.6 | 149.3 | 14.7 | 242.4 | 44.3 | 259.9 | 3,354.2 |
| 1995 | 3,103.1 | 184.4 | 14.7 | 203.7 | 52.0 | 329.4 | 3,887.4 |
| 1996 | 3,393.7 | 191.8 | 16.1 | 188.1 | 61.3 | 336.9 | 4,188.0 |
| 1997 | 3,897.3 | 164.4 | 12.6 | 198.8 | 113.7 | 426.8 | 4,611.6 |
| 1998 | 5,260.1 | 321.6 | 15.8 | 211.8 | 198.4 | 483.4 | 6,491.1 |
| 1999 | 4,738.0 | 292.6 | 15.3 | 275.1 | 196.9 | 508.6 | 6,026.5 |
| 2000 | 4,498.8 | 243.9 | 13.6 | 302.0 | 130.0 | 497.2 | 5,685.5 |

Source : Ministry of International Trade and Industry, 2001. (1USD = RM3.80)

Currently, Malaysia is the world's largest supplier of medical gloves, catheters and latex thread. The latex-based industries have expanded rapidly as the world demand for these products has been upward in recent years. Mainly latex goods and rubber gloves in particular made the impressive export performance of the industry possible. In 2000, rubber gloves topped as the country's largest rubber product export with a value of RM3, 333 million and the breakdown for the export of latex goods from January till December 2000 is shown in Table 2.3 (Malaysian Rubber Board, 2001).

Table 2.3 : Exports of Latex Goods from Malaysia, 2000

| **Latex Goods** | **Value ('000 RM)** |
|---|---|
| Surgical gloves | 827,472 |
| Household, examination and industrial gloves | 2,505,191 |
| Other articles of apparel | 153,555 |
| Ballons | 23,934 |
| Latex thread | 416,105 |
| Condoms | 60,435 |
| Catheters | 1,078 |
| Catheters, cannules and the like | 442,073 |
| Finger stalls | 7,184 |
| Teats and soothers | 2,517 |
| Other hygienic and pharmaceutical rubber articles | 26,812 |
| Foam products | 32,480 |
| TOTAL | 4,498,836 |

Source : Malaysian Rubber Board (2001).

According to the Malaysia Statistic Department, 2000, the rubber gloves industry consumed 190,703 tonnes of natural rubber i.e. approximately 55% of the total natural rubber (NPC, 2000). Table 2.4 indicates the natural rubber consumption in five main categories of rubber product, by product sector in Malaysia in 2000 (MARGMA, 2001).

Table 2.4 : The natural rubber consumption in five main categories of rubber product, by product sector in Malaysia in 1998.

| **Products** | **Total Consumption (tonnes)** |
|---|---|
| Latex products (i.e. rubber gloves, rubber thread, catheters and other latex products) | 259,266 |
| Tyres and tubes | 52,251 |
| Manufacture of other rubber products i.e. rubber compounds, rubber bands and rubber sheeting | 19,668 |
| Other rubber products | 6,229 |
| Footwear | 3,145 |
| All other manufacturing industries consuming natural rubber | 4,251 |
| **Total** | **334,810** |

Source : MARGMA (2001).

The major export markets for Malaysian latex goods are United States of America, European countries, Japan and Australia. In the first quarter of 2001, exports to US was valued at RM367, 059.90, followed by exports to United Kingdom with a value of RM68, 879.80. Japan is the third largest importer of rubber gloves (MARGMA, 2001).

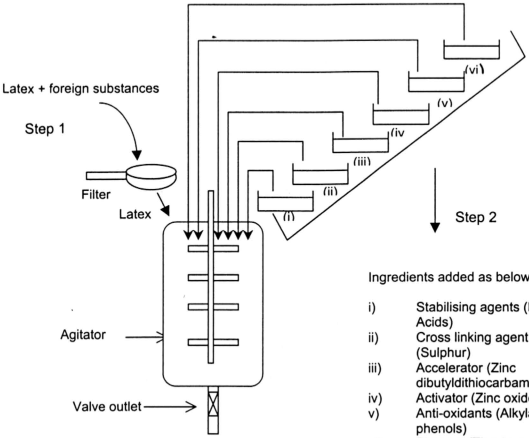
## 2.2 Rubber Gloves Manufacturing: Processes Involved

### 2.2.1 Definition of Latex

The most important component in the rubber gloves manufacturing is the latex concentrate. Latex itself is the milky substance that many plants exude when they are cut. However, it is commonly associated with the natural rubber (NR) tree, *Hevea braziliensis*. Latex is a mixture of the rubber phase and non-rubber phase and it has 36% solid content (Subramaniam, 1993). The rubber phase contains hydrocarbon chains, lipid and protein, while the non-rubber phase is made up of bottom fraction such as dirt, dispersing matter and microbes, serum and alpha-carotene pigment particles known as particle-frey Wyssling. These particles produce the yellowish and reddish colour in latex.

NR latex is harvested from the *Hevea* tree by a process of shallow cuts in the bark, called tapping. As the latex coagulates on exposure to air, the tapped liquid is preserved with 0.7% ammonia on latex by weight (Nordin and Lim, 1999). This preserved liquid is known as latex concentrate. Preservation is an important step as it reduced the stinky smell of the natural latex and prohibits the growth of microbes on the latex itself.

The second step involved the addition of additives such as fatty acid soap (stabiliser), sulphur (cross-linking agent), zinc dibutyldithiocarbamate (accelerator), zinc oxide (activator), alkylated phenols (anti-oxidants) and titanium dioxide (pigment) into the latex concentrate in a sequence of batch operations. This step is known as latex compounding as shown in Figure 2.1. By introducing the additives into the latex, it transforms the latex into a range of materials suitable for different types of applications. The latex compound is then left to mature for one day before sending to latex-based manufacturers such glove manufacturers for the manufacturing of rubber gloves (RRIM, 1988).



Ingredients added as below orders:

- i) Stabilising agents (Fatty Acids)
- ii) Cross linking agent (Sulphur)
- iii) Accelerator (Zinc dibutyldithiocarbamate)
- iv) Activator (Zinc oxide)
- v) Anti-oxidants (Alkylated phenols)
- vi) Pigment (Titanium dioxide)

The above orders can be changed but it has been proven to be the most suitable formulation.

Step 3

The mixture will be kept for several hours or days, depending on the process requirement. This stage is known as MATURATION.

Figure 2.1: Latex Compounding Process

### 2.2.2 Manufacturing Process

*a) Dipping*

Coagulant dipping and an automatic chain drive system are often used in the rubber gloves manufacturing process. Dipping is the most important stage of the process. Heated ceramic former pre-coated with coagulant and detackifier, calcium nitrate and calcium carbonate respectively are firstly immersed into the latex compound solution to pick up a layer of coagulated latex. The calcium nitrate acts as a coagulant and causes the latex compound to coagulate over the formers, and thus formed the shape of the formers, while the calcium carbonate provides an anti-tack barrier between the rubber and formers. This will facilitate the subsequent removal of the finished gloves. Correct dipping techniques and conditions and a proper latex compound ensure a smooth and uniform thickness of latex deposit onto the formers. The dwell time is normally varied between 5 to 20 seconds.

*b) Beading*

While still in the wet gel state, the cuffs of the newly formed gloves are rolled back by rotating beading brush to form beads. Beaded cuffs give strength to the gloves as well as enhancing the ease of donning the gloves by users later.

The water-soluble substances or residues such as coagulant, soaps and serum found in the newly formed gloves will be removed through the water-leaching stage. A post-leaching step is carried out to reduce the potential allergenic effects of residual chemicals in the gloves. A sufficient time of leaching is required to obtain a good product.

Drying removes the water content in the gel to the lowest possible value as fast as possible. There are many methods of drying such as by applying direct gas heating, by use of infrared rays, by hot air or by steam. During the drying and curing stage, some of the material in the latex matrix is forced to the outer surface of the gloves. This process reduces the water-soluble extractable and calcium nitrate extractable from approximately 1.0% to 0.2% and 0.09% to 0.04% respectively according to Ansell Healthcare Inc. (Ansell Health Care, 2001).

Vulcanisation at a temperature of $100^0$C to $120^0$C for 15 to 20 min gives the product the desired strength after drying (Careplus Malaysia Manufacturing Process Page, 2001). This process involved the formation of longer polymer chains of the molecules in the latex and thus increased the strength of the gloves. Sulphur which acted as a vulcanisation agent was added in to assist in the vulcanisation process. Two other components, namely the zinc oxide and accelerator were also added to speed up the vulcanisation process.

After the drying and vulcanisation steps, the dried gloves are powdered through a step called powdering. Powdering is required to prevent the gloves from sticking after removal from the formers. Cornstarch, magnesium carbonate and calcium carbonate are some the common dusting powders used.

