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Recalcitrant industrial wastewater treatment by membrane bioreactor (MBR)

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Abstract

Membrane Bioreactor (MBR) process consists of a biological reactor integrated with membranes that combine clarification and filtration of an activated sludge process into a simplified, single step process. The membrane is an absolute barrier to suspended matter and microorganisms and it offers the possibility of operating the system at high mixed liquor suspended solids (MLSS) concentration. The implication of maintenance of high MLSS are— requirement of a smaller footprint and operation at high solids retention time (SRT) under low F/M ratio, hence, yielding reduced excess sludge. Operating as an MBR allows conventional activated sludge plants to become single step processes, which produce high quality effluent potentially suitable for reuse. Accordingly, over the past decade, submerged MBR processes have experienced unprecedented growth in domestic and municipal wastewater treatment/reuse. Application of MBR technology for industrial wastewater treatment has also gained attention because of the robustness of the process. Theoretically, maintenance of long SRT in MBR is in favor of the retention and development of special microorganisms, which may lead to better removal of refractory organic matter and make the system more robust to load variations and toxic shocks. Although in general MBR exhibits much improved overall treatment of concentrated industrial wastewater as compared to conventional activated sludge process, literature suggests that the conceptual expectation of enhanced biodegradation of hardly biodegradable compounds in MBR does not often come true. Very often the improved removal has been attributed to the adsorption of target compounds on sludge, which implies that further treatment of the periodically withdrawn, toxic compound-laden sludge would be required. Improved biodegradation to certain extent has been reported in a few studies; however the underlying factors leading to such improvement still remains to be elucidated. This chapter provides a comprehensive review of the studies dealing with recalcitrant industrial wastewater treatment by MBR, and casts light on the strategies to achieve enhanced biodegradation of hardly biodegradable industrial pollutants in MBR.

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Recalcitrant industrial wastewater treatment by membrane bioreactor (MBR)

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ABSTRACT

Membrane Bioreactor (MBR) process consists of a biological reactor integrated with membranes that combine clarification and filtration of an activated sludge process into a simplified, single step process. The membrane is an absolute barrier to suspended matter and microorganisms and it offers the possibility of operating the system at high mixed liquor suspended solids (MLSS) concentration. The implication of maintenance of high MLSS are— requirement of a smaller footprint and operation at high solids retention time (SRT) under low F/M ratio, hence, yielding reduced excess sludge. Operating as an MBR allows conventional activated sludge plants to become single step processes, which produce high quality effluent potentially suitable for reuse. Accordingly, over the past decade, submerged MBR processes have experienced unprecedented growth in domestic and municipal wastewater treatment/reuse. Application of MBR technology for industrial wastewater treatment has also gained attention because of the robustness of the process. Theoretically, maintenance of long SRT in MBR is in favor of the retention and development of special microorganisms, which may lead to better removal of refractory organic matter and make the system more robust to load variations and toxic shocks. Although in general MBR exhibits much improved overall treatment of concentrated industrial wastewater as compared to conventional activated sludge process, literature suggests that the conceptual expectation of enhanced biodegradation of hardly biodegradable compounds in MBR does not often come true. Very often the improved removal has been attributed to the adsorption of target compounds on sludge, which implies that further treatment of the periodically withdrawn, toxic compound-laden sludge would be required. Improved biodegradation to certain extent has been reported in a few studies; however the underlying factors leading to such improvement still remains to be elucidated. This chapter provides a comprehensive review of the studies dealing with recalcitrant industrial wastewater treatment by MBR, and casts light on the strategies to achieve enhanced biodegradation of hardly biodegradable industrial pollutants in MBR.

INTRODUCTION

Membrane Bioreactor (MBR) process is a hybrid system amalgamating membrane separation with biological treatment [1]. Operating as an MBR allows conventional activated sludge plants to become single step processes, which produce high quality effluent potentially suitable for reuse. Over the past decade, submerged membrane bioreactor (MBR) processes have experienced unprecedented growth in domestic and municipal wastewater treatment owing to several advantages including excellent effluent quality, low sludge production, small foot print, and flexibility in future expansion [1,2]. Application of MBR technology for industrial wastewater treatment has also gained attention because of the robustness of the process.

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High organic loadings and very specific, biorefractory, inhibiting and difficult to treat compounds are the major characteristics of industrial waste streams that render alternative treatment techniques such as the MBR desirable. The technical features of the reactor play an important role in solid separation and biomass selection. However, it is important to highlight that industrial wastewater may heavily influence the microbial selection process within an MBR because of the presence of refractory compounds [3]; and the efficiency in the removal of the organic load depends on the type of industrial process that has been implemented and consequently on the quantity of non-biodegradable compounds.

Although MBRs in recent years have been proved to be effective and economically feasible for treatment of various kinds of high strength, refractory, and/or toxic wastewaters, the mechanisms of refractory chemical oxygen demand (COD) removal still remain to be well-documented. The researchers are yet to reach at a consensus about the underlying reason(s) of their superiority—whether this is due to the development and maintenance of special degrading microbes or simply due to the maintenance of higher biomass concentration and longer sludge retention time (SRT). This chapter addresses this question by providing a comprehensive review of the studies dealing with recalcitrant industrial wastewater treatment by MBR and offers unique insights into this matter.

BACKGROUND

Inception of the MBR technology

Biological treatment technologies have been utilized in wastewater reclamation for over a century. Out of the many different processes employed, the activated sludge system has proven to be the most popular [4]. Increasing volumes of wastewater combined with limited space availability and progressively tightening environmental standards has promoted the development of new intensive biotechnological processes for wastewater treatment. The implementation of membranes within the treatment sequence of a water pollution control facility was initially limited to tertiary treatment and polishing. Ultra-filtration, micro-filtration, or reverse osmosis units were utilized in areas where discharge requirement were very stringent or direct reuse of the effluent was desired [4]. High capital and operational costs as well as inadequate knowledge on membrane application in waste treatment were predominant factors in limiting the domain of this technology. However, with the emergence of less expensive and more effective membrane modules and the implementation of ever-tightening water discharge standards, membrane systems regained interest. Membrane modules have evolved from being utilized solely in tertiary wastewater treatment to being integrated into secondary wastewater treatment. These systems are now most commonly referred to as membrane bioreactors (MBRs). **Figure 1** summarizes the evolution of membrane use in wastewater treatment and demonstrates the basic differences in the treatment trails.

*Insert **Figure 1** near here*

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By the mid 1990s, the development of less expensive submerged membranes made MBRs a real alternative for high flow, large scale municipal wastewater applications [5]. Over 1,000 MBRs are currently in operation around the world with approximately 66% in Japan, and the remainder largely in Europe and North America. Out of these installations, about 55% use submerged membranes while the rest have external membrane modules [6].

Advantages and Limitations

There are several advantages associated with the MBR technology which make it a valuable alternative over other treatment techniques. The MBR system is particularly attractive when applied in situations where long biological solids retention times are necessary, and physical retention and subsequent hydrolysis are critical to achieving biological degradation of pollutants [7].

First of all, the retention of all suspended matter and most soluble compounds within the bioreactor leads to excellent effluent quality capable of meeting stringent discharge requirements and opening the door to direct water reuse [1]. The possibility of retaining all bacteria and viruses results in a sterile effluent, eliminating extensive disinfection and the corresponding hazards related to disinfection by-products. Since suspended solids are not lost in the clarification step, total separation and control of the solid retention time (SRT) and hydraulic retention time (HRT) are possible enabling optimum control of the microbial population and flexibility in operation.

The absence of a clarifier, which also acts as a natural selector for settling organisms, enables sensitive, slow-growing species (nitrifying bacteria, bacteria capable of degrading complex compounds) to develop and persist in the system even under short SRTs [8,9].The membrane not only retains all biomass but also prevents the escape of exocellular enzymes and soluble oxidants creating a more active biological mixture capable of degrading a wider range of carbon sources [10].

MBRs eliminate process difficulties and problems associated with settling, which is usually the most troublesome part of wastewater treatment. The potential for operating the MBR at very high solid retention times without having the obstacle of settling, allows high biomass concentrations in the bioreactor. Consequently, higher strength wastewater can be treated and lower biomass yields are realized [11]. This also results in more compact systems than conventional processes significantly reducing plant footprint making it desirable for water recycling applications [12]. The low sludge load in terms of BOD forces the bacteria to mineralize poorly degradable organic compounds. The higher biomass loading also increases shock tolerance, which is particularly important where feed is highly variable [13]. The increased endogenous (autolytic) metabolism of the biomass [14] under long SRT allows development of predatory and grazing communities, with the accompanying trophic-level energy losses [15]. These factors, in addition to resulting in lower overall sludge production, leads to higher mineralization efficiency than those of a conventional activated sludge process. High molecular weight soluble compounds, which are not readily biodegradable in conventional systems, are retained in the MBR [16]. Thus, their residence time is prolonged and the possibility of oxidation is improved. The system is also able to handle fluctuations in nutrient concentrations due to extensive biological acclimation and retention of decaying biomass [17].

The disadvantages associated with the MBR are mainly cost related. High capital costs due to expensive membrane units and high energy costs due to the need for a pressure gradient have characterized the system. Concentration polarization and other membrane fouling problems can lead to frequent cleaning of the membranes, which stop operation and require clean water and chemicals. Another drawback can be problematic waste activated- sludge disposal. Since the MBR retains all suspended solids and most soluble organic matter, waste-activated-sludge may exhibit poor filterability and settleability properties. Additionally, when operated at high SRTs, inorganic compounds accumulating in the bioreactor can reach concentration levels that can be harmful to the microbial population or membrane structure. Details on this aspect is available in the literature [1,2,18].

RECALCITRANT WASTEWATER TREATMENT

Micropollutants

Several pharmaceuticals, ingredients of personal care products and so-called endocrine disrupting compounds (EDCs) (hormones and chemicals, which are suspected to have an impact on humans and wildlife hormone systems) are detected in surface waters all over the world. Most of those compounds are of anthropogenic origin and wastewater treatment plant (WWTP) effluents are important point discharges for the presence of endocrine disrupting compounds and residuals of pharmaceuticals in rivers, streams and surface waters.

The presence of elevated concentrations of natural or anthropogenic chemicals under suspicion as endocrine disrupters (EDCs) [19] in the aquatic environment has initiated comprehensive analytical research activities. These EDCs which can cause severe interferences in the hormonal systems of aquatic organisms [20] are discharged with wastewater treatment plant (WWTP) effluents into receiving waters because of incomplete elimination during wastewater treatment. Concentrations of natural and anthropogenic estrogens in effluents of WWTPs as major point sources for these compounds can still reach levels high enough to induce estrogenic effects in aquatic organisms [21].

Wastewater reclamation has been attracting attention as a potential countermeasure for alleviating water shortage problems. To ensure the safety of reclaimed water, enhanced treatment for toxic trace chemical pollutants, such as endocrine disrupting chemicals (EDCs), is required. The membrane bioreactor (MBR) is an effective wastewater treatment process developed in recent decades, and is a potential technique for wastewater reclamation. Although the effluent quality of MBR is generally better than that of conventional treatment processes, it is unknown whether it is effective enough to remove EDCs. The available studies indicate that the MBR has the potential to remove EDCs, but the fate of EDCs in the treatment process is not yet clear. Moreover, because of the hydrophobicity of many EDCs, the excess sludge would also be a potential source of risks. Thus, it is necessary to investigate the performance of the MBR in

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removal of EDCs. **Figure 2** compares the fate of two micropollutants during treatment in a conventional and MBR process as reported in a specific study [22].

*Insert **Figure 2** near here*

Endocrine disrupting chemicals (EDCs) are potentially harmful chemicals during wastewater reclamation. Bisphenol A (BPA) is a typical EDC. It is used to synthesize polycarbonates and epoxy resins, flame retardants, and other specialty products. Furthermore BPA is applied as a constituent of dental sealants, as developing agent in the coating of thermal papers and as an anti-oxidant in the production of plasticizers and processing polyvinyl chloride. BPA removal using a submerged membrane bioreactor (MBR) was investigated by Chen et al.[23]. For comparison, a conventional activated sludge reactor (CASR) was simultaneously tested using the same BPA sludge loadings as the MBR. The results showed that MBR could remove BPA a little more effectively than CASR under conditions of equal sludge loadings ranging from 0.046 to 10.2 g kg^{-1} d^{-1}. However, MBR could bear much higher volume loadings than CASR and still achieve the same BPA removal efficiencies. In MBR, HRT did not significantly influence the removal of BPA. The results also showed that the contributions of sludge adsorption to BPA removal were quite low in both reactors. In addition, one metabolite of BPA biodegradation, 4-hydroxy-acetophenone, was detected. These results suggested that biodegradation dominated the BPA removal process.

