Membrane Bioreactor (MBR) as an Advanced Wastewater Treatment Technology

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Abstract The development and application of a membrane bioreactor (MBR) for full-scale municipal wastewater treatment is the most important recent technological advance in terms of biological wastewater treatment. The MBR is a suspended growth-activated sludge system that utilizes microporous membranes for solid/liquid separation instead of secondary clarifiers. It represents a decisive step forward concerning effluent quality by

delivering a hygienically pure effluent and by exhibiting a very high operational reliability. Advanced MBR wastewater treatment technology is being successfully applied at an ever-increasing number of locations around the world.

In this chapter, the authors have covered several aspects of MBR, with an exhaustive overview of its operational and biological performance. Different configurations and hydraulics of MBR are presented, with attention given to the fouling phenomenon and strategies for reducing it. Also, the high quality of MBR effluent is discussed, whereas in comparison with CAS removals of organic matter, ammonia, phosphorus, solids, bacteria and viruses are significantly enhanced. Emphasis has been given to the improved capability of MBR to remove organic contaminants present at trace concentration levels ($ng\,L^{-1}$, $\mu g\,L^{-1}$ and $mg\,L^{-1}$), which to the authors' knowledge represents a first attempt to summarize the published literature on this subject. Finally, advantages and disadvantages of MBR over CAS are concerned. In conclusion, MBR represents an efficient and cost-effective process that copes excellently with the growing needs for transforming wastewater into clean water that can be returned to the hydrological cycle without detrimental effects.

Keywords Biological performance · Membrane bioreactor (MBR) · Trace organic pollutants · Virus removal · Wastewater treatment

Abbreviations

ABT	Aminobenzothiazole
AEO	Alcohol ethoxylates
AHTN	6-acetyl-1,1,2,4,4,7-hexamethyltetraline
AOB	Ammonium oxidizing bacteria
APs	Alkylphenols
APEOs	Alkylphenol ethoxylates
BOD	Biological oxygen demand
BPA	Bisphenol-A
BT	Benzothiazole
CAS	Conventional activated sludge
COD	Chemical oxygen demand
2,4-D	2,4-dichlorobenzoic acid
DBPs	Disinfection by-products
DEET	Meta-N,N-diethyl toluamide
DO	Dissolved oxygen
2,4-DP	2-(2,4-dichlorophenoxy) propionic acid
E1	Estrone
E2	17β-estradiol
EBPR	Enhanced biological phosphorus removal
ED	Electrodialysis
EDCs	Endocrine disrupting compounds
EDI	Electro deionization
EDTA	Ethylenediamino tetraacetate
EE2	17α-ethinylestradiole
EPS	Extracellular polymeric substances
F/M	Food-to-microorganism ratio
FS	Flat sheet

GAOs	Glycogen accumulating organisms
HF	Hollow fiber
HHCB	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyran
HRT	Hydraulic retention time
LAS	Linear alkylbenzene sulphonates
MBR	Membrane bioreactor
MBT	Mercaptobenzothiazole
MCPA	(4-chloro-2-methylphenoxy)-acetic acid
MCPP	Mecoprop
MF	Microfiltration
MLSS	Mixed-liquor suspended solids
MLVSS	Mixed-liquor volatile suspended solids
MTBT	Methylthiobenzothiazole
MWCO	Molecular weight cut-off
NF	Nanofiltration
NOB	Nitrate oxidizing bacteria
NP	Nonylphenol
$NPEC_x$	($x = 1, 2$) nonylphenol mono, di-carboxylates
$NPEO_x$	($x = 1, 2, 3$) nonylphenol mono, di, tri-ethoxylates
NSA_x	($x = 1, 2$) naphthalene mono, di-sulfonates
OHBT	Hydroxybenzothiazole
OP	Octylphenol
OPEOs	Octylphenol ethoxylates
P^3	persistent polar pollutants
PAC	Powdered activated carbon
PAHs	Polycyclic aromatic hydrocarbons
PAN	Polyacrylonitrile
PAOs	Phosphate accumulating microorganisms
PE	Polyethylene
PES	Polyethylsulphone
PhACs	Pharmaceutically active compounds
pI	Iso-electric point
PP	Polypropylene
PVDF	Polyvinylidene difluoride
RO	Reverse osmosis
SMP	Soluble microbial products
SPC	Sulfophenyl carboxylates
SRT	Solids retention time
SS	Suspended solids
SVI	Sludge volume index
TC	Total Coliform
TCEP	Tris-(2-chloroethyl) phosphate
TCPP	Tris-(chloropropyl) phosphate
TKN	Total Kjeldahl nitrogen
TN	Total nitrogen
TSS	Total suspended solids
UF	Ultrafiltration
VSS	Volatile suspended solids
WWTP	Wastewater treatment plant

1
Introduction

Membrane bioreactor (MBR) technology, which combines biological-activated sludge process and membrane filtration has became more popular, abundant, and accepted in recent years for the treatment of many types of wastewaters, whereas the conventional activated sludge (CAS) process cannot cope with either composition of wastewater or fluctuations of wastewater flow rate. MBR technology is also used in cases where demand on the quality of effluent exceeds the capability of CAS. Although MBR capital and operational costs exceed the costs of conventional process, it seems that the upgrade of conventional process occurs even in cases when conventional treatment works well. It can be related with increase of water price and need for water reuse as well as with more stringent regulations on the effluent quality. Along with better understanding of emerging contaminants in wastewater, their biodegradability, and with their inclusion in new regulations, MBR may become a necessary upgrade of existing technology in order to fulfill the legal requirements in wastewater treatment plants (WWTPs).

The idea for coupling the activated sludge process and membrane separation was firstly reported by research conducted at Rensselaer Polytechnic Institute, Troy, New York, and Dorr-Oliver, Inc. Milford, Connecticut, US [1, 2]. The first MBR installation (Membrane Sewage System-MST) was made by Dorr-Oliver, Inc., with flat sheet ultrafiltration plate and frame membrane. It did not gain much interest in North America but it had considerable success in Japan in the 1970s and 1980s. Before the 1990s, most of the installed MBRs were used for industrial water treatment. With the development of submerged membranes, firstly introduced by Yamamoto et al. [3], the number of MBRs treating municipal wastewater increased while the MBR market is currently experiencing accelerated growth. The global MBR market doubled over the last 5-year period and in 2005 it has reached a market value of $217 million in 2005 with a projection for the year 2010 of $360 million [4].

The MBR process can be configured in many different ways depending on project-specific nutrient removal objectives. Anoxic zones before or after the aerobic treatment may be used for denitrification, depending on the effluent nitrate and total nitrogen requirements. Anaerobic zones may be used to achieve enhanced biological phosphorus removal in any of its possible configurations.

2
Membrane Classification

The membrane process is a very important separation process in water and wastewater technology, which becomes increasingly competitive and is supe-

rior to the traditional water technology with proven performance and process economics. The most widely applied membrane separation processes are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), electrodialysis (ED) and electro deionization (EDI), whereas the first four processes produce permeate and concentrate. The separation ranges are as follows: 100 to 1000 nm for MF, 5 to 100 nm for UF, 1 to 5 nm for NF, and 0.1 to 1 nm for RO. Firstly, application of membrane-based technologies in wastewater treatment was focused on tertiary treatment of secondary effluent, so as to obtain a high-quality final effluent that can be reused for different purposes. However, over the past 10 years, MBRs have emerged as an effective secondary treatment technology, whereas membranes applied are usually in the range of those of MF and UF.

Membranes are usually made from different plastic and ceramic materials, but metallic membranes also exist. The most widely used materials are celluloses, polyamides, polysulphone, charged polysulphone and other polymeric materials such as polyacrylonitrile (PAN), polyvinylidene difluoride (PVDF), polyethylsulphone (PES), polyethylene (PE), and polypropylene (PP). All of these polymeric materials have a desirable chemical and physical resistance. They are also hydrophobic, and it is known that hydrophobic membranes are more prone to fouling than hydrophilic ones due to the fact that most interactions between the membrane and the foulants are of hydrophobic nature [5, 6]. All commercially available membranes are therefore modified by chemical oxidation, organic chemical reaction, plasma treatment, or by grafting to achieve more hydrophilic surface. This modification process usually differs one membrane from another together with the method of fabrication of the membrane module.

3
Types of Membrane Bioreactor Configurations

Membrane separation is carried out either by pressure-driven filtration in side-stream MBRs (Fig. 1) or with vacuum-driven membranes immersed directly into the bioreactor, which operates in dead-end mode (Fig. 2) in submerged MBRs. The more common MBR configuration for wastewater treatment is the latter one, with immersed membranes, although a side-stream configuration is also possible, with wastewater pumped through the membrane module and then returned to the bioreactor.

The energy consumption required for filtration in submerged MBR is significantly lower (Table 1). Both configurations need a shear over the membrane surface to prevent membrane fouling with the constituents of mixed liquor. Side-stream MBRs provide this shear through pumping, as with most other membrane processes, whereas immersed processes employ aeration in the bioreactor to provide it. Shear enhancement is critical in promot-
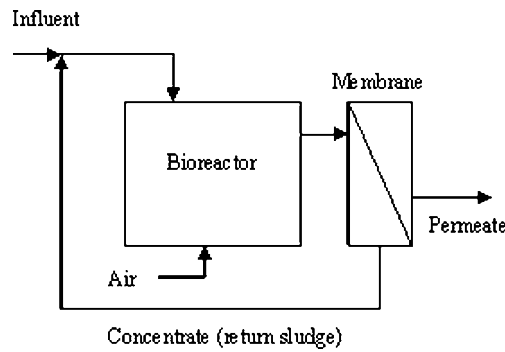
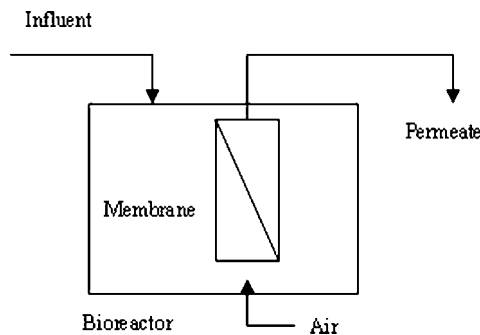**Fig. 1** Side-stream MBR with external pressure-driven membrane filtration

Fig. 2 Submerged MBR with internal vacuum-driven membrane filtration

Table 1 Comparison of filtration conditions for tubular and immersed MBRs [8]

	Side-stream tubular membrane	Submerged membrane
Manufacturer	Zenon	Zenon
Model	Permaflow Z-8	ZeeWeed ZW-500
Surface area [m^2]	2	46
Permeate flux [$L\,m^{-2}\,h^{-1}$]	50–100	20–50
Pressure [bar]	4	0,2–0,5
Air flow rate [$m^3\,h^{-1}$]	–	40
Energy for filtration [$kWh\,m^{-3}$]	4–12	0.3–0.6

ing permeate flux and suppressing membrane fouling, but generating shear also demands energy, which is probably the reason for submerged configuration predominance. Also, in side-stream MBR module fouling is more pronounced, due to its higher permeate flux. Pumping of activated sludge induces shear stress to microbial flocs, causing them to break-up, which leads to a decrease in particle size and releasing of foulant material from the flocs [7].

This may significantly promote the membrane fouling rate. In Table 1 filtration conditions are presented for tubular and immersed MBRs [8].

The configurations of MBR are based on either planar or cylindrical geometry. There are five principal membrane configurations currently employed in practice:

1. Hollow fiber (HF)
2. Spiral-wound
3. Plate-and-frame (i.e., flat sheet (FS))
4. Pleated filter cartridge
5. Tubular.

In the HF module, large amounts of HF membranes make a bundle, and the ends of the fibers are sealed in epoxy block connected with the outside of the housing (Fig. 3). The water can flow from the inside to the outside of the membrane, and also from the outside to the inside, which is produced differently by different manufacturers. These membranes can work under pressure and under vacuum (Fig. 4).

The spiral-wound configuration is mostly used for the NF and RO process. The membranes are wound around the perforated tube through which permeate goes out (Fig. 5). The spiral-wound modules are manufactured in standard dimensions by all major manufacturers, which makes their installation easier and membrane production less costly. Many membrane modules can be installed together in series or parallel in plants with high capacity (Fig. 6).

Plate-and-frame membrane modules comprise of FS membranes with separators and/or support membranes. The pieces of these sheets are clamped onto a plate. The water flows across the membrane and permeate is being collected through pipes emerging from the interior of the membrane module in a process that operates under vacuum (Fig. 7).

There are also membrane configurations such as plated filter cartridge and tubular module, but they are not so widely used as the other three mod-
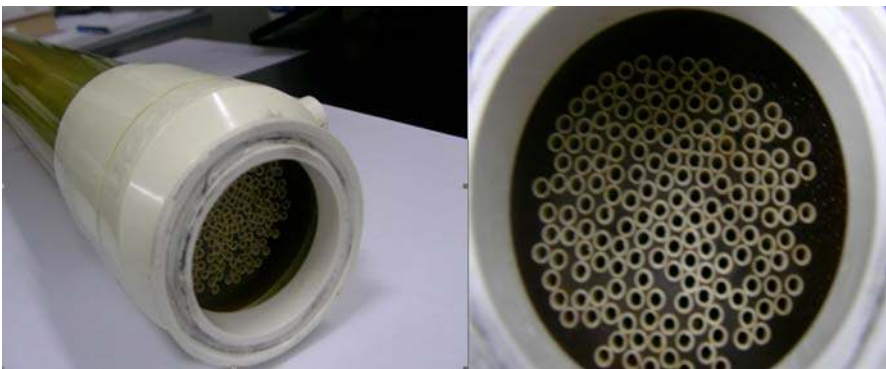

Fig. 3 Hollow-fiber (HF) membrane module

Fig. 4 Hollow-fiber (HF) immersed membrane module (Zenon, Canada) filtrating activated sludge under vacuum

Fig. 5 Spiral-wound membrane part

ules. Typically, tubular membranes are encased in pressure vessels and mixed liquor is pumped to them and they are predominantly used for side-stream configurations. HF and FS modules are mostly immersed directly in mixed liquor with permeate drawn through the membranes using vacuum pumps. In the case of HF membranes, use of 0.8 mm to 1.5 mm fine screen upstream of membranes is recommended to protect the membranes from hair
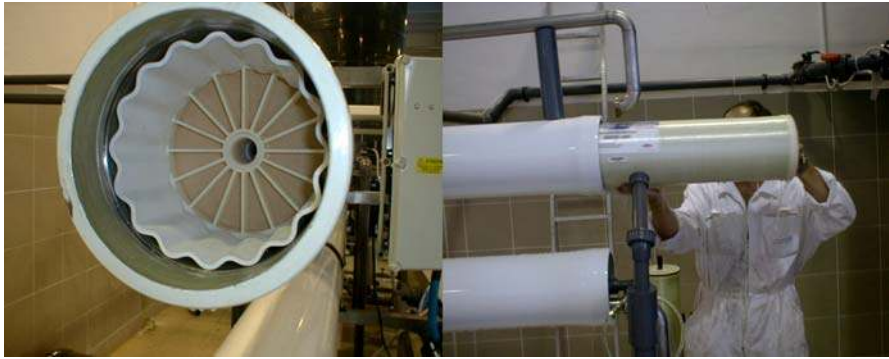
Fig. 6 Connection of the spiral-wound elements

Fig. 7 Plate-and-frame immersed membrane module (Kubota, Japan)

and other stringy materials that can result in excessive cleaning frequencies. A fine screen of 2–3 mm is usually employed for FS membrane systems.

4
Hydraulics of Membrane Bioreactor

4.1
General

During MBR wastewater treatment, solid–liquid separation is achieved by MF or UF membranes. The basic principle is that the feed water passes over the membrane surface and the product is called permeate, whereas the re-
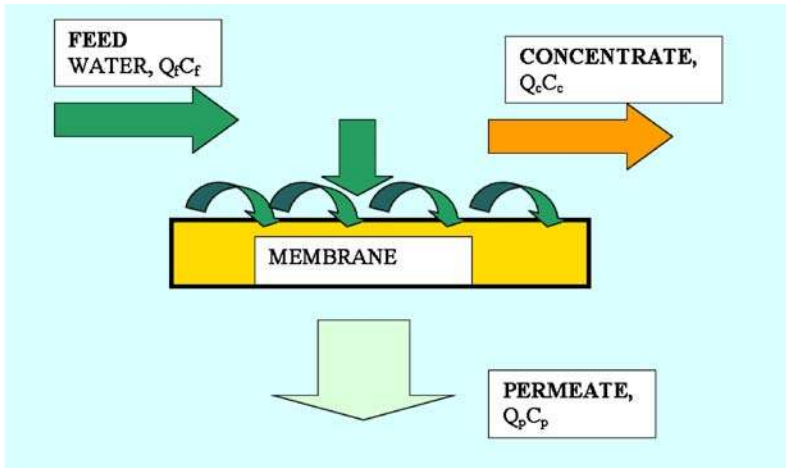
Fig. 8 Basic principle of membrane filtration

jected constituents form concentrate or retentate (Fig. 8). A membrane is simply a two-dimensional material used to separate components of fluids usually on the basis of their relative size or electrical charge. The capability of a membrane to allow transport of only specific compounds is called semi-permeability. This is a physical process, where separated components remain chemically unchanged. Components that pass through membrane pores are called permeate, while rejected ones form concentrate or retentate.