*b) Stripping*

The final stage of the process known as Stripping involved the removal of the finished gloves from the formers. Stripping is done either manually or semi-automatically using air-jets. Gloves when stripped from the formers are often damp from the steam, which is often trapped between the gloves and the formers. It is important that these gloves are dried thoroughly prior to the electronic testing, a step to detect defective gloves. As such these gloves must be dried through two stages of drying to ensure that the dampness and any moisture in the gloves are completely removed. Stripped gloves are subjected to further treatment offline and quality inspection before they are packed for sale in 100 pieces per box.

## 2.3 Generation of Effluent and Its Characteristics

### 2.3.1 Generation of Effluent

Through out the whole rubber gloves manufacturing process, four types of effluent are generated. Figure 1.1 shows the different sources of effluent generation in the overall process (Zaid, 1988).

Effluent A comes from the water used to clean the formers online and offline. This kind of effluent contains residual acid or detergent used to clean the formers. It is important that the formers are thoroughly cleaned before the manufacturing process starts. Presence of residuals on the formers will eventually affect the quality of the end products.

In the latex dipping stage, the coagulant-precoated formers will be dipped into the latex compound solution. A layer of coagulated latex will be formed on the formers. When this step is completed, the tank needs to be washed. The washing is usually carried out once every fortnight or every three weeks. Two types of effluent are generated from this stage. The first type (Effluent B) is the washing water used to clean the dipping tank. The second type is actually the sludge from the tank itself, formed from the sediments or residuals in the latex compound or the coagulants.

The main source of effluent (Effluent C) comes from the leaching stage. Leaching tank discharge constitutes a major source of effluent pollution. It contains pollutants, particularly water-soluble substances, leached out from the product when they are washed with water or other chemicals.

Effluent is also generated during the cleaning of latex compounding tanks. The effluent (Effluent D) contains mainly washwater from ball mill, latex containers etc. and the uncoagulated latex and sludge.

These effluents are channelled or transferred into the WWTP to be equalised and further treated chemically and biologically prior to discharging into the rivers or receiving waters (see Appendix II).

### 2.3.2 Characteristics of Effluent

Table 2.5 shows the characteristics of untreated effluent from different types of latex based industries (Zaid, 2001). It was observed that the effluent from rubber gloves and latex thread plants exhibited a high level of COD and BOD as compared to effluent generated from other industries such as catheters and condoms. The ratio of BOD to COD for the rubber gloves plant effluent varied from 0.2 to 0.7, and thus indicates that biological processes could be used to treat this type of effluent particularly in the secondary treatment.

The effluent is also relatively neutral with an average pH of 6.8. However it contains a rather high level of suspended solids (SS) as compared to effluents from factories manufacturing catheters and latex threads. The SS could be due to the compounded latex and the coagulant used in the manufacturing process. In addition, the effluent contains fairly high amount of nitrate content, which is due to the usage of calcium nitrate as a coagulant in the manufacturing process (Zaid, 1997).

A study on five examination gloves factories effluent was carried out by Zaid (1988), and it was found that the effluent exhibited similar trend for BOD/COD ratio, i.e. ranged from 0.4 to 0.7 with an average of about 0.5, as shown in Table 2.6.

Table 2.5 : Characteristics of Untreated Effluents from Latex-based Industries

| Parameter | Rubber gloves | | Catheters | | Latex thread | | Condoms | | Mixed Products | | Other Products | | EQA | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Range | Mean | Range | Mean | Range | Mean | Range | Mean | Range | Mean | Range | Mean | Std A | Std. B |
| PH | 2.1-10.2 | 6.8 | 2.7-10.6 | 6.0 | 2.5-7.6 | 4.6 | 6.23-7.64 | 6.98 | 5.24-8.98 | 6.86 | 5.34-7.82 | 6.75 | 6-9 | 5.5-9 |
| COD | 98-3058 | 770 | 43-428 | 211 | 1723-8107 | 4837 | 140-613 | 311 | 199-1088 | 490 | 130-11553 | 3354 | 50 | 100 |
| BOD₅ (at $20^0$C) | 20-2170 | 276 | 36-103 | 64 | 482-6080 | 2781 | 37-237 | 109 | 57-244 | 148 | 22-6145 | 1635 | 20 | 50 |
| Total solids | 160-8423 | 2025 | 207-1897 | 928 | 583-3863 | 2109 | 360-720 | 504 | 517-3180 | 1374 | 40-11707 | 4100 | | |
| Suspended solids | 7-2413 | 236 | 13-97 | 51 | 47-197 | 97 | 13-30 | 22 | 50-182 | 95 | 33-747 | 272 | 50 | 100 |
| Total nitrogen | 1-90 | 37 | 8-50 | 19 | 18-80 | 62 | 7-65 | 31 | 35-66 | 52 | 0.82 | 53 | | |
| Ammoniacal nitrogen | 0-58 | 23 | 2-25 | 8 | 9-55 | 38 | 2-56 | 23 | 24-48 | 35 | 0-40 | 28 | | |
| Nitrate nitrogen | 1-68 | 14 | 0-7 | 2.7 | 5-40 | 24 | 3-8 | 6 | 7-22 | 13 | 2-19 | 11 | | |
| Free chlorine | 0-116 | 11 | 0-0.9 | 0.2 | 0-7.1 | 1.4 | 0-0.4 | 0.1 | 0-92 | 26.7 | 0-3.6 | 0.9 | 1.0 | 2.0 |
| Oil & grease | 3-202 | 24 | 5-16 | 9 | 23-350 | 92 | 3-8 | 6 | 9-14 | 17 | 9-40 | 25 | UD | 10.0 |
| Zinc | 0.3-103 | 12.5 | 0.4-9.4 | 4.6 | 14-356 | 139 | 1.6-4 | 2.9 | 1.8-14 | 6.8 | 0.7-18 | 6.9 | 1.0 | 1.0 |
| Lead | 0.1-1.1 | 0.5 | 0-0.3 | 0.1 | 0-1.1 | 0.3 | 0-0.1 | 0.03 | 0-1.1 | 0.23 | 0-0.9 | 0.4 | 0.1 | 0.5 |
| Iron | 0.2-8.2 | 1.4 | 0-5.5 | 2.1 | 1.1-3.2 | 1.6 | 0.5-21 | 7.5 | 0.1-5.6 | 2.4 | 0.5-1.3 | 1.3 | 1.0 | 5.0 |

Note : All values except pH are expressed in mg/L. UD - Undetected

EQA – Environmental Quality Regulations (Sewage & Industrial Effluent, 1979)

Source : Zaid (2001)

Table 2.6 : Characteristic of Untreated Effluent from Examination Glove Manufacturing Factories.

| **Parameter** | **Factory** | | | | |
|---|---|---|---|---|---|
| | **A** | **B** | **C** | **D** | **E** |
| pH | 7.72 | 7.72 | 6.83 | 6.98 | 7.11 |
| Total solids | 2435 | 948 | 638 | 696 | 1346 |
| Volatile solids | 1728 | 622 | 564 | 596 | 914 |
| Suspended solids | 361 | 125 | 54 | - | 48 |
| Volatile Suspended Solids | 259 | 96 | 65 | - | 48 |
| COD | 1237 | 259 | 117 | 316 | 734 |
| BOD | 435 | 121 | 79 | 163 | 372 |
| BOD/COD ration | 0.4 | 0.5 | 0.7 | 0.5 | 0.5 |
| Total nitrogen | 135 | 50 | 23 | 38 | 81 |
| Ammoniacal nitrogen | 91 | 29 | 4 | 12 | 35 |
| Nitrate | 340 | 300 | 41 | 118 | 286 |
| Sulphate | 167 | 55 | 44 | - | 72 |
| Phosphate | 8 | 2 | 3 | - | 6 |
| Volatile fatty acids | 99 | 21 | 11 | - | 81 |
| Zn | 9 | 1 | UD | 1 | 4 |
| Fe | 3 | UD | 2 | 2 | 4 |
| Mg | UD | 9 | 1 | UD | 2 |
| Ca | 10 | 2 | UD | 19 | 1 |
| Pb | UD | UD | UD | UD | UD |
| Ni | UD | UD | UD | UD | UD |

UD = Undetected

All parameters except pH are expressed in mg per litre.

Source : Zaid (1988)

## 2.4 Types of Effluent Treatment

### 2.4.1 Treatment Technology

In complying the Third Schedule of the Environmental Quality Regulations (Sewage and Industrial Effluents) 1979, most of the latex-based manufacturing factories have installed suitable systems for treatment of their effluents. There are six types of effluent treatment systems often used by the latex-based industry in Malaysia as given in Table 2.7 (Zaid, 2001). Basically, these systems can be divided into two main treatments i.e. the primary treatment, which involved chemical-physical treatment of the effluent and secondary treatment, a biological process where microorganisms are used to treat the effluent.

