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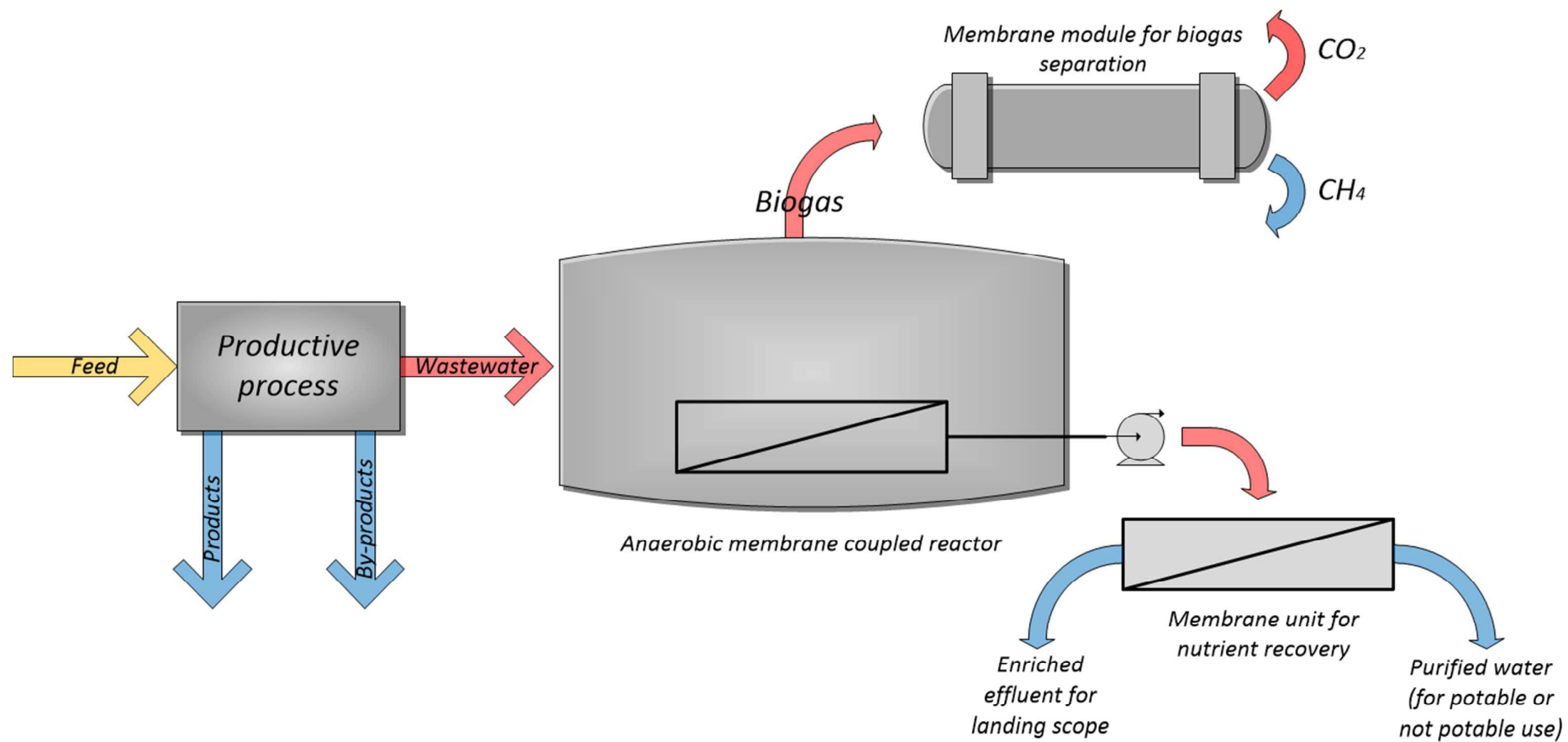
Membrane applications for biogas production processes and purification: an overview on a smart alternative for process intensification

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Abstract

Biogas is the result of a complex process of conversion that takes place because of the metabolic activity of various kinds of bacteria. The anaerobic digestion (AD) plants are characterized by many different criticisms, which risk producing a failure condition; one of this is the washout phenomena that imply a premature removal of the active biomass, owing to a vigorous adduction of organic matter. There is also the possibility of generating an excess of digestate with high nitrogen and phosphorous content that can induce water eutrophication if freely left in nature. In this sense, the use of membrane can be useful; with their high separation power, they can be employed both for the stabilization of the exhausted digestate and the enhancement of the solid retention time (SRT). Membranes are promising even in the field of biogas final separation for bio-methane production. Various kinds of setup have been tested so far for CO_2 capture and the results push to think in a possible stable application for anaerobic digestion plants. Therefore, membranes are a good choice for the development of advanced processes optimized for both the gas and semi-liquid phase handling.

Graphical abstract

1. Introduction

Biochemical conversion processes for the development of gaseous and liquid fuels are an attractive solution for the use of waste material and the production of useful resources.

In particular, AD is based on the activity of a numerous group of bacteria, capable of exerting their metabolic action on various type of substrates. This biochemical process comprises various steps, which should not be seen as consecutive phases, but as different actions of the same metabolic chain.

Like any other natural spontaneous process, AD presents many difficulties, which can greatly affect the results of the operations. First of all there is the problem of temperature, in fact, reproducing an environment compatible with the bacteria is fundamental.

Low temperature determines low rate for the metabolic reactions, which become more difficult; this is why psychrophilic AD is not so pursued, with the exception of cold regions [1] [2]. Instead, increasing the temperature there is the possibility of obtaining a higher chemical oxygen demand (COD) removal and biogas production, while methane concentration remains always similar [3]. pH, alkalinity and volatile fatty acids (VFA) concentration are also important for a good result. The optimal pH interval is 7.0-8.0. Below 6.5, the acidity of the medium is too high for allowing methanogenic activity. Above 8.5, instead, there is a clear accumulation of ammonia with inhibition phenomena.

Another problematic parameter is the SRT that can be defined as the time spent by solid particles inside the digester. When the material is subtracted from the fermenting device, a part of the active biomass is removed and this implies the necessity of a process recovery. If this new biomass formation is not enough to compensate the previous removal, there is the failure of the entire procedure. Beyond this extreme condition, the interval of possible choice for the value of SRT is wide, as it is visible in figure 1.

Figure 1 [4]

A bigger retention time induces a stronger alteration of the organic matter and, in so doing, a smaller final volume of residuals and a bigger gas production. Furthermore, with a long SRT it is possible guarantying a kind of acclimation in

the case of toxic compounds adduction. However, it is fundamental remaining above 10 days [4]; this value can be deduced considering the characteristic time of methanogenic bacteria. In fact, it is known that they present higher generation time than acidogenic bacteria, therefore, a short SRT can just induce a methanogens washout and a bigger VFA production. It is evident that SRT gives the chance of shifting the composition of the microbial population, acting in this way on the efficiency of volatile solids destruction [5]. The typical design values of SRT as a function of temperature are reported in table 1.

Table 1 [6]

It is immediately clear that in the case of no recycle or liquid withdrawal absence, hydraulic retention time (HRT) and SRT are the same thing. This is not the case of membrane coupled anaerobic bioreactors (AnMBR), which exploit the action of a membrane device to selectively remove just the liquid phase.

In this way, it is possible to operate with different value of HRT and SRT at the same time, providing the possibility of a volume reduction and an organic loading rate (OLR) increasing.

This type of configuration is common for both aerobic and anaerobic treatment of wastewater [7] [8]; but in this second case there is the real possibility of developing a gaseous fuel capable of feeding the thermal request of the whole process.

The application of membrane for biogas plants does not stop here. A tedious problem is that of the possible discharge and treatment of the digestate. In fact, even if it is true that it has amendment properties for the soil [9], there is also the problem of total nitrogen content that is high and goes beyond agricultural purposes. This is why many attempts have been tried up to know for reducing this concentration [10]. Membrane filtration, in particular, is good for the recovery of macronutrients from various kind of wastes [11], so it can also be employed for the post-treatment of digestate, in order to obtain an easily dischargeable residual.

The necessity of pursuing an enhancement of biogas production must be coupled with the possibility of its easy application. Moreover, as it was said for the digestate treatment, it is fundamental trying to find sustainable solution even for the product refining. As it is known, biogas is made of various compounds: CH_4 (40-70 % vol.); CO_2 (30-60 % vol.); NH_3; H_2O and H_2S in traces. Lower concentration of the diluting components also implies higher heating of combustion. It would be important arrive near the value of $803*10^6$ J/kmol, that is to say the heating capacity of pure methane. In this way, it could be possible producing bio-methane, useful for the natural gas grid or vehicles application.

Even in this field, membrane are promising and have stimulated a big curiosity [12] [13].

Therefore, the possibility of developing advanced membrane biogas plants, capable of good performances and easy final separations is real and it will be critically investigated in this paper.

In particular, the first part will be devoted to the use of membrane filtration for conditioning the hydrodynamic behavior of a typical digester. Then the nutrients membrane recovery techniques for liquid management will be investigated, and finally the attention will be focused on the gaseous product purification.

2. Biogas from wastewater: an alternative substrates to solid biomass

Despite of the big nomenclature variability present in literature, the different types of anaerobic digesters can be classified in terms of solid content as in table 2 [14] [15].

Table 2

Even in the case of low solid concentration (e.g. various type of wastewaters), there is the possibility of having a highly energetic medium.

This explain why anaerobic digestion of wastewater has gained such a success [16]. Moreover, many different industrial sectors are responsible of a big production of liquid waste with high organic content. This problem of stabilization and reuse becomes nearly vital in the Mediterranean area that combines a deep industrial development with a traditional heritage. Slaughterhouses, cheese production centers, distilleries and olive oil mills are just a few of all the possible providers of nutrient wastewaters.

Therefore, in every case in which there is a productive activity with a contingent formation of wastewater (compatible with biological activity), there is also the chance of using it for biogas production.

The different technological solutions that have been employed in the last years for wastewater treatment can be summarized as in figure 2 and 3; some of them will be further explored in the next sections.

Figure 2 [17]

Figure 3 [17]

3. Anaerobic high rate reactors: main criticisms

Generally, in the field of biogas production the technological possibilities are three: standard rate digesters, high rate digesters and two-stage digesters [18]. In the first case, the fermenting medium is not mixed or heated; there is a natural stratification that is far from allowing homogeneity. In the high rate digesters, instead, an external action of mixing and heating determines a great increase of the process rate, and the possibility of a volume decrease. Sometimes a second vessel follows the high rate digester and gives the chance to promote a decanting action of the outlet stream and the recycle of the active sludge [18].

The undifferential removal of material from the digester cannot prevent the active biomass withdrawal, this is why a possible coupling with membrane has been studied [19] [20] [21]. The possibility is very interesting especially in the case in which the classical technique of natural biofilm formation and granulation do not provide acceptable results.

In fact, one of the most common choice for municipal wastewater treatment is the Upflow Anaerobic Sludge Blanket (UASB) [22]. With this type of configuration, the possibility of separating HRT and SRT is partially explored, because biomass agglomerates in form of bigger particles or flocs ad goes to the bottom of the vessel. This produces a clarified zone from where it is possible to withdrawn, guarantying a high value of SRT and a low value of HRT.

Actually, the process of granulation is not so easy to describe [23] [24] [25] and it can be greatly influenced by the operative conditions. For example, it was found that the natural agglomeration is favored by high liquid upflow velocity and short HRT [26] [27] [28], with different conditions, there is the risk of producing a low dense and porous biofilm. Instead, a high shear strength is capable of inducing a thinner and compact layer [28]. Even the value of the OLR must be chosen in a proper way, because a big increase in the start-up phase can induce a massive formation of biogas that can alter the granulation process, owing to the rising bubbles. It is also easy to understand that the substrate composition can change the results, because with its variation there is the alteration of the cellular activities and the nature of extracellular polymers (ECP) produced [29] [30].

All these different aspects, combined with the necessity of avoiding extreme condition for temperature [31], make the UASB an improvable alternative.

The biggest problem is that of the start-up, because it requests strict control and long time. In the first phase of utilization, a not well-developed active biomass does not allow efficient COD removal and there is the necessity to increase the HRT in order to avoid the washout of the microbial seeds. For example, for the treatment of municipal wastewater at 20°C, a start-up period of 60 days was found to be enough for a COD removal of 80-85% [32]. A longer period, of exactly 120 days, was employed, instead, for the treatment of a Lurgi coal gasification wastewater [33]. Even if the periods are always long, there is a certain difference between the various choices reported in literature. This discrepancy can be justified considering the different operative condition and nutritional capacity of the various substrates. For example, in the case of the Lurgi coal gasification wastewater, the need of long start-up time is due to the low biodegradability and high inherent toxicity that makes the acclimation harder [33].