Mass balance of the solute in the process can be presented by the equation:

$$Q_f c_f = Q_p c_p + Q_c c_c \,, \tag{1}$$

where Q_f – feed flow rate; c_f – solute concentration in feed flow; Q_p – permeate flow rate; c_p – solute concentration in permeate; Q_c – solute concentration in concentrate; c_c – solute concentration in concentrate.

Membrane rejection of solutes can be calculated according to the following equation:

$$R = \frac{c_f - c_p}{c_f} \,, \tag{2}$$

where C_f represents concentration of solute in feed flow and C_p represents its concentration in permeate.

The fraction of feed flow converted to permeate is called yield, recovery or water recovery (S). Water recovery of the membrane process is given with the equation:

$$Y = \frac{Q_p}{Q_f} \,, \tag{3}$$

where Q_p is the permeate flow and Q_f is the feed flow.

Recovery is normally close to 100% for dead-end filtration, while it varies significantly for cross-flow filtration depending on the nature and design of membrane process. Permeate flux (usually denoted as J) is the volume of water passed through a unit area of membrane per unit of time and it is often normalized to a standard temperature. The common unit for J is usually $L\,m^{-2}\,day^{-1}$, and most of the available data for MBR is given in that manner rather than in SI units. MBR membranes generally operate at fluxes between 10 and $100\,L\,m^{-2}\,h^{-1}$. The flux is related to its driving force which is transmembrane pressure (TMP or ΔP) while the membrane performance can be estimated from the membrane permeability (K), which is calculated as permeate flux per unit of TMP and is usually given as $L\,m^{-2}\,h^{-1}\,bar^{-1}$.

4.2
Membrane Fouling

A decrease in the permeate flux or increase in TMP during a membrane process is generally understood by the term "fouling". Fouling occurs as a consequence of interactions between the membrane and the mixed liquor, and is one of the principal limitations of the MBR process. There has been done a lot of research on this subject [9], so it is of interest to describe the fouling in more details. Fouling of membranes in MBRs is a very complex phenomenon with diverse relationships among its causes, and it is very difficult to localize and define membrane fouling clearly. The main causes of membrane fouling are:

1. Adsorption of macromolecular and colloidal matter
2. Growth of biofilms on the membrane surface
3. Precipitation of inorganic matter
4. Aging of the membrane

As a measure of fouling, resistance (R), which is inversely related to K, is often used. R is given by:

$$R = \frac{\Delta P}{\eta J} \,, \tag{4}$$

where η stands for permeate viscosity in ($kg\,m^{-1}\,s^{-2}$). This total filtration resistance consists of a number of components, which can be divided as: membrane resistance, resistance of the fouling layer on the membrane surface, and resistance offered by the membrane-solution interfacial region. Membrane resistance is a function of characteristics of membrane material such as thickness and pore size, and it determines the flux through the membrane for filtration of one-component liquid, i.e., clean water. For MBRs, membrane resistance is often given as its inverse value called "clean water permeability", which is normally within the range of a few hundred to a few thousand $L\,m^{-2}\,h^{-1}\,bar^{-1}$. The resistance of the fouling layer is associated with the fil-

tration mechanism, which is dependent on the membrane characteristics and characteristics of filtered solids, while membrane-solution interfacial region resistance is associated with concentration polarization. Concentration polarization is a phenomenon of solute tendency to accumulate within the boundary liquid layer of near-stagnant fluid adjacent to membrane surface. Since liquid velocity within this layer is close to zero, the only mode of mass transport is diffusion, which is significantly slower then convective transport in the bulk solution. As a consequence, resistance to filtration occurs. The thickness of the boundary layer is dependent on system's hydrodynamics and can be decreased by promoting the turbulence of liquid flow.
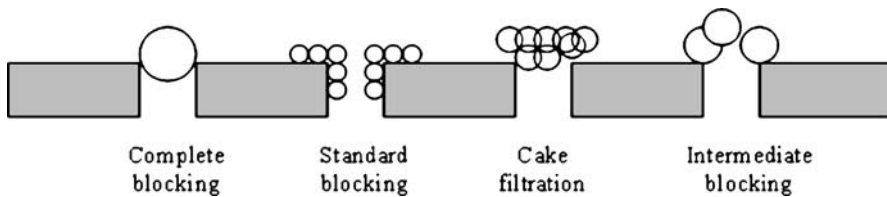

| Complete | Standard | Cake | Intermediate |
| blocking | blocking | filtration | blocking |

Fig. 9 Fouling mechanisms

According to recognized mechanisms (Fig. 9), the fouling on the membrane occurs as:

1. Complete blocking caused by occlusion of pores by the particles with no particle superimposition
2. Intermediate blocking caused by occlusion of pores by particles with particle superimposition
3. Standard blocking where particles smaller than the membrane pore size deposit onto the pore walls thus reducing the pore size
4. Cake filtration where particles larger than the membrane pore size deposit onto the membrane surface

Many authors tried to divide total filtration resistance (R_t) on three components [5, 10–13] (Eq. 5):

$$R_t = R_m + R_c + R_f , \tag{5}$$

where R_m is the membrane resistance, R_c is the cake resistance and R_f is the fouling resistance. It is assumed that fouling consists of two separate processes, one being cake fouling caused by suspended particles that form a cake layer on the membrane surface, and the other type associated with adsorption of smaller colloid and soluble matter on the membrane surface and in the membrane pores. To therefore determine the divided resistances, the measurement of R_m with clean water and R_t with activated sludge is done. Then another subsequent clean water filtration with fouled membrane is performed, which gives $R_m + R_f$ value and the R_c can then be calculated by

subtraction. This model neglects the coupling of synergistic effects on fouling, which may occur among different activated sludge components.

Similar to the above approach, in an attempt to make a distinction among different constituents of activated sludge, relative contribution of biomass fractions on fouling has been intensively investigated by fractionation of activated sludge into suspended solids, colloids, and solutes. This fractionation is usually performed by centrifugation of biomass and subsequent filtration of the supernatant through 0.45 μm filter for separation of colloid from soluble matter. Again, this approach does not take into account all the interactions among fractions, but it represents an interesting approach to clarification of the fouling phenomenon. The results of these studies, recently reviewed by Judd [4], vary significantly in assessment of the relative contributions of components to fouling. Despite variations in the published results, it is generally accepted that fouling caused by suspended solids is less than that of supernatant. Moreover, Chang et al. [13] reported a faster fouling rate with the effluent of biological process than with the activated sludge and concluded that suspended solids can act as a dynamic layer over the membrane surface, which can slow the penetration of soluble fouling species that cause fouling. Ng et al. [14] also reported greater filtration resistance from mixed-liquor supernatant than from the biomass. With regards to the fouling mechanism, it is generally assumed that soluble and colloid materials are responsible for pore blocking, while suspended solids contribute mainly to cake layer resistance. Again, one has to be aware of the fact that biomass itself is responsible for a composition of soluble and colloid material in the liquid phase, and that composition of supernatant is a function of the physiological state of the suspended phase, i.e., biomass.

Among the constituents of the supernatant, extracellular polymeric substances (EPS) have gained a lot of attention as possible important foulants in MBR [5, 15, 16]. EPS is a general term for various types of macromolecules found outside the cell surface, most commonly carbohydrates and proteins. They are normally produced by microorganisms as a construction material necessary for the development of microbial aggregates, such as biofilms or flocs, or used as a protective barrier around the bacteria. Apart from the EPS that are bound in microbial flocs, EPS can be found in the water phase as free EPS. Substances in this category originate from the break up of flocs and cell lyses, or they can be introduced by the influent. Another group of substances overlapping the EPS is called "soluble microbial products" (SMP). This group contains a wider range of substances that can also be defined as soluble EPS. The presence of EPS is desirable in CAS because it helps formation of microbial flocs and makes them easier to settle, but due to its heterogeneous nature EPS can form hydrated gel which can act as a barrier to permeate flow in MBR. Little is known about the circumstances that influence EPS production and their possible release to the water phase. Many operating parameters including substrate composition and organic loading

rate appear to affect EPS, with solid retention time (SRT) probably being the most significant factor [17]. Generally taken, the EPS level may be lower when fewer disturbances, such as starvation, oxygen or essential nutrient depletion, are introduced to the biomass. Rosenberger et al. [18] found a correlation between polysaccharide concentration in the supernatant of mixed liquor and high fouling rates of submerged membrane. The concentration of polysaccharides of microbiological origin was influenced by temperature and stress situations to microorganisms.

Fouling can be divided from the practical point of view on:

1. Reversible fouling that can be removed from the membrane by physical cleaning
2. Irreversible fouling removed by chemical cleaning
3. Irrecoverable fouling that cannot be removed by any cleaning

Physical cleaning in MBRs is normally achieved either by back-flushing or by relaxation (stopping the permeate flow and continuing to scour the membrane with air bubbles). Physical cleaning is a simple and short method (usually lasting less then 2 min) of fouling suppression which demands no chemicals and generally it is less likely that it will affect the membrane material. The latest published data [4] on the cleaning regime of full-scale plants suggests that presently most of MBR facilities use relaxation rather than back-flushing. However, by means of physical cleaning it is not possible to remove all the material deposited on the membrane. Chemical cleaning is a more effective method, which is able to remove more strongly the adsorbed deposits. Chemical cleaning is carried out mostly with sodium hypochlorite and sodium hydroxide for organic deposits removal, or with acidic solutions for removal of lime or other inorganic deposits. Cleaning is performed by soaking the membrane in the cleaning solution or by adding the cleaning agent into the back flush water. Most MBRs employ chemical maintenance cleaning on a weekly basis, which lasts 30–60 min, and recovery cleaning when filtration is no longer sustainable, which occurs once or twice a year. Deposits that cannot be removed by available methods of cleaning is called "irrecoverable fouling". This fouling builds up over the years of operation and eventually determines the membrane life-time. Development of the fouling given as pressure transient for these three types of fouling for the continuous operation are presented on Fig. 10.

MBRs are normally operated under a constant flux. Since the fouling rate increases roughly and exponentially with the flux, MBR plants operate at modest fluxes and preferably below the so-called critical flux. The critical flux concept, firstly introduced by Field et al. [19], assumes that in MF/UF processes exists a flux below which a decline of permeability with time does not occur, and above which fouling occurs. In MBR operations, critical flux is normally defined as the highest flux under which a prolonged filtration with constant permeability is possible. Critical flux is often determined by the flux-
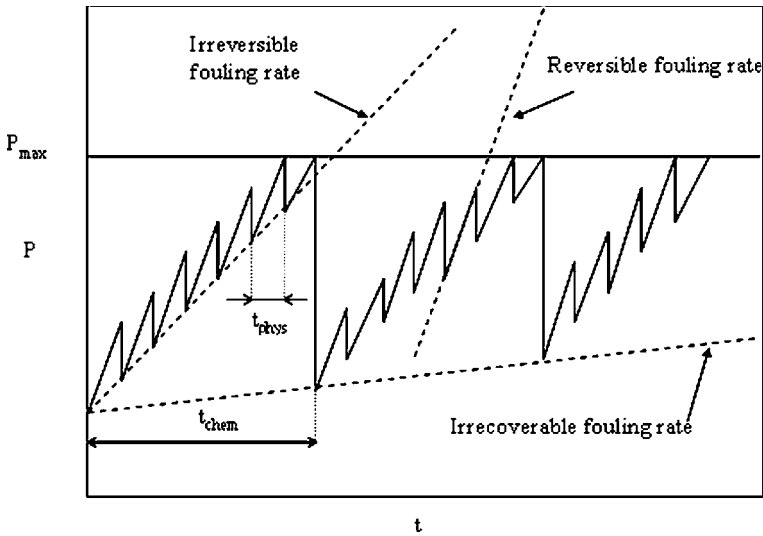
Fig. 10 Fouling rates for different types of fouling (t_{phys} – duration of physical cleaning cycle, t_{chem} – duration of chemical cleaning cycle)

step method, in which the flux is incrementally increased in number of steps with fixed duration, and the increase in TMP is recorded. It is then possible to observe the apparent flux where fouling occurs, observed as a significant TMP increase or deviation in linearity of K. The critical flux definition in its strong form demands that K obtained during filtration in sub-critical conditions equals K obtained during clean water filtration. It is possible to achieve such results when filtration media has defined characteristics regarding the size of the particles. In MBR operation, however, due to the complexity of the mixed liquor, some irreversible fouling constantly occurs, which makes it impossible to achieve the sub-critical conditions as for the strong form of the critical flux. Nevertheless, this concept is widely accepted in MBR operations as a tool that can provide useful guide value for the appropriate operating flux.

Pollice et al. [20] reviewed the sub-critical fouling phenomenon in MBR. From the reviewed data it is evident that even sub-critical operation inevitably leads to fouling. This fouling is often reported to follow a two-stage fouling pattern [21, 22], which includes slow TMP increase over a long period of time, followed by a rapid increase after some critical time period. In the work of Zhang et al. [23], this pattern is extended with an initial period of conditioning fouling. In cited work, fouling in MBR under sub-critical conditions three stages are introduced, which include:

1. Initial conditioning fouling
2. Slow fouling
3. Sudden TMP jump

During the initial conditioning fouling reported also by Ognier et al. [24] and Jiang et al. [25] interactions take place between the membrane surface and soluble components of the mixed liquor. This fouling is usually rapid (measured in hours), irreversible by nature, and occurs even for zero flux operation [23]. In the second stage, slow fouling, the membrane surface is gradually covered by biopolymers such as EPS, which changes the properties of the membrane surface and makes attachment of the microbial flocs to the membrane surface easier. Thus, biofilm growth on the membrane surface may be promoted. Over time, complete or partial pore blocking takes place. This blocking is expected to be inhomogeneous since the air and the liquid flow are distributed unevenly in MBR. With regions of membrane more fouled than others, flux locally varies, thus exceeding the critical flux in some areas of the membrane surface, which then leads to a sudden TMP jump characteristic for operation above the critical flux. The other explanation for the sudden TMP jump may be the change of properties of the fouling cake on the membrane surface due to its compression.

4.3
Methods to Control Fouling

To control the fouling that inevitably occurs in MBR operation, several key parameters can be modified. The most important strategies are concentration polarization suppression, optimization of physical and chemical cleaning protocols, pre-treatment of feed wastewater, and mixed-liquor modification. Fouling related to concentration polarization can be reduced either by promoting turbulence or by reducing flux. As mentioned above, both MBR configurations need shear over the membrane surface to prevent this type of fouling. As with most other membrane processes, side-stream MBRs provide shear through pumping, which increase cross-flow velocity, whereas immersed processes employ aeration around the membrane to provide shear stresses.

Aeration intensity over the submerged membrane surface is recognized as the key operational parameter in preventing cake formation on the membrane surface in the submerged configuration [26–28]. Membrane permeability and critical flux have been shown to increase roughly linearly with aeration rate, up to a level above which no further increase is observed. Liu et al. [29] investigated critical aeration intensities for different sludge concentration and fluxes, drawing a quantitative correlation between those parameters. However, increasing membrane aeration is normally prohibitively expensive. Since membrane aeration contributes significantly to the energy demand, much development has been focused on reducing aeration whilst maintaining membrane permeability. A development has been achieved in aeration efficiency with new jet aeration and cyclic aeration systems. It is often in practice to use different aeration systems for biological system and for

membrane fouling control, in order to insure most efficient energy use for both systems demands.

Reducing the permeate flux always reduces fouling, but at the same time this strategy demands a more installed membranes, which then contributes to the capital cost of MBR installation. In other words, flux can be maintained below the critical value to ensure stable operation with little or negligible increase in TMP, thus decreasing cleaning frequency and consumption of chemicals, or total installed membrane area can be reduced on the behalf of frequent cleaning. The latter strategy is called intermittent operation. In practice, most submerged MBRs treating municipal wastewater operate at net fluxes of 20–30 L m^{-2} h^{-1} with the relaxation period every 10 min and period-ical maintenance chemical cleaning every few months.

As mentioned above, pre-treatment of feed wastewater through screening is necessary for both HF and FS membrane modules. HF membranes have a tendency for aggregates of hair and other debris to collect at the top of the membrane elements. These aggregates usually cannot be significantly removed by back-flushing. FS modules are somewhat less prone to such clogging, but they too need a feed-water pre-treatment, though with coarser screens.

The properties of the mixed liquor that affect the fouling propensity can also be altered to minimize fouling. The production and release of EPS could be influenced by changing the biological state of biomass, usually by SRT modification as mentioned above, but it is rarely done in practice. To decrease the ESP or SMP concentration, mixed liquor is mostly modified through addition of chemicals. The use of flocculants and coagulants such as alu-minum or ferric chloride has been investigated in an attempt to minimize fouling [10, 30]. Also, the addition of adsorbent reagents such as powdered ac-tivated carbon (PAC) has been found to improve the membrane performance by decreasing the level of organic compounds with potential for membrane fouling [14, 31]. Recently, a commercial product, a cationic polymer-based compound called MPE50 manufactured by Nalco Company has been de-veloped and tested at full-scale to enhance membrane performance.

