2.0 LITERATURE REVIEW

2.1 LANDFILLING OF WASTE

Waste is generated in every human activity. Any material or product that has no value in the perception of the generator or the consumer is considered waste. The definition of waste may vary from country to country but whatever the form of the waste, it requires proper treatment and disposal.

Solid wastes are defined as wastes arising from human and animal activities that are normally solid and unwanted. The main sources of solid wastes are domestic or residential. Other sources include municipal services, commercial, institutional, industrial and agricultural activities. Municipal Solid Waste (MSW) is mainly household wastes including some commercial and institutional wastes. MSW is highly heterogeneous and its composition depends on factors such as living standard, geographical location, cultural habits of individuals, type of housing and seasons (Agamuthu & Nather, 1997).

The production of MSW has doubled or tripled in some industrial countries over the last two decades (George *et al.*, 1999). Developing countries which are becoming industrial nations are also producing MSW at an alarming rate but the techniques and facilities for the waste treatment in these countries are not being developed at the same rate as for the waste production.

In 1997, the total solid waste generated throughout Malaysia was 5.6 million tones or 15 000 tonnes.d^{-1} and of this 80% was domestic waste about 12 100 tonnes.d^{-1} and the rest about 3 100 tonnes.d^{-1} was commercial waste (Agamuthu, 2001). The

MSW generated increased to 6.0 million tones in 1998, with average of 0.5 to 0.8 kg per capita per day. Per capita waste generation increased from 0.70 kg per person in the 1990's to 1.2 kg per person in 2000. By the year 2000, production of domestic and commercial waste was 7.0 million tones.year^{-1}. One quarter of the solid waste was generated in the Klang Valley. Table 1 shows the waste generation in the major urban areas in Malaysia. Kuala Lumpur generated about 3000 tonnes of solid waste daily (in 2000) and it is at 4000 tonnes now.

Table 1: Solid waste generated in major urban areas in Peninsular Malaysia (Agamuthu, 2001).

	Solid waste generated (tonnes.d^{-1})		
Urban centre	1970	1980	1990
Kuala Lumpur	98.8	310.5	586.8
Johor Bahru	41.1	99.6	174.8
Ipoh	22.5	82.7	162.2
Georgetown	53.4	83.0	137.2
Klang	18.0	65.0	122.8
Kuala Terengganu	8.7	61.8	121.0
Kota Bharu	9.1	56.5	102.9
Kuantan	7.1	45.2	85.3
Seremban	13.4	45.1	85.2
Melaka	14.4	29.1	46.8

Source: ICM/ICE,1994.

Waste generation within Malaysia was found to depend very much on the sources of MSW. The rate of generation varied greatly depending on the premises (house, shop etc), affluence of population (low income or high income), occupation or business. Housing area generates the largest amount of waste (Figure 9)

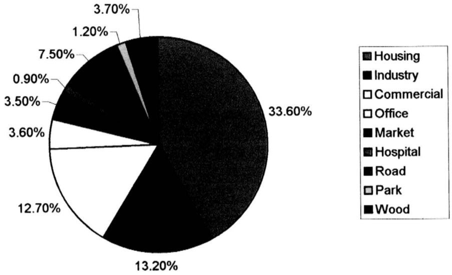


Figure 9: Waste generation in Malaysia (Agamuthu, 2001)

Malaysians generate about 72% compostable wastes (Table 2) comprising organic waste, paper, textile/leather and wood. The amount of plastic waste, which accounts for 16% is considered very high and is typical of a fast developing nation (Agamuthu, 2001). Table 2 compares wastes characteristics of Malaysia compared with that of the United States of America.

The composition of MSW reflects the affluence of the society, their way of life, their economic status and their social behaviour. The characteristics of MSW change with time as the society evolves to the needs of development. Treatment and disposal of solid waste vary from one country to another and depend on the type of waste, composition, infrastructure, land availability, labour, economic aspects, recycling strategy, public awareness, calorific value of waste, energy availability and demand, and environmental impact.

Table 2: Malaysian and US municipal solid waste characteristics (% by weight)

Waste composition	Malaysia	US
Organic/food waste	32.0	10
Yard waste	-	15
Paper	29.5	38
Textile/leather	3.4	7
Wood	7.0	-
Plastics	16.0	10
Rubber	2.0	-
Glass	4.5	6
Ceramics	0.4	-
Ferrous metal	3.7	8
Non-ferrous metal	0.6	-
Others	0.9	3

Source: Ridhuan (1995); cited from Agamuthu (2001).

Landfilling is one of the primary technologies used to dispose of solid wastes. Methods of depositing waste vary widely but, in general, good operating practice requires that waste is spread and compacted in layers and that all exposed surfaces are covered regularly, at least at the end of each working day, with an inert material. The maximum depth of face recommended in the UK is 2.5 m, with a daily covering of at least 15 cm (Debra & Timothy, 1998). Regular covering helps to reduce nuisance pests and to improve the visual impact of the landfill operation. Compaction helps to eliminate vermin within the landfill itself. Many other wastes can be co-deposited in a municipal waste landfill site including household, commercial, industrial and street cleaning wastes, dewatered sludge from sewage treatment plants, drainage waste except hazardous and toxic wastes, and hospital waste (Agamuthu,2001).

A landfill site may be viewed as a huge outdoor biological reactor, in which the waste decomposes over time. The increase of temperature within the landfill can rise to a fire hazard if the site is not properly managed. Settlement of materials will occur as decomposition proceeds. Pollution problems may arise from two main sources:

1. If water is allowed to come in contact with the waste, then an obnoxious mineralized leachate is produced.
2. Gases are generated from the biodegradation of the waste.