This difficult arises with every kind of wastewater characterized by high solid concentration. In fact, there could be an accumulation of inert particles and slow biodegradable solids, which lead the bacteria concentration to low level, producing their inability of reaching good COD removal. For example, in the case of potato-maize wastewater treatment [34] this accumulation was observed with high OLR (>10 g_{COD}/Ld) and low HRT (>1 d).

As it was already underlined, temperature is one of the most problematic parameter, not only for its effect on the metabolic rate, but also for the influence on the macroscopic properties of the fermenting mixture, which can determine a bad working of a UASB. In particular, temperature is able to affect the rheology of the ECP. In the case of the extracellular polysaccharides produced by a *Pseudomonas Oleovorans* NRLL B-14682, a decrease of steady shear and dynamic rheological parameters was detected with the increasing of temperature [35]. This is the results of a bigger mobility of the polymeric chains that obstacles bio-flocculation and settling ability. Therefore, the enhancement of biological reactions rate is accompanied by an increase of turbidity of the outlet stream and excessive biomass removal [36] [37].

Settling can also be worrying in the case of high lipids content, because they can produce a hydrophobic layer around the biomass particles inducing their floatation and in so doing the biomass discharge from the UASB. This is not the only problem that arises with this type of material, in fact, an excessive scum formation, with problem of plug at the gas outlet, was observed [38]. Actually, the difficulties with high grease and fat content do not stop here because of the inhibitory effect they can induce. It is known that lipids can be easily hydrolyzed in long chain fatty acids with high toxic power for gram-positive microorganism [39], like the methanogens.

Another problem related to the use of UASB, which can be partially solved with the use of membrane, is that of the salinity [40] [41]. A high concentration of salts induces a strong osmotic pressure that can force water going out the cells, producing a deep stress for the microorganisms [42] [43]. This is why the residues that comes from the sea-food processing are so difficult to handle [44] [45] [46]; without considering the possibility of their high calcium concentration. In fact, low concentration of calcium can be useful for the sludge settling, but beyond certain limit (abt. 200 mg/L) there is the rise of a series of complications like: the precipitation of $CaCO_3$; the cementation of the blanket; the reduction of the methanogenic activity [47] [48].

Considering all the information reported so far, it is possible to understand the main criticisms of classical anaerobic high rate processes.

4. Anaerobic membrane reactors: state of the art

AnMBR appeared for the first time in 1978 [49] as a combination of anaerobic digestion and a cross-flow membrane. The idea was developed in order to obtain a process capable of a major stabilizing action for the effluent wastewater. In fact, in origin, the anaerobic treatment of the organic waste employed just a vessel with short residence time. In this condition, the performances were limited and did not allow a drastic reduction of the pollutant power of the starting wastewater.

Since this first attempt, it was clear that with a membrane module the global rate of the process could be enhanced of 3-4 times, with a biochemical oxygen demand (BOD) removal of 85-95% and an effluent with low nitrate concentration [49]. With this work a huge speculation about the theme of anaerobic membrane reactors started. Actually, in the first step of the research the main problem was associated to the cost of the membrane unit, which was high for thinking to a large-scale application. This is why the membrane anaerobic reactor system (MARS) developed by Dorr-Oliver never overcame the pilot scale [50].

A good knowledge enhancement was obtained with the help of different research projects. Aqua Renaissance, in particular, was an intense attempt in Japan for promoting anaerobic membrane reactor as a useful process for wastewater treatment [51]. All the works included in this project were barely contemporary to the development of the ADUF (anaerobic digestion ultrafiltration) process in South Africa [52]. This was the first time in which self-made membranes were employed for the development of the ultrafiltration unit connected to the anaerobic digester. This curiosity is not surprising, because acting on the feature of the membrane (pore size, thickness, smoothness) it is possible to exert a certain effect: on the flux, on the extent of the fouling and on the durability of the system.

All the first studies were based just on the search of a good setting and the evaluation of the enhancement of the anaerobic treatment produced by ultrafiltration or microfiltration units.

This led to a configuration similar to the one in figure 4, which was found in various examples [53] [54] [55].

Figure 4

Actually, it is not obligatory to operate under pressure; in fact, the permeation can be induced with suction through a submerged membrane unit (SAnMBR). A typical scheme is that in figure 5.

Figure 5

These types of systems were systematically studied starting from the end of the 90's [56] and they still continues catching huge attention [57]. The innovation is also in the possibility of recirculating the gaseous stream for generating a cleaning action and fouling reduction for the membrane module. The concept comes directly from the processes of aerobic wastewater treatment in which the airflow is employed for partially remove the cake on membrane surface. Even if the biogas recirculated stream cannot be regular as an air stream, it gave promising results [58].

Actually, the problem of membrane fouling has gained a big importance in the last decade and it has been treated by different points of view [59] [60]. The rising transport resistance is one of the major difficulty that limits the use of this type of technology. Moreover, there is also the necessity of guarantying proper conditions for the anaerobic digestion process that can be easily altered. This is why AnMBR are not so commonly employed as a full-scale wastewater treatment. One exception is the Kubota's submerged anaerobic membrane reactor process that was used for the stabilization of all the wastes that comes from the agro-industry [61]. This patented process is based on the contemporary use of a solubilization tank followed by a digester with submerged membranes and it was used for the construction of less than 20 full-scale plants based in Japan and America [61]. In so doing, it is possible retaining methanogenic bacteria, removing all the inhibitors of the anaerobic fermentation process. The results obtained are positive with a total volume reduction of three-five times.

Considering all the materials that can be found in literature, it is possible summarizing as in table 3.

Table 3

Reference
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5. Type of possible wastewater

As it is visible from table 3, AnMBR were tested for the treatment of various kinds of wastewaters. In fact, in order to assess the feasibility of any type of technology, it is fundamental showing its capacity of producing a beneficial effect with moderate cost. In this case, the problem is even more complex because there is the double necessity of guarantying a high rate process and a good energetic integration with biogas production.

AnMBR showed great performances with various kinds of substrates; the only doubts are connected to the possible treatment of wastewaters with high organic strength and low particulate content [96]. In this case, membrane application is not so advantageous because the bigger capital cost and technical difficulties make the traditional high rate process (UASB, EGSB) the best solution. In fact, it is cheaper promoting a process based on a spontaneous flocculation even if the start-up time is bigger, in so doing it is possible having at the end of the initial phase a performance that is comparable with an AnMBR.

Most of the lab-scale works are made using synthetic wastewaters, in order to reveal possible anomalies before any further investigation.

For example, the effluents released by tapioca starch factories were easily simulated using an aqueous solution made with starch and additional salts, in order to reproduce the original salinity [97]. In that case, it was fundamental trying to understand the possibility of incorporating the anaerobic digestion process with the economy of tropical countries, which highly exploit this crop.

Obviously, a synthetic mixture is useful for a preliminary examination of the potentiality of a certain waste, because it cannot completely describe the complexity of the original scenario that is perturbed by many variables. This why in most of the cases the attention was focused on waste materials as directly produced by process industry.

There are many possibilities, which come from food and industrial processing in general; these materials are often pollutants and can obtain a second life with a natural process of degradation. For example, food-wastes usually have high organic content (1000-85000 mg_{COD}/L) and high solid concentration (50-17000 mg/L) [7]; they are massively produced in global economy and they can be transformed in useful resources more easily than raw materials [98]. This huge nutritional power can sustain anaerobic digestion and it should allow high OLR. Considering some of the works found in literature [76] [99] [100], dealing with the AnMBR for food waste, it is possible to find out a suggested OLR that is bigger than 10 kg_{COD}/m^3 d with an HRT of few hours. These results must be compared with the ones obtained using traditional processes. In particular, the OLR that can be tolerated with high rate processes is similar to the one used for AnMBR [101] [102], the big difference is in the HRT that is generally of various days. The possibility of treating food-processing residuals, with low HRT means a faster process that is therefore more captivating.

Many other productive activities generate highly useful wastewater; it is not easy making a resume because the typical features depend on the type of activity considered.

For example, there is the case of the textile wastewaters, which come from the fibers treatment. Considering the large amount of water used by this sector, it is not surprising that the problem of waste valorization has become important. Moreover, there is a big variability of the main characteristics according with the type of transformation, as it is visible from table 4.

Table 4 [103]

One of the most attractive possibility is the reduction of various kind of dyes; in particular, azo dyes are the most worrying because of their aromatic nature.

It is not possible finding a unique type of microorganism or enzyme that is capable to reduce every azo dyes, this is why the attention goes directly to those natural processes, which are based on a metabolic chain, of various microorganisms, like anaerobic digestion.

In particular, using a SAnMBR it was possible promoting immediate azo dye removal (more than 90%), even with high influent concentration [104]. The only problem observed was connected with the considerable amount of VFA in the effluent stream together with the aromatic amines derived by azo dyes cleavage. This results was justified assuming the inability of methanogens to metabolize the aromatic amines and assuming a moderate inhibition at high influent concentration of azo dyes [104].

Another possibility that has been tested with anaerobic membrane reactor is that of wastewater generated by paper treatment. Even in this case there is a huge variability according to the type of process and wood employed [105]. An interesting resource is the evaporator condensate of kraft pulp mill, which has a high methanol concentration [106]. Good overall performances were obtained employing a SAnMBR equipped with a flat sheet microfiltration membrane [107]: COD removal reached the average level of 93-99% without particular toxic actions. Moreover, there is the possibility of using the residuals from pulping and paper mill operations, which have captured a certain attention for their high nutritional capacities [108] [109].

Actually, in the field of AnMBR, the most exploited substrates are the municipial wastewaters, which are streams with low organic content and high particulate concentration. Anaerobic treatments have obtained a so big attention in this field because of the possibility of removing any air addition and promoting the formation of a gaseous product capable of sustaining part of the costs. In particular, municipal wastewaters have been tested with CSTR, UASB and EGSB membrane coupled reactors. The results obtained with short HRT (0.8-120 h) and good OLR (0.23-12.5 kg_{COD}/m^3 d) are promising in term of COD removal [110]. This implies the possibility of generating a permeate stream of non-potable water that can be used for other purposes.

Despite of the membrane beneficial effect, some problems connected to the use of municipal wastewaters remain. In particular, there is the possibility of a high pharmaceuticals content that can inhibit microbial activity [111]. Antibiotics, in particular, are responsible of a bactericidal effect. However, this possibility is negligible in a large-scale process, in fact, comparing the experimental data obtained with and without pharmaceuticals traces just a drop in methane biogas concentration was observed [112].

Another problem that is typical of municipal and industrial wastewater is that of the heavy metals content. A two years monitoring activity of a biological wastewater treatment system in Gdansk allowed finding out a fluctuating concentration of cadmium, copper, lead and zinc (0.01-0.8 mg/L) in the influent wastewater stream [113]. Moreover this concentrations tend to increase during the anaerobic digestion owing to the degradation of the organic compounds and the removal of material in the form of methane and carbon dioxide [113]. The major problem associated with heavy metals is that of the irreversible binding with the enzymes produced by bacteria, which become incapable of acting their usual role.

Considering all the topics analyzed so far, it is clear that membrane coupled anaerobic digesters combine all the capacity and difficulties of a traditional fermenter with the power and criticisms of membranes. Their optimization is even more complex because of all the possible substrate mixtures and technical arrangements.

6. Type of filtration and fouling problems

In the field of AnMBR the most common solutions are essentially two: microfiltration and ultrafiltration membrane. Small pores with a mean diameter that is comprised in the range 10-1000 Å characterize ultrafiltration membranes [114], which are capable to retain even colloids and macromolecules according to their cut-off. Generally, to qualify the performance of a membrane, it is necessary estimate the flux that undergoes a rapid decline when used for wastewater. There is an initial drop that is caused by the formation of a cake layer and pore blocking action; then, with the passing of days, there is a farther slow drop caused by a densification effect.

The resulting gel layer is made by solid particles, macromolecules, microorganisms and their ECPs. In general, once the gel layer has appeared, it is impossible a further increase of the flux through the ultrafiltration membrane with any operative conditions. Therefore, in order to avoid any unuseful energy consumption, it is better working with a pressure drop capable of guarantying a flux near the critical value.

Actually, the situation is even more complex because of the possibility of a gel layer removal due to the eddies near the membrane surface which produce a flux recovery and a result that is better than the predicted one [115].