The cleaning protocol is mainly dictated by designed operational net flux as explained above. Usually the protocol suggested by the manufacturer is followed as a guideline, and the majority of the installed plants work in the sub-critical regime. However, cleaning protocol has been studied inten-sively by many researchers where the key parameters of interest are duration and frequency of the cleaning and the back-flush flux. Less frequent, longer back-flushing (600 s filtration/45 s back-flushing) has been found to be more efficient then more frequent but shorter back-flushing (200 s filtration/15 s back-flush) [25]. To optimize the back-flush duration, Smith et al. [32] de-veloped a generic control system based on TMP monitoring. Membrane re-laxation, which is the most common practice for fouling control, encourages the diffusive back-transport of foulants away from the membrane surface, which is enhanced by air scouring. Relaxation allows longer filtration periods

between chemical cleanings, and despite some reports that it may not be a feasible practice for large-scale MBRs [33], it is widely used in practice.

Although intensive research has been done on this subject, membrane fouling in MBRs needs further attention in order to understand the complex interactions among biologically active and constantly changing filtration media, hydrodynamic conditions of the filtration process, and the membrane itself.

5
Biological Performance of Membrane Bioreactor

5.1
Microbiological Aspects

In the biochemical stage of wastewater treatment, organic carbon and nutrients are removed from wastewater by microbes. These microbes live and grow enmeshed in EPS that bind them into discrete micro-colonies forming three-dimensional aggregated microbial structures called flocs. The ability of microorganisms to form flocs is vital for the activated sludge treatment of wastewater. The floc structure enables not only the adsorption of soluble substrates but also the adsorption of the colloidal matter and macromolecules additionally found in wastewaters [34, 35]. The diversity of microbial community in activated sludge is very large, containing prokaryotes (bacteria), eukaryotes (protozoa, nematodes, rotifers), and viruses. In this complex microsystem, bacteria dominate the microbial population and play a key role in the degradation process [34].

MBR technology with biochemical and sludge-separation stage integrated into one step implies a continuous generation of new sludge with the consumption of feed organic materials, while some sludge mass is decayed by endogenous respiration. Endogenous respiration involves consumption of cell-internal substrate, which leads to a loss of activity and slightly reduced biomass. Endogenous respiration implies all forms of biomass loss and energy requirements not associated with growth by considering related respiration under aerobic conditions: decay, maintenance, endogenous respiration, lyses, predation, and death. It can be both aerobic and anoxic, though under anoxic conditions it is a lot slower and especially protozoa are considerably less active under denitrifying conditions (slower predation) [36].

Endogenous respiration of a microbial community in MBR can be encouraged by very high sludge age, i.e., high sludge concentration. The energy available to microorganisms is determined by the supply of substrate. By increasing the SRT, which increases biomass concentration, it would be theoretically possible to reach a situation where the amount of energy provided equals the maintenance demand. This concept was first introduced

by Pirt [37], where maintenance energy is defined as the amount of bio-chemical energy strictly necessary for sludge endogenous respiration. Microorganisms satisfy their maintenance energy requirements in preference to producing additional biomass. Therefore, under the conditions of decreased nutrient supply, external substrate is used only for the upkeep of bacterial vial functions, while the amount of bacteria is not changed. Moreover, the higher the biomass concentration, the lower the sludge loading, i.e., food-to-microorganism (F/M) ratio (g COD gTSS^{-1} day^{-1}) becomes [38]. When the sludge loading becomes low enough, little or no excess sludge is produced [3, 39–42]. Low et al. [41] reported a sludge production reduced by 44% when increasing a biomass concentration in an MBR from 1.7 to 10.3 g L^{-1}. In various studies on applications of MBR in wastewater treatment, zero sludge production was established at different F/M ratios, obviously depending on feed compositions which determine the growth of microbial populations [43–45].

However, there is an optimal biomass concentration (i.e., SRT) for a successful operation of MBR. Biomass retention results in a slow-growing population with high sludge ages, where cell dormancy and death reduce the viability of population [46, 47]. An example of changes in sludge yield and biomass concentration with sludge age are presented on a Fig. 11 (HRT—hydraulic retention time, k-rate constant for endogenous metabolism, k_d-rate constant for biomass decay) [48].

Several explanations are suggested for this phenomenon. Since MBR sludge acts as a non-Newtonian fluid by increasing the mixed-liquor sus-pended solids (MLSS) concentration, the viscosity of sludge increases exponentially. This results in mass transfer limitations for both the oxygen and substrate, which increases aeration costs as well as causing extensive membrane fouling [49]. On the other side, at lower MLSS concentrations, more specific surface area is available for the uptake of a substrate and enzyme production, and the enzymatic activity is higher. Thus, when operating at
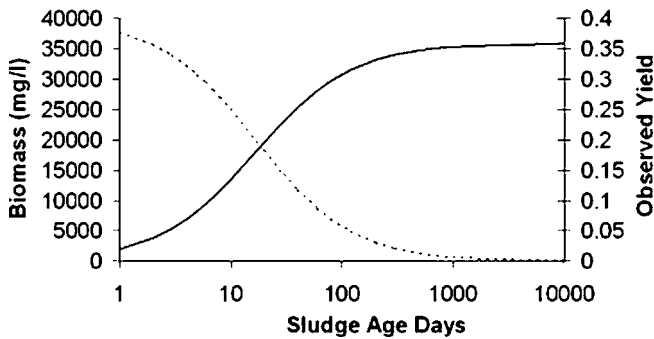

Fig. 11 Net observed yield $\cdots$ and biomass concentration as a function of sludge age in a MBR, HRT=2.7 h, Y=0.4, $k = 0.07$ d^{-1}, $k_d = 0.06$ d^{-1} [48]

low SRT response of the system in degradation of xenobiotic waste should be faster. Moreover, the chances of genetic mutation and adaptation of microorganisms to different organic loadings should be greater [46]. Horan et al. [50] also noted that at high sludge ages the solubility of substrate becomes rate-limiting.

Ng et al. [51] studied the performance of MBR at low SRT (0.25–5 days). They indicated that modification of sludge morphology, i.e., proliferation of non-flocculating microorganisms, could have a positive impact on removal performance. In addition, recent works of Wilen et al. [52] showed that the surface properties and the structure of biological flocs in activated sludge are correlated to the chemical constituents of EPS, and can be significantly influenced by the operating condition. However, some investigations have given completely opposite results. Massé et al. [53] observed a decrease in floc size at higher SRTs. This could be due to lower production of EPS, which is responsible for the formation of flocs or other cell aggregates. Moreover, growth of non-flocculating bacteria is enhanced because they are more exposed to the present substrate than when they are arranged into macro-flocs.

Some authors believe that there should be a minimal rate of sludge wasting in order to keep an optimal range of sludge concentration in MBR [46, 54–56]. When no sludge is withdrawn from the reactor, accumulation of inorganic compounds can be expected [16, 56–58]. Retention and accumulation of non-biodegradable compounds in the bioreactor could lead to microbial inhibition or toxicity, which limits the alternatives available for excess sludge disposal. Several works have described a possible negative long-term effect of accumulation of recalcitrant compounds on process stability [40, 59–62]. Non-biodegradable solids (solids that are not metabolized under present conditions) are either present in the influent or they are produced in the microbial process. Their forming can also be a result of protozoan activity, which may not degrade the bacterial cell walls fully, leaving behind the inert material. However, inerts are not ultimately inert: it is possible that degradation of inert material occurs by slow-growing bacteria, which will depend on the SRT [63]. Many studies have reported a stable performance of MBR during long operating periods, with a dynamic balance of active biomass and inorganic fraction during long-term operating periods [40, 58, 64]. In these studies, the mixed-liquor volatile suspended solids (MLVSS) to MLSS (MLVSS/MLSS) ratio was used as an indicator of the amount of viable sludge, and it was found to be relatively constant. Pollice et al. [65] explained this phenomenon by a possible hydrolysis and/or enzymatic solubilization of inert matter.

Taking into account all of the above-mentioned aspects of SRT control in MBR, SRT should be chosen in such a way to avoid both the adverse effects of accumulated non-biodegradable substances resulting from low sludge discharge and also an excessive production of sludge at low sludge ages. High sludge ages are one of the main advantages of MBR, consider-

ing that in conventional treatment processes long SRTs are impossible because of bad settling ability of sludge at high concentration and withdrawal of suspended solids with the effluent. Typical values for MLSS concentration in MBR vary from 10 to 25 g MLSS L^{-1}, while in CAS they are around 1.5–5 mg MLSS L^{-1} [44, 66].

Besides the "prolonged SRT" strategy, sludge decay rate in MBR could be boosted by disintegration of some part of sludge. The most common way for achieving this is sludge lyses. Lyses imply death and the breaking apart of cells, and therefore loss of bacteria. The autochthonous substrate formed contributes to the organic loading and is reused in microbial metabolism. Since the biomass growth on this substrate cannot be distinguished from the growth on the original organic substrate, it is called cryptic growth, and it was first introduced by Ryan et al. [67]. Limiting step for cell lyses is the degradation of the cell wall, and in order to accelerate it, physical or chemical treatment can be used [68]. Canales et al. [69] managed to improve the endogenous metabolism in an MBR by inducing cell death and lyses with a thermal treatment. Biomass was extracted and treated at three different temperatures (50, 70, and 90 °C) (see Fig. 12), while the hydrolysates were recycled to the bioreactor. Thus, improvement of endogenous metabolism was obtained by cryptic growth with both HRT and SRT were very low (2 and 10 h, respectively).

Other techniques for establishing cryptic growth in an MBR are ultrasound disintegration [70], ozone-induced biodegradation [71–73], and alkaline treatment [74]. Experimental results showed that by ozonization, excess sludge production could be reduced significantly, and biological performance of mineralization and nitrification would not be inhibited [71]. The ozone
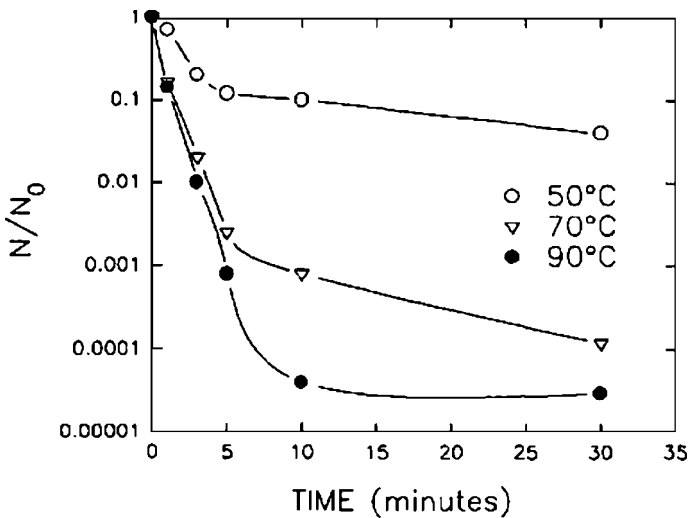

Fig. 12 Death kinetics of *P. Fluorescens* at different temperatures [69]

dosing rate is directly proportional to the amount of sludge to be treated. For example, in a study of Sakai et al. [72], it was found to be 0.034 kg O_3 per kg of suspended solids (SS).

On the other side, growth of controllable predators has been successfully tested for reducing excess sludge production in bench and pilot-scale reactors [75]. Grazing fauna mainly consists of protozoa and metazoa. These higher organisms consume bacteria, while decomposition of substrate remains unaffected. During energy transfer from low to high trophic levels, energy is lost due to inefficient biomass conversion. Under optimal conditions, the total loss of energy will be maximal, and the total biomass production thus will be minimal [49].

Environmental factors that influence and limit microbial growth are temperature and pH value, i.e., the acidity or alkalinity of the aqueous environment. Temperature has a profound effect not only in governing the rate of the treatment but it also affects bacterial composition. Chiemchaisri et al. [76] investigated performances of MBRs at various temperatures and noted a reduction in the number of strict aerobic bacteria when temperature was lowered, suggesting a limited oxygen transfer, partly due to reduced viscosity of mixed liquor at lower temperatures. The temperature range for optimal performance of MBR was found to be from 15 to 25 °C, while the treatment efficiency deteriorated as the temperature decreased to 10 °C. As far as pH is concerned, autotrophic metabolism is considered impaired outside the optimal pH range (7.2–8.5) [77].

How to operate MBR systems efficiently remains a topic of argument because there is a lack of information on the development of microbial community structure in the reactor [57]. The characteristics of sludge morphology (dispersed bacteria, lower amount of large filamentous bacteria, floc densification) certainly play an important role in the removal efficiencies, but they also affect sludge filterability and fouling mechanisms. Under the high organic loading conditions (i.e., low SRT), foaming and sludge bulking may rise.

In particular, the modification of sludge structure induced by membrane separation compared to a settling separation is still unclear. Because MF and UF membrane retain dispersed bacteria as well as colloidal and supra-colloidal material, the biological medium in MBR can be significantly different from those produced in an activated sludge [78]. It can be assumed that if operated at high sludge ages, bacteria in MBR face conditions of extreme competition for the inflowing substrates. However, microbiology and physiology of MBR are far from being understood.

5.2
Nitrification/Denitrification and Phosphorus Removal

An irrational use of agricultural fertilizers and pesticides and the discharge of incompletely treated industrial and municipal wastewater results in high ni-

trogen and phosphate concentration in surface water and groundwater. This enrichment usually leads to an excessive eutrophication of lakes and other water bodies, promoting an excessive growth of certain weedy species. Since both nitrates and phosphates are rate-limiting for the process of eutrophication (extraordinary growth of algae), their removal is of crucial importance for successful wastewater treatment. Nitrate and nitrite-contaminated water supplies are also related to several diseases such as methemoglobinemia occurring in infants, also called "blue baby disease" [79]. Moreover, these two compounds can induce mutations of DNA, causing gastric cancer [80].

Biological nitrification is an oxic process of conversion of ammonia to nitrite (NO_2) and then to nitrate (NO_3). Following nitrification, nitrogen can be removed from wastewater by reducing nitrate to nitrogen gas (N_2) in the process of anoxic denitrification. Because of the low growth rate and poor cell yield of nitrifying bacteria, nitrification is generally a rate-limiting step in biological nitrogen removal performance. The key requirement for nitrification to occur is that the net rate of accumulation of biomass (and hence the net rate of withdrawal of biomass from the system) is less than the growth rate of nitrifying bacteria [81]. Long SRTs applied in MBR prevent nitrifying bacteria from being washed out from the bioreactor, improving the nitrification capability of the activated sludge. Moreover, nitrifiers are less endangered by faster-growing heterotrophic bacteria, which are better competitors for the ammonia nitrogen (NH_3-N). Many studies have proven that MBR can operate as a high-rate nitrifying technology that can be applied in the nitrification of wastewater containing a high concentration of ammonia nitrogen [82]. Chiemchaisri [82] and Muller [40, 83, 84] found that more than 80% of the influent total Kjeldahl nitrogen (TKN) could be nitrified to NO_3 in an MBR. On the other hand, the denitrification process requires anoxic conditions in order to occur. To enhance denitrification, usually an anoxic tank is added upstream from the aerated tank. Anoxic conditions can also be introduced by operating MBR in an intermittent aeration mode, even when regarding submerged MBR, which needs permanent bubbling. In the intermittently aerated MBR, ammonium is nitrified mostly to nitrate and most phosphates are removed during the aerobic period (aeration), where the accumulated nitrate is completely denitrified during the anoxic period (non-aeration), and phosphorus (P) is taken up. The net P removal is achieved by wasting sludge after the aerobic period when the biomass contains a high level of polyphosphates (polyP) [85].

P is found in wastewater as phosphates (orthophosphates, condensed phosphates, organic phosphate fractions), and it can be eliminated either by precipitation and/or adsorption, or by luxury uptake. Only a small amount of phosphorus is used for cell metabolism and growth (1–2% of the total suspended solids (TSS) mass in the mixed liquor) [86]. Precipitation and adsorption processes require an appropriate pH, the presence of iron or calcium ions, etc. In WWTPs, luxury uptake of P is accomplished by the introduc-

tion of an anaerobic phase in the wastewater treatment line ahead of the aerobic phase and recycling of sludge through the anaerobic and aerobic phase [87]. Exposing mixed liquor to an anaerobic/aerobic sequence selects phosphate accumulating microorganisms (PAOs) due to a competition between PAOs and other aerobic organisms. This competition mechanism is based on a complete anaerobic uptake of the lower fatty acids by the polyP organisms (i.e., PAOs), which assures that in the aerobic phase, no fatty acids are left. The polyP organisms use the stored internal substrate during aerobic conditions while other aerobic organisms are lacking substrate. This process is usually referred to as the enhanced biological phosphorus removal (EBPR) process. EBPR process can be established in MBR treatment unit by operating it in intermittent aeration mode. Moreover, phosphorus removal will be significantly improved in an MBR by a physical retention of PAOs, whose size is typically larger than $0.5\ \mu m$. Since an MF membrane ($0.2\ \mu m$) will act as a physical barrier to retain the PAOs in the reactor, sufficient biomass is provided for the EBPR mechanism to take place [88, 89].

Intermittently aerated MBR can achieve nitrogen and phosphorus removal by a simultaneous nitrification and denitrification, P-uptake and P-release in the same reactor in accordance with time cycle of aeration and non-aeration. However, even though intermittent aeration was successful in removing nitrogen, P removal was difficult to achieve at a higher level [83, 90]. This is probably due to the inhibition by nitrate. In the anaerobic stage, nitrate reduces phosphate release, and in the aerobic stage it diminishes its uptake. Denitrification has more capability than phosphorus release with respect to the competition of substrate [91]. This is because nitrate will be utilized as a final electron acceptor in the growth of non-polyP heterotrophs. Thereby, the amount of substrate available for polyP organisms is reduced and hence the removal of phosphorus is lowered. There are some studies that confirm the ability of polyP organisms for denitrification, however, not all PAOs can use nitrate as an electron acceptor [92].

