

# FS-BIO-008

**TECHNOLOGY FACT SHEETS  
FOR EFFLUENT TREATMENT PLANTS  
OF TEXTILE INDUSTRY**

## **ANAEROBIC DIGESTION**

***SERIES: SECONDARY TREATMENTS***

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**ANAEROBIC DIGESTION (FS-BIO-008)**

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## 1.- INTRODUCTION

In the anaerobic treatment the organic matter is decomposed into biogas, methane ( $\text{CH}_4$ ) and carbon dioxide ( $\text{CO}_2$ ), process in which a different oxygen molecule acts as a terminal electron acceptor. Methane production occurs in different natural environments, such as swamps, lakes, rivers and sea sediments, as well as in the digestive organs of ruminant animals, where the redox potential is around  $-300\text{mV}$ . It is estimated that anaerobic digestion with methane formation is responsible for the complete mineralization of 5 to 10% of all the organic matter available on the earth.

Anaerobic digestion represents an accurately balanced ecological system, where different populations of microorganisms present specialized functions, and the breakdown of organic compounds is usually considered a two stage process. In the first stage, a group of facultative and anaerobic bacteria converts, by hydrolysis and fermentation, the complex organic compounds (proteins, carbohydrates and fats) into simpler organic compounds, mainly volatile fatty acids (VFA), as well as carbon dioxide and hydrogen gases. In the second stage, the organic acids and hydrogen are converted into methane and carbon dioxide. This conversion is performed by a special group of microorganisms, namely methanogens, which are strictly anaerobic. These microorganisms have two main functions, produce methane which enables the removal of organic carbon and they keep the hydrogen ( $\text{H}_2$ ) partial pressure low enough to allow conditions in the medium for fermenting and acid producing bacteria to produce soluble compounds such as acetic acid.

## 2.- MICROBIOLOGY OF ANAEROBIC DIGESTION

Anaerobic digestion can be considered an ecosystem where several groups of microorganisms work interactively in the conversion of complex organic matter into final products, such as methane, carbon dioxide, hydrogen sulfide, water and ammonia, besides new bacterial cells.

Anaerobic digestion can be subdivided into various metabolic pathways, with the participation of several microbial groups, each with a different physiological behavior, as illustrated in Figure 1 and described in the following items.

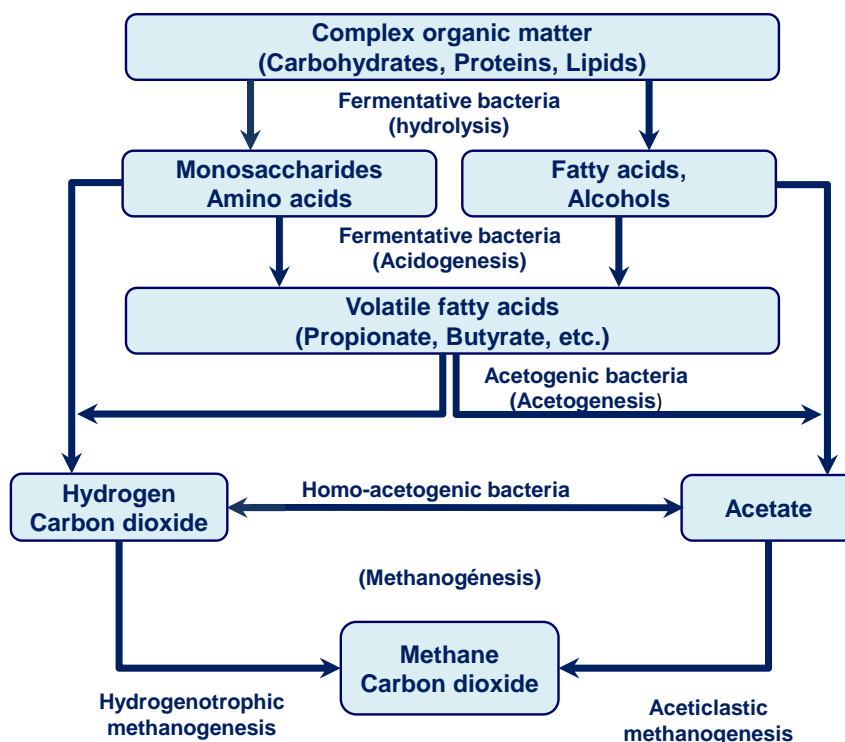


Figure 1. Metabolic pathways and microbial groups involved in anaerobic digestion (Lettinga et al. (1996).