Any air present within the waste is normally used up quickly, so that most decomposition takes place anaerobically. In a municipal waste, methane, carbon dioxide, ammonia and hydrogen sulfide gases are generated due to anaerobic decomposition of the waste. These gases dissolved in water and some react with the water or dissolved constituents of the infiltrating water. For example, carbon dioxide combines with water to form carbonic acid, which then dissolves minerals from the wastes (Debra & Timothy, 1998).

Anaerobic decomposition of wastes consist of three stages:

1. Hydrolysis – during which complex organic substances, like polysaccharides, proteins and fats, are hydrolyzed by extracellular enzymes to monomers, like amino acids and long-chain fatty acids.
2. Acidification – during which short-chain volatile fatty acids, carbon dioxide and water are produced.
3. Methanogenesis, during which the products of acidification are converted, directly or indirectly by previous transformation of volatile fatty acids into acetic acid, to methane and carbon dioxide.

From a microbial point of view, bacterial groups responsible for acidification and methanogenesis are very different. Acidification is performed by both strictly anaerobic and falcutative microorganisms, which have the maximum activity at a pH ranging 4.4 to 6.6, while methanogenesis by strict anaerobes, which grow between 6.6 and 7.6, and the pH optima range from 7.0 to 7.2 (Bruce *et al.,* 1989).

2.1.1 Leachate formation mechanisms

Leachate results from the contact of water with solid waste. Other contributors to leachate generation include groundwater inflow, surface water runoff, moisture from emplaced waste and biological decomposition Some leachate results from moisture present in the waste when it is disposed although most leachate is generated as a result of rainfall infiltrating into the solid waste. Studies in United Kingdom indicated an infiltration rate of about 55% (Campbell, 1982). Leachate that infiltrates into the landfill either is absorbed and stored by the landfilled material or it migrates through the landfill under the force of gravity, ultimately being intercepted by the liner system. Liner systems are designed and constructed to prevent leachate from migrating into the soil and groundwater underneath the landfill, but this leachate must be properly removed, stored, treated and disposed.

The quantity of leachate produced is impacted by the following factors: precipitation, type of site, groundwater infiltration, surface water infiltration, waste composition and moisture content, preprocessing of waste (baling or shredding), cover design, depth of waste, climate, evaporation, evapotranspiration, gas production and density of waste (Barlaz & Ham, 1993). Continuous production of leachate will occur once the absorptive capacity of waste has been satisfied. Leachate quantity is site specific and ranges from zero in arid states to nearly 100 percent of precipitation in wet climates during active landfill operation. Leachate production from new landfills occur at relatively low rates, then increases as more waste is placed and larger areas are exposed to precipitation. Leachate production reaches a peak just before closure and then declines significantly with the provision of surface grading and interim or final cover (Debra & Timothy, 1998).

The process of landfill leachate generation passes through five phases (Figure 10) namely Initial Adjustment Phase (Phase 1), Transition Phase (Phase 2), Acid Phase (Phase 3), Methane Fermentation Phase (Phase 4) and Maturation Phase (Phase 5) (Debra & Timothy, 1998). In Phase 1, most of the biodegradable components in municipal solid wastes begin to undergo bacterial decomposition. Biological decomposition occurs under aerobic conditions because of air trapped within the landfill.

In the Transition Phase (Phase 2), oxygen is depleted and anaerobic conditions begin to develop. pH of the leachate drops due to the presence of organic acids and the effect of the elevated concentration of CO_2 within the landfill. In Phase 3, the Acid Phase, because of the acids produced during this phase, the pH of the leachate drops to values of 5 or lower. The BOD, COD and conductivity of the leachate will increase significantly during Phase 3 due to the dissolution of the organic acids in the leachate. A number of inorganic constituents, principally heavy metals, will be solubilized in this phase. Many essential nutrients are also removed from the leachate and if the leachate is not recycled the essential nutrients will be lost from the system.

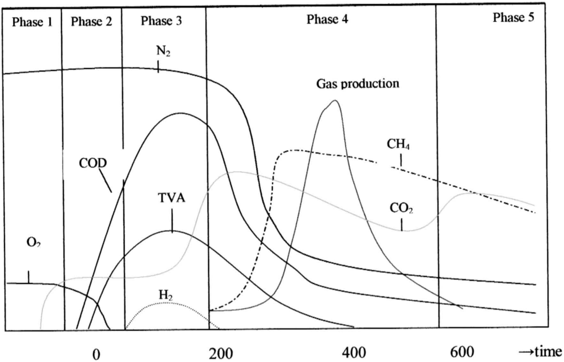


Figure 10: Typical production pattern of landfill leachate (Tchobanoglous, *et al.*, 1993).

In the Methane Fermentation Phase (Phase 4), acids and the hydrogen gas produced are converted to CH_4 and CO_2. The pH of the leachate will rise to the range between 6.8 and 8.0. The concentrations of BOD, COD and the conductivity value of the leachate will decrease. With higher pH values, fewer inorganic constituents are solubilized, and this results in the reduction of the concentration of the heavy metals present.

The Maturation Phase (Phase 5) occurs after all the readily biodegradable organic has been converted to CH_4 and CO_2. During this phase, the leachate will often contain higher concentration of humic and fulvic acids, which are difficult to process further biologically (Tchobanoglous, *et al.,* 1993).

The concentrations of the pollutants vary with the different phases (Table 3). The concentrations of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total volatile acids (TVA), ammonia and conductivity are much higher during the acid formation phase (Phase 3).