In addition, intermittently aerated MBR showed an unstable nitrogen removal in its application to treat domestic sewage of rural settlements because of incomplete denitrification [93]. Stable nitrification can be maintained as long as the oxygen concentration is high enough [94]. Chiemchaisri et al. [83] found that by lowering the dissolved oxygen (DO) concentration, nitrification was significantly inhibited, although it recovered completely after raising the DO concentration to 1 mg/L. Nitrosomonas and Nitrospira-like bacteria were identified as the predominant ammonium (AOB) and nitrate-oxidizing bacteria (NOB) in an MBR, respectively [95]. Both of these are obligate aerobic and under anoxic conditions are unable to store or utilize their substrate. The absence of oxygen may provoke stress and damage of their metabolism, NOB being the more sensitive [96].

There is much research on the effect of SRT on MBR performance as far as nitrification/denitrification and phosphorus removals are concerned. Ac-

cording to Cicek et al. [46], there is a decrease in nitrification rate at very low SRT (2 days), supposedly due to a partial loss of nitrifying microorganisms. On the other side, Li et al. [57] observed a decreasing trend of nitrifiers when increasing the sludge concentration, i.e., solids retention time. Another study confirmed a negative influence of long SRT on nitrification performance [56], which was explained by impeded oxygen and substrate transfer owing to an increase in MLSS concentration. Similar observations on the effect of SRT on phosphorus removal were taken by Yoon et al. [97], who recorded a decreased P removal at long SRT. In this case, it is probably due to a fact that PAOs undergo competitive conditions with glycogen-accumulating organisms (GAOs) at SRTs longer than 20 days [98].

These findings indicate that a compromise should be found between a sufficiently long SRT necessary to prevent the washout of nitrifiers, and a negative influence of too long SRT (decreased mass transfer due to poor aeration, competition with GAOs, etc.). However, over 90% removal of NH_3-N is usually achieved in MBR systems, almost independent on the SRT [56, 65]. Pollice et al. [65, 99] investigated a performance of an MBR system which start-up was done without any sludge inoculum. The system was fed on municipal sewage in order to favor biomass selection based on the imposed operating conditions. Biodegradation of the influent chemical oxygen demand (COD) and complete nitrification were consistently obtained already in the first days of operation. The ammonium oxidation performance over the whole experiment showed a typical nitrification start-up curve with initial $N-NO_2$ production followed by complete nitrification that occurred only 10 days after the start-up of the plant. As far as HRT is concerned, several studies noted a complete nitrification in an MBR operating with a HRT as low as 2 h [39, 100].

Other important factors that are to be considered for nitrogen removal are alkalinity, temperature, and organic and nitrogen loads (C/N ratio, i.e., biological oxygen demand (BOD) to total nitrogen (TN) ratio) [101, 102]. The BOD/TN ratio must be high enough to denitrify the nitrogen to be nitrated. Though this ratio is an important factor to be considered for successful nitrogen removal, it depends upon the components of organic matter that were readily degradable, such as volatile fatty acids [101]. As far as temperature is concerned, it is considered that it has to be maintained below 40 °C to ensure sufficient nitrification. If the temperature is controlled, a nitrification rate usually over 99% can be gained in spite of variations of inflow TN concentration [101].

Aerated MBR offers two major advantages in the elimination of phosphorus: complete removal of all particles (containing usually up to 0.1 mg of P per mg of total solids (TS)), and aeration, which prevents the phosphate release that occurs under anoxic conditions. Furthermore, there is an increasing interest for the application of MBR as a technology for phosphorus recycling, since the P-content of sludge is expected to increase when prolonging SRT [86].

Much research has confirmed that MBR is a highly viable wastewater treatment technology regarding nitrification-denitrification and phosphorus removal. With optimized design and operating parameters it warrants high effluent quality in terms of ammonia, nitrates, and phosphates present in wastewater. Current European regulation describes guidelines for total phosphorus and nitrogen in treated effluent to $1–2\,mg\,L^{-1}$ and $10–15\,mg\,L^{-1}$, respectively [86]. More stringent regulations are expected to come into force soon in some countries, which fulfillment will require improvements in the existing treatments and the implementation of additional ones.

5.3
Removal of Organic Matter and Suspended Solids

Knowledge about COD removal mechanisms that occur when mixing an activated sludge with real wastewater is still scarce. The microbial response to dynamic conditions in a real wastewater treatment unit can be different from a simple increase in cell number (i.e., growth of microbial population), and include other substrate-removal mechanisms like sorption, accumulation, and storage [103]. There have been several investigations on treatment efficiencies of MBR and CAS processes operating under comparable conditions that have shown significantly improved performance of an MBR in terms of COD, NH_3-N and SS removals [3, 30, 40, 51, 83, 104–111]. There are several factors that may contribute to the lower organic carbon content of MBR effluents as compared to CAS processes, like longer retention times, smaller floc sizes, etc.

Côté et al. [100, 112] attributed the improved COD removal to the avoidance of biomass washout problems commonly encountered in activated sludge process, as well as to complete particulate retention by the membrane. Membrane rejection of a significant amount of soluble organic molecules and colloids makes their removal more effective due to a higher lyses activity in the reactor induced by elevated concentrations of these compounds. Higher sludge ages that are achieved by long SRTs allow more complete mineralization of biodegradable raw water organics, but also an adaptation of microorganisms to less biodegradable compounds. Therefore, biomass can acclimatize to wastewater without being restricted to fast-growing and floc-forming microorganisms. In a study of Al-Malack et al. [95], COD removal efficiency in immersed MBR was found to increase significantly with increase in MLSS concentration, however, the effect of SRT on permeate COD became insignificant for MLSS concentrations above of $3\,g\,L^{-1}$, which probably means that the organic loading rate was not high enough to show a significant difference at higher biomass concentrations. Since typical sludge concentrations for immersed MBRs are between 15 and $25\,g\,L^{-1}$, elimination of organic matter and turbidity is almost independent on SRT, and average removals normally achieved for COD and SS are over 90 and nearly 100%, respectively [112].

Better performance of MBR operated at long SRTs can also be explained by the presence of dispersed bacteria that are advantageous in the overall population competition when substrate concentration becomes very low, i.e., at low F/M ratio and high sludge age. Flocs in a bioreactor were found to be smaller (Fig. 13) [56], which can explain enhanced mass transfer for both oxygen and carbon, thus enabling a higher removal rate and more adaptability to changes in the influent quality and quantity [53, 113]. In another study it was demonstrated that the flocs were more active and displayed greater species diversity [104].

The overall capacity of biomass to degrade different carbon substrates does not change significantly at different SRTs, which confirms that MBR is capable of degrading a wide variety of carbon substrates in a similar fashion. This robustness of MBR treatment regarding turbidity and organic matter removals was confirmed in several studies [114]. Xing et al. [58] recorded high treatment efficiency regardless of the absolute level of sludge concentration in the MBR, and unaffected by variations in SS and volatile suspended solids (VSS) influent concentrations. In another study, in spite of large fluctuations in the influent, COD effluent COD was always low and extremely stable, because upon the addition of organic substrates, biomass responded immediately with increased respiration activity [114]. It is assumed that there is an upper limit for organic loading rate in an MBR under which degradation performance is independent of biomass concentration and organic loading rate. Rosenberger et al. [44] found that for organic loading rates lower than $7 \, \text{kg COD m}^{-3} \, \text{day}^{-1}$, COD removal in MBR was high and stable regardless of MLSS concentration and composition of microbial culture. Moreover, another study reported that the mineralization process was not impaired nor with the shifts in the morphological composition of microbial population, or even with the occurrence of high numbers of filamentous bacteria [44]. Pollice et al. [65] tested a performance of MBR when its start-up was done without any sludge inoculum. Biodegradation of the influent COD as well as complete
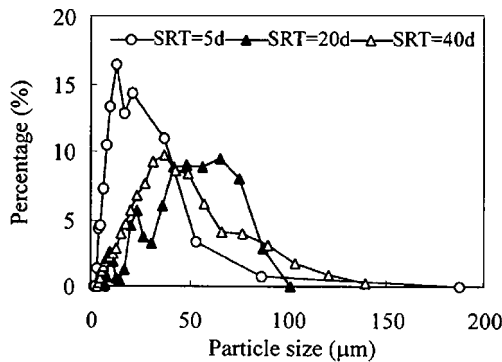

Fig. 13 Sludge particle size distributions at different SRTs [56]

nitrification were consistently obtained already in the first days of operation, which demonstrated the high responsiveness of MBR. In aerated MBR, COD loss is also a result of the production of volatile compounds that are released from the system under aerated conditions [92].

Concerning turbidity removal, due to a complete retention of particulate matter by the membrane, there are no suspended solids found in the MBR effluent, unlike the effluent of a conventional process. The UF/MF membrane can capture all SS in the reactor because of its fine pore size [115]. Therefore, non-biodegradable organic compounds are removed through filtration of particulates and discharged with the sludge. Gander et al. [116] reported that membrane contribution to the removal of organic matter was approximately 30%, this roughly equating to the insoluble fraction that was removed via active biomass. In another study with an external membrane module, total COD removal was 97% on average, where 85% was removed by the bioreactor and only 12% resulted from membrane separation [58].

As far as HRT is concerned, results of Sun et al. [113] indicated a clear influence of the operation time on biomass concentration (Fig. 14). Short HRT brings up a higher concentration of biomass because the volumetric organic loading is bigger (more food is supplied to microorganisms), although the oxidation of organic matter might not be complete. On the other hand, Chaize et al. [39] recorded a complete nitrification and organics removal at HRT of only 2 h.
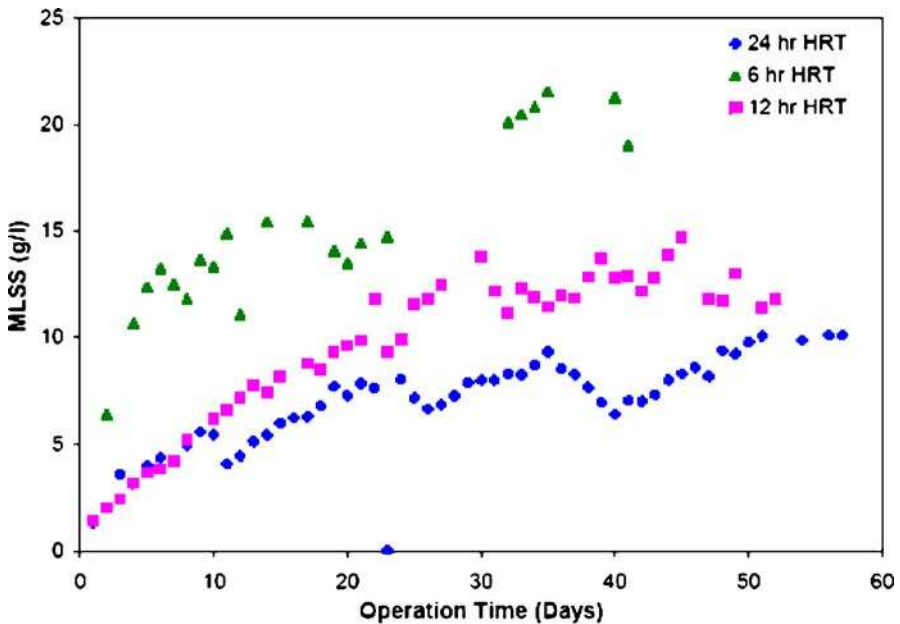

Fig. 14 Growth of MLSS concentrations in submerged MBR at different HRTs [113]

Aeration flow is also one of the main factors that affect the biochemical process of BOD and COD removals. The right amount of oxygen needs to be provided to the microorganisms in response to their three specific demands:

1. carbonaceous BOD (conversion of the carbonaceous organic matter in wastewater to cell tissue and various end products),
2. nitrogenous BOD (in the process of nitrification ammoniacal nitrogen is oxidized to the intermediate product nitrite, which is then converted to nitrate),
3. inorganic COD (oxidation of reduced inorganic compounds within the wastewater) [117].

Biomass characteristics such as SMP and EPS strongly influence the oxygen transfer, so therefore they will determine the rate of organics removal. These compounds are also widely recognized as the main membrane foulants [118]. SMP is soluble and thus is in the liquid phase and EPS is bounded to cells and makes a part of the solid phase. In order to reach the active sites on the bacterial cell membrane, the oxygen needs to penetrate the liquid film surrounding the flocs and then diffuse through the floc matrix (EPS) [117]. EPS amounts differ with changes in microbial state and operating conditions of the bioreactor. In the intermittently aerated MBR they increase in proportion to the non-aeration time [119]. Nevertheless, Ujang et al. [89] reported no significant difference in COD removal efficiency when varying aeration and non-aeration time, indicating that in intermittently aerated MBR organic matter can be degraded both under aerobic and anaerobic conditions. Also, over-aeration can bring about poor sludge characteristics such as bad floc structure and rather low sludge volume index (SVI), which can then be related to fouling [101].

In conclusion, immersed MBR is strongly capable of resisting shock-loadings, and variations in the inflow turbidity and organic matter content have no effect on their removal efficiencies. The removal of organic pollutants in terms of COD and SS has been proven to be very high and a good-quality effluent can be achieved during long-term operation. However, how to operate MBR systems efficiently remains a topic of argument because there is a lack of information on the development of microbial community structure in MBRs during nitrification [57]. It is important to distinguish among these different contributions to the overall COD removed, in order to better understand the dynamics of the process and to build-up a useful basis for process designing and modelling.

5.4
Bacteria and Virus Removal

Microbiological water quality is usually measured by monitoring the organisms that might indicate that the water is contaminated with fecal material

or that disinfection is inadequate. These organisms are referred to as "indicator organisms", and they are not harmful to health but they coexist in high quantities where pathogens are present. The most common indicator organisms used are total coliform (TC) in drinking water quality control, while for wastewater evaluation fecal coliform and bacteria *Escherichia coli* are used. On the other side, viruses are expected to be more suitable indicator organisms than bacteria since they are much smaller and harder to straining than bacteria, and also considered to be more resistant to common disinfectants [120]. The removal of enteric viruses requires specific attention, given their low infective dose, long-term survival in the environment, and low removal efficiency in the conventional wastewater treatment. Due to the difficulty in assaying animal viruses, bacteriophages have been suggested as viral indicators because they closely resemble enteric viruses in terms of structure, morphology, size, and behavior [121]. A variety of bacteriophages have shown potential as model organisms for monitoring virus-removal in drinking water treatment plants [122], such as F-specific RNA coliphages (viruses infecting *E. coli*). MS-2 is the most-studied F-RNA coliphage, and it is often used as an indicator because of its being the smallest ($0.02–0.025\,\mu m$) among viruses and relative hydrophobicity, which makes it a good worst-case strain and therefore representative to address the ability of pathogen removal.

If these pathogens (i.e., microorganisms capable of causing diseases) are not removed by water treatment or disinfection and stay present in water, consumers may suffer infectious diseases like cholera, polio, typhoid, hepatitis, and a number of other bacterial, viral, and parasitic diseases. Sewage treatment may reduce the numbers by ten to ten thousand-fold, depending on the nature and degree of treatment. However, even tertiary treatment of sewage will not eliminate all viruses. In well-functioning biological plants, as many as $10^6\,\text{CFU}\,\text{L}^{-1}$ resistant coliform bacteria were found in the effluent [123, 124], while this number is much larger when counting with the existence of smaller viruses. In the production of potable water, a limited number of bacteria are acceptable, which also depends on the type of bacteria. The average content of viruses in drinking water should be only around 10^{-8} viruses L^{-1}. Hence, given their low infective dose, long-term survival in the environment and low removal efficiency in the conventional wastewater treatment, enteric virus removal requires specific attention. For their elimination, the most important step in potable and wastewater treatment is disinfection, during which the number of pathogenic organisms in water is lowered to an acceptable value. Primary methods of disinfection are chlorination, chloramines, ozone, and ultraviolet light. Other disinfection methods include chlorine dioxide and treatment with potassium permanganate. These processes are often accompanied by mutagenic/carcinogenic and toxic disinfection by-products (DBPs), which are potentially harmful to humans and aquatic organisms. Another disadvantage of chemical sterilization methods is that they kill the present microorganisms without removing the dead ones,

which are a source of pyrogens (compounds that can cause a rise of a body temperature).

One of the most advanced options for disinfection is MBR treatment, where removal of microorganisms is achieved by filtration. Membrane treatments have been proved to be very efficient in reducing vegetative bacteria [125–127]. Ottoson et al. [126] noted a 5 log removal of *E. coli* and 4.5 log removals of enterococci. These reductions are in line with the MBR removal rates of *Faecal coliforms* and *Faecal streptococci* (up to 7 log) reported by Ueda et al. [128]. Phages and spores are not as efficiently removed as bacteria, though their elimination can be successfully increased by submerging a membrane module in the reactor for a few weeks, which allows a membrane-attached biofilm to develop [126, 129, 130]. Some investigations have shown that membranes were capable of removing viruses completely (UF) or significantly (MF) under appropriate conditions [116]. If the pore sizes of the membrane are smaller, then viruses can be removed by size exclusion. Cooper and Straube [131] found that RO can effectively remove viruses from wastewater without any additional treatment.