## 2.1.- Hydrolysis and acidogenesis

The first phase in the anaerobic digestion process consists in the hydrolysis of complex particulate material into simpler and dissolved materials, which can penetrate through the cell membranes of the fermentative bacteria. The hydrolysis of solid materials usually occurs slowly in anaerobic conditions. Several factors may affect the degree and rate at which the substrate is hydrolysed:

- Substrate composition (e.g. lignin, carbohydrate, protein and fat contents)
- pH of the medium
- Concentration of ammonium ( $\text{N-NH}_4^+$ )
- Operational temperature of the reactor
- Residence time of the substrate in the reactor
- Concentration of products from hydrolysis (e.g. volatile fatty acids)

The soluble products from the hydrolysis phase are metabolized inside the cells of the fermentative bacteria and are converted into several simpler compounds. The compounds produced include volatile fatty acids, alcohols, lactic acid, carbon dioxide, hydrogen, ammonia and hydrogen sulfide, besides new bacterial cells. The acidogenic phase is carried out by a large and diverse group of fermentative bacteria.

## 2.2.- Acetogenesis

Acetogenic bacteria are responsible for the oxidation of the products generated in the acidogenic phase. The most important acetogenic substrates are propionate and butyrate, but they also metabolized lactate, ethanol, methanol and even  $\text{H}_2$  and  $\text{CO}_2$ . The products generated are acetic acid, hydrogen and carbon dioxide.

During the formation of acetic and propionic acids, a large amount of hydrogen is formed, causing the pH in the aqueous medium to decrease. However, there are two ways by which hydrogen is consumed in the medium: (i) through the methanogenic microorganisms, that use hydrogen and carbon dioxide to produce methane; and (ii) through the formation of organic acids, such as propionic and butyric acids, which are formed through the reaction among hydrogen, carbon dioxide and acetic acid.

Among all the products metabolized by the acidogenic bacteria, only hydrogen and acetate can be directly used by the methanogenic microorganisms. However, at least 50% of the biodegradable organic matter is converted into propionic and butyric acids, which are later decomposed into acetic and hydrogen by the action of the acetogenic bacteria.

## 2.3.- Methanogenesis

The final phase in the overall anaerobic degradation process of organic compounds into methane and carbon dioxide is performed by the methanogenic bacteria. They use a limited number of substrates: acetic acid, hydrogen, carbon dioxide, formic acid, methanol, methylamines and carbon monoxide. The methanogenic bacteria are divided into two groups, according with their affinity for the substrate and the amount of methane produced: (i) Aceticlastic methanogens, that forms methane from acetic acid and methanol, and (ii) Hydrogenotrophic methanogens, that produces methane from hydrogen and carbon dioxide. The aceticlastic methanogens are responsible for about 60 to 70 of all the methane produced.

## 3.- ENVIRONMENTAL FACTORS

Microorganisms present in an anaerobic habitat, in this case an anaerobic reactor, can vary rapidly and frequently due to changes in the supply of nutrients or in the physical conditions. Both environmental characteristics, physical and chemical, influence microbial growth. Physical factors usually act as selective agents, while chemical factors can or cannot be selective. Some elements, such as carbon and nitrogen, which are usually required in large amounts, can be very important in the selection of prevailing species. Micronutrients, which are required in very small amounts, generally have little or no selective influence.

Anaerobic digestion is particularly susceptible to the strict control of the environmental conditions, as the process requires an interaction between fermentative and methanogenic organisms. Special attention should be given to the methanogenic microorganisms, as they are considered high vulnerable to changes in the environmental conditions.

The main environmental factors to be considered in the anaerobic digestion are discussed below.



### 3.1.- Nutrients

For biological treatment process to perform successfully the inorganic nutrients necessary for the growth of microorganisms should be supplied. If the needed concentration of nutrients is not added it is necessary to compensate the system either by applying lower loads or by allowing reduced efficiency of the system.

