

Review

Catalytic Ozonation and Membrane Contactors—A Review Concerning Fouling Occurrence and Pollutant Removal

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Abstract: Membrane filtration has been widely used in water and wastewater treatment. However, this process is not very effective for the removal of refractory organic compounds (e.g., of pharmaceutical origin). Coupling membrane filtration with ozonation (or other Advanced Oxidation Methods) can enhance the degradation of these compounds and, subsequently, the incidence of membrane fouling (i.e., the major problem of membrane uses) would be also limited. Ozonation is an efficient oxidative process, although ozone is considered to be a rather selective oxidant agent and sometimes it presents quite low mineralization rates. An improvement of this advanced oxidation process is catalytic ozonation, which can decrease the by-product formation via the acceleration of hydroxyl radicals production. The hydroxyl radicals are unselective oxidative species, presenting high reaction constants with organic compounds. An efficient way to couple membrane filtration with catalytic ozonation is the deposition of an appropriate solid catalyst onto the membrane surface. However, it must be noted that only metal oxides have been used as catalysts in this process, while the membrane material can be of either polymeric or ceramic origin. The relevant studies regarding the application of polymeric membranes are rather scarce, because only a few polymeric materials can be ozone-resistant and the deposition of metal oxides on their surface presents several difficulties (e.g., affinity etc.). The respective literature about catalytic membrane ozonation is quite limited; however, some studies have been performed concerning membrane fouling and the degradation of micropollutants, which will be presented in this review. From the relevant results it seems that this hybrid process can be an efficient technology both for the reduction of fouling occurrence as well as of enhancement of micropollutant removal, when compared to the application of single filtration or ozonation.

Keywords: catalytic membranes; ozonation; hybrid process; fouling control; micropollutant removal

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1. Introduction

Water is a key issue for the development of nations worldwide. However, many freshwater sources are contaminated and in some cases this contamination is considered to be irreversible. Water is also crucial for industrial processes, although around 80% of it is consumed by agriculture, livestock, and energy production (water, energy, and food nexus) globally [1,2]. The freshwater sources are also stressed by the continuous increase of the world's population. The lack of water supplies is not the only problem that needs to be addressed. Billions of people lack access to safe drinking water, or they have little or no sanitation. As a consequence, millions of people die annually from diseases transmitted using unsafe water. In both industrialized and developing countries, a growing number of contaminants are continuously entering water sources, mainly due to human activities. These substances can be, e.g., heavy metals, distillates [2], or micropollutants (MPs), such as pharmaceuticals, perfluorinated compounds, disinfection by-products, gasoline additives, etc. [3]. Figure 1 shows the impact of emerging contaminants in the aqueous ecosystem.

Public health and environmental concerns combined with the development of technology has led to efforts for further decontamination of waters that previously were considered to be clean [2]. Energy and water are the main challenging sectors, which are interconnected [4]. More effective and lower cost decontamination and disinfection methods are needed without further stressing the environment or endangering human health by the application of treatment itself. In recent years, the relevant published research about water treatment and especially regarding the emerging contaminants has significantly increased, as Figure 2 shows [2].

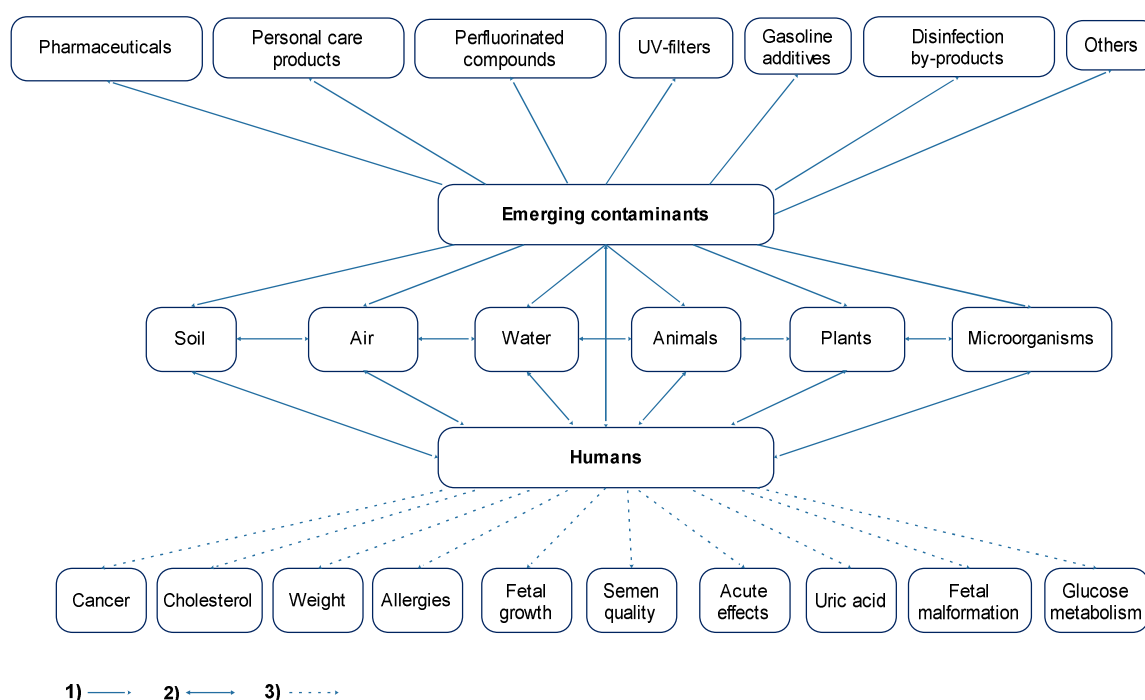


Figure 1. (1) The impact of micropollutants in soil, air, water, animals, plants, and microorganisms; (2) the interactions between them; and (3) the potential adverse effects of human exposure to micropollutants and their sources (Adapted from [3]).

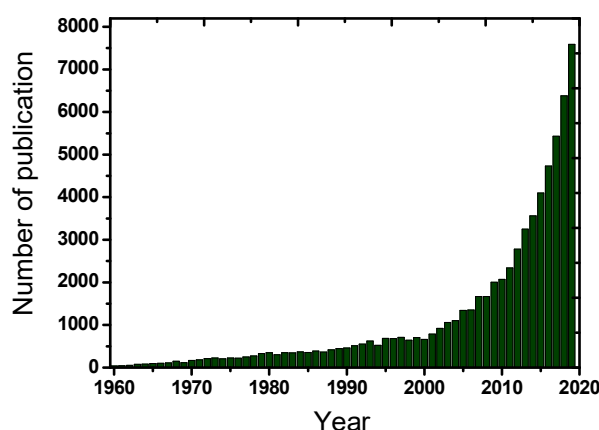


Figure 2. Number of yearly published scientific articles about emerging contaminants, as can be found from a relevant literature search in Science Direct.

The application of conventional methods (i.e., coagulation–flocculation, adsorption, and ion exchange) can effectively address several of these problems, but they are sometimes costly, both economically and in terms of energy [2,5]. Membrane technology can be a viable solution, because it is presently both energy-efficient and cost-effective [4]. It is a reliable technology that has been intensively researched and used for years. Membranes present many advantages, such as: (1) rather easy maintenance; (2) compact modular construction; (3) low chemical content in the treated effluent; and (4) high separation efficiency. In recent years, Advanced Oxidation Processes (AOPs) have proved to be effective technologies particularly for water treatment, and especially for the removal of MPs. The application of AOPs combined with membrane filtration has recently attracted research interest mostly for disinfection purposes, as well as for the removal of refractory organic pollutants and for membrane anti-fouling. Among these hybrid technologies is the combination of catalytic ozonation and membrane filtration [6]. There are three main types of catalytic ozonation coupled with membrane filtration, i.e., (a) ozonation occurring before membrane filtration, (b) ozonation occurring after membrane filtration, and (c) simultaneous ozonation and membrane filtration [7]. The third hybrid process can take place with the use of catalytic membranes, which is the major subject of this review. Catalytic membrane ozonation is a promising process that improves the anti-fouling properties of the membrane, enhances the removal of organic pollutants, and means that the catalyst deposited onto the membrane surface does not need to be recovered for potential reuse [8].

In this review, the major features of catalytic membranes and their applications in ozonation processes will be presented. In particular, the relevant literature has been reviewed and discussed, especially from the material (e.g., organic/inorganic) and the application (e.g., fouling/removal of MPs) points of view. Certain specific applications have also been analyzed.

2. Membrane Filtration

There are many different membrane separation processes although in all of them membrane plays the same role, i.e., it is the physical interface/barrier that allows the differential passage of materials (dissolved or particulate), according to the specific properties of the membrane itself, the solute, and the solvent [9].

2.1. Membrane Materials

Membranes can be fabricated and/or modified by using many materials. According to their material, membranes can be divided in two basic categories, i.e., organic (polymeric) and ceramic (inorganic) membranes.

2.1.1. Organic Membranes

Organic membranes are made of polymeric materials, such as cellulose acetate (CA), polyimide (PI), poly-acrylonitrile (PAN), polyvinyl-alcohol (PVA), polyether-sulfone (PES), polyether-imide (PEI), polyvinylidene fluoride (PVDF), polypropylene (PP), and polytetrafluoroethylene (PTFE) [4]. Polymeric materials in general may offer a wide variety of shapes (i.e., hollow, spiral-wound, flat-sheet, etc.) and properties [4,10]. Their main advantages are shown in Table 1. The most critical disadvantage is the fouling appearance. The presence of proteins, organic/inorganic compounds (dissolved or particulate), microorganisms, and microbial communities can block the membrane surface, due to the hydrophobic nature of both the constituents to be separated and the membrane surface. The hydrophobicity of organic membranes generally increases fouling phenomena, which in turn can increase the operational cost and decrease the membrane's efficiency and lifetime [4].