It was found in these studies that the main role in the removal of bacteria as well as viruses plays a biofilm formed on the membrane surface. In the absence of biofilm, virtually no phage removal was observed, while in its presence better phage removal was observed at higher sludge concentrations. It has been suggested that mechanisms for this removal comprise a physical component due to pore size reduction, a chemical component due to viral adsorption on the biofilm, and a biological component resulting from the predation of phage by other microorganisms. Given enough time for a biofilm to develop, the removal improves significantly because the membrane surface gets fully covered with gel layers, while internal blockage and partial coverage (presumably by EPS) are observed in the membrane pores [95, 117]. In the study performed by Shang et al. [117] the membrane alone showed poor virus removal. This was to be expected since the average pore size of the membrane fibers (0.4 μm) was much larger than the size of the bacteriophage MS-2 (0.02 μm). The overall removal increased substantially with the presence of biomass and biofilm. Similar results were found by Lv et al. [132] for the elimination of the phage T4 in two membrane modules with pore sizes of 0.22 and 0.1 μm. In the second one, a membrane alone could block most phages from leaking by direct membrane interception, while cake and gel layer played a significant role on the phage removal for the 0.22 μm membrane module. Phages are also expected to associate with biomass flocs and then get removed by flocculation or cell adsorption in the aeration tank [117].

There is evidence that pore size does not necessarily describe the ability of a filter to remove particles from solutions [127]. Besides gel layer at membrane surface, important factors for adsorption of viruses on membranes are chemical composition of membrane, ratio of membrane pore diameter to virus diameter and hydrophobic and electrostatic interactions. The charge of

most viruses will be negative under the conditions present in most wastewater effluents (i.e., pH 6–7). Neutral net charge at the iso-electric point (pI) of a virus leads to maximum virus–virus coagulation. Aggregation may therefore further promote virus retention by membranes. It has also been noted that the presence of particular ions promotes virus aggregation compared to buffers at low pH alone.

For electrostatic interaction of viruses, the thickness of the double-layer as described by Gerba [129, 133] plays the most important role, which is governed by the pH and the presence of salts in the bulk solution (Fig. 15).

Increasing the salt concentration (for example its thickness) is reduced (Gouy layer around the virus is decreased) and thus virus adsorption to membrane surfaces is facilitated. Gerba showed that certain salts have a positive effect on both electrostatic and hydrophobic interactions.

pI of a virus is a parameter relevant for its electrostatic interactions and relative hydrophobicity. By knowing a virus's pI it is possible to predict the likelihood of its adsorption to a charged surface as long as the suspending conditions are known, at the first place pH of a bulk solution. Van Voorthuizen et al. [129] observed that the retention of bacteriophage MS-2 at its pI and in the presence of salts was significantly higher when using a hydrophobic membrane compared to the hydrophilic one. If a solution's pH is greater than the pI of a virus, hydrophobic interaction could play the major role in maintaining virus-filter adsorption due to the increased electrostatic repulsion at higher pH levels [133]. On the other hand, the pI of a virus can differ within the same strain due to the fact that different viruses have different protein coatings that surround the virus. In addition, metals and other substances present in water could form complexes with these protein coatings, which will have an impact on adsorption characteristics and the measured pI [129].
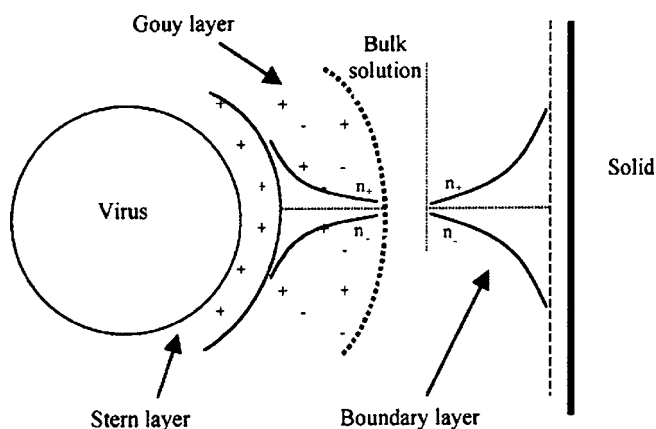

Fig. 15 Schematic illustration of virus structure with electrokinetic double layers [129]

The presence of human enteric viruses is a major risk associated with wastewater reuse.

As sewage mixes with the receiving water, viruses are carried downstream and the length of time they remain detectable depends on temperature, their degree of absorption into sediments, penetration of sunlight into the water, pH, and other factors. Consequently, enteric viruses can be found in sewage-polluted water at the intakes to water treatment plants. In recent years, the reuse of wastewater for non-potable reuse has gained much attention. MBR effluents were found to be compliant with the EU Bathing Water Directive (EC/160/75) including parameters such as total coliforms, *Faecal coliforms*, *Streptococcus faecalis* as *Salmonella* spp. and *Coliphages* [134]. However, how to cope with wastewater when different types of viruses coexist and how to dispose the virus-bearing excess sludge must be studied further.

6
Removal of Trace Organic Compounds by a Membrane Bioreactor

WWTPs treating wastewater from municipalities and industries have been shown as major sources of many environmental pollutants. These pollutants usually originate from synthetic chemicals that have been used widely for industrial, agricultural, and household purposes. Compounds like pharmaceutically active compounds (PhACs), industrial chemicals, and pesticides are produced worldwide on a 100 000 t scale. After their usage for the intended purpose, a large fraction of these substances will be discharged into the wastewater unchanged or in the form of degradation products that are often hardly eliminable in conventional WWTPs. Depending on the efficiency of the treatment and chemical nature of a compound, they reach WWTP effluents and surface waters in certain concentration. In the worst case, they are present in drinking water, in spite of expensive treatment steps.

Although the exact effect of consistent exposure to trace organic contaminants is still unclear, there is no more doubt that it has significant adverse consequences for public health. For example, antibiotics and their metabolites can significantly increase antibiotic resistance in the population. Synthetic hormones can act as endocrine disruptors by mimicking or blocking hormones and disrupting the body's normal functions. Due to their polarity, they can be eliminated during wastewater treatment only incompletely. Polar poorly degradable compounds were detected in high and comparable concentrations in the effluents of numerous WWTPs all over Europe. A proper wastewater treatment as mandatory in the European Union due to the Urban Wastewater Treatment Directive (91/271/EEC) will not eliminate polar pollutants completely [135]. Therefore, to avoid such contaminants, emissions with WWTP effluents would have to be reduced by their advanced treatment or by avoidance and replacement measures for the respective pollutant. One of the

most promising technologies is MBR technology. The potential of MBR to efficiently remove hazardous substances from wastewater is often highlighted. Besides the fact that there is a physical retention of all the molecules larger than the molecular weight cut-off (MWCO) of the membrane, hydrophobic substances also tend to accumulate onto the sludge and therefore they are removed from the effluent. Furthermore, as all the bacteria are held back, there are better adapted to mineralizing of micropollutants present in the reactor.

6.1
Removal of Pharmaceutically Active Compounds

Most pharmaceutical substances are by nature biologically active and hydrophilic so that the human body can absorb them easily, and persistent in order to avoid the degradation before having a curing effect. Depending on the pharmacology of a medical substance, it will be excreted as a mixture of metabolites, as unchanged substance or conjugated with an inactivating compound attached to the molecule [136]. Once they enter a WWTP, pharmaceutical residues are usually not completely degraded or retained by adsorption to sludge. Hence, they pass through wastewater treatment and end up in the receiving waters in certain percentage. Their removal in WWTPs is variable and depending on the properties of the substance and process parameters (i.e., SRT, HRT, and temperature) [137, 138]. A large number of PhACs are hardly eliminated and therefore detected in WWTP effluents. The presence of PhACs in surface, drinking, and wastewaters is well documented in literature [136, 139–147]. Although present in low environmental concentrations, drugs can have adverse effects on aquatic organisms. These effects are rather chronicle than acute toxic effects, depending on the exposure factor (bioavailability), degradability, and susceptibility of the compound in question [148]. The results reinforce concerns about excreted pharmaceutical compounds from wastewater systems that may end up in the water supply, potentially resulting in adverse effects for humans and the environment.

The most important removal pathways of organic compounds during wastewater treatment are biotransformation/biodegradation, adsorption to the sludge (excess sludge removal), and stripping by aeration (volatilization). Considering low values of Henry coefficients (K_H) of most of the PhACs detected in wastewater streams [149], stripped fraction removed by volatilization can be neglected [150]. In most of the studies, two processes of abiotic (adsorption) and biotic degradation (transformation by microorganisms) could not be distinguished, and the term "removal" usually refers to a conversion of a certain micropollutant to compounds other than the parent compound.

The membrane-activated sludge process is expected to enhance trace-organics removal to a greater extent than the conventional treatment (Fig. 16). There are many reasons for this assumption: higher sludge age, higher
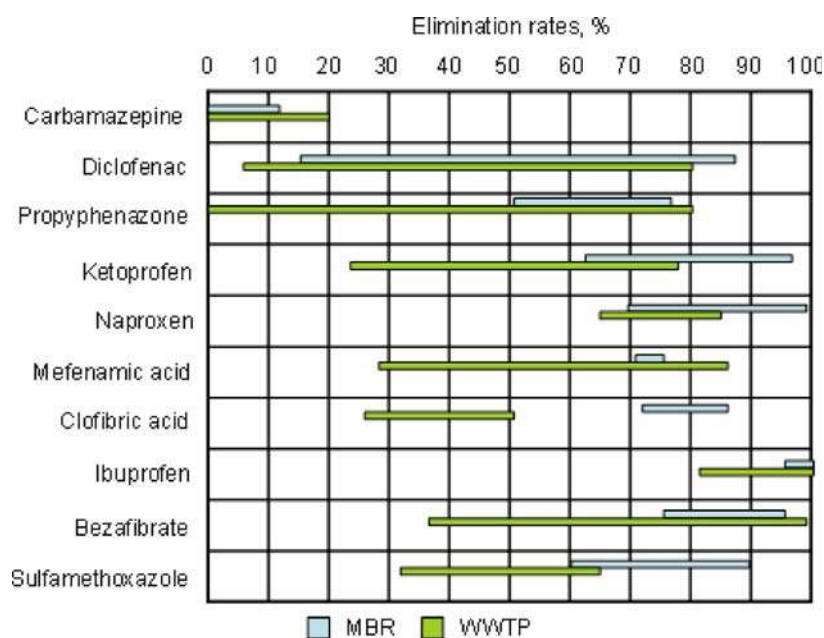
Fig. 16 Elimination rates of PhACs in MBR and CAS treatment [156]

biomass concentration, complete retention of solids and microorganisms, etc. Several studies have been conducted that confirmed an advantage of MBR over CAS when reduction of pharmaceuticals is concerned [151–155]. Radjenović et al. [155, 156] found significantly improved removal of lipid regulators and cholesterol lowering statin drugs (gemfibrozil, bezafibrate, clofibric acid and pravastatin), β-blockers (atenolol and metoprolol), antibiotics (ofloxacin and erythromycin), anti-ulcer agent (ranitidine) and some analgesics and anti-inflammatory drugs as well (propyphenazone, mefenamic acid, and diclofenac).

Still, some authors report comparable elimination rates for these two processes [137, 146, 157]. The current understanding of biotransformation of PhACs in WWTPs and MBRs, and of their biodegradation pathways and mechanisms is still incomplete. Although the biodegradation of some pharmaceuticals in batch reactors has been described, it is still unclear how this information relates to biotransformation processes under real conditions of WWTPs.

Qunitana et al. [154] investigated microbial degradation of several pharmaceuticals and performance of MBR in their elimination from wastewater. They found a formation of potentially stable metabolites during ketoprofen and bezafibrate transformation, which may deserve further attention when analyzing removal of PhACs in wastewater treatment technologies. In laboratory degradation experiments, ketoprofen yielded two metabo-

lites formed along the biphenyls, biphenyl ethers and related compounds pathway [154, 158]. Bezafibrate was hydrolytically cleaved along the amide bond yielding one well-degradable metabolite (4-chlorobenzoic acid) and another metabolite that was not mineralized [154]. Ibuprofen, bezafibrate and naproxen were degraded only with the addition of external carbon source (co-metabolism), whereas diclofenac was not transformed [154]. In the same study, the only two metabolites found in wastewater were hydroxyl-ibuprofen and 4-chlorobenzoic acid detected in the MBR influent, while in the effluent they were not present. Considering the fact that it is still uncertain what kind of adverse effect on humans and the environment these compounds can have, monitoring of these pharmaceutical by-products should be established in WWTPs. Due to the lack of knowledge about the metabolites of PhACs, the non-existence of adequate analytical methods, and a possible sampling inaccuracy, usually no firm conclusion about their biotransformation can be made.

Joss et al. [150] performed batch biodegradation experiments with CAS and MBR sludge. Based on the average results for kinetic biodegradation constants (K_{biol}, $kg_{SS}^{-1} d^{-1}$), they established three different classes of compounds according to their susceptibility to biological degradation:

1. compounds with $K_{biol} < 0.1 \, kg_{SS}^{-1} d^{-1}$, that have no removal (e.g., carbamazepine, diclofenac, diazepam),
2. partially removed compounds, $0.1 < k_{biol} < 10 \, kg_{SS}^{-1} d^{-1}$, (e.g. roxythromycin, fenoprofen, acetylsalicilic acid, naproxen, bezafibrate, clofibric acid, fenofibric acid, gemfibrozil, piracetam, and some iodinated contrast agents),
3. compounds removed with more than 90% efficiency, $k_{biol} > 10$, (e.g., ibuprofen and acetaminophen).

However, there are many literature data contradictory to these results. Good elimination in CAS has been reported for both indomethacine and diclofenac [143]. Removals of bezafibrate were over 80% in some investigations [137, 143]. The discrepancy in results of existing publications on this matter could be due to different pharmaceuticals concentrations and/or sludge origin (sludge age, wastewater composition, etc.). When performing batch experiments, their outcome will also depend on the way of handling sludge prior to the experiment.

Many studies have confirmed a complete biodegradation of a non-steroidal anti-inflammatory drug ibuprofen to hydroxyl-ibuprofen and carboxy-ibuprofen in WWTP and MBR, whereas removals higher than 95% have been reached [106, 137, 141, 146, 154, 159]. Although a very high elimination of this drug during wastewater treatment has been reported by several authors, it is frequently found in surface and ground waters [160–162]. This is no surprise considering its wide usage and high therapeutic doses prescribed for the treatment of pain, dysmenorhea, inflammation, and fever, which makes

it one of the most important pharmaceutical contaminants found in WWTPs. Also, Stumpf et al. [163] found that hydroxyl-ibuprofen was quite stable during conventional treatment in WWTP, while carboxy-ibuprofen, the main metabolite in humans, disappeared. Moreover, pharmacologically active isomer of ibuprofen is the most prominent form detected in environmental samples, which could be explained by the fact that microorganisms mainly utilize its inactive isomer [141]. This change in enantiomeric composition points to biological dissipation of ibuprofen rather than other processes such as sorption and uptake by the sludge.

In short-term biodegradation tests with pilot sewage plant and biofilm reactor, clofibric acid and diclofenac turned out to be very persistent [153, 164, 165]. However, such pilot plants may not be adequate simulations of the actual processes occurring during wastewater treatment. In some WWTPs, attenuation of 50–70% of diclofenac has been reported [106, 137, 143, 145, 166]. Ternes et al. [143] recorded 51% elimination of clofibric acid during conventional wastewater treatment. However, literature data on this subject is still very contradictory. Many studies have reported extremely low efficiency of conventional treatment in the removal of diclofenac (only 10–30%) [137, 142, 146, 167]. Clofibric acid has also been found to be a refractory contaminant during wastewater treatment [145]. Kimura et al. [125] related the persistence of diclofenac and clofibric acid in both MBR and CAS processes to the presence of chlorine in their structures, which makes them hardly degradable. Moreover, in batch experiments with MBR and CAS sludge Joss et al. [150] showed no difference between their biodegradation constants (K_{biol}) of diclofenac, which were low in both cases ($\leq 0.1\,\mathrm{L\,g_{SS}^{-1}\,d^{-1}}$), whereas for clofibric acid K_{biol} determined with CAS sludge was greater than with MBR sludge (0.3–0.8 and 0.1–0.23 $\mathrm{L\,g_{SS}^{-1}\,d^{-1}}$, respectively). On the other hand, Radjenović et al. [155] noted a significant improvement in removal of these compounds when using MBR unit. Elimination in MBR of diclofenac and clofibric acid were 87% and 72%, compared to 50% and 28% found in CAS, respectively. Clara et al. [106] noted an improvement in elimination of diclofenac during MBR treatment with prolonging the SRT. González et al. [168] suggested that faster diminution of diclofenac was because of better acclimation of microorganisms to the MBR influent water. Besides possible changes in microbial consortia during its adaptation to wastewater contaminants, another explanation for better performance of MBR could be higher sorption potential of sludge, as the organic matter content is higher with respect to the CAS sludge. Moreover, according to the results of the EU project POSEIDON [169], sorption processes are relevant for the elimination of diclofenac. Clofibric acid can perhaps be sorbed to sewage sludge particles in acidic conditions, since considering its pK_a value (4.91) it will exist in non-ionic form, which makes it more hydrophobic [170].

