2. LITERATURE REVIEW

2.1 Considerations on sewage treatment in developing countries

The deleterious impacts caused by the discharge of raw sewage or poorly treated effluents on natural resources and public health are well known. One of the main arguments for justifying this situation in developing countries is the high cost of sanitation facilities provision and the lack of capital resources to invest in the sector.

The scarcity of resources is habitually responsible for deficient maintenance of the infrastructure and includes inadequate human resources as the most important constraint (i.e. shortages of skilled manpower, insufficiently experienced and lacking adequate training and motivation). This factor also includes lack of material resources like spare parts, electricity, chemicals, laboratory facilities, and equipment for maintenance tasks. Therefore, the development of suitable wastewater treatment technologies for developing countries evidently needs to be addressed. In this way, a wider set of reliable technological options able to cope with the above mentioned constraints must be developed and promoted accordingly.

In the case of Latin America, a considerable amount of work on sustainable wastewater treatment options has been and is being currently developed. Different groups from Brazil, Peru and Colombia, in collaboration with European Universities mainly from the UK and the Netherlands, are working on the improvement and adaptation of different technologies for domestic sewage treatment. Diverse types of anaerobic reactors, WSP and other natural wastewater treatment methods (mainly constructed wetlands) are the main options evaluated for sustainable wastewater management strategies in the region. Nevertheless, despite the relative simplicity of some technologies such as high-rate anaerobic reactors, about 10,400 small municipalities with less than 20,000 inhabitants in Latin America and a few thousand rural settlements in the Andean Region (Mascareño and Balbi, 1995) are in need of simpler but more efficient and affordable technologies.

In this sense, Peña (2002) found that WSP are a good option for small municipalities located in flat lands of Colombia. However, the development of improved ponds requiring less area per inhabitant would make WSP technology a more feasible option for both small rural communities and Andean settlements facing land area availability and low ambient temperature restrictions. This result may cautiously be extended to other natural treatment systems and anaerobic technologies in the perspective of developing a sustainable wastewater management strategy for the whole of the Andean region in Latin America.

2.2 Anaerobic treatment of domestic wastewater

A thorough look over the trends in wastewater treatment show that aerobic systems have been more developed hitherto than anaerobic systems. However, the former require higher amounts of capital resources and skilled manpower compared to the latter. This is partly due to the very nature of aerobic wastewater treatment, which requires an external source of oxidant (e.g. oxygen is the natural oxidant of organic matter used in aerobic wastewater treatment). As reported by van Haandel and Lettinga (1994), in conventional aerobic metabolism about 67 percent of the organic matter is converted to cell mass by a process called anabolism. This feature has profound implications for the running costs of aerobic treatment systems due to the large daily biological sludge production that requires further treatment and safe disposal.

In contrast to this, anaerobic digestion, which is a fermentative process, exhibits important features such as the production of stable final products and also a much lower cell mass output. According to van Haandel and Lettinga (1994), only around 3 percent of the organic matter present in the wastewater is converted to cell mass. The other 97 percent is converted via catabolism into CH_4 and CO_2 as stable end-products. Thus, in anaerobic treatment systems, the daily biological sludge production is much lower and this reduces the costs of its further treatment and disposal. Additionally, the CH_4 produced is a suitable source of energy readily available for different purposes.

Figure 2.1 presents the fractions of organic matter converted via anabolism (cell mass production) and catabolism (stable end-products) for both conventional aerobic and fermentative metabolisms.

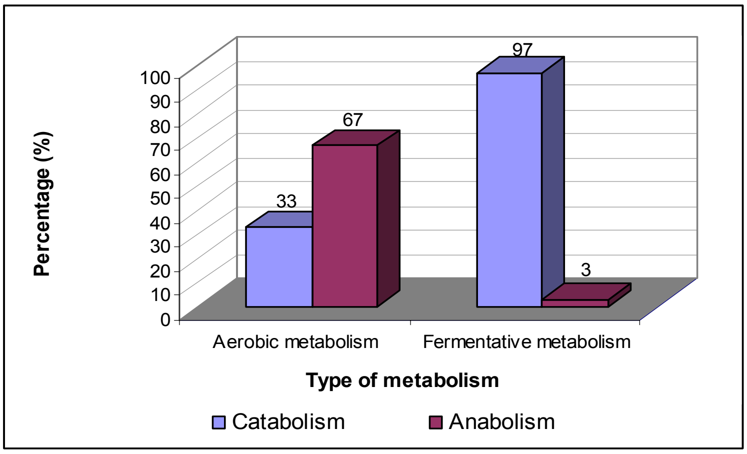

Figure 2.1 Fractions of organic matter converted via anabolism and catabolism in both conventional aerobic and anaerobic metabolisms.

Furthermore, anaerobic digestion processes are very appropriate for tropical and subtropical countries with average temperatures above 15 ºC. Nevertheless, promising results at even lower temperatures have been reported elsewhere (Lettinga, 1995).

Anaerobic digestion encompasses a complex consortium of microorganisms. Earlier work on the biochemical processes as well as the microbial species involved in anaerobic digestion suggested that these could be classified into three main categories (Toerien *et al.,* 1970). A flow diagram of the main process steps is shown in Figure 2.2.

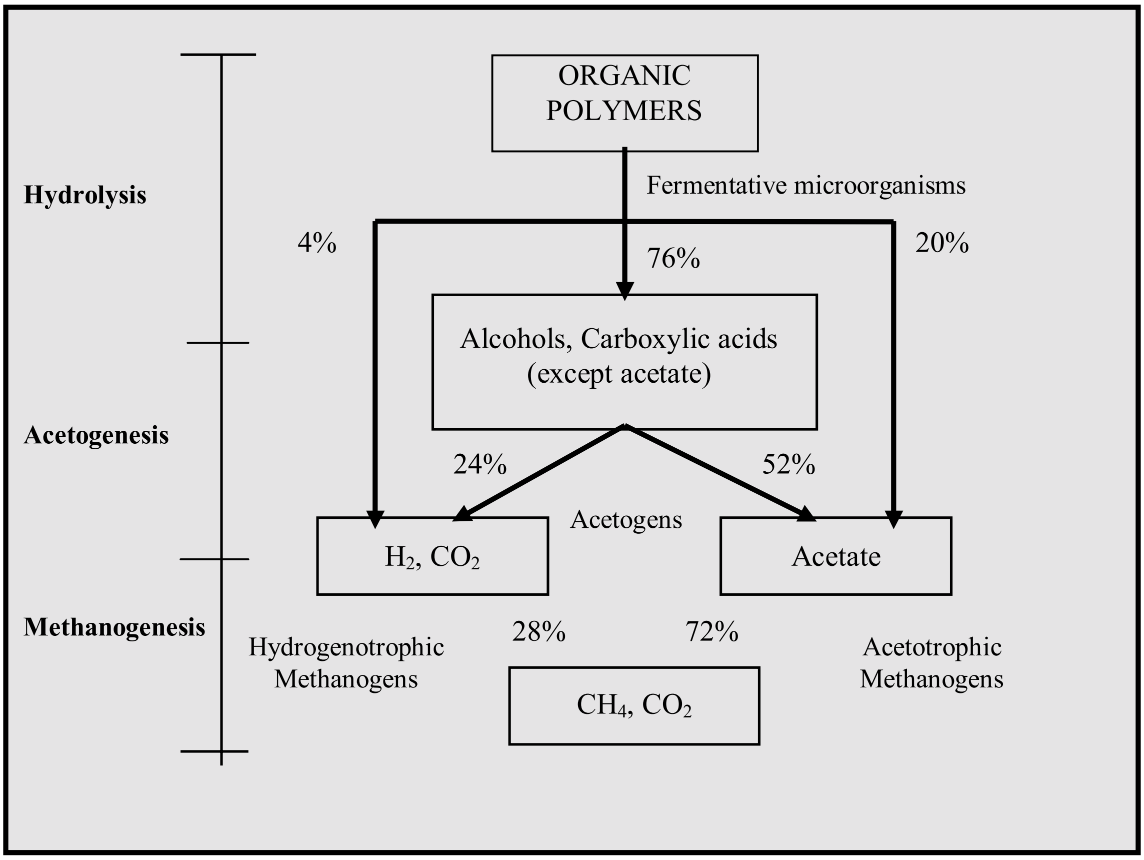

Figure 2.2 Anaerobic decomposition of organic matter.
Source: Droste (1997), taken from Zehnder *et al.* (1982).

Hydrolysis. This stage refers to the breakdown of large, complex soluble and insoluble molecules into smaller ones that can be transported into the cells and metabolised. Extra cellular enzymes associated with the primary fermentative bacteria carry out this preliminary task. Proteins are converted via polypeptides to amino acids, carbohydrates are degraded to soluble sugars, and lipids are transformed into long chain fatty acids and glycerine (van Haandel and Lettinga, 1994). Hydrolysis is an energy consuming process and the fermentative bacteria responsible for this step do not form methane (Droste, 1997).

Formation of acids and acetogenesis. The products of hydrolysis are converted into organic acids by the fermentative acidogenic bacteria (e.g. *Clostridium* spp.). They convert sugars, amino acids, and fatty acids into organic acids like acetic, propionic, formic, lactic, and butyric or succinic acids; and alcohols and ketones, acetate, CO_2, and H_2 (Bitton, 1994). The products from this stage vary with the type of bacteria and environmental conditions (i.e. temperature, pH and redox potential).

The acetate and H_2-producing bacteria called acetogenic bacteria such as *Syntrobacter wolinii* and *Syntrophomonas wolfei* (McInernay *et al.*, 1981) (quoted by Bitton, 1994), transform the products of acidogenesis into acetate, hydrogen and carbon dioxide, which are the substrate for the methanogens. From Figure 2.2, approximately 72 per cent of the influent COD is converted to acetate. There may be formation of carbon dioxide or hydrogen along with the acetate depending on the oxidation state of the original organic matter (van Haandel and Lettinga, 1994). In complex substrates such as sewage, both processes are likely to occur simultaneously.

Methanogenesis. This stage comprises the production of methane from acetate or from the reduction of CO_2 by acetotrophic and hydrogenotrophic methanogens. The acetotrophic methanogens (also known as acetoclastic archaea) convert acetate into CH_4 and CO_2 according to the following reaction.

$$CH_3COOH \rightarrow CH_4 + CO_2 \tag{2.1}$$

Based on experimental data and thermodynamic considerations the following reaction for acetate conversion to methane was proposed by Zeikus (1975):

$$CH_3COOH + 4H_2 \rightarrow 2CH_4 + 2H_2O \tag{2.2}$$

The most common acetoclastic methanogens found in reactors treating substrates with a high volatile fatty acids concentration are from the genera *Methanosarcina* and *Methanosaeta* formerly called *Methanothrix* (Patel and Sprott, 1990). According to Zinder (1988), *Methanosarcina* spp. are coccoid bacteria with doubling times around 1.5 d, and *Methanosaeta* spp. are sheathed rods, sometimes growing as long filaments with doubling times near 4 d.

Meanwhile, the hydrogen-utilising methanogens help to maintain the low partial pressures needed for the conversion of volatile fatty acids and alcohols to acetate, Speece (1983). This bacterial group converts hydrogen and carbon dioxide into methane following the next reaction:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (2.3)$$

There is a synergistic relation between the hydrogen producers and the hydrogen scavengers. Small variations in hydrogen concentration can change the products of the acid-forming phase. Harper and Pohland (1987) found that as the hydrogen partial pressure rises, hydrogen oxidation becomes more thermodynamically favourable than acetate degradation and acetate concentration is therefore increased. The degradation of other substrates such as alcohols is also inhibited by high hydrogen concentrations. Hydrogen is an important intermediate product in the metabolic processes despite its very small net production.

It is suggested that overall hydrogen partial pressures are below 10^{-4} atm for stability and good performance in anaerobic systems. This pressure corresponds to a 10^{-8} M solution, which assures continuous production of acetic acid from influent and intermediate organics without inhibiting the acetate utilisation capacity (Harper and Pohland, 1987).

Henze and Harremoes (1983) found that hydrogenotrophic methanogens grow faster than acetotrophic methanogens, the latter generally being the rate limiting with respect to the conversion of complex macromolecules in sewage to biogas. Some authors group together the first stages of anaerobic digestion and call them acid fermentation, whereas the last phase is called methanogenic fermentation.

All the features previously described make the anaerobic treatment of wastewater a very important field of research where improvements and new developments are needed to overcome the environmental problems faced by several industrialising countries around the world.

In the following sections, the terms *anaerobic treatment* or a*naerobic digestion* will be indifferently used when referred to sewage treatment.

2.2.1 Principles of anaerobic treatment

Bacterial metabolism. This is the most important mechanism for the removal of organic matter in any biological sewage treatment system. It refers to the use of the organic material, either as a source of energy or as a source for the synthesis of cellular mass. Bacterial metabolism comprises two well-defined processes: catabolism occurs when organic matter is used as energy source and it is consequently transformed into stable end-products; and anabolism refers to the conversion and addition of the organic matter into cell mass.

Anabolism consumes energy and it is only possible if catabolism takes place at the same time in order to supply the energy needed for cell synthesis. Therefore, these two biochemical processes are interdependent and simultaneous.