Also, these membranes present rather low chemical resistance and therefore can be unstable against ozone (oxidative agent). In particular, the polymers with carbon double bonds, such as PES and PEI, can react with ozone and decompose. Fluoropolymers, such as PTFE or PVDF, as well as polymers without functional groups that may exhibit reactivity towards ozone, such as poly-dimethyl-siloxane (PDMS, which has a dense non-porous morphology), are more suitable for ozone applications. When compared to fluoropolymers, PDMS is less resistant towards oxidizers other than ozone, including UV; however, its longer-term use in water treatment ozonation applications is still pending. Due to its availability in various sizes and relatively lower cost, PDMS is considered an appropriate “model” membrane material for smaller-scale investigations of coupled membrane/ozonation processes [11]. The resistance of polymers against ozone can be visually understood by the investigation of dos Santos et al. [12], examining the resistance of various commercial polymeric membranes (PEI, PES, PP, PDMS, PVDF, PTFE) after contact with gaseous ozone. Figure 3 shows SEM microphotographs and simple photographs of these materials before and after the application of 4 h of ozonation at 5.25 g/h dose at ambient temperature. In this study, except for PVDF and PTFE, the PDMS membrane also seems to be an ozone-resistant polymer; however, PTFE seems to be an ideal polymeric material for membrane contactors and for other applications, such as CO₂ separation. Due to its inherent hydrophobicity, PTFE presents less wettability, and it is more stable in gas-involving processes. However, based on the relatively lower cost of PVDF membranes and their comparable performance to PTFE ones, they still remain the membranes of first choice for several relevant applications [13].

2.1.2. Ceramic Membranes

Ceramic membranes are frequently used in water and wastewater treatment processes, due to their specific advantages, as shown in Table 1 [14]. Many inorganic materials have been used for the fabrication of ceramic membranes, such as α -Al₂O₃, TiO₂, ZrO₂ [6], as well as different combinations of them, i.e., TiO₂-SiO₂, TiO₂-ZrO₂, Al₂O₃-SiC, etc. [4]. The TiO₂-based membranes have received particular attention, due to their unique properties, such as chemical stability, good fouling resistance, and specific semi-conductive and photo-catalytic properties [15]. The chemical stability of these membranes increases generally in the order of SiO₂, Al₂O₃, ZrO₂, and TiO₂, while their thermal stability increases in the order of SiO₂, TiO₂, Al₂O₃, and ZrO₂ [16].

Table 1. Main advantages of organic and ceramic membranes [4,10,15,16].

Organic Membranes	Ceramic Membranes
Lower cost	Good selectivity
Flexibility	Robustness
Scalability	High productivity
Elasticity	Chemical, mechanical, and thermal stability
Resistance to fatigue	Controlled pore size

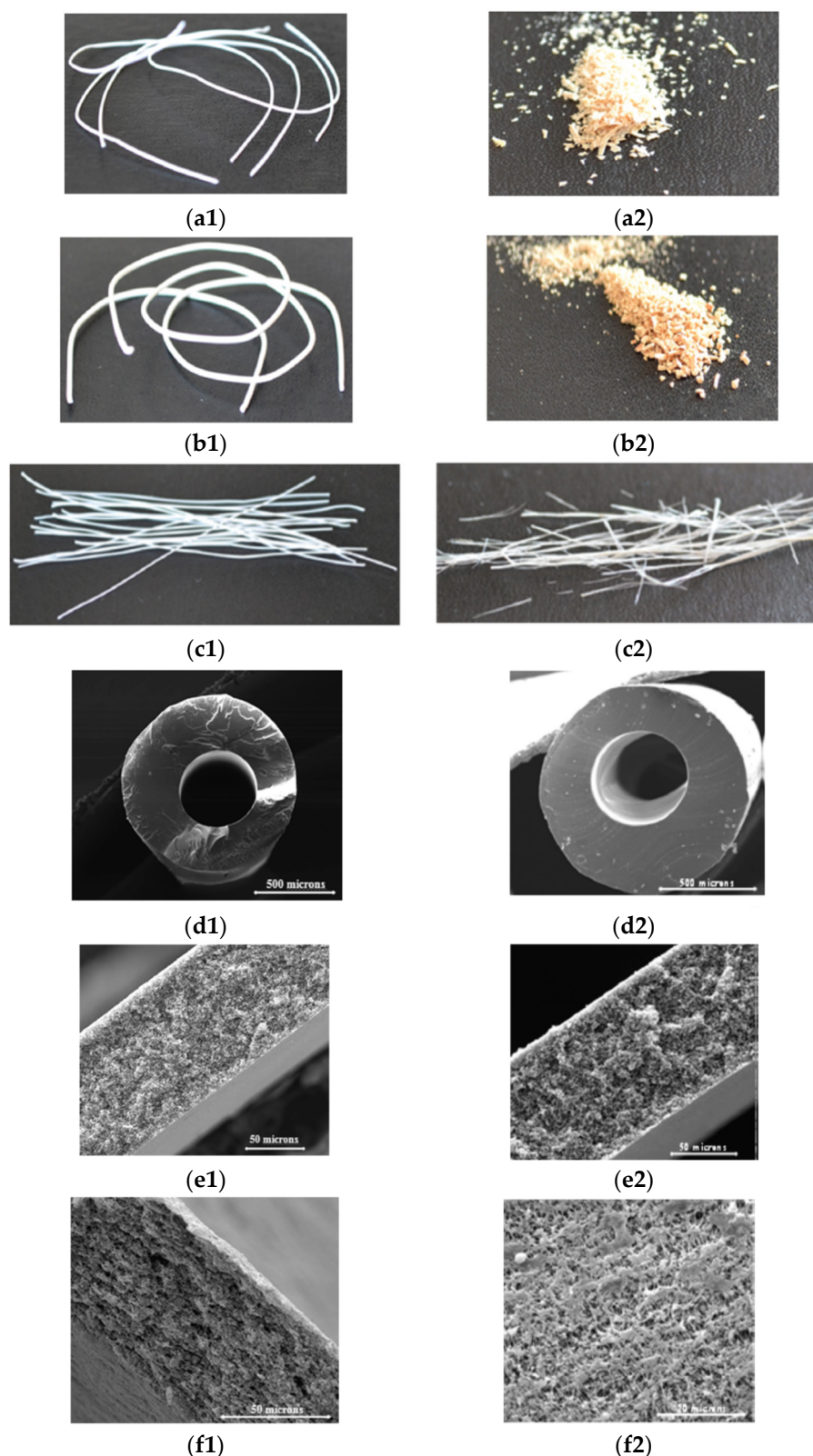


Figure 3. Simple and SEM microphotographs of commercial polymeric membranes before: PES (a1), PEI (b1), PP (c1), PDMS (d1), PVDF (e1) and PTFE (f1), and after the application of 4 h of ozonation: PES (a2), PEI (b2), PP (c2), PDMS (d2), PVDF (e2) and PTFE (f2) (Adapted from [12]).

Compared to organic membranes, the ceramic ones present higher chemical and mechanical stability, porosity, permeability, and hydrophilicity, longer lifetimes, lower operational cost, and greater recyclability [14,16,17]. Furthermore, the surface of ceramic membranes can be more easily coated with metal oxides, which can act as catalysts and hence improve their efficiency. However,

their capital/construction cost is still higher and the materials are more brittle than the polymeric ones [17]. The chemical stability of ceramic membranes makes them a suitable choice for oxidation process applications [18]. However, large-scale applications are still rather limited, due to the higher operational cost and mechanical fragility [19]. The higher hydrophilicity of ceramic membranes is associated also with lower fouling [16] and higher wettability as compared to organic membranes [20].

Nevertheless, when water comes into contact with a hydrophilic surface, it penetrates the membrane pores and can create gas transfer problems [20]. Kukuzaki et al. [21] showed that the mass-transfer coefficient of a hydrophilic porous glass membrane was four orders of magnitude lower than the hydrophobic-surface modified. By contrast, Hofs et al. [16] studied five different membranes, i.e., four ceramic (TiO_2 , ZrO_2 , Al_2O_3 , SiC) and one polymeric (PES-PVP), and observed that the ceramic membranes and in particular the TiO_2 and SiC -based showed lower reversible and irreversible fouling, i.e., the most hydrophilic membrane fouls the least.

2.2. Fouling Occurrence

Recently, the applications of membrane filtration processes have increased rapidly, due to the substantial reduction of the membrane's capital and operational costs [17]. Although membrane filtration can achieve higher water quality [15], when compared to most conventional methods (coagulation–flocculation, adsorption, and ion exchange) [5,15], it still presents an important critical limitation, i.e., the fouling incident, which can reduce flux and leads to reduced efficiency and higher operational cost [15].

There are in general four different types of fouling, i.e., (1) complete pore blocking, (2) intermediate pore blocking, (3) standard pore blocking, and (4) the formation of surface cake layer (Figure 4). These types can affect the filtration and are being affected differently by the operation process characteristics [22]. The formation of cake filtration does not block the membrane pores as the previous ones do, but can create a layer on the external surface, leading to the increase of hydraulic resistance [23]. The fouling resistance can be divided into three major types, i.e., adsorption, reversible, and irreversible fouling.