Microfiltration, instead, is based on the use of membranes with bigger pores (0.1-10 μm) [114] and it is traditionally employed for bacteria removal from water. Even in this case there is a progressive flux decline determined by membrane fouling that has a similar mechanism as the one previously described [116]. The problem of water flux is of crucial importance because it determines the practical feasibility of AnMBR. For example, using a commercial ultrafiltration membrane in a lab-scale AnMBR a flux decline of 90% was observed in 20 days of usage [53]. This worrying fouling action was due to inorganic and organic materials. In particular, struvite ($MgNH_4PO_4 \cdot 6H_2O$) was identified as the major inorganic foulant [53]. Its formation is generally induced by the contemporary presence of magnesium, ammonium and phosphate ions in the broth and it is responsible of a strong fouling action.

This is why some attempts have been tried in order to reduce this action. In particular, there is the possibility of employing a kind of backfeeding [62]. This technique was considered useful because in long time operations backflushing with permeate was not capable of recovering water flux to the original value [62]. In particular, the operation of backfeeding consists in the sporadic adduction of an acidic feed solution in the membrane module that induces a pH drop and a deeper cleaning action. A lower pH obstacles struvite precipitation and helps in removing this solid phase that has grown inside the pores. The big difference from backflushing is in the possibility of feeding the bioreactor using the membrane module, which undergoes a recovery effect owing to the weak acidity of the solution.

Actually, the scenario is highly influenced by the constructive materials of membrane, this is why, in the same conditions, inorganic and organic membranes gave different results [64]. For example, comparing the performance of a hydrophobic polypropylene membrane with a zirconia skinned inorganic membrane a different behavior of the flux was observed. Organic membrane gives a stronger flux reduction with a faster reaching of a steady state condition. Inorganic membrane, instead, after a consistent initial drop, does not reach a steady state flux in a period of 150 hours and it guarantees a better overall performance.

The different behavior was explained in term of surface smoothness. The hydrophobic polypropylene membrane had a rough surface that ensured a strong adhesion of solid particles; this action was absent in the case of the inorganic membrane, which did not give rise to cake layer (figure 6).

Figure 6

It was estimated that the bigger foulant of the inorganic membrane was again struvite that was not so abundant in the organic membrane [64]. Therefore, the precipitation is easier on the surfaces, which have a kind of chemical similarity with the precipitate. In a perfectly similar way, the hydrophobic flocs tend to accumulate more easily on a similar surface.

The problem of the interaction between particles and surface was studied even in connection with the treatment of pulping residues [117]. In particular, it was found, with a polyvinylidene fluoride membrane of 70000 Da, that the cake layer was made primarily by the smallest flocs present in the fermenting medium with higher bound ECP and even the microorganism were different from the ones in the bulk. This is related to the concept that a potential gradient between the bulk and the surface membrane is the base of the separation process and it determines this diversification inside the system.

A composite structure [117] was also identified in the growing cake, which is generally made by: a dense layer strictly attached to the membrane, a porous layer and a loose upper part made of gel-like substances. The elemental analysis

of the cake layer demonstrated even in the case of pulping wastewater the possible presence of struvite [117], which was already identified as an aggressive foulant.

As it was briefly said, ECPs are another important agent that can promote the formation of an adhesive layer. They are made essentially by proteins and polysaccharides and the ratio between these compounds can influence the adhesive properties even more than their real quantities [118]. A bigger proteins concentration is responsible of a stronger hydrophobicity of microbial flocs; owing to this condition the flocs tend more easily to organize themselves in a sticky layer against membrane.

It was also found that microbial communities in the bulk phase and in the cake layer are not completely the same [117]. Considering that different microorganisms can produce different type and quantities of ECPs, it is easy realizing that there must be some specific bacterial population involved in the starting of biofouling action [119].

Even temperature can affect the magnitude of biofouling phenomena. In particular, thermophilic digestion generates a larger amounts of fine flocs (<15μm), biopolymers and soluble products [82]. This situation determines bigger difficulties in the process management with the impossibility of operating at the same water flux as the mesophlic case and with the necessity of a frequent readjustment. First of all, with higher temperature there is a stronger production of soluble microbial products, which can alter membrane performances [120] [121]. This action is also accompanied by a stronger production of biopolymers clusters, that is to say, substances with bigger dimension than soluble microbial products and independent by bacteria activity [82] [122] . Even a higher ratio between proteins and polysaccharides was detected in the thermophilic sludge [82] with all the problematic effects already described. However, the most significant and alarming effect related to thermophilic AnMBR is the stronger production of small flocs. A bimodal particle size distribution was detected in different works [19] [82] [123] [124]. Therefore, in the case of thermophilic AnMBR, the bulk sludge is made of dispersed aggregates and big flocs. The smallest particles (1-10 μm) are considered responsible for the formation of a quite dense layer against membrane surface, acting a key role in the flux decline mechanism. The formation of these fine particles is induced and favored by two contemporary effects: the proceeding of the demolition process and the action of the shear stress into the membrane module [125] that determines the disruption of the microbial aggregates. All this generates a progressive reduction of the mean diameter during the entire operations [19].

The themes discussed so far are sufficient for understanding the complexity of the hydrodynamic behaviour of an AnMBR. In this case, the typical problems of membrane management are deeply connected with the biological nature of the operation, which evolves in respect of its microbial vocation.

7. Membrane fouling control

The possible implementation of membrane on a large-scale anaerobic digestion process is dependent by the possibility of a flux control. In fact, when appreciable fluxes require excessive transmembrane pressure there is the necessity of recovering membrane performances with a proper cleaning action.

To overcome the fouling problems there are different routes which can be followed:

- change of the operation strategy;
- inhibition of foulant production;
- alteration of membrane surface properties;
- modification of broth characteristics.

Acting on the hydrodynamic behavior of the filtration module it is possible inducing the reduction of transport resistance and in so doing recovering the flux. This is the meaning of a change of operative strategy and it can be pursued in various way. First, there is the already cited possibility of backflushing, which consists in a temporary inversion of the permeation through the membrane owing to a high pressure in the permeate side.

This cleaning action was highly studied for both ultrafiltration and microfiltration in anaerobic and aerobic reactors. Generally, the system is backflushed for a few seconds and with a certain frequency (for 5-10 s every 3-15 min)[126]; the main effect is a drastic reduction of the concentration polarization resistance, while just a few decrease of the internal fouling can be produced with this type of action [126].

Moreover, there is a certain dependency of the result from the nature of the foulant agents, this why backflushing showed better performances with yeasts rather than bovine serum albumins [127]. In fact, the effect of the recovering procedures is deeply linked with the nature of the interactions between membrane and foulants; some compounds like albumins are capable of a bigger adhesion and they do not allow a proper and complete restore. Considering that a wastewater for biogas production is made of many constituents it is easy understanding that there could be some limitations for the beneficial effects of backflushing.

Another possibility that is very similar to the one previously described is that of the backpulsing. In this case, the inversion of the filtration through the membrane is much more frequent and fast, like a pulse. The results are absolutely positive with a good flux enhancement [128]; even in this case the results push to suppose the impossibility

of a complete internal fouling removal [128]. As it was for backflushing, there is the necessity of optimizing the operation, remaining inside the bonds imposed by the material resistance. In fact, it is easy understanding that the long exposure to the intermittent stress can seriously damage the membrane used.

Another possibility is based on the use of gaseous streams different from air or oxygen, which can alter the anaerobic environment required for the biochemical conversion. For example, in the case of ceramic anaerobic membranes, which are able to tolerate higher pressure, the possibility of employing N_2 backflushing was explored [129]. More in particular, with a pore membrane size of 1 μm, a filtration time of 16 min with backflushing intervals of 40 s and a transmembrane pressure of 1.0 kg_f/cm^2 demonstrated to be the best solution [129]. The results of the optimization is highly dependent from the type of the membrane employed and it is not surprising that smaller pores lead to the necessity of a more frequent recovering activity [129].

The possibility of using inert gases for membrane care is also at the base of all those reactors, which employs biogas sparging systems [82] [117] [83].

The rising bubbles are capable of promoting a certain removal of the foulant layer and, above all, with their mixing action they can cause a drop of the concentration polarization resistance [130]. This type of arrangement is not defect-free in fact some problems can arise.

For example, recycling the biogas inside the fermenter means increasing the CO_2 concentration in the liquid and the resulting pH drop can induce some inhibition effects [131]. Methane, instead, does not produce negative effects because of the law solubility in the liquid phase, therefore, it is right assuming a condition of no accumulation in the broth.

Acting on the recycled gas flow means acting on the intensity of the shear against membrane and in so doing on the ECPs production. Long exposure to high shear stress induces a smaller production of floc-associated ECPs; this can be justified not only in terms of a worse generation of total ECPs but also in terms of a smaller production of flocs-ECPs resistant to the erosion effect [132]. Obviously, there is a kind of adaptive mechanism of the biomass that is able to change its activity according to the shear condition of the surrounding media.

A scouring action of the membrane surface can be produced with the addition of powdered activated carbon (PAC) to the mixture to be filtered [80] [133] [134]. Not only these particles are able to produce a mechanical scouring action, but they are also responsible of a buffer effect against VFA and they can adsorb fine colloids on their surface avoiding the adhesion on membrane [80]. Even an increase of the resistance to compression has been showed [135], this implies the possibility of having a porous cake with a looser resistance. Considering all the aspects seen so far it is clear that this technique (based on broth alteration) improves the performance of a membrane reactor owing to a double action that is both mechanical (erosion of the cake layer) and physical (adsorption of possible adhesive compounds). Obviously, the optimal concentration of particles in the liquid to be treated is also affected by economical estimation; one solution has to be considered appreciable until it can produce the same beneficial effect with a smaller cost.

There is also the possibility of employing zeolites for conditioning the behavior of the fermentation broth [136], in fact, they are capable to reduce the ammonium concentration preventing struvite precipitation. In particular, the experiments conducted with clinoptilolite (a natural zeolite) showed a flux enhancement of the 15-20% in the case of a ceramic membrane [136]. This fact is not surprising because these natural materials are well known for the ability of ions exchanging. Obviously, the global performances are greatly affected by the physical and chemical properties of the system. The overall performance is a combination of two effects the cation exchange and the adsorption on pore walls. In particular, the ion exchange mechanism prevails at lower ammonium concentration, that is to say, when this amount is comparable to the cations entrapped inside the zeolite; adsorption, instead begins to prevail at higher concentrations.

As it was proved by many studies [137] [138] [139], the development of a cake layer is connected to the morphology of the membrane surface. This explains why many attempts have been done in order to develop a surface conditioning technique capable of promoting a slower flux decrease. In this sense, it is remarkable the case of the graft polymerization that induces the attachments of functional groups on the membrane substrate. The functionalizing membrane action can be promoted by the use of UV rays [140] [141] [142], plasmas [143] [144] or ozone [145] and the result is the induction of a certain hydrophilic behavior that can limit the hydrophobic interaction between proteins and membrane.

Obviously, the different techniques can be combined together for promoting a better membrane recovery, for example, graft polymerization and backpulsing were tested in conjunction with a polypropylene membrane [146]. In this particular case, the drop of the interactions between foulant and membrane produced a higher efficiency for the backpulsing action. As it was already underlined, a big contribution to the cake layer formation comes from the microbial activity. This is why a certain effort for the limitation of this action has been tested [147] [148]. The main objective is trying to disrupt the quorum sensing mechanism, which also contribute to the biofilm formation. This

9

method can give good results even just with the addition of free [149] or immobilized [150] *Acylase I* to the fermentation broth in the membrane bioreactors (MBR). This enzyme can destroy the *N-acetyl homoserine lactone*, an autoinducer of Gram-negative bacteria, providing a beneficial effect in term of biofouling reduction. Considering all the problems of cost and stability connected to the use of free enzymes, also the strategy of bacterial quorum quenching has been tried [151]. In this second case, recombinant microorganisms (capable of a high enzymes production) are entrapped in a precise region of the MBR in order to prevent their dispersion. Therefore, using a membrane and developing a "microbial-vessel", it is possible putting in contact the broth with the microorganisms responsible of the anti-fouling enzymes production.

In our knowledge, a possible application of this technique to AnMBR has not been tested yet. Even in anaerobic conditions there is the development of a quorum sensing mechanism, therefore, even in this case an enzymatic or bacterial quenching action could be helpful.

Finally, it is important underlining that a big effort has been tried in the last years in order to develop a procedure for the production of membranes capable of good performances without complex treatments.

Patterned membranes are the main results of this type of approach. They are prepared inducing the formation of precise patterns on the flat surface with soft lithographic techniques. Pyramid type and prism type membranes (figure 7) have been recently tested showing a certain flux enhancement in comparison with traditional flat-sheet membranes [152].

Figure 7 [152]

It is also possible producing patterned hollow fiber membranes adopting a patterned nozzle during the fabrication [153].