Table 3 : Characteristics of landfill leachate from different phases (Debra *et al.*, 1998)

Parameter	Phase 2 Transition	Phase 3 Acid formation	Phase 4 Methane formation	Phase 5 Final maturation
BOD, mgL^{-1}	100-10000	1000-57000	600-3400	4-120
COD, mgL^{-1}	480-18000	1500-71000	580-9760	31-900
TVA, mgL^{-1} as Acetic acid	100-3000	3000-18800	250-4000	0
BOD/COD, mgL^{-1}	0.23-0.87	0.4-0.8	0.17-0.64	0.02-0.13
Ammonia, mgL^{-1}	120-125	2-1030	6-430	6-430
pH	6.7	4.7-7.7	6.3-8.8	7.1-8.8
Coductivity, (μmhoscm^{-1})	2450-3310	1600-17100	2900-7700	1400-4500

2.1.2 Leachate composition and characteristics

The characteristics of the leachate are highly variable depending on the composition of the waste, rate of water infiltration, refuse moisture content and landfill design, operation and age (Bruce *et al.*, 1989). Typical characteristics of the landfill leachate in Malaysia namely Taman Beringin Landfill, Air Hitam Landfill and Sabak Bernam Landfill are shown in Table 4. The concentration of landfill leachate is high in NH_4-N, COD, BOD and heavy metals.

Table 4: Characteristics of landfill leachate (Agamuthu, 1999).

	Taman Beringin Landfill	Air Hitam Landfill	Sabak Bernam Landfill
Years in operation	16	5	7
Alkalinity	3750-9375	1540-9000	1200-1550
Hardness	211-1200	314-672	310-850
pH	7.85-8.75	7.6-8.84	7.95-8.10
Conductivity, μS	8.80-35.4	8.64-33.50	8.10-16.20
Chloride	875-2875	1652-3200	420-1820
Sulfate	40-79	18.5-110	36-52
TSS	420-1150	410-1250	111.60-920
TS	10300-13680	13930-15380	-
COD	1960-5500	1724-7038	1250-2570
BOD	562-1990	1120-1800	726-1210
Total-P	6-28	6-22	5.8-17.2
Total-N	104-1014	131-930	-
Amm. N	2.1-47	1.88-32.00	3.1-8.0
Total-C	1380-2573	1610-2890	1230-2060
Ca	28-376	47-177	110-440
Ba	0-0.3	0.01-0.13	-
K	402-1940	719-1818	540-980
Ni	0-0.60	0.13-0.95	-
Cd	0-0.15	0.0001-0.23	0-0.001
Cu	0.15-0.46	0.05-0.49	0-0.02
Fe	3.2-17.42	3.6-15.7	2.0-8.6
Pb	0-3.45	0-5.37	0-0.03
Na	1530-5640	2616-5660	1287-1670
Mg	31-109	41-105	55-96
Al	1.13-33.1	1.4-6.6	-
Zn	1.0-4.7	1.0-5.4	1.4-2.0
Cr	0.04-0.70	0.24-0.94	-

(All in mgL^{-1} except otherwise stated)

The average amount of leachate generated in a landfill is 150 L.tonne^{-1} of waste (Agamuthu, 2001). Leachate composition is very different in terms of organic and inorganic pollutant concentrations (Campbell, 1982).

Organic contaminants of leachate are primarily soluble refuse components or decomposition products of biodegradable fractions of waste. The organic compounds include organic acids, ketones, aromatic compounds, chlorinated aromatic compounds, ethers, phthalates, halogenated aliphatic compounds, alcohols, amino-aromatic compounds, nitro-aromatic compounds, phenol, heterocyclic compounds, pesticides, sulfur substituted aromatic compounds, polyaromatic hydrocarbons, polychlorinated biphenyls and organophosphates. The class of organic compounds found at highest concentration in leachate is generally volatile organic acids (VOAs) produced during the decomposition of lipids, proteins and carbohydrates. Aromatic hydrocarbons, including benzene, various xylenes and toluene, are also frequently found at lower concentrations. These compounds are considered to be constituents of gasoline and fuel. Non-volatile classes of compounds such as phenolic compounds may be degradative products of lignin. A small complex fraction found in several leachates contained nicotine, caffeine and phthalate plasticizers (Campbell, 1982).

The dominant organic class in leachate shifts as the age of the landfill increases due to the ongoing microbial and physical or chemical processes within the landfill. An investigation of leachates obtained from landfills operated from one to 20 years found that, the relative abundance of high molecular weight humic-like substances, decreases with age, while intermediate-size fulvic materials showed significantly smaller decreases (Campbell, 1982). The relative abundance of organic compounds present in these leachates was observed to decrease with time in the following order : free VOAs, low molecular weight aldehydes and amino acids, carbohydrates, peptides, humic acids, phenolic compounds and fulvic acids.

A variety of heavy metals are frequently found in landfill leachates, including zinc, copper, cadmium, lead, nickel, chromium and mercury. Again, these metals are either soluble components of the refuse or are products of physical processes such as corrosion and complexation. Heavy metal concentrations in leachate do not appear to follow patterns of organic indicators such as COD, BOD, nutrient or major ions. Heavy metal release is a function of characteristics of the leachate such as pH, flow rate and the concentration of complexing agents (Debra & Timothy, 1998).

The age of a landfill is an important factor that affects the composition of the leachate. For example the ammonium concentrations show only slight increase during the first few years of operation after which the concentration remain almost constant (Campbell, 1982). Young leachates show a high organic load due to large amount of volatile fatty acids; the value of BOD_5 : COD ratio greater than 0.4 indicates a good biodegradability. As biochemical reactions proceed, COD and BOD_5 values decline sharply together with BOD_5 : COD ratio which drops below 0.1 after methanogenesis is established. This shows that a very low biodegradability of old leachates is due to biorefractory organic compounds. Destruction of volatile fatty acids which comprise most of the biodegradable substrates, is also evidenced by pH increase (Campbell, 1982).

The amount of rainfall can also affect the leachate composition. A survey carried out by Ehrig (1983), on 20 German landfills, aged from zero to 15 years, showed that the yearly amount of leachate, at a mean rainfall of 750 $mm.y^{-1}$, is 15 to 20% and 25 to 50% of rainfall for waste with high and low compaction, respectively.