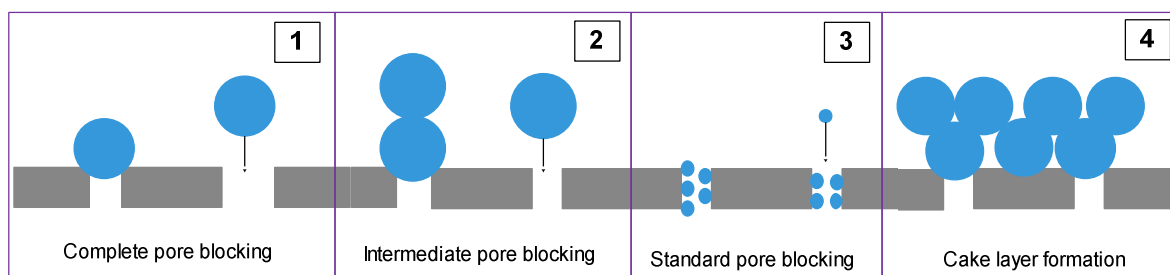


Figure 4. Schematic diagram of the four types of membrane fouling proposed by Hermia (Adapted from [23]).

Pore size, smoothness, hydrophobicity, and surface charge can substantially influence the fouling degree of a membrane. Smaller porous membranes have lower fouling potential and are less difficult clean after fouling than the larger ones [24]. The smaller porous membranes reject a wide range of treated materials and as a result a cake layer may be formed, which is more reversible during the cleaning cycle [25]. Cheng et al. [26] showed that when reducing the membrane surface roughness, this could decrease the accumulation of contaminants on the “valleys” of membrane surface and therefore, to reduce membrane fouling. Also, Vrijenhoek et al. [27] found that at the initial stage of fouling more particles were deposited on a rougher surface, rather than on a smoother one, but as the cake layer is forming, the consequences of roughness become less significant [25].

Hydrophobic degree is another characteristic on which fouling degree of the membrane depends. Hydrophilic membranes, due to their electrostatic charged surface groups are considered to be more fouling tolerant [24]. Therefore, if the hydrophilic properties of membranes' surface can

change, then the level of foulants that is adsorbed onto this surface could be reduced [25]. Furthermore, crucial role plays the electrostatic interactions between the membrane surface and the organic molecules. Zhu et al. [24] showed that a positively charged surface, such as that of alumina, can attract the negatively charged organic molecules, while the surface of TiO₂ membrane, because it is negatively charged at the same pH range, would attract the positively charged molecules. Most NOM are negatively charged molecules, therefore the TiO₂-based membrane is less likely to be fouled. Similar observations were made by Gonder et al. [25]; membrane fouling was reduced at the alkaline conditions (pH values around 10), due to the increased strength of electrostatic repulsion between the surface of the membrane and the components of the effluent.

The effects of fouling occurrence can be decreased by the application of appropriate pre-treatment methods. The most applicable pre-treatment methods are coagulation, adsorption, pre-oxidation, and pre-filtration. Table 2 shows the possible applications of the most commonly used pre-treatment methods for the fouling control plus the major advantages and disadvantages of these methods.

Table 2. Main pre-treatment processes applicable for fouling control: major applications, advantages, and disadvantages.

Pre-Treatment Process	Foulants	Advantages	Disadvantages	References
Coagulation	Viruses, humic/fluvic acids, proteins, polysaccharides with acid groups, colloids	Flux improvement	Requires proper dose	[25,28–31]
		Reversible fouling reduction	May exacerbate fouling	
		Decrease colloids and NOM concentration	Produce solid wastes	
		Low cost	Ineffective in mitigating the fouling by hydrophilic neutral organics	
		Easy operation	No removal of small molecules	
Adsorption	Humic/fluvic acids, small organic acids, some DBPs, pesticides, and other synthetic organic compounds	Flux improvement	Possible exacerbation of membrane fouling	[25,28]
		Small molecules removal	Difficult in removing PAC powders from treatment facilities	
		Cost competitive method		
Pre-oxidation	Viruses and organic contaminants	Flux improvement	Formation of by-products, such as DBPs (chlorination), bromated (ozonation), precipitates (permanganate)	[25,28,30,31]
		Decrease of organic pollutants concentration	May damage membranes incompatible with oxidants	
		Suppress microbial growth	May be ineffective in suppressing the growth of some microbiota resistant to oxidation	
Pre-filtration	Particulate and colloidal organic/inorganic substances, microbiota	Flux improvement	Performance of pre-filters may deteriorate and be difficult to recover	[25,28]
		Can remove colloidal matter and suspended solids	May require pre-treatment (e.g., coagulation or pre-oxidation) to enhance the efficacy	

An alternative way to eliminate the disadvantages of the applicable pre-treatment methods is the appropriate combination of them, which is called integrated (or couple, hybrid) pre-treatment. Such hybrid systems are coagulation–filtration, adsorption–flocculation, ozonation–GAC filtration, and ion-exchange–coagulation. However, these combinations may increase the capital cost of the treatment system, but if membrane fouling can be efficiently reduced as a result, then the overall

operational costs will be decreased and they can become cost-effective techniques [16,32]. Very few studies have been reported to detail the cost analysis of an integrated system. Most of these studies are focused on desalination plants, which used membrane systems as pre-treatment methods. Wolf et al. [33] performed such an analysis and observed that the capital cost was a little higher for the hybrid system (0.2452 \$/m³) as compared to the conventional one (0.2377 \$/m³), but showed also 22% higher flux and lower cleaning frequency. Some relevant results were reported by Valladares et al. [34] calculating that the application of pre-treatment for Forward Osmosis (FO) was found to increase the capital cost by 17%, while through energy management the operational cost was reduced by 56%, i.e., substantial savings were achieved.

All the major membrane-based treatment processes, i.e., microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and Reverse Osmosis (RO), have been used for the removal/separation of organic etc. pollutants in water and wastewater treatment operations [9]. However, membranes are a physical barrier, and they can only separate, e.g., the organic pollutants from the feed water, rather than degrade them. For the integrated abatement of organic pollutants, membrane filtration must be combined usually with an oxidation process, such as ozonation. By the application of this hybrid system the pollutants can be efficiently degraded and the retentates (concentrates) can be easier disposed. From this point of view, the coupling of membrane filtration with ozonation can be a promising method for the simultaneous degradation of pollutants and for the reduction of membrane fouling [7].

3. Ozonation

Ozone is a strong oxidant agent that can be used in water and wastewater treatment operations for the removal/oxidation/destruction of organic/inorganic pollutants, as well as of microorganisms. Ozone can participate into the respective oxidation reactions via two major routes, i.e., (1) it can directly react with the pollutants, or (2) it can be decomposed into hydroxyl radicals and these (more) reactive species can then react with the contaminants [35]. Certain metals, such as arsenic and iron, can be oxidized (and subsequently removed) by the application of direct oxidation with ozone, but the refractory organic compounds, such as nitrobenzene and MTBE (Methyl Tert-Butyl Ether), can only be degraded by the application of hydroxyl radicals, which are considered among the strongest oxidative species. Ozone decomposes into hydroxyl radicals by a 3-step mechanism, which involves initiation reactions, radical chain reactions, and a termination step. The overall reaction of ozone decomposition into hydroxyl radicals is:



Therefore, three molecules of ozone can produce two molecules of hydroxyl radicals via the radical chain reaction (second mechanism step). The initial decomposition reaction is that of ozone with the hydroxyl ion. More specific information about the more complex ozone reaction mechanisms can be found in the reference of Gottschalk et al. [36].

The main disadvantages of the ozonation process are considered to be the relatively slow oxidation/reaction time and the high energy requirements [22]. Although ozone is used frequently, especially in water treatment applications (mainly for disinfection purposes), its production cost is still quite high. The high cost is mainly a function of pure mass-transfer operation and its production process [37]. For example, the daily energy cost for a conventional ozone production system that treats 0.38 hm³/day of wastewater, when the average ozone dose, ozone concentration, and energy cost is 1.0 mg/L, 10% wt. and 0.10\$/kWh respectively is 346 \$/day [38]. Ozone is an unstable gas such that in order to react with a compound/contaminant it must be transferred from the gas into the liquid phase [37]. Ozone cannot be stored, because it decomposes quite fast into oxygen, so it must be produced in situ and consumed directly. The off-gases of ozonation process consist usually of 10% ozone and about 90% oxygen, which have no further use. Also, ozone has rather low partial pressure (0.01 atm) in air (according to the Henry's law) [39] and except for the difficulty to be diffused/dispersed/transferred into the liquid phase (indicating a weak driving force), the obtained dissolved ozone in the solution can be subsequently easily escaped into the gas phase at ambient

temperature. Overall, the efficiency of the ozonation process is considered rather low and several ways to improve it have been proposed [40].

The conventional ozone (contact) reactors are based on bubble diffusers, injectors and static mixers [40]. However, such processes can almost never consume completely the ozone added in water. Therefore, an ozone destructor must be subsequently used in order to destroy the residual ozone from the off-gases [41]. Furthermore, these types of reactors present rather small mass-transfer rates, because they are producing bubbles with quite small contact area (interface). The contact area may be decreased further, due to the possible presence of surfactants in the wastewaters. These organic substances can stabilize the bubbles' surface, creating unwanted foams in the reactor surface [42]. Due to the low use efficiency, an excess amount of ozone is necessary to be produced/added in order to be able to achieve the required ozone dose [43]. An alternative way to resolve the foaming issue is the addition of appropriate anti-foaming agents, but these chemical substances contribute to an additional water pollution problem. A more eco-friendly approach for both aforementioned major problems is probably the use of membranes as ozone diffusers/contactors [42]. The respective European project WaterCatox showed that a membrane contactor can increase the ozonation system efficiency by 3–6 times over the conventionally used reactors [44] and at the same time it does not create bubbles and offers better reliability in the addition of ozone dose [42].