One fundamental aspect is the "fidelity of the pattern", that is to say, the similarity of the master and replica mold. Obviously, it should be the highest possible because only in this way there is the chance of predicting the performance of the separation process. There are many variables and operative aspects that can greatly affect the fidelity of the pattern; the molecular weight and the concentration of the polymer in the casting dope are probably the most important, and they can be easily controlled during the preparation phase [154]. Instead, acting on the height and the shape of the pattern, it is possible producing a certain action on the water flux and the biofouling. The experimental evidences show that increasing the height of the pattern (in the case of a prism-patterned membrane) it is possible producing a higher flux and a smaller extent of the biofouling action [154]. While the first results can be easily justified considering that a major height means a bigger area, the second evidence is connected to the intensity of the shear stress produced against the patterned wall.

Another option that is also based on micro-fabrication techniques is that of the micro-sieve membranes. The most captivating feature is in the possibility of obtaining huge fluxes (two or three order of magnitude larger than traditional membranes) with moderate operative conditions. The non-tortuous pores and their uniform and geometrically organized distribution on the layer (figure 8) is responsible of such a good performance.

Figure 8 [155]

Moreover, the possibility of having a strictly narrow pore size distribution implies the chance of making a real resolution of the complex mixtures fed to the membrane device.

The applicability of this alternative for the wastewater treatment showed great results in term of biofouling management. More in particular, adopting UV-curable polyurethane acrylate as starting material for the preparation of a microsieve membrane, it is possible developing a layer with a low surface energy, which also implies a lower biofouling tendency [156]. Obviously, with the passing of time, there is a certain pore blocking action, but despite this, the huge increase of the flux is enough for justifying the interest for this alternative in the field of membrane bioreactor management.

8. *Membrane process for the recovery of useful resources from digestate*

Once the substrate is completely exhausted, it should be removed from the anaerobic digester and handled in the proper way. Considering that the active plants are quite numerous nowadays, it is easy understanding that there is a real need of developing simple processes for the reduction of the residual and a possible recovery of useful resources from them. In this sense, membranes can represent a valid alternative.

Conventionally, the digestate is just left in storage tanks and periodically used for fertilizing, there are also other options briefly explained in figure 9.

Figure 9 [157]

Essentially, the two things that could be important to separate from a digestate are phosphorous and nitrogen. In particular, the last one is more problematic because of the gaseous loss in form of ammonia and the possibility of the eutrophication of the aquifers. This risk is less strong in the case of phosphorous because of its ability to adhere to the soil particles [158].

A membrane process should be able to originate a permeate, made of water, useful for other application, and a concentrated retentate rich of the nutrients cited above, suitable as fertilizer and easy to storage. In this sense, ultrafiltration and microfiltration can be used for the removal of solid particles and macromolecules, while nanofiltration and reverse osmosis allow a further purification of water.

The first critical issue is related to the quality of the permeate; it is necessary obtaining water for agricultural or potable use. This last option requires an extreme purification in accordance with the international and local standards. In the European Community these limits are clearly explained in the text of the directive 98/83/EC, whose statements are briefly summarized in table 5.

Table 5

The experimental evidence shows that *E. Coli* can be almost completely removed both with ultrafiltration and microfiltration membranes [159]. This capacity is mainly due to the dimension of the bacteria that is bigger than the average pore size of both type of membranes. Even various type of parasites like *Nematode* can be completely excluded from the permeate [159].

Not only membranes should be capable of a good retention, but also a big attention should be paid to the contamination of the permeate side, which could be reached by undesired microorganisms [160]. This, combined to the possible presence of nutrients traces, can induce the formation of thick biofilm even on the permeate side of the membrane with the generation of an unacceptable water.

The problem looks even more complex if it is analyzed in term of finding the optimal solution for the contemporary removal not only of the microorganisms and inert solid particles but also of the heavy metal. Actually, their concentration in a well-functioning anaerobic digester cannot be so high in order to prevent inhibition phenomena [161]. More in particular, the results obtained for the co-digestion of sunflower hulls and poultry manure shows a limited concentration of heavy metals (Ni, Zn, Cu, Pb, Cr, Cd, Hg) [162], which is however high if compared to the bounds imposed for purified water. It is possible to state that this content is mainly due to manure and the seed sludge [162], in fact, different metals are often used to enrich the feedstuff of the animals [163].

Generally, the most exploited solution for metals removal from wastewater and liquid digestates is represented by nanofiltration and reverse osmosis [164] [165] [166]. The separation power of this type of membranes can be enhanced with the use of surfactants additives or water-soluble polymers capable of complexing the metal ions. More in particular, beyond a critical concentration, the surfactants aggregate in micelles, which capture the metal ions, making more difficult the transport through the membrane [167] [168]. Similarly, polymer-enhanced filtrations use the capacity of polymer ligands to create complexes with a weight bigger than the cut-off of the chosen membrane. A number of different polymers have been tried in the last years. Chitosan [169] [170], polyethylenimine [171] and polyacrylamide [172] are just some of the possible alternatives.

It is not infrequent also the use of electrodialysis, a membrane process based on the use of an electric field and an ion-exchange membrane. Originally employed for the treatment of seawater and the production of salt, electrodialysis gave promising results even for the recovery of chromium [173] [174], copper [175] [176] and lead [177] ions.

As it was previously said, water is not the only good resource that can be obtained from the treatment of the digestate. The interest for the production of fertilizers, based on phosphorous and nitrogen, easy to storage and capable to avoid the unconditioned discharge of anaerobic digestate, is demonstrated by the intensive research in the field of struvite crystallization [178] [179] [180]. This salt is made by the combination of magnesium, nitrogen and phosphorous based ions and it can work as a slow-release fertilizers.

The possible application of membranes for this scope is not free of difficulties. For example, using a reverse osmosis membrane, helped by a vibratory shear action, for a clarified digestate, a removal of 93% and 59% for nitrogen and phosphorous respectively was achieved [181]. This not so high performance was improved with a second filtration stage that allowed reaching a final removal of 95% for total nitrogen and 69% for phosphorous. Furthermore, this type of arrangement gave prove of an unstable behavior, with the risk of not respecting continuously the limitation imposed for water reuse [181].

The results cited above are less encouraging than the ones found by another research group [182]. More in particular, with a single stage vibratory enhanced filtration, it was possible providing the 96.4% removal of total nitrogen and 98.1% removal of phosphorous from the permeate [182]. This discrepancy is not surprising because of the big amount

of variables that can greatly perturb the results of such an operation. One of these is temperature; in fact, it is capable of modifying the viscosity of the feed acting to the rate of filtration and it alters the dissociation equilibria too. For example, increasing the temperature there is a bigger concentration of free ammonia rather than ammonium and this produce a bigger loss of ammonia as a gas, owing to the reduced solubility. The equilibria are also highly affected by pH and dilution conditions. This is enough for supposing that different conditions can produce apparently unmatchable experimental results.

Actually, very high performance for nitrogen recover were also obtained using submerged hollow fibers ultrafiltration membranes [183]. Lab-scale experiments with high ammonia starting concentration gave great removal efficiency, up to 98.5% [183].

The physical conditions of the digestate are also capable of acting on phosphorous and metal recovery. For example, a prior acidification of the sludge can provide a great increase of phosphorous extraction with the possibility of obtaining a higher concentration in the permeate side of a microfiltration system [184]. With this type of system, the nutrient recovery and concentration does not concern the retentate side, but the permeate; this is why it is necessary providing an extraction agent. Deionized water is enough for guarantying a stronger nitrogen recovery, while it is not good for enhancing phosphorous recovery, which prefers lower pH condition [184]. A similar trend can be observed even for metals, which are bound to solid particles and can be released in an easier way with the help of an acidic solution, in fact, hydrogen ions can replace metal ions on solid surface amplifying the extraction effect [184].

A smarter technique, originally used with MBRs, is based on forward osmosis [185] [186].

Figure 10

As it is visible in figure 10, the action of such a device is based on the use of a drawn solution with a lower chemical potential and the wastewater to be treated with a higher chemical potential. This gradient induces a water flux from the wastewater side to the drawn solution side, therefore there is the concentration of the sludge and the dilution of the drawn solution at the same time. The outputs of the whole process are a concentrated sludge stream, enriched in term of nutrient and a purified water stream useful for agricultural purposes.

More in particular, the reconcentration of the drawn solution is based on a reverse osmosis or a membrane distillation unit [187] [188].

The results of this type of operation are promising even in the field of digestate treatments [189]. The major advantage is the possibility of managing the fouling phenomena in a better way. In fact, the forward osmosis stage preserves the reverse osmosis membrane, of the second stage, from a rapid flux decline. This possibility is even more appreciable considering that the specific energy consumption enhancement, induced by the forward osmosis pretreatment, is modest [189].

Even the recovery of volatile fatty acids from a discharged digestate can be attempted with membrane technology [190] [191]. Considering the low molecular weight of these compounds (butyric acid, propionic acid, acetic acid, valeric acid, ecc.), it is normal thinking to nanofiltration as a suitable route for separation. They are so attractive because they can be obtained from a residual of another process and they can find application in many field of petrochemical and fuel industry [192].

The experimental results, obtained starting from an anaerobic digestate (pretreated with microfiltration membrane for solid removal), push to think to a possible application of the concept to the real anaerobic digesters. In fact, a retention up to 72.23% was achieved with the production of a retentate highly enriched in term of volatile fatty acids. This promising result, obtained with a composite polyvinyl alcohol-aromatic cross-linked polyamides membrane, was gained at 9 unit of pH. In this condition, the acids are almost completely present in dissociated form, so it is plausible thinking to a charge effect that obstacles acids permeation [193].

In the specific case of a membrane coupled anaerobic digester, which is already equipped with a microfiltration or ultrafiltration module for the retention of the active biomass, it is reasonable thinking to a successive nanofiltration or reverse osmosis module capable of giving almost clear water and a retentate enriched in nutrients. In this specific case is even more easy because there is not the real necessity of thinking to a pretreatment of the exhausted digestate, which already comes from a separation device.

9.   *Methods for biogas separation*

The only component that makes biogas an interesting resource is methane; this is why a huge attempt has been made in the years for finding a cheap purification system.

The removal of CO_2 is generally conducted using one of these technologies: water absorption; amine absorption; pressure swing adsorption, cryogenic technologies and membrane technologies.

Absorption is probably the most common solution; it requires a solvent capable of capturing the components of interest (CO_2 and H_2S in the case of biogas separation) and two columns, one is for the absorption action and one for the recovery of the solvent. A possible choice is represented by water, which has a certain capacity of capturing carbon dioxide, as demonstrated by the solubility data reported in table 6.

Table 6 [194]

Generally, the water scrubbers are operated at room temperature and at a pressure higher than the atmospheric one (less than 15 bar [195] [12] [196]); this choice is determined by the thermodynamic constraints reported above. In the first column, water falls from the up and cleans biogas from the acid compounds. The second column instead promotes CO_2 desorption just with a pressure drop. Considering that a complete removal of H_2S from water cannot be provided in the regeneration column, it is impossible recycling all the water stream, in order to avoid accumulation in the recycling loop [12].

This option can be enhanced using amine solution. In particular, monoethanolamine and diethanolamine have been widely employed for this purpose. Triethanolamine, instead, did not gained the same success because of the high steric hindrance that determines a less effective action.

Despite of the bigger purities of the final methane, there are some problems connected to the use of this type of process. First, there is the risk of contamination of the environment because of the possible loss of these chemical agents. Then there is the problem of pressure; generally, these scrubbers work at atmospheric pressure and this produces the necessity of an intense compression of the final product to satisfy the gas grid standard.

Pressure swing adsorption is becoming an even more common research theme in the last decades. It is based on the use of non-toxic microporous or mesoporous solids and it can induce limited capital costs [197]. Moreover, choosing a proper solid adsorbent, it is possible obtain the contemporary removal of water, hydrogen sulfide, carbon dioxide and other impurities, reaching an excellent purification of methane. Natural and synthetic zeolite are the most typical choice owing to their huge selectivity. In some cases the separation is promoted by a stronger interaction of carbon dioxide with the solid substrate; in other circumstances, instead, it is not a question of interaction, but the separation is promoted by a difference in the diffusion rate inside the microporous or mesoporous structure [198]. Most of the works found in literature propose a moderate overpressure for the adsorption phase and an atmospheric pressure for the desorption stage [199]. This means that the resulting methane stream needs a compression even in this case.

There is also the possibility of applying cryogenic techniques, which exploit a temperature drop at high pressure for promoting the condensation of carbon dioxide.

Table 7 [194]

The boiling point temperatures reported in table 7 are enough for understanding that a good separation can be obtained reaching the condensation temperature of carbon dioxide.