Carbamazepine is an established drug used for the control of psychomotor epilepsy. It is also used in the treatment of trigeminal neuralgia and

bipolar depression. Concentrations to several hundred nanograms per liter of this pharmaceutical have been detected in different surface waters [142]. Poor elimination of this neutral drug has been reported previously by many authors [144, 146, 157, 171]. Carbamazepine does not adsorb onto the sludge [169]. Also, the pore size of MF membranes usually applied in wastewater treatment processes does not allow any further retention of the molecule. Therefore, carbamazepine passes both WWTP and MBR without any reduction and effluent concentration in the range of influent ones were measured in many studies [137, 145, 146, 157, 172, 173]. As is often the case, effluent concentrations of carbamazepine are detected to be greater than the influent ones. This could be explained by the presence of its input conjugate compounds that are being retransformed during treatment into the original compounds [143].

Unexplained variations of concentration over time can also be observed for sulphonamide antibiotics, probably also because of unknown conjugation and deconjugation processes that may occur during contact with activated sludge. For example, a significant amount of sulfametoxazole enters WWTP in metabolized form as N_4-acetyl-sulfamethoxazole that can be converted back to the original compound [174]. Variable elimination percentages of sulfamethoxazole can also be associated with the dependence of its biotic degradation on the presence of easily biodegradable organic matter in wastewater, which is submitted to changes in both MBR and CAS systems [175].

Theoretically, trace organic removal should be better in MBR than in CAS because of high SRT and sludge retention on membranes. This enables biological adaptation and changes in microbial consortia, whereas synthesis of specialized enzymes for biodegradation of micropollutants is induced. Data from literature show that higher sludge age often reached in MBRs may significantly improve the removal of specific compounds [146, 152]. For compounds like trimethoprim and macrolide antibiotics azithromycin, erythromycin, and clarithromycin, a clear increase in transformation was found at sludge ages of 60–80 days [152]. In the same study, higher reduction of roxythromycin was observed already at 33 days SRT. Clara et al. [106] reported higher removal of diclofenac when increasing SRT in an MBR. However, Joss et al. [146] found no improvement in degradation of micropollutants with increased SRT (i.e., carbamazepine, naproxen, diclofenac, ibuprofen, roxythromycin, and bezafibrate).

In general, the more hydrophobic the chemical is, the amount adsorbed will be greater.

However, there are many factors that may contribute to the ultimate concentration of organic pollutants in sewage [176]. Urase et al. [170, 177] reported higher elimination of diclofenac, indomethacin, and some other acidic PhACs (clofibric acid, ibuprofen, ketoprofen, fenoprofen, gemfibrozil, naproxen) during CAS and MBR treatment in acidic operational conditions. It was postulated that this was due to their increased hydrophobicity since these compounds did

not exist in ionic form in the acidic pH, which resulted in adsorption onto sludge particles. For example, the elimination rate of diclofenac was more than 90% when pH was in the range of 4.3–5.0, compared to around 10–15% removal at neutral pH. On the other hand, propyphenazone and carbamazepine do not have functional groups to form ions, and their removal was not affected by the pH. Jones et al. [178] detected no adsorption of ibuprofen, salbutamol, acetaminophen, and propranolol hydrochloride to sewage sludge. In the same study, some removal to solids of mefenamic acid was indicated. However, this compound has frequently been found in WWTP effluents.

There are several mechanisms responsible for the sorption of a certain organic compound onto the activated sludge: adsorption onto bacterial lipid structure, sorption onto polysaccharide structures outside bacterial cells, and chemical binding to bacterial proteins and nucleic acids [179]. Kumagai et al. [180] reported greater biosorption of pharmaceuticals having a more significant protein binding. However, in real sewage, pharmaceuticals are likely to be out-competed for sorption sites by other hydrophobic contaminants, which means that a greater proportion of them will remain in the aqueous phase than the expected one. Besides hydrophobic processes that are taking place, a number of other reactions like complex formations with metal ions, ion exchange, and hydrogen bindings decide about the partition of the organic compound between the solid and the liquid phase [181].

Since for adsorption processes the organic fraction, i.e., VSS of the sludge is relevant [182], MBR sludge is expected to have higher sorption potential, as the organic matter content is higher in respect to the sludge of the CAS. Literature data indicates irrelevant sorption coefficients (K_d) values for most of the pharmaceuticals investigated by now, with the exception of macrolide antibiotics azithromycin and clarithromycin [183, 184]. For other PhACs like acetaminophen, naproxen, indomethacin, ibuprofen, fenoprofen, diclofenac, roxithromycin, bezafibrate, clofibric acid, fenofibric acid, gemfibrozil and N_4-acetyl-sulfamethoxazole, sorption effects can be neglected [150]. In this case, biological transformation can be estimated by direct comparison of the soluble concentration in the influent and effluent. Joss et al. [146] used an approximation to assess if the sorbed amount is significant or not (Eq. 6):

$$L_{sorbed} \leq 0.1 L_{sol, out} \,,\qquad\qquad\qquad\qquad\qquad (6)$$

where L_{sorbed} is the load of the compound sorbed onto sludge ($g\,m^{-3}_{WW,\,treated}$), and $L_{sol,\,out}$ is the soluble load in the effluent ($g\,m^{-3}_{WW,\,treated}$).

In the same study, biodegradability of pharmaceuticals was estimated in MBR and CAS sludge. Transformation rate constants were similar in two types of sludge for most of the compounds. However, in some cases they differed quite a lot, like for gemfibrozil and fenofibric acid, where k_{biol} in MBR was ten times smaller than for CAS sludge, and also MBR degradation of piracetam and bezafibrate was conducted at a significantly higher rate (Fig. 17).
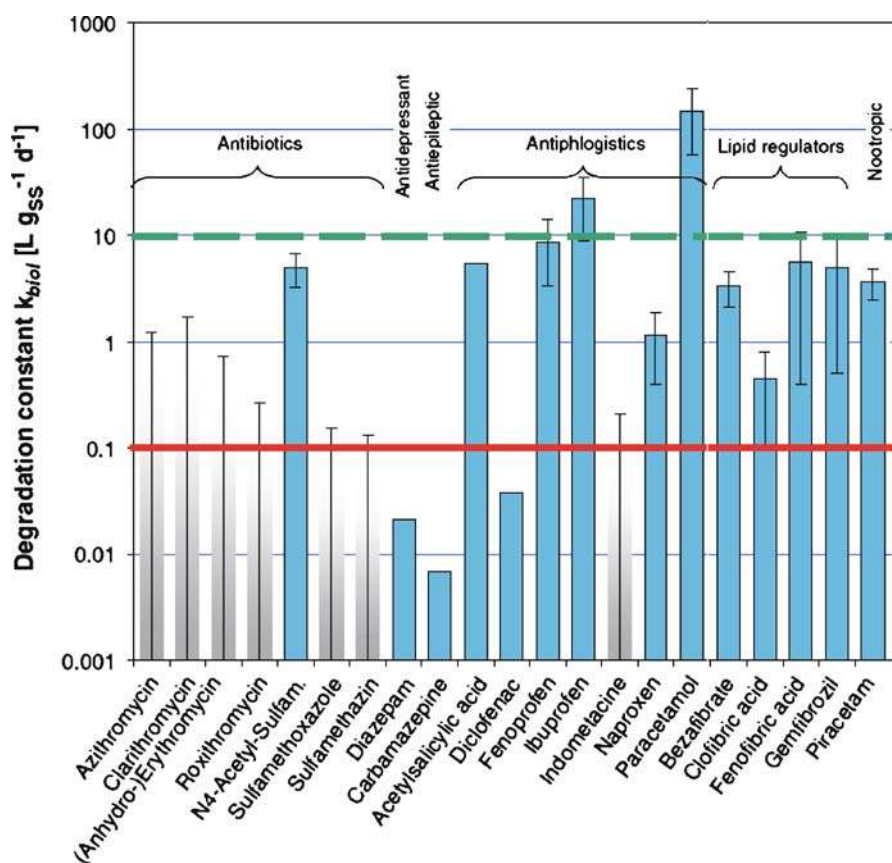
Fig. 17 Kinetic degradation constants of pharmaceuticals observed in sludge from nutrient-removing municipal WWTPs: the average of CAS and MBR batch experiments is indicated. The *error bars* indicate the 95% confidence interval. The lines at K_{biol} 0.1 and 10 L g_{SS}^{-1} d^{-1} indicate limits for less than 20% and more than 90% removal expected from nutrient-removing municipal wastewater treatment. The *faded columns* indicate values from which experimental resolution allows only identifying an upper limit for K_{biol} (*upper error bar*) (adopted from Joss et al. [150])

Knowledge about the removal of trace organic compounds by MBR is very limited. There have been several investigations conducted on the efficiency of WWTPs in removing PhACs from wastewater and its comparison with advanced MBR treatment [106, 137, 146, 150, 151, 153–155, 177]. For most of the investigated PhACs, MBR effluent concentrations were usually significantly lower than in the effluent of a conventional treatment. They are removed from wastewater during membrane treatment by sorption, degradation, or a combination of both. Better removal of readily biodegradable micropollutants in the MBR could be due to smaller flock size of sludge, which enhances mass transfer by diffusion and therefore increases the elimination. Considering the

composition of sludge originating from a membrane bioreactor (specialized microorganisms, large portion of active biomass in suspended solids) improved removal is to be expected. In general, no relationship has been found so far between the structures of micropollutants and their removal during wastewater treatments.

Urbanization and constant population growth is likely to keep increasing the quantity of wastewater discharged to WWTPs. Also, considering fast development of pharmaceutical industry and general aging of population, it can be assumed that PhACs will be more consumed and with a more diverse array, with development of new compounds that have unknown fate and effects on the environment. At the same time, the demand for clean water increases as well. Therefore, new technologies for wastewater treatment like MBR will have increasing interest. Although the efficiency of MBR as a barrier for micropollutants such as PhACs is still not clear, it seems to be a promising mean for their removal.

6.2
Removal of Hormones

Estrogenic substances have been identified and quantified in a wide variety of environments associated with industrial and municipal effluents, as well as urban and agricultural runoffs [185–191]. Negative adverse health effects on aquatic organisms which could be attributed to endocrine disrupting compounds (EDCs) are reported by several authors [192, 193]. EDCs are substances that interfere with the hormone system of animals and human beings. When absorbed into the body, they either mimic or block hormones and disrupt the body's normal functions. This disruption can happen through altering normal hormone levels, halting or stimulating their production, or changing the way they travel through the body, thus affecting the functions that these hormones control. According to a description by the European Commission (CEC 1999), an endocrine disruptor is "an exogenous substance or mixture that alters function(s) of endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub) populations". Two different classes of substances causing endocrine disruption can be identified: natural substances, including natural sexual hormones (estrogens, progesterone and testosterone) and phytoestrogens (chemicals produced by plants that act like estrogens in animal cells and bodies), xenobiotic substances, including synthetic hormones as the contraceptive 17α-ethinylestradiole (EE2) as well as man-made chemicals and their by-products (e.g., pesticides, cleaning agents, flame retardants, etc.).

Sumpter et al. [194] documented feminization of male and sexually immature fish caused by stimulation of vitellogenin synthesis in male fish by EDCs. Guillette et al. [195] noted changes in gonads of alligators. Several studies confirm that human estrogens, mainly 17β-estradiol (E2), estrone (E1) and

EE2 are responsible for a significant part of the endocrine-disrupting effects seen in the aquatic environment [185, 196]. They are known to have a strong biological impact already at very low concentrations of 0.1–0.5 ng L^{-1} [197]. Xenoestrogens like nonylphenol (NP) and bisphenol-A (BPA) are not as estrogenically active as for example E2, but due to their widespread production, they can be found in the environment at much higher concentrations [185].

Human excretion is thought to be the principal source of estrogens and progesterone. Although they undergo various transformations in liver of humans and mammalians (oxidation, deoxydation, hydroxylation and methylation), estrogens are principally excreted as inactive polar conjugates of glucuronide acid and sulphate [198]. However, these conjugates can be cleaved in WWTP due to the presence of β-glucoronidase and arylsulfatase enzymes of a bacterial sludge, and they reform original compounds [186, 199, 200]. Therefore the estrogenicity of the effluent is greatly increased, since the estrogenic potentials of conjugated forms of estrogens are clearly much lower [201].

Since EDCs are suspected to enter rivers, streams, and surface water through the effluents of WWTPs, the elimination of these substances in these treatment plants is of elementary interest. Different processes of varying efficiency are applied. Regarding conventional wastewater treatment, some authors consider that in current European activated sludge treatment plants with a HRT no greater than 14 h, the elimination of estrogens and progesterons present in the influent is not complete [186, 199, 202–204]. However, results obtained by now are very diverse, and efficiencies over 90% have been reported for E1, E2, and EE2 in various municipal WWTPs [151, 184, 185, 205–208]. Slightly lower removal of E1 is frequently detected in WWTPs, which is probably due to the conversion of E2 to E1 during the treatment and the cleavage of glucuronides [186, 209]. Advanced water-purification techniques like UV radiation, ozonization, or activated charcoal may significantly improve the removal of endocrine disrupters, but these techniques are not broadly applied because of their high cost.

Membrane bioreactor technology is a possibility to enhance the removal of EDCs.

Factors like high sludge ages and low organic loads could not yet be correlated to improved degradation capacity, although biomass compositions might influence hormone removal in MBRs [210]. Servos et al. [201] found that EE2 was not degraded under non-nitrifying conditions, while nitrifying sludge could oxidize it to more hydrophobic compound. Vader et al. [201] also showed that the EE2 degradation capability of sludge was associated to the nitrifying activity. This phenomenon is probably a reflection of improved biological diversity and growth conditions in these systems resulting in increased biological transformations. Synthetic estrogens in general exhibit greater resistance to the activated sludge process [211].

Besides aerobic biodegradation, sorption is also hypothesized as one of the main mechanisms for the elimination of hormones in the aquatic en-

vironment. However, there is no clear agreement about its relative importance [211]. Although E1 and E2 are relatively water soluble, a significant fraction can be associated with organic particles or colloids in the treatment systems, potentially influencing their degradation and ultimate fate [56]. Clara et al. [212] investigated sorption behavior of BPA, E2, and EE2. High adsorption potential to sewage sludge could be observed for these substances, with no saturation levels detected. However, at high pH values typical for WWTPs (due to the application limestone or milk of lime for sludge conditioning) it was observed a release of the adsorbed fractions of all three investigated substances. Several researchers have shown that higher pH values (pH > 11) led to an almost complete desorption of EDCs (ex. BPA), which generally exhibits phenolic character [212, 213]. Also, in the experiments of Reddy et al. [200] acidic pH showed to be the best method in preventing dissociation of the steroid conjugates to free steroids.

In a study by Joss et al. [205], the MBR elimination of natural estrogens E1 and E2 was seen to be higher than in the CAS sludge by the factor of 2–3. Higher removal rates in MBR compared to CAS could be explained by the smaller flock size of MBR sludge: it was measured to be $10–100\ \mu m$ for MBR flocks and $100–500\ \mu m$ for CAS [56]. The thickness of the boundary layer is estimated to be $10–20\ \mu m$ for MBR and $20–30\ \mu m$ for CAS flocks [205]. Although there is no information available as to where various estrogen degradations take place throughout the flock, on the flock surface (e.g., on the outer biofilm layer) or in the bulk medium (e.g., catalyzed by extracellular enzymes), it is considered that the size of flocks may also contribute to degradation activity of the sludge.

Among natural hormones, E2 is considered as highly biodegradable, while EE2 is slowly biodegradable [186, 214]. The removal of E2 was always recorded to be high regardless of pH [177]. In another study, the same authors found pH conditions irrelevant for the sorption of E1, E2, EE2, and BPA [170]. These estrogens do not have hydrophilic functional groups and therefore the decrease in pH has no effect on their water–sludge partition coefficient (K_p) [170]. A linear relationship was found between their $\log K_p$ and logarithm of K_{ow} (octanol-water partition coefficient, $\log K_{ow}$) values, which means that adsorption of compounds increases linearly with an increase in its hydrophobicity [170].

Generally, the micro and ultrafiltration membranes do not display a barrier effect to hormones, but compared to conventional secondary and tertiary systems, a high removal can be expected due to full particle retention promoting the adsorption onto the sludge flocks. Schäfer et al. [213] showed that particles of activated sludge could not only act like adsorbents of hormones but also like a dynamic membrane or rejecting layer for micropollutants. Although a certain estrogenic activity could be expected in MBR effluent (due to the cleavage of estrogen conjugates, or dissolution of particles due to digestion process that may release estrogens by desorption), membrane tech-

nology represents a good combination of different mechanisms for removal of endocrines. On one side, smaller floc sizes and higher sludge activity enhance biodegradation, and on the other particle size exclusion enables retention of the adsorbed compounds.

6.3
Removal of Surfactants and Their Degradation Products

Surface active substances are an extensively used group of chemicals, e.g., domestic detergents, pesticide formulations, industrial products, etc. Several main classes of surfactants (e.g., linear alkylbenzene sulphonates (LAS), alkylphenol ethoxylates (APEOs) and alcohol ethoxylates (AEO)) have shown very high ubiquity in the environment, thus presenting a serious environmental problem. Among the APEOs, octylphenol ethoxylates (OPEOs) and nonylphenol ethoxylates (NPEOs) are the two most common surfactants on the market. NPEOs account for about 80% of the total APEOs consumption: they are widely used in industry, agriculture, and households as detergents, emulsifiers, wetting agents, spermicides, and pesticides, etc [215]. Approximately, 500 000 tons are produced annually worldwide, 60% of which ends up in the aquatic environment [216, 217]. Anionic surfactants LAS are mainly used in laundry detergents and cleaning agents.