2.1.3 Leachate Collection and Storage (LCS)

When leachate is intercepted by the barrier layer of a liner system, it must be routed from the liner through the use of drainage layers. Leakage through a barrier liner, either as a result of permeation through the material or leakage through a hole or imperfection, increases with an increasing depth of leachate on the liner. Leachate collection systems are therefore designed to minimize the depth of leachate above the liner. The materials that make up the Leachate Collection and Storage (LCS) are typically permeable soils such as sand and gravel, or synthetic drainage devices such as a geonet (synthetic membrane). Leachate drains from the LCS to a series of trenches that typically contain large diameter pipes surrounded by a blanket of gravel. If necessary, a geotextile fabric filter is used to separate the gravel from other drainage materials such as sand in the LCS. The trenches themselves are sloped and ultimately drain to a sump or lift-station. The sump contains a pump that is used to remove leachate from the landfill. A storage system must be provided for leachate at the landfill site and may be part of a leachate treatment system. Typical storage systems include lined surface impoundments and both closed and open tanks (Debra & Timothy, 1998).

2.1.4 Leachate treatment

Leachate accumulated within a landfill or collected from drainage systems designed to protect waters may need to be disposed of and treatment may first be needed to reduce its polluting potential.

Several techniques have been used in laboratory studies, pilot scale and to a lesser extent full scale test for the treatment of leachate from domestic and hazardous waste landfill. On the whole, the objective for the treatment of leachate must reflect the disposal outlet selected. However the concentration of organic pollutants, the presence of inorganic comtaminants and the variable and unpredictable nature of leachate make its treatment difficult.

The chosen treatment depends on the quantity of leachate, available land space, age of the landfill, the required treatment efficiency (which depends on the ultimate receiving water or soil), the cost of available energy source and available capital as well as operating budget.

Leachate treatment techniques which are advanced and tested include aerobic, anaerobic, physical-chemical processes, combination with municipal sewage treatment and with recirculation. The effectiveness of leachate treatment processes varies with leachate from landfill of different ages. Biological treatment was found to be more effective in treating leachate from a relatively young landfill (Loukidou & Zouboulis, 2000). Aerobic biological decomposition is recommended for low-strength (COD < about 500 mgL^{-1}) leachates. For medium-strength (COD range of approximately 500 to 5000 mgL^{-1}) leachates, on the other hand, the choice could be either aerobic or anaerobic. Often, however, potentially toxic metals may have to be removed by pretreatment (such as chemical precipitation). Physical and chemical methods showed better performance in treating old leachates (Keenan *et al.*, 1983)

The aerobic biological treatment processes for leachate involve one or more of the following techniques: activated sludge treatment, contact aeration, rotary disc, deep shaft, oxidation ditch, trickling filters, aerated lagoon treatment (Uloth & Mavanic, 1977; Chian & DeWalle, 1976; cited Agamuthu & Nather, 1997), suspended carrier biofilm reactor (Welander *et al.*, 1998), enzymatic treatment using Sequencing Batch (Bio) Reactor (SBR) (Zouboulis *et al.*, 2001), ultrafiltration-biologically activated carbon (UF-BAC) process (Massoud *et al.*, 1996), moving bed biofilm process followed by a granular activated carbon (GAC) moving bed biofilm processes (Loukidou *et al.*, 2000). These methods will remove the organic matter (COD and BOD) and nitrogen.

The anaerobic biological treatment processes include up-flow anaerobic filter (Chian & DeWalle, 1976 cited Agamuthu & Nather, 1997); anaerobic filter (Bae *et al.*, 1997) and up-flow anaerobic study blanket (UASB) reactor at 37 ^{0}C followed by electrochemical oxidation of 2000 mgL^{-1} of chloride (in the form of sodium chloride) and at a current density of 32.3 Macm^{-2} (Wang *et al.*, 2001).

Physical-chemical methods consist of the addition of chemicals to precipitate, flocculate and coagulate solids or to oxidize inorganic and organic components (Uloth & Maranic, 1977; cited in Agamuthu & Nather, 1997); activated carbon (Pohland, 1976; cited in Agamuthu & Nather, 1997), ion exchange adsorption, reverse osmosis

(Angelo *et al.*, 1999), nanofiltration (Marttinen *et al.*, 2002; Trebouet *et al.*, 2001), air stripping (Keenan *et al.*, 1983 cited in Agamuthu & Nather, 1997), a coagulation process combined with Fenton Oxidation (Yoo *et al.*, 2001), a combination of Classical Fenton reaction with UV light (Kim *et al.*, 1997), fixed-bed adsorption and ozonation (Fettig *et al.*, 1996) and electrochemical oxidation (Chiang *et al.*, 1995). The physicochemical method removes or reduces COD, metals, suspended solids and colour. The processes used include sedimentation with coagulation, sand filtration, ozone oxidation, activated carbon adsorption and chelating resin adsorption (Agamuthu, 2001).

2.2 WATER POLLUTION

Pollution refers to the introduction by human action, directly or indirectly, of substances or energy into the environment, resulting in deterioration effects of such in a nature as to endanger human health, harm living resources or ecosystem and impair or interfere with amenities and other legitimate uses of the environment (Owens & Owens, 1991) Whereas, water pollution may be defined as any chemical or physical change in water detrimental to living organisms. Although the causes of water pollution may be natural, the majority results from human activities. Water pollution is a serious environmental problem which destroys the aesthetic value of water bodies such as lake, river and seas. It also creates an adverse impact on organisms living in such habitats.

One of the most common types of water pollutants apart from disease-causing agents, oxygen-demanding wastes, inorganic plant nutrients, organic chemicals, sediment of suspended matter, radioactive isotopes and heat, is the water-soluble inorganic chemicals (Todd & Mc Nulty, 1976). Inorganic pollutants consist of acids, salts and compounds of toxic metals such as mercury and lead. High levels of these chemicals can make the water unfit for drinking, harm fish and other aquatic life, decrease crop production and accelerate corrosion of equipment that come into contact with the water.