Fermentative catabolism. Anaerobic digestion is a fermentation process applicable to wastewater treatment. Fermentative catabolism occurs in the absence of an oxidant element and it takes place without the transfer of electrons (van Haandel and Lettinga, 1994). The following general equation describes the process of anaerobic digestion:

$$CxHyOz + \frac{(4x - y - 2z)}{4} H_2O \rightarrow \frac{(4x - y + 2z)}{8} CO_2 + \frac{(4x + y - 2z)}{8} CH_4 \tag{2.4}$$

According to this equation, there is a production of methane, which is the most reduced organic compound that exists. In this sense, anaerobic digestion can be regarded as the ultimate fermentative process. Carbon dioxide, which is a more oxidised compound, is also produced and both gases escape from the liquid phase as the so-called biogas. The CH_4 produced keeps the capacity for electron transfer as no oxidation of organic material occurs during the treatment process.

The energy effect for oxidative catabolism when oxygen or nitrate is the oxidant exceeds that of fermentative catabolism significantly (van Haandel and Lettinga, 1994), as shown by the following reaction:

$$C_2H_4O_2 + 2O_2 \rightarrow 2CO_2 + 2H_2O + 207kcal \tag{2.5}$$

According to Equation (2.5), the oxidation of acetic acid with oxygen releases a free energy of 207 kcal/mol. If it follows the anaerobic digestion path instead, the following reaction occurs:

$$C_2H_4O_2 \rightarrow CH_4 + CO_2 + E_{dig} \tag{2.6}$$

The free energy (E_{dig}) released from reaction (2.6) may be calculated taking into consideration firstly the free energy released during methane oxidation according to the following reaction:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 191kcal \tag{2.7}$$

By combining (2.5) and (2.6), reaction (2.4) is obtained and consequently the free energy balance is given by:

$E_{dig} + 191 = 207$ kcal/mol $\qquad E_{dig} = 16$ kcal/mol

In conclusion, the released free energy from anaerobic digestion of acetic acid is equivalent to only 8 percent of the free energy released from oxidation of the same compound. Therefore, the remaining 92 percent is kept as chemical energy in the form of CH_4.

Anabolism. Anabolism causes growth of the bacterial mass and it can be measured by the increase in volatile suspended solids concentration (VSS). Meanwhile, catabolism can be estimated by the methane production. The entire combined effect of these two processes can be determined from the reduction in the substrate concentration (organic matter). The yield coefficient (Y) correlates the bacterial mass formed from anabolic activity, and the metabolised mass of organic material (Metcalf and Eddy, 1991).

$$Y = -dX / dS \tag{2.8}$$

Where Y is the yield coefficient, X is the volatile solids concentration, and S represents the organic material concentration. The value of Y is practically constant for most organic compounds, but it depends on the nature of the associated catabolic reaction (van Haandel and Lettinga, 1994). Figure 2.3 provides a schematic representation of substrate utilisation by bacterial metabolism.

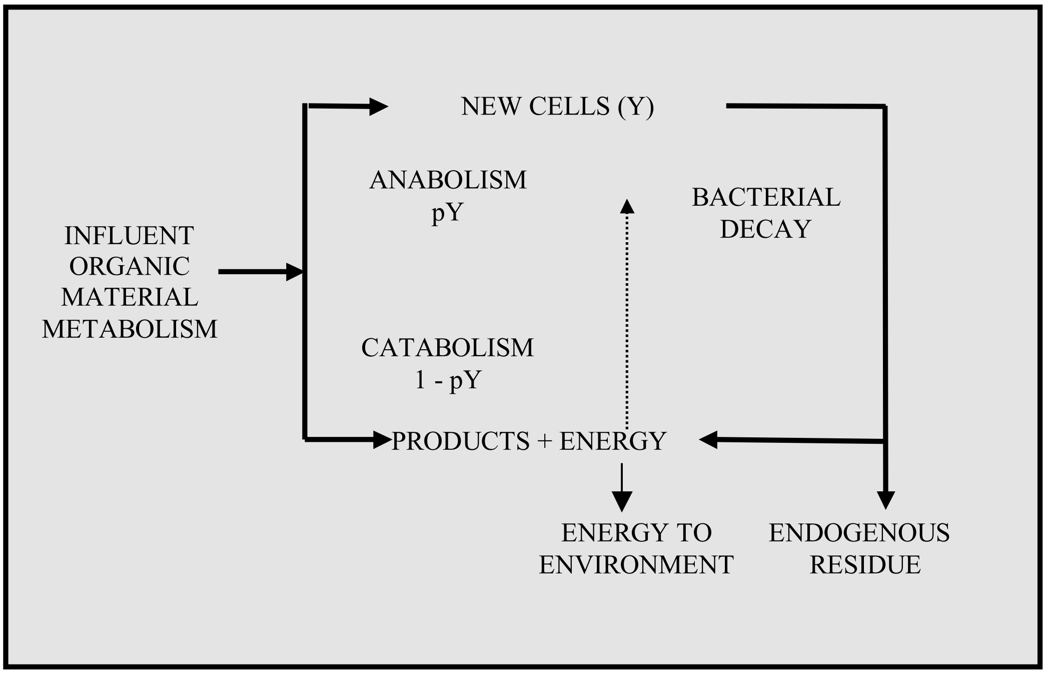

Figure 2.3 Bacterial metabolism (anabolism and catabolism) and bacterial decay.
Source: Van Haandel and Lettinga (1994).

According to Marais and Ekama (1976), the value of Y in oxidative metabolism is around 0.45 gVSS/gCOD. McCarty (1990) reported a value of Y between 0.02-0.03 gVSS/gCOD for methane-producing bacteria. Consequently, the production of bacterial mass in aerobic wastewater treatment plants exceeds that in an anaerobic system.

From Figure 2.3, the constant (p) denotes the COD value of a unit mass of microorganisms, determined as volatile suspended solids (VSS). In accordance with different experimental results, the value of (p) is around 1.48 (van Haandel and Lettinga, 1994). In the case of aerobic metabolism, when 1 kg of COD is metabolised, it results in 0.45 kg VSS, then a fraction of pY = 1.48 * 0.45 = 0.67 of the metabolised organic matter is anabolised and the other 0.33 is then catabolised. For anaerobic metabolism Y is about 0.02 gVSS/gCOD and the anabolised fraction is then pY = 1.48 * 0.02 = 0.03. The remaining 0.97 is the large fraction of the organic matter that is converted into methane (van Haandel and Lettinga, 1994).

Bacterial decay. Microbial growth is controlled by the abundance or lack of nutrients and electron acceptors, as well as the production and accumulation of inhibitory metabolites (Bitton, 1994). The bacterial population is thus subject to decay and part of this biomass itself is biodegradable and undergoes metabolism, as it constitutes another source of organic matter (van Haandel and Lettinga, 1994). This process is known as endogenous respiration. Several experimental results demonstrate that the decay rate of bacteria follows a first-order kinetics given by:

$$dX_v / dt = - K_e X_v \tag{2.9}$$

According to Droste (1997), the values of the decay rate constant (K_e) for anaerobic cultures at temperatures in the range of 30-40 ºC (adapted from Henze and Harremoës, 1983), fall in the following ranges: for acid formers K_{ea} = 0.08-6.1 d^{-1}; for methane formers K_{em} = 0.01-0.04 d^{-1}, and for the overall process K_e = 0.01-0.04 d^{-1}, but typically 0.03 d^{-1}. From these values, it can be seen that the decay rate of methanogenic bacteria is very low; this explains why anaerobic biosolids remain active for long periods without feeding.

2.2.2 Anaerobic digestion kinetics

Kinetics refers to the relation between the velocity at which a reaction occurs and the substrate utilisation rate. Most of the expressions formulated to describe the kinetics of microorganisms metabolism are based on the Monod model. This model has been widely accepted and used in biological treatment because of its mathematical simplicity and the relative easiness to estimate the kinetic parameters. Previous work by Lawrence and McCarty (1969) and Lawrence and McCarty (1971) found that Monod kinetics were reasonably satisfactory for methanogenesis in anaerobic digestion. Thus, if anaerobic digestion exhibits Monod-type kinetics, the bacterial growth rate (μ) is related to the concentration of the limiting substrate (S) by following Equation (2.10).

$$\mu = \mu_m S / (K_s + S) \tag{2.10}$$

where μ = specific growth rate (d^{-1})

μ_m = maximum specific growth rate (d^{-1})

K_s = Monod constant or half-saturation constant (mg COD/l)

Barthakur *et al.* (1991) point out that several dynamic simulation models have been developed based on a continuous multiculture system corresponding to major bioconversion steps in anaerobic digestion with the assumption of culture growth following Monod-type kinetics. However, several researchers have declared doubts about the validity of applying the Monod model to anaerobic wastewater treatment (Grady *et al.,* 1972; Pfeffer, 1974; Chen and Hashimoto, 1980), given the complex composition of such a substrate. Kinetic data on anaerobic biodegradation of domestic sewage are scarce. Therefore, more information on this is needed in order to improve reactor design and performance (Castillo *et al.,* 1999).

From Equation (2.10), at high substrate concentrations, the ratio $S / (K_s + S)$ approximates unity and the bacterial growth rate becomes a zero-order reaction. In other words, it turns out to be independent of the substrate concentration. Meanwhile, if the substrate concentration is low (with S values well below K_s), the bacterial growth rate becomes proportional to the substrate concentration, which is a feature of a first-order reaction. As an example, Figure 2.4 taken from van Haandel and Lettinga (1994) shows specific growth rate values as a function of substrate concentration for the archaea *Methanosaeta* spp. and *Methanosarcina* spp. The maximum specific growth rates of these acetate-consuming organisms are $\mu_m = 0.1$ and $0.3\ d^{-1}$, respectively. Meanwhile, the half-saturation constant or affinity constant (K_s) corresponds to the substrate concentration at the half maximum specific growth rate value. For *Methanosaeta* spp. and *Methanosarcina* spp. these values are $K_s = 30$ and 200 mg/l acetate, respectively.

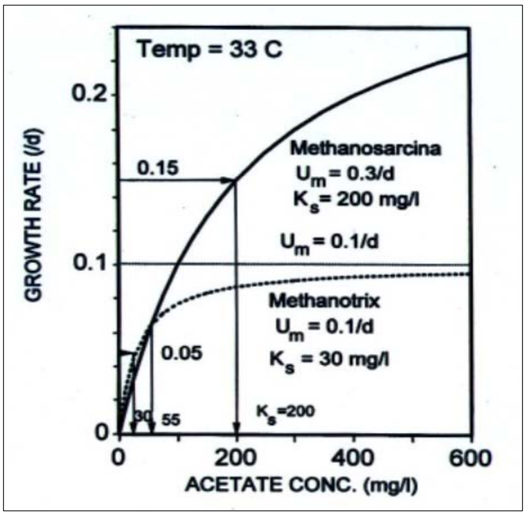

Figure 2.4 Monod kinetics model for *Methanosaeta* spp. and *Methanosarcina* spp. specific growth rate.

Source: van Haandel and Lettinga (1994).

At low acetate concentrations the specific growth rate of *Methanosaeta* spp. becomes higher than that of *Methanosarcina* spp., thus, the methanogenic population will be predominantly composed of the former. However, above an acetate concentration of 55 mg/l, *Methanosarcina* spp. will out-compete *Methanosaeta* spp. and become the dominant acetate-consuming organism (van Haandel and Lettinga, 1994).

A minimum substrate concentration is required in order to maintain a steady state bacterial growth in the reactor. It must be enough to sustain a growth rate of the bacterial population greater than its loss rate due to lysis and endogenous decay mechanisms; therefore $\mu_m \geq K_e$. This can be expressed mathematically by substituting in the Monod equation (2.10) the specific growth rate (μ) with the endogenous decay constant (K_e) (Terzis, 1994):

$$K_e = \mu_m S / (K_s + S) \tag{2.11}$$

Solving for S:

$$S_{min} = K_s K_e / (\mu_m - K_e) \tag{2.12}$$

The value of S_{min} given by (2.12) is the lowest value of the substrate concentration, which can be obtained in the treatment system. Given the sequential steps in the anaerobic treatment of sewage (hydrolysis, acetogenesis and methanogenesis), the minimum substrate concentration under these conditions will be equal to the sum of the minimum concentrations for the different processes (van Haandel and Lettinga, 1994). There is no way to achieve lower effluent substrate concentrations than S_{min} under any process loading at fixed environmental conditions (Terzis, 1994).