Lyko et al.[24] studied the suitability of MBRs with regard to the elimination of estrogenic trace contaminants for Municipal wastewater treatment and landfill leachate treatment. Investigations of phase distributions of the trace contaminants were conducted. The possibility of enhancement of the EDC rejection by the membrane filtration unit was also investigated. A significantly higher concentration appeared in the supernatant compared to the permeate concentration. They concluded that the ultrafiltration membrane was able to partly remove the macro-molecular DOC of the wastewater, while micropollutants tended to adsorb and associate with these removed macromolecules.

Schroder [22] operated a conventional biological wastewater treatment plant (BWWTP) and a membrane bio-reactor (MBR) to treat municipal wastewater. The endocrine disrupting compounds (EDCs), 4-nonylphenol (4-NP) and bisphenol A (BPA; 2,2-bis-(4-hydroxyphenyl)-propane), were spiked into the feed. Additionally, the effluents were treated with ozone (O_3). Reduction of Chemical Oxygen Demand (COD) was observed with 95 ± 2%. The elimination achieved without applying ozone were > 98 or 97.8 % for 4- NP and BPA in MBR treatment and > 98 and 91.6 % under conventional treatment. Mass balance proved biodegradation as the main elimination mechanism for 4-NP and BPA in both treatment processes.

In a study by Spring et al. [25] a pilot scale MBR was more effective at removing cholesterol, coprostanol, stigmastanol, estrogenic species (E1, EE2), and BPA to low ng/L levels than a full scale convensional activated sludge plant receiving the same wastewater. The authors opined that the lower effluent concentrations achieved by the MBR may be a function of the membrane or the increased SRT.

Yeast estrogen screen (YES) bioassay and liquid chromatography−mass spectrum−mass spectrum (LC−MS−MS) analysis were performed by Hu et al. [26] to investigate the fate of active and potential endocrine disrupting compounds in 3 pilot-scale and 2 lab-scale membrane bioreactor (MBR) systems. Compared with the overall estrogenicities of sewage treatment plant (STP) effluents from references, the MBR systems studied have relatively good performance in the removal of estrogenicity. Estrone (E1) was removed with relatively high efficiency (80.2−91.4%), but 17β-estradiol (E2) was removed with moderate efficiency (49.3−66.5%) by the MBRs. However, the experimental results indicated that after the treatment by MBR, substantial amounts of E1, estrone-3-sulfate (E1-3S), estrone-3-glucuronide (E1-3G), and 17β-estradiol-glucuronides (E2-G) passed through treatment systems and entered into the aquatic environment. The reduction in the levels of overall equivalent E1 (68.4%) and that of overall equivalent E2 (80.8%) was demonstrated for the pilot-scale MBR-B. For alkylphenol compounds, bisphenol A (BPA) was removed well with a removal efficiency of 68.9 −90.1%, but 4-nonylphenol (4-NP) concentration was amplified (removal efficiency of −439.5 to −161.1%) after MBR treatment which could be caused by the transformation of its parent compounds, nonylphenol polyethoxylates (NPnEOs). The amounts of adsorbed estrogens per kg dry mass was relatively low, due to short hydraulic retention time and high mixed liquor suspended solids in MBRs, compared to that in STPs.

Synder et al. [27] conducted investigations to determine the efficacy of various membranes for the removal of endocrine disruptors, pharmaceuticals, and personal care products. Microfiltration and ultrafiltration were found to reject very few target compounds; however, some loss of steroidal type compounds was observed. Nanofiltration and reverse osmosis were capable of significant rejection of nearly all target compounds, though compounds were detectable at trace levels in permeates. A membrane bioreactor (MBR) system was tested at pilot scale using primary effluent as the feed water. The results of the MBR experiment showed that while the MBR is effective for reducing the concentration of many EDC/PPCPs, several compounds are unaffected and very few compounds are reduced to below the MRL. The removal is likely related to biodegradability of the individual compound. For instance, in each experiment naproxen, acetaminophen, ibuprofen, and caffeine experienced significant removal through the MBR. These compounds were previously shown to be rapidly biodegraded.

Eight pharmaceuticals, two polycyclic musk fragrances and nine endocrine disrupting chemicals were analysed by Clara et al. [28] in several waste water treatment plants (WWTPs). A membrane bioreactor in pilot scale was operated at different solid retention times (SRTs) and the results obtained are compared to conventional activated sludge plants (CASP) operated at different SRTs. The SRT is an important design parameter and its impact on achievable treatment efficiencies was evaluated. Different behaviours were observed for the different investigated compounds. Some compounds as the antiepileptic drug carbamazepine were not removed in any of the sampled treatment facilities and effluent concentrations in the range of influent concentrations were measured. Other compounds as bisphenol-A, the analgesic ibuprofen or the lipid regulator bezafibrate were nearly completely removed (removal rates 490%). The operation of WWTPs with SRTs suitable for nitrogen removal (SRT 4-10 days at 10°C) also increases the removal potential regarding selected micropollutants. No differences in

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treatment efficiencies were detected between the two treatment techniques. As in conventional WWTP also the removal potential of MBRs depends on the SRT. Ultrafiltration membranes do not allow any additional detention of the investigated substances due to size exclusion. However, MBRs achieve a high SRT within a compact reactor. Nonylphenolpolyehtoxylates were removed in higher extend in very low-loaded conventional WWTPs, due to variations of redox conditions, necessary for the degradation of those compounds.

Chen et al. [29] conducted a pilot-scale test with a two-phase anaerobic digestion (TPAD) system and a subsequent membrane bioreactor (MBR) treating chemical synthesis-based pharmaceutical wastewater. The TPAD system comprised a continuous stirred tank reactor (CSTR) and an upflow anaerobic sludge blanket-anaerobic filter (UASBAF), working as the acidogenic and methanogenic phases, respectively. The wastewater was high in COD, varying daily between 5789 and 58,792 mgL^{-1}, with a wide range of pH from 4.3 to 7.2. The wastewater was pumped at a fixed flow rate of $1m^3$ h^{-1} through the CSTR, the UASBAF and the MBR in series, resulting in respective HRTs of 12, 55 and 5 h. Almost all the COD was removed by the TPAD–MBR system, leaving a COD of around 40mg L^{-1} in the MBR effluent. The MBR influent (the UASBAF effluent) COD fluctuated in a range of 4326–9246mgL^{-1} in the initial period of 21 days, corresponding to COD loading rates of 20.8–44.4 kgm^{-3} day^{-1}, and then decreased gradually to 1005 mgL^{-1}at day 51 and thereafter leveled off. The COD removal of the MBR remained constant at a rate of approximately 99% throughout the experiment. The pH of the MBR effluent was found in a narrow range of 6.8–7.6, indicating that the MBR effluent can be directly discharged into natural waters.

Weiss et al. [30] studied the potential of a lab-scale membrane bioreactor (MBR) to remove polar pollutants from municipal wastewater for industrial and household chemicals over a period of 22 months parallel to a conventional activated sludge (CAS) treatment. For half of the compounds, such as benzotriazole, 5-tolyltriazole (5-TTri), benzothiazole-2-sulfonate and 1,6-naphthalene disulfonate (1,6-NDSA), removal by MBR was significantly better than in CAS, while no improvement was recorded for the other half (1,5-NDSA, 1,3-NDSA, 4-TTri and naphthalene-1-sulfonate). The influence of operational conditions on trace pollutant removal by MBR was studied but no significant effects were found for variation of hydraulic retention time (7 h–14 h) and sludge retention time (26 d–102 d), suggesting that the lowest values selected have already been high enough for good removal. The authors contended that MBR is neither superior for well degradable compounds that are already extensively degraded in CAS treatment nor for recalcitrant compounds that are not amenable to biodegradation. However, for most compounds of intermediate removal in CAS treatment (15–80%), among them pharmaceuticals, personal care products and industrial chemicals, the MBR is clearly superior and reduces the effluent concentration by 20–50%.

The fate of two differently labelled radioactive forms of 17α-ethinylestradiol (EE2) in a laboratory-scale MBR was studied by Cirja et al. [31]. The MBR, specially designed for studies with radioactive compounds, was operated using a synthetic wastewater representative of that emanating from pharmaceutical industry and the activated sludge was obtained from a large-scale MBR treating pharmaceutical wastewater. By applying in MBR a concentration of 8 g/L mixed liquor solid suspension and a sludge retention time of 25 days over the whole test period (35 days), the removal performance of C-, N- and P-ranged between 80% and 95%. Balancing of radioactivity could demonstrate that real mineralization is <1%, while radioactivity mainly remained sorbed in the reactor, resulting in a removal of approximately 80%. The same metabolite pattern in the radiochromatograms for the two different labelling protocols led to the assumption that the elimination pathway does not involve the removal of the ethinyl group from EE2 molecule.

Bernhard et al.[32] studied the biodegradation of selected non-adsorbing persistent polar pollutants (P3) during wastewater (WW) treatment by comparing a lab-scale membrane bioreactor (MBR) running in parallel to activated sludge treatment (AST). The investigated P3 are relevant representatives or metabolites from the compound classes:pesticides, pharmaceuticals, insect repellents, flame retardants and anionic surfactants. Analyses of all these P3 at low ng/L levels with sufficient standard deviations was performed in WW influents and effluents. Non-degradable micropollutants, such as EDTA and carbamazepine were not eliminated at all during WW treatment by any technique. However, the MBR showed significant better removals compared to AST for the investigated poorly biodegradable P3, such as diclofenac, mecoprop and sulfophenylcarboxylates. The application of such an MBR optimized in terms of sludge retention time may lead to a reduction of these P3 in the water cycle.

Kimura et al. [33] studied the ability of submerged MBRs to remove pharmaceutically active compounds (PhACs). Experiments were conducted at an existing municipal wastewater treatment facility, and the performance of the MBRs was compared with that of the conventional activated sludge (CAS) process. Six acidic PhACs (clofibrie acid, diclofenac, ibuprofen, ketoprofen, mefenamic acid, naproxen) and one acidic herbicide (dichloprop) were investigated. Compared with CAS, MBRs exhibited much better removal regarding ketoprofen and naproxen. With respect to the other compounds, comparable removal was observed between the two types of treatment. Removal efficiencies of the PhACs were found to be dependent on their molecular structure such as number of aromatic rings or inclusion of chlorine.

The degradation of three estrogens, two endocrine disruptors and ten pharmaceutical substances in a membrane separation bioreactor was experimentally examined by Urase et al. [34]. Higher removal of acidic pharmaceutical substances was obtained in the case of lower pH operation because of the increased tendency of adsorption to the sludge particles. The target substances attached to the sludge were not accumulated in the reactor and they were biologically degraded. The membrane used in this study was a microfiltration membrane which has much larger pores than target substances. However, the permeate concentration was lower than the water phase concentration in the reactor probably due to activated sludge deposition onto the membrane surface. The additional removal by the membrane was increased with the time elapsed, though the removal was not significantly high for the relatively hydrophilic compounds.

The elimination of 14 pharmaceuticals, 6 hormones, 2 antibiotics, 3 personal care products (PCPs), and 1 flame retardant chemical during drinking water and wastewater treatment processes at full- and pilot-scale was investigated by Kim et al. [35]. MBR system was found to be efficient for hormones (e.g., estriol, testosterone, androstenedione) and certain pharmaceuticals (e.g., acetaminophen, ibuprofen, and caffeine) with approximately 99% removal. However, the results showed that MBR treatment did not decrease the concentration of erythromycin, TCEP, trimethoprim, naproxen, diclofenac, and carbamazepine.

Radjenovic et al.[36] reported on the performances of full-scale conventional activated sludge (CAS) treatment and two pilot-scale membrane bioreactors (MBRs) in eliminating various pharmaceutically active compounds (PhACs) belonging to different therapeutic groups and with diverse physico-chemical properties. Both aqueous and solid phases were analysed for the presence of 31 pharmaceuticals included in the analytical method. The most ubiquitous contaminants in the sewage water were analgesics and anti-inflammatory drugs ibuprofen (14.6–31.3 mg/L) and acetaminophen (7.1–11.4 mg/L), antibiotic ofloxacin (0.89–31.7 mg/L), lipid regulators gemfibrozil (2.0–5.9 mg/L) and bezafibrate (1.9–29.8 mg/L), β-blocker atenolol (0.84–2.8 mg/L), hypoglycaemic agent glibenclamide (0.12–15.9 mg/L) and a diuretic hydrochlorothiazide (2.3–4.8 mg/L). Also, several pharmaceuticals such as ibuprofen, ketoprofen, diclofenac, ofloxacin and azithromycin were detected in sewage sludge at concentrations up to 741.1, 336.3, 380.7, 454.7 and 299.6 ng/g dry weight. Two pilot-scale MBRs exhibited enhanced elimination of several pharmaceutical residues poorly removed by the CAS treatment (e.g., mefenamic acid, indomethacin, diclofenac, propyphenazone, pravastatin, gemfibrozil), whereas in some cases more stable operation of one of the MBR reactors at prolonged SRT proved to be detrimental for the elimination of some compounds (e.g., β-blockers, ranitidine, famotidine, erythromycin). Moreover, the anti-epileptic drug carbamazepine and diuretic hydrochlorothiazide by-passed all three treatments investigated. Furthermore, sorption to sewage sludge in the MBRs as well as in the entire treatment line of a full-scale WWTP was observed. Among the pharmaceuticals encountered in sewage sludge, sorption to sludge could be a relevant removal pathway only for several compounds (i.e., mefenamic acid, propranolol, and loratidine). Especially in the case of loratidine the experimentally determined sorption coefficients (Kds) were in the range 2214–3321 L/kg (mean). The results obtained for the solid phase indicated that MBR wastewater treatment yielding higher biodegradation rate could reduce the load of pollutants in the sludge. Also, the overall output load in the aqueous and solid phase of the investigated WWTP was calculated, indicating that none of the residual pharmaceuticals initially detected in the sewage sludge were degraded during the anaerobic digestion. Out of the 26 pharmaceutical residues passing through the WWTP, 20 were ultimately detected in the treated sludge that is further applied on farmland.