In a sanitary landfill there is little risk or evidence of either pollution or nuisance at the surface, but there is some risk of groundwater pollution. Landfill leachate may cause water pollution if it contaminates either surface or groundwater supplies.

The stages involved in the production of water pollution from a landfill site may be summarized as follows (David, 1981):

1. Water enters the waste. Some water will already be contained in the waste as received, while some will be generated by biodegradation. Additional water may come from infiltrating rainfall, liquid waste, surface water drainage, spring issue or by tipping direct into standing water. Good practice requires the latter three sources to be eliminated by proper site selection or by preliminary engineering works, for example to divert surface water drains. In addition, the use of an impermeable top cover and good grading to aid surface run-off from the site should minimize rainfall infiltration.
2. The leachate leaves the landfill site. This may occur either laterally or vertically. Lateral movement may occur where the permeability of the waste is reduced by high-density compaction. Care is necessary to prevent the contamination of surface water by leachate 'springs'.

3. The leachate passes through the rock structure beneath the site, moving first through any unsaturated zone until it reaches the water table. The concentration of contaminants may be attenuated by physical processes such as dispersion, by chemical interactions with the rock minerals and by biodegradation.
4. Once in the saturated aquifer, the leachate mixes with the water and travels with it to a borehole or other extraction point. The contaminated water is then combined with water coming from elsewhere and may thus enter a drinking water supply.

2.2.1 Groundwater pollution caused by leachate

The most serious problem by far is groundwater contamination. As water percolates through any material, various chemicals in the material may dissolve in the water and get carried along in process called leaching. The water with various pollutants in it is called leachate. As a water percolates through municipal solid waste (MSW), a noxious leachate is generated that consist of residues of decomposing organic matter combined with iron, mercury, lead, zinc and other metal. The nature of the landfill site and the absence of precautionary measures funnel this 'witches brew' directly into groundwater aquifers (Bernard & Richard, 1996).

Studies on the movement of leachate through soils indicate so far that the distance the contaminants travel depends on the composition of the soil, its permeability and the type of contaminant. Organic materials that are biodegradable do not travel far, but inorganic ions and refractory organics can. Furthermore, the rate of movement through some soil may be so slow that the full impact of contaminant travel may not be realized for years. Since natural purification processes are limited, treatment of leachate should be considered when large quantities are expected and a potential water pollution problem exists (Mantell, 1975).

The migration or retention of contaminants in the ground depends on the nature of both the contaminant and the material through which it flows. Groundwater is the vehicle that carries the contaminants, so the migration of contaminants depends on groundwater flow. Retention of contaminants depends on mineralogical and physical characteristics of the medium.

Groundwater moves freely through permeable rock units called aquifers but less freely through relatively impermeable aquifers. Consequently, the best aquifers are also the most susceptible to contamination, whereas the poor aquifers are relatively immune. In a humid region groundwater heads are highest under hills and lowest in valleys because the water table follows the land surface rather closely. Thus groundwater moves from upland zones of recharge to lowland zones of discharge. The dry-weather flow of streams consists mostly of groundwater discharge, which must be balanced by an equivalent amount of recharge in order to satisfy the requirements of continuity. Depending on these controls, water may move only a short distance underground before returning to the surface, or it may be in part of the groundwater for hundreds of years.

2.2.2 Water Quality Standard.

For the year 2000, a total of 901 stations located within 120 river basins were monitored (DOE, 2000). Out of these 901 monitoring stations, 388 (43.1%) were found to be clean, 391 (43.4%) slightly polluted and 122 (13.5%) polluted. In terms of water quality on the basis of river basins, 34 river basins (28.3%) were clean; 74 (61.7%) slightly polluted and 12 (10%) polluted.

Analysis of heavy metals in 5325 water samples revealed that almost all the samples complied with the Interim Water Quality Standards for arsenic (As), mercury (Hg), cadmium (Cd), chromium (Cr), lead (Pb) and zinc (Zn), except for iron (Fe) with 80% compliance (DOE, 2000).

2.3 MICROALGAE

Microalgae are single-celled aquatic organisms that are photosynthetic oxygenic autotrophs that are typically smaller and less structural complex than land plants (Graham & Wilcox, 2000). Microalgae are microorganisms that undergo a simple cell division cycle, in most cases without a sexual type stage enabling them to complete their cell cycle within a few hour. Microalgae are abundant and ancient organisms that can be found in virtually every ecosystem in the biosphere.

For billion of years, microalgae have exerted profound effects on our planet and its biota and they continue to do so today. People from many cultures, ancient and modern have used microalgae for a variety of purposes (Graham & Wilcox, 2000). Microalgae play an important role as the primary producer in the aquatic food chain. It is the natural food of fish and shell fish and is required during certain development stages of crustaceans and mollusks (de Pauw & Persoone, 1998).

For millennia, people throughout the world have collected microalgae for human food (eg: *Chlorella, Spirulina* and *Dunaliella)*. More recently microalgae have begun to play important roles in biotechnology (Graham & Wilcox, 2000). Algal Biotechnology is the application of microalgae for the production food, feed, fine chemicals as well as for environmental bioremediation (Phang *et al.,*1994). The concept of Algal Biotechnology is basically the utilization of photosynthetic machinery for the production of valuable biomass and transfer of solar radiation into chemical energy.

Microalgae have been commercially utilised as nutritional supplements for many years (Apt & Paul, 1999). The dried algal biomass produced from *Chlorella* (Lee, 1997), *Dunaliella* and *Spirulina* (Vonshak, 1997) have dominated the commercial opportunities. The *Chlorella* industry is growing at annual rate of 2% and there are at least 46 plants producing *Chlorella* as health food in Asia, especially in Japan and Taiwan (Kawaguchi, 1980).