In practice, the effluent substrate concentration may be greater than the minimum achievable because otherwise a very long retention time would be required. Due to this fact, there will be a net growth of cellular mass within the reactor and after some time of operation, the system will become full of biomass. Thus, at some time, wastage of the excess biomass becomes unavoidable. If the rate of wastage is equal to the net production rate of sludge then a constant biomass concentration will be established in the reactor. A very important operational parameter, the sludge age, or the average sludge residence time (θ_s), is related to the effluent substrate concentration and it is given by the following ratio:

$$\theta_s = \text{mass of solids in the reactor / solids wastage rate}$$

Therefore, a mass balance for a steady-state reactor without accumulation of biomass renders (van Haandel and Lettinga, 1994):

$$(dX/dt)_w = (dX/dt)_g + (dX/dt)_d \tag{2.13}$$

or:

$$X/\theta_s = X\mu - XK_e \tag{2.14}$$

Solving for θ_s:

$$\theta_s = 1 / (\mu - K_e) \tag{2.15}$$

where X = biomass concentration (mg VSS/l)

μ = specific growth rate (d^{-1})

K_e = decay rate constant (d^{-1})

θ_s = sludge age (d^{-1})

w, g, d = wastage, growth and decay, respectively

By substituting μ from equation (2.15) into equation (2.10), the following expression is obtained for effluent substrate concentration in a completely mixed reactor:

$$S = K_s (K_e + 1/\theta_s) / [\mu_m - (K_e + 1/\theta_s)] \tag{2.16}$$

Equation (2.16) shows that the effluent concentration depends on the values of three kinetic constants (K_s, μ_m, K_e) and the sludge age (θ_s) as a process variable. The minimum sludge age (θ_{sm}) can be calculated from equation (2.16) when the effluent substrate concentration S is equal to the influent concentration. This occurs when conversion of organic matter does not take place. It must be noticed that the influent substrate concentration is much higher than K_s value, so that removal of organic matter effectively takes place. Under these considerations, equation (2.16) simplifies to:

$$\theta_{sm} = 1 / (\mu_m - K_e) \tag{2.17}$$

On the other hand, by replacing (2.17) in equation (2.12) the following expression for the minimum substrate concentration (S_{min}) in terms of θ_{sm} is obtained (Terzis, 1994):

$$S_{min} = K_s K_e \theta_{sm} \tag{2.18}$$

Equation (2.18) reveals an association between S_{min} and θ_{sm} that is substrate specific and represents the lower limit of the effluent substrate concentration essential for adequate process operation (Terzis, 1994).

Elefsiniotis and Oldham (1993) hold that the sludge age or average sludge residence time (θ_s) is an operational parameter, which can be used as a selective factor by imposing stress on bacterial consortia. It affects the mixture of organisms that eventually predominate in the system because it tends to select them in accordance with their generation times. These researchers concluded that if the same microbial community is responsible for the conversion of particulate organic matter to volatile fatty acids (VFA), then θ_s below a certain value poses a limit on acidogenic activity causing an accumulation of intermediate soluble products. It is therefore evident that longer θ_s values facilitate the conversion of soluble metabolic intermediates from the acidogenic phase to the end-products of methanogenesis.

Another important kinetic constant is the specific substrate utilisation rate (k, kg COD/kg VSS d), which indicates the maximum mass of substrate that can be metabolised per unit mass of bacteria per unit of time. It is calculated as the ratio of the maximum specific growth rate (μ_m) and the yield coefficient (Y) as follows:

$$k = \mu_m / Y \tag{2.19}$$

As an example, Table 2.1 presents experimental values of the most important kinetic constants for both acid and methanogenic fermentation when pure anaerobic cultures are grown in readily degradable wastes under favourable laboratory conditions.

Table 2.1 Kinetic constants for anaerobic cultures at temperatures in the range 30-40 °C.

Kinetic constant	**Range**	**Typical**	**Remark**
Acid Formers.			
k, [gCOD/gVSS/d]	9.5-176	13	For the Monod model
K_s, [g/l]	0.023-31	0.2	
Y, [gVSS/gCOD]	0.12-.054	0.15	
K_e, [d^{-1}]	0.08-6.1	0.5	
Methane Formers.			
k, [gCOD/gVSS/d]	1.8-17	13	For the Monod model
K_s, [g/l]	0.002-3.9	0.05	
Y, [gVSS/gCOD]	0.02-0.28	0.03	
K_e, [d^{-1}]	0.01-0.04	0.02	
Overall Process.			
k, [gCOD/gVSS/d]	-	2.2	
K_s, [g/l]	0.2-.04	1.0	For a Monod kinetic model
Y, [gVSS/gCOD]	0.024-0.21	0.18	
K_e, [d^{-1}]	0.01-0.04	0.03	

Source: Droste (1997).

Van Haandel and Lettinga (1994) point out that when the substrate is sewage the situation is more complicated because new factors affect the kinetics of the reactions involved. Firstly, the sludge mass will have an inorganic fraction due to the flocculation of inorganic material in the influent or generation of insoluble salts. Such a fraction in many cases will account for more than 50 per cent in raw sewage. Secondly, depending on the operational conditions of the system, there may be a fraction of biodegradable and particulate organic matter present in the sludge mass. Consequently, the anaerobic sludge will contain a small methanogenic fraction. Thirdly, since bacteria remain in the treatment reactor for a very long period, then decay and accumulation residues become important. This is especially true for the acid formers, which decay at a higher rate than methanogens. Combination of the factors already mentioned will result in an anaerobic sludge with a maximum substrate utilisation rate (k) much lower than that of pure cultures and may be between 0.05 to 0.50 gCOD/gVSS/d.

Van Haandel and Lettinga also argue that available kinetic expressions for anaerobic digestion are of very limited value for the prediction of organic load removal efficiency or for the design of a system with a certain specified effluent quality. However, various studies carried out by different researchers (Han and Levenspiel, 1987; Diaz and Howell, 1987; Barthakur *et al.*, 1991; Elefsiniotis and Oldham, 1993; Hoh and Cord-Ruwisch, 1996 and Droste 1997) show that, although kinetics and modelling of anaerobic processes is a difficult task, it is necessary in order to predict operating conditions and effluent quality. The designer as well as the modeller must be aware of the basis on which kinetic coefficients are determined and therefore apply the model consistently.

As pointed out by Terzis (1994), some kinetic constants like Y, K_e, and μ_m have been widely researched under various environmental conditions. In contrast, K_s values have not been determined as often and much less is known about their dependence on environmental factors like temperature and pH.

2.2.3 Modelling of anaerobic digestion

Improvements in anaerobic process design, its control, modelling and kinetics have to consider that all governing mechanisms and chemical reactions are biologically mediated. Thus, anaerobic microbiology and biochemistry dictate process evolution. Additionally, hydrodynamics and mass transfer phenomena affect the biochemical reactions whenever the process is placed into a particular reactor configuration (Harper and Suidan, 1991). The intrinsic complexity of anaerobic treatment processes makes their modelling difficult. Nevertheless, several attempts have tried to develop models for suspended growth processes (Droste, 1997).

An underlying principle is that a model must be consistently applied with the assumptions and conditions upon which it was developed. Wentzel and Ekama (1997) argue that, given the complexity of biological wastewater treatment processes, designs based on practical experience only will no longer provide optimal performance; hence, design procedures based on fundamental behavioural patterns are required. Nonetheless, Harper and Suidan (1991) point out that researchers must carefully differentiate scientific desires from engineering needs in order to interpret data usefully within the limits of experimental design and current analytical capabilities. The latter issue becomes essential given the difficulties involved in understanding the complexity of anaerobic processes variables.

General kinetic model. A model of the overall anaerobic process considers only a single biomass and lumps substrates together. In many situations, methane formation controls the rate of process performance and this fact validates the overall model, as the kinetic coefficients will largely reflect those of the methane formers (Droste, 1997). A completely mixed reactor (CSTR) with suspended growth without recycling is examined in the following paragraphs. The mass balance considering a Monod removal rate expression is given by:

Accumulation = Input - Output + Generation

$$\frac{dS}{dt}V = QS_o - QS_e - \frac{kX_vS_e}{K_s + S_e}V \tag{2.20}$$

where S_e = effluent COD [M/L^3]
S_o = influent COD [M/L^3]
X_v = VSS in the reactor [M/L^3]
k = overall rate constant [T^{-1}]
K_s = Monod constant [M/L^3]
t = [T]

The biomass balance equation for net biological growth is:

$$\frac{dX_v}{dt}V = QX_o - QX_v + Y\frac{kX_vS_e}{K_s + S_e}V - K_eX_vV \tag{2.21}$$

where X_o = influent VSS (It is negligible) [M/L^3]
Y = overall yield coefficient [M/M]
K_e = overall decay rate constant [T^{-1}]
Q = flow rate [L^3/T]
V = reactor volume [L^3]

The equation for methane production depends on the rate of substrate removal and the conversion factor for COD to methane, which is 0.25 g CH_4/g COD removed.

$$Q_m = 0.25\frac{kX_vS_e}{K_s + S_e}V \tag{2.22}$$

where Q_m = methane production [M/T]

The above equations apply when the influent substrate concentration is mainly soluble organic matter. This model must be used with caution since it is highly simplified (Droste, 1997). It must be noticed that operating data and kinetic constants for a given wastewater and process are less likely to be directly applicable for different reactors or liquid wastes.

Definition of terms in the substrate and biomass solids balances is straightforward when the organic matter is predominantly soluble. However, a non-recycling CSTR is a suitable choice for wastes with high content of suspended solids. Thus, if the raw influent contains a significant amount of suspended solids, the VSS in the reactor comprise a mixture of biomass and partially degraded influent VSS. Since the influent VSS content is generally not acclimated anaerobic biomass, it is erroneous to use total VSS within the reactor in the kinetic expressions.

According to Chung and Neethling (1990), only 40-50 per cent of biomass from a high solids waste in a suspended growth reactor was viable. This represented only 5-

10 per cent of the total VSS in the reactor. Nonetheless, distinction between anaerobic VSS and other organic particulates is exceptionally difficult to perform. Despite this limitation, it is possible to carry out experiments with variable influent VSS and variable operating conditions to fit a model that realistically describes the process performance under all conditions (Droste, 1997).

Specific models. Barthakur *et al.* (1991) proposed a kinetic model for substrate utilisation and methane production in the anaerobic digestion of complex organic feeds. The model assumes that anaerobic digestion occurs in three stages. First, extracellular hydrolysis of complex compounds converted into soluble assimilable substrate. This step is assumed as a first order reaction with respect to the concentration of hydrolysable substrate (S). Pavlostathis and Gossett (1986) demonstrated the validity of this assumption by carrying out experimental work. Thus:

$$\frac{dS}{dt} = -K_h(S - S_h) \tag{2.23}$$

where S_h = concentration of hydrolysed substrate [M/L^3]

K_h = hydrolysis rate coefficient (T^{-1})

Secondly, the transport of hydrolysed substrate into the cell is considered as directly related to the difference in concentrations of this substrate outside and inside the cells and to the concentration of active cell biomass X. Thus, if the hydrolysed substrate entering the cells metabolises rapidly, then the intracellular concentration tends to be zero ($S_u \cong 0$). Moreover, when the uptake of hydrolysed substrate is not rate limiting with respect to hydrolysis, the following relationship holds:

$$\frac{dS}{dt} = -k(S_h - S_u)X = -kS_hX \tag{2.24}$$

where k is the transport rate coefficient of the hydrolysed substrate [T^{-1}]. The combination of (2.23) and (2.24) gives:

$$S_h = \frac{K_hS}{kX + K_h} \tag{2.25}$$

A multiculture complex that utilises the hydrolysed assimilable compounds carries out the entire anaerobic treatment process. The different microbial cultures interact with each other behaving as an organic whole. Consequently, the kinetic constants in this model are related to the multiculture complex and are global in scope

(Barthakur *et al.,* 1991). Hence, the last stage of this model refers to the utilization of readily assimilable substrates for cell growth and product formation. A Monod kinetic model can describe the latter process according to:

$$\mu = \frac{\mu_m S_h}{K_s + S_h} \tag{2.26}$$

where K_s is the Monod constant with respect to hydrolysed substrate [M/L^3]. By replacing the value of (S_h) from equation (2.25), equation (2.26) becomes:

$$\frac{\mu}{\mu_m} = \frac{S}{K_s kX / K_h + K_s + S} \tag{2.27}$$

Under steady-state conditions in a continuous CSTR without recycling, the following relationships hold:

$$\mu = 1/\theta \tag{2.28}$$

$$F = (S_0 - S)/\theta \tag{2.29}$$

where θ is the hydraulic retention time (HRT) [T], F is the volumetric substrate removal rate [M/L^3-T], S_o is the influent hydrolysable (biodegradable) substrate concentration [M/L^3] and S is the hydrolysable substrate concentration in the effluent or in the reactor [M/L^3]. In order to simplify the model, maintenance energy and microbial decay are considered small, so the biomass yield coefficient (Y) is constant.

$$X = \frac{FY}{\mu} = Y(S_o - S) \tag{2.30}$$

Substituting equation (2.30) in (2.27) yields the following expression:

$$\frac{\mu_m}{\mu} = \frac{K_s kY}{K_h}\frac{S_o - S}{S} + \frac{K_s}{S} + 1 \tag{2.31}$$

According to Barthakur *et al.* (1991), equation (2.31) is the basic equation for substrate utilisation in the anaerobic digestion of complex organic wastes. If $S \gg K_s$, which may be the case in the practical anaerobic digestion of complex feeds (such as sewage), the second term of the right hand side in (2.31) becomes negligible and the equation changes to:

$$\frac{\mu_m}{\mu} = C\frac{S_o - S}{S} + 1 \qquad \text{Where: } C = \frac{K_s k Y}{K_h} \tag{2.32}$$

This equation is very similar to the one obtained by Chen and Hashimoto (1980) and Chen and Hashimoto (1978) as quoted by Barthakur *et al.* (1991). If the substrate is readily hydrolysable, K_h may be very large in relation to the other values. For the extreme case of a soluble and assimilable substrate like glucose, $K_h = \infty$, and the first term of the right-hand side of (2.31) becomes close to zero. Under such conditions equation (2.31) yields the Monod equation. Therefore, equation (2.31) is a generalised expression that holds well in two extreme cases.