In this way, there will be the production of a liquid phase made by: carbon dioxide, water, hydrogen sulfide and ammonia. While the gas phase will contain methane and small traces of hydrogen and other compounds (nitrogen, oxygen, carbon monoxide), which can be accidentally present in biogas.

All the technologies analyzed so far have been developed in the past years for the gas upgrading in various field of petrochemical and chemical industry.

In the case of a biogas plant, which is finalized just for the feed of a power station, it is not important reaching a so high methane purity and there is the problem of a fluctuating behavior with a sometimes-modest production. In such a situation, membranes can be the most appropriate solution. First, there is the possibility of developing modular separation systems, capable of satisfying different requests, and they are also perfect for a case in which there is a not so high gas production and a big carbon dioxide formation [200]. In fact, the size and the cost of a traditional scrubber are more influenced by the carbon dioxide percentage in the feeding than the gas flow rate [200].

Actually, this is not a defect-free alternative and many doubts continue to push in the direction of a stronger research. For example, there is the problem of the product purity that is sometimes less than the one obtained with absorption system. Another topic that causes many debates is that of plasticization [201], a swelling effect induced by the CO_2 sorption and accompanied by a selectivity loss. Summarizing it is possible to state that a good membrane for CO_2 separation and biogas upgrading must have the following features [202]:

- high carbon dioxide permeability and selectivity;
- a moderate cost;
- a certain resistance to plasticization and aging effects;
- a good resistance to any kind of alteration produced by chemical agents or high temperature conditions.

10. Polymeric membranes: an overview on the commonly used materials and main features

Membrane purification of biogas is generally conducted using all that options that have been tested for carbon dioxide removal from various type of flue gases and natural gas.

The first attempts for gas deacidification were tried with cellulose membranes [203]. Cellulose is a polymer that can be found even in living systems; it is made by a linear sequence of glucosyl residues connected with a β1-4 linkage. Beyond these first approaches, the real beginning was represented by cellulose acetate membranes [204] [205] [206]. In a dense cellulose acetate layer, the transport can be described with a solution diffusion mechanism, typical of all dense polymeric membranes. According to this explanation, the gas molecules dissolve in the polymer and then diffuse owing to a concentration gradient and this is why permeability depends from solubility and diffusivity at the same time (equation 1).

$$P_i = D_i * S_i \ (eq.1)$$

A good membrane separation requires that the permeability of the target component is higher than the permeability of all the others. This means having a pronounced selectivity, defined as in equation 2.

$$\alpha_{i,j} = \frac{P_i}{P_j} = \frac{D_i * S_i}{D_j * S_j} \ (eq.2)$$

Generally, the diffusivity of the component i is described with an Arrhenius dependency from temperature (equation 3).

$$D_i = D_{0i} * e^{-\frac{E_{Ai}}{RT}} \ (eq.3)$$

In equation 3, the two parameters (the activation energy and the front factor) are related in some way with the characteristics of the penetrant and the polymer and they can be connected each other with the relationship expressed by equation 4.

$$\ln(D_{0i}) = a * \frac{E_{Ai}}{RT} - b \ (eq.4)$$

In equation 4, a has always a value of 0.64 and b depends just on the state of the polymer (it is 9.2 for polymers in rubbery state, 11.5 for glassy polymers).

Moreover, the activation energy depends from the size of the penetrants and the nature of the polymer; a valid description of this dependence is provided by equation 5.

$$E_{Ai} = c * d_i^2 - f \ (eq.5)$$

d_i is a diameter representative of the penetrant (e.g. the kinetic diameter), c and f instead change their value according to the nature of the base polymer.

Combining all the equations seen so far, it is possible developing the following expression for the selectivity.

$$\ln \alpha_{i,j} = - \left[\left(\frac{d_j}{d_i} \right)^2 - 1 \right] * \ln P_i + \left\{ \ln \left(\frac{S_i}{S_j} \right) - \left[\left(\frac{d_j}{d_i} \right)^2 - 1 \right] * \left[b - f * \frac{1-a}{RT} - \ln S_i \right] \right\} \ (eq.6)$$

Equation 6, deeply analyzed elsewhere [207], is a clear demonstration of the strong connection between selectivity and permeability, which are involved in a negative correlation.

The dependency of the solubility from the operative conditions can be expressed using the so-called dual-mode sorption model (reported in equation 7).

$$S = \frac{C}{p} = S_D + S_H = K_D + \frac{C_H' * h}{1 + h * p} \ (eq.7)$$

14

It is like assuming that the sorption of the gas in the cellulose acetate membrane (but also in a generic polymeric layer) is made of two contributions: the simple dissolution (S_D) and the Langmuir adsorption term (S_H) typical of a porous solid.

The weight of the two terms changes according to the distance from the glass transition temperature of the polymer. If the working conditions are below the glass transition temperature, the polymeric chains are rigid and essentially incapable of consistent movements; in this case, the polymer is in the glassy state. Instead, beyond the glass transition temperature, the thermal energy is enough for allowing the movements of the chains producing a rubbery state.

Generally, this rubbery state is assumed as an equilibrium condition, while a glassy polymer can be considered as a hypothetic liquid matrix with a dispersed solid inside.

The experimental results for a cellulose acetate membrane are perfectly compatible with this type of description [206] and they also underline a certain sensibility to the problem of plasticization. In fact, the micro-voids, which are present in the glassy polymer structure, block some CO_2 molecules producing a swelling action of the membrane matrix that is damaged. This negative action is empirically demonstrated by the selectivity loss that appears increasing considerably the CO_2 concentration in the feeding side [206].

Despite these problems, which are common to other materials, cellulose acetate membranes gave prove of good performances, with carbon dioxide and hydrogen sulfide removal higher than 90% [208] and a CO_2/CH_4 selectivity higher than 20 [202].

The silicone rubber membranes represent another solution commercially available. Nowadays they are employed for the treatment of the gas, which comes from the oil production [209]. More in particular, these membranes allow the movements of bigger hydrocarbons, avoiding the passage of methane and ethane. The high permeability that they show is connected to the large free volume among the chains [203] [210]. A very low glass transition temperature and a good flexibility also characterize all this type of polymers.

In order to get a bigger mechanical resistance, it is useful adopting a copolymerization process. In this way, the other monomers can be chosen in order to enhance the stability of the base polymer and provide a material capable of higher performance for industrial processes.

However, it is clear that pushing on the rubber behavior it is possible promoting a flux enhancement, while a glassy behavior is responsible of a major selectivity.

Another option is represented by polysulphone membranes, which are probably one of the most exploited solution [211] [212] [213]. The interest for this type of material was stimulated by its mechanical and thermal stability, which determine also the possibility of an easy spinning action for hollow fibers production.

Even for polysulphone membranes, a dual-mode sorption model can be adopted [214]. The empirical analysis also shows that the selectivity is deeply linked with the thickness of the layer. A higher thickness can induce a higher selectivity, with an upper limit of a 22.4 for the CO_2/N_2 case [214]. Actually, it is not so easy making any kind of prediction, because of the big variability of structure that can be produced changing even the additives for the preparation. More in particular, non-solvent additives increase the non-miscibility of the spinning dope and accelerate their precipitation, producing a structure with finger like cavities. Reducing these agents, instead, the final structure will be more similar to a sponge [212]. This mechanism is not just typical of polysulphone membranes, but of all polymeric membranes in general.

Another interesting type of material is represented by polycarbonates, which are synthetized by the reaction of carbonic acid and bisphenol-A. Considering the difficulty of the polymeric chains in organizing a compact structure, it is not surprising that polycarbonates membrane are characterized by a considerable CO_2 permeability (around 40 barrers), combined with a high selectivity comprised between 15 and 25 [215].

Polyimides, instead, are obtained from a condensation reaction of a polyamic acid. Acting on the nature of the precursor is always possible producing particular feature in the resulting polymer and, in so doing, in the final membrane. In this sense, 6-FDA is probably one of the most studied precursor because of its ability of inducing high permeability and a good separation power [215]. Polyimides are generally characterized by high glass transition temperature and a certain hydrophobicity; this implies a perfect match with an operation like biogas treatment. In fact, the presence of moisture cannot affect considerably an hydrophobic layer as a polyimides membrane [216].

In addition, the interest exerted by polyarilates is remarkable. They are produced by a reaction of a dioil with chloride acid; the performance obtained are not among the best possible, even if a permeability of 85 barrers is sometimes reported in literature [215].

Beyond any empirical and phenomenological approach to the problem of polymers design for membrane production, some principles are clear by now. One of these is the importance of having polar groups in the polymer structure. First of all, there is the possibility of a CO_2 solubility enhancement, in fact, considering the series polybutadiene - polytetramethylene oxide - polyethylene oxide the CO_2 solubility goes from 0.89 to 1.4 cm^3/cm^3 atm [217]. The

stronger interactions of polar groups with carbon dioxide are also responsible of a delay action of CO_2 diffusion in the polymeric bulk. For the same reason, there is also a reduction of the CO_2 permeability [217]. The total effect on the selectivity, instead, is quite difficult to explain. The enhancement effect on solubility, accompanied by a not so high delay effect on CO_2 diffusivity, should guaranty a good selectivity. The polar groups are also capable of inducing a packed glassy structure with an inherent sieving power. Despite this, a depressing action on selectivity was discovered in the case of benzylic amine substituents on a polysulfone structure. More in particular, the CO_2/CH_4 permselectivity of a polysulfone-CH_2-NH_2 (51%) membrane, was found sensibly lower than the one of a non-substituted polysulfone membrane [218].

One exception is represented by ether oxygen, which combines the positive actions already mentioned of polar groups, with a not so high depressing action on CO_2 permeability [217]. This explains why polyethylene oxide membrane have captured so many attention in the field of gas separation [219] [220] [221]. Moreover, other trends of research are pushing in the direction of the use of low molecular weight polyethylene oxide or polyethylene glycol. In fact, choosing a small chain, polymer it is possible creating thin supported films that are liquid at moderate temperatures and capable of high performance [222] [223].

Another chance for overcoming the high crystallinity problem is using copolymers in which polyethilene oxide segments are combined with hard fragments that inhibit crystallization, avoiding a compact arrangement of the chains [224] [225].

It is fundamental remember the chance of crosslinking that is used not just for polyethilene oxide membranes but in all those cases in which is fundamental conditioning the original properties of the material for inducing an anti-plasticization behavior or a bigger durability. Crosslinking implies a connection of different polymeric chains with the use of chemical agents, UV light or physical methods [203].

Actually, it is not so easy controlling such an operation; it is fundamental guarantying a certain extent but, at the same time, it should be not so enhanced in order to prevent excessive brittleness of the material. Even the result in term of permselectivity can be unexpected. For example, with a modified polyimide membrane, increasing the crosslinking extent, it is possible having a big increase of He/N_2 selectivity and a considerable decrease of CO_2/N_2 selectivity [226].

A special role in the conditioning techniques for membrane capacity improvements is represented by thermal rearrangement reactions. This type of treatment is a post fabrication alternative induced by high temperatures (350-450°C) [227] [228].

Starting from a hydroxyl-containing polyimides membrane, it is possible inducing a rearrangement of the chains to a fully aromatic benzoxazole product, according to the mechanism reported in figure 11 [227].

Figure 11

This transformation is responsible of macroscopic effects, as the reduction of the density, but also of microscopic changes, mainly due to the formation of a product with a stiff structure. This stiffness is mainly induced by the high energy barriers to rotation of the two aromatic fragments.

A possible application for biogas upgrading is plausible because of the great increase of CO_2 permeability obtained. It is like developing a structure full of microvoids, appropriate for molecular separation, which reduces drastically the transport resistance. The effect on the permeability is obviously accompanied by a contemporary effect on the selectivity that is deeply connected with the extent of the thermal treatment [227]. In general, the performances are surprising with a CO_2/CH_4 selectivity and a CO_2 permeability that go beyond the upper limit of a typical polymeric membrane (figure 13) [229]. It is plausible assuming that the big permeability is the effect of the huge porosity, while the selectivity is the result of the shape of the cavities, which show a narrow neck region [229]. Moreover, no effects of plasticization are monitored, even at high CO_2 partial pressure.

All these particular features make thermally rearranged membrane a promising alternative to classical glassy polymeric membranes.

11. Carbon molecular sieve membranes

Carbon molecular sieve membranes are produced by pyrolysis of a polymeric precursor already available in form of membrane. Despite the big separation potentiality, these materials are not so frequent in an industrial contest [202] [230]. The major drawbacks are: the excessive brittleness, that implies the impossibility of using high pressure; an excessive sensibility to water and oxidizing agents; the possibility of a progressive pore blocking action [230].