The dynamics of 12 micropollutants in a membrane bioreactor (MBR) was studied when treating synthetic sewage by Reif et al. [37]. The selected substances corresponded to different therapeutic groups such as antiepileptics (carbamazepine), tranquillisers (diazepam), analgesics (ibuprofen, naproxen, diclofenac), antibiotics (roxithromycin, erythromycin, sulfamethoxazole, trimethoprim) and three polycyclic musk fragrances (galaxolide, tonalide, celestolide). These micropollutants were spiked into the synthetic wastewater fed to the reactor at environmentally relevant concentrations ranging from 10 to 20 μg/L. The MBR was operated at a sludge retention time (SRT) of 44–72 days, since a high value of this parameter is considered as crucial for the

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removal of these micropollutants. Under these conditions, different fates are observed depending on pharmaceutical and personal care products (PPCPs) characteristics. Hydrophobic organic substances, like musk fragrances, are partially sorbed onto the sludge. This explains the partial removal observed in the reactor, with an overall efficiency around 50%. Other substances, like the anti-inflammatories ibuprofen and naproxen, are not sorbed but they are eliminated almost completely (98% and 84% of removal, respectively). On the other hand, substances like carbamazepine or diclofenac show a recalcitrant character and their elimination from the effluent is very limited, below 9%.

The biodegradation of selected priority acidic pesticides MCPP, MCPA, 2,4-D, 2,4-DP and bentazone and the acidic pharmaceutical diclofenac was investigated using a membrane bioreactor (MBR) and a fixed-bed bioreactor (FBBR) by Gonzalez et al.[38]. A pilot plant MBR was fed with raw water spiked with the selected compounds. The experiment was repeated every week during four weeks to enhance the adaptation of microorganisms. In order to further study the biodegradability of these compounds, degradation studies in a FBBR were carried out. All the samples were analysed by solid phase extraction-gas chromatography-mass spectrometry (SPE-GC-MS). The results indicate that in the MBR compounds except for bentazone were eliminated within the first day of the experiment at rates ranging from 44% to 85%. Comparing these results with the degradation rates in the FBBR showed that in the latter only MCPP, MCPA 2,4-D and 2,4-DP were degraded after a much longer adaptation phase of microorganisms.

The elimination of sulfonamides, macrolides and trimethoprim from raw wastewater was investigated in several municipal wastewater treatment plants by Gobel et al.[39]. Primary treatment provided no significant elimination for the investigated substances. Similar eliminations were observed in the secondary treatment of two conventional activated sludge (CAS) systems and a fixed-bed reactor (FBR). Sulfamethoxazole, including the fraction present as N4-acetyl-sulfamethoxazole, was eliminated by approximately 60% in comparison to about 80% in a membrane bioreactor (MBR) independent of the solid retention time (SRT), indicating a positive correlation of the observed elimination to the organic substrate concentration. The elimination for macrolides and trimethoprim varied significantly between the different sampling campaigns in the two CAS systems and in the FBR. In the MBR, these analytes were eliminated up to 50% at SRT of 16±2 and 33±3 d. Trimethoprim, clarithromycin and dehydro-erythromycin showed a higher elimination of up to 90% at a SRT of 60–80 d indicating a correlation with reduced substrate loading (SL). Together with the high SRT, the SL may lead to an increased biodiversity of the active biomass, resulting in a broader range of degradation pathways available.

A pilot-scale study on pharmaceutical wastewater treatment by a membrane bioreactor (MBR) process in southern Taiwan was presented in a paper by Chang et al.[40] A 10 m^3/day capacity MBR plant consisting of an aeration tank and a membrane was installed to remove organic matter (measured in terms of chemical oxygen demand (COD)). The performance of the MBR was monitored for a period of 140 days. The removal of COD was on average over 95%. The effluent did not contain any suspended solids. The results indicated that the MBR system has potential as a means of treating high-strength and fluctuating strength wastewater with consistent performance.

Xu et al. [41] harvested biomass from a membrane bioreactor (MBR) and a sequencing batch reactor (SBR), and conducted sorption experiments over a range of temperatures. Sorption of 17α-ethinylestradiol (EE2) to activated sludge was spontaneous (ΔG values were between -16 and -11 KJ/mol), enthalpy-driven (ΔH values were -37 KJ/mol (MBR) and -48 KJ/mol (SBR)), and entropy-retarded (ΔS values were -74 (MBR) and -119 J/mol/K (SBR)). Although EE2 is nonpolar, hydrophobic interactions were not dominant driving forces. The thermodynamic data also suggested that EE2 sorption to biomass was primarily physisorption, but it also included low-level chemisorption. The FT-IR results suggested that chemical reactions were not significant enough to shift the detectable chemical bonding characteristics of the biomass functional groups. Results suggested that sorption is an important mechanism for removal of 17α-ethinylestradiol (EE2) in biological wastewater treatment.

Yi et al. [42] operated a membrane bioreactor (MBR) and a conventional bioreactor (CBR) under various conditions to assess the biomass characteristics and evaluate the ensuing effects on the partitioning and sorption hysteresis of 17α-ethinylestradiol (EE2). When the biomass was grown without nitrogen limitation, the biomass mean particle size had a dramatic effect on the observed partitioning coefficient (K_d) and on sorption hysteresis index (HI). MBR K_d (0.33–0.57 L/g) values were equal to or larger than those of the CBR (0.25–0.33 L/g). Under nitrogen-deficient conditions, the correlations between the biomass particle size and Kd and HI were poor, likely because of extracellular polymeric substances. The K_d and HI were determined for initial EE2 concentrations between 100 and 1000 μg/L. Changing the SRT did not affect particle size, and the effects on K_d and HI were not dramatic.

In a review of the factors influencing the removal of organic micropollutants from wastewater, Cirja et al.[43] concluded that sorption and biodegradation are the dominant removal processes in CTP and in MBR, which are influenced by operation conditions like sludge retention time (SRT), biomass concentration, temperature, pH value, dominant class of micropollutants, etc.

Hydrophobic compounds (NP, EE2, etc.) can be removed from the influent via adsorption to the sludge particles present in the system. Compounds containing complex structure (e.g., alkyl chain branching) and toxic groups (e.g., halogens and nitro group) show higher resistance to biodegradation processes. When SRT in the wastewater treatment system is high enough (at least 8 d) the removal of organic compounds through biodegradation processes is enhanced. The temperature of wastewater treatment seems to play an important role; WWTP in countries with average temperature of 15– 20°C may better eliminate micropollutants as in cold countries with a temperature mostly under 10°C. The seasonal temperature changes between summer and winter influences the biodegradation and removal of micropollutant. The pH value influences the removal of micropollutants from wastewater. Although few studies focused on this parameter, the control of pH value might be a solution for the removal of micropollutants in WWTP. The pH of industrial wastewater is often subject to variations and may also negatively influence the removal of the micropollutants.

By comparing CTP and MBR, they opined that there is no real difference between the two investigated systems concerning the removal of different classes of micropollutants. Nevertheless, the removal rates differ from one compound to the other and the rates of removal depend on the physico-chemical characteristics of the xenobiotic, e.g., hydrophobicity, chemical structure, pKa, etc. Hydrophobic compounds are removed from the liquid phase via adsorption, and possibly through biodegradation processes when the SRT is high enough. Owing to the compactness of MBR plant and the high organic load that can be applied, this process is promising concerning the removal of micropollutants, which are eliminated at high SRT and biomass concentration.

Dye wastewater

Large amounts of dyes are annually produced and applied in many different industries, including the textile, cosmetic, paper, leather, pharmaceutical and food industries [44]. There are more than 100,000 commercially available dyes with an estimated annual production of over 7 $x10^5$ tons, fifteen percent of which is lost during the dyeing process [45]. The textile industry accounts for the two-thirds of the total dyestuff market and consumes large volumes of water and other refractory chemicals for wet processing of textiles [46]. The chemical reagents used are very diverse in chemical composition, ranging from inorganic compounds to polymers and organic products.

The presence of even trace concentration of dyes in effluent is highly visible and undesirable [47].The release of colored wastewater in the ecosystem is a remarkable source of esthetic pollution, eutrophication and perturbations in aquatic life. Dye effluent usually contains chemicals, including dye itself, which are toxic, carcinogenic, mutagenic, or teratogenic to various microbiological and fish species. Concern arises, as many dyes are made from known carcinogens such as benzidine and other aromatic compounds. Also azo- and nitro-compounds have been reported to be reduced in sediments by microorganisms, consequently yielding potentially carcinogenic amines that spread in the ecosystem. The presence of dyes or their degradation products in water can also cause human health disorders such as nausea, hemorrhage, ulceration of skin and mucous membranes, and can cause severe damage to kidney, reproductive system, liver, brain and central nervous system. Virtually all the known physico-chemical and biological techniques have been explored for decolorization [47], none has emerged as a panacea [48].

You et al. [49] compared the performance of the membrane bioreactor (MBR) and sequencing batch reactor (SBR) process for treating real textile dyeing wastewater. The microbial diversity of the MBR process was also identified by a combined culturing method and molecular biotechnology. The sludge retention time (SRT) and hydraulic retention time (HRT) were 20 days and 48 hours, respectively. The results show that the removal efficiencies for color, COD, BOD, and SS with the MBR process were 54, 79, 99, and 100%, respectively, all higher than the corresponding parameters for the SBR process: 51, 70, 96, and 60%. All the above four parameters for the MBR effluent meet the criteria of the Taiwan EPA, while on the other hand for the SBR process, only color and COD meet the Taiwan EPA effluent criteria. Furthermore, the genus *Microbacterium*, especially the *Microbacterium aurum*, was the most predominant population, contributing 70.6% of the total isolates, and might be responsible for the degradation of the dyeing wastewater. Another two textile dyeing degradation bacteria, *Paenibacillus azoreducens* and *Bacillus sp*., as predominant bacteria in MBR sludge, were also observed.

Rozzi et al. [50] tested the post- treatment of secondary wastewater (80% textile, 20% municipal) on a pilot scale low-pressure reverse osmosis (RO) module, to produce a polished effluent to be recycled into the textile factories. Two different flow sheets were used. In the first one, the feed to the RO was pre-treated in a coagulation and filtration unit. In the second one, a membrane hollow fibre reactor was used to separate the activated sludge from the permeate which was fed to the RO module. Compared to the conventional biological treatment, the MBR permeate was obviously free of suspended solids and measured concentrations were lower for most parameters. As an average, soluble COD was 30–40% lower, absorbance was 20–30% lower and anionic and non ionic surfactants were 30–50% lower. It is noteworthy that an appreciable biological activity also took place inside the MBR, as evidenced by lower soluble COD concentration in the outflow as compared to the stream entering the box of the membrane module. Both MBR and coagulation plus dual media filtration ensured that SDI values are obtained which are suitable for the feed of the low-pressure RO module. On account of the stability, however, the MBR permeate seemed to allow for a more regular and constant operation of the RO module, with a lower decrease in the specific flux against time.

Malpei et al. [51] tested a pilot plant membrane bioreactor in parallel with a full-scale activated sludge wastewater treatment plant fed on the wastewater from a textile factory. The possibility to upgrade the final effluent for internal reuse was investigated. The application of MBR process for the production of purified water to be reused in a dyeing textile factory appeared feasible. The residual SST, COD and absorbance of the permeate make it suitable for reuse in some operations of the dyeing cycle such as the first washing. Compared to the existing extended aeration WWTP, the pilot MBR made it possible to obtain higher COD removal and colour abatement, besides a much higher removal efficiency for suspended solids and microorganisms.
Lubello et al. [52] ran a pilot MBR plant in parallel to one existing WWTP (activated sludge + clariflocculation + ozonation) for the treatment of textile wastewater (**Figure 3**). The aim was to investigate the possibility of realizing wastewater reclamation. On average, removal efficiency of the pilot plant (93% for COD, and over 99% for total suspended solids) was higher than that of the WWTP. Color was removed as in the WWTP. Anionic surfactants removal of pilot plant was lower than that of the WWTP (90.5 and 93.2% respectively), while the BiAS removal was higher in the pilot plant (98.2 vs. 97.1).