In 1995, efforts directed towards microalgae mainly focussed on protein production for human and animal nutrition (Venkatamaran & Becker, 1984). At present, microalgae are viewed as potential sources of single cell protein (SCP) to serve as an important supplementary protein source in the human diet. The crude protein in microalgae ranges around 50% of the microalgal biomass, for example 50-60% in *Scenedesmus* and 56-62% in *Spirulina* (Soeder, 1980).

Many species of microalgae are commercially-valuable materials due to the abundant presence of proteins, carbohydrates, lipids and pigments (Cohen, 1997). Microalgae are also regarded as an important source of unconventional protein, polyunsaturated fatty acids (PUFA) (e.g. γ-linolenic acid, eicosapentaenoic acid and docosahexanoic acid), carotenoids, astaxanthin and β-carotene. In recent years, considerable attention has been directed at unicellular algae for the production of oils and fatty acids containing long-chain polyunsaturated fatty acids (LC-PUFAs) as nutritional supplements (Cohen *et al.*, 1993). A number of algal groups have been identified for the production of high levels of LC-PUFA (Cohen, 1997). New algal products are being developed for use in the mass commercial markets. The algal derived LC-PUFA, mainly docosahexaenoic acids (DHA) are used as supplements in human nutrition and animals. Large-scale production of algal fatty acids is possible through the use of heterotrophic algal production (Apt & Paul, 1999).

Algal products have also been developed into pharmaceutical and research products. Algal products include high-value specialized chemicals, fine chemicals, vitamins, health foods, human food products and aquaculture larval feed products. Therefore, several pilot plants producing several microalgal species specially on *Chlorella, Spirulina, Dunaliella, Pavlova,* (Borowitzka & Borowitzka, 1989) have been established. There are now well established microalgal production plants in Taiwan (*Chlorella, Spirulina*), Thailand, Japan, China, USA, India, Italy, Israel (*Spirulina*), USA (*Dunaliella*) and Australia (*Dunaliella* and *Chlorella*).

2.3.1 Microalgae cultivation system

Microalgae cultivation systems can be divided into three major systems, based on the raw materials used; open system, wastewater system and enclosed bioreactor.

i. The open system where a selected algal strain is grown in a clean process using freshwater, mineral nutrients and additional carbon sources. The algae, produced in this systems are intended to be utilized mainly as food for human or animals. Open systems have the advantages of being cheaper and easier to construct and operate (Tredici & Materassi, 1992). The open system, developed in the 1940's (Becker, 1980) includes high rate algal pond (HRAP) and ranges from the circular ponds where the culture is stirred by a rotating arm, to raceways with the culture is mixed by paddlewheels. Open systems are shallow so that all algal cells can accumulate maximum solar energy to produce high production.

ii. Wastewater system where sewage or industrial wastewater is used as culture medium without the addition of minerals and external carbon. In such plants, the algal population consist of several species in the presence of high amount of bacteria. The main function of this system is the treatment of wastewater. The harvested biomass can be used as animal feed, if not contaminated with toxic compounds, or as substrate for energy production.

iii. Cultivation of algae in an enclosed system (fermenter) under sunlight or artificial light, with cells being grown in a completely autotrophic medium. Culture of algae in the enclosed system reduces contamination. Under this system, algae can be grown in plastic bags of various shapes and sizes placed on the ground. Tubular photobioreactors were later developed as efficient enclosed culture systems (Tredici & Materassi, 1992).

2.4 HIGH RATE ALGAL POND (HRAP)

The concept of the HRAP was developed by Oswald and co-workers in the mid-fifties (Oswald *et al.*, 1957) and the systems are in place in various countries around the world. The HRAP is being developed to provide a maximum yield of algae and reduction of wastewater organics. The typical system consists of a primary settlement lagoon, a shallow 0.2 to 0.6m deep meandering open channel, the HRAP, in which the effluent is propelled by a paddlewheel to prevent settling. The function of the paddlewheel is to provide mixing and not oxygenation, as sufficient oxygen is produced by the high algal biomass achieved in the HRAP (Phang *et al.*, 2001). Mixing in the HRAP helps the interchange of carbon dioxide and oxygen in the system. The paddlewheel mixing system also requires less energy and reduces the stress forces on the algal cells (Borowitzka & Borowitzka, 1989).

Most ponds are operated at average velocities from 10 to 30 $\mathrm{cmsec^{-1}}$ to avoid deposition of algal cells (Dodd, 1986). The slow paddlewheel mixing (15 $\mathrm{cms^{-1}}$) keep the algal cells in suspension to maximize the light capturing and dissolved nutrient assimilation by both algal and bacterial cells. The slow mixing also creates turbulence in the algal culture, which facilitates light-dark regime fluctuation as well as increase in the transfer rates between the growth medium and the cultured organisms (Grobbelaar, 1993). An optimized flow pattern will maximize exposure of the algae to favourable light conditions thereby maximizing the quantity of algal oxygen production and reducing the area or volume requirement of the HRAP. The HRAP is an economical, intensive system for controlled aerobic wastewater or sewage treatment (Shelef & Soeder, 1980). It is one of the most economical and practical way to cultivate algae while contributing oxygen for biodegradation of organic matter.

One of the most important features of the HRAP is the culture depth (0.1 to 0.3m). The minimal depth prevents light attenuation. Together with mixing, these characteristics maximize autrotrophic algal growth in unlimited light and nutrient absorption and the heterotrophic bacterial biodegradation resulting in high treatment efficencies. Retention time of waste treatment in a HRAP range from two days (in mid-summer) to six days (during the winter) (Shelef & Soeder, 1980). The time period required allows the absorption of organic matter into the microbial biomass and resulting in the oxidization of organic matter in a few hours under high dissolved oxygen condition (Oswald, 1991).