Some of the nutrients necessary for the nutritional stimulation of the methanogenic microorganisms are: nitrogen, phosphorus, sulfur, iron, cobalt, nickel, molybdenum, selenium, etc.

Generally nitrogen is required in larger concentrations for the growth of microorganisms. Under anaerobic conditions, the nitrogen in the forms of nitrite and nitrate is not available for bacterial growth, as it is reduced to nitrogen gas and released to the atmosphere. Ammonia and the fraction of organic nitrogen released during the degradation are the main sources of nitrogen used by microorganisms.

Nitrogen requirements are based on the empirical chemical composition of the microorganisms. According to Lettinga *et al.* (1996) the following relations can be used:

- *Biomass with low yield coefficient (Y ~ 0.05 g VSS/g COD)*  
COD:N:P = 1000:5:1  
C:N:P = 330:5:1
- *Biomass with high yield coefficient (Y ~ 0.15 g VSS/g COD)*  
COD:N:P = 350:5:1  
C:N:P = 130:5:1

The phosphorus in anaerobic processes should be approximately in the relation 1/5 a 1/7 of that established for nitrogen. Most of the microorganisms are capable of using inorganic phosphorus.

### 3.2.- Temperature

Temperature is one of the most important physical factors in the selection of microbial species. Three temperature ranges can be associated with microbial growth in most of the biological processes

*Psychrophilic range:* between 4 and approximately 15 °C

*Mesophilic range:* between 20 and approximately 40 °C

*Thermophilic range:* between 45 and 70 °C

The microbial formation of methane may occur in a wide temperature range (0 to 97 °C). Two temperature levels have been associated with the anaerobic digestion, one in the mesophilic range (30 to 35 °C), and another in the thermophilic range (50 a 55 °C). Most of the anaerobic digesters have been designed in the mesophilic range.

It is very important to maintain an uniform temperature in the reactor, once the anaerobic process is considered very sensitive to abrupt temperature changes, which may cause an unbalance between the microbial populations and the consequent failure of the process.

The methanogenic microorganisms prevailing in anaerobic digesters operated in the mesophilic temperature range belong to the genera *Methanobacterium*, *Methanobrevibacter* y *Methanospirillum*, which are hydrogen using organisms; and to the genera *Methanosarcina* y *Methanosaeta*, which are organisms that use acetate to produce methane.

The Arrhenius equation is frequently used to quantify the effects of temperature on biochemical reactions:

$$K = K_0 \times e^{\left(\frac{-E}{R-T_{abs}}\right)}$$

where:

K = reaction rate

K<sub>0</sub> = constant

E = activation energy

R = gas constant (1,98 cal/mole.K)



$T_{abs}$  = absolute temperature (K)

According to the experimental data, the maximum growth rate increases as the temperature rises, until a maximum growth value is reached. From this maximum value, the maximum growth rate decreases quickly. This decrease results from two competitive processes: (i) bacterial synthesis, and (ii) bacterial decay, each represented by the Arrhenius equation, so that the net growth rate can be expressed as follows:

$$K_{net} = K_1 \times e^{\left(\frac{-E_1}{R-T_{abs}}\right)} - K_2 \times e^{\left(\frac{-E_2}{R-T_{abs}}\right)}$$

where:

$K_{net}$  = net growth rate  
 $K_1$  = bacterial synthesis rate  
 $K_2$  = bacterial decay rate

### 3.3.- pH, alkalinity and volatile fatty acids

These three environmental factors are closely related to each other, being equally important to the control and suitable operation of anaerobic processes. The pH affects the process in two ways: (i) directly to the organisms, or (ii) indirectly, affecting the toxicity of a number of compounds.

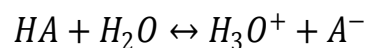
The methanogenic microorganisms have an optimum growth in the pH range between 6.6 and 7.4, although stability may be achieved in a wider pH range, between 6.0 and 8.0. The optimum pH depends on the type of microorganism involved in the anaerobic process, as well as on the type of substrate.