Table 2.7 : Types of Effluent Treatment System Adopted by the Latex-based Industry

| System | Treatment Units | No. of Factories |
|---|---|---|
| A | Chemical Flocculation and Activated Sludge | 33 |
| B | Chemical Flocculation with DAF and Activated Sludge | 6 |
| C | Chemical Flocculation with DAF and Trickling Filter with Activated Sludge | 6 |
| D | Chemical Flocculation with DAF and Biofilter with Activated Carbon Filter | 5 |
| E | Chemical Flocculation and UASB with Aerated / Facultative ponds | 4 |
| F | Chemical Flocculation and Aerated / Facultative ponds | 5 |
|  | TOTAL | 59 |

Note: DAF : Dissolved Air Flotation, UASB : Upflow Anaerobic Sludge Blanket

Source : Zaid (2001).

### 2.4.2 Primary Treatment

In the primary treatment, a portion of the coarse, suspended and floating solids, grease and organic matters are removed from the wastewater. This removal is usually accomplished with physical operations such as screening and sedimentation. A considerable amount of organic matter is often observed in the effluent from the primary treatment. In addition, it exhibits a relative high BOD.

Often, chemicals are added to the wastewater to alter the contaminants chemically to enhance their removal by physical processes through precipitation. This is known as physico-chemical techniques. Chemical precipitation is used as a means of improving the performance of primary settling facilities. The degree of clarification of the effluent is influenced by the amount of chemical added to the untreated wastewater. It is possible to remove 80 to 90% of the suspended solids, 50 to 80% of the $BOD_5$, and 80 to 90% of the bacteria with chemical precipitation. In comparison, well-operated primary sedimentation tanks operating without the addition of chemicals have demonstrated removals of 50 to 70% of suspended solids, 25 to 40% of the $BOD_5$ and 25 to 75% of the bacteria (Metcalf and Eddy, 1991).

#### 2.4.2.1 Chemical Coagulation

Coagulation is a chemical technique directed towards destabilisation of colloidal particles. It is employed to remove waste materials existing in the effluent in suspended or colloidal form. Colloids consist of particles with size ranging from

0.1nm to 1mm and they generally do not settle out nor be removed by conventional physical treatment processes. The electrical properties possessed by the colloids create a repelling force and prevent agglomeration and settling. A bound layer of water surrounds the stationary-charged layer on the surface. In this layer ions of opposite charge are drawn from the bulk solution to produce a rapid drop potential. This drop within the bound water is known as the Stern Potential. A more gradual drop, called the Zeta Potential, occurs between the shear surface of the bound-water layer and the point of electro-neutrality in the solution. A schematic representation of the resulting colloidal state is shown in Figure 2.2 (McGhee, 1991).

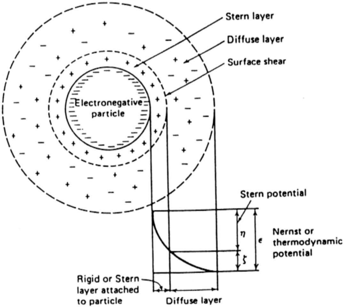


Figure 2.2 : A schematic representation of the resulting colloidal state (Gouy-Stern Colloidal Model)

Coagulation results from two basic mechanisms: perikinetic or electrokinetic coagulation, in which the zeta potential is reduced by ions or colloid of opposite charge to a level below the *van der Waals* attractive force. In orthokinetic coagulation, the micelles aggregate and form clumps, which agglomerate the colloidal particles. The addition of high-valence cations depresses the particle charge and the effective distance of the double layer, thereby reducing the zeta potential. As the coagulant dissolves, the cations serve to neutralise the negative charges on the colloids. This occurs before visible floc formation, and rapid mixing will then help to form microflocs. These microflocs will serve to neutralise and coat the colloidal particles. The mechanism of the coagulation process is shown in Figure 2.3 (Eckenfelder, 1989).

#### 2.4.2.2 Flocculation

The destabilised particles and chemical precipitates resulting from coagulation process usually settle very slowly. Flocculation process will assist in the agglomeration of the colloids with a hydrous oxide floc. The rate of flocculation depends on several factors such as the number of particles present, the relative volume, which they occupy, and the velocity gradient (G) in the basin. While coagulation process is often known as flash mixing since it involves a rapid mixing process, flocculation involves slow mixing as the microflocs formed during coagulation process are then brought into contacts in order to promote their agglomeration.

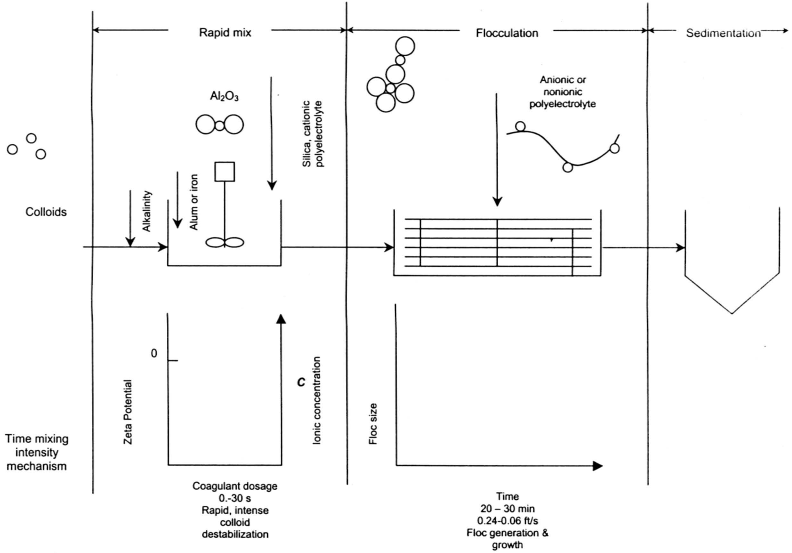


Figure 2.3 : Mechanisms of Coagulation

Colloidal particles in rubber glove manufacturing plant effluent comprise mainly organic and heavy metals such zinc (Nordin and Zaid, 1997). Chemical flocculation is seen as an indispensable step for the removal of the toxic and hazardous chemicals from the effluent prior to biological treatment. Chemical flocculation was reported to remove 99% of zinc content in the effluent from rubber thread manufacturing factory (Subbiah *et. al.*, 2000)

A prototype effluent treatment system for rubber glove manufacturing was designed by the Rubber Research Institute of Malaysia (RRIM) in 1996 and commissioned in 1997. Results showed that removal of COD, BOD and zinc from the treatment plant were 48.4%, 75% and 85.9% respectively. The chemical flocculation stage itself managed to remove 46.6%, 78% and 65.4% of the above mentioned parameters (Nordin and Zaid, 1997). The results proved that the chemical flocculation step is important as it assists in reducing a significant amount of pollutants in the effluent prior to the secondary treatment. It actually helps to reduce the load of subsequent treatment.

A survey carried out by RRIM on the existing effluent treatment plants showed that the removal of COD by chemical flocculation varied from 33.1% to 48.7% (Zaid, 1992b and 1992c). Similarly removal of BOD was 26.7% to 43.1% and zinc from 40.0% to 75.9% (Zaid, 1991c)

### 2.4.2.3 Primary Sedimentation

The chemical precipitates, which are formed in coagulation and flocculation processes, tend to agglomerate while settling as a result of interparticle collisions. These settled solids will then be removed from the effluent by sedimentation. Thus, sedimentation is the separation of readily settleable solids and floating material from wastewater, by gravitational settling, and thus reduces the suspended solids content in the effluent. The floating flocs will then flow into the biological tank for further treatment.

Primary sedimentation tanks are often used as a preliminary step, ahead of biological treatment. These tanks will help to reduce the load on the biological treatment units. An efficiently designed and operated primary sedimentation tank is known to be able to remove 50 to 70% of the suspended solids and 25 to 40% of the $BOD_5$ (Metcalf and Eddy, 1991). However, actual removals vary considerably with the characteristics and age of the waste.

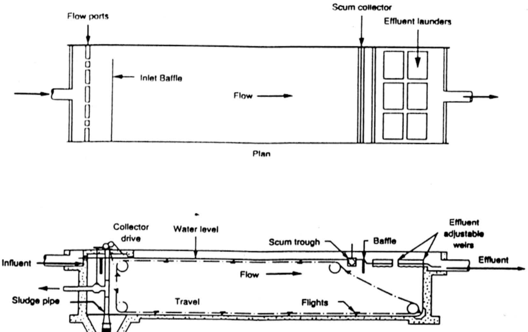
There are two main designs of sedimentation tanks i.e. mechanically cleaned circular or rectangular sedimentation tanks. The size of installation, local site conditions, local rules and regulations, economic reasons and other factors will determine the selection of the type of sedimentation unit.