The HRAP system has been widely used to treat wastewater such as sewage, pig slurry, tapioca waste, palm oil mill effluent and rubber effluent and have yielded high algal biomass production. For examples the first HRAP in Malaysia was tested by the Rubber Research Institute of Malaysia for secondary treatment of rubber effluent (Nordin & Mohd Zin, 1989). A hydraulic retention time of six days was found sufficient to treat the rubber effluent. Assuming a completely-mixed flow regime, the first-order total nitrogen removal rate of coefficient was 0.339 day^{-1}. They also found that the land requirement for a HRAP system was 40% that for a facultative system.

In Singapore, the HRAP was successfully tested for piggery-waste treatment (Lee *et al.*,1980). HRAP's from 125 to 1230 m^2 were used. The single- loop raceway design was used with pond walls at 50 cm above ground. The channel width was from 1.5 to 7.0 m. Mixed velocity was from 18 to 20 cm sec^{-1} once every four hours for 15 to 30 minutes each time. The operating depth was 20 cm. Loading rate from 175 to

200 kg.ha^{-1}.d^{-1} and retention time from four to eight days were used. At eight days retention time, the BOD, COD and ammonia removals were 89%, 76% and 64% respectively. The Gross Biomass Productivity ranged from 14.3 to 20.5 g m^{-2}.d^{-1} for a loading rate of 200 kg BOD ha^{-1}.d^{-1}.

In Thailand, *Spirulina* is cultured in digested tapioca starch effluent (TSE) in HRAP (Tanticharoen,1992). The 6m x 26m x 0.5 m raceway ponds produce up to 10 g m^{-2}.d^{-1} algal biomass when sodium bicarbonate and nitrogen fertilizer is supplemented in the effluent.

The HRAP is being investigated for treatment of rubber effluent from latex concentrate factory and generation of *Chlorella* biomass at the Institute of Postgraduate Studies, University of Malaya (Phang, 1991; Geetha *et al.*, 1991). Using HRAP of 4 m^2 surface area and pond depth of 0.2 m, the algal biomass peaked between day six and eight while COD, ammonia and phosphate removal reached 98.6%, 96.6% and 94.6% respectively. The algal biomass obtained reach 360 mg.DW.L^{-1} which had average protein, lipid and carbohydrate contents of 55%, 12.5% and 22% respectively. Total carotenoids reached 2.42 mg.g^{-1} dry weight (Phang *et al.*, 1994).

In the Philipines, the HRAP was used to treat human sewage producing algal biomass with high quality protein (Adan & Lee, 1980). Table 5 gives examples of research using HRAP system to treat a variety of wastewaters.

Table 5 : Review of algal yield and the efficiency of waste treatment using the HRAP system.

Ref	Site	Substrate	Yield	Comments
1	Australia	Primary treatment industrial effluent	25 t ha^{-1} yr^{-1}	95% BOD and 72% COD removal, yield used as high protein concentrate for livestock
2	Israel	Municipal waste	44.2 gm^{-2}d^{-1}	92% BOD and 84% COD removal, production of *Scenesdesmus* sp., *Euglena* sp., *Chorella* sp.
3	Philipines	Domestic wastewater	50.0 t ha^{-1} yr^{-1}	90% BOD and >80% NH_3 removal.
4	Thailand	Domestic wastewater	41.0-72.3 mgL^{-1}	49% BOD and 66% N_2 removal Retention time of 4 days.
5	Singapore	Anaerobic digester and	5.4-25.2 gm^{-2}d^{-1}	89% BOD and 64% NH_3-N removal. Culture depth 20 cm, retention time 4-16 days. Production of *Chlorella* sp.
6	USA	piggery wastewater	23.5 t ha^{-1} yr^{-1}	
7	USA	Swine wastewater	0.04 kg.m^{-2}	81% BOD and 64% COD removal
8	Vietnam	Anaerobic liquor of swine wastewater	7-10 gm^{-2}d^{-1}	*Spirulina platensis* culture
9	USA	Underground water, minerals and cat ions	18.0 t ha^{-1} yr^{-1}	Commercial production of algae
10	Hawaii	Inorganic media	20 t ha^{-1} yr^{-1}	Commercial production of algae
11	Taiwan	Inorganic media	300 t . yr^{-1}	Commercial production of *Chorella* sp.
12	Japan	Inorganic media	20.2 t ha^{-1} yr^{-1}	Commercial production of *Spirulina* sp.
13	Thailand	Tapioca wastewater withNaHCO$_3$ and N_2 fertilizer	36 t. yr^{-1}	Commercial production of *Spirulina* sp. for fish and livestock feed
14	Malaysia	Palm oil effluent	5.5-6.4 gm^{-2}d^{-1}	*Euglena* sp. and *Chorella* sp.
15	Malaysia	Anaerobically digested sago starch effluent	14-18 gm^{-2}d^{-1}	*Spirulina platensis*
16	Malaysia	Rubber effluent	5.5-10 gm^{-2}d^{-1}	*Chorella* sp.

References: 1. Dodd and Anderson, 1977; 2. Shelef *et al.*, 1978; 3. Adan and Lee, 1980; 4. Edwards *et al.*, 1980; 5. Lee *et al.*, 1983; 6-7. Lincoln and Hill, 1980; 8-12. Sassaon, 1991; 13. Tantichareon *et al.*, 1992; 14. Phang, 1990; 15. Phang *et al.*, 2000; 16. Phang *et al.*, 2001; (cited Miah, 2001).

2.4.1 Algal –pond processes

The processes occurring in the algal ponding system are shown in Figure 11. Algal activities occur mainly in the upper layer of the pond, the oxygen has to be supplied throughout to the aerobic bacteria for the breakdown of the complex organic matter to the simple forms utilizable by the algae. The amount of mixing would determine the balance between the aerobic processes and the anaerobic processes which take place at the pond bottom.