3.1. Membrane Contactors

Membrane contactors are appropriate modules that can help the transfer of a constituent between a gas and a liquid phase and they are frequently used in ozone-based processes. The membrane is the interface that allows the two phases to flow separately. The main advantages and disadvantages of the membrane contactors are shown in Table 3 [45]. The introduction of this technology increases substantially the capital cost of ozonation process, but as counterbalance it decreases also the operational cost (due to limited ozone losses) and increases the process efficiency [41]. More information about the capital cost of ozonation by membrane contactors can be found in Plumlee et al. [46].

The membranes that used as contactors in the ozonation processes must have three important attributes, i.e., (1) long-term stability to ozone exposure, (2) surface hydrophobicity, and (3) porosity [11]. The most membrane contactors are polymeric membranes, but the use of these materials in ozone-based processes is rather limited, due to the oxidation reactivity of ozone and the potential quick destruction of these membranes. Therefore, ceramic membranes are more frequently used. These membrane types are mostly tubular, while the polymeric membranes can be also available as flat-sheet or hollow-fiber configurations. The hollow-fiber membrane contactors present certain advantages, when compared to the other mentioned membrane types, such as [45]:

- Larger membrane area per unit volume of membrane module
- Higher productivity
- High self-mechanical support
- Good flexibility
- Easy handling from fabrication to operation.

Except for their shape, ceramic membranes usually require appropriate surface modification before their use to increase hydrophobicity. Relevant studies have shown that the hydrophilic membranes present much lower efficiency as gas–liquid contactors than the hydrophobic ones [41], because the higher degree of hydrophobicity prevents the membrane's surface wetting and the flooding of pores [11]. The capillary forces in a hydrophilic membrane allow water to penetrate into its pores and may cause severe operational problems [41]. In the case of membrane contactors, the wetting phenomenon can increase the membrane resistance to the mass-transfer process and decrease the respective mass-transfer coefficient of gases. Complete prevention of wetting can only occur theoretically with a super-hydrophobic membrane, minimizing diffusion through the pores of the membrane. The wetting of pores with the exception of the specific structure of the membrane

material, also depends on the properties of the aqueous solution to be treated, in particular the relevant operating conditions (i.e., pressure and flow rate), type of liquid, and concentration of pollutants. E.g., liquids presenting lower surface tensions can more easily penetrate the membrane pores than the liquids with higher surface tensions. The presence of organic compounds in the liquid phase decreases the surface tension, depending also upon the organic compounds concentrations [47]. In case of inherent hydrophobic materials (e.g., certain organic polymers) Khaisiri et al. [13] reported that the order of membrane gas absorption is following the order: PTFE>PVDF>PP, which is not the same as the respective hydrophobicity order: PTFE>PP>PVDF, because the hydrophobicity of materials is not the only property that can affect the membrane's wettability. Other relevant properties may include also pore size and porosity. Higher porosity and bigger pore sizes can increase the membrane wettability [47].

Table 3. Main advantages and disadvantages of membrane contactors [26,45,48].

Advantages	Disadvantages
Higher mass transfer	Mass-transfer resistance from the membrane itself
Operating flexibility	Wetting of membrane pores
Scale-up simplicity	Sensitive to impurities
Absence of dispersion between the fluid phases	Membrane fouling
Compact structure	Life duration of a membrane (quicker replacement)
Operation with low pressure drops	Only mild operating conditions can be applied (polymeric membranes)
Higher interfacial area	
Easy recycling of effluent mixture	
Increase conversion in equilibrium limited reactions	
Overall higher efficiency	

Janknecht et al., 2004 [42] studied the mass transfer of ozone, using three different membrane materials. For their investigation they chose two ceramic membranes (alumina and cordierite/ $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) and an organic (PTFE) one. The second ceramic membrane was modified (to obtain higher hydrophobicity) with an appropriate silane ($\text{C}_8\text{F}_{17}\text{C}_2\text{H}_4\text{Si}(\text{OMe})_3$). Ozone mass transfer was found to increase with increasing membranes surface hydrophobicity, noting that materials with inherent hydrophobic features can give better results, when compared to laboratory modified hydrophobic materials. The residual water within the pores is the major limiting factor to ozone mass transfer. The pores of PTFE seem to be the ideal membrane material to overcome this limitation, due to its inherent hydrophobic features. Furthermore, PTFE presents high resistance to ozone [42].

The most investigated membrane contactors for ozone diffusion are based on the application of direct ozonation. Ozone alone is considered to be incapable of mineralizing refractory organic compounds, because it has low reactivity against them and it is a rather selective oxidant agent [49]. Thus, the application of membrane contactors might be restricted only for the cases of ozone-resistant compounds treatment, such as the MPs. In the latter case their degradation can be significantly improved by the combination of a membrane contactor with a proper catalyst, leading to the catalytic ozonation process [43].

3.2. Catalytic Ozonation

Catalytic ozonation can be divided in two main categories, based on the type of catalyst that will be applied, i.e., *homogeneous* catalytic ozonation (using mainly dissolved transition metals) and *heterogeneous* catalytic ozonation (using mainly specific solid materials). A variety of solids have been examined in several catalytic ozonation publications, which can be broadly classified into the following four groups [49]:

- Metal oxides, e.g., γ -Al₂O₃ [50], TiO₂ [51], ZnO [52]
- Metal or metal oxides on appropriate supporting materials, e.g., Ni-AC [53], Co-FeOOH [54]
- Minerals, e.g., zeolites [55,56], clinoptilolite [57]
- Carbons, e.g., Activated Carbon (AC) [53], Graphene Oxide (GO) [58]

Regardless of the type of catalytic ozonation the main goal of this process is the higher efficiency of oxidation system, or the use of reduced ozone amount to reach the same efficiency, when compare to the application of single ozonation. That requires the acceleration of the hydroxyl radicals production, which present an electro-chemical potential of 2.7 V, i.e., they more powerful oxidant agents than the singly ozone (2.07 V) and also, they can participate unselectively in the oxidation reactions taking place (another difference with the aforementioned ozone selectivity). Although the hydroxyl radicals are usually the predominant radical species in the catalytic ozonation systems, many researchers have shown that the formation and participation of other oxidizing species, such as organic or oxygen radicals, are also possible [36].

Catalytic ozonation has been studied extensively; however, there is a lack of understanding, concerning the detailed reaction mechanism taking place. In general, catalytic ozonation can occur only when ozone or organic molecules or both are being adsorbed in the catalyst surface. Ozone can be adsorbed, but when it is dissolved in the liquid phase, this adsorption cannot be easily proved [59]. Organic molecules usually are poorly adsorbed on the catalyst surface, but many researchers have shown that even this minor adsorption can play an important role in the overall reaction result. Kermani et al. [60] combined three metal oxides, synthesizing the nano-tri-metallic oxide Fe₃O₄@SiO₂@TiO₂ for the removal of catechol. The investigation of pH values has showed that the optimal pH value was 8, because at this pH a synergistic effect between adsorption and ozonation took place. The point of zero charge of this catalyst was 6.18, while the catechol pK_a is 9.45. Therefore, at pH 8 the catalyst and the organic compound were of opposite charge and as a result, the adsorption process was favored. Dadban Shahamat et al. [61] and Farzadkia et al. [62] studied the deposition of magnetic Fe₃O₄ in AC surface; the point of zero charge of modified material was found to be 7.7. In the 1st study the optimum pH value was 6, because the pK_a of examined MP was 4.11, while in the 2nd case the optimum pH value was 8, because the targeted phenol is a basic compound (pK_a = 9.9).

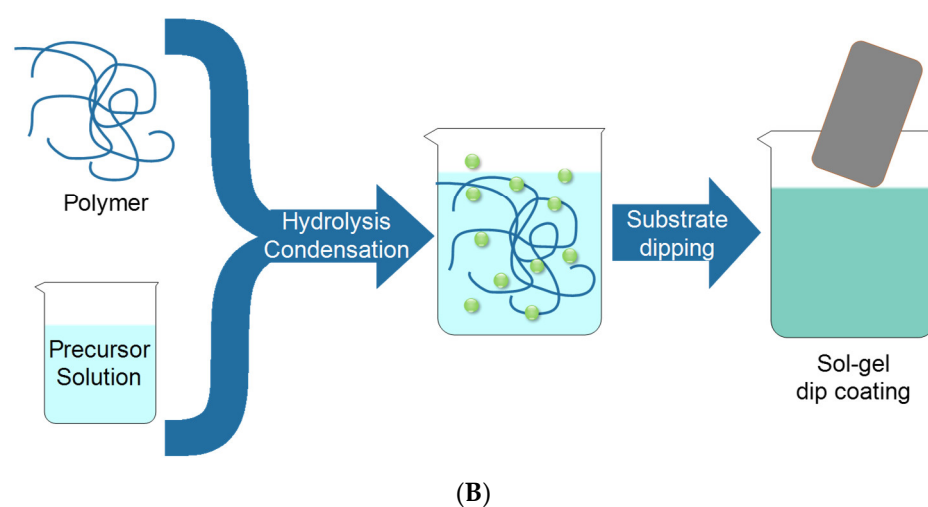
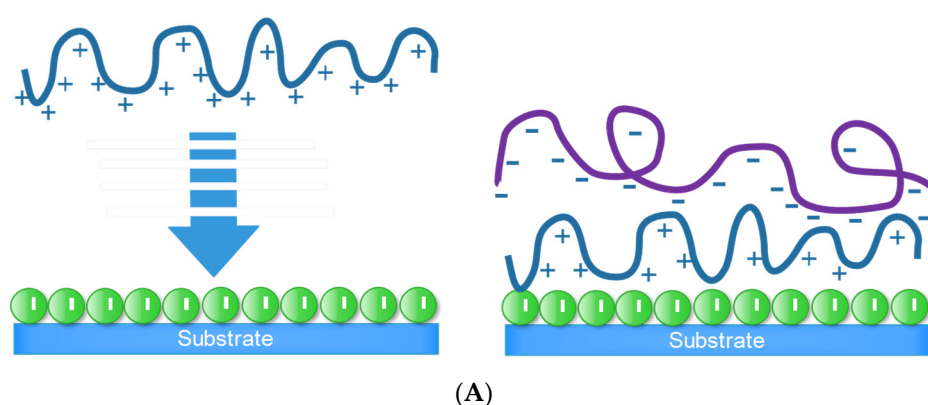
A hybrid process of ozonation and membrane filtration can be performed by following the three modes, i.e., (1) membrane filtration followed by ozonation, (2) ozonation followed by membrane filtration, and (3) ozonation and membrane filtration taking place simultaneously. The use of catalytic ozonation process before or after the membrane filtration is rather seldom applied. Only very few studies have been found to investigate such systems [63–65]. Usually, the hybrid catalytic ozonation—membrane filtration system is applied by the 3rd mode, in which the oxidation and filtration processes are carried out simultaneously [7]. By that point the heterogeneous catalytic ozonation can be sub-classified in two groups, i.e., the single heterogeneous catalytic ozonation, when the solid material is added to the system usually in powdered form (i.e., as suspension) [49], and the membrane catalytic ozonation, when the solid catalyst is preliminary deposited onto a membrane. Then the Catalytic Membrane Contactor (CMC) is transformed into a unit that acts simultaneously as a contactor (improving the ozone diffusion/transfer) and as a reactor (for the oxidation of organic compounds) [10]. As a general rule, when the catalyst is immobilized onto the membrane surface, its catalytic activity is usually lower than when it is used as an aqueous suspension [8].