Furthermore, in the case of complex organic substrates (generally expressed as COD or VSS) a part of the substrate is usually refractory to biodegradation. As pointed out by Barthakur *et al.* (1991), the refractory coefficient R is defined as S_r / S_{To}, where S_r and S_{To} are the refractory and total COD or VSS concentrations in the influent respectively. Denoting the effluent total COD or VSS concentration by S_T, the following relationships are derived:

$$S_o = S_{To}(1 - R), \qquad S = S_T - RS_{To} \tag{2.33}$$

By substituting equations (2.28) and (2.33) in (2.31), and rearranging terms:

$$S_T = S_{To}\frac{(1 - R)C + K_s / S_{To}}{\mu_m\theta + C - 1} + R \tag{2.34}$$

Equation (2.34) shows the relationship between influent and effluent concentrations of total COD or VSS taking into account hydrolysis, transport of hydrolysed substrate into the cells, cell growth and the substrate refractory fraction.

Barthakur *et al.* (1991) propose a kinetic expression for methane production based on the derivation of Chen and Hashimoto (1978). If B describes the specific methane yield in litres at standard temperature and pressure (STP) per gram of COD or VSS added to the reactor and B_o denotes the maximum specific methane yield in litres at STP per gram of COD or VSS at infinite retention time, then the following relationship arises:

$$\frac{S_o - S}{S} = \frac{B}{B_o - B} \tag{2.35}$$

Substitution of equation (2.35) in equation (2.31) yields:

$$\frac{\mu_m}{\mu} = C\frac{B}{B_o - B} + \frac{K_s}{S} + 1 \tag{2.36}$$

This expression represents the kinetic equation for methane fermentation. However, taking into consideration the refractory fraction given by equation (2.33), the above expression changes to:

$$\frac{B}{B_o} = 1 - \frac{C + K_s / (S_{To} - RS_{To})}{\mu_m \theta + C - 1} \tag{2.37}$$

Equation (2.37) shows that, at constant influent substrate concentration, as θ approaches ∞, *B/B*$_o$ approximates unity. Furthermore, equation (2.37) includes a term for end-product formation in anaerobic digestion (methane production) and so this last expression is the complete model proposed by these authors. The non-linear least squares technique allows the estimation of the kinetic parameters μ_m, C, K_s, B_o and the refractory coefficient R, as described in detail in the original paper of Barthakur *et al.* (1991).

Other models. The two models already presented are mainly for the design of anaerobic systems. However, more comprehensive models have been proposed to simulate the behaviour of anaerobic systems in a non-steady state regime. The work of Hoh and Cord-Ruwisch (1996) formulates a modified Michaelis-Menten rate equation combined with a thermodynamic term on a purely theoretical and mathematical basis. Consequently, the model never predicts thermodynamically unfavourable reactions. Thus, an equilibrium constant (K) is included in the new model in order to develop an equation from the reversible kinetic scheme (Alberty, 1953; Haldane, 1930; Stryer, 1988) for anaerobic treatment processes and other biological reactions that proceed close to equilibrium.

Guiot (1991) formulated a mathematical model to predict soluble COD removal efficiency and methane productivity in a hybrid up-flow sludge bed-filter using synthetic soluble sugar waste. This author estimated critical values of solids and hydraulic retention times. Kiely *et al.* (1997) carried out the development of a mathematical model for the anaerobic digestion process and to simulate methane production, using experimental data for the calibration of process parameters. This model comprises a set of 28 equations, which were solved by numerical methods to simulate observed pH, ammonium (NH_4) and methane (CH_4) production. The overall simulation of the reactor, which treated the organic food fraction of municipal solid waste, was satisfactory, in accordance with the 19 model parameters and 13 model variables considered.

Jeyaseelan (1997) proposed a simple mathematical model for anaerobic treatment processes. This model based on Monod kinetics is applied separately to the acid and methane formation stages. One basic assumption of this model is to consider municipal wastewater as a mixture of carbohydrates, proteins, lipids and a very small proportion of other materials. The results showed that treatment efficiencies could be modelled as a function of hydraulic retention times as well as substrate composition. The kinetic constants either should be determined experimentally or collected from the literature. This model can also be used to set operating parameters such as BOD loadings, retention times and temperatures that will produce any desired reactor efficiency within practical limits.

The technical literature contains different models to describe anaerobic digestion processes performance. Some of them are useful to forecast removal efficiencies based on kinetic features as well as substrate composition. Others are more applicable to the design and operation of various reactor configurations. According to Wentzel and Ekama (1997), these mathematical models have proved to be the most suitable tool for the design and operation of biological wastewater treatment systems. Since they provide quantitative descriptions, it is then possible to make predictions of the system's response and efficiency. Consequently, design and operational criteria coupled to field data will allow the optimisation of system performance.

2.3 Anaerobic wastewater treatment technologies

Conventional anaerobic processes. Classical anaerobic treatment technologies date from the end of 19th century when M.Mouras applied an airtight chamber (resembling a septic tank) to the treatment of sewage. This experience was described in the French journal *Cosmos* and was called "Mouras' automatic scavenger" (McCarty, 2001). Later on, Cameron and Imhoff developed the septic and Imhoff tanks in England and Germany, respectively. These two systems are primary treatment units with biological treatment of the settled solids. In 1935, after these early developments, the sewage treatment works of Chicago were constructed and they consisted of a battery of Imhoff tanks treating a flow of 1.8 million cubic meters a day, as reported in the *Water and Sewage* report in 1935. Ever since, research and implementation of engineered anaerobic treatment processes for solids reduction have been progressing.

Paradoxically, this oldest form of wastewater treatment was not developed further and was applied only eventually in ponds for high-strength wastewaters. Nowadays, the anaerobic treatment of dilute wastes like sewage remains as a challenge (Droste, 1997). The first large application of anaerobic treatment to raw wastewaters was in the 1950s, when the anaerobic contact process was developed. This anaerobic process has a similar configuration to that of a recycling activated sludge process.

Anaerobic ponds are another conventional or classic low-rate anaerobic process. They are man-made reservoirs of up to five metres depth that receive raw wastewater. This technology can be classified as a dispersed growth system. The main removal mechanisms are the sedimentation of suspended solids, which once settled undergo anaerobic digestion. These treatment units are frequently uncovered and mixing of the liquid phase may occur due to advection, convection, turbulence caused by rising biogas bubbles, but also because of wind currents and solar energy. Anaerobic ponds have been extensively applied to sewage treatment, particularly as a pre-treatment step in a series of WSP. According to van Haandel and Lettinga (1994), the sewage retention time in anaerobic ponds varies from two to five days and BOD_5 removal efficiencies are around 50-70 per cent.

High-rate processes. In contrast to conventional or classical anaerobic processes, these new systems are characterised by a mechanism for biosolids retention. There are two methods for this: first, systems based on immobilised biomass, that is, attached to a support media. To this category belong the upflow or downflow anaerobic filters (Figures 2.6a and 2.6b) and the sludge bed reactors operating either in a fluidised or expanded mode (Figures 2.6c and 2.6d).

Secondly, systems based on liquid-solid phase separation. In these reactors, the biosolids return to the digestion zone after removal in a special device. The contact process falls in this category. This is the anaerobic equivalent of the activated sludge process and it uses an external settler (Figure 2.6e). Another example is the upflow anaerobic sludge blanket reactor (UASB), which uses an internal settler (Figure 2.6f). However, in some systems there is not a specific separation device, that is, the reactor also functions as a settler (Figure 2.6g).

The treatment objectives must be formerly defined in order to compare the different anaerobic treatment systems (van Haandel and Lettinga, 1994). This will largely depend upon the local situation at the treatment site and the possibilities for effluent reuse. Nevertheless, the system chosen should offer the highest possible organic load removal efficiency at the shortest possible HRT. Since the kinetics of anaerobic treatment processes are not yet sufficiently developed to allow predictions of the above-mentioned relationships, it is necessary to establish empirical associations based on experimental results.

Figure 2.5 below shows different configurations of high-rate anaerobic wastewater treatment systems. Most of them have been applied to a great variety of industrial wastes; however, there are several variations and new experimental designs to be tested (Droste, 1997).

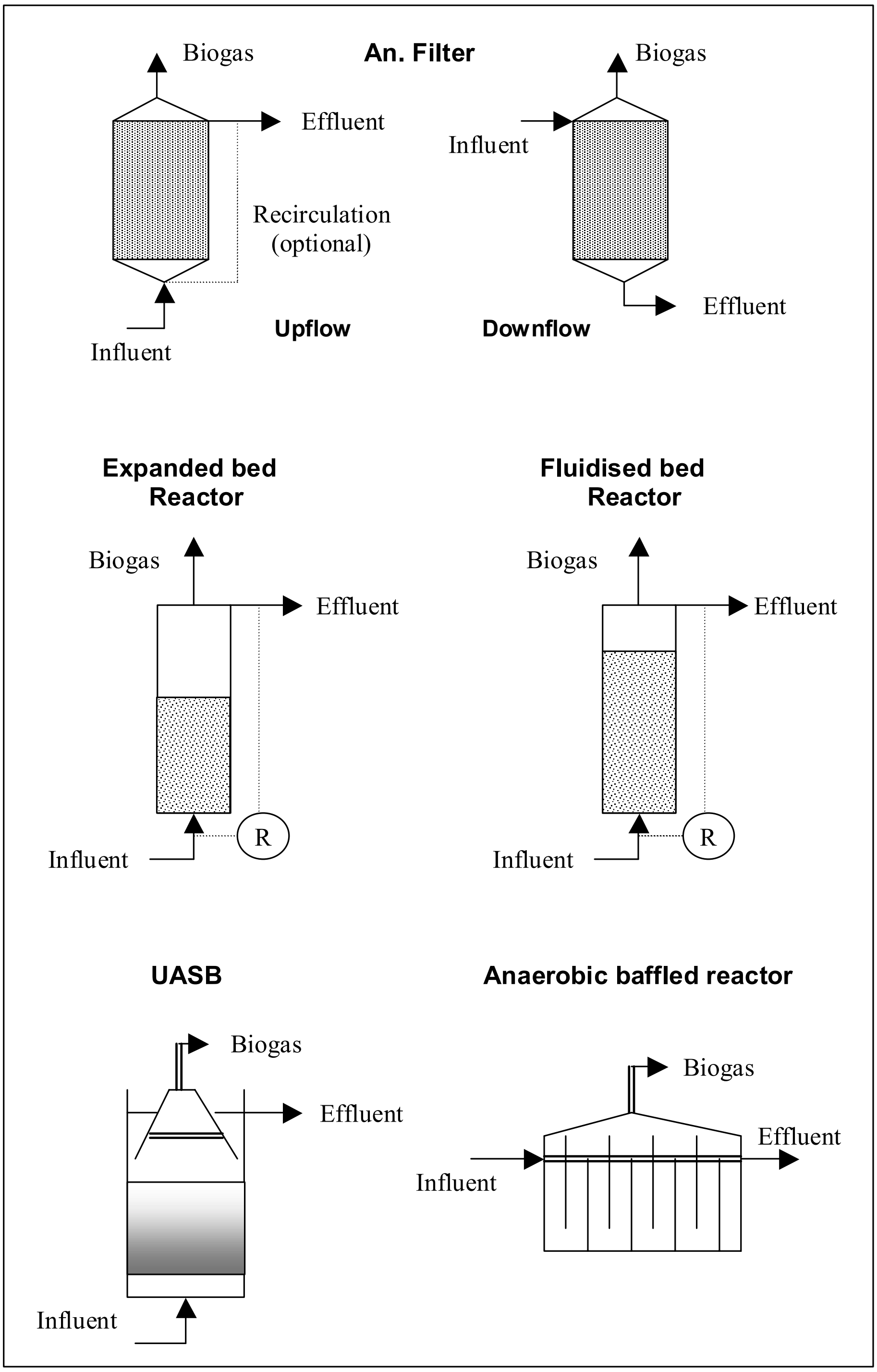

Figure 2.5 High-rate anaerobic treatment processes.

Figure 2.6 shows the total COD removal efficiency as a function of the HRT in different anaerobic reactor configurations. The four straight lines on the left show the removal efficiency of high-rate reactors whereas the line on the right depicts the removal of an anaerobic pond.

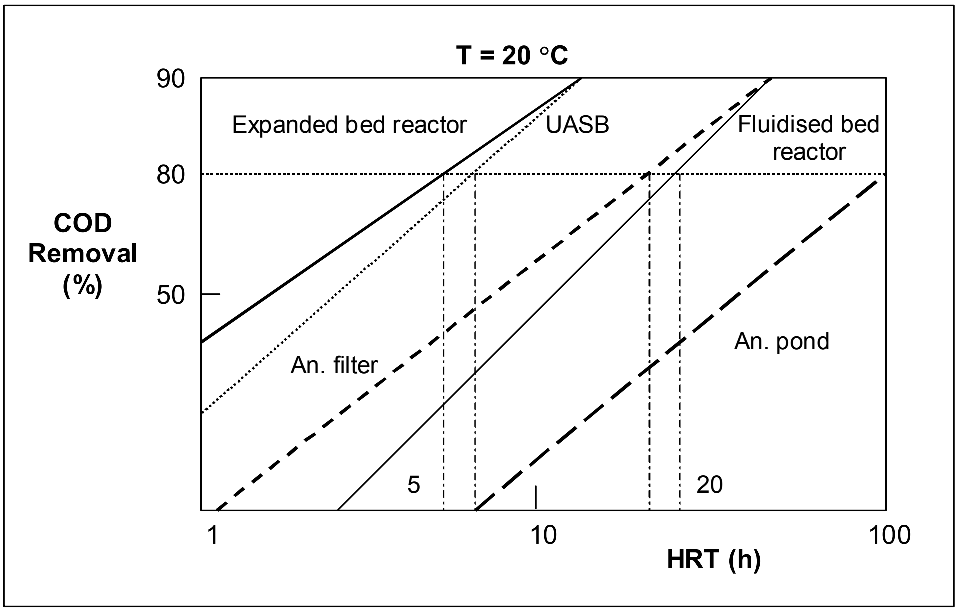

Figure 2.6 Removal efficiency of organic load as a function of retention time in different anaerobic treatment systems.