Obviously, a big series of positive aspects makes these membranes so interesting for researchers. First, they are characterized by a strong thermal stability; this is not a secondary aspect, especially for the possible application in the petrochemical industry [231]. Then they are almost inert to many of the chemical agents typical of industrial processes and they can be produced easily in form of flat sheets or fibers (according to the shape of the precursor).

Probably the most interesting aspects is the possibility of acting on the permeability and selectivity of the layer changing the pyrolysis conditions [232] [233]. In particular, starting with a hollow fiber polyimide membrane, it was possible to see that an inert gas is capable of accelerating the carbonization of the substrate, also inducing a higher permeability than the one obtainable with a vacuum pyrolysis [233]. More recent results, instead, show the small effect of inert gas flow rate, pushing to think that oxygen has the most important role [232]. Therefore, changing the oxygen exposure conditions it is possible manipulating the CO_2 separation power.

This is just a brief overview on the big potentialities of carbon molecular sieve membranes, which could be applied even for biogas purification. Actually, in our knowledge, there is not a systematic study about the potentiality of this type of membranes for biogas upgrading. Probably this gap depends from the fact that it is still a new concept that has been implemented just in lab-scale application for general estimations.

12. Facilitated transport membranes

The research of new possibilities for overcoming the tradeoff of selectivity and permeability led to an increasing attention on the so-called facilitated transport membranes. They are made of a polymeric structure with an insert, which act as a carrier. More in particular, this carrier is capable of reacting, in a reversible way, with carbon dioxide. Therefore, the classical transport is accompanied by the facilitated transport mechanism, which is possible just for the objective compound.

It is clear that the reversible interaction with the carrier are just a tool for increasing the selectivity of the membrane without penalizing the permeability.

In figure 12, a possible transport mechanism for a facilitated transport membrane is proposed [234].

Figure 12 [234]

It is clear from the figure that there could be also a certain movement of methane through the polymeric base of the membrane, but essentially, it will remain almost in the retentate.

Considering that for biogas application, the main objective is removing CO_2 and H_2S, the carrier should be able to interact with an acidic compound. In this sense, it is interesting considering all that works about facilitated transport membranes, which incorporate basic carriers such as amines and imines.

More in particular, in the case of an amine carrier the interaction with CO_2 can be described with a zwitterions mechanism [235]. First CO_2 reacts with the amine giving the zwitterions; then there is a deprotonation that leads to the formation of the carbamate ion, which in presence of water can degenerate to form bicarbonate ion. Carbonate and carbamate ions are the form in which CO_2 can move in the layer reaching the other side.

If the membrane is just made of a solution in a microporous structure then there is the risk of a washout of the carrier or its evaporation. This why immobilization by electrostatic forces is more common than liquid membranes. In this way, the carrier cannot move freely and CO_2 passes from one functional group of the polymeric chain to another as in figure 7.

The results obtained with these membranes are promising for biogas upgrading. For example, with a cross-linked polyvinyl alcohol membrane, with both mobile and fixed amine, it is possible reducing the CO_2 from 17% to 100 ppm (with a flow rate of 60 mL/min)[235]. It is a drastic reduction and above all the high initial concentration is perfectly compatible with a scenario in which the raw mixture is biogas.

Another solution, that was tested directly with biogas, is represented by polyvinylamine-polyvinylalcohol blend membrane [236]. The carrier is fixed in the polymeric structure and CO_2 reversibly reacts with the amino groups. The results obtained using low pressure (2 atm) and room temperature are good with a CO_2/CH_4 selectivity of 40 and a permeance of 0.55 m^3/m^2 h bar.

The possibility of operating at nearly room condition is of primary importance for biogas treatment, because most of the anaerobic digesters operate in condition of small overpressure, so developing a system with a compression in the middle is of primary importance. Actually, despite of the good selectivity at low pressure, there is the problem of the surface area, which tends to increase rapidly, for a certain amount of biogas to treat, with the decreasing of pressure. This is why the optimization process indicates that the best scenario is the alternative based on two modules in series, equipped with polyvinylamine-polyvinylalcohol blend membrane, and operating at a pressure of 20 and 10 bar respectively.

Another competitive option that has been recently tested in condition of high pressure is based on the use of a water insoluble amino-starch derivative, for the preparation of a polyethersulfone membrane[237]. The ammino-starch content is of primary importance for the regulation of the overall performances. In fact, its increase can help the CO_2 sorption, reducing the CH_4 sorption at the same time. The presence of the amine group suggests a facilitated transport, exactly as in the cases already mentioned. The membranes were synthetized in form of dense or

17

anisotropic layers, but in both the cases they gave proves of remarkable performance, with a selectivity of 58.23 and 61.2, for asymmetric and dense membrane respectively, at a pressure of 27 bar and with a synthetic mixture similar to biogas (30% CO_2, 70% CH_4) [237].

While most of these options are not commercially available, another alternative is produced on large scale. More in particular, nanofiltration membranes for water treatment, showed good performance for CO_2 separation from humidified gaseous stream [238]. This good behavior was supposed to be the results of the presence of piperazine functional groups and free amine within the membrane structure.

All the discussion above is a clear demonstration of the big potentiality of facilitated transport membranes for a problem like biogas upgrading that remains a complex issue.

13. Mixed matrix membranes

Mixed matrix membranes try to combine the positive features of polymers with the high selectivity of other materials. This is why the attention is focused mainly on those materials that have a highly inherent separation power such as: zeolites; carbon nanotubes; metal organic frameworks or covalent organic frameworks.

More in particular, it is well-known that polymeric membranes presents a negative connection between selectivity and permeability [239]. Choosing a material with a high permeability generally means obtaining a not so high selectivity.

Figure 13 [239]

Coupling polymers with inorganic fillers, it is possible going up that limit clearly visible in figure 8 obtaining better performances.

The improved behavior of membrane after the addition of inorganic fillers can be estimated using the simplified model of Maxwell [240].

$$P_c = P_m \circ \frac{n * P_f - (1-n) * P_m + (1-n) * (P_f - P_m) * \varphi_f}{n * P_f + (1-n) * P_m - n * (P_f - P_m) * \varphi_f} \ (eq.0)$$

In the previous equation P_c is the permeability of the composite membrane, P_m is the permeability of the polymeric matrix, P_f is the permeability of the filler material, φ_f is the volume fraction of the filler and n is the shape factor of the particles.

This equation comes from the analogy with the problem of the current circulation, generated by a field, in a dielectric materials made of different phases. It shows a good agreement with experimental data in the case of low filler concentration. In case of high concentration, instead, it is possible making an estimation using the Bruggeman equation [240].

$$\frac{\left(\frac{P_c}{P_m}\right) - \left(\frac{P_f}{P_m}\right)}{1 - \left(\frac{P_f}{P_m}\right)} * \left(\frac{P_c}{P_m}\right)^{-\frac{1}{3}} = 1 - \varphi_f \ (eq.9)$$

Both equations predicts an increase of the maximum selectivity with the fillers concentration, this explains why their presence is so useful.

Handling a high solid concentration can be quite difficult, especially in the preparation phase. In fact, there is always the risk of obtaining a non-homogenous layer with particles aggregates in the inner part of the layer. The solution to the problems are essentially three [241]:

- increasing the base polymer viscosity for reducing the sedimentation rate of solid particles;
- reducing drastically the preparation time of the composite layer;
- adopting nanoparticles that are not able to precipitate in a rapid way.

There is also the risk of an accumulation of the particles in the surface area; this happens because of the convective motion, which appear operating at high temperature [242].

Another aspect that makes preparation of mixed matrix membranes not so easy is related to the interactions between the fillers and the polymer matrix. If there is not a perfect contact and some gaps remain there is the risk of producing a selectivity drop, because, obviously the gases will choose the easiest way for reaching the other side of the membrane [243]. There is also the possible risk of a matrix rigidification around the filler particles, with a consequent permeability decrease. Obviously, the non-homogeneity can be a characteristic not just of the matrix but also of the

filler, therefore it is possible having a reduced permeability region within particles surface or, in an opposite way, there could a portion highly permeable owing to a bigger porosity [243].

In all these cases, the prediction power of Maxwell model appears moderate and various correction can be tried in order to improve its predictions [241].

In the field of CO_2 removal, zeolites are one of first materials that have been tested for the creation of mixed matrix membranes. More in particular, adopting hydrophilic zeolites with high Al concentration it is possible adsorbing polar compounds such as H_2S, while hydrophobic zeolites are more appropriate for polar compounds as CO_2 [244].

The possible choices that have been tested for the creation of mixed matrix membrane are numerous and they can be summarized as in table 8 [13] [245].

Table 8

Despite the big flexibility of zeolites, a certain attention has been gained in the last years by MOFs (metal-organic frameworks). These materials can have an incredibly high surface area (>6000 m^2/g) [246] and their features are also tunable according to the nature of the organic ligands employed [246]. Essentially, they can be described as coordination polymers comprising metal ions with organic linkers. These ones can also provide a bigger stability of the composite layer because of the major affinity with the polymeric bulk.

The first big result connected to the application of MOFs, that is interesting even for biogas application, is represented by the use of copper (II) biphenyl dicarboxylate-triethylenediamine [247]. The bigger gained mobility of CO_2 across the membrane was inspiring for the search in this field that now also comprises new established choices such as MOF-5 [248] and zeolitic imidazolate framework (ZIF) [249] [250].

This research trend is parallel to the use of carbon nanotubes, that is to say graphitic sheets organized in tubes with a diameter of few nanometers. Obviously, the presence of these channels inside the polymer matrix represents an improvement of the permeability, while, the difference in the adsorption energy between different compounds is responsible of the big selectivity.

Some of the experimental results collected in the last years are resumed elsewhere [247], and greatly show the big potentiality of these composite materials, which have all the elements for an application to a mixture as biogas.

14. Membrane for biogas refining: a still open research field

Despite of the big quantity of theoretical and experimental study about the feasibility of membrane for carbon dioxide removal from various type of gases, there is still a certain gap in the field of biogas applicability.

In literature, there are some works, which attest the promising potentiality of membranes for this type of application [251] [252] [253]. Most of the studies are based on lab-scale devices, which are tested with synthetic mixtures.

Actually, there is a kind of mismatch between the evolution of the study about the materials to be used and the actual technological development of a fully organized process. What appears immediately clear is the lack of a specific study about the monitoring, control and maintenance of membrane modules for biogas upgrading. Probably this gap is connected to the relatively young origin of this type of separation in such an area of study. It is not a negligible aspect because absorption technology are based on a well-established knowledge that allows a perfect understanding of any aspects. Therefore, absorption will continue to be the most exploited solution in large scale processes until a user-friendly configuration for membrane separation will not be reached.

The most desired advances in the field of biogas purification can be summarized as follows:
- a major research of cheaper materials;
- the development of simple modules, which can be easily guided by unprepared users;
- a bigger limitation of negative phenomena such as plasticization;
- a bigger attention to the problem of monitoring and control of large-scale purification plants;
- an appreciable enhancement of the trade-off between permeability and selectivity;
- the development of consolidate protocols for the preparation of well performing polymeric blends and composite membranes.

15. Cost estimation and economical analysis

The importance of biogas in the energetic scenario of highly industrialized and still developing countries is well established nowadays. It has been estimated that in the EU-15 the use of renewable energies has grown up from 300 TWh in 1995 to 400 TWh in 2005, with biogas as the most popular alternative derived from biomass use [254]. Moreover, the previsions for the future are quite generous with an estimated biogas production for the European member States of approximately 756 000*10^9 kJ in 2020 [254].

The big success of such an alternative is mainly due to the possible easy integration with an already existing productive framework. The starting raw materials are essentially wastes coming from other activities; therefore, only employing them in the immediate neighborhoods it is possible obtaining an appreciable gain. For example, the biogas potential of the Long Island (New York) area has been estimated as the 12% of the total energy produced starting from traditional sources in the same area and this total amount can be directly obtained from local wastewater treatment plants, solid waste management centers and agricultural activities [255].

Despite these general considerations, there is still some difficulties in the estimation of the real economic potential of an anaerobic digestion plant. First of all the operative and capital costs strongly depend on the final use of biogas, which can be directly burnt in a stationary plant for electricity generation, or it can be refined for gas grid injection. In this second case, the separation devices induce an increase of the capital and operative cost, but they contemporary generate a final product with bigger value.

The choice of the upgrading technique is connected to different aspects, as shown in figure 14.

Figure 14

The energy requirements are essentially related to all those operations, comprised in the refining process, which are fundamental for the transformation of the raw stream in a biomethane stream. A good review of energy requirements and total costs for different alternatives is already present in literature [256] and it can be summarized as in figure 15.