4. Applications of Hybrid Catalytic Membrane—Ozonation Systems

The selection of appropriate material that will be deposited onto the membrane surface is based mainly on the catalytic activity of it and its specific physico-chemical characteristics. The formation of coating can affect the surface morphology of the membrane and change its initial properties. For example, the hydrophobicity of membrane may be affected by its roughness. Furthermore, the deposition of coating can change the surface charge and subsequently, the separation performance and fouling behavior of the membrane can be also modified [66]. The catalytic performance and the

properties of the membrane itself are also highly depending on the applied coating method. The most commonly used methods for this purpose are: layer-by-layer technique [18,67–69], sol-gel [6,15,24,70–73] and phase inversion methods [74,75]. Figure 5 is an illustrative presentation of these three methods.

In recent years, many researchers have coupled ceramic membranes with ozonation to enhance the production of hydroxyl radicals, to increase the membrane performance and to prevent its fouling. Ceramic membranes modified with nanoparticles proved to prevent fouling and present higher efficiencies, regarding the removal/destruction of organic compounds/pollutants. Catalytic membranes are those deposited with an appropriate material, usually a metal oxide, which presents catalytic activity. However, some membranes are prepared from materials with inherent catalytic activity and therefore, can enhance the production of hydroxyl radicals without any further modification. The most commonly applied relevant materials are Al_2O_3 , TiO_2 , and ZrO_2 . Zhu et al. [24] showed that the combination of ozone with a Al_2O_3 membrane gave better results, concerning membrane fouling, while the application of TiO_2 , due to its surface charge and smoothness is more tolerant and can be easier cleaned, simply by backwashing. Another interesting substrate material for membrane is cement. Hydrate cement contains insoluble alkaline products and metal oxides. These alkaline products, such as calcium silicate hydrate, can increase the pH value of aqueous solution and subsequently, the ozone decomposition. The cementitious membrane present sufficient catalytic performance and in combination with its low capital cost makes it a promising candidate for the catalytic ozonation process [48].



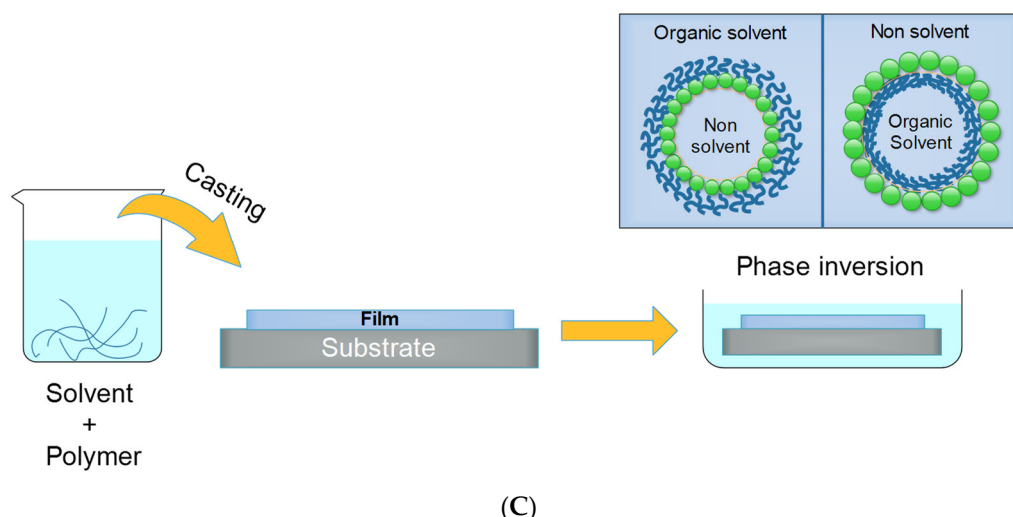


Figure 5. The most common coating methods; (A) layer-by-layer technique, (B) sol-gel, (C) phase inversion method.

4.1. Fouling Control

Prevention of membrane fouling is a difficult problem to solve in water treatment processes, which can lead to higher operating costs and poor product yield [4]. To deal with this problem in recent years ceramic membranes have been coupled with the AOPs, such as photo-catalytic and catalytic ozonation. Ozonation has the advantage of hydrophobic NOM compounds degradation into simpler hydrophilic molecules [19,76]; however ozone has rather low reactivity with the neutral and hydrophilic fractions of NOM. An enhancement of removal for these fractions was observed with the application of catalytic ozonation [19]. The most used oxides that have been applied as coatings to improve fouling control are iron and manganese oxides.

Karnik et al. [67] fabricated an iron oxide catalytic ceramic membrane for the treatment of drinking water by ozonation. They observed that although the catalytic membrane enhanced the NOM and fouling reduction, the UV-254 adsorbing compounds did not present any particular differences of higher removal rates than with the uncoated membrane. As a result, UV-absorbing compounds can be better reduced by ozonation in the bulk solution, rather than with the application of surface catalytic reactions. For the same purpose Park et al. [19] coated a γ - Al_2O_3 membrane with iron oxide nanoparticles. From the flux experiments it was obvious that the combination of ozone with the catalytic membrane can decompose/mineralize and alter the characteristics of NOM and as a consequence, membrane fouling was also significantly reduced.

A titania membrane coated with manganese oxide was studied by Wang et al. [14]. They observed that by increasing the ozone dose (5–20 $\mu\text{g/s}$ as injection rates), the fouling decreased both in the virgin and in the coated membrane. However, the coated membrane needed 33% less ozone dose to present similar efficiency. In the absence of the oxidant, the fouling was greater in the case of virgin membrane than of the coated membrane. This is mainly due to the different surface charge of each membrane. The point of zero charge of manganese oxide ($\text{pH}_{\text{pzc}} = 2.8\text{--}4.5$) is lower than that of titania oxide ($\text{pH}_{\text{pzc}} = 4.1\text{--}6.2$). At the pH value of treated water (around 8), the coated membrane was more negatively charged than the TiO_2 surface and therefore, the Mn oxide membrane show a stronger repulsion from its surface the negatively charged NOM compounds. As a result of the stronger repulsive electrostatic forces, the organic deposition was reduced and membrane fouling was lower. Cheng et al. [26] also used manganese oxide to coat a titania membrane. In this investigation three types of MnO_2 were used; a commercial oxide and two lab-prepared oxides. The 1st lab-prepared oxide was prepared by reducing KMnO_4 with the addition of MnCl_2 , while in the 2nd case the reduction was achieved with the addition of $\text{Na}_2\text{S}_2\text{O}_3$. These membranes were abbreviated as C- MnO_2 , M- MnO_2 , and S- MnO_2 , respectively. The fouling in these membranes was mainly caused by the formation of a surface cake layer, as Figure 6 shows, but the combination of

membrane filtration with ozone was found to decrease this layer, reducing both types of fouling (reversible and irreversible) and improving the flux recovery by the application of simple hydraulic backwash.

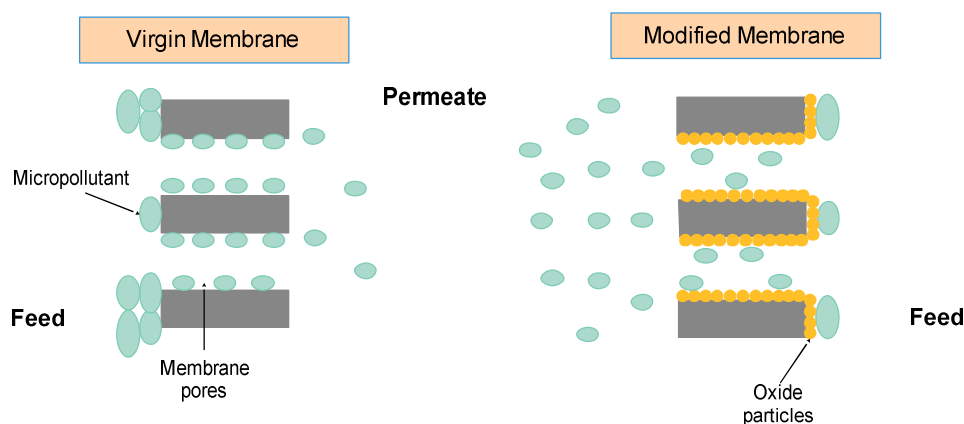


Figure 6. The influence of oxide presence in membrane fouling (Adapted from [26]).