Source: Van Haandel and Lettinga. (1994).

As shown in this figure, high-rate anaerobic reactors achieve COD removal efficiencies of around 80 percent at HRT varying from 5 to 20 hours, depending on reactor configuration. Meanwhile, according to these authors, an anaerobic pond treating the same wastewater at equal temperature would require about four days HRT to attain a similar total COD removal efficiency.

2.4 Anaerobic pond technology

An anaerobic pond (AP) is a man-made basin into which wastewater flows to undergo anaerobic treatment as a function of water temperature, HRT and volumetric organic load. According to Mara *et al.* (1992) anaerobic ponds are 2-5 m deep and receive volumetric organic loads usually over 100 g BOD/m^3-d, which is equivalent to more than 3000 kg BOD/ha-d for a depth of 3 m. Anaerobic ponds are devoid of oxygen throughout their depth and exhibit the anaerobic metabolism features already described. These units are used as the first treatment stage for high-strength wastewaters in systems comprising a series of ponds. In this way, anaerobic ponds produce a reduction in influent organic load of 50 percent or more (Droste, 1997).

However, the work of Mara *et al.* (1992) and Mara and Mills (1994) has shown that anaerobic ponds work extremely well in warm climates. In such conditions and provided that the pond has been properly designed and is not significantly underloaded, it will achieve around 60 per cent BOD removal at 20 °C and as much as 75 per cent at 25 °C. In contrast to the long retention times reported by van Haandel and Lettinga (1994), wastewaters with a BOD of up to 300 mg/l can be treated in an anaerobic pond of 1 day retention time at temperatures above 20 °C in order to achieve these removal efficiencies.

Pearson (1996) points out that one of the most significant advances in pond technology over recent years has been the development of reliable design procedures for odour-free anaerobic ponds (Mara and Mills, 1994; Pescod, 1996), which has for a long time been one of the main criticisms against anaerobic pond implementation. Modern anaerobic ponds operate with a minimum hydraulic retention time of 1 day and their inclusion in a pond system provides a land area saving of over 75 per cent at temperatures above 16 °C. In the treatment of industrial wastewaters, AP are able to sequester heavy metals as insoluble sulphides, to treat effluents with large concentrations of grease, oil residues and organic solids (Pearson, 1996). Furthermore, Oragui *et al.* (1995) reported that sewage treatment in anaerobic conditions rapidly inhibits *Vibrio cholerae*. Hence, the incorporation of AP in cholera-prone locations should be given serious consideration from the public health point of view.

Criticism of pond technology is decreasing due to new economic scenarios that force a more rational and informed evaluation upon what is the most appropriate sewage technology for a particular location. Likewise, existing scientific data support how pond technology has advanced from the concept of holes in the ground full of sewage to one of a robust and affordable technology at the forefront of wastewater reclamation practices (Pearson, 1996). Nowadays, the better understanding of ponds process microbiology and the consequent refinements in process, physical design and operational strategies have brought forward a reliable and efficient operation of pond systems, eliminating many of the past horrors that gave this technology a bad reputation over the last few decades.

2.4.1 Process functioning and performance

The overall treatment process in an anaerobic pond is described by the basic mechanisms and concepts introduced in Section 2.2. However, Figure 2.7 is useful to present in more detail some of the specific bacterial interactions likely to occur in anaerobic ponds.

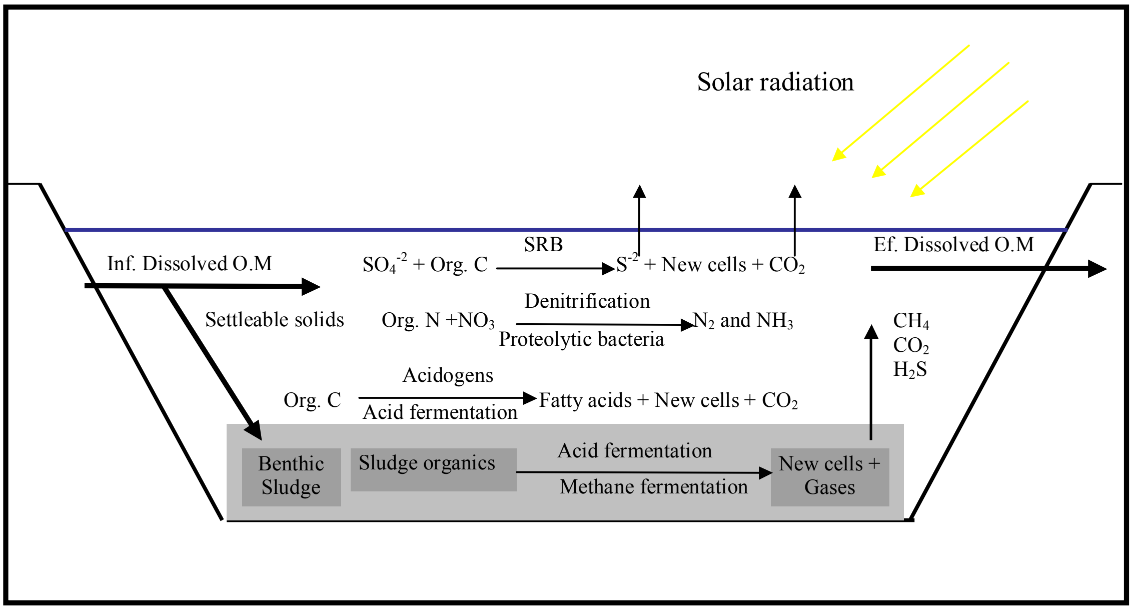

Figure 2.7 Schematic representation of the main biochemical reactions in anaerobic ponds.
Source: Adapted from Almasi and Pescod (1996).

Taking into consideration the principles of anaerobic treatment discussed in Section 2.2.1 and according to Figure 2.7, the removal of organic matter in AP is due to the sedimentation of settleable solids and their subsequent anaerobic digestion in the resulting sludge layer. In this sense, anaerobic ponds function much like open septic tanks, where BOD removal is their principal objective (Mara *et al.,* 1992). Anaerobic digestion is particularly intense at temperatures above 15 °C. Intense methanogenic activity occurring at the bottom of the pond (biosolids bed) releases biogas whose main components are CH_4 and CO_2 in proportions of about 70 and 30 per cent, respectively. Marais (1970) found that methane production increases sevenfold for every 5 °C rise in temperature with the maximum rate being achieved in the thermophilic range.

It must be noticed that gas bubbling may resuspend a fraction of the settled solids together with part of the bacterial population developed in the sludge layer. This fact may eventually have two different effects. Firstly, the resuspended solids might enhance contact between the dissolved organic matter present in the liquid phase and the bacterial cells attached to the biosolids particles, therefore, a potential removal of soluble organic matter can occur. Secondly, depending on the biogas bubbling intensity some of the resuspended solids may escape in the pond effluent contributing towards a higher effluent COD/BOD content. Because of this, the removal efficiency of the pond will decrease. Oldham and Nemeth (1973) reported this effect by thorough visual examination of three bench-scale anaerobic ponds treating wastewater from a commercial hog-raising facility.

Organic load removal. Oldham and Nemeth (1973) hold that AP have been either condemned or praised as a wastewater treatment process simply because there has been a lack of meaningful data to adequately design the process rather than just build it. These authors also argued that it is possible to design and build AP that will predictably remove up to 80-90 per cent of the influent BOD_5. The liquid retention time, pond temperature, nutrient availability and pond geometry are the main design and operating parameters that affect the organic load removal in AP. The geometry of the lagoons is very important to provide a given HRT, especially if conditions in the bottom biosolids layer generate a high degradation rate. Likewise, the flow patterns along the pond are related to its geometry, which in turn influences the fractions of dead zones and short-circuiting (i.e. affecting the theoretical HRT) and hence the overall removal efficiency of the reactor. In such situations, the uncontrolled resuspension of settled solids due to gas bubbling from the biosolids layer will produce a poorer effluent quality (Oldham and Nemeth, 1973). Table 2.2 shows some of the data obtained by these authors on the performance of laboratory-scale anaerobic ponds treating the effluent from a commercial hog-raising facility at different temperatures under a semi-continuous flow regime. These data show that total BOD_5 removal varied very little in relation to flow rate and temperatures above 18 °C. In contrast, the organic fraction directly degraded was very sensitive to flow rate and temperature variations.

The question of how organic matter is removed was approached by closely monitoring the gas production from the reactors before and after the daily influent feedings. The released biogas was composed of 68 per cent CH_4, 30 per cent CO_2 and the remaining two per cent accounted for H_2S, H_2O and N_2. The authors of this study concluded that the mechanisms of BOD_5 removal in bench-scale AP varied substantially with temperature and HRT.

Toprak (1995a) researched the primary treatment of sewage in two laboratory-scale anaerobic waste stabilisation columns operated in a repeated batch model. The rate constant for soluble COD removal was 0.325g SCOD/g MLVSS d. Other findings from this study recommend a maximum SCOD loading rate of 0.15 kg SCOD/m^3 d and a minimum HRT of 4 days which is too long in comparison with the much shorter HRT figures reported by Mara *et al.* (1992) for a similar sewage strength and a comparable organic load removal.

Table 2.2 Total BOD_5 removals in bench-scale anaerobic ponds and percentage of BOD_5 removed by direct degradation.

Temperature (°C)	**Influent flow rate Q (l/d)**	**Influent BOD (mg/l)**	**Effluent BOD (mg/l)**	**BOD removed (%)**	**Q (CH_4) (l/d)**	**BOD removed by direct degradation (%)***
30	0.5	9175	1010	89	1.22	83
	1.0	9760	1170	88	1.84	59
	2.0	9950	1590	84	3.89	64
	4.0	9950	1095	89	4.76	37
25	0.5	9175	1100	88	1.14	78
	1.0	9760	1170	88	1.64	53
	2.0	9950	1690	83	2.62	43
	4.0	9950	1195	88	4.16	32
18-23	0.5	9175	1190	87	1.00	69
	1.0	9760	1465	85	1.28	42
	2.0	9950	1940	81	1.98	34
	4.0	9950	1790	82	3.35	28
10	1.0	9760	5515	44	0.17	11
	2.0	9950	7265	27	0.44	22
	4.0	9950	5820	42	N.D	N.D

N.D: Not determined.

* Amount removed = CH_4 (l/d) x 0.96 x 1/0.35 ($BOD_5/BOD_u = 0.96$)

Source: Oldham and Nemeth (1973).

It has been widely recognised that AP play a major role in the treatment of wastewaters with high contents of solids and organic matter concentrations (Mara *et al.* 1992; Toprak, 1995b; Saqqar and Pescod, 1995; Pearson, 1996).

In order to keep anaerobic conditions within the pond, these treatment units are designed based on volumetric BOD_5 loading (λ_v). Due to the scarcity of reliable data, the development of a suitable design equation for AP has not yet been achieved. Nevertheless, the results of the Kenyan pond study (Mara *et al.,* 1990) indicate that the general recommendations given by Mara and Pearson (1986) can be used safely for design purposes in tropical regions. The design recommendations given in Table 2.3 are based on Meiring *et al.* (1968) for the limits of λ_v values, that is, the volumetric loading in AP should lie between 100-400 $gBOD_5/m^3$ d, with the former to maintain anaerobic conditions and the latter to avoid odour release provided, that raw wastewater contains less than 500 mg SO_4^{2-}/l.

As pointed out by Mara *et al.* (1992), the upper limit for design is set at 300 g BOD_5/m^3 d in order to provide an adequate margin of safety with respect to odour release. However, the results obtained in a more recent research carried out by Pearson *et al.* (1996) in northeast Brazil, suggest that maximum design volumetric loadings for

AP can be increased to 350 g BOD_5/m^3 d at 25 °C, rather than restricting it to 300 g BOD_5/m^3 d at all temperatures above 20 °C

Table 2.3 Design values of permissible volumetric loading and percentage BOD_5 removal in anaerobic ponds as a function of temperature.

Temperature (°C)	**Volumetric loading (λ_v) (g BOD_5/m^3 d)**	**BOD removal (%)**
< 10	100	40
10 - 20	20T - 100	2T + 20
> 20	300	60 *

T, Temperature in °C.
* Higher values may be used if local experience indicates that this is appropriate.

Source: Mara *et al.* (1992).

These results also showed that some operational loss in AP efficiency occurs at HRT less than one day, although the ponds under study did not fail or cause odour problems. Mara *et al.* (1983) reported a mean annual BOD_5 removal of 75 per cent in an optimally loaded pond with a 0.8 d (19.2 h) HRT operating at 25-27 °C.