*Insert **Figure 3** near here*

Lubello et al. [53] carried out another experimental study in order to evaluate the feasibility of upgrading a conventional activated sludge WWTP treating municipal and textile wastewaters to a membrane bioreactor (MBR). The MBR pilot plant was fed with mixed municipal–industrial wastewaters during the first experimental period and with pure industrial wastewaters during the second. According to the experimental results the MBR permeate quality was always superior to the conventional WWTP one and it was suitable for industrial reuse in the textile industry. The

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advantages of the MBR system compared to the conventional WWTP were summarised as follows: lower effluent COD value (27 mg/L versus 60 mg/L); very little standard deviation of the effluent quality; no problems due to filamentous microorganisms (which, on the contrary, grow abundantly in the WWTP oxidation tank because of high influent non-ionic and anionic surfactant concentrations); no peaks of solids, COD, $N\text{-}NO_2^-$, $N\text{-}NH_4^+$ (always 0.2 mg/L) in the effluent; complete nitrification during all the first period even at temperatures below 6 °C. While feeding only with industrial wastewater, because of gradual accumulation of heterotrophic biomass, a decrease of the permeate COD was observed (from 140 to 70 mg/L in 40 days, with a mean value of 102 mg/L). The low concentration of nitrogen in textile wastewater compared to the organic content (N/COD = 0.015) determined a reduction of autotrophic biomass activity, but did not affect the heterotrophic growth in the MBR because of the very high sludge age. The biomass retention in the MBR reactor allowed heterotrophic bacteria growth without the need to add nutrients.

Brik et al. [54] investigated the capability of MBR to achieve a water quality meeting reuse criteria. A laboratory-scale MBR unit was fed with textile wastewater originating from a polyester finishing mill. Removal capacity was examined at VLRs ranging between 0.35 and 3.6 g/(l day). In addition, the effect of nutrient addition was studied. COD removal was found to vary between 60 and 95% with reduced COD levels at lower VLRs tested. Nutrient addition slightly enhanced effluent quality. Sludge yield obtained were between 0.01 and 0.1 gMLSS/gCODremoved. At similar sludge loading rates specific sludge production rates were approximately 50% higher when nutrients were added. A distinct relationship between sludge growth and colour removal could be observed. Above an sludge growth rate of 0.3 g/(l day), colour removal was above 87% for all wavelengths examined. They contended that if reuse of MBR treated wastewater is intended, additional polishing steps must be considered as MBR effluents did not reach the required quality for water reuse. In order to upgrade MBR effluent, nanofiltration as a post-treatment was suggested.

As most of the biodegradation of dye generally takes place at very low oxygen levels, unlike a conventional MBR operated at aerobic condition, anoxic or anaerobic conditions are required for an MBR for dye wastewater treatment. Accordingly, Yun et al. [55] studied an anoxic-aerobic MBR sequence for dye wastewater treatment. The treatment efficiencies of COD and the dye between aerobic and anoxic MBR were compared. The average COD removal efficiency was 94.8% and 27.0% when DO concentration was 6.0 mg/L and 0.3 mg/L, respectively. Whereas, the dye removal efficiency increased from 72.9% to 86.6% with decreasing DO concentration from 6.0 to 0.3 mg/L. Generally, it is known that under aerobic condition a synthetic azo dye cannot be degraded and can only be removed by adsorption to microbial cells followed by sludge withdrawal. This removal rate by the adsorption has been reported to be about 30%. However, a 72.9% removal efficiency is still high compared to the 30% in aerobic condition. In another view, biofilm formed on the membrane surface may be under an anoxic or an anaerobic state even in the aerobic reactor due to limitation in mass-transport. Therefore, it could be said that this 72.9% of dye removal efficiency in aerobic reactor could be attributed to both adsorption to bacterial cells (activated sludge) and partial degradation inside the membrane biofilm. The opposite tendency in treatment efficiency between COD and dye as a function of DO level suggested that an alternative operation of aerobic and anoxic phases is indispensable to efficiently biodegrade both COD and dye molecules in dye wastewater treatment with MBR.

A laboratory-scale membrane bioreactor (MBR) with a gravity drain was tested by Zheng et al. [56] for dyeing and printing wastewater treatment from a wool mill. Results showed that excellent effluent quality could meet the reuse water standard in China. The average removal rates of COD, BOD5, turbidity and color were 80.3%, 95.0%, 99.3% and 58.7%, respectively. Due to its compact design, simple operation and easy maintenance, MBR with a gravitational filtration system has low energy consumption and is cost-effective to build and operate. If the life expectancy of the membrane is set for 3–4 years and the membrane flux is set at 15 $l/m^2.h$, such a MBR would be very competitive.

Hoinkis et al.[57] studied the design and start up a new, innovative, integrated process using membrane technology for wastewater reuse on a large scale in the Klingelmeyer laundry, Germany. The large scale plant was designed for wastewater treatment capacity of $200m^3$/day. The integrated process comprises a membrane bioreactor (MBR) with submerged plate and frame microfiltration membranes as the principal cleaning unit. The results of the pilot agree with those of the large-scale plant. The chemical oxygen demand (COD) removal efficiency was around 90%; the average flux was approximately 14 L/m^2 h. The MBR permeate provides a water quality that can be used as washing water since it fully meets the requirements of the washing process.

Schoeberl et al. [58] developed for a specific textile finishing company strategies for water recycling and recovery of valuable chemicals. A comprehensive study of the company's resource consumption and emission profile was performed. On this basis selected end of the pipe and integrated recycling options were further examined in detail. When treating the mixed wastewater flow, a combination of a membrane bioreactor and subsequent nanofiltration proved to meet all requirements for reuse. However, this approach is associated with considerable technological effort and potentially high costs. As an alternative, a relatively simple and straightforward process was tested to treat only the washing effluents by means of ultrafiltration. Based on results obtained from the ultra filtration experiments, a process integrated recycling concept was proposed. By its implementation water consumption can be cut down by 87.5% within the washing process. Furthermore total COD emissions can be reduced by 80%, and as washing agents are partly recycled, consumption for the washing process can be lowered by 20%.

Membrane bioreactor can be easily integrated into an industrial process allowing a quasi-total reuse of waters (it is as well one of the reasons that the membranes separation are very used in the industries). This reuse of wasted effluents allows the reduction of the manufacturing cost. The objective of a study by Badani et al. [59] was to determine the operating conditions of an external membrane bioreactor for the treatment of waste of textile industry. The pilot-plant includes a reactor of 500 L in which an adapted biomass was developed. For the three considered feed outputs, the experiments showed that the average rejection of the COD is 97%, the rate of elimination of the ammoniac nitrogen is 70%, whatever the age of sludge is. A 70% of reduction of the color of the treated effluent was observed.

Tannery wastewater

The high complexity of the tannery wastewater matrix originates from a wide range of components such as: raw materials (skins) residues, excess dosage of reagents including a high concentration of proteins, lipids and salts (sulphide, sulphate and chloride), tanning agents such as natural and synthetic tannins (in the case of vegetal tanning), dyes and surfactants[60]. The choice of the treatment process is strictly related to the presence of significant fractions of slowly hydrolysable and inhibiting compounds requiring technologies such as MBR, granular biomass, etc., which increase the sludge age and consequently the capacity to degrade substrates usually not biodegraded in conventional wastewater treatment plants.

In leather tanning industrial areas sulphide management represents a major problem. Biological sulphide oxidation to sulphur represents a convenient solution to this problem. Elemental sulphur is easy to separate and the process is highly efficient in terms of energy consumption and effluent quality. However, it has been shown that the yield of the sulphide oxidation process depends on the features of the selected microbial community [61]. As the oxidation process is performed by specialized bacteria, selection of an appropriate microbial community is fundamental for obtaining a good yield. Vannini et al. [62] explored an MBR in this context. Their data clearly showed that an efficient process of sulphide oxidation to elemental sulphur took place in the experimental MBR. Furthermore, after the start-up phase, the process proceeded in a very stable way, as long as the influent sulphide concentrations did not exceed 900 mg l^{-1}. The control of the ORP from -380 to -400 mV was shown to be an operative tool for regulating air input to achieve optimal sulphide oxidation. They attributed the satisfactory removal to the maintenance of an appropriate microbial community in the MBR which has key relevance for the efficiency of the sulphide oxidation process.

A pilot-scale membrane bioreactor (MBR) and a conventional activated sludge plant (CASP), treating the same tannery wastewaters under the same operating conditions, was compared by Munz et al.[60] in order to evaluate the overall treatment efficiency, the presence and distribution of Gram negative bacteria and the kinetics of nitrifying bacteria. Process efficiency was evaluated in terms of organic and nitrogen compounds: the MBR showed a higher COD removal (+4%) and a more stable and complete nitrification. The Gram negative bacteria were detected by fluorescent in situ hybridization (FISH) with phylogenetic probes monitoring of alpha-, bita- and gamma-Proteobacteria, of the main ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria of the Nitrobacter and Nitrospira genera. The results showed that the main differences between the two sludges were: the higher abundance of alpha- and gamma-Proteobacteria in the MBR bioreactor and the presence of AOB aggregates only on the surfaces of MBR flocs. Finally, the titrimetric (pH-stat, DO-stat) tests showed similar values of the kinetic parameters of the nitrifiers both in MBR and CASP sludge.

Artiga et al. [63] used an MBR during 120 days for treating two different wastewaters with different characteristics. During the first 50 operating days the unit was fed with an influent similar to the streams generated in wineries. From day 50 onward, the MBR treated a wastewater generated in a tannery factory. The major differences between the wastewaters were the absence of both suspended solids and particulate chemical oxygen demand (COD) in the winery stream and the presence of these compounds in the wastewater from the tannery. Efficiency of the MBR was high: COD removal efficiency above 97% was obtained with winery wastewater, and about 86% during the period in which the tannery wastewater was used. COD concentration in the permeate of the unit varied between 60-80 mg COD/L during the whole experimental period, despite the differences in both wastewater characteristics and the operating conditions applied. Biomass concentration, in terms of volatile suspended solids (VSS), ranged between 0.5 and 15 g VSS/L. Apparent biomass yield was estimated at 0.14 g VSS/g COD and 0.16 g VSS/g COD for winery and tannery wastewater, respectively. A drop in the oxygen transfer efficiency was observed when the system operated with biomass concentrations above 8 g VSS/L.

Munz et al.[64] carried out experiments to ascertain the role of tannins in the treatment of vegetable tanning wastewater with MBR and CASP. In particular, it was possible to conclude that: the COD is removed more efficiently (4% more) and the nitrification process appears to be more complete in comparison with the CASP. The removal of phenols, which can be associated with the presence of tannins, did not differ greatly between the two.

Bench scale membrane bioreactors were operated by Chung et al. [65] to investigate the treatment efficiency of tannery wastewater with high organic and nitrogen contents and the optimum operating conditions were derived. The optimum ratio of the volume of anoxic denitrification tank to aerobic nitrification tank was 50% when denitification/nitrication MBR process was used to treat tannery wastewater. It was also found that supplementation of phosphorus to maintain COD:T-P ratio of 100:1 was needed to achieve the best performance. Under these conditions, the effluent COD and T-N were 160 and 54 mg/L, respectively which satisfied the effluent limits for the tannery wastewater.

Landfill leachate

Landfill leachate can broadly be defined as the liquid produced from the decomposition of waste and infiltration of rainwater in the landfill. Generation of leachate occurs when moisture enters the refuse in a landfill, dissolves the contaminants into liquid phase and becomes sufficient to initiate a liquid flow. Leachate varies from one landfill to another with fluctuations that depend on short and long-terms due to variations in climate, hydrogeology and waste composition [66]. Due to this, improvements in landfill engineering are aimed at reducing leachate production, collection and treatment prior to discharge [67]. Characterisation and treatment of landfill leachate has only taken place within the last 40 years. Nitrification is generally readily achievable, with >95% removal of ammonia reported through the exclusive application of biological techniques to the treatment of both young and old leachates [68-70]. However, chemical oxygen demand (COD) removal is considerably more challenging, with removal efficiency values from 20% to over of 90% reported according to leachate characteristics (origin and age), process type and process operational facets [71-73] Such process schemes generally comprise some combination of biological and physical and/or chemical treatment with key operational determinants being organic loading rate and the related hydraulic retention time (HRT).