Cornael et al. [66] prepared a catalytic membrane, by applying the layer-by-layer technique and during the preparation sintering the hydrated MnO_2 (initially used) was reduced to $\alpha\text{-Mn}_2\text{O}_3$. The flux of catalytic membrane was then compared to the uncoated membrane. The catalytic membrane was found to improve the oxidation of foulants, which were deposited on the membrane surface. Increasing the amount of manganese oxide, by increasing the number of the coating layers did not lead to further increase of permeate flux, even after the application of extended ozonation. The membrane coated with 20 layers showed improved flux recovery, when compared to the uncoated membrane. The same was observed by Karnik et al. [67]. Also, the increase of coating layer thickness did not found to accelerate the catalytic procedure [66].

On the other hand, Chen et al. [77] coated an $\alpha\text{-Al}_2\text{O}_3$ ceramic membrane with TiO_2 and a Ti-Mn layer for the treatment of aquaculture wastewater in a fish farm. It was found that the Ti-Mn coating improved the anti-fouling capacity of membrane. In the presence of ozone, the Ti-Mn/ TiO_2 / Al_2O_3 membrane present much higher permeate flux, while the permeate flux of TiO_2 / Al_2O_3 membrane was kept decreasing. The Ti-Mn layer/catalyst present stronger catalytic activity than TiO_2 . For the first half hour, the removal turbidity increased rapidly with each experiment as impurities deposited on the membrane surface reduced the porosity and pore size of the membrane, causing more suspended/particulate matter to be retained. The removal efficiency of turbidity for the TiO_2 / Al_2O_3 membranes without the presence of ozone was only 55%, while it was up to 100% for both TiO_2 / Al_2O_3 and Ti-Mn/ TiO_2 / Al_2O_3 membranes combined with ozone. The membrane coated with Ti-Mn showed the stronger ability to decompose fine organic constituents than the membrane coated with TiO_2 . The average particle size of fine solids in permeate was around 20 nm for the Ti-Mn/ TiO_2 / Al_2O_3 membrane coupled with ozone, which is smaller than the case of TiO_2 / Al_2O_3 membrane relevant application (≈ 100 nm). Hydroxyl radicals (HO^\bullet) can decompose various pollutants into smaller fractions, as well as to break down larger diameter solids into smaller ones. Accordingly, the average particle size of fine solids in permeate was about 400 nm for the TiO_2 / Al_2O_3 membranes without ozonation, i.e., nearly four times larger than that with the application of ozone. The two types of modified membranes achieved similar results, and both were found to meet the water quality criterion, regarding the aquaculture water reuse. The specific structure of the Ti-Mn/ TiO_2 / Al_2O_3 membranes may be another factor to provoke higher efficiency. The Ti-Mn oxides distributed equally on the membrane surface, as well as on the inner walls of pores, indicating that the catalytic ozonation not only occurs on the membrane surface, but also in the inner pores of membrane.

Copper oxide (CuO) was examined by Scarati et al. [8] as catalytic coating. As with previous publications, it was shown that the deposition of a metal oxide in the surface of membrane without the application of ozone did not decrease the fouling of membrane. However, with the application of

ozone in both cases the flux value was 60% lower than the initial one. In the case of CuO-coated membrane the flux was completely re-established after 60 min, while in the uncoated membrane the establishment was not observed even after 360 min. These findings confirmed that the fouling was caused by the presence of NOM. The same experiment was conducted in continuous mode. The results were almost the same and the flux re-establishment was performed faster than the case of uncoated membrane. The permeate flux recovery was partly contributed to the oxidation caused by the formation of hydroxyl radicals, but also to the formation of gaseous bubbles, scrubbing/scouring and cleaning the membrane surface.

Guo et al. [71] used a ceramic membrane, coated with CuMn_2O_4 particles, for the treatment of a Waste Water Treatment Plant (WWTP) effluent and they observed that the fouling was significantly reduced by adding ozone to the system. Effluent Organic Matter (EfOM) of WWTP could be degraded or changed by the application of single or catalytic ozonation and this procedure was found to decrease the fouling of virgin membrane. The surface coating reduced the fouling of membrane, because of the catalytic ozonation activity, caused by the CuMn_2O_4 surface. Higher (normalized) permeate flux and shorter recovery time were achieved with the modified membrane. The use of catalytic membrane in combination with ozone was found to enhance the degradation of EfOM, containing unsaturated groups from the larger molecular weight compounds degraded to smaller ones, which was helpful for the reduction of membrane fouling.

In most cases ceramic membranes have been used in catalytic ozonation systems, because the substrate material is simpler to be coated. However, Yu et al. [29] coated a PVDF (polymeric) membrane with MnO_2 nanoparticles. They observed that there was not any detectable additional pressure loss by the presence of coating at the beginning of process operation and the presence of MnO_2 surface layer was found to lower the fouling rate. For the initial 10 days of operation the increase of Trans-Membrane Pressure (TMP) of both membranes was very small, partly as a consequence of ozone presence, limiting the development of biological activities and the bio-accumulation onto membranes. The characteristics of cake layer formation on the surface of membrane were found to alter sufficiently by the exposure to $\text{O}_3/\text{HO}^\bullet$, enabling a near-complete removal during the routine backwashing. Much of the strongly hydrophobic organic matter content was changed into either weakly hydrophobic or hydrophilic fractions. As the hydrophobic organic matter is much easier to be adsorbed onto the hydrophobic PVDF membrane pores, the conversion of hydrophobic organic compounds to hydrophilic ones should mitigate the inner membrane fouling, especially for the $\text{MnO}_2\text{-O}_3$ system. The lower concentration of polysaccharides in the hybrid system enables the cake layer to be more easily removed during the subsequent backwash cleaning process. The polysaccharides can cause the formation of flocs, which would be attached on the surface of membrane and as a result, to cause irreversible internal fouling. After continuous operation for 70 days, the coated membrane was nearly the same as an unused membrane, leading overall to less organic matter adsorbed in the membrane pores.

Unlike other researchers Hu et al. [15] and Zhu et al. [24] wanted to examine the effects of residual ozone concentration and they applied only a single dose of ozone at the beginning of filtration procedure. Ozone single injection at the beginning of the process can maintain the permeate flux at higher level, reducing the initial fouling. This is mainly due to the oxidation of organic substances/pollutants by the application of direct ozonation and/or oxidation by HO^\bullet , or by other radical species produced from ozone decomposition. However, at the end of this process membrane fouling was not prevented. Ozone is an unstable molecule that decomposes fast. Therefore, at the beginning of this process the catalytic ozonation process was taking place, while at the end the membrane was used just for filtration purposes and the cake layer was eventually formed.

4.2. Removal of Micropollutants

MPs usually are smaller than the Molecular Weight Cut-Off (MWCO) of most MF and UF membranes. [78]. NF membranes are more suitable for MPs separation, since they can still operate at rather low pressures, but they have smaller pore sizes, around the size of the MPs [22]. The removal

of MPs by a NF membrane is mainly influenced by the surface charge. Negatively charged NF membranes can remove/separate easier the negatively charged solutes than the naturally or positively charged ones. This is due to the respective electrostatic interactions between the solutes and the membrane surface [79]. Therefore, it is very important the physico-chemical interactions between the membrane and the MP to be better understood [22].

4.2.1. Factors Affecting the Removal of MPs

There are four main factors that can influence the catalytic performance of a membrane and subsequently, the removal of MPs, i.e.,

- Coating times
- Pore size
- Preparation method of the metal oxide to be used
- Adsorption capacity

Coating Times

Guo et al. [18] proved that the coating times influence significantly the removal of MPs, as noticed also for the case of fouling. The increase of coating times increases the active component content onto the membrane surface, resulting in higher efficiency. In this research the best results were obtained, when the ceramic membrane was coated repeatedly for 80 times. The same was observed by Scarati et al. [8]. An increase in the catalyst (CuO) loading was found to favor the decomposition of ozone and to enhance the production of hydroxyl radicals; as a result, the removal of 1,4-dioxane and its secondary by-products was also increased. The loading of 0.484 mg/cm² was considered to be the upper limit for the respective enhancement; after the achievement of this limit the MPs and Total Organic Carbon (TOC) removal did not show any further improvement. In that point the CuO particles covered almost entirely the ceramic membrane surface and made it more efficient for the catalytic ozonation process.

The soaking time was found to be also a relevant important parameter; longer soaking times can lead to the adsorption/attachment of more active (catalytic) material onto the membrane surface, resulting in higher MPs removal. Guo et al. [71] observed that after 120 min of soaking time the catalytic activity of membrane was not further improved; as in the previous case, the CuMn₂O₄ particles probably covered almost entirely the membrane surface, or the increased amount of coated CuMn₂O₄ particles was then more effective for the catalytic ozonation. Lee et al. [70] observed that although at even higher metal oxide loading the removal of MPs and TOC did not further enhanced, the ozone decomposition can be increased, because there were more active sites to enhance its decomposition. Sun et al. [74] showed that the catalyst loading is also important for the case of polymeric membranes; the nitrobenzene removal rate was gradually increased with an increase of nano-TiO₂ (catalyst) dosage.