### a. *Regular Sedimentation Tank*

Rectangular Sedimentation Tank allows the use of common-wall construction in plants containing multiple basins, and thus offer a reduced likelihood of short circuiting and allow optimum use of land area. Figure 2.4 shows a typical rectangular primary sedimentation tank. The influent enters from one end of the tank, and flows through the tank to the opposite end at a very slow rate. The slow flow will enable the coagulated solids to settle down at the bottom of the sedimentation tank. A chain scrapper scraps the solids into a sludge hopper located at the bottom of the tank. Meanwhile, a skimmer at the surface of the tank skims off the floating matters or scum found at the surface of the effluent. Thus, a sedimentation tank actually removes both the settleable and floating solids in the effluent.

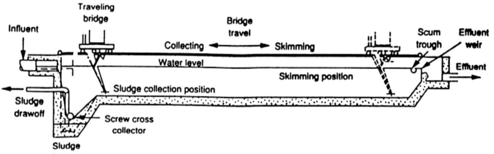
### b. *Circular sedimentation tank*

Circular sedimentation tanks are commonly used in small plants, which contain only a few units. In addition circular sedimentation tanks have a minimum perimeter for a given area and as such may be more economical in such circumstances. Figure 2.5 shows a center-flow circular sedimentation tank (Hammer and Hammer, 1996). The concept of a circular sedimentation tank is similar to the rectangular type, except for the location of influent pipe. In this design, the influent enters through a horizontal pipe at the bottom of the tank, and flows up through a central vertical pipe or at the side around the clarifier and flows down through the channel. A rotating scrapper, also known as collector arm plows the settled solids to the centre of the tank. The sludge is then draw off either by gravitational process or by means of pumps. A



Elevation

(a)



Elevation

(b)

Figure 2.4 : Typical Rectangular Sedimentation Tanks – (a) Chain-and-flight collector and (b) Travelling-bridge collector.

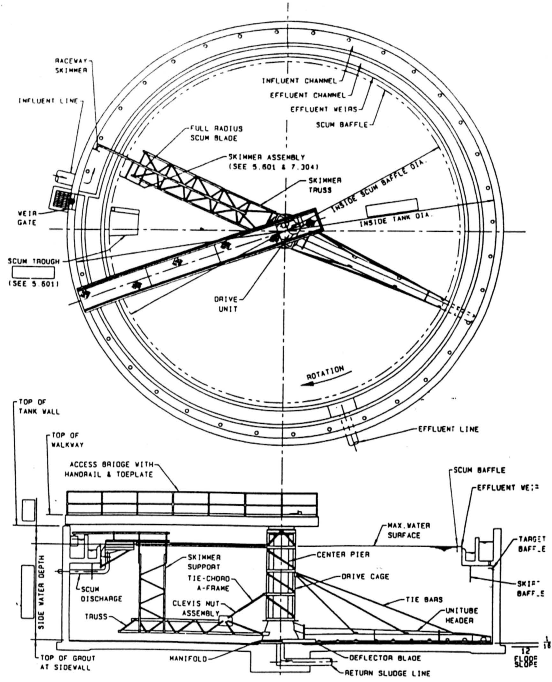


Figure 2.5 : A Typical Circular Primary Sedimentation Tank

skimmer skims off the floating materials or scum at the surface.

The efficiency of a sedimentation tank depends largely on the characteristic of the effluent itself i.e. the content in the wastewater. For example, for municipal waste containing high soluble organic matter, the sedimentation stage may be able to reduce less than 20% of the BOD, while industrial wastes that contribute settleable solids may experience a BOD removal as high as 60% (Hammer and Hammer, 1996).

#### 2.4.2.4 Flotation

While the primary sedimentation tank is often used as the first step of pollutant removal in the effluent, there are other more advanced technologies, which have similar application such as dissolved air flotation (DAF), cavitational air flotation (CAF), centrifuge and rotary screen. Flotation is used for the removal of suspended solids and oil and grease from effluent, and is also applicable for the separation and concentration of sludge (Eckenfelder, 1989). It involves a process where the solid or liquid particles are separated from a liquid phase by introducing air bubble into the liquid phase. The pressurised air bubbles attach to the particulate matters and subsequently rise to the surface, where they are skimmed off.

In the flotation process, very small and light particles that are difficult to settle or require a longer settling period could be removed more thoroughly and quickly from the effluent. Sedimentation process could not perform such function.

Dissolved Air Flotation (DAF) system is basically a gravity separation process whereby the separation of two phases is achieved by increasing the specific gravity (SG) difference of the two phases. The SG change could be achieved by attaching air bubbles to one of the phases. Air is dissolved in the water to a saturating point under a pressure of 3 to 5 atmospheres (Meyers, 1984). This is followed by the depressurising process where an immediate expansion of the water through a valve to atmospheric pressure occurs. The pressure drop causes sudden expansion and the gases will form micro bubbles which nucleate onto the solid particles or liquid droplets of one phase. These micro bubbles in the range of 30 to 80 microns become intimately attached to the solid particles and subsequently, with lower effective specific gravity and buoyant force, the contaminants will rise to the surface leaving a clear water phase below.

In normal practice, the inflow of the wastewater is pressurised by means of a pump within the range of 275 to 350 kPa (Metcalf and Eddy, 1991). Air is introduced into the suction pipeline. A residence time ranging from 30 to 60 seconds for the entire flow in the tank ensures maximum dissolving of air in the water. However, the saturation of air in water is directly proportional to pressure, and inversely proportional to temperature.

The density of the air/solid bubble particle combination is given by:

$$Pa = \frac{VgPg + VsPs}{Vg + Vs} \quad \text{.........................................Equation 2.1}$$

But the density of gas ($Pg$) is much lower than the density of solid ($Ps$), therefore $Vg/Ps$ approaches 0 and

$$\Rightarrow \quad Pa \approx \frac{VsPs}{Va + Vs} \quad \text{.........................................Equation 2.2}$$

where,

$Pa$ = density aggregate

$Pg$ = density gas

$Ps$ = density solid

$Vs$ = volume solid

$Vg$ = volume aggregate

$Va$ = volume air.

The ratio of air to solids is given by the equation:

$$\frac{A}{S} = \frac{1.33\, Ca\, (Pf - 1)}{Cs} \quad \text{................................Equation 2.3}$$

where,

$A$ = Air

$S$ = solids

$Cs$ = solids concentration (mg/l)

$Ca$ = air solubility (cc/l)

$P$ = pressure (atm)

$f$ = fraction of air dissolved (0.5 – 0.9).

DAF tanks are designed with different shapes and forms. The common forms are the circular upward radial flow DAF (Figure 2.6), the horizontal, rectangular 'plug-flow' type DAF (Figure 2.7) and more recently the 'Tilted Plate Flotator' (TPF) (Figure 2.8), which incorporates a corrugated plate pack as secondary separation chamber, is common. These plates increase the surface area, which enhances the separation of solids or liquids from the water phase. Sufficient and effective surface area is one of the major factors that influence the rise velocity and as such determines the degree of separation. Whilst surface area is critical, the depth of the DAF tank does not play a significant role in the process.

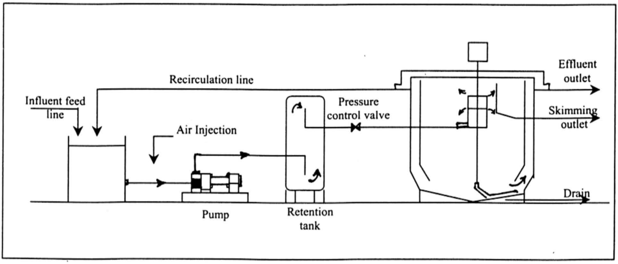


Figure 2.6 : Circular Upward Radial Flow DAF

According to Meyers, 1995, the effectiveness of DAF for the reduction of BOD depends largely on the chemical pre-treatment method applied. Conventional DAF plants using single-pass solid blade scrapers generally could achieve solid contents in the sludge within the range 4 to 8% (for protein sludges), whereas dual finger scraper can achieve higher content (10 to 12% for chicken slaughterhouse; 14 to 16% for a fish-finger processing plant).