Figure 15

Despite of the lower average value that can be found for amine scrubbing, there is a wide discrepancy of the results of different authors. This is quite common, especially in the case of membrane processes, because different modules, equipped with different membrane, can produce completely different results. Changing, the type of membrane implies acting on the permeability and in so doing on the pressure necessary for the separation; considering that the compression costs are one of the most significant element in the development of a chemical process, is not surprising having such a dispersion of values.

The specific membrane features are also relevant for the quantification of methane losses, which represent a waste of a useful product and, in so doing, an indirect cost. Acting on the type of membrane means changing the selectivity and the overall performance of the device, therefore, in the case of a simple polymeric membrane it is not surprising finding that methane concentration in the permeate is not so low. Adopting extremely selective materials implies a reduction of this undesired effect but also an exponential increase of the capital costs, without considering that most of the newest highly selective membranes have been tested just in lab scale applications.

Moreover, a membrane separation for biogas upgrading can be organized according to different process schemes (single stage separation, single stage with recycle, multistage processes) [12]. Changing the main structure, it is possible acting on the compression cost, the total area required and the CH_4 recovery for a certain desired value of CH_4 purity.

Even for the digestate treatment, the cost problem is not so easy to handle, with membrane being the effective solution in some situations and not in others. A widely used correlation for the estimation of the capital costs of a membrane for wastewater treatment is given by equation 10 [257].

$$C(\text{\pounds}) = 2 * c_{membrane} \left(\frac{\text{\pounds}}{m^2}\right) * \frac{Q\left(\frac{L}{h}\right)}{J\left(\frac{L}{h\,m^2}\right)} \quad (eq.\,10)$$

The previous amount is always accompanied by other costs related to all the other components generally present in a full-scale process.

While in the case of biogas refining, a big contribution was represented by the compression costs, in the case of the digestate treatment a certain amount is related to the use of pumps. Actually, a pump is cheaper if compared with a compressor; therefore, its effect on the capital costs is generally negligible; the operative costs, instead, are strictly dependent on the flowrate to be treated.

Finally, there is the problem of maintenance and membrane recovery that in this second case is quite worrying. Actually, it is not so easy making some general considerations, because, as it was already seen, different methods can be implemented for the fouling reduction. Even the frequency of the recovery action is variable according to the

nature of the wastewater to be treated. All this variability is probably the reason why a systematic economical assessment for AnMBR is still missing in our knowledge.

16. Conclusion and final remarks

This review paper provides a deep insight in the field of membrane separation for biogas production processes.

All the considerations starts from the material that has been produced in the last years about MBRs, AnMBRs and membranes for CO_2 separation. Even if these themes are quite common in the scientific literature, a systematic study of their combination for the improvements of anaerobic digestion process is still missing.

Developing a digester equipped with membrane both for the liquid and gas treatment can solve the problems typical of the traditional processes.

First, there is the possibility of conditioning the hydrodynamic behavior of a high rate digester, acting on those critical aspects that limit a UASB, especially in the start-up phase. The improvements of the solid retention time also induces a further increase of the overall rate, allowing a higher OLR.

Membranes also provide an easy way for the digestate management. It is possible recovering water for potable or agricultural purposes and producing a concentrated sludge enriched in nutrient. The main objective is inducing a reduction of the volume required for the storage of the digestate and a final product with a high concentration of phosphorous and nitrogen, useful as a fertilizer.

The semiliquid digestate produced by anaerobic digesters, can be treated with ultrafiltration or microfiltration membranes. A more intense purification can be realized with reverse osmosis membrane, combined with a forward osmosis membrane.

The main limit is represented by the fouling action. Many alternatives can be found for the reduction of this natural phenomenon, which is due not only to the inert solids deposition but also to the microbial activity.

The progressive reduction of the flux is the most worrying aspect, because in a full-scale process the rate should be acceptable. Therefore, a kind of compromise between separation power and rate should be reached.

The anaerobic digester can be equipped with a subsequent membrane module for gas separation. The possible choices are numerous: polymeric membranes, mixed matrix membranes, carbon molecular sieves, facilitated transport membranes.

Even in this case there is a certain lack of knowledge, because most of the works found in literature deals with lab-scale applications. Despite this, it is clear that membranes can represent a green alternative for biogas purification because of the possibility of avoiding all those chemical agents employed for absorption.

This paper just wants to offer a complete view of all the possible applications of membranes in a contest in which their use is not so well established. Despite this, a further and more extensive analysis should be realized in order to verify the economical and technical profitability of this membrane-based transformation for a full-scale process.

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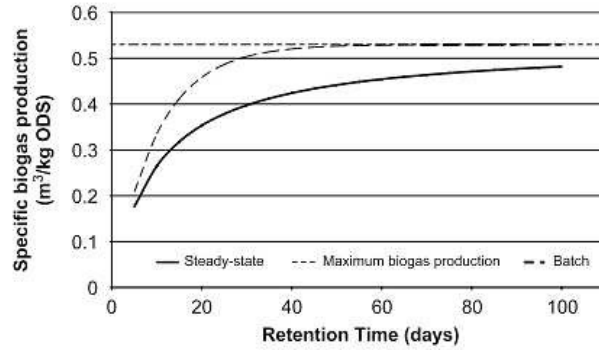
Figures

Figure 1 Specific biogas production as a function of solid retention time [4]
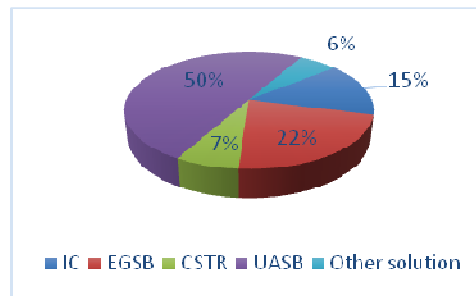

Figure 2 Anaerobic reactor technologies as monitored in the period 1981-2007 (2266 total plants analyzed) [15]
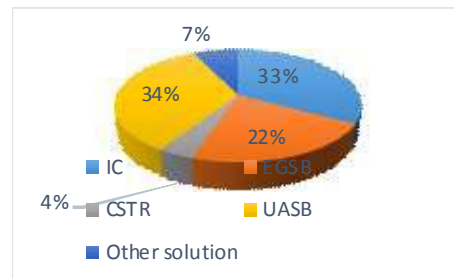

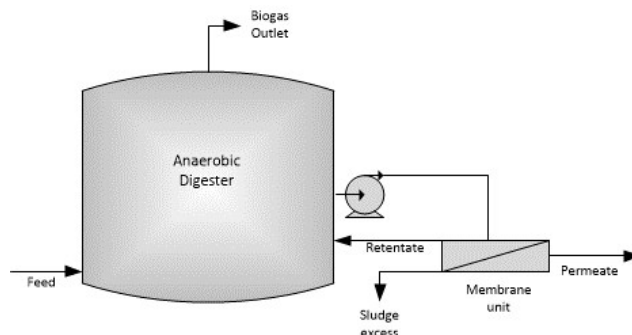*Figure 3 Anaerobic reactor technologies as monitored in the period 2002-2007 (610 total plants analyzed)*[15]

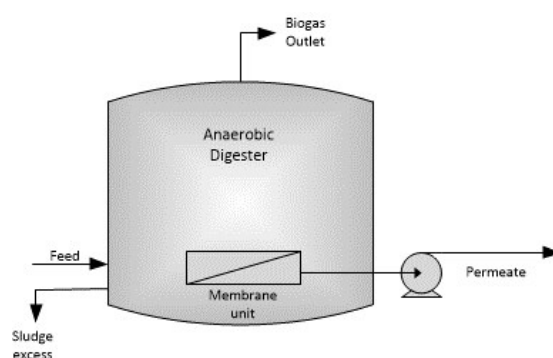*Figure 4 A typical arrangement for anaerobic membrane reactors*

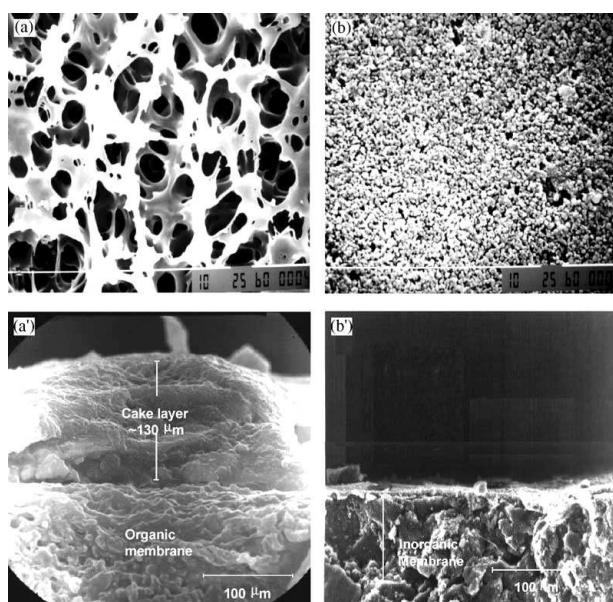*Figure 5 A typical arrangement for a submerged anaerobic membrane reactor*

Figure 6 SEM analysis of the surface of the organic (a) and inorganic (b) membrane before use; cross sectional view of the organic (a') and inorganic (b') membrane after 70 days of use [62]
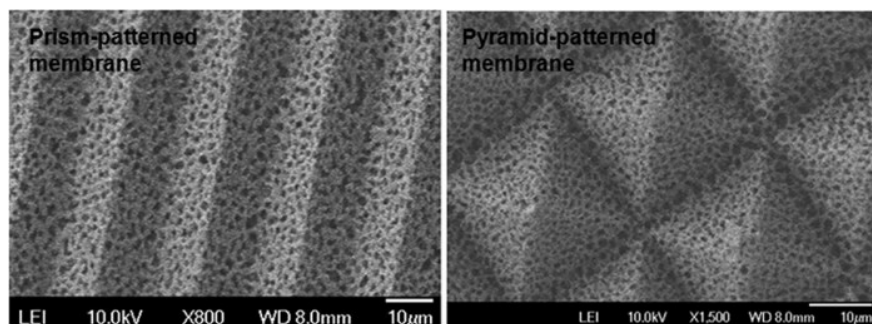
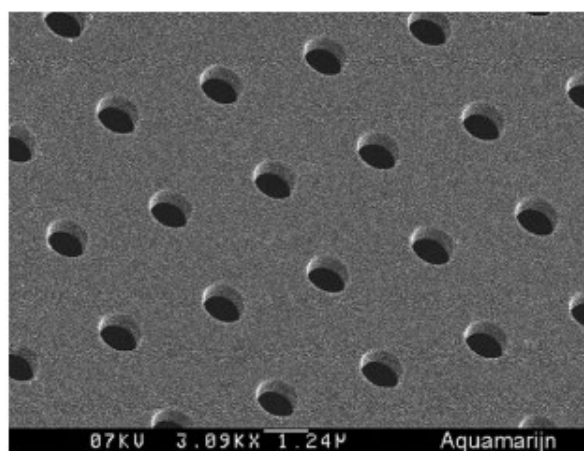*Figure 7 SEM images of two different patterned membranes [150]*
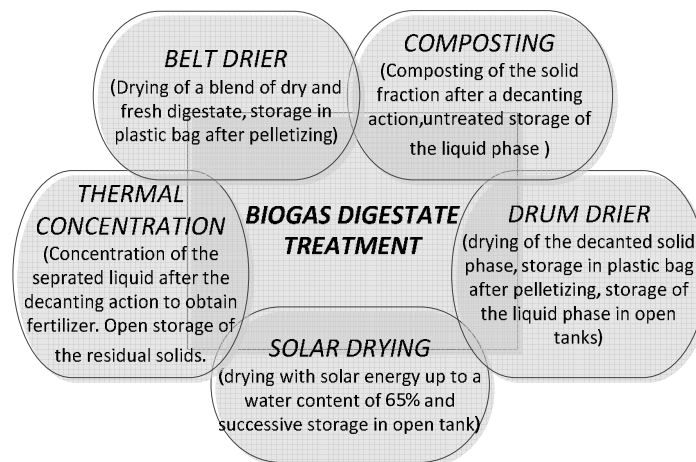

Figure 8 SEM image of a microsieve membrane [153]

Figure 9 Conventional treatments of anaerobic digestate [155]