In view of the high strength of the landfill leachate, Visvanathan et al. [74] utilized an aerobic thermophilic membrane bioreactor (MBR) for treating raw landfill leachate from two landfill sites in Thailand. Thermophilic process offers several advantages such as rapid biodegradation rates, low sludge yields, rapid inactivation of pathogenic microorganisms and high loading rate, thus reducing the retention time for treatment and capital cost. One of the major restraints in the aerobic thermophilic process, however, is the poor bacterial flocculation and problems associated with foams. Poor bacterial settling characteristics result from certain suspended microorganisms which make the separation of biomass difficult and thus limits the overall treatment efficiency. Looking into this aspect, an aerobic thermophilic membrane bioreactor (MBR), being able to filter wide ranges of biomass sizes, could be an attractive option for treating high strength landfill leachate. In the study, the leachates from these sites were mixed in different proportions to produce a BOD/COD ratio of 0.39, 0.57, and 0.65. The COD, ammonia, and TKN composition of the mixed leachate was 12,000, 1700 and 1900 mg/L, respectively. BOD was supplemented with glucose and soy protein. At a hydraulic retention time (HRT) of 24 hrs the COD removal rate increased from an average value of 62–79% while ammonia removal efficiency decreased from 75 to 60% with gradual increase in BOD. Furthermore, a high BOD removal efficiency (97–99%) was also observed. Lapara and Alleman [75] stipulated that ammonia removal phenomenon in thermophilic condition is governed by temperature, mixing and pH, and inhibition of biological nitrification occurs at temperatures greater than 43°C. Although the ammonia removal efficiency dropped with increasing BOD/COD ratio, in view of the substantial COD removal this system appeared interesting.

Laitinen et al. [76] treated landfill leachate from a composting field of a Finnish municipal waste landfill with sequencing batch reactor (SBR) and a submerged membrane bioreactor (MBR) fed batch-wise. Considerably long HRT (SBR=4d, MBR=9d) and reasonable solids retention times (SBR=10-40 d, MBR=35-60 d) were applied. In SBR, suspended solids concentration in effluent was up to 89% smaller than influent suspended solids concentration. However, sometimes bulking reduced the efficiency. The preliminary results with MBR start-up showed that it is free from bulking problems and compared to feed concentration the retention was over 99% of suspended solids. It also increased the retentions of both BOD_7 and ammonium nitrogen to >97% and reduced variations. Phosphorus retention was >88%.It was concluded that both the SBR and MBR remove total ammonia nitrogen effectively. However, the sludge was escaping from the SBR unit whenever the process was disturbed and thus quite high suspended solids, BOD_7, and phosphorus concentrations were observed. MBR effluent was significantly better in quality and had lower variations.

Alvarez-Vazquez et al. [77] presented a review of quality and biological treatment of landfill leachate. They showed that conventional *ex-situ* treatment normally demands multistage process treatment schemes, which may encompass both aerobic and anaerobic technologies alongside chemical precipitation and/or oxidation. This was contrasted with the more recent membrane bioreactor technology, which generally demands much reduced pre and post-treatment and has a much reduced footprint compared with conventional biotreatment. From their review, it appeared that reasonable COD removal values are attained from the more recent membrane bioreactor

(MBR) technology. Critical assessment of data from existing plants on a common basis revealed a clear distinction in performance with the membrane bioreactor data. MBR-based treatment schemes appear to achieve greater COD removal, a mean of around 80% across all installations, for less biotreatable feed waters (BOD/COD = 0.03–0.16), than conventional systems which achieve COD removals of around 63% at feed water BOD/COD ratios of 0.21–0.3 (**Figure 4**). Moreover, they do so at generally lower HRTs, and thus correspondingly higher loading rates (1–3 kg $CODm^{-3}$ d^{-1} compared with less than 0.25 kg $CODm^{-3}$ d^{-1} for conventional treatment schemes) and so lower footprints. It was apparent that MBR technologies demand downstream treatment for enhanced COD removal in much the same way as a conventional biological process plant, but none-the-less provide greater COD removal than conventional systems and moreover permit downstream polishing by nanofiltration because of the highly clarified effluent provided by the membrane. Membrane bioreactors generally offer increased COD removal for less biodegradable feeds and at a much smaller incurred footprint.

*Insert **Figure 4** near here*

Oil contaminated wastewater

In petroleum refinery, the combination of complex processes induces different wastewaters. The main processes inducing wastewaters are: storage, desalination, fractionation, thermal and catalytic cracking, reforming, polymerization, alkylation, isomerisation and solvent refining [78]. Wastewaters coming from those different steps of the process lead to the production of a wastewater containing organic compounds. The composition of this wastewater is a function of the processing units involved and generally contains: hydrocarbons (aliphatic or aromatic), phenolic compounds (phenol, methylphenol, dimethyphenol), sulphur, mercaptans, oil, solvents or chlorines.

Olive oil extraction process generates large amounts of dark liquid effluents called olive mill wastewaters (OMWs) as high as 0.5–0.8 m^3 for 1 ton of olive fruits treated. These effluents result from the mixture of "vegetation water" coming from the olives, and water added during the process. OMW is one of the most contaminated effluents. It is characterised by the variety of pollutants it contains which vary with place, age of growth, season, year, etc. The OMW is a foul smelling acidic wastewater composed of water (83–92 wt%), organic matter (4–16 wt%) and minerals (1–2 wt%). The organic load is so high with biological oxygen demand (BOD) up to $100 gL^{-1}$ and chemical oxygen demand (COD) up to 200 g L^{-1}. These values are about 300 times higher than those of a typical municipal sewage. Because of their antibacterial effects, phenolic compounds of the organic are the most problematic compounds encountered in the OMW [79]. **Table 1** compares COD removal during olive mill wastewater treatment by different processes [80].

*Insert **Table 1** near here*

The number of publications devoted to the application of membrane bioreactors to oil contaminated wastewater is still low and the main attention is focused on the study of the process feasibility and some operating conditions [81,82].

Kurian et al. [83] studied aerobic MBRs operating at room temperature (20 °C) and at lower thermophilic range (45 °C) for the treatment of dissolved air flotation (DAF) pretreated pet food wastewater. The particular wastewater was characterized by oil and grease (O & G) concentrations as high as 6 g/L, COD of 51 g/L, BOD of 16 g/L and volatile fatty acid (VFA) of 8.3 g/L. The performances of the two systems in terms of COD, BOD and O & G removal at varying hydraulic retention time (HRT) were compared. COD removal efficiencies in the thermophilic MBR varied from 75% to 98% and remained constant at 94% in the conventional MBR. The O & G removal efficiencies were 66–86% and 98% in the thermophilic and conventional MBR, respectively. Interestingly, high concentrations of VFA were recorded, equivalent to 50–73% of total COD, in the thermophilic MBR effluent. The observed yield in the thermophilic MBR was 40% of that observed in the conventional MBR.

The use of a submerged membrane bioreactor for the treatment of industrial oil contaminated wastewater was investigated using microfiltration hollow fiber membranes by Bienati et al.[84]. The membrane bioreactor worked with a hydrocarbon concentration ranging from 600 to 1500 mg/L in a sub-critical flux regime. The sludge concentration ranged from 14 g/L to 28 g/L. The MBR was able to treat wastewater with high removal efficiency (about 98%), under low hydraulic retention time (about 10 h) and high biomass concentration.

The use of a crossflow membrane bioreactor (CF–MBR) in treating wastewater discharged by a petroleum refinery was investigated by Rahman et al. [85]. The performance of the CF–MBR process was evaluated at MLSS concentrations of 5000 and 3000 mg/l. The process performance was measured in terms of the hydraulic efficiency as well as the COD removal efficiency. The results of the investigation showed that a COD removal efficiency of more than 93% was obtained at both MLSS values. The study also showed that hydraulic retention time did not have a significant effect on the system’s performance.

Dhaouadia et al. [80] undertook an experimental study of olive mill wastewater (OMW) treatment in an external ceramic membrane bioreactor (MBR). The main objective of this work was the study of OMW treatment feasibility using an MBR with a biomass specially acclimated to phenol. The used reactor, equipped with an external ceramic microfiltration membrane gave stabilized permeate flux, around 92 L $h^{-1}m^{-2}$, with zero suspended solid and no phenolic compounds. No fouling problems occur during all the experiments. The chemical oxygen demand (COD) remains quite high, and its abatement can be achieved by enhancing the oxygen transfer to the mixed liquor contained in the MBR. The combination of biological and membrane separation for the OMW treatment seemed to be an effective alternative in the reduction of the environmental impact of the olive oil extraction processes effluents. The authors contended that OMW treatment in a membrane bioreactor can be used as a pre-treatment stage, essentially for phenolic compounds removal before a conventional biological process. Since the MBR biomass concentration is no longer controlled by secondary clarifier solids loading limitation, the ability of MBR to operate at high MLSS concentration permits a high amount of phenolic compound retention on biomass surface. No specific measurements in this work were done to evaluate the phenolic compound bioconversion. Nevertheless slow rate phenolic compounds biological conversion has been reported in the literature. In MBR, the membrane filtration step provides an effluent with high quality in terms of suspended solid, the phenolic compounds adsorbed on suspended solid remains within the retentate phase and the obtained permeate is thus phenols free.

Phenol and its derivatives are widely used as raw materials in the petrochemical industry and in oil refineries. Phenolic compounds due to their high toxicity inhibits micro-organisms or even eliminates them from municipal biological wastewater treatment plants [86]. Barrios-Martinez et al. [87] showed the feasibility of the MBR treatment of a synthetic effluent containing a large amount of phenol. Using a biomass acclimated to phenol degradation, the critical conditions of membrane separation were determined: TMP= 100 kPa (1 bar) and v=5ms^{-1}. The membrane bioreactor process was evaluated in terms of membrane performance and biological degradation. The experiment of phenol degradation proved the effectiveness of the step of activated sludge acclimation, since a steady state was reached in a few hours. No phenol was detected in the permeate and a large quantity of phenol (50 g day^{-1}) was degraded. The absence of suspended matter, the removal of a substantial amount of phenol and a good performance on organic substance removal show the excellent performances of MBR.

Galil et al. [88] evaluated practical possibilities to upgrade existing wastewater treatment facilities to MBR technology, in order to obtain high quality effluent for sustainable reclamation and reuse of industrial wastewater. Three different types of industrial wastewaters were biologically treated by MBR working on hollow fiber technology: (a) paper mill; (b) food production; (c) fuel port facilities. The MBR received preliminarily treated effluent by anaerobic, chemical and physical processes, respectively. The experimental work in this study indicated that biological treatment of industrial wastewater containing contaminants characterized by hydrophobicity and/or by low biodegradability would require the adaptation of the MBR operating conditions, by lowering cell residence time and MLVSS in the bioreactor and by increasing the amounts of excess biosolids accordingly. The effluent was of high quality and could be considered for reuse in paper mill and food production.

Trials in a MBR with a high activated sludge concentration of up to 48 g/1, showed that oily wastewater also containing surfactants was biodegraded with high efficiency [81]. During the different loading stages of the MBR operation a removal rate of 99.99% could be achieved for fuel-oil as well as lubricating oil at a hydraulic retention time of 13.3 h. The maximum biodegradation of fuel oil amounted to 0.82 g hydrocarbons degraded per day, and g MLVSS and average values of 0.26-0.54 g hydrocarbons g^{-1}MLVSS d^{-1} could be achieved. The average removal of COD and TOC during the experiment was 94-96% for fuel oil 97, and 98% for lubricating oil, respectively. Due to the high removal efficiency of oily pollutants and the complete retention of suspended solids by the ultrafiltration unit, the MBR system shows good potential for application in industry for process wastewater recycling purposes. This study showed the superiority of MBR in comparison to plain filtration (**Table 2**).

*Insert **Table 2** near here*

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To extend the service life and to improve the quality of degreasing solutions from surface refining processes in the metal working industry a process based on a membrane bioreactor (MBR) with submerged multi-channel fiat sheet ceramic membranes was developed by Blocher et al.[89]. This MBR-based regeneration process combines the retention by membranes and the biodegradation of oils/grease. The objective was to retain the biomass as well as the hydrocarbons in the bioreactor by the microfiltration membranes to enhance biodegradation. Simultaneously, low retention of surfactants is aimed at since these substances have to be returned to the degreasing bath. The multi-channel flat sheet ceramic membranes, which had an average pore diameter of 0.3 μm, fulfilled the objective of retaining the hydrocarbons to a high extent while allowing relatively high permeation of the surfactants (in order to minimise additional dosing). Permeate was free of solid matter and hydrocarbon concentration was reduced by 85-90% (compared to the feed). The reduction in non-ionic surfactants was only 25-40%. Compared to conventional ("open") biological regeneration, a five fold increase in volumetric biodegradation rate was achieved due to the higher biomass concentration.