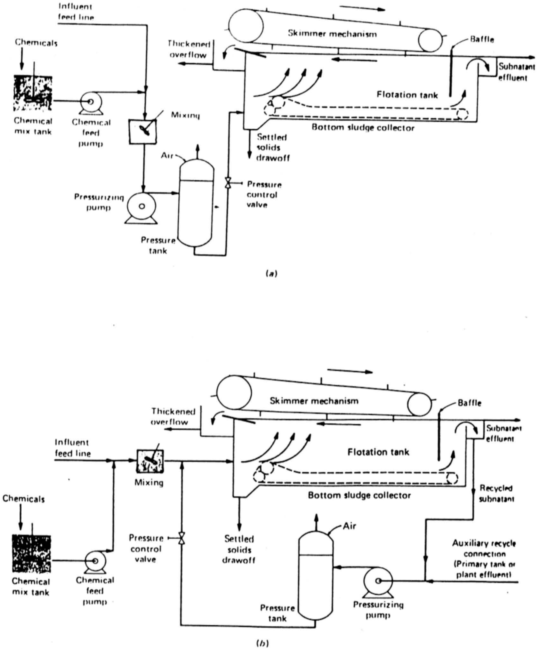


Figure 2.7 : Horizontal Tank Type DAF (a) without recycle and (b) with recycle

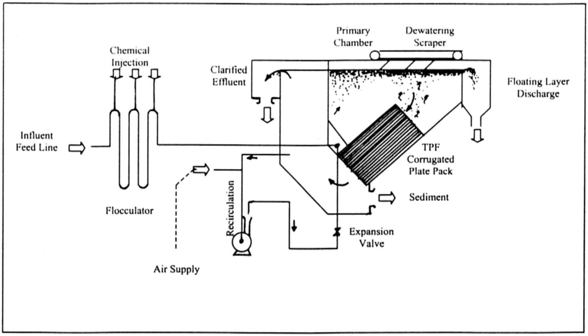


Figure 2.8 : Tilted Plate Flotation DAF

The percentage of BOD reduction by DAF process in other industries is shown in Table 2.8. Thus, an optimal chemical pre-treatment helps to maximise the separation of the contaminants and minimise the chemical costs. In Table 2.9, a comparison of chemical pre-treatment methods for poultry slaughterhouse effluent in Sidney was carried out (Hopwood, 1978 and Cooper and Denmead, 1979). It was found that ferric chloride, as primary flocculant is the most economical system.

Table 2.8 : The Use of DAF in WWTPs for Various Industries

| Industry | % Reduction | | |
|---|---|---|---|
| | BOD | SS | Grease |
| Pet Food Manufacturer | 72.3 | 99.6 | 96.6 |
| Fish Finger Processing | 70.0 | 95.7 | 96.0 |
| Hamburger Pattle Manufacturer | 81.4 | 99.8 | 99.3 |
| Cosmetics Manufacturer | 81.4 | 97.4 | 99.9 |
| Silk Screen Printing | 99.87 | 99.6 | 90.3 |

Source : Meyers (1984).

Table 2.9 : Comparison of Chemical Pre-Treatment Methods for a Poultry Slaughterhouse Effluent, with Different Types of Chemicals Prior to DAF.

| Method | Reduction (%) | | |
|---|---|---|---|
| | BOD | SS | Grease |
| Alum, polyelectrolyte, DAF | 73 | 95 | 93 |
| Ferric chloride, polyelectrolyte, DAF | 82 | 90 | 88 |
| Acid, alum, lime polyelectrolyte, DAF | 80 | 87 | 86 |
| Acid, ferric, lime (I) | (I) 80 | 92 | 88 |
| Polyelectrolyte, DAF (II) | (II) 89 | 89 | 86 |
| Acid, lignosulfonate, DAF, lime | 75 | 84 | 90 |
| Acid, HMP, DAF, lime | 75 | 80 | 90 |

Source : Meyers (1984)

Besides slaughterhouse, DAF has been used in numerous applications such as tannery, starch mill, latex-industries, vegetable, petroleum refinery effluent, electro-plating and others. DAF can be installed at downstream of biological treatment where it replaces the conventional clarifier.

In the electro-plating, metal finishing and paint industries, heavy metals are often precipitated out as metal hydroxide. Sedimentation after the precipitation stage is unable to remove the bulky sludge with low solids content. DAF which functions opposite of sedimentation would easily concentrate the solids content of the sludge produced and proportionately reduce the volume of sludge. In fact, one of the key successes of DAF, is its capability to maximise the solids content of the sludge. Every time the solids content is doubled, the sludge volume is halved.

DAF is very useful in separating the emulsion from the water phase of the soluble oil and oil emulsions effluent. Oil emulsions, which usually contain heavy metals, would undergo the neutralisation step to precipitate out the heavy metals prior to separation in the DAF plant.

Considerable amount of research has been carried out on the treatment of starch mill effluents to recover product for reuse. One of the product recovery methods involve the application of DAF. Starch mill effluent has a BOD value of 10,000 mg/l, SS of 5,000 mg/l, and is generally unstable and easily acidified by bacteria. Almost half of the BOD is soluble and does not respond readily to conventional chemical-physical treatment techniques. However, DAF managed to overcome this problem, reducing the BOD concentration to 4,900 mg/l and SS to 150 mg/l, with a 60% and 96.9%

respectively. It also essentially recovers the insoluble starch. Eventually, with the recovery of insoluble but valuable starch from the effluent, the sewerage charges were also reduced. Annual savings for a starch mill located in Melbourne, Australia is very significant. It was reported that although BOD was reduced by only 60%, the saving in Melbourne Sewer Board amounted to AUS$356,000.00 (Meyers, 1984).

In the latex-based industries, DAF is often installed right after the chemical treatment, replacing the conventional primary sedimentation tank. In a study involving the upgrading of effluent treatment system for a condom manufacturing plant located in Negeri Sembilan, a DAF unit was installed up-front to remove the suspended solids prior to biological treatment (Meyers, 1995). Along other improvements to the plant, it was reported that the performance of the effluent treatment plant has improved tremendously, as shown in Table 2.10.

### 2.4.3 Secondary Treatment

#### 2.4.3.1 General

Secondary treatment systems are intended to remove the soluble and colloidal organic matter, which remain after the primary treatment. Biological treatment involves the application of a controlled natural process where microorganisms are used to remove soluble and colloidal organic material from the waste, and are in turn removed themselves. The removals of these organic matters are usually measured as BOD, total organic (TOC), COD and SS.

Table 2.10 : Effluent Treatment Plant Performance for a Condom Manufacturing Plant (Case Study)

| | *BOD* | *COD* | *SS* | *O & G* | *Zn* |
|---|---|---|---|---|---|
| *Raw Effluent* | | | | | |
| Average | 551 | 934 | 840 | 20 | 2.7 |
| Range | 51-740 | 234-1120 | 684-912 | 9-23 | 0.5-11.6 |
| *After DAF* | | | | | |
| Average | 160 | 360 | 50 | 4 | 1.6 |
| Range | 18-180 | 70-140 | 16-92 | 1-9 | 0.1-0.84<br>0.4-1.9 |
| % Reduction | 71 | 61 | 94 | 80 | 41 |
| *Final Discharge (Treated Effluent)* | | | | | |
| Average | 9 | 32 | 15.3 | 4 | 0.5 |
| Range | 4-20 | 8-44 | 2-48 | 0-9 | 0.4-0.6 |
| % Reduction | 94 | 91 | 69 | - | 69 |
| Std. B | 100 | 50 | 1.0 | 10.0 | 100 |
| Std. A | 20 | 50 | 50 | ND | 1.0 |

ND – Non Detectable

Source : Meyers, (1995), Unpublished data.

There are five major biological processes commonly used in the wastewater treatment systems, namely aerobic processes, anoxic processes, anaerobic processes, combined aerobic, anoxic, and anaerobic processes, and pond processes. These groups can be subdivided further as seen in Table 2.11 (Metcalf and Eddy, 1991). The aerobic and anaerobic cycles, shown in Figures 2.9 and 2.10 are basically natural-occurring processes.

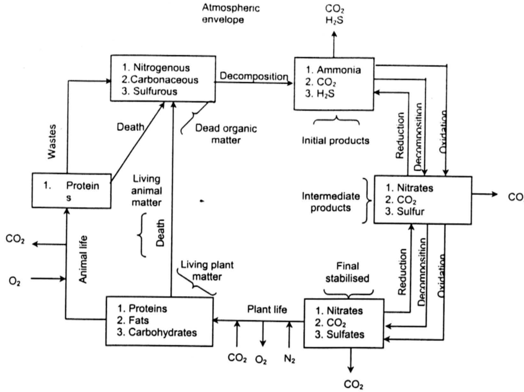


Figure 2.9 : The Aerobic Cycle in nature

### 2.4.3.2 Aerobic Processes

Aerobic treatment processes basically involve the usage of microorganisms to convert dissolved organic material in the effluent to new cellular material. The microorganisms consist of mixed or heterogeneous population and generally divided into three main groups i.e. a) strict aerobes, b) strict anaerobes, and c) facultative organisms. The bacteria, viruses, algae, fungi, protozoa, rotifers, and other types of microbes help to degrade the organics and subsequently remove the degradable organics from the wastewater. The removal process involves a few stages, including mass transfer, adsorption, absorption and biochemical enzymatic reactions.