Regarding the stability of the process, it is important to remark that acidogenic bacteria are less sensitive to pH than the methanogenic bacteria, which means that acidogenic bacteria can be active at low pHs, even for pH values as low as pH 4.5. In practice, this means that the production of acids in a reactor can continue freely, although the methane production has been practically interrupted due to low pH.

The acidogenic bacteria have an optimum growth rate in the pH range between 5.0 y 6.0, with a higher tolerance to lower pH values. Therefore, pH control aims mainly at eliminating the risk of inhibition of the methanogenic microorganisms by the low pH values, thus avoiding the failure of the process.

#### 3.3.1.- Alkalinity and buffer capacity

The buffer capacity can be understood as the capacity of a solution to avoid changes in the pH. A buffer solution consists of a mixture of a weak acid and its corresponding salt, thus avoiding both the increase and decrease of the pH. The following generic equations are applied:



$$K_A = \frac{[H_3O^+] \times [A^-]}{[HA]}$$

$$pH = pK_A + \log \frac{[A^-]}{[HA]}$$

The buffer capacity reaches its maximum when  $pH = pK_A$ , that is when  $(A^-) = (HA)$ .

The two main factors that affect the pH in anaerobic processes are carbonic acid and volatile acids. In the pH range between 6.0 y 7.5, the buffer capacity of the anaerobic system depends almost completely on the carbon dioxide/alkalinity system, which, in equilibrium with the dissociation of the carbonic acid, tends to regulate the concentration of the hydrogen ion.

The amount of carbonic acid in solution is directly related to the amount of  $CO_2$  in the gaseous phase, once a balance is established between the amounts of  $CO_2$  in the liquid phase and in the gaseous phase. The portion of  $CO_2$  dissolved in the liquid phase can be established by Henry's law:



$$[CO_2] = K_H \times P_{CO_2}$$

where:

$CO_2$  = saturation concentration of  $CO_2$  in water

$K_H$  = constant of Henry's law (mole/atm.L)

$P_{CO_2}$  =  $CO_2$  partial pressure (atm)

The relation between alkalinity and pH is given by the following expression:

$$pH = pK_1 + \log \frac{[HCO_3^-]}{[H_2CO_3^*]}$$

where:

$pK_1 = \log (1/K_1)$

$K_1$  = constant of apparent ionization ( $4,45 \cdot 10^{-7}$ , a 25 °C), that is related to all the  $CO_2$  dissolved in the liquid

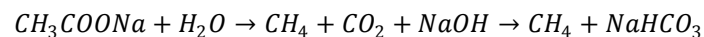
$$[H_2CO_3^*] = [CO_2] + [H_2CO_3] \cong [\sim CO_2(liq)]$$

The concentration of  $H_2CO_3^*$  can be obtained by calculating the partial carbon dioxide gas pressure.

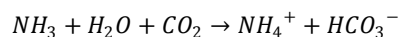
### 3.3.2.- Ratio between alkalinity and volatile fatty acids

The ratio between alkalinity and volatile fatty acids during anaerobic digestion is based on whether alkalinity of the system is able to neutralize the acids formed in the process and buffer the pH in case of accumulation of volatile fatty acids. Both the alkalinity and the volatile fatty acids derive primarily from the decomposition of organic compounds during digestion, as follows:

- Conversion of volatile fatty acids. For example, the digestion of sodium acetate can lead to the formation of sodium bicarbonate



- Conversion of proteins and amino acids, with formation of ammonia ( $NH_4^+$ ). The combination between ammonia and carbonic acid in solution leads to the formation of ammonia bicarbonate.



### 3.3.3.- Determination of alkalinity

In the control anaerobic reactors, the systematic determination of alkalinity is more important than the evaluation of pH. This is due to the logarithmic scale of pH, meaning that small pH decreases imply the consumption of a large amount of alkalinity, thus reducing the buffering capacity of the medium.