Almasi and Pescod (1996) developed design models based on a full factorial experimental design for the organic load removal in two laboratory-scale anoxic ponds. Organic matter removal in terms of BOD_5 was 70-85 per cent at 25 °C, whereas at 10 °C it decreased to 60-70 per cent. The maximum volumetric organic load applied to the experimental ponds was 100 g BOD_5/m^3 d, which is one third of the value normally applied to an anaerobic pond working at 20 °C. Therefore, a full-scale anoxic pond designed on the basis of volumetric load will occupy a greater volume compared to an anaerobic pond with a similar removal efficiency.

Nitrogen and phosphorus removal. Primary anaerobic treatment of sewage does not effectively remove nutrients. As pointed out by van Haandel and Lettinga (1994), results from determinations of nitrogen and phosphorus concentrations before and after UASB treatment showed that ammonia increased from 35 to 53 mg N/l and orthophosphate from 5.5 to 9.9 mg P/l. The likely mechanism for such increases may be the mineralisation of organic compounds containing organic nitrogen and phosphorus. Nutrient removal can only be achieved in a separate post-treatment step.

According to Mara *et al.* (1992), in anaerobic ponds organic nitrogen is hydrolysed to ammonia by hydrolytic bacteria in the first stage of anaerobic digestion. The effluent of anaerobic ponds generally contains a higher concentration of ammonia nitrogen than the raw wastewater, unless the time of travel in the sewer is long enough to allow urea conversion before reaching the treatment plant.

Volatilisation of ammonia seems to be the only likely nitrogen removal mechanism occurring to some extent in AP. As discussed by Middlebrooks *et al.* (1982), ammonia assimilation into algal biomass and some degree of biological nitrification/denitrification are the other two mechanisms likely to occur in WSP. However, these two are characteristic of facultative and maturation ponds only. Soares *et al.* (1996) found a very low removal of nitrogen in AP. These data clearly showed a change in the chemical forms of nitrogen present in the AP liquid rather than an effective removal of it.

Soares *et al.* (1996) carried out two experiments with mean temperatures of 22.3 °C and 25.6 °C respectively. The HRT in the AP was only one day. Typically, neutral mean pH values and very low dissolved oxygen levels were detected in the AP in both experiments. Ammonia concentrations in the AP effluent during both experiments increased about 29 percent when compared to the concentration in raw sewage. This was due to ammonification and a low loss of NH_3 by volatilisation given the pH values registered in the ponds. This research reported an overall total nitrogen removal between 87-92 percent, with final effluent concentrations at the end of the whole ponds series in the range 2.7-4.3 mg N/l. Most of the nitrogen removal took place in the maturation ponds series after a total HRT of 19.6 days.

Silva *et al.* (1995) carried out a study on a WSP system and found that mean pH values in AP were neutral and dissolved oxygen concentrations were nearly zero at a mean temperature of 23 °C. Meanwhile, ammonia concentration increased from 32.5 mg N/l in the raw sewage to nearly 42 mg N/l in the AP due to the biological conversion of organic compounds such as proteins and urea hydrolysis by the likely action of urease under anaerobic conditions as reported by Ideliovitch and Michail (1981). The reduction of organic nitrogen in the AP was about 50 per cent. Sedimentation and further degradation of the particulate organic material as well as biological degradation of the soluble organic matter seemed to be the key mechanisms involved. TKN removal followed the same trend of ammonia nitrogen. Mean concentrations of TKN dropped a little in the AP (from 53.9 to 50.0 mg N/l) and decreased continuously throughout the pond system down to 11.6 mg N/l in the tertiary maturation ponds. The HRT in the AP was one day and the total HRT in the ponds series was 18.8 days.

Regarding phosphorus removal in WSP and particularly in anaerobic ponds, there are few data available in the literature. Mara *et al.* (1992) argue that the efficiency of total phosphorus removal in ponds systems depends on how much P leaves the water column and enters the pond sediments compared to the quantity that returns through mineralisation and resolubilization. The phosphorus removed from the liquid phase enters the pond sediments as organic P in the algal biomass but also precipitates as inorganic P at pH values above 9.5. These mechanisms are however most likely to take place in maturation ponds. Surampalli *et al.* (1995) published a work on phosphorus removal in ponds by using chemical addition of alum, ferric chloride and lime in several ponds systems in the United States. The applications of alum and ferric chloride produced consistently high quality effluents with concentrations varying from 0.5 to 15 mg P/l. However, there is a lack of coherent evidence on the removal efficiency of phosphorus carried out by the natural biological processes involved in WSP systems.

Sulphate conversion. The principal potential source of odour in domestic sewage is hydrogen sulphide, which is formed mainly by the anaerobic reduction of sulphate by sulphate-reducing bacteria (SRB) such as *Desulfovibrio* (Mara *et al.,* 1992). Once hydrogen sulphide is formed in aqueous solution, a hydrogen sulphide-bisulphide-sulphide equilibrium is established according to the pH value in the liquid phase. Figure 2.8 shows the interdependent relationship between H_2S, HS^- and S^{2-} at different pH values.

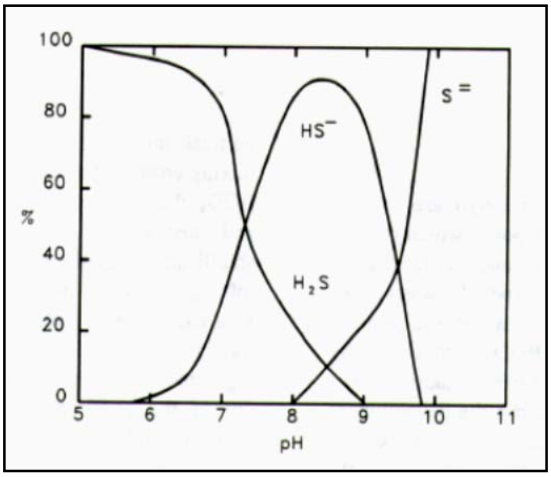

Figure 2.8 Effect of pH on hydrogen sulphide-bisulphide-sulphide equilibrium.
Source: Mara *et al.* (1992) from (Sawyer and McCarty, 1978).

In a well-designed AP the pH value normally found is around 7.5. Hence, most of the sulphide is present as the odourless bisulphide ion according to Figure 2.8. Odour problems are caused by escaping hydrogen sulphide (H_2S), which follows Henry's law.

The gas molecules seek to achieve a partial pressure in the air above the pond that is in equilibrium with their concentration in the liquid phase. Gloyna and Espino (1969) (quoted by Mara *et al.,* 1992) concluded that odour is not a problem if recommended design loadings are not surpassed and the sulphate concentration in the raw wastewater is less than 500 mg SO_4^{2-}/l. Veenstra *et al.* (1995) working on a WSP system in the Yemen republic reported that sulphate levels decreased from 30-40 to 10-20 mg S-SO_4^{2-} /l in the AP whereas the total sulphide concentration rose to a maximum of 15 mg S^{2-}/l, due to anaerobic sulphate reduction. The unbalanced S mass balance over the AP may be due to S accumulation in the sludge and evaporation of H_2S formed by active sulphate reduction. At the prevailing pH of 6.9-7.6 found in this study, the non-dissociated part (30-50% of the total sulphide) may cause odour and toxicity problems.

A more comprehensive research carried out by Visser (1995) showed that the occurrence of sulphate reduction processes in anaerobic wastewater treatment systems has advantages and disadvantages. The main disadvantages are:

Since a fraction of the organic compounds in the wastewater is used for the reduction of sulphate, this results in a lower methane yield and therefore negatively affects the overall energy balance of the process. Moreover, the quality of the biogas is reduced as part of the sulphide ends up as H_2S.

A fraction of the sulphide will also be present in the effluent of the anaerobic reactor contributing to a lower overall treatment efficiency of the system. In such situation, post treatment to remove sulphide is essential.

Sulphide is an inhibiting compound for anaerobic bacteria, including methanogenic (MB), acetogenic (AB) and even sulphate reducing bacteria (SRB). Sulphide accumulation may cause a severe inhibition of the treatment process resulting in its total failure.

On the other hand, Visser (1995) points out the following advantages of this process: the application of sulphate reduction in combination with the biological sulphide oxidation to elemental sulphur can be used for the removal of oxidised sulphur compounds from wastewaters.

Heavy metals present in wastewaters can be removed by the formation and precipitation of metalsulphides. This will also reduce potential toxicity problems to the anaerobic digestion process.

In wastewaters containing sulphites, the reduction of this very toxic compound to the less toxic sulphide will increase the potential of anaerobic treatment implementation.

As pointed out by Visser (1995), the biological treatment of wastewaters with high levels of sulphate consists of two steps. First, sulphate is dissimilatory reduced to sulphide. At this stage, the ability of SRB to compete with MB for the available organic substrate and their sensitivity for toxic levels of sulphide are important factors to consider. Secondly, anaerobic purple and green sulphur bacteria oxidise the sulphide from the first stage to elemental sulphur as a final product.

In the case of wastewaters containing low sulphate concentrations (i.e. domestic sewage), SRB are able to use several intermediates of the anaerobic mineralisation process. Therefore, under sulphidogenic conditions two reactions can occur. Oxidation of fatty acids with more than two carbon atoms by SRB plus oxidation of acetate by acetotrophic SRB (ASRB) and molecular hydrogen by hydrogenotrophic SRB (HSRB). However, in the oxidation of fatty acids two patterns can be distinguished: firstly, incomplete oxidation with acetate and sulphide as the end products; and secondly, a complete oxidation with CO_2 and sulphide as end products. SRB form a group of strict anaerobic bacteria, which can be divided into two main subgroups (Visser, 1995):

(a) SRB oxidizing the substrate incompletely with acetate as the end product: to this subgroup belong the genera *Desulfovibrio, Desulfotomaculum, Desulfomonas, Thermodesulfobacterium* and *Desulfobulbus*; and

(b) SRB oxidizing the substrate completely to carbon dioxide: to this subgroup belong the genera *Desulfobacter, Desulfococcus, Desulfosarcina, Desulfobacterium* and *Desulfonema*. An interesting feature of the SRB is their ability to perform acetogenic oxidation in syntrophy with HMB.

Wu *et al.* (1992) found that in granular sludge adapted to a VFA mixture and brewery wastewater in absence of sulphate, the SRB conduct the acetogenic oxidation of ethanol and especially propionate. However, obligatory hydrogen producing AB and MB have to compete with SRB for substrates such as hydrogen, acetate, propionate and other fatty acids when sulphate is present in the wastewater. The outcome of this competition will determine to what extent sulphide and methane are produced. The importance of this competition increases with a decrease in the COD/[SO_4^{2-}] ratio of the wastewater.

Lovley *et al.* (1982) and Lovley (1985) (quoted by Visser, 1995) stated that, because of the more effective consumption of hydrogen by HSRB, they would keep the hydrogen level below the threshold value of the HMB. In that case, hydrogen utilisation by the HMB becomes energetically unfavourable.

On the other hand, several studies have shown that acetate is entirely converted into methane, even under an excess of sulphate content (Hoeks *et al.,* 1984; Mulder, 1984; Rinzema *et al.,* 1986). Nevertheless, other authors reported a predominance of ASRB (Rinzema and Schultz, 1987; Choi and Rim, 1991; Stucki *et al.,* 1992). Hence, the outcome of acetate competition seems to be unpredictable (Rinzema, 1988).

At low sulphate concentrations, (this can be the case in AP treating domestic wastewater) the growth of ASRB will be sulphate limited, thus enabling AMB to outcompete them. Consequently, at high COD/[SO_4^{2-}] ratios, the oxidation of compounds such as hydrogen and propionate by SRB is likely, whilst AMB will degrade acetate.

Pathogen removal in AP. The removal efficiency of pathogens in wastewater treatment plants is one of the most important treatment objectives for the public health protection specially when effluent reuse schemes are implemented. In conventional plants, pathogenic microorganisms are removed in tertiary treatment units. However, in natural treatment systems such as WSP, the pathogens are progressively removed along the ponds series with the highest removal efficiency taking place in the maturation ponds (Mara *et al.,* 1992).

Knörr and Torrella (1995) reported a higher removal efficiency of total coliforms in anaerobic ponds when compared to the facultative lagoons. The latter units were however more efficient at removing faecal coliforms due to disinfection mechanisms such as photo-oxidation, high pH levels and sunlight radiation; all of them mediated by algae (Mara and Pearson, 1986). Some figures from this research carried out at a WSP system in the Mediterranean coast of Spain showed removals of one log unit for total coliforms in the AP. Meanwhile, the viral removal efficiency measured through coliphage reduction was very poor in the AP. Observed concentrations of Salmonellae were frequently higher in the effluent from the AP than in the raw sewage.

Arridge *et al.* (1995) working on an experimental WSP complex in Northeast Brazil found a one log unit removal in the AP for each of the following indicators: faecal coliforms, faecal streptococci and *Clostridium perfringens.* Salmonellae were reduced from 130 to 70 MPN/100 ml and *Vibrio cholerae* O1 was reduced from 40 to 10 MPN/l respectively. In-pond survival studies indicated that significant removal of *V. cholerae* occurs when the sulphide concentration is ≥ 3 mg/l, thus indicating the need to include AP at the head of the series. Oragui *et al.* (1993) reported a reduction of *V. cholerae* numbers in an AP from 485 to 28 CFU per litre, which is equivalent to 94 per cent removal. Thus, AP appears to be essential for high levels of *V. cholerae* removal.