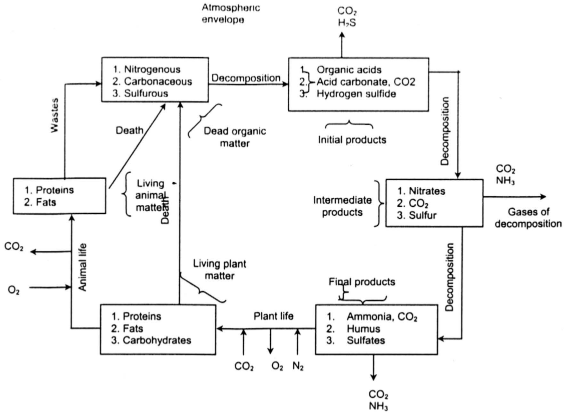


Figure 2.10 : The Anaerobic Cycle in nature

As indicated in Table 2.11, the aerobic processes can be divided into a) suspended growth, b) attached growth and c) combined suspended-and attached growth processes. These three main categories can be further subdivided into more specific type of aerobic treatments. However, the common aerobic biological treatment units include a) activated sludge, b) aerated lagoons, c) trickling filters, d) rotating biological contactors, e) facultative lagoons and f) oxidation ponds.

Table 2.11 : Major biological treatment processes used for wastewater treatment

| Type | Common Name |
|---|---|
| *Aerobic Processes:*<br>a. Suspended-growth | Activated-sludge process<br>• Conventional (plug-flow)<br>• Complete-mix<br>• Step aeration<br>• Pure oxygen<br>• Sequencing batch reactor<br>• Contact stabilisation<br>• Extended aeration<br>• Oxidation ditch<br>• Deep Tank (90ft)<br>• Deep shaft<br>Suspended-growth nitrification<br>Aerated lagoons<br>Aerobic digestion |
| b. Attached-growth | Trickling filters<br>• Low-rate<br>• High-rate |
| c. Combined suspended and attached-growth processes | Activated biofilter process, trickling-filter solids-contact process, biofilter activated-sludge process, series trickling-filter activated-sludge process |
| *Anoxic Processes*<br>a. Suspended-growth | Suspended-growth denitirication |
| b. Attached-growth | Fixed-film denitification |
| *Anaerobic Processes*<br>Suspended-growth | Anaerobic digestion<br>• Standard rate, single-stage<br>• High-rate, single-stage<br>• Two-stage<br>Anaerobic contact process<br>Upflow anaerobic sludge-blanket |
| Attached-growth | Anaerobic filter process<br>Expanded bed |
| *Combined aerobic, anoxic, and anaerobic processes*<br>Suspended-growth | Single or multi-stage processes, various proprietary processes |
| Combined suspended- and attached-growth | Single or multi-stage processes |
| *Pond processes* | Aerobic ponds<br>Maturation (tertiary) ponds<br>Facultative ponds<br>Anaerobic ponds |

### a. Activated Sludge System

In the activated-sludge process, soluble and insoluble organics are removed from the effluent stream, and converted into a flocculent microbial suspension that is readily settleable. These setteable suspensions are subsequently removed by gravitational solids liquid separation techniques. The removal of the biodegradable organics from the effluent by the microorganisms, involves two distinct metabolic processes, namely respiration and synthesis. The respiration process is a microbiological process where it involves the oxidation of organic or inorganic substance to produce energy and end products such as carbon dioxide and water. The energy produced is subsequently utilised to synthesise new microbial cell enzymatically. The equation for the process is expressed below:

Respiration:

$$\text{Organics} + a'O_2 + N + P \xrightarrow[K]{\text{Cells}} a \text{ new cells} + CO_2 + H_2O$$
$$+ \text{ non biodegradable soluble residue}$$

..............................Equation 2.4

where

$a$ = fraction of organic removed that is synthesised to cell mass,

$a'$ = fraction of organic removed that is oxidised to end products for energy, and

$K$ = rate coefficient and is a function of biodegradability of the organic in the effluent.

During the endogenous phase, the food supply decreases, causing the death rate of microorganisms exceeding their growth rate. In the natural process, the bacteria would live on the dead bacteria and oxidise them to carbon dioxide and water. The organisms also undergo progressive auto-oxidation in their cellular mass. The equation for this process is expressed as below:

Endogenous phase:

$$\text{Cells} + b'\text{O2} \xrightarrow[b]{} \text{CO2} + H_2O + N + P + \text{non-biodegradable cellular residue} \quad \text{.............Equation 2.5}$$

Where

$b$ = fraction per day of degradable biomass oxidised, and

$b'$ = oxygen required for this oxidation.

In Figure 2.11 (Hammer and Hammer, 1996), raw influent flowing into the aeration tank is used as food by the bacteria living in the wastewater. With the presence of dissolved oxygen in the wastewater, the bacteria metabolised the organics and produced new bacterial growth. The co-existing protozoa feed on a portion of the bacterial cells for energy to reproduce. A portion of the bacteria dies, and thus release the cell contents to the solution for re-synthesis. The organic matter is removed from the wastewater by synthesis into microbial and other end products, and is subsequently separated out through gravitational separation in a clarifier or secondary sedimentation tank. The settled floc is then recycled into the aeration tank, while the clarified effluent is discharged.

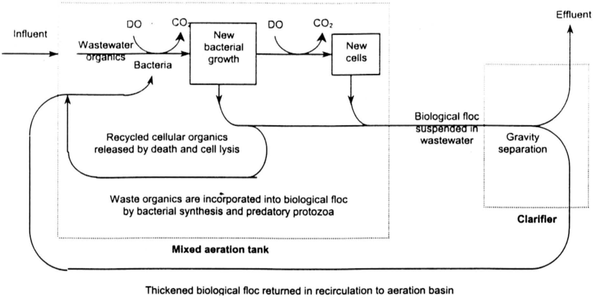


Figure 2.11 : Activated sludge process

There are four main parameters that influence an activated sludge process design, i.e. a) hydraulic retention time (HRT), b) BOD loading per unit volume, c) food-to-microorganism ratio (F/M), and d) sludge age (SRT).

a) HRT is expressed as:

$$\theta = \frac{V}{Q} \quad \text{..........Equation 2.6}$$

where

$\theta$ = hydraulic retention time (d),

$V$ = volume of aeration tank ($m^3$), and

$Q$ = wastewater inflow ($m^3/d$) {sludge recycle excluded).

b) BOD loading is expressed as:

$$BOD\ loading = \frac{(Q\ x\ S_o)}{V} \text{ ..............................Equation 2.7}$$

where

$BOD\ loading$ = kg of BOD applied for unit volume of aeration tank (kgBOD/m$^3$), and

$S_o$ = influent BOD to aeration tank (mg/l).

c) F/M is expressed as:

$$\frac{F}{M} = \frac{S_o}{\theta X} \text{ ..................................................Equation 2.8}$$

where

$\frac{F}{M}$ = Food-to-microorganism ratio, d$^{-1}$, and

$X$ = concentration of volatile suspended solids in the aeration tank (mg/l) (X is also known as mixed liquor suspended solids (MLSS) or mixed liquor volatile suspended solids (MLVSS).

d) Sludge age is expressed as:

$$SRT = \frac{X\ x\ V}{(SS_e\ x\ Q_e) + (SS_w\ x\ Q_w)} \text{ .......................Equation 2.9}$$

where

$SRT$ = sludge age or mean cell residence time (d),

$X$ = MLSS or MLVSS (mg/l),

$SS_e$ = suspended solids in wastewater effluent (mg/l),

$Q_e$ = quantity of wastewater effluent (m3/d),

$SS_w$ = suspended solids in wastewater sludge (mg/l), and

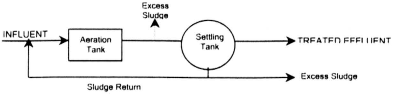
$Q_w$ = quantity of wastewater sludge (m3/d).

In Figure 2.12, five types of activated sludge systems with different modification can be observed (Sastry, 1995). These five types, namely (i) the Conventional Activated Sludge, (ii) Step Aeration, (iii) Contact Stabilisation, (iv) Complete Mix Plant and (v) Oxidation Ditch, are the common designs for effluent treatment plants. Compared to the original experiments developed by Arden and Lockett in 1914, there have been many modified and improved activated-sludge processes since then.

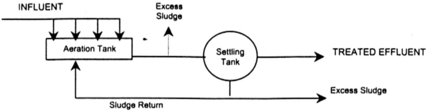
### *i. Conventional Activated Sludge*

In the Conventional Activated Sludge, wastewater is treated in an aeration basin together with high concentration of biological sludge. The concentration in the aeration tank is maintained by recycling the sludge from the secondary sedimentation tank. Air supply is tapered along the length of the tank to provide greater aeration at the head-end where raw wastewater and return activated sludge are introduced.