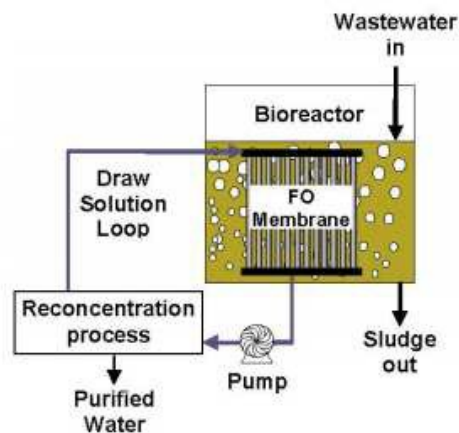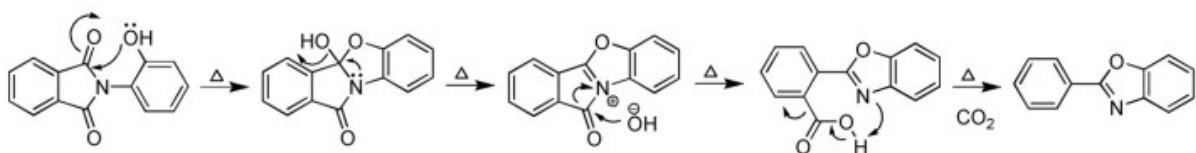*Figure 10 A schematic representation of an OsMBR* [183]

Figure 11 A proposed mechanism for thermal rearrangement of hydroxyl-containing polyimides
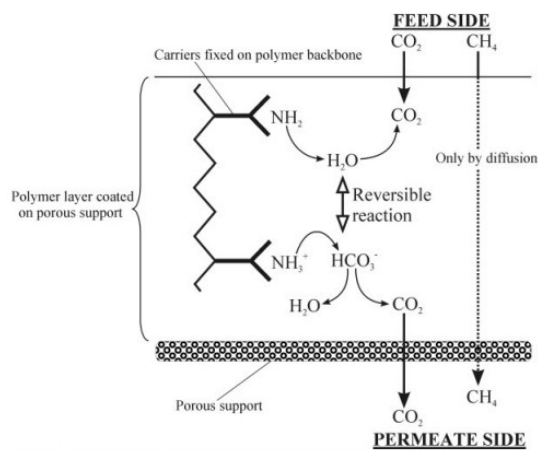

Figure 12 The transport mechanism through a facilitated transport membrane [233]
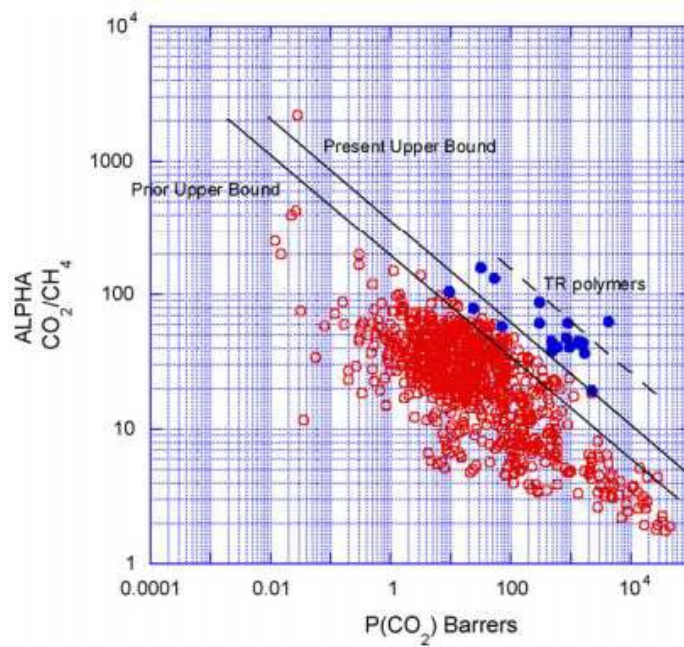
Figure 13 Correlation of selectivity and permeability for polymeric membranes [238]

Tables

Table 1 SRT values for the design of a mixed digester [6]

Operating temperature [°C]	Minimum SRT [d]	Maximum SRT [d]
18	11	28
24	8	20
30	6	14
35	4	10
40	4	10

Table 2 A possible classification of anaerobic digestion processes according to solid content (the reported ranges were deducted taking into account the variability presents in literature)

Solid Content [%]	Wet anaerobic digestion	Semi-dry anaerobic digestion	Dry anaerobic digestion
	7:15	15:20	25:40

Table 3 A brief review of the scientific production about AnMBR

Type of wastewater	Type of membrane	Volume [L]	Efficiency	Reference
Raw wastewater from alcohol fermentation	Tubular ceramic membrane (0.45 μm)	5	COD removal=90 to 95% (OLR=2-7 kg_{COD}/m^3 d)	[60]
Synthetic wastewater (Glucose=10000 mg/L)	Polypropylene membranes modified by ozone treatment (0.2 μm)	4.5	-	[61]
Raw wastewater from alcohol fermentation	Hydrophobic polypropylene membrane (0.2 μm), zirconia skinned inorganic membrane (0.14 μm)	5	COD removal>90% (OLR=3-3.5 kg_{COD}/m^3 d)	[62]
Artificial wastewater; slaughterhouse effluent; Sauerkraut brine	Ceramic cross-flow membrane (0.2 μm)	7	COD removal>97(OLR=6-8 g_{COD}/L d)	[63]
Wastewater from food processing	Polyethersulfone ultrafiltration membranes (20000 to 70000 Da)	0.5	COD removal>90% (OLR<2 kg_{COD}/m^3 d) COD removal>80% (OLR=2-4.5 kg_{COD}/m^3 d)	[64]
Sewage sludge	Polysulphone membrane (0.1 μm)	-	COD removal=98.8% (OLR=0.1 kg_{COD}/m^3 d)	[65]
Synthetic substrate (460±20 mg $_{COD}$/L)	Polyethylene membranes (0.4 μm)	3	COD removal=90% (HRT=3 h)	[56] [66] [67]
Synthetic wastewater	Polysulphone microfiltration membranes	3.7	-	[68] [69] [70] [71]

	(0.2 µm)			[72]
Raw domestic wastewater	Stork WFFX 0281 (100 kDa)	50	COD removal>76% (OLR=0.8-1.2 g_{COD}/L d)	[73]
Cheese whey	Ceramic membrane (0.2 µm)	27	COD removal=98.5% (OLR=19.78 g_{COD}/l d)	[74]
Swine manure	Polyethersulfone membrane (20000 Da)	6	COD removal>86% (1-2 g_{VS}/Ld)	[75]
Municipial wastewater	Stork WFFX 0281 membrane (100000 Da)	50	COD removal>88% (OLR=0.23-2 g_{COD}/L d)	[76]
Landfill leachate	Capillary ultrafiltration module (polymeric membrane 0.1µm)	29	COD removal=90% (OLR of 2.5 kg $_{COD}$/m^3 d.	[77]
Sucrose-based synthetic feed (4 g_{COD}/L)	Polyethylene membrane (0.4 µm)	3	COD removal=98% (OLR=16 g_{COD}/L d)	[78]
Synthetic saline sewage (465±20 mg $_{COD}$/L)	Polyethylene membrane (0.4 µm)	3	DOC removal=99% (with 35 g NaCL/L)	[79]
Kraft evaporator condensate (COD:N:P=100:2.6:1)	Polyvinylidene fluoride membrane (70000 Da)	10	COD removal=97-99% (OLR=3.1 kg_{COD}/m^3 d in thermophilic condition, OLR=12.2 kg_{COD}/m^3 d in mesophilic condition)	[80] [81]
Synthetic substrate (10-17 g_{COD}/L)	Ceramic Al_2O_3 membrane (0.2 µm)	2	-	[82]
Synthetic sewage	Polyvinylidene fluoride ultrafiltration membrane coated with 1% PEBAX 1657 (100000 Da)	10	COD removal>96% (OLR=5 kg_{COD}/m^3 d)	[83]
Synthetic municipal wastewater	Poly-tetrafluoroethylene membrane (1 µm)	4	COD removal>95% at 25 °C, COD removal>85% at 15 °C (OLR=1 kg_{COD}/m^3 d)	[84]
Dilute municipal wastewater	Membrane filter by PCI Membrane Systems, Inc., Milford, OH (0.1 µm)	10	COD removal=64% (OLR=0.03-0.11 kg_{COD}/m^3 d)	[85]
Sucrose	Flat sheet Kubota membrane (0.4 µm)	11	-	[86]
Municipal wastewater	Polyvinylidene fluoride membrane (140000 Da)	80	COD removal=90% (0.26 L_{CH4}/$g_{COD-removal}$)	[87]
Municipal wastewater (COD= 630 ± 82 mg/L)	Polyether sulfone ultra-filtration membrane (38 nm)	350	COD removal=90% (OLR= 0.6-1.1 g_{COD}/L d)	[88]
Suspended marine microalga *P. Tricornutum*	Kubota microfiltration membrane module (0.4 µm)	8	COD removal=52.2 % (OLR=1- 6 g_{COD}/L d)	[89]
Ethanol thin stillage	Polyvinilydene fluoride membrane (0.08 µm)	12000	COD removal=98 % (OLR=4.5- 7 kg_{COD}/m^3 d)	[90]
Synthetic wastewater (cheese whey:sucrose=1:1)	Kubota microfiltration membrane module (0.4 µm)	11	COD removal=94 % (OLR=1.5- 10 g_{COD}/L d) COD removal=33 % (OLR=1.5- 10 g_{COD}/L d)	[91]
Domestic wastewater	Polyethersulfone membranes (0.2 µm)	7	COD removal= 92 ± 5% (OLR=170-660 mg_{COD}/Ld)	[92]
Sludge and coffee grounds (85:15)	Chlorinated polyethylene (0.2 µm)	15	COD removal= 44.5-66.8% (OLR=2.2-23.6 kg_{COD}/m^3 d)	[93]
Synthetic wastewater	Cellulose triacetate membrane	3.6	TOC removal>96%	[55]

Table 4 Main characteristics of the typical wastewaters of textile industry [101]

Process	COD [g/L]	BOD [g/L]	TS [g/L]	TDS [g/L]	pH [-]	Colour (ADMI)	Water usage [L/kg]
Desizing	4.6-5.9	1.7-5.2	16.0-32.0	-	-	-	3-9
Scouring	8.0	0.1-2.9	7.6-17.4	-	10-13	694	26-43
Bleaching	6.7-13.5	0.1-1.7	2.3-14.4	4.8-19.5	8.5-9.6	153	3-124
Mercerizing	1.6	0.05-0.1	0.6-1.9	4.3-4.6	5.5-9.5	-	232-308
Dyeing	1.1-4.6	0.01-1.8	0.5-14.1	0.05	5-10	1450-4750	8-300

Table 5 European limitation for potable water (directive 98/83/EC)

Biological parameters	
Parameter	**Value**
Escherichia coli (E. coli)	0 in 250 mL
Enterococci	0 in 250 mL
Pseudomonas aeruginosa	0 in 250 mL
Colony count 22 °C	100 in 1 mL
Colony count 37 °C	20 in 1 mL
Chemical parameters	
Parameter	**Limit concentration**
Nitrate	50 mg/L
Nitrite	0.50 mg/L
Arsenic	10 µg/L
Benzene	1.0 µg/L
Nickel	20 µg/L
Chromium	50 µg/L
Mercury	1.0 µg/L
Cadmium	5.0 µg/L
Hydrogen ions	6.5-9.5 pH unit

Table 6 Carbon dioxide solubility in water expressed as weight of CO_2 in 100 weights of H_2O [192]

Pressure [atm]	Temperature [°C]					
	18	25	35	50	75	100
25	3.86	-	2.56	1.92	1.35	1.06
50	6.33	5.38	4.39	3.41	2.49	2.01
75	6.69	6.17	5.51	4.45	3.37	2.82
100	6.72	6.28	5.76	5.07	4.07	3.49

Table 7 Boiling temperature of the compounds that can be present in biogas [192]

Compounds	Boiling temperature [°C]		
	p=1 atm	p=10 atm	p=20 atm
Hydrogen	-252.5	-241.8	-
Nitrogen	-195.8	-169.8	-157.6
Carbon monoxide	-191.3	-161.0	-149.7
Oxygen	-183.1	-153.2	-140.0
Methane	-161.5	-124.8	-108.5
Carbon dioxide	-78.2	-39.5	-18.9
Hydrogen sulfide	-60.4	-0.4	25.5
Ammonia	-33.6	25.7	50.1
Water	100	180.5	213.1

Table 8 Main features of the commonly used zeolites for mixed matrix membrane[13,245]

Type of zeolite	Pore size [nm]	Si/Al	Pore volume [cm^3/g]
3A	0.29	1	0.197
4A	0.4	1	0.2
5A	0.4-0.5	1	0.28
13X	0.74	1.2	0.36
KY	0.74	2.6	0.47
Silicalite 1	0.53-0.56	>500	0.18
SSZ-13	0.38	11.8	-