Pore Size

Another important factor that influences the catalytic membranes performance is the pore size. The pores of the membrane can act as micro-reactors and provide high specific surface areas within a confined reaction environment. The micro-reactor can reduce the mass-transfer limitations of heterogeneous catalytic ozonation. On the micro-scale, efficient interphase mass transfer could be achieved by the molecular diffusion, due to short diffusion path in the catalytic ceramic membrane micro-pores, causing the catalytic reactions to be limited mainly by the intrinsic reaction kinetics instead of other mass-transfer limitations [70]. Zhu et al. [24], who evaluated the performance of two different membranes (TiO₂, Al₂O₃) in an ozonation system, observed that the TiO₂ membrane can achieve much higher reductions, regarding color, absorbance (A_{254nm}) and TOC content. This is mainly attributed to the smaller pore size of the used TiO₂ membrane, when compare e.g., to Al₂O₃ (i.e., 0.004 μ m vs. 0.58 μ m respectively for the dry materials), which allowed only the smaller organic compounds to pass through its pores and rejected the colored organic compounds with relatively

larger molecular weights during the filtration process. However, the optimal pore size (as all the other examined factors) presents a limit. When Guo et al. [18] changed the membrane pore size from 50.0 nm to 20.0 nm, the removal efficiency decreased, because the $\text{MnO}_2\text{-Co}_3\text{O}_4$ nanoparticles coating on the ceramic membrane were also decreased.

Preparation Method of the Metal Oxide

Cheng et al. [26] tried to prove that not only the kind/type of the membrane is important for its catalytic activity, but also the preparation method of the respective oxide deposited on it. For that purpose, they used three different types of MnO_2 , including commercial available MnO_2 , and two lab-prepared MnO_2 , i.e., M- MnO_2 and S- MnO_2 , by reducing KMnO_4 with the addition of stoichiometric amounts of MnCl_2 and $\text{Na}_2\text{S}_2\text{O}_3$, respectively. The lab-fabricated metal oxides had more hydroxyl groups than the commercial one and these membranes showed higher catalytic activity. The commercial membrane showed only a slight activity with an increased efficiency of 3.1%, when compared to the virgin one, whereas the M- MnO_2 and S- MnO_2 membranes improved the removal efficiencies by 12.9% and 19.4%, respectively.

The importance of hydroxyl groups in the production of hydroxyl radicals was pointed out also by Wang et al. [48] in the case of the cementitious catalytic membrane. A schematic reaction of ozone with the hydroxyl groups is shown in Figure 7. Although several researchers have pointed out the significant role played by the hydroxyl groups in the catalytic ozonation procedure (e.g., [80,81]), others (e.g., Zhang et al. [82]) have found contradictory results. They examined several Fe oxy-hydroxides, which present catalytic activity following the order: $\gamma\text{-FeOOH} < \beta\text{-FeOOH} < \alpha\text{-FeOOH}$, while the surface hydroxyl radical densities follow a different order: $\alpha\text{-FeOOH} < \gamma\text{-FeOOH} < \beta\text{-FeOOH}$. They mentioned that although the surface hydroxyl groups can influence the process of catalytic ozonation, not all of them possess the same catalytic activity, but the weaker ones can favor better the production of hydroxyl radicals. On the other hand, Cheng et al. [26] investigated the role of membrane shape during the catalytic ozonation process. They observed that the different shape and channels of coated ceramic membranes show no significant differences, regarding the MPs removal.

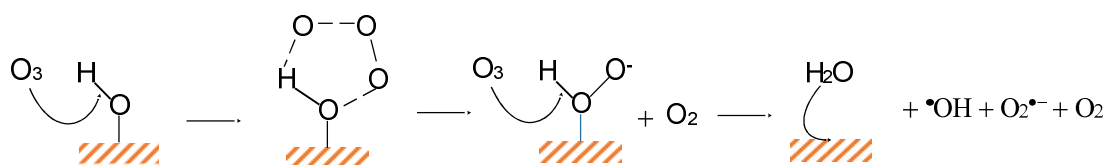


Figure 7. Scheme of ozone reactions with the hydroxyl groups on the FeOOH surface for the production of hydroxyl radicals (Adapted from [83]).

Adsorption Capacity

The adsorption of MPs in the catalytic surface allows the oxidative species to be in better contact with the organic molecules to be removed or destroyed. Sun et al. [74] observed that nitrobenzene can be adsorbed onto the nano- TiO_2 surface; therefore, to increase the surface area (S_{BET}) of the metal oxide, resulting in the increase of adsorption efficiency. Furthermore, Heng et al. [84] took advantage of the adsorption process to promote the MPs degradation. The $\gamma\text{-Al}_2\text{O}_3$ coating on a ZSM-5 membrane did not enhance ozone decomposition, but the removal of phthalates and their by-products (e.g., carboxylic acids, ketones, aldehydes) increased. The presence of $\gamma\text{-Al}_2\text{O}_3$ was capable of adsorbing and retaining the MPs on its surface, being in the reaction zone for longer (residence) time and as a result, their degradation was enhanced.

4.2.2. Removal Efficiencies and Mechanistic Aspects

Wang et al. [48] used a virgin cementitious membrane, as a catalyst for the removal of p-chloronitrobenzene (p-CNB). The adsorption of this molecule on the membrane was negligible. Compared to the application of ozone alone, the presence of membrane catalyst in the ozonation

system increased the p-CNB degradation by more than 50% and the reduction of TOC was also similar. Approximately 40% of the initial TOC was removed, whereas less than 10% was removed with the application of single ozonation process. The surface hydroxyl groups of metal oxides and particularly, of aluminum oxide and iron oxides were neutrally charged, because their pH_{pzc} are near the treated water pH value. The neutral surface charge can favor the contact of ozone molecules with the surface and subsequent, the production of hydroxyl radicals [85–88]; the relevant mechanism is shown in Figure 8. Furthermore, these researchers have studied the influence of reaction medium during the catalytic ozonation process. Three types of water sources were tested: deionized water, filtered water from a drinking water treatment plant and river water. The removal efficiency in the first two types of water was higher. The differences in the examined matrixes lie mainly in the concentrations of bicarbonate and NOM in the treated water, which are considered to be typical hydroxyl radical scavengers, commonly existing in natural waters and therefore, influencing negatively the p-CNB removal efficiency.

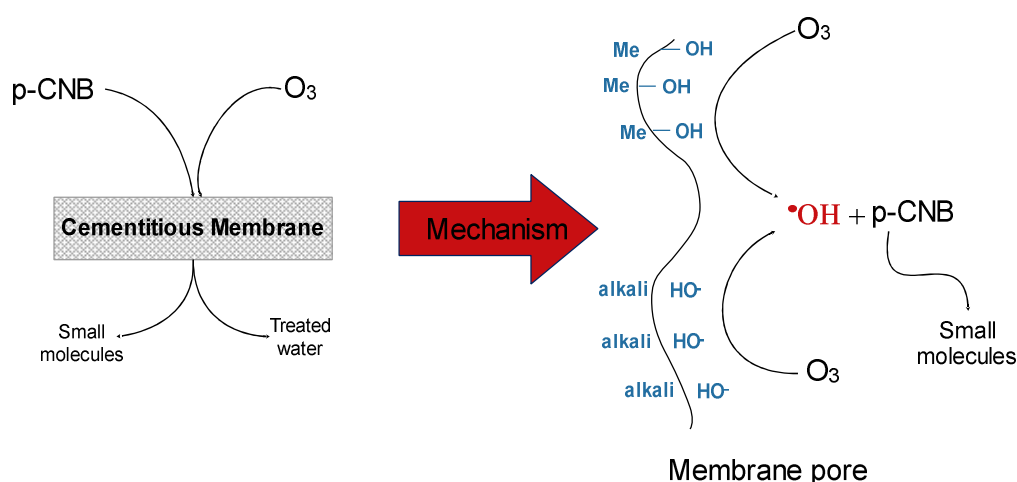


Figure 8. Main radical mechanisms regarding the removal of p-CNB by the synergistic effect of a cementitious catalytic membrane and ozone application (adapted from [48]).

Unlike the aforementioned cementitious membrane, in most other cases the researchers have deposited metal oxides onto membrane surfaces to enhance membrane catalytic activity. Lee et al. [70] deposited onto an alumina membrane Mn or Ce content to improve the removal of bisphenol-A (BPA) from water. The alumina membrane, used in this study, initially did not show any catalytic activity. The modified Mn-CCM membrane was capable of adsorbing 55% BPA after 1 h of operation time, but this did not enhance the TOC removal. However, the modified Ce-CCM membrane was found to exhibit much stronger mineralization capability of the examined organic pollutant. Nearly 38% TOC was removed within 13.7 s treatment time. The main oxidative species except the ozone molecules were the hydroxyl radicals and the superoxide ions ($O_2^{\bullet-}$). The Ce-CCM membrane showed the highest Reactive Oxygen Species (ROS) generation with $0.14 \mu\text{mol HO}^\bullet/\text{L}$ and $8.78 \mu\text{mol } O_2^{\bullet-}/\text{L}$ detected, while the Mn-CCM membrane produced much lower amounts of ROS with only $0.06 \mu\text{mol HO}^\bullet/\text{L}$ and $3.59 \mu\text{mol } O_2^{\bullet-}/\text{L}$. The ratio of Ce(IV)/Ce(III) has increased from 2.52 to 3.55 after reaction, indicated that a partial oxidation of Ce(III) to Ce(IV) had also taken place during the process. On the other hand, the proportion of Mn(IV) increased from 9.8 to 14.4% after reaction. These observations proved that the catalytic ozonation process was based, in this case, on the electron transfer between the metal ions and the O_3 molecules.