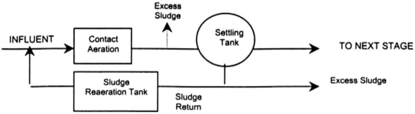
1. *Conventional Activated Sludge*



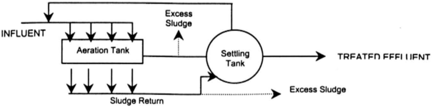
2. *Step Aeration*



3. *Contact Stabilisation*



4. *Complete Mix Plant*



5. *Oxidation Pond*

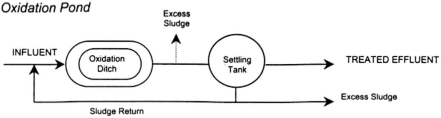


Figure 2.12: Schematic diagrams of Activated-sludge Systems with different modifications

### *ii. Step Aeration*

Step Aeration is similar to conventional activated sludge, except the introduction of its wastewater into the aeration tank is at several points. These multiple entries of substrate into the aeration tank increase the removal of soluble organics by adsorption and higher BOD loading per unit volume.

### *iii. Contact Stabilisation System*

In the contact stabilisation system, recycled sludge is aerated separately in a sludge reaeration tank prior to mixing with the incoming wastewater. The retention time in the sludge aeration tank is twice to four times as in the conventional activated sludge system.

### *iv. Complete Mix System*

In the complete mix system, wastewater and sludge flows are introduced at several points in the aeration tank. The mixed liquor is collected through the effluent channels which then flows into the secondary sedimentation tank. The recycled sludge is introduced at the head-end of the raw wastewater inflow.

### *v. Oxidation Ditch*

Oxidation ditch is one form of extended aeration system. It has a ditch and a rotor which provides continuous aeration from 24 to 36 hours. This process is based on the concept of low organic loading, long aeration time, high MLSS concentration and low F/M ratio. The BOD removal efficiency by this system is high.

### b. Aerated Lagoons

Besides activated sludge system, aerated lagoons are also employed as secondary treatment. The aerated lagoons process is essentially the same as the conventional extended-aeration activated sludge process, except that an earthen basin usually 2 to 4 m deep is used for the reactor (Ahmad *et. al.*, 1979 and Zaid *et. al*, 1997). Oxygen required by the process is supplied continuously by surface or diffused aerators. The aerators also support the mixing and suspension of microbial floc in the basin.

This system generally comprises of two units. The first unit involves the application of mechanical surface aerators, which are designed to ensure that the solids do not settle at the bottom of the lagoon. The second unit acts as a settling tank and is used to remove the solids (see Figure 2.13). Compared to other systems, aerated lagoons employ minimal equipment. The principal equipment is the surface aerator. As such, aerated lagoons are known to be one of the low cost biological treatments and are commonly used for municipal and industrial wastewater. Aerated lagoons have low sensitivity to toxicity, pH disturbances and load variation, thus enabling them to handle various types of wastewater (Ahmad, 1982). Sludge produced from this system is low and the nutrient demand is less compared to activated sludge system (BOD:N:P = 100:1:0.2) (Ahmad and John, 1985, Getha *et. al.*, 1994). However, there are disadvantages with aerated lagoons. The most obvious disadvantage is its requirement for large area, which many factories could not accommodate.

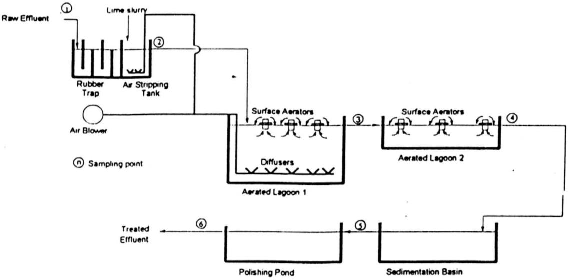


Figure 2.13 : Schematic Diagram of Aerated Lagoon System

BOD removal is a function of aeration period, temperature and nature of the wastewater. It is expressed as:

$$\frac{S}{S_o} = \frac{1}{1 + k\dfrac{V}{Q}} \qquad \text{..........................Equation 2.10}$$

where

$S$ = effluent $BOD_5$ concentration (mg/l),

$S_o$ = influent $BOD_5$ concentration (mg/l),

$k$ = overall first-order $BOD_5$ removal-rate constant ($d^{-1}$),

$V$ = volume ($m^3$), and

$Q$ = flowrate ($m^3/d$).

Removal efficiency of BOD for different types of industries employing the aerated lagoon system is shown in Table 2.12 (Eckenfelder, 1989), ranging from 45-98%.

Table 2.12 : Summary of average parameter and BOD removal efficiency for aerobic and facultative ponds.

| Industry | Area (m2) | Depth (m) | Detention (d) | Loading (kg/m2.d) | BOD removal (%) |
|---|---|---|---|---|---|
| Meat & poultry | 5,261 | 0.91 | 7 | 0.008 | 80 |
| Canning | 27,924 | 1.77 | 37.5 | 0.016 | 98 |
| Chemical | 125,454 | 1.52 | 10 | 0.018 | 87 |
| Paper | 339,940 | 1.52 | 30 | 0.012 | 80 |
| Petroleum | 62,727 | 0.46 | 25 | 0.003 | 76 |
| Wine | 28,328 | 1.52 | 24 | 0.025 | |
| Dairy | 30,352 | 1.22 | 98 | 0.002 | 95 |
| Textile | 12,545 | 0.46 | 14 | 0.018 | 45 |
| Sugar | 80,938 | 1.28 | 2 | 0.010 | 67 |
| Rendering | 8,903 | 0.91 | 4.8 | 0.004 | 76 |
| Hog feeding | 24,281 | 0.91 | 8 | 0.040 | |
| Laundry | 809 | 1.22 | 94 | 0.006 | |
| Miscellaneous | 60,704 | 1.52 | 88 | 0.006 | 95 |
| Potato | 102,387 | | 105 | 0.012 | |

Source: Eckenfelder (1989).

## 2.5 Treatment of Effluent from Rubber Glove Manufacturing Industries

While there has been rapid expansion on the rubber product manufacturing industries, the treatment of its effluent has also not been neglected. In fact, extensive research has been carried out especially by Rubber Research Institute of Malaysia (RRIM), to establish the most suitable treatments for the effluent generated from these industries.

It was reported that in 1992 there were about 135 rubber products manufacturing factories actively operating in Peninsular Malaysia (Zaid, 1992b). However, only 35 of this total had actually constructed treatment plants (WWTPs) to treat the effluent prior to discharge (Table 2.13), with rubber gloves manufacturing factories leading the number. The few common systems adopted by the industries are a) flocculation and activated sludge, b) flocculation, anaerobic digestion & aerated lagoon, c) flocculation & aerated lagoon, d) anaerobic / facultative ponding, and e) flocculation and sand filtration, as in Table 2.14 (Zaid, 1992b).

In 1999, the number of rubber product manufacturers increased to 271 (Abdul Halim, 1999), with latex-based products occupying the top spot with 126 companies. A nation-wide survey carried out by the Technical Committee for the Rubber Based Industry Waste, from July to September 1999. The committee comprises of Department of Environment (DOE), Malaysian Rubber Board (LGM), Kualiti Alam Sdn Bhd (KA), Malaysian Rubber Product Manufacturers' Association (MRPMA), Malaysian Rubber Glove Manufacturers' Association (MRGMA), Association of Malaysian Medical Industries (AMMI) and Federation of Malaysian Manufacturers

Table 2.13 : Treatment of Wastewater from Rubber Products Manufacturing Industry in Malaysia

| Product | No. of Factories in Operation | No. of Factories with WWTPs |
|---|---|---|
| Rubber gloves | 87 | 20 |
| Rubber thread | 5 | 3 |
| Catheters | 5 | 0 |
| Condom | 3 | 0 |
| Swim caps | 1 | 0 |
| Balloons | 3 | 0 |
| Rubber toys | 2 | 0 |
| Finger cots | 1 | 0 |
| Foam products | 5 | 1 |
| Teats and soothers | 1 | 0 |
| Mixed products | 22 | 11 |
| TOTAL | 135 | 35 |

Source : Zaid (1992b)

Table 2.14 : Types of Wastewater Treatment Systems Adopted by the Rubber Products Manufacturing Industry in Malaysia

| Types of Wastewater Treatment System | No. of Factories Adopted | % Total |
|---|---|---|
| Flocculation & Activated Sludge | 25 | 71 |
| Flocculation, Anaerobic Digestion & Aerated Lagoon | 2 | 6 |
| Flocculation & Aerated Lagoon | 1 | 3 |
| Anaerobic/Facultative Ponding | 5 | 14 |
| Flocculation & Sand Filtration | 2 | 6 |
| TOTAL | 35 | 100 |

Source : Zaid (1992b)

(FMM). From the survey, 33 out of the 60 latex-based factories use the chemical flocculation with activated sludge for the treatment of the effluent generated from their respective factories (Zaid, 2001) (see Table 2.7). One of the main tasks of this committee was to address the problems faced by the industry in complying with the effluent discharge standard.