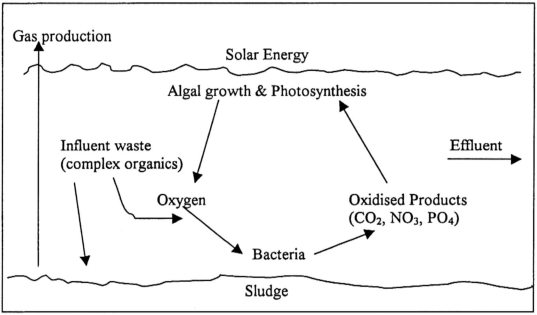


Figure 11: Process occurring in the algal pond (Martin, 1991).

Good mixing increases the pond's ability to handle increased organic loads. Supersaturation with photosynthetic Dissolved Oxygen (DO) occurs during sunshine hours and is usually sufficient to meet the demands of both algal and bacterial respiration at night. DO levels vary from 2.0 g $m^{-2}hr^{-1}$ in midmorning to 0.03 g m^{-2} hr^{-1} at late evening. The aerobic processes may be represented as:

Aerobic bacteria

$(CH_2O)x + xO_2 \rightarrow xCO_2 + xH_2O$

Protein (organic nitrogen) $\rightarrow NH_3 \rightarrow NO_2 \rightarrow NO_3$

Organic sulfur → sulfate

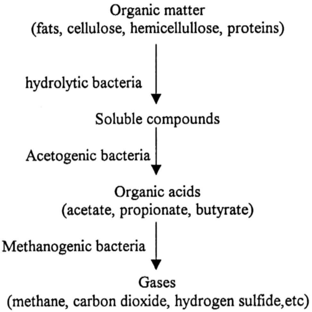
Organic phosphate $\rightarrow H_3PO_4 \rightarrow CaPO_4$

Algal production

$106\ CO_2 + 90H_2O + 16NO_3 + PO_4 + \text{light energy} \rightarrow C_{106}\, H_{180}\, O_{45}\, N_{16}\, P_1 + 154.5\ O_2$

One gram of algae produced in wastewater is equivalent to the production of 1.3 – 1.8 g of DO. Algal cells consists of 55% carbon, 9% nitrogen and 1% of phosphorus.

The anaerobic processes may be shown as follows:



In the upper layer of the pond, rapid algal growth depletes CO_2 and bicarbonate, increasing the pH to levels as high as 11. At this high pH, calcium, magnesium and phosphorus precipitates while ammonia is lost to the atmosphere. High pH also inhibits algal and bacterial growth. These limitations prevent the pond from achieving high efficiency treatment.

The major external influencing factors for algal growth are light and temperature (Goldman, 1979). In outdoor mass cultures, the algal yields are closely correlated with irradiance (Ayala *et al.*, 1988). Studies have been conducted to correlate between growth and light for mass culture of microalgae in the outdoor culture systems (Vonshak *et al.*, 1982; Fontes *et al.*, 1987; Vonshak & Richmond, 1988; Richmond & Hu, 1997). The highest specific growth rate (μ) is achieved at the lowest cell density when mutual shading and light limitation are minimal. With increasing population density, the μ decreases because of light limitation. In dense cultures, not all the cells receive the maximum amount of light at all the time. If the cells are mixed appropriately, resulting in an alternating high-light/low-light regime, algal growth is enhanced (Laws *et al.*, 1983; Grobbelaar, 1994). For example, the growth of *Spirulina plantesis* becomes saturated at a range of 150 to 200 $\mu mol.s^{-1}.m^{-2}$, which is 10 to 15% of the total solar irradiance in the range of 400 to 700 nm (Vonshak, 1997).

Temperature is an important environmental factor, which affects all metabolic activities. It also affects nutrient availability and uptake, as well as other physical properties of the cells aqueous environment. In outdoor cultures, temperature varies throughout the diurnal cycle. In the morning, the pond temperature varies from 15 to 20 ^0C and the optimal temperatures in the range of 35 to 38 ^0C are reached only in the early afternoon. In tropics, optimal temperatures occurs earlier during the day but at night and at early morning temperature fall below the optimum temperature (Vonshak, 1997). Such trends are advantageous as it reduces the night biomass loss due to lower respiration rate. It has been demonstrated that relatively high temperature at night can increase respiration rate, which may result in higher night biomass loss (Grobbelaar & Soeder, 1985; Torzillo *et al.*, 1991).

During the wastewater treatment by algal culture, the CO_2 for algal growth originates both from the availability in relation to pH as well as the organic carbon substrates through bacterial activity. Azov (1982) has suggested that free CO_2 may be limiting in dense algal cultures with high pH values although Lincoln and Hill (1980) noted that bacterial respiration produce sufficient free CO_2 from organic matter to retard the depletion of the HCO_3 to CO_2 reservoir, thus minimizing the pH rise.

The successful operation of algal treatment systems depends upon establishing a dynamic equilibrium between algal O_2 production and bacterial O_2 consumption (Goldman 1979; Lincoln & Hill 1980). The algal and bacterial interaction is normally considered as a symbiotic relation in nature (Allen & Garrett 1977). The algae utilize CO_2 and the nutrients produced through aerobic bacterial degradation of the organic matter provided by the wastewater. The algae subsequently release oxygen by photosynthesis. This oxygen is utilized by bacteria. Thermodynamic conditions indicate that nearly 300 bacterial units are required to ensure the necessary CO_2 supply per algal unit. Under the practical conditions of the HRAP system the algae and bacteria ratio is about 1:250 and an alternative source of CO_2 may be considered to keep the system in thermodynamic equilibrium. Gideon *et al.* (1979) found the algae: bacteria ratio of about 1: 100 in HRAP used for waste treatment.