In order to develop full scale process and design information, Sutton et al. [90] conducted field pilot studies for several months. These pilot studies involved assessing system performance and developing system design information in the treatment of wastewaters from metalworking automotive plants. The results of the pilot studies provided the basis for the design of a full scale demonstration MBR system for treatment of industrial oily wastewaters. The extent of the process information developed and the positive nature of the performance results observed provide a high degree of assurance that cost-effective full-scale MBR systems can be designed and installed, and can be expected to perform technically at a level equal to or better than a conventional oily wastewater treatment system.

Some other recalcitrant wastewater

Wastewater from acrylonitrile, butadiene and styrene (ABS) plant includes high total Kjedahl nitrogen (TKN)/COD ratios as an index of biodegradation-refractory characteristics. The feasibility and the treatment efficiency of treating acrylonitrile-butadiene-styrene (ABS) industrial wastewater by an aerated submerged membrane bioreactor (ASMBR) were investigated by Chang et al. [91]. Throughout long-term investigation, biomass, biological oxygen demand (BOD5,) chemical oxygen demand (COD), total organic carbon (TOC) and permeate flux were measured to evaluate the MBR performance. The results show that a hydraulic retention time (HRT) of 18 h leads to the highest biomass concentration, a maximum mixed liquor suspended solids (MLSS) value of approximately 35 g/L. The membrane bioreactor led to superior COD and BOD_5 removal in ABS wastewater compared to the conventional biological treatment.

Two lab scale wastewater treatment plants treating hospital wastewater in parallel were compared by Pauwels et al. [92] in terms of performance characteristics. One plant consisted of a conventional activated sludge system (CAS) and comprised an anoxic and aerobic compartment followed by a settling tank with recycle loop. The second pilot plant was a plate membrane bioreactor (MBR). The wastewater as obtained from the hospital had a variable COD (Chemical

Oxygen Demand) ranging from 250 to 2300 mg l^{-1}. Both systems were operated at a similar hydraulic residence time of 12 hours. The reference conventional activated sludge system did not meet the regulatory standard for effluent COD of 125 mg l^{-1} most of the time. Its COD removal efficiency was 88%. The plate MBR delivered an effluent with a COD value of 50 m g l^{-1} or less, and attained an efficiency of 93%. The effluent contained no suspended particles. In addition, the MBR resulted in consistent operational parameters with a flux remaining around 8-10 l m^{-2} h^{-1} and a transmembrane pressure < 0.1 bar without the need for backwash or chemical cleaning. The CAS and the MBR system performed equally well in terms of TAN removal and EE2 removal. The CAS system typically decreased bacterial groups for about 1 log unit, whereas the MBR decreased these groups for about 3 log units. Enterococci were decreased below the detection limit in the MBR and indicator organisms such as fecal coliforms were decreased for 1.4 log units in the CAS system compared to a 3.6 log removal in the MBR.

Cicek [93] summarized the potential applications of the MBR technology for the treatment of wastewater from agricultural sources. He opined that anaerobic digestion coupled with an aerobic/anoxic membrane bioreactor could be utilized for treating manure and wastewater from livestock operations to levels suitable for direct reuse or safe discharge to surface water bodies. Wastewater generated from industries such as slaughterhouses, meat, dairy, egg, and potato processing and liquor production could potentially be treated with MBRs resulting in compact systems producing high quality reusable water.

INNOVATIVE MODIFICATIONS TO MBR DESIGN

Researchers have put forward different modifications to conventional design of MBR in order to enhance removal performance and/or mitigate membrane fouling. Such modified designs include anoxic/aerobic MBR [55, 93], Biofilm MBR [94], thermophilic MBR [83], Bio-augmented MBR [110], adsorbent-added MBR [122] etc. This section will focus on the latter two types of MBR in conjunction with recalcitrant compounds removal.

Bio-augmented MBR

Bioaugmentation is the application of indigenous or genetically modified organisms to bioreactors or other polluted waste sites in order to accelerate the removal of undesired compounds [95]. Bioaugmentation usually help conventional biodegradation processes work faster, or may provide additional, exogenous biological agents to polluted systems and improve the transformation processes [96-97]. Bioaugmentation has been demonstrated to enhance the removal of many specific pollutants such as phenols, chloroaniline, chlorobenzoate, resin acid, etc. [98-100]. However, the bioaugmentation does not always work because of the washout of the inoculants from the system [101]. Specifically, unstable removal efficiency and uncertain ecological risk make bioaugmentation using genetically engineered microorganism (GEM) seem unreliable in the conventional biological treatment processes. Several characteristics of MBR, such as membrane interception and long sludge retention time, help to prevent washout of inoculants. Also the ecological risk that may arise from leakage of genetically modified microbes would be minimal in case of MBR. However successful application of bioaugmentation techniques is dependent on the identification and isolation of appropriate microbial strains, and

Hai, F. Ibney., Yamamoto, K., Nakajima, F. & Fukushi, K. (2010). Recalcitrant industrial wastewater treatment by membrane bioreactor (MBR). In S. Gorley (Eds.), Handbook of Membrane research: Properties, Performance and Applications (pp. 67-104). New York: Nova Science Publishers.
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their subsequent survival and activity, once released into the target habitat. Hence to fully exploit the augmented MBR system, the microbial population structure, dynamics and the survival of the added microorganisms should be better understood.

Qu et al. [102] studied the removal performances of Bromoamine acid (1-amino-4-bromoanthraquinone-2-sulfonic acid, BAA) which is widely used in synthesis of anthraquinone dyes and also the microbial population changes in a laboratory-scale membrane bioreactor (MBR) augmented with Sphingomonas xenophaga QYY. While a previous study by the same group [103] reported the inability of conventional activated sludge to degrade BAA, in the present study it was demonstrated that after 30 days of acclimation, the non-augmented MBR system was able to degrade bromoamine acid (BAA) to some extent. They contended that the activated sludge used for inoculation in the latter study possessed the indigenous BAA-degrading populations and since the membrane module could maintain the biomass, it could achieve BAA removal. However, with increase of influent BAA concentration, the removal ratio was decreased. Also, the dynamic and structure of bacterial populations were not kept at a normal level. On the other hand, the augmented MBR showed higher removals (more than 90% and 50% color and COD removals, respectively) (**Figure 5**). By ribosomal intergenic spacer analysis (RISA), it was found that BAA-utilizing populations gradually increased to become the dominant species in the non-augmented MBR. The augmented MBR possessed relatively stable treatment abilities, in which the introduced strain QYY could be persistent and co-exist well with the indigenous populations.

*Insert **Figure 5** near here*

Liu et al. [104] reported efficient and stable atrazine removal after a start-up period in a membrane bioreactor (MBR) bioaugmented with genetically engineered microorganism (GEM). The removal efficiency was above 90%. Atrazine is one of the persistent organic pollutants (POPs) and it has been used widely in agriculture and forestry in the world for more than fifty years. Unsatisfactory treatment of of atrazine containing wastewater in biological processes has been reported. Under prolonged hydraulic retention time (HRT) of 5-7 d, only 40–90% of atrazine could be removed by the wild type atrazine-degrading strain or mixed microbial consortium in the conventional biological treatment processes [105-107]. In the current study, GEM containing an atrazine chlorohydrolase gene was applied to enhance atrazine removal from wastewater. The start-up period was found to be the key step to realize efficient and stable atrazine removal. In the start-up period, atrazine removal was unstable and inefficient and the GEM population varied greatly. After the start-up period, stable and high efficiency of atrazine removal could be obtained and the GEM population remained constant. The shortest start-up period was 2 days and the longest one was 12 days under different operation conditions. Initial influent atrazine loading, operation temperature and initial density of GEM affected the start-up period greatly. High initial influent atrazine loading, high operation temperature and large initial density of GEM were favorable to shorten the start-up period. The variation of GEM density was influenced by operation conditions and showed close relationship with atrazine removal in the start-up period.

Ghyoot et al. [108] examined the behaviour of a 3-chlorobenzoate (3CBA) degrading Pseudomonas putida BN210 carrying the self-transferable clc-element containing the clc-genes for 3CBA metabolism in a conventional activated sludge system (CAS) and a membrane separation bioreactor (MBR). Although molecular techniques indicated that strain BN210 disappeared or survived only in low cell numbers in both the reactors, the MBR showed higher resistance towards shock loading of 3CBA in terms of improved COD removal. Respirometry showed that the MBR sludge was less destabilized by 3CBA shock loadings than the CAS sludge. Molecular characterization of the isolates strongly suggested that in the MBR the *clc*-element had been *in situ* disseminated from the initial inoculum to contaminant bacteria, which had invaded the reactor and which finally became the dominant strains to continue 3CBA degradation. Possibly high biomass concentrations in the MBR stimulated transfer of the *clc*-element from strain BN210 to autochthonous bacteria. Also, autochthonous 3CBA degrading bacteria might benefit from specific conditions in the MBR.

Wichitsathian et al. [109] investigated biological treatment of medium-age landfill leachate in a membrane bioreactor operated with mixed yeast culture termed as yeast based membrane bioreactor (YMBR). The leachate was characterized with a chemical oxygen demand (COD) concentration of 7000–9000 mg/L, biochemical oxygen demand (5 days) to chemical oxygen demand ratio (BOD_5/COD) of 0.35–0.45 and total Kjeldahl nitrogen (TKN) of 1800–2000 mg/L. The performance was assessed with and without ammonia stripping. The average COD and TKN removal efficiency without ammonia stripping ranged between 52–66 and 14–28%, respectively. The performance of the membrane bioreactor improved with ammonia stripping in terms of both COD (72–76%) and TKN (82–89%) removal efficiency. Performance comparison with a mixed bacteria-based MBR revealed that though the difference was not significant in terms of COD removal, the YMBR showed better removal efficiency in terms of BOD_5. The molecular weight cut-off showed that the degradation pathway of the leachate by bacterial and yeast are different. In regard to membrane fouling, the YMBR showed better performance with lower trans-membrane pressure as well as longer operating time. This superior performance of the YMBR could be due to the structure of yeast cells which are larger in size as well as reduced soluble extracellular polymeric substances (EPS) production, which are the main cause of membrane biofouling.

Hai et al. [110] developed a submerged membrane bioreactor containing a mixed microbial community dominated by the white-rot fungus *Coriolus versicolor* for the treatment of textile dye wastewater. Under controlled temperature (29±1°C) and pH (4.5±0.2), and applied HRT of 15 h, the reactor accomplished around 97% TOC and 99% color removal from the synthetic wastewater (TOC = 2 g/L; dye = 100 mg/L) for a prolonged period of observation. The results showed that the dye having high biosorption was retained by the sludge-layer on the membrane, and was subsequently degraded by fungi. Thus de-coupling of the dye retention time and HRT was possible in the membrane-coupled fungi reactor and satisfactory dye removal even under low titer of fungal activity (due to the presence of bacterial contamination) was achieved applying reasonable HRT.

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Adsorbent added MBR

A solution used to increase the biodegradation of the slowly biodegradable compounds is the adsorbent addition in the bioreactor. The addition of adsorbents into a biological treatment system allows removing various toxic or non-biodegradable organic substances from the wastewaters and reduces their toxic effects on microorganisms [111]. Slowly biodegradable or toxic compounds are adsorbed and thereby their residence time within the reactor increases, which gives appropriate time for biodegradation [112].

In the available studies, powdered activated carbon (PAC) has been predominantly used as the adsorbent. The main features of PAC use in conventional activated sludge processes are:

-autotrophic [113] and heterotrophic [114,115] microorganism protection from load peaks of inhibiting compounds;

-PAC bioreactivation [116,117];

-refractory organic compounds degradation by biological activated carbon [111];

- increase of activated carbon adsorption in presence of a biofilm [118,119];

-increase of sludge settleability and dewaterability [120].

Frequent addition of fresh adsorbent is inevitable in conventional systems. Due to the high maintenance costs of PAC, successful results achieved in laboratory and pilot scale experiments have found little application on full scale plants. However, this not a problem in case of MBR due to membrane retention and application of long SRT. Biofilm could grow on the activated carbon surface and develop a specific population for the degradation of the toxic compound. The membrane will separate the activated carbon and the sludge from the treated water. In this way, for a given PAC concentration, the decrease of excess sludge removal causes the reduction of PAC maintenance cost. **Figure 6** [121] illustrates the hybrid PAC-membrane-biodegradation concept.