To determine separately the portions of bicarbonate alkalinity and of alkalinity of the volatile acids, the titration of the sample can be performed in two ways (Ripley, 1986):

- *Titration up to pH 5.75:* the first stage of titration provides the partial alkalinity (PA), practically equivalent to the bicarbonate alkalinity
- *Titration up to pH 4.3:* the second stage of titration provides the intermediate alkalinity (IA), practically equivalent to the alkalinity of the volatile acids

The interest of determining the alkalinity in two stages refers to the significance of the IA/PA ratio. IA/PA Values higher than 0.3 indicate the occurrence of disturbances in the anaerobic digestion.



### 3.3.4.- Alkalinity necessary for the process and chemical products

From the operational point of view is desirable to maintain high levels of alkalinity in the system, because high concentrations of volatile fatty acids could be buffered without causing a significant drop in the pH. However, if an alkalinity has to be supplemented then the selection of chemical products have to be evaluated in terms of applicability and economy. The minimum acceptable alkalinity requirement depends on the concentration of the organic matter because it determines the generation of volatile acids in the system.

Several chemical products can be used to control the pH of anaerobic digesters that can be separated in two groups:

- Products that provide bicarbonate alkalinity directly: NaOH, NaHCO<sub>3</sub>, NH<sub>4</sub>HCO<sub>3</sub>
- Products that react with carbon dioxide to form bicarbonate alkalinity: CaO, Ca(OH)<sub>2</sub>, NH<sub>3</sub>

Lime is normally the cheapest source of alkalinity but, as it is very insoluble product, it can cause operational problems. If the concentration of carbon dioxide is insufficient to react entirely with lime, the final pH may be very high which can be as harmful as a low pH.

Sodium bicarbonate is easy to handle, is very soluble, and, unlike lime, it neither requires carbon dioxide nor increases pH substantially when excessively dosed. The use of ammonia as a source of alkalinity depends substantially on the local conditions. For example, the use of ammonia might be prohibitive because the effluent will contain an excessive amount of ammonia.

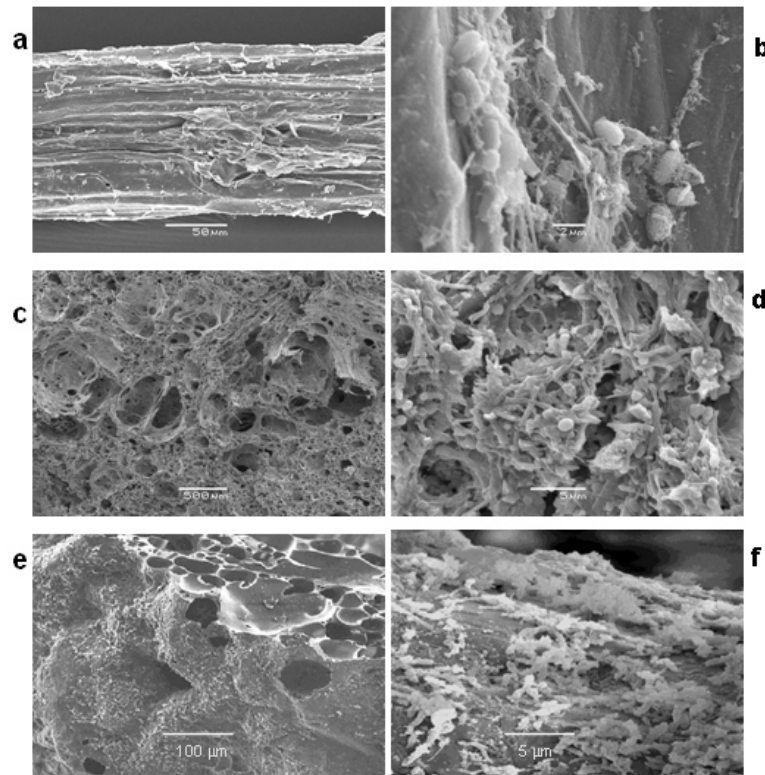
## 4.- BIOMASS IN THE ANAEROBIC SYSTEMS

A biological treatment process tends to be economical if it can be operated at low hydraulic retention times and at sufficiently long solids retention times to allow microorganisms growth. The development of high rate anaerobic processes capable of maintaining a large amount of active biomass even when operated at low hydraulic retention times, allows to operate the reactors at high volumetric loads.