The results obtained from other experiments carried out in an innovative WSP system located at the same site revealed an equal trend to the one already reported, thus showing that pond performance was reproducible. In this sense, the first order rate constants for faecal bacterial removal calculated in the AP were 2.76 d^{-1}, -0.09 d^{-1} and 1.00 d^{-1} for FC, salmonellae and *V. cholerae* respectively.

Oragui *et al.* (1995) reported the removal of one log unit for rotaviruses in the AP of the experimental WSP complex located in Campina Grande in Northeast Brazil. The concentration of rotaviruses was measured as fluorescent foci per litre (ff/l). Additionally, one log unit FC removal was recorded, but *Clostridium perfringens* removal was nearly zero in AP. Almasi and Pescod (1996) found an *E. coli* removal of 1.5 to 1.9 log units in two laboratory-scale anoxic ponds under both warm (25 °C) and cool conditions (10 °C). The removal rates for *Streptococcus faecalis* were approximately the same as those for *E. coli* with a mean removal efficiency value of 92.6 per cent. These authors also found that influent sulphate concentration had an insignificant effect on *E. coli* removal.

Grimason *et al.* (1993) studied the occurrence and removal of *Cryptosporidium* spp. oocysts and *Giardia* spp. cysts in eleven WSP systems located in towns across Kenya. The results from this study showed that a significantly higher concentration of *Giardia* cysts was detected in raw sewage compared to anaerobic pond effluent. Oocysts and cysts were detected in three out of five AP effluents examined. The concentration ranges were 2.25-50 oocysts/l and 133.3-230.7 cysts/l respectively. As the majority of oocysts, cysts and organic removal occurred in primary ponds receiving raw sewage, this indicates that adsorption of oocysts and cysts onto settleable solids is probably the main removal mechanism for protozoan parasites in these reactors.

Grimason *et al.* (1996a) working at the Eldoret WSP system in Kenya found that the median *Giardia* cyst concentration in raw wastewater samples was $3x10^3$ cysts/l. All the effluent samples examined along the pond series were positive for *Giardia* cysts and the median concentration detected in the AP effluent was 225 cysts/l. These figures represent a removal efficiency of 92 per cent in the AP.

On the other hand, Grimason *et al.* (1996b) reported *Ascaris* sp. ova removal efficiency between 80-90 percent at the AP of Kitale and Eldoret in Kenya. Nevertheless, the removal efficiency of *Ascaris* sp. ova at the AP in Nakuru was less than 40 percent. As pointed out by Grimason *et al.* (1996a), the removal of pathogens in WSP systems, especially protozoan parasites, is a subject that clearly warrants further investigation. These authors hypothesise that several factors affect the rate at which protozoan parasites settle in pond systems. The most significant include the terminal settling velocity of the parasite, temperature inversion, methane bubbling and sediment disturbances. Bartone (1985) argues that thermal stratification and sludge accumulation seem to increase the potential for short-circuiting and consequently reduce the hydraulic retention time, thereby enabling the rapid transportation of viable pathogens through the ponds.

2.4.2 Environmental conditions

Physical as well as chemical factors affect the habitat of microorganisms and consequently the anaerobic sewage treatment process. The most important environmental factors to take into consideration are temperature, pH, Redox Potential (ORP), degree of mixing, nutrient requirements, ammonia and sulphide control and the presence of toxic compounds in the influent (Droste, 1997; Van Haandel and Lettinga, 1994).

Temperature. As temperature rises, the rate of reaction also increases, but in biological systems, such increases are not as great as for chemical reactions. In anaerobic treatment, there are two optimal ranges for producing methane: 30-40 °C (the mesophilic range is between 15-40 °C) and 50-60 °C (the thermophilic range is above 40 °C). In order to have a reasonable methane production rate, the temperature should be maintained above 20 °C. This fact makes application of the AP more attractive in tropical regions with sewage temperatures above 20 °C. Methane production rates are doubled for each 10 °C temperature increase in the mesophilic range (Droste, 1997). The relationship between loading rate and temperature is proportional, so that when temperature decreases the loading rate must decrease in order to sustain the same degree of treatment. On the other hand, the operation in the thermophilic range is not very practical because of the high energy requirements for reactor heating.

pH in the reactor. This is the most important process control parameter in anaerobic reactors. According to Zehnder *et al.* (1982), the optimum pH range for all methanogenic bacteria is between 6.0 and 8.0, but the optimum value for the group as a whole is close to 7.0. van Haandel and Lettinga (1994) reported the same observation and also pointed out that, since acidogenic populations are notably less sensitive to pH variations, acid fermentation will predominate over methanogenic fermentation. The latter may result in souring of the reactor contents. Thus, the system must contain adequate buffering capacity to neutralise the production of volatile acids and carbon dioxide, which dissolves at the operating pressure (Droste, 1997). Excess alkalinity or ability to control pH must be available to protect against the accumulation of excess volatile acids. Anaerobic processes can operate over a wide range of volatile acid concentrations, from less than 100 mg/l to over 5000 mg/l if proper pH control is carried out. Alkalinity requirements vary with the waste, type of process and system operation. The weak acid-base systems have a great influence and in particular the carbonic system is often determinant as its concentration generally exceeds that of other systems, such as phosphate, ammonia or sulphide (van Haandel and Lettinga, 1994).

Redox potential. Some authors argue that ORP itself is not a good indicator of process functioning and it has to be monitored along with other parameters in order to have a complete picture of reactor performance (Speece, 1996). Nevertheless, ORP provides information on the electrochemical equilibrium of a particular aqueous environment. Accordingly, either the reducing or the oxidising power of such environments can be characterised by ORP readings. Figure 2.9, taken from Charpentier *et al.* (1998), shows the correlation between ORP and the corresponding redox pairs encountered in biological wastewater treatment.

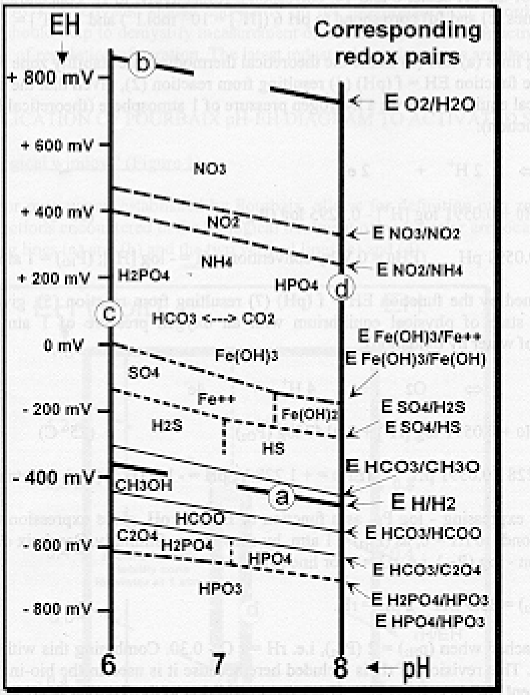

Figure 2.9 Correlation between Eh values and redox pairs in waters.
Source: Charpentier *et al.* (1998).

Carbonaceous organic matter in the form of VFA is present in highly reducing environments (Eh values between –600 to –400 mV) whereas H_2S and SO_4^{2-} are present at higher Eh values (-300 to –100 mV). Meanwhile, the more oxidised forms of nitrogen are in the other extreme of the scale at positive Eh values higher than +400 mV.

Therefore, in the case of anaerobic bioreactors as AP, ORP measurements along with pH provide good information on process functioning and stability since these parameters correlate to the presence of VFAs, H_2S and SO_4^{2-} in the water column.

Degree of mixing. The importance of mixing for improving anaerobic process performance was recognised in the 1940s by Babbitt and Baumann (1958) (quoted by Droste, 1997). The separation of digestion from other processes and the application of mixing were the first major advances in anaerobic treatment. Mixing is an important factor in pH control and maintenance of even environmental conditions. It distributes buffering agents throughout the reactor volume and prevents localised build-up of high concentrations of intermediate metabolic products, which may inhibit methanogenic activity. On the contrary, inadequate mixing propitiates the development of adverse microenvironments. Moreover, mass transfer limitations of substrate from the bulk liquid to the surface of biosolids particles are related to different transport mechanisms, which in turn are affected by mixing intensity (Pavlostathis and Giraldo-Gomez, 1991). Consequently, mass transfer limitations to and from biosolids aggregates may cause significant substrate removal inefficiencies.

Nutrient requirements. Acidogenic and methanogenic bacteria have low growth rates for a given amount of substrate and this feature results in less nutrient requirements compared to aerobes. The normal composition of microorganisms is typically assumed to be $C_5H_7NO_2$ for both aerobes and anaerobes. Meanwhile, phosphorus content is about one fifth of nitrogen content on a weight basis (Droste, 1997). As an example, for a typical activated sludge process, this yields a COD: N: P ratio of 100:5:1 on a mass basis. On the other hand, anaerobic systems produce 20 per cent or less of the amount of sludge produced in aerobic systems for the same substrate and so N and P requirements should decrease proportionally.

Ammonia and sulphide control. Anaerobic bacteria can acclimatise to high ammonia concentrations, but large fluctuations can be detrimental to the process. Free ammonia is much more toxic than the ammonium ion and it occurs more at high pH values. Wastes with high contents of proteins will generate significant amounts of ammonia that in turn increases alkalinity. Wastes containing blood can produce enough ammonium bicarbonate to raise the pH beyond the optimal range and this requires acid addition for pH correction. In most cases, the protein content of wastes is not high enough to cause ammonia toxicity problems. The latter has been confirmed by the work of Vavilin *et al.* (1995) who found that only high levels of ammonia, around 900 mg N/l caused failure of an anaerobic system fed by cattle manure.

At the same time, sulphide can be formed in the process due to the reduction of sulphates:

$$8H^+ + SO_4^{\ 2-} + 8e \rightarrow S^{2-} + 4H_2O \qquad (2.38)$$

Sulphides are inhibitory to methanogens and sulphate-reducers themselves, but according to results of Rinzema (1988), a sulphide concentration of up to 50 mg/l (normally expected in anaerobic sewage treatment systems) is far lower than the minimum concentration causing toxicity problems. Parkin *et al.* (1990) confirmed this result as they found that under an influent sulphate concentration of 1250 mg S/l the high resulting hydrogen sulphide content inhibited methanogenic archaea.

Toxic compounds. Other compounds such as heavy metals and chloro-organics affect the rate of anaerobic digestion even at very low concentrations. Apart from sulphide, oxygen is also a potentially toxic compound, which can enter the reactor together with influent flow. However, the presence of these compounds at inhibitory concentrations is unlikely in domestic wastewater. In 1979, a procedure called the biochemical methane potential (BMP) test (analogous to the BOD test) was defined to assess the methane potential of a waste. Owen *et al.* (1979) modified the BMP and developed a toxicity assay. Although these procedures have not been incorporated into *Standard Methods* (1992), they are widely used in the field (Droste, 1997).

2.4.3 Hydrodynamics of anaerobic ponds

Hydrodynamics is one of the most important features to be considered at the design stage and subsequent operation of a reactor. However, very often this crucial factor tends to be overlooked in current design procedures. Juanico (1991) highlights the fact that the efficiency of most wastewater treatment processes largely depends on the hydraulic characteristics of the treatment units. In this sense, the two ideal patterns in reactors are plug flow and completely mixed flow. These can yield different results in terms of size of the reactor and distribution of products (Levenspiel, 1979).

Engineers commonly design process reactors to approach one or the other of these flow regimes because both are often optimum and they are simple to treat. Nevertheless, full-scale reactors always deviate from these ideals according to three somewhat interrelated factors. Levenspiel (1999) defined these factors as: the retention time distribution (RTD) of material flowing through the vessel, the state of aggregation of the flowing material and the earliness and lateness of material mixing in the vessel.

The factors already mentioned play an important role depending on the situation under consideration. Levenspiel (1999) argues than in some cases one of these three factors can be ignored, but in others, all of them can become crucial. Frequently, much of the reactor behaviour relies on the reaction time (t_{rx}), the time for mixing (t_{mix}), and the time to stay in the vessel (t_{stay}). Based on these different times, the following cases can occur for a single flowing fluid:

- If $t_{rx} \gg t_{stay}$ then little reaction takes place, so plug flow and mixed flow will give the same conversion;
- If $t_{rx} \approx t_{stay}$ then only RTD need to be known, whether plug flow, mixed flow or somewhere in between as determined by the RTD curve;
- If $t_{rx} \ll (t_{stay}$ or $t_{mix})$ all three factors enter the picture to influence reactor behaviour;
- As a special case if the reaction rate is of first order, then only RTD needs to be known no matter what the (t) values may be.

Flow pattern models in ponds. Early work by Meron *et al.* (1965) showed that BOD reduction in ponds is directly related to the hydraulic retention time (HRT) in the basin. Fritz *et al.* (1979) pointed out that hydraulic regimes in ponds and their effect on biological processes were not well known at that time. These authors recommended that attempts at approaching near-plug-flow conditions with laboratory ponds should be pursued given that baffled ponds have been shown to have improved performance. In this sense, Arthur (1981) holds that pond design methods remain largely empirical and most of them emphasise either temperature or solar radiation as the only limiting factors in wastewater treatment. The results from this study showed that a greater degree of treatment is achieved in a series of units rather than in a single pond for the same total HRT. Mixed reactors had higher treatment efficiency in terms of BOD removal compared to unmixed reactors. Marais (1970) holds that detention times less than seven days will allow a good degree of influent blending due to wind and thermal mixing.