*Insert **Figure 6** near here*

Hai et al. [122] explored a PAC-added membrane-coupled fungi reactor for textile dye wastewater treatment. The synthetic textile wastewater containing either or both of two structurally different azo dyes was continuously fed. Compared to the Acid Orange II dye (simpler structure), higher biosorption but slower biodegradation of the polymeric dye (Poly S119) was observed in sterile batch tests. In the membrane bioreactor (MBR), although a relative abundance of fungi (66%) without any specific control of bacterial contamination could be maintained, unlike in pure fungus culture, enzymatic activity was below detection limit. Nevertheless, >99% removal of Poly S119 was consistently achieved under a dye loading of 0.1 g $L^{-1}d^{-1}$ (HRT= 1 day). Comparison of the reactor-supernatant (SQ) and the membrane-permeate (PQ) qualities (31% improvement) revealed the significant contribution of the membrane to the overall removal (biosorption, cake layer filtration, biodegradation) of Poly S119. Contrary to the faster removal of Orange II in batch test, membrane-permeate quality revealed 93% removal of the dye in MBR (corresponding SQ= 82%). However, excellent (>99%) stable removal of Orange II or of both the dyes together, as well as stable enzymatic activity was observed following addition of powdered activated carbon (PAC) in the MBR. In accordance with real textile wastewater, dye contributed only 5% of the TOC loading (0.944 g $L^{-1}d^{-1}$) in this study. In contrast to low TOC removal by fungi alone, the MBR containing mixed microbial community steadily achieved >98% removal, which improved further to >99% after PAC addition. Improved decolorization due to adsorption and close contact of dye as well as dye-degrading enzyme on powdered activated carbon (PAC), which was added into the MBR, was observed in this study. Simultaneous PAC adsorption within fungi MBR thus resulted in multiple advantages including adsorption of dye and prevention of enzyme washout, eventually leading to enhanced dye-degradation.

Munz et al. [123] operated a pilot scale membrane bioreactor (MBR) with the addition of powdered activated carbon (PAC) to analyze improvements in effluent quality and the filtration process. The results refer to a pilot plant monitoring stretched over a period of 594 days: 380 without PAC, 123 with a PAC concentration of 1.5 g/L and 91 with 3 g/L. The sludge residence time and hydraulic retention time were maintained between 30 and 90 days and 50 and 100 hours, respectively. Improvements in COD removal were found to be low, but not negligible, and greater than the PAC adsorption effect alone. COD removal stability appeared to increase as PAC concentration increased. No effects were observed on the nitrification processes. The filtration process was evaluated in terms of sludge filterability, fouling rate and fouling reversibility. The fouling rate decreased with an increasing PAC concentration and showed complete reversibility both in presence and in absence of PAC.

Lesage et al. [121] compared a membrane bioreactor (MBR) and a hybrid membrane bioreactor (HMBR) coupling membrane separation, biological activity and adsorption on powdered activated carbon (PAC) in order to remove a toxic compound. The two processes were compared in terms of water treatment efficiency, membrane fouling and biological sensitivity to the toxic compound. Experiments were performed with synthetic wastewater and 2,4-dimethylphenol (DMP) was chosen as a molecule representative from toxic compounds present in effluents from the oil industry. This study showed the interests of the hybrid process in comparison with a conventional MBR, due to the positive effects of PAC adjunction: results pointed out that addition of activated carbon could structure the biomass, deposit at the membrane surface, and decrease proteins and carbohydrates concentrations in the HMBR supernatant that allows a reduction of membrane fouling. Results show that PAC adjunction slightly reduces sludge production in the HMBR. Toxic injection inhibits the biological activity in the MBR whereas the biological activity is maintained in the HMBR, with a biodegradation of the toxic compound after an acclimation period.

Thuy et al. [124] investigated the treatability of phenolic compounds by using two membrane-bioreactor systems, namely: activated sludge coupled with MBR (AS-MBR) and biological granular activated carbon coupled with MBR (BAC-MBR). Initially, the system was fed with phenol (500 mg/L) followed by adding 2,4-dichlorophenol (2,4-DCP). Phenol, 2,4-DCP, TOC

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and COD removal were higher than 98.99% when the organic load ranged between 1.80 and 5.76 kg/m^3.d COD. In addition to MBR system development, removal mechanisms were also investigated. Relatively low values of phenol adsorption on GAC and biomass, and high maximum substrate removal rates obtained from a biokinetic experiment, proved that the removals were mainly due to biodegradation. Analysis of sludge indicated a significant difference in the sludge characteristics of the two reactors. The high EPS content in BAC-MBR led to higher viscosity and poor sludge settling properties. The relationship between sludge properties and EPS components revealed that settleability had no direct correlation with EPS, though it was better correlated to protein/carbohydrate ratios.

Adding iron salt or iron hydroxide to sludge mixed liquor in an aeration tank of a conventional activated sludge processes (bioferric process) can simultaneously improve the sludge's filterability and enhance the system's treatment capacity. In view of this, Haiyan et al. [125] added $Fe(OH)_3$ to a submerged membrane bioreactor (SMBR) to enhance the removal efficiency and to mitigate membrane fouling. Bioferric process and SMBR were combined to create a novel process called Bioferric-SMBR. A side-by-side comparison study of Bioferric-SMBR and common SMBR dealing with dyeing wastewater was carried out. Bioferric-SMBR showed potential superiority, which could enhance removal efficiency, reduce membrane fouling and improve sludge characteristic. When volumetric loading rate was 25% higher than that of common SMBR, the removal efficiencies of Bioferric-SMBR in terms of COD, dye, and NH_4^+-N were 1.0%, 9.5%, and 5.2% higher than that of common SMBR, respectively. The transmembrane pressure of Bioferric-SMBR was only 36% of that in common SMBR while its membrane flux was 25% higher than that of common SMBR. The stable running period in Bioferric-SMBR was 2.5 times of that in common SMBR when there was no surplus sludge discharged. The mixed liquor suspended solids concentration of Bioferric-SMBR was higher than that of common SMBR with more diversified kinds of microorganisms such as protozoans and metazoans. The mean particle diameter and specific oxygen uptake rate of Bioferric-SMBR were 3.10 and 1.23 times the common SMBR, respectively.

INSIGHT INTO RECALCITRANT COMPOUND REMOVAL IN MBR

Some key benefits of the membrane bioreactor may be claimed in comparison to the conventional activated sludge systems and plain filtration processes:

- High biomass concentration in combination with the filtration effect, which increases the actual concentration of the pollutants in the bioreactor and therefore their bio-availability, lead to enhanced biodegradation efficiencies.
- The implementation of a biological stage enhances membrane permeate quality due to the degradation of the pollutants.
- Biodegradation leads to lower actual concentrations of the pollutants in the feed stream of the filtration unit.
- Another advantage of the membrane bioreactor is that the major part of the pollutants is mineralized. In comparison to membrane filtration where high volumes of concentrate are produced, only small amounts of surplus sludge have to be disposed.

This chapter presents comprehensive review of a large number of papers reporting on recalcitrant compound degradation in MBR. Based on that, the following insight can be offered:

Studies suggest that build up of heterotrophic bacteria having special degrading capacity [39,53,62] or easier acclimatization [80,87] is possible in MBR due to the complete retention of biomass by membrane and application of longer SRT. Accordingly better and/or stable removal performance may be expected in MBR.

For moderate to considerably biodegradable compounds, the volumetric biodegradation rate in MBR may improve due to high biomass concentration. For instance, compared to conventional biological process, a five fold increase in volumetric biodegradation rate was achieved in case of an oil-contaminated wastewater due to the higher biomass concentration [89]. However, that may not be the case for the hardly biodegradable or non-biodegradable compounds. For instance, no differences in treatment efficiencies were detected between the two treatment techniques while treating micropollutant containing wastewater [28]. As in conventional process the removal potential in MBRs also depends on the SRT. However, MBRs achieve a high SRT within a compact reactor. Conversely, other studies have reported that MBR is neither superior for well degradable compounds that are already extensively degraded in conventional treatment nor for recalcitrant compounds that are not amenable to biodegradation [30, 32]. However, they agreed that for most compounds of intermediate removal in conventional treatment, the MBR is clearly superior.

The ability of MBR to operate at high MLSS concentration permits a high amount of recalcitrant compound retention on biomass surface. The membrane filtration step provides an effluent with high quality in terms of suspended solid; hence the recalcitrant compounds adsorbed on suspended solid remains within the retentate phase where they may undergo biodegradation [34]. However, if the biosorbed compound is non-biodegradable, when the sludge is withdrawn, that toxic compound-laden sludge will require further appropriate treatment. At times, significant retention of soluble organics on the cake-layer over the membrane and subsequent biodegradation may occur [55, 110].

CONCLUSION

The MBR system is particularly attractive when applied in situations where long biological solids retention times are necessary and physical retention and subsequent hydrolysis are critical to achieving biological degradation of pollutants. Nevertheless, the removal rates differ from one compound to the other and the rates of removal depend on the physico-chemical characteristics of the xenobiotic.

In some cases enhanced biodegradation by development of special microbes may occur due to high MLSS and long SRT, but sometimes the improvement is more due to adsorption on biomass, retention by membrane and subsequent biodegradation. Often measures like bio-augmentation or addition of PAC have to be adopted to achieve enhanced removal. The superiority of the MBR lies in the fact that it is compatible with such additional measures. Application of such strategies

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in case of conventional wastewater systems would not be effective. New developments in this field are expected to lead to excellent solutions to treatment of recalcitrant industrial wastewater.

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Recalcitrant industrial wastewater treatment by membrane bioreactor (MBR)

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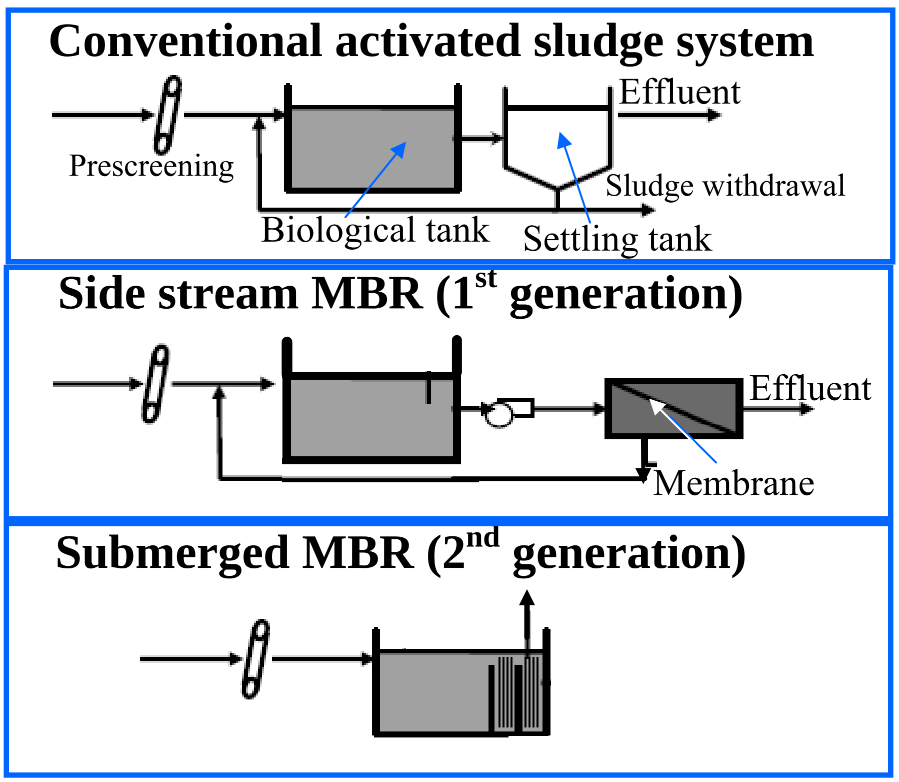

Figure 1: Evolution of membrane use in conjunction with bioreactor

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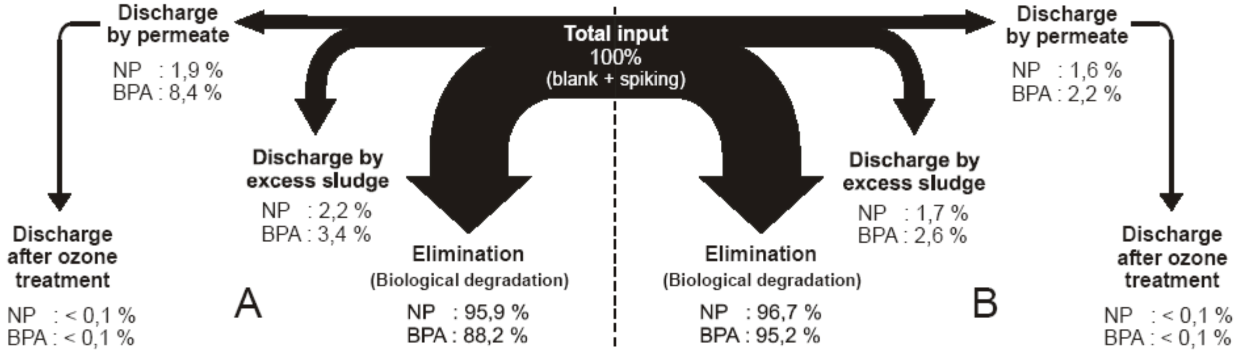

Figure 2: Mass flow chart demonstrating the fate of two micropollutants [4-nonylphenol (NP) and bisphenol A (BPA)] during treatment by (A) conventional, (B) MBR process, and after subsequent O_3 treatment steps (Adapted from [22])