The retention of high activity biomass in the high rate anaerobic processes depends on a series of factors and mechanisms, which are discussed in the following sections.

### 4.1.- Retention of biomass by attachment

The habitats of microorganisms in aqueous systems, such as anaerobic digesters, are very diverse and their growth depends on factors such as temperature, stratification and nutrient availability. Often the microorganisms overcome the instability of the living environment when adhered to a surface (Figure 1). The immobilization of microorganisms by adhesion is possible on fixed surfaces (e.g. anaerobic filter) or on moving surfaces, such as expanded and fluidized bed processes.



**Figure 1.- Microorganisms adhered to a different surfaces forming a biofilm: (a) sisal fibre waste (mag. x 500), (c) pumice stone (mag. x 35) and (e) porous glass beads surface and cross section (mag. x 150) before microbial colonization, and after colonization with anaerobic microbial biofilms: (b) sisal fibre waste (mag. x 6000), (d) pumice stone (mag. x 3000) and (f) porous glass beads (mag. x 2300) (Mshandete et al., 2008).**

#### 4.2.- Retention of biomass by flocculation

Bacteria grow into flocs, which can be separated from the liquid phase by sedimentation allowing to obtain an effluent with low concentration of suspended solids. The phenomenon of flocculation is important in upflow anaerobic sludge bed reactors (UASB).

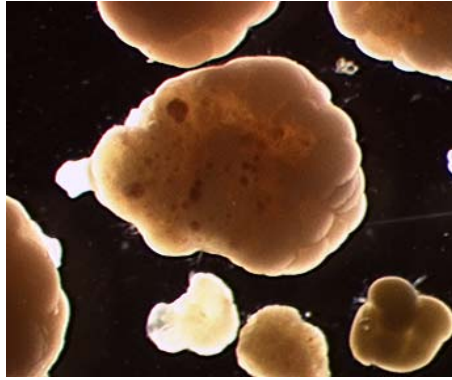
#### 4.3.- Retention of biomass by granulation

In terms of waste water treatment, the granulation phenomenon is basically restricted to UASB reactors. The mechanisms controlling the selection and generation of granules are related to physical, chemical and biological factors:

- The wastewater characteristics (concentration and composition)
- The compression of the sludge particles and the superficial rate of biogas liberation
- The ideal conditions for the growth of methanogenic bacteria
- The presence of divalent cations
- The hydraulic loading rate of the liquid through the sludge bed

The granules usually have a defined shape and can be several millimeters in diameter (Figure 2). Using a reactor with granules presents several advantages:

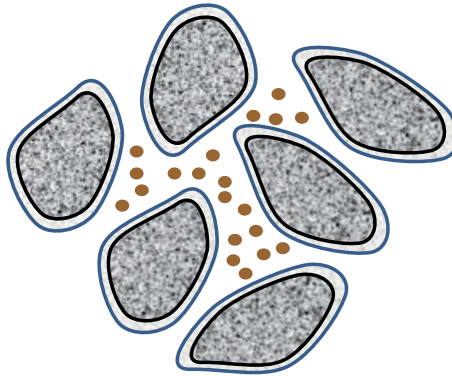
- The microorganisms are normally densely packed
- The granules exhibit good settleability
- The no need of a carrier material enables the maximum use of the reaction volume of reactor



*Figure 2.- Image of a granule.*

#### 4.4.- Interstitial biomass retention

The retention of biomass occurs in the interstices of a fixed support medium (Figure 3). The support surface is used for growth of the attached biomass while the support voids are occupied by microorganisms that grow dispersed.



*Figure 3.-Interstitial biomass retention.*

### 5.- ANAEROBIC TREATMENT TECHNOLOGIES

In recent decades several anaerobic treatment systems capable of retaining high levels of microorganisms have been developed. High sludge concentrations can be obtained by physical retention and or immobilization of anaerobic sludge. High biomass concentration enable the application of high organic loading rates, while maintaining long solids retention times (SRT) and relatively short hydraulic retention times (HRT).

#### 5.1.- Single stage anaerobic reactors

The process is based on two stages. In the first stage the organic matter is converted to methane and carbon dioxide in a completely mixed reactor. In the second stage the treated material is directed to a settler to separate the treated stream (clarified) and sludge, which is returned to the first stage reactor.