Numerous data on primary and ultimate biodegradation of LAS have been reported. It is expected for these compounds to undergo a primary degradation of up to 93–97%. Very high levels of biodegradation (97–99%) have been found in some WWTPs using aerobic processes [105, 218–220]. Therefore, LAS are generally regarded as biodegradable surfactants, with a breakdown mechanism that involves degradation of the straight alkyl chain, the sulphonates group and finally the benzene ring [221, 222]. Yet, biological degradation of LAS in WWTP is not complete since aerobic breakdown intermediates sulfophenyl carboxylates (SPC) are regularly found in WWTP effluents. In a study that covered eight municipal WWTPs in Western Europe, SPCs were detected in median effluent concentrations of 57 µg/L [223]. Besides their biological removal, the process of adsorption to sludge particles also occurs in WWTP. Berna et al. [224] reported that a significant proportion of LAS in raw sewage (10–35%) adsorbs to particulate matter. Moreover, longer alkyl chains confer greater hydrophobicity, thus increasing their adsorptive tendency [225]. LAS elimination in MBR unit has been reported to be very similar to a conventional treatment by several authors [105, 226, 227]. Both LAS and SPCs were reported to be removed to a high extent in these two treatment processes (96–98%) [228]. However, Bernhard et al. [228] studied elimination of persistent polar pollutants (P^3) pollutants in MBR and CAS, whereas MBR showed a significant improvement when removal of LAS is considered, and a slightly better performance regarding the attenuation of the concentration of SPC.

WWTP can eliminate parent compounds of NPEOs rather efficiently [227, 229–231]. However, in WWTPs APEOs degrade into more toxic shorter-chain APEOs and alkylphenols (APs) such as NP, octylphenol (OP), NP mono-, di-, and triethoxylates (NPEO1, NPEO2, and NPEO3) and NP carboxylates (NPEC1 and NPEC2). Many studies have reported on their wide occurrence in the environment [232–235]. It was observed a change in distribution of NP, NPEOs, and NPECs between WWTP influent and effluent [236, 237]. Ahel at al [237] noted that in the primary effluent NPEOs were the most abundant class (82.4%), while in the secondary effluent over 70% were metabolic products, the most abundant being NP1EC and NP2EC (46.1%) (Fig. 18).

Therefore, whereas in the influent NP and NP1EO are the main fractions, in the effluent NP1EC and NP2EC are the predominant ones [137, 237]. There is a concern that the concentration levels of these metabolites present in the environment may be sufficient to have endocrine disrupting effect on wildlife and humans [187, 238]. Moreover, during chlorination of wastewater, the residues of alkylphenolic compounds can be transformed into even more persistent halogenated derivatives that can reach drinking water systems [139].

Compared to conventional treatment, MBR technology has the advantage of giving an effluent with lower concentration of lipophilic metabolites. This is probably due to a better adaptation of microbial consortia which become more capable of degrading persistent NPEO oligomers (NPEO1 and NPEO2) [226]. The elimination efficiencies of parent nonylphenolic compounds in MBR unit and CAS treatment have been reported to be similar (> 90%) [226, 239]. In a study by González et al. [227], CAS treatment was
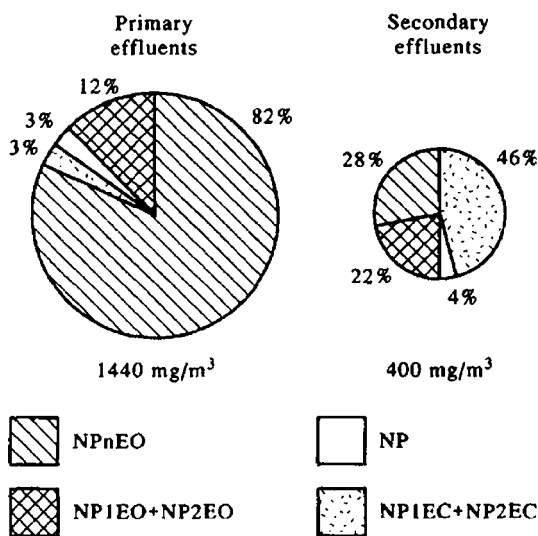

Fig. 18 Relative abundance of NPEOs and their metabolites in primary and secondary effluents (weight-based average value of 11 WWTPs in the Glatt Valley, Switzerland) [237]
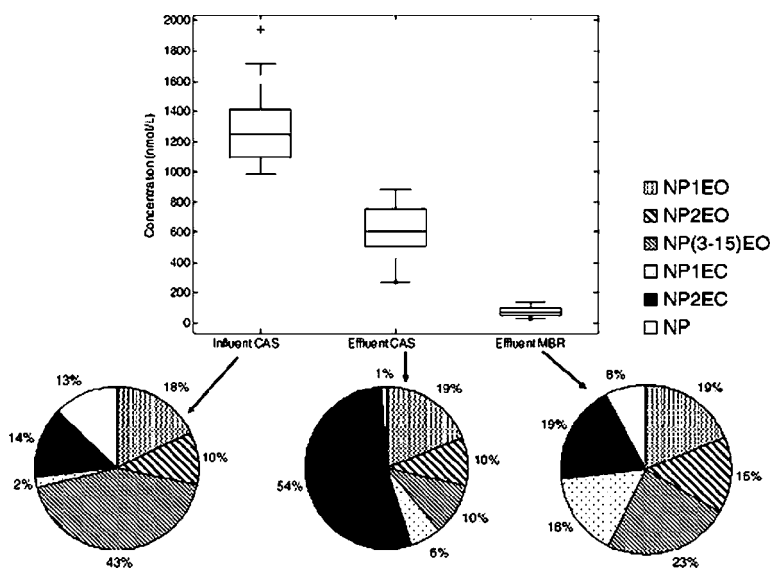
Fig. 19 Boxplot (calculated on a molar basis) and average composition of NP compounds in influent, CAS effluent and MBR effluent [227]

found to be generally inefficient in removing nonylphenolic compounds with overall elimination around 54%, while the ultimate elimination efficiency in the MBR reached 94%. The distribution of the nonylphenolic compounds in the MBR effluent showed rather proportional percentages of all species (23% of the parent compounds, 35% NPECs, 34% short ethoxy chain NPEOs and 8% NP) with overall much lower concentration of potentially estrogenic metabolites as compared to the CAS effluent (Fig. 19).

Considering that the primary biodegradation of APEOs results in the formation of various persistent metabolites that are usually poorly removed even in most efficient WWTPs and have a significantly enhanced removal in the MBR, membrane technology gives room for expectation that with this alternative wastewater treatment the ecological risk associated with alkylphenolic compounds as well as other ionic and non-ionic surfactants can be drastically reduced. The utilization of MBRs in municipal WWTPs may ensure efficient elimination and biodegradation of APEO-derived EDCs, thus reducing the ecotoxicity of effluents posed by those compounds.

6.4
Removal of Sulfonated Organic Compounds, Pesticides, Musk Fragrances and Other Micropollutants

Sulfonated organic compounds are frequently used in industrial processes [240–243] and often found in municipal effluents [240, 244]. Reemtsma

et al. [245] studied the performance of MBR system in eliminating naphthalene sulfonates and benzothiazoles. Technical mixtures of naphthalene monosulfonates (NSAs) and disulfonates (NDSAs) are widely used as dispersants in industrial processes. Benzothiazoles are a class of industrial chemicals that are used as fungicides, corrosion inhibitors and vulcanization accelerators. They reported very similar efficiencies of MBR and CAS treatment in eliminating naphthalene sulfonates for most of isomers, except for 1,7- and 2,7-NDSA who were subjected to more complete degradation in MBR system, probably due to low substrate supply and a high sludge age [245]. In both treatments disulfonates were poorly removed, while the removal of NSAs was a lot better (1-NSA and 2-NSA were had removal rates greater than 99%). This was probably due to better capability of MBR sludge to biodegrade these micropollutants, since due to their great polarity and low molecular weight removals by sorption and membrane rejection can be excluded [245].

In the same study, benzothiazoles were removed by membrane treatment with an average of 87%. However, strong differences were reported for various benzothiazoles: while the concentration of benzothiazole (BT) was lowered for only 37%, up to 99% of mercaptobenzothiazole (MBT) was degraded. Practically no removal was noted for aminobenzothiazole (ABT), hydroxybenzothiazole (OHBT), and methylthiobenzothiazole (MTBT). In another study, two MBRs operating in parallel with CAS treatment were monitored in Berlin, Germany [246]. Performance of two membrane units regarding the removal of benzothiazoles was significantly better than in the treatment (43% and 10%, respectively). The greatest difference in efficiency between MBR and CAS was detected for BT, which was removed significantly better in the MBR (70%) [246]. The process of the aerobic degradation benzothiazoles is largely unknown: although some benzothiazoles are degraded in activated sludge system, most of laboratory data on the pathways of their biodegradation are inconclusive.

Pesticides continue to be the focus of many environmental studies and contamination of water resources by pesticide residues is one of the major challenges for the preservation and sustainability of the environment. Inappropriate use of pesticides can give rise to severe and long-lasting ecological damage through pesticide-containing wastewaters that enter the environment. Acidic herbicides such as phenoxy acids (MCPP, MCPA, 2,4-D, 2,4-DP) and bentazone represent an important class of pesticides used not only in the control of weeds in crops but also as algicides in paints and coatings and roof-protection agents. Bernhard et al. [228] compared removals of several persistent polar pollutants in MBR and CAS. In the case of pesticides, some of them were found to be poorly degradable in both WWTP and CAS (e.g., atrazine, bentazone, isoproturon), while 2,4-dichlorobenzoic acid was rapidly eliminated in both treatments. González et al. [168] also noted a good MBR removal of 2,4-D and persistence of bentazone on the other side. For compounds like MCPP and MCPA, the importance of acclimation period was emphasized, con-

sidering that their degradation was significantly higher after a lag period of microorganisms [168]. However, the advantage of MBR in comparison with other investigated processes is high unit-volume removal rate. For example, in other investigated treatments of 2,4-D polluted wastewaters such as conventional activated sludge processes [247, 248], sequential batch reactors [249], and the anaerobic fluidized bed reactor [250], it was found to be very low, even at highest elimination efficiencies (0.02 to 0.3 kg 2,4-D m^{-3} day^{-1}). Significant improvement in biodegradation when using MBR instead of CAS treatment was reported for insect repellents and metabolites Bayrepel, Bayrepel acid and DEET [228]. These compounds were very persistent during conventional treatment, but achieved high removals in the membrane unit.

Polar compounds can spread along a partially closed water cycle after discharge with municipal wastewater and occur in raw waters used for drinking water production. For compounds like ethylenediamino tetraacetate (EDTA), TCPP, and TCEP, their potential to spread with the water along its flow path and penetrate into groundwater from infiltrated surface waters has been shown in several studies [251–253]. EDTA is utilized in many industrial applications and in households and has been proven to be widely distributed in aquatic systems [254]. EDTA was detected in very high medium concentration in European municipal WWTP effluents and surface waters, 60 $\mu g\,L^{-1}$ and 3.7 $\mu g\,L^{-1}$, respectively [223]. This compound showed an extremely recalcitrant behavior during conventional and membrane treatment as well [228]. Another poorly degradable compound in both CAS and MBR is flame retardants (TCEP, TCPP) [228]. Moreover, no enhancement in their removal could be observed when increasing SRT [228]. For the compounds that cannot be removed effectively, new emission limits should be set and also certain strategies for their avoidance, in order to prevent their entrance into closed water cycles.

Benzotriazoles are a class of high-production-volume chemicals that are used as corrosion inhibitors in various industrial processes and in households. They were detected in WWTP effluents and surface waters [140, 255]. Treatment of municipal wastewater by MBR instead of CAS also improves the removal of benzotriazoles (61 and 37% on average, respectively) [256]. Also, MBR was able to cope with elevated influent concentrations without responding with elevated effluent ones, and stability of performance with changes in temperature between summer and winter was found to be greater in the membrane unit [256].

Submerged MBR also showed to be very efficient when treating polymeric industrial wastewater, like high-strength acrylonitrile-butadiene-styrene wastewater [257]. Moreover, very high removal of metals and polycyclic aromatic hydrocarbons (PAHs) was noted in submerged ultrafiltration MBR operating in alternate aerobic/anoxic cycles mode [258].

Musk fragrances tonalide and galaxolide are generally removed to the same extent (85%) in MBR and CAS, with slightly lower effluent concentrations in the MBR unit [106, 137]. As both substances are very hydrophobic, for

an estimation of the mass flux, specific K_ds have to be included. Sorption co-efficients of these compounds were determined to be 5200 and 7900 L kg^{-1} for galaxolide in CAS and MBR sludge, respectively, and 10 800 and 16 000 L kg^{-1} for tonalide, respectively [259]. Diurnal variation pattern of tonalide (AHTN) and galaxolide (HHCB) were paralleled by the nitrogen load, suggesting that human excretion was a major source of these micropollutants, as well as it was the case with PhACs [146]. Their elimination was around 50% during biological wastewater treatment, which was estimated to be mainly due to their sorption onto sludge particles [146].

Polar compounds may occur in WWTP effluents because of their persistence during the activated sludge treatment or because of their incomplete microbial degradation. Sorption of these polar pollutants to wastewater solids can be neglected. However, there can be present significant ionic interactions, especially for organic cations. Moreover, concentrations of metabolic products may increase after wastewater treatment, even though the compound is degradable, provided that their formation proceeds faster than its further transformation. General concern about the presence and behavior of organic micropollutants and restrictive legislation on their management and final destination invite to enhance the actual treatment processes and to find a reliable alternative.

7
Advantages and Drawbacks of MBR Technology

A need for the development of MBR technology arose mainly from the limitations of the CAS process. It is of interest here to describe CAS in more detail, since it has been used successfully for almost a century in wastewater treatment. CAS in its most simple manner consists of a primary physical treatment that includes screening of gross solids and sedimentation of settleable solids followed by biological treatment with activated sludge, and subsequent secondary sedimentation where activated sludge in the form of flocs is separated from treated water by gravitational force. The biological step is carried out in an aerated bioreactor in the presence of mixed microbial culture, where pollutants from water are degraded by microorganisms and turned into microbial biomass and gases such as carbon dioxide, water, and inorganic nitrogen products. This stage may include an anoxic zone preceding the aerobic zone within the single reactor or a separate post-denitrification reactor to achieve a complete nitrogen removal. Also, preliminary anaerobic zone for biological removal of phosphorus is available. The settled sludge is returned to the bioreactor while excess sludge additionally grown during the process is being constantly removed. Essentially, the process uses aerobic microbial biodegradation of organic matrix presented in wastewater in the same manner as the natural microbial community in the water bodies would, if given enough time

and oxygen. The final products of the process are treated water and excess sludge. Treated water is usually discharged into water bodies such as lakes and rivers, while excess sludge ends up mostly as a fertilizer in agriculture or it is disposed of on land. Some countries like Germany and Switzerland forbade the use of secondary sludge in agriculture and excess sludge is incinerated together with hazardous wastes. In any case, the processing of this sludge, which includes operations like thickening, anaerobic stabilization, chemical conditioning, dewatering and thermal reduction [260], represents a cost and a problem that has to be dealt with. Land application of sewage sludge in agriculture is very restricted owing to the presence of potentially toxic substances, i.e., heavy metals, pathogens, persistent organic pollutants, etc. Critical shortage of available land coupled with new, more-stringent regulations for design and operation of landfills have caused prices of their sighting, building, and operating to rise sharply. Incineration is usually the final option for sewage sludge treatment due to an abundant ash generation, which has a high content of heavy metals and is generally toxic.

Therefore, high sludge production is one of the main drawbacks of CAS. Currently, reduction of sludge wasting is a major challenge of biological wastewater treatment. Excess sludge processing and disposal could account for about 50–60% of the total cost of wastewater treatment [261, 262]. The ideal way to solve the problem of sludge post-treatment and disposal is to reduce its production. To reduce the production of biomass, the wastewater process must be engineered in such a way that substrate utilization is diverted from assimilation of carbon for biosynthesis to non-growth activities of a microbial community. In activated sludge plants, the sludge-yield coefficient (Y) is typically 0.5. [263]. According to Urbain et al. [264], the yield coefficient for an aerobic membrane separation process treating municipal wastewater (488 ± 143 mg COD/L) was 0.23 kgSS kgCOD$_{removed}^{-1}$. Pollice et al. [99] reported a production of sludge in an MBR of 0.12 gVSS gCOD$_{removed}^{-1}$, which was in accordance with previously reported yields for MBRs [34, 42, 65, 263]. This advantage of MBR, together with the abandonment of energy-demanding sludge recirculation loop in CAS, contribute to better competitiveness of membrane technology compared to the conventional one.