Several studies have revealed that WSP normally exhibit no ideal flow patterns, which exceed the limits of the two ideal extremes mentioned before (Thirumurthi, 1969). In many cases, there are also changes between thermal stratification with hydraulic short-circuiting during the day and convective overturn caused by nocturnal cooling (Marais, 1966). In the latter case, the flow conditions may be similar to the plug flow pattern. Ferrara and Harleman (1980) based on experiments on the hydraulics of ponds concluded that a completely mixed tank reactor (CSTR) model is appropriate for dynamic process modelling.

Uhlmann *et al.* (1983) argue that despite the amount of useful detailed information on WSP available from the literature, there is still a need for a generalized design procedure that produces more realistic results than the equations commonly used which are mostly based on empirical formulae.

Nowadays, it is well understood that pond efficiency is a function of both the biochemical transformations and the hydrodynamic phenomena occurring within the pond (Polprasert and Bhattarai, 1985). Ponds are complex reactors encompassing the existence of many microbial species and the occurrence of diverse transport phenomena. Figure 2.10 shows a dimensionless plot of typical dispersion patterns found in different reactor configurations.

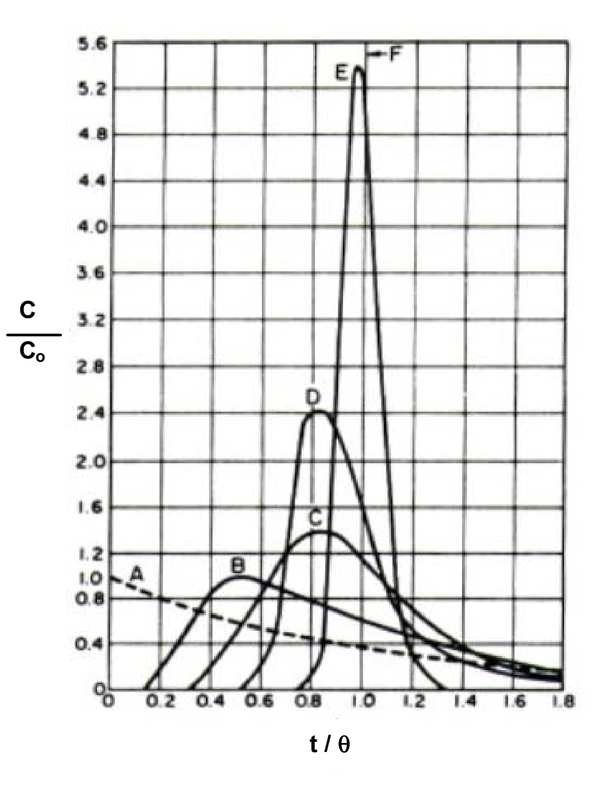

Figure 2.10 Typical dimensionless dispersion curves for reactors.
Source: Polprasert and Bhattarai (1985).

The horizontal scale is the ratio of the actual time a certain concentration appears at the outlet (t) to the detention period of a tank (θ). The vertical scale is the ratio of the actual concentration of tracer (C) to the concentration that would be obtained if the tracer slug were instantaneously mixed with the entire tank contents (Co).

Curve A is the theoretical response curve for a completely mixed reactor and the vertical line at F represents the ideal response curve for a plug flow reactor. Curves B, C, D and E show the flow patterns characteristic of partially mixed conditions. These are the sort of response curves expected from ponds since they normally lie between completely mixed and plug flow extremes (Polprasert and Bhattarai, 1985). Ponds with relatively large L/W ratios may approach the mixing characteristics of curves E and F and are most desirable because of their minimum short-circuiting fraction. Wehner and Wilhelm (1956) proposed the following equation for chemical reactors, which exhibit first-order kinetics and non-ideal mixing conditions under any sort of inlet and outlet arrangements.

$$\frac{C}{C_o} = \frac{4ae^{1/2\delta}}{(1+a\ )^2 e^{a/2\delta} - (1-a\ )^2 e^{-a/2\delta}} \tag{2.39}$$

In which: $a = \sqrt{1+4K\theta.\delta}$

where C = remaining substrate concentration in pond effluent [M/L^3]

C_o = initial input substrate concentration to the pond [M/L^3]

K = general reaction rate coefficient [T^{-1}]

θ = hydraulic retention time of the pond [T]

δ = dispersion number (dimensionless)

Equation (2.39) is valid for ponds in which reactions are occurring uniformly throughout the pond depth at a rate coefficient *K*. Ponds approaching the completely mixed regime have high (δ) values and the opposite is true for ponds approaching the plug flow regime (Polprasert and Bhattarai, 1985). However, as pointed out by Agunwamba *et al.* (1992), there is an implicit difficulty involved in the determination of the dispersion number (δ), whose accuracy inevitably affects that of the proposed model. In ponds, (δ) is usually determined by tracer studies as suggested by Levenspiel (1999). Although some researchers have tried to derive some predictive equations based on the geometry and hydraulic properties of the ponds (Polprasert and Bhattarai, 1985; Ferrara and Harleman, 1981; Arceivala, 1981), the values of (δ) found experimentally differ from those obtained from the predictive equations. Additionally, Wood (1987) argues that an inappropriate experimental model to describe either the hydrodynamic behaviour or the process kinetics in ponds can only give a misleading interpretation of experimental results (i.e. a continuous flow process is not adequately described by a batch or even a semi-continuous experimental model).

The mixed flow reactor model for conversion of input materials following a first order reaction has been also used to design WSP. Levenspiel (1999) concludes that this model describes correctly the conversion of substrate regardless of its degree of segregation (i.e. tendency to clump) for first order reactions. This model is given by:

$$S = \frac{S_o}{1 + k\theta} \tag{2.40}$$

where S = remaining substrate concentration in pond effluent [M/L^3]

S_o = initial influent substrate concentration to the pond [M/L^3]

k = first order reaction constant [T^{-1}]

θ = hydraulic retention time of the pond [T]

Apart from the geometric features of the ponds and the organic and hydraulic loads applied, there are also environmental factors such as temperature variations, evaporation and rainfall regimes, wind speed and direction, which affect the hydrodynamics of these units. James (1987) emphasises that wind action is generally sufficient to ensure that ponds function as partly or completely mixed reactors, and therefore it promotes a distribution of retention times. Llorens *et al.* (1992) working on a deep WSP in Spain found that marked thermal stratification appeared in spring-summer. The presence of this phenomenon caused a vertical distribution with distinct concentration gradients across the thermocline. In the absence of thermal stratification, the pond functioned as a completely mixed reactor with almost constant concentrations throughout the water column.

Marecos do Monte and Mara (1987) hold that the hydrodynamic transport processes within a WSP are controlled by the shape of the unit, the positioning of the inlets and outlets and the degree of wind-induced mixing. The results obtained by these researchers in two facultative WSP systems in Portugal showed that the flow in the ponds is strongly affected by dispersion and it is far from either plug flow or completely mixed regimes. The long tails of the RTD curves obtained from tracer studies (similar to curve B in Figure 2.10) suggest the presence of a significant component of short-circuiting. Consequently, the mean actual HRT for these particular ponds was shorter than the theoretical HRT. The values of the dispersion number (δ) in these ponds varied from 0.371 to 0.595. Moreno (1990) carried out a hydraulic study of five facultative WSP located in different regions of Spain. The results indicated that a CSTR model could be used to describe the hydraulic behaviour of the ponds evaluated. The actual

HRT values were typically shorter than the theoretical HRT. Although the plug flow model has been used in some cases to design WSP, its predictions are far too optimistic regarding the real efficiency attainable in these systems.

Peña *et al.* (2000), after carrying out dispersion studies in two full-scale APs treating sewage, found that these units showed large deviations from plug flow since dispersion number values were between 0.06 and 0.08. The results also showed that APs should rather be designed based on a CSTR model as the very nature of in-pond anaerobic digestion processes induces mixing via biogas bubbling. Accordingly, mixing and contact in these reactors need to be optimised by reducing short-circuiting and dead zones. The latter may be achieved by introducing simple but effective engineering interventions such as baffling or hydraulically induced stirring. Nevertheless, further research is needed on this subject.

On the other hand, Shilton (2000) argues that the ability to predict flow patterns and its correlation to pond treatment performance would be a valuable tool for design engineers. Furthermore, hydraulics is the only process variable that can be controlled to some extent during design and operation of ponds systems. Thus, HRT is the overriding factor for the correct functioning of WSP units. Pond hydrodynamics is strongly influenced by geometric features (shape), provision of baffling, inlet/outlet arrangements and hydrological regimes. The ability to predict the interaction of these factors and their relationship to pond treatment performance is likely to be achieved by the application of computational fluids dynamics (CFD) (Shilton *et al.,* 2000).

Previous work carried out by Wood *et al.* (1995), Wood *et al.* (1998) and Shilton (2000) show the potential of CFD to improve the design of new facilities and to upgrade existing malfunctioning pond systems. Nevertheless, the hydrodynamics of AP in particular seem to be a very complex subject given the interactions between liquid, solid and gas phases coexisting in the pond. Therefore, the experience and knowledge gained from high-rate anaerobic reactors [e.g. expanded granular sludge bed reactors (EGSB), UASB, fluidised sludge bed reactors (FSBR)] may be applicable to the improvement of AP hydrodynamics and process performance. Concepts such as enhanced contact, complete mixing, mass transfer effects and reactor configurations have to be innovatively applied if more efficient but simple AP are going to be developed.

Fortunately, an important amount of work done on high-rate anaerobic reactors can be applied to testing new AP configurations. As an example, the hydrodynamics and degree of mixing that occur within anaerobic baffled reactors (ABR) strongly influence the extent of contact between substrate and microbial consortia, thus controlling mass transfer and potential reactor performance (Barber and Stuckey, 1999). These authors recommend low HRT values when treating low strength wastewater since this will enable better mass transport due to improved hydraulic mixing. Nevertheless, research on hydrodynamics of ABR has not taken into account biogas mixing effects, biomass particle size and the rate at which biosolids aggregates move throughout the reactor.

Long (1990) pointed out that wastewater has to come into close contact with the anaerobic sludge to achieve a good conversion of the organic biodegradable matter. In a UASB system, this contact occurs in both the sludge bed and the sludge blanket. The reactor contents are mixed by both wastewater upflow and rising biogas bubbles. The production of biogas, apart from mixing, also contributes to the creation of the sludge blanket at the top of the bed. The behaviour of the liquid and solid phases is interdependent and influences process performance. Fluid flow patterns are affected by the influent distribution over the bottom of the reactor and also by the movement of the biogas bubbles.

More recently, Mulder *et al.* (2001) hold that mass transport limitations should be reduced as much as possible in order to exploit optimally the available biomass in the reactor. Reactor hydrodynamics is therefore a vital factor for substrate conversion efficiency. Consequently, more work is needed for the development of reactors where both sufficient biomass growth and its effective retention can be accomplished.

To date, most of the research on hydrodynamic behaviour and process performance of WSP reported in the literature corresponds to facultative and maturation ponds. As pointed out by Saqqar and Pescod (1995), most of the technical literature shows that complete analysis of performance data and comprehensive studies on AP are not available. Additionally, there are no available relationships to be used for the design of AP based on fundamental biological treatment process. Consequently, a satisfactory performance model has not been formulated for these reactors yet.

Design of AP is currently based on empirical criteria that have been developed through experience. These criteria are based on either volumetric organic loading or hydraulic retention time values (Saqqar and Pescod, 1995). However, it is likely that organic matter removal efficiencies in conventional AP can be improved if better mixing and contact patterns are enhanced within these primary treatment units. This topic certainly deserves further research since likely improvements to obtain a high-rate

AP may have significant technical and economical implications for WSP technology as a whole.

The literature review presented earlier may be summarised in three main aspects. First, the foundations and principles of anaerobic wastewater treatment, which include basic concepts of bacterial metabolism, kinetics of anaerobic treatment and modelling of the biological process. This part of the literature review provides the conceptual background to understand most of the interactions that normally occur in any anaerobic reactor configuration.

The second part comprises the review of general information on the most commonly used high-rate and low-rate anaerobic reactors for domestic wastewater treatment. A particular emphasis is made on anaerobic reactors currently used in tropical countries. Although the application of anaerobic biotechnology in tropical countries has been successful, there is still a need for developing efficient and yet simpler reactor configurations to solve the water pollution problems faced by small municipalities, rural towns and low-income communities.

The last part of the literature review deals with the state of the art of anaerobic ponds. Waste stabilisation pond technology is one of the most widely used treatment systems in the Andean region of Latin America and anaerobic ponds are usually the first step in the ponds series. Nevertheless, the performance of the current AP configuration may be improved by applying to it some of the basic concepts discussed in the earlier parts of the literature review. Thus, the improvement of mixing and the consequent enhanced contact and reduced mass transfer limitations may result in a significant positive impact on the removal rates of organic matter in AP. Most of the references quoted in Section 2.4, together with widely accepted knowledge on high-rate anaerobic reactors plus the conceptual framework of anaerobic digestion, seem to suggest that an improved mixing intensity coupled with better biomass retention and longer sludge retention times within the reactor could lead to the development of a high-rate AP configuration.

Therefore, the experimental work, results, discussion and conclusions of this research are primarily related to the latter part (Section 2.4) of the literature review Chapter. Sections 2.1, 2.2 and 2.3 of the literature review provide the global picture and conceptual framework to continue further research based on the results and conclusions reported herein.