#### 5.2.- Anaerobic filters (AF)

The upflow anaerobic filter contains a stationary carrier material, in which the populations of anaerobic microorganisms are established (Figure 4). The sludge retention is based on: (i) the attachment of a biofilm to the solid carrier material and (ii) the sedimentation and entrapment of sludge particles between the interstices of the packing material, formation of very well settling sludge aggregates. Various types of synthetic packing material have been investigated and natural material such as gravel, coke and bamboo segments as well. Therefore it is crucial the selection of the support material, shape, size and weight. The average residence time of solids in the reactor is usually above 20 days. The feed can be carried out both upstream and downstream.

The most important characteristics of a biological treatment are the solids retention time and the concentration of microorganisms present in the medium. The long solids residence times in the reactors, associated with the



short hydraulic detention times, provide the anaerobic filter with a great potential for application to the treatment of low concentration wastewater. The main advantage of this technology is the low production of solids, although maintain good contact between the sludge and wastewater can be tricky. A disadvantage of the anaerobic filter is the accumulation of biomass at the bottom of the upflow reactors, where it can lead to blockage or the formation of shorts circuits.

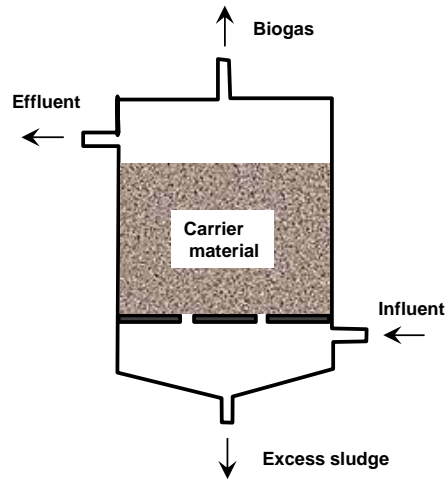


Figure 4.- Schematic representation of an upflow anaerobic filter.

### 5.3.- Upflow anaerobic sludge blanket reactor (UASB)

The anaerobic sludge bed reactors are by far the most used systems in the anaerobic treatment of wastewater. The sludge retention in the reactor is based on the formation of easily settling sludge aggregates (flocs or granules), and on the application of an internal gas-liquid-solids separation system.

The best known example of this concept is the upflow sludge bed reactor (UASB) (Figure 5). The wastewater moves in an upward mode through a dense sludge bed and is treated by the microorganisms to produce biogas. The required good contact between the sludge and wastewater is accomplished (i) by feeding the wastewater as uniformly as possible over the bottom of the reactor, or (ii) as a result of the agitation caused by the production of biogas. The washout of sludge aggregates is prevented by separating the produced biogas using a gas collection zone installed at the top of the reactor.

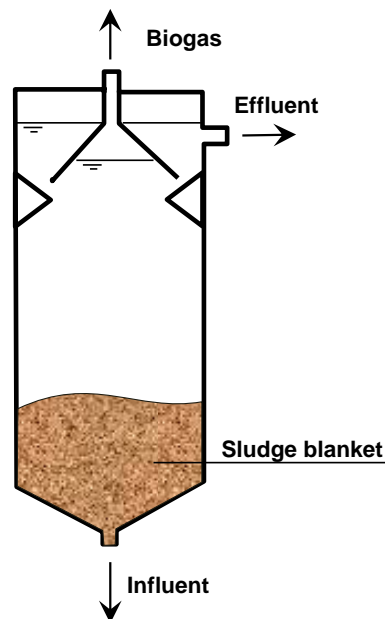


Figure 5.- Schematic representation of an upflow anaerobic sludge bed reactor (UASB).



#### 5.4.- Expanded granular sludge bed anaerobic reactor (EGSB)

The expanded granular sludge bed (EGSB) is a variant of the sludge bed reactors and are considered a second generation (Figure 6). It differs primarily in the higher speed of upward flow of wastewater. The increase in flow allows partial bed expansion, improving the contact between biomass and the stream to be treated. The high surface velocities of the liquid in the reactor are achieved through the application of a high effluent recirculation rate. Simultaneously inactive segregation of small particles suspended in the sludge occurs.