The limiting step in the conventional treatment is the separation of sludge from the treated water. Without a good sedimentation in secondary settler, parts of the sludge end up in treated water, which leads to poor removal efficiency. It should be noted that during the normal operation of CAS per each kg of BOD$_5$ removed up to 0.6 kg of microbial biomass is formed [265], so if the separation of activated sludge is not properly carried out, the whole treatment process loses its purpose. Sedimentation of sludge is influenced by the characteristics of microbial flocs as a function of their physiological state. In other words, the biological process must be operated in such a way to allow the formation of easily settling microbial flocs. Sludge with poor settling characteristics is often called "bulking sludge", and in most cases this prob-

lem occurs due to the growth of filamentous bacteria. In filamentous growth, bacteria form filaments of single-cell organisms that attach end-to-end and normally protrude out of the sludge floc. Common filamentous organisms are *Sphaerotilus natans*, *Microthrix parvicela* and *Thiothrix* spp. The main reasons for bulking are low DO concentration, low F/M ratio, and nutrient deficiency. At such conditions of low substrate concentration, filamentous organisms, due to their increased surface-to-mass ratio can compete better for substrate and overgrow the floc-forming organisms. While DO concentration can be provided by a proper aeration system, problems with variations in wastewater flow rate and composition can seriously affect the CAS process. The usual measures for bulking control are the addition of flocculants like ferric chloride and aluminum sulphate to the settler, or chlorination of return sludge (0.002 to 0.008 kg of chlorine per kg of MLSS per day) since filamentous bacteria is more sensitive to oxidative agents. Also, if the design of the plant allows, bulking can be mitigated by setting the operational parameters (such as the F/M ratio) high enough to enhance the growth of floc-forming organisms. By doing so, microorganisms of the activated sludge are kept in the exponential growth phase in which they produce a large amount of excess biomass. To achieve high F/M, the MLSS in the aeration basin has to be kept low (around $3–5\,\mathrm{g\,L^{-1}}$ dry mass weight) while the concentration of the organic matter in the feedwater needs to be high. These conditions are usually easy to achieve with municipal wastewater with a small amount of industrial wastewater and drainage water. In the cases where drainage water dilutes the wastewater significantly, or industrial wastewater adds its components to the influent, the efficiency of CAS can be seriously lowered due to a poor sedimentation of microbial flocs.

The quality of CAS effluent is another important issue. Firstly, microbiological contamination of the effluent may be significant since there is no physical barrier between activated sludge and treated water. A correlation has been reported between the occurrence of eye and ear infections in humans and their contact with water where recreational use occurs (e.g., rivers or lakes) that has been receiving CAS effluents [266]. This problem is even more pronounced if hospitals discharge their wastewater into sewage without treatment, because of the increased number of pathogens that may be found in raw sewage and in the effluent.

Also, there is a problem with specific compounds whose biodegradation depends on specialized microbial species. If such species have a slow growth rate they will be washed out with the excess sludge during the constant and fast sludge disposal rate (i.e., short SRT) of CAS treatment. As a consequence, specialized slow-growers may not develop in sufficient number to degrade efficiently some trace pollutants. Emerging contaminants in municipal wastewater and their fate in the environment have become an issue of importance for the legislators and decision-makers. Since the design of most municipal WWTPs does not allow operation at longer SRTs, they may not be

suitable for degradation of some organic micropollutants. To overcome the limitations of conventional treatment with activated sludge, MBR technology can be successfully employed. While bacteria in activated sludge decompose and degrade organic matter from the wastewater, membrane separates them from the treated water, thus replacing the secondary settler used in CAS. The simple change from one physical separation technique to another leads to quite complex changes in the process characteristics. It affects the sludge characteristics in several ways.

During CAS wastewater treatment, the bacterium present can survive in the bioreactor only in the form of flocs because the ones that do not settle are discharged with the treated water. Also, due to its short SRT, it is necessary for all microorganisms to grow fast or otherwise they will be washed out from the bioreactor. In other words, microbial population in CAS is selected among fast-growing and floc-forming species. On the contrary, in the case of MBR, the bacterial ability to settle and to grow fast is of negligible importance. MBR works at much longer SRTs, which can be measured in months rather than days. As an illustration, the SRT for a full-scale MBR for municipal water treatment (Porlock, UK, 1900 m^3/d) was reported to be 30–60 days [4] in comparison with the typical SRT of the conventional process with activated sludge, which ranges from 3 to 15 days [260]. In such conditions, slower-growing species with the ability to decompose less-biodegradable compounds have the opportunity to proliferate. In other words, in MBR selection among microorganisms is primarily made by their capability to degrade the substrate, which is also the primary purpose of the treatment process.

Without demand for settling of the sludge, the F/M ratio can be set much lower, thus allowing operation at much higher MLSS concentrations, which consequently leads to higher volumetric efficiency of the process. Given the reduction in bioreactor volume, the elimination of secondary clarifiers and the elimination of granular media filters, MBR typically has a much smaller footprint relative to CAS, when achieving the same discharge limits. Due to this footprint reduction, other concerns such as esthetics and odors can be more easily addressed.

A low F/M ratio means that less substrate is available per unit of biomass. According to the maintenance concept introduced by Pirt [37], part of the energy contained in the supplied substrate is used for maintenance functions that are independent of growth rate. When the energy supplied to the bioreactor is lowered, the biomass ceases to grow and to utilize the substrate for maintenance. In this manner, the sludge production in the process is much lower, or does not occur at all. Very low sludge production in pilot MBR operations are reported [16], but it is often impractical for full-scale operations to keep F/M too low. The design of such plants would include very high MLSS concentrations that can promote membrane clogging, or large bioreactors, which contributes to the initial capital cost. Moreover, high MLSS concentration reduces aeration efficiency, which is possibly the most significant problem with maintenance of

high MLSS concentration. Nevertheless, due to the low F/M ratio, there is a significant decrease of sludge production in MBR in comparison to CAS, which then decreases the cost of excess sludge handling.

As water reuse and reclamation increases, MBR technology can make reclaimed water more accessible by achieving the reclaimed water treatment standards in nearly a single step, thus reducing the complexity of these systems. Further, the use of reclaimed water reduces the stresses on other water bodies by reducing the need for water withdrawals and by reducing pollutant loading. In the United States, reclaimed water is being used to augment drinking water supplies. Required treatment involves multiple steps, typically culminating in RO. In wastewater treatment, RO typically is preceded by MF or UF to reduce RO membrane fouling. Therefore, implementation of an MBR process provides the flexibility to install RO without the expense of a pre-treatment process.

With the use of UF membranes (effective pore size of $0.04\,\mu m$) instead of CAS, most of the pathogens of concern in wastewater can be significantly removed from the effluent. The membranes provide an additional barrier to *Faecal coliform*, *Cryptosporidium*, and *Giardia* even in processes that use MF membranes due to a dynamic film layer over the membrane that reduces the effective filtration pore size [267]. In addition, the clarity of the effluent produced by the MBR process is consistently below 0.1 nephelometric turbidity units (NTU), which is comparable to drinking water standards. This low turbidity can result in an effluent highly amenable to final disinfection using ultraviolet light. Membrane filtration followed by ultra-violet (UV) treatment results in a highly disinfected effluent.

MBR systems do not require any more significant operational attention, in each case much less than CAS process. A process control of an MBR system is reduced to monitoring the MLSS concentration, occasional adjustments of the chemical feed rates, and scheduling membrane recovery cleaning. Therefore, MBR is a much better solution for the small plants where CAS is non-feasible due to its requirement for constant attention and monitoring.

On the other side, the cost of oxygen demand is superior in MBR. Energy consumption of MBR comes from power requirements for pumping feed water, recycling retentate, permeate suction (occasionally) and aeration [268]. The two MBR configurations have substantial differences in terms of aeration. In the side-stream configuration, aeration is supplied by fine bubble aerators that are highly efficient for supplying oxygen to the biomass. In submerged MBRs, the aeration mode is turbulent and cross-flow is generated, which scours the membrane surface and provides oxygen to the biomass. Aeration cost in the latter-mentioned configuration represents around 90% of the total costs, whereas in side-stream MBR, only ∼20% derives from it [269]. However, energy consumption of the side-stream system is usually two orders of magnitude higher than that of submerged systems. These low costs of submerged MBRs are associated with low fluxes, which in turn increase capital costs and

footprints. Also, packing density influences the final cost of MBR: low packing densities of membrane modules mean that higher specific area of membrane is required to produce the same flux, which increases the energy requirements.

There are certain drawbacks for wider implementation of MBR technology. MBR is widely viewed as being a state-of-the-art technology but is also sometimes seen as high-risk and prohibitively costly compared to CAS and other more established technologies. MBRs were historically perceived as suitable only for small-scale plants with high operator skill requirements, and the key operating expenditure parameters such as membrane life unknown [4]. Many of these drawbacks are no longer true. Perhaps the biggest challenge to companies active in the market is to persuade decision-makers of the capability of MBRs and what benefits they will undoubtedly bring to the customer. In the past, there were an insufficient number of full-scale MBR treatment plants to convince decision-makers of the reliability of this advanced treatment. Presently, there are a number of examples of successful implementation of MBRs across the range of applications, and there is certainly less reason to be suspicious of this technology.

8
Application and Cost Analysis of a Membrane Bioreactor

MBRs became commercially available more than 10 years ago, and their market has continued to grow. In the beginning of their application, the customers were put-off by the high-costs, appropriate operating skills, and high-level maintenance labor. However, the technology was improved, and now there are many manufacturers of MBRs, including Zenon Environmental, Kubota, Ionics/Mitsubishi rayon, USFilter, Aqua-Aerobics7Pall and Norit X-flow. There are more than 2200 MBR installations in operation or under construction worldwide [270]. The main world MBR providers and characteristics of their systems are presented in Table 2.

Kubota (Japan) has installed most of the world's MBRs while Zenon (Canada) dominates in regard to installed capacity having almost four times more water treated through their membranes than Kubota [4]. Zenon has installed about 85% of North American installations, which comprise about 11% of the world's MBR market. Asian markets (mostly in Japan and South Korea) have employed MBR technology mostly for small-scale domestic applications. In general, most of the MBRs in operation are medium or small-scale plants. More than 85% of Kubota's MBRs have flows less than 200 m^3 d^{-1} while out of 219 MBR plants that treat municipal wastewater in North America, only 17 exceed 10 000 m^3 d^{-1}. The largest capacity plant in operation is in North America (Traverse City, MI), which operates at 26 900 m^3 d^{-1}, while the largest MBR worldwide currently is in Kaarst, Germany (48 000 m^3 d^{-1}) with total membrane area of 84 480 m^2 [4]. Both of these plants operate with Zenon

Table 2 Comparison of the main MBR systems (adapted from Yang et al. [270])

	Kubota (Japan)	Mitsubishi-Rayon (Japan)	Zenon (Canada)
Number of installations[a]	1538 (1138 + 400)	374 (170 + 204)	331 (204 + 127)
Membrane Configuration	FS Vertical immersion	HF Horizontal immersion	HF Vertical immersion
Pore size (μm)	0.4	0.1/0.4	0.04
Material	Chlorinated PE	PE	PVDF
Module size (m^2)	0.8	105	31.6
Cleaning method	Relax	Relax	Backpulse and relax
Cleaning frequency (min/min)	1/60	2/12	0.5/15
Recovery method	Chlorine backwash	Chlorine backwash	Chemical soak

[a] Municipal WWTPs + Industrial WWTPs

membranes. Leading manufacturers have exponential growth in the number of installed MBRs and their cumulative capacity in the last decade. Although the market is still dominated by Zenon and Kubota, there is a wide range of MBR systems available, however most are still at the development stage. The photographs of typical Zenon and Kubota membranes are presented in Figs. 20 and 21, respectively.

Fig. 20 Kubota flat sheet MBR

Fig. 21 Zenon hollow-fiber MBR, ZeeWeed 500a membranes

The side-stream MBRs that were predominant before the 1990s are still present on the market but they hold a smaller share. The main manufacturers of side-stream MBR systems are Norit X-Flow, Millenniumpore and Novasep-Orelis. Most of the side-stream MBRs today treat industrial wastewaters or landfill leachates.

Municipal wastewater treatment is both the earliest and largest application of MBR, and it is predicted that this will continue to be its primary use. Due to its small footprint and potential for reuse of high-quality effluent, MBR is capable of coping with population growth and limited space. For industrial applications where more stringent regulations are imposed, it provides an effluent that can be safely discharged into the environment. The main applications of membrane technology reported in industry are for treatments of heavily loaded wastewaters such are oily wastewaters [62], or discharges from tanneries [245] and textile industries [271]. Promising applications also exist in treating landfill leachate, chlorinated solvents in manufacturing wastewater, and for groundwater remediation.

Energy usage for membrane aeration is a significant operating cost for any membrane bioreactor facility. Yoon et al. [272] calculated the total variable operational cost of MBR by summing the decreasing sludge-treatment cost and increasing aeration cost (see Fig. 22). Since minimized sludge production implies maximized aeration cost, and vice versa, they considered the existence of an optimum point between these two extreme cases, where
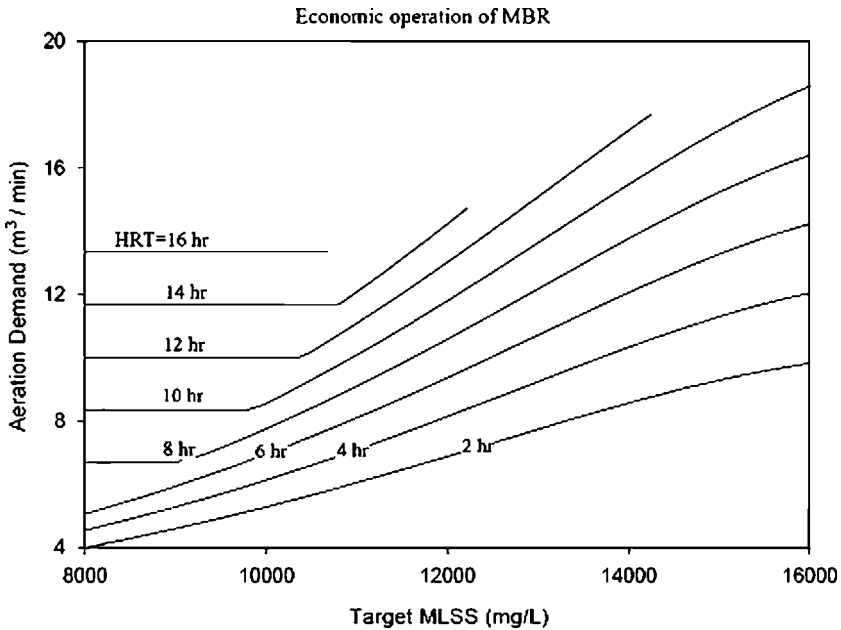
Fig. 22 Aeration demand for biodegradation of organic matters as a function of target MLSS and HRT. Flow rate and COD of influent were 1000 m³ day⁻¹ and 400 mg L⁻¹, respectively [272]

the total operational cost is minimized. They concluded that for reasonable ranges of HRT and MLSS sludge treatment cost overwhelms aeration cost, so the most adequate strategy for MBR cost reduction would be maintenance of low sludge production conditions. High SRT in an MBR means a high MLSS concentration and low F/M ratio, which enables application of short HRT. However, sludge production is obviously inversely proportional to HRT when MLSS is mixed. The shortest HRT and the minimum sludge production cannot be achieved simultaneously.

Furthermore, overall membrane cost has decreased exponentially over time for all main manufactures. Relative decrease for Kubota MBR systems and cost of Kubota membrane over the years is given in Fig. 23 [273]. As can be seen, the membrane whole-life costs decreased more than eight times in last 15 years, which has considerably closed the gap in prices between ASP and MBR technologies. Since the expected membrane lifetime has increased and enough full-scale plants have been successfully operated and proven to be reliable, the MBR technology is becoming increasingly competitive, and its future market position should be guaranteed.

Despite its relative youth, MBR technology has developed over a decade to a mature product available for all sizes of application, in domestic, municipal, or industrial sector. Further improvement of the process will increase
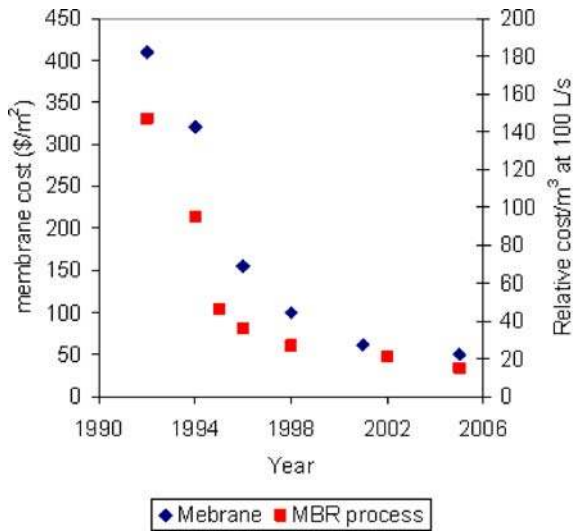
Fig. 23 Relative cost decrease of Kubota membranes and MBR systems (adopted from Kennedy et al. [273])

its cost-effectiveness and MBR technology is expected to play a key role for wastewater treatment in the next years, in Europe as well as worldwide. To date, European countries with the highest number of full-scale MBR plants are England, France, Germany, Belgium, and the Netherlands. MBR markets are expected to open in other countries as well: in dry southern states like Spain, Greece, and Italy, due to their water shortages, and in Central and Eastern European countries (such as Hungary, Poland, Bulgaria, etc.) that will be obligated to develop their wastewater treatment technologies and adapt them to the standards and environmental legislation of the European Union.

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