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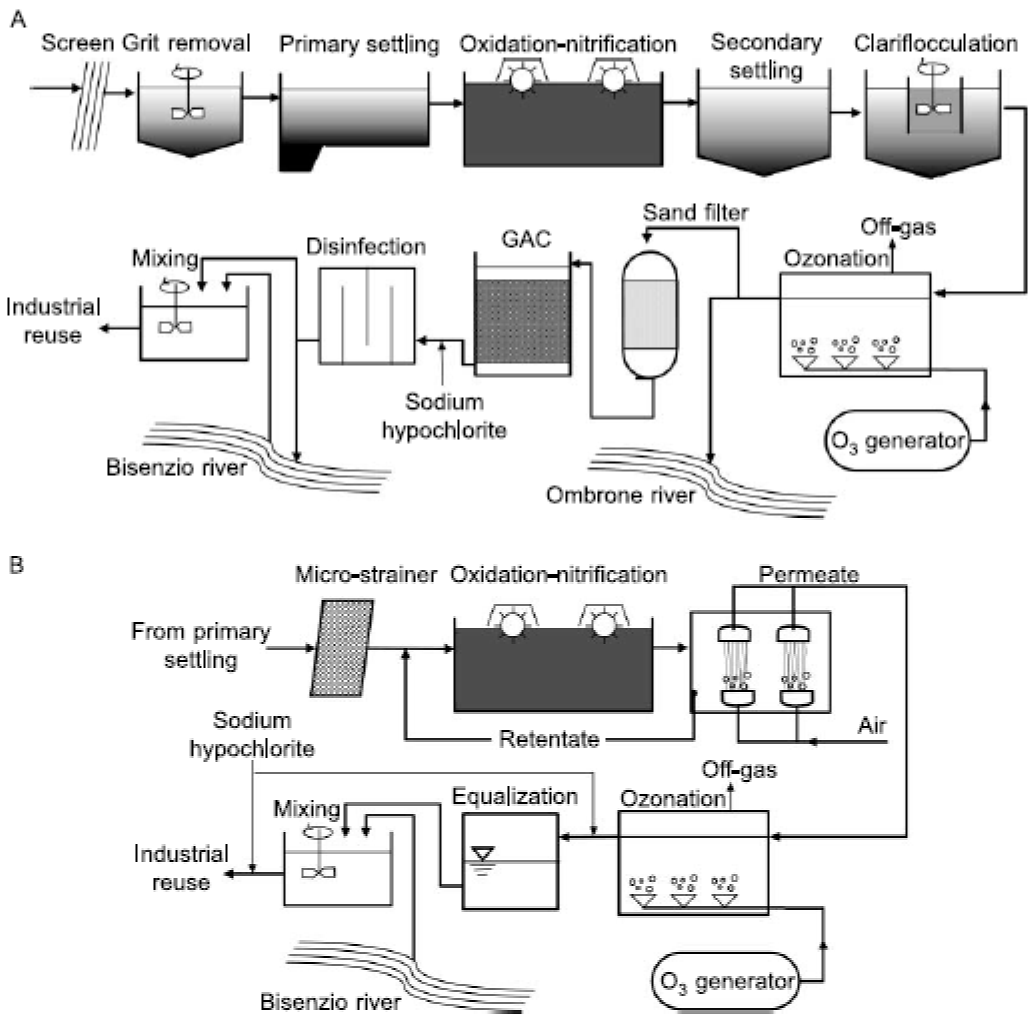

Figure 3: Schematic of two textile wastewater treatment options (A) Conventional process-based elaborate treatment trail, (B) MBR-based more compact treatment scheme (Adapted from [52])

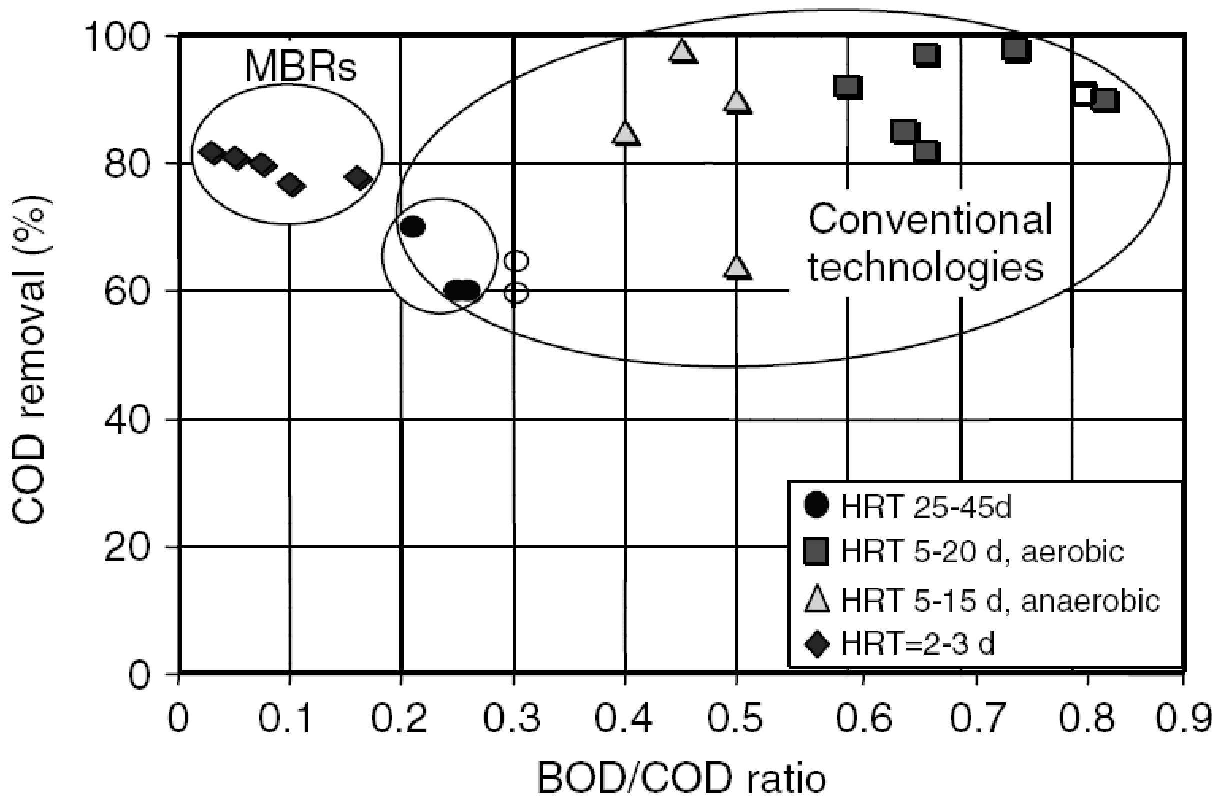

Figure 4: COD removal vs leachate BOD/COD ratio for different HRT ranges, full-scale plant; open data points refer to two-stage processes, hatched areas represent comparable data. (Adapted from [77])

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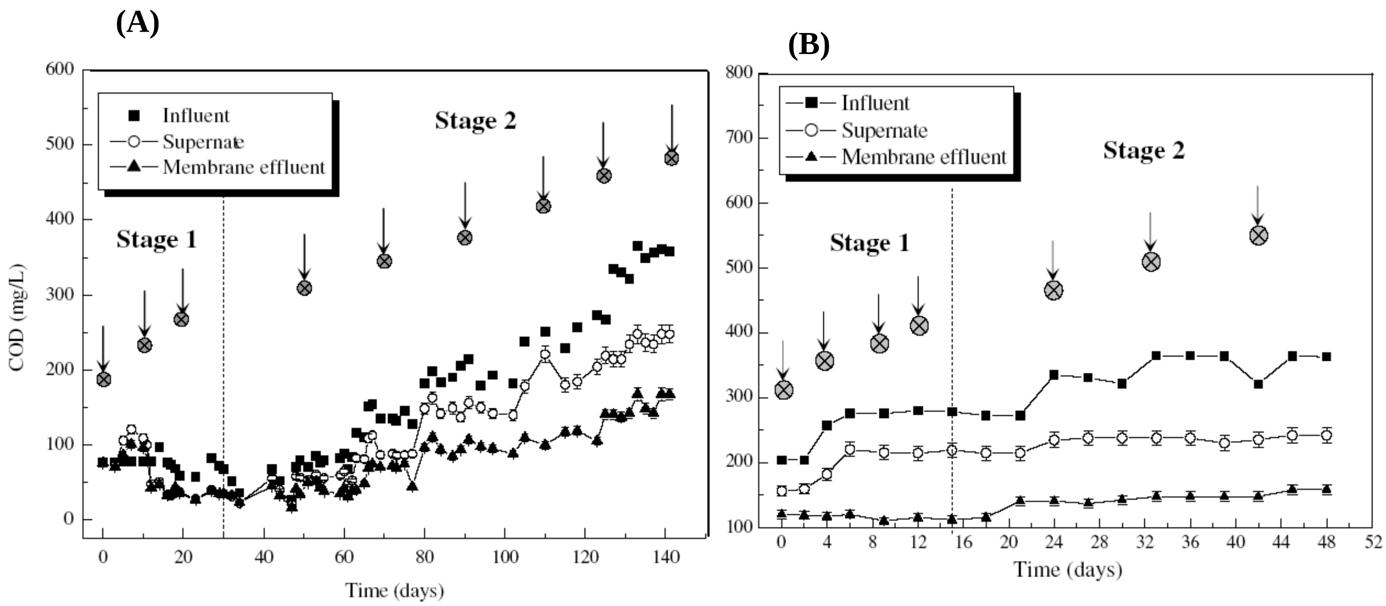

Figure 5: COD removal from wastewater containing the recalcitrant compound Bromoamine acid (BAA) in a non-augmented (A) and bio-augmented (B) MBR system. (Adapted from [102])

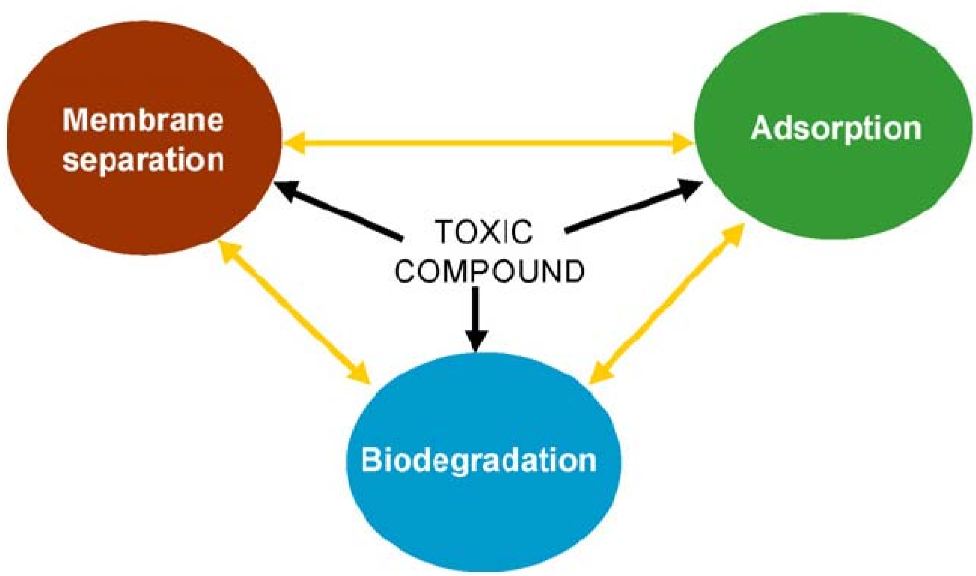

Figure 6:Schematic of hybrid adsorption—membrane separation—biodegradation process for toxic compound degradation (Adapted from [121])

Table 1: COD removal during olive mill wastewater treatment by different processes (Adapted from [80])

Process	Phenol inlet (mg L^{-1})	Phenol removal (%)	COD inlet (mg L^{-1})	COD removal (%)
Electrochemical	1520	>90	1,475–6,545	35–15
Electro-coagulation	nd	nd	4,850	52
UASB reactors	nd	nd	5,000	70
GAC reactor	720–1420	70–74	10,256–26,211	32–65
Fungal laccase	3700	65	43,000	5.3
Pleurotus spp.	3400	69–76	140,000	nd
MBR	5410	>92	1,500–5,300	81–37

Table 2: Comparison of operation parameters between industrial-scale applied ultrafiltration systems treating oil-contaminated wastewater from machine factoring and the membrane bioreactor system (Adapted from [83])

	Membrane bioreactor	Membrane application
COD (mg l^{-1})	129–131	373
Oil (ppm)	0.036–0.35	1
COD removal efficiency (%)	97	85.6
Oil removal efficiency (%)	99.9	99.2

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