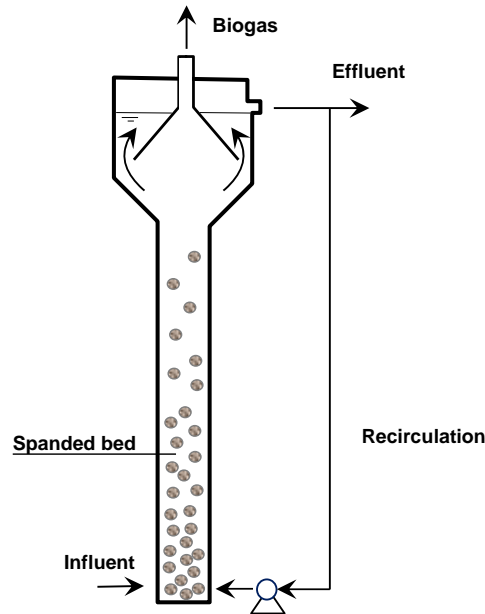


Figure 6.- Schematic representation of an expanded granular bed (EGSB).

#### 5.5.- Other anaerobic reactors

In addition to the anaerobic treatment technologies mentioned above, there are other anaerobic systems. Anaerobic sequencing batch reactor (ASBR) consists of a set of anaerobic reactors operated in a batch mode using a fill and draw method. A certain amount of the raw wastewater is supplied to the anaerobic reactor, after the supernatant liquid of a previous batch has been discharged. Then mixing of the reactor contents is started in order to enable the settled viable sludge to contact the wastewater and to eliminate the organic matter. After a sufficient period of reaction time, the sludge is allowed to settle and the supernatant solution is discharged. The next cycle is then started.

Anaerobic membrane bioreactors (AMBR) are a more recently option, but have high interest in those cases where traditional technologies do not work properly. This likely is the case when extreme conditions prevail such as high salinity and high temperatures, or wastewaters containing refractory and/or toxic compounds. Industrial scale experiences have shown that under those conditions sludge immobilization by granule formation does not develop successfully, affecting negatively the sludge retention. The main drawback of AMBR is the high cost of membranes.

### 6.- APPLICATIONS AND EXPERIENCES OF ANAEROBIC DIGESTER IN TEXTILE INDUSTRY EFFLUENT TREATMENT

Biological processes are often more sustainable and more effective processes from an economic point of view. Anaerobic processes may be more attractive than aerobic processes since it can be used to treat recalcitrant compounds under aerobic conditions, consume less energy and produce new sources of energy as methane or alcohol as fuel.

The textile industry generates effluents with a strong environmental impact. In dyeing and finishing lines, i.e. between 100-200 liters of wastewater are generated per kg of textile product. This effluent typically presents a high content of organic matter, since in the dyeing process up to 50% of the dyes are not fixed in the tissues and thus discharged in the effluent. Contaminants in wastewater of textile industries vary widely due to the use of batch operations in the dyeing process and the use of different dyes in each batch.

The salt content is also an important subject in the textile industry effluents, which varies between 30 and 100 g/L in the dye bath. After dilution with washing water, the usual salt concentration in the effluent is 2-3 g/L. The wastewater treatment with a salt content from the textile industry is viable and has been demonstrated on a pilot scale, being both anaerobic filters with AMBR suitable for the treatment of this type of effluent (Georgiou and Aivasidis, 2012; Xiao and Roberts, 2010).

New configurations of reactors have been developed more recently for the treatment of effluents from the textile industry (Wang et al., 2015), such as the anaerobic reactor where the internal circulation has been changed (MIC) and an external water circulation has been installed in order to increase the mass transfer between the sludge and the substrate.

In stationary conditions, a removal of organic matter 85% has been achieved, and color removal increased from 77% to 90% throughout the experiment. Also, the biomass concentration increased from 66.1% to 75.9%. However, it is important to note that excessive upward hydraulic speed (40.9 m/h) produces the disintegration of the granule and therefore a decrease in the removal efficiency of organic matter.

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