In the survey it was also reported that generally most of the latex-based industries are able to comply with the regulatory standards of DOE. For the 60 factories surveyed, 8 factories (13.3%) complied with the COD limit of Standard A and 27 factories (45.0%) complied with Standard B. Meanwhile, 38 factories (63.3%) complied with BOD Standard A and 52 factories (86.7%) with Standard B. Details of compliance are shown in Table 2.15.

Table 2.15 : Status of Compliance of Latex-based Industry with the Effluent Discharge Standards

| Parameter | Standard A | | | Standard B | | |
|---|---|---|---|---|---|---|
| | Limit | Factories Complied | | Limit | Factories Complied | |
| | | No. | % | | No. | % |
| pH | 6.9 –9.0 | 56 | 93.3 | 5.5-9.0 | 57 | 93.3 |
| COD | 50 | 8 | 13.3 | 100 | 27 | 45.0 |
| BOD5 | 20 | 38 | 63.3 | 50 | 52 | 86.7 |
| Suspended solids | 50 | 38 | 63.3 | 100 | 52 | 86.7 |
| Free Chlorine | 1.0 | 41 | 68.3 | 2 | 46 | 76.7 |
| Oil & Grease | UD | 11 | 18.3 | 10 | 60 | 100 |
| Zinc | 1.0 | 33 | 55.0 | 1.0 | 33 | 55.0 |

Note : UD = undetected, all parameters except pH, are expressed in mg/l.

Total number of factories = 60

Source : Zaid (2001).

### 2.5.1 Flocculation – Activated Sludge System

The activated sludge process has been used extensively for the treatment of effluent from the rubber product manufacturing factories and other types of industries in Malaysia. In the two reports (Zaid, 1992a and Ahmad *et. al.*, 1986), they have clearly shown that the chemical flocculation and activated sludge systems is the most common effluent treatment system being applied by the rubber products manufacturing industry in Malaysia. A schematic diagram of complete treatment plant based on the activated sludge system is shown in Figure 2.14 (Zaid, 1993b).

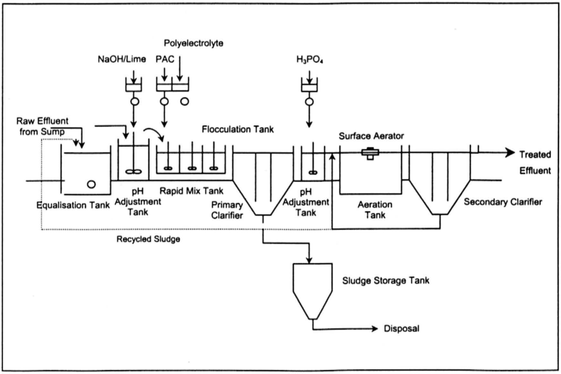


Figure 2.14 : Typical Schematic Diagram of the Flocculation and Activated Sludge System

In Figure 2.14, the equalisation step of raw effluent was carried out in the Equalisation Tank. In order to achieve a good flocculation, pH of the effluent was first adjusted to approximately pH11. Lime or caustic soda (NaOH) was added to acquire the alkalinity condition. The flocculated materials are then settled in a primary sedimentation tank and subsequently removed as sludge, comprise mainly zinc and other metallic elements. The pH of the clarified liquor is adjusted back to neutral prior to further treatment in aeration tank. Phosphoric acid is added to attain the neutral condition, which works best with activated sludge process. The phosphoric acid also increases the level of phosphate required by the aerobic bacteria in the aeration tank. Besides phosphoric acid, urea (N source) is also added to maintain the essential COD/N/P ratio for these bacteria. The activated sludge process helps to remove the remaining pollutants such BOD, COD, nitrogen, etc. Biological sludge would be settled and removed at the secondary clarifier, while the clarified effluent is discharged to receiving water. Zaid and Nordin (1991a) reported the removal efficiency of COD, BOD and zinc for wastewater treatment plants of 5 rubber glove manufacturing factories ranged from 48-93%, 44-97% and 20-58% respectively. All these 5 treatment plants adopted flocculation and activated sludge system.

The flocculation followed by activated sludge system has been proven to be an effective system in treating the effluent from rubber glove manufacturing industries. It was reported that this treatment system effectively removed 98% BOD, 96% COD, and 65% suspended solids from the examination glove manufacturing effluent, as shown in Table 2.16 (Zaid, 1993b). Similar results have been reported by Zaid (1988) in a performance study on the flocculation and aeration systems in the treatment of effluent from two examination glove manufacturing factories (factory A and B). Removal of BOD for factory A was 99%, while for factory B was 95%. 94% of COD was successfully removed for factory A, 87% for factory B; and for SS 89% and 92% were removed respectively.

Table 2.16 : Performance of Activated Sludge System in the Treatment of Examination Glove Manufacturing Factory WWTP.

| Parameter | Raw Influent | Treated Effluent | % Removal |
|---|---|---|---|
| pH | 7.18 | 7.94 | - |
| Total Solids | 2457 | 964 | 61 |
| Suspended Solids | 241 | 84 | 65 |
| COD | 2011 | 85 | 96 |
| BOD | 1336 | 27 | 98 |
| Total Nitrogen | 180 | 99 | 45 |
| Ammoniacal Nitrogen | 126 | 72 | 43 |
| Nitrate | 340 | 14 | 96 |
| Zinc | 32 | 3 | 91 |

Source : Zaid (1993b)

### 2.5.2 Flocculation, anaerobic digestion and aerated lagoon system

This system is commonly adopted in the rubber thread manufacturing industries. Sodium sulphide and polyelectrolyte are used as flocculants and dosed in at the primary treatment stage. Zinc and other metallic components would be removed at this stage. Subbiah *et. al* (2000) found that this system was able to reduce sludge production by approximately 90%.

The clarified wastewater is further treated in a high rate anaerobic digestion system (upflow anaerobic sludge blanket or UASB reactor) for the removal of COD and BOD. The liquor is further treated in a number of aerated lagoons. The UASB reactor was able to reduce 90% of COD (Subbiah and Alui, 1999). Similar observation was reported by Zaid (1993a and 1994). While activated sludge system is controlled by solids recycle and its performance is dependent on the separation of solids in the settling tank, fluidised bed used biomass support particles such as sand for microbial growth and attachment. Since the biomass concentrations in fluidised bed are often higher compared to activated sludge system, the overall volumetric rates of carbon conversion in UASB are higher. In addition, the cost of UASB system is lower and it requires smaller land area as secondary treatment. A prototype effluent treatment system comprises a rubber trap, a chemical flocculation unit, a primary sedimentation tank, anaerobic and aerobic fluidised beds and a secondary sedimentation tank as designed and commissioned by RRIM (Nordin and Zaid, 1997). Results from the commissioning exercise have indicated the removal of COD, BOD and zinc to be 48.4%, 75% and 85.9%, respectively.

Often the liquor from anaerobic digestion requires further aerobic treatment prior to discharge into the receiving water. This is to ensure that the treated effluent meets the regulatory standard limits set by the DOE. Conclusion from the report of Abdullah (1994) confirms the necessity of an aerobic treatment system after an anaerobic treatment. He found that the removal efficiency for BOD, COD and zinc in a thread manufacturing wastewater treatment plant which adopted chemical-flocculation and UASB is 56%, 53% and 99%, respectively, but is insufficient to meet the DOE's regulatory requirements.

### 2.5.3 Flocculation-Aerated Lagoon System

Chemical flocculation followed by aerated lagoon system is more commonly adopted by latex concentrate industries, as compared to latex-based manufacturing industries. However, this system was not as effective as activated sludge treatment. Observation by Zaid (1991b) on a rubber thread manufacturing factory which adopted this system, has lower removal efficiency for BOD, COD and SS, as compared to activated sludge and UASB. It was only able to achieve 10% COD removal, 30% BOD removal and 88% zinc removal. Chick (1981) and John and Ong (1979) reported removal of 90% to 95% for effluent from latex concentrate factories.

### 2.5.4 Flocculation-DAF-Activated Sludge System

Since the Flocculation-Activated Sludge System, Flocculation, Anaerobic Digestion and Aerated Lagoon System, and Flocculation-Aerated Lagoon System methods have already been tested for the rubber glove manufacturing effluent, a different design treatment was investigated in this study. In this investigation, chemical flocculation-DAF, followed by activated sludge system, is considered as another option to treat the rubber glove manufacturing effluent. DAF replaces the conventional clarifier, and has been found to be more efficient in removing the solids especially the chemical sludge prior to biological treatment.