Zhu et al. [6] deposited CeO_2 on a TiO_2 membrane to examine the removal of tetracycline by the application of ozone. The removal of tetracycline and humic acids was enhanced by the catalytic membrane. As in the previous cases, the predominant oxidative species are hydroxyl radicals that were produced by the ozone decomposition onto the membrane surface. During the first stages of this study ozone was not been applied in the treatment system. The removal of tetracycline was more than 60% after the first 2 h, due to the adsorption process. However, the removal rates were

continuously decreased and after 6 h of the process operation the removal of the pollutant was less than 10%. In that point ozone was fed to the system and the concentration of the pollutant decreased by 85%, due to its transformation/destruction.

Guo et al. [71] used a ceramic membrane modified/deposited with CuMn_2O_4 particles to enhance the removal of benzophenone-3 (BP-3), as compared to the respective virgin membrane and to the application of single ozonation. Furthermore, in the ozonation process $\text{O}_2^{\cdot-}$ was produced and that generation was enhanced during catalytic ozonation. Therefore, the presence of catalytic membrane enhanced the ozone self-decomposition to $\text{O}_2^{\cdot-}$ that initiated the chain reaction and the production of HO^{\cdot} radicals. Additionally, the modified membrane can also promote secondary interactions between ozone and the catalyst/organic chemicals to form H_2O_2 that also promotes the molecular ozone decomposition into HO^{\cdot} . During the catalytic ozonation $3.27 \mu\text{mol/L}$ H_2O_2 was produced. The large weight molecules were degraded to small molecules, or transformed to hydrophilic ones. The large number of surface hydroxyl groups on the modified membrane increased the number of potential catalytic sites for the decomposition of ozone, which generates the aforementioned ROS. The efficiency in terms of BP-3 removal was 76.6%.

Karnik et al. [89] used salicylic acid (SA) as a model compound to investigate an ozonation-membrane filtration system. They coated a CéRAM membrane with iron oxide. At higher pH values the reaction mechanism was based on the hydroxyl radical reactions. The results showed that the salicylate ion was adsorbed to the membrane, whereas the SA did not. The synergy between sorption and oxidative reactions with the hydroxyl radicals may lead to a greater decrease of SA concentration in the hybrid process in comparison with the application of single ozonation process. With the application of hybrid process, the SA by-products were formed at lower concentrations.

Several researchers have also used organic catalytic membranes for the removal of MPs. In most cases PVDF was selected as the virgin membrane. Sun et al. [74] doped it with nano- TiO_2 to examine the removal of nitrobenzene. Under acidic conditions the removal rates of pollutants by the application of all three treatment processes (i.e., adsorption, ozonation and catalytic ozonation) are rather very low, but the removal rates can increase with an increase of pH values. The efficiency of the adsorption was almost stable after pH 6. At basic pH values the decomposition of ozone is accelerated, but when the pH value was higher than 10, the nitrobenzene removal rate was reduced, because in alkaline conditions the HO^{\cdot} can be decomposed into O^- and H^+ . Therefore, the nitrobenzene removal rate is higher in alkaline conditions than in acidic ones and the best removal rate was obtained at the pH value 10. Also, the removal of nitrobenzene increased with an increase of ozone dose. In this research the applied ozone dosages were very small (i.e., $0.46 \mu\text{g/L}$ – $1.63 \mu\text{g/L}$), but the respective removal efficiencies were quite high. With the use of $1.63 \mu\text{g/L}$ ozone, the nitrobenzene was removed by almost 70% ($14.4 \mu\text{g/L}$) within 20 min treatment time.

Zhu et al. [73] used the same catalytic membrane for the treatment of municipal wastewater. Organic matter was degraded by the production/presence of high oxidizing HO^{\cdot} radicals. Membrane filtration reduced only the larger molecular weight organic compounds, whereas the Chemical Oxygen Demand (COD) reduction due to this process was rather small (27.6%), although after the application of pre-treatment by ozone aeration, the removal of COD increased. Ozone can degrade the existing macro-molecular compounds into smaller ones. However, the so produced micro-molecules cannot be effectively removed by the PVDF membrane. The residual ozone after the contact/reaction tank was contacting a TiO_2 modified membrane and through the catalytic ozonation process the organic matter with molecular weight above 10 kDa was almost completely removed, while the effect of this procedure on the smaller size molecules (i.e., <10 kDa) was found to be lower. The catalytic ozonation with the application of a nano- TiO_2 doted PVDF membrane may follow two major pathways: (1) nano-organics can be preliminary adsorbed on the membranes' surface and further on they can be easier oxidized, and (2) nano- TiO_2 catalytic ozonation can produce more HO^{\cdot} radicals, which are powerful oxidative species and can react/destroy unselectively the present organic matter.

Li & Yeung [90] used a coated PVDF-MF-membrane as ozone gas distributor and catalytic contactor. For the first time a carbon-based material was used as a coating agent. This modification

helped the organic pollutants to be retained in the reaction zone for longer times, resulting in higher N,N-diethyl-meta-toluamide (DEET) conversion. The degree of mineralization remains identical for the PAC-coated, as well as for the uncoated PVDF membrane. This is due to the refractory nature of the intermediately produced by-products by the DEET ozonation. Mixing ferrihydrite nanoparticles with PAC (and creating the CAT catalyst) before the coating onto PVDF membrane did not found to increase the DEET removal, but improved the overall mineralization of DEET, particularly when applying longer reaction times. Ferrihydrites showed greater adsorption capacities against the carboxylic and oxygenated compounds that are the major by-products of ozonation procedure. The DEET adsorption on PAC and CAT materials, acting as catalysts, was rapid and reached 83% and 80% respectively, while the TOC removal by CAT was 20% higher than in the case of PAC.

All the researchers observed that the catalytic membrane ozonation follows a mechanism based on radicals. The predominant radical species in most cases were the hydroxyl radicals. In some cases both hydroxyl radicals and superoxide ions were found to participate in the catalytic reaction [70]. However, Scarati et al. [8] noticed that when they used a CuO-coated membrane for the 1,4-dioxane oxidation/removal the primarily oxidative species were the $O_2^{\bullet-}$. These radicals that formed on the CuO-coated ceramic surface could also contribute to the removal of fouling. The catalytic ozonation may promote the production of more intermediates, thus eventually increasing the acute toxicity. The obtained results were not very promising and this membrane maybe not suitable for catalytic reactions. Although the production of superoxide ions is a part of ozone decomposition mechanism for the formation of hydroxyl radicals (e.g., [36,91]), it seems that in this case the decomposition pathways were different. All the aforementioned studies are summarized in Table 4.

Table 4. Summary of catalytic membranes (main characteristics, conditions, efficiency) used for MPs removal.

MP	Catalytic Membrane	Membrane Characteristics	Conditions	Efficiency	Reference
Tetracycline	CeO ₂ -TiO ₂ /α-Al ₂ O ₃	Thickness = 1.5 μm Particle size = 13 nm S _{BET} = 71.3 m ² /g Pore size = 9.0 nm MWCO = 80 kDa	C _m = 5 mg/L Co ₃ = 2.5 mg/L TMP = 2 bar	SAP < 10% (600 min) COP > 80% (200 min)	[6]
1,4-dioxane	CuO/α-Al ₂ O ₃ -ZrO ₂	One channel L = 25 cm D = 1 cm Pore diameter = 50 nm A = 47.12 cm ² MWCO = 10 kDa Cover density = 0.90 mg/cm ²	C _m = 200 mg/L Co ₃ = 60 mg/L pH = 4–5.5 T = 25 ± 1 °C TMP = 0.25 bar	SAP = ng ⁽¹⁾ COP ≈ 65% (350 min)	[8]
Nitrobenzene	Ni foam/PVDF	Flat sheet Thickness = 210 μm Porosity = 76% Pore size = 0.2 μm	C _m = 30 mg/L Co ₃ = 50 mg/L pH = 7 current density = 1 mA/cm ²	Electrolysis = 23% COP = 55% Electrolysis-COP = 85% (120 min)	[43]
p-CNB	Cement (MF)	Pore size = 0.3–8.2 μm 19.97%wt Si 7.57%wt Ca	C _m = 15 mg/L Co ₃ = 2.5 mg/L pH = 6.5 HRT = 10 min TMP = 60 Kpa	SAP ≈ 0 SOP ≈ 28% COP = 90%	[48]
BPA	Mn ₂ O ₃ /Al ₂ O ₃	S _{BET} = 35.4 m ² /g 4.2 mg/g Mn	C _m = 3 mg/L Co ₃ = 4 mg/L HRT = 13.7 min Reaction time = 60 min	SAP = 55% (1h) SOP = 84% COP ≈ 98%	[70]
BTZ				SAP < 5% SOP = 57% COP ≈ 55%	
CA				SAP < 5% SOP = 49% COP ≈ 55%	
BTA				SAP < 5% SOP = 84% COP ≈ 80%	
BTZ				SAP < 5% SOP = 57% COP ≈ 57%	
CA				SAP < 5% SOP = 49% COP ≈ 40%	

BP-3	CuMn ₂ O ₄ /ZrO ₂ /α-Al ₂ O ₃	R ₁ = 187 ± 17nm Thickness = 125–145 μm	C _m = 2 mg/L C _{O₃} = 1 mg/L pH = 7 ± 0.25	SAP ≈ 8% SOP = 47.4% COP = 76.6%	[71]
Nitrobenzene	Nano-TiO ₂ /PVDF	Membrane area = 12 × 15 cm ²	C _m = 48.08 μg/L C _{O₃} = 2.5 mg/L pH = 8 T = 25 °C TMP = 5 × 10 ⁴ Pa	SAP = 18.4% SOP = 25.7% COP = 59.5% (20 min)	[74]
Salicylic acid	Fe ₂ O ₃ /CéRAM	D = 10 mm L = 25cm A = 41.2 cm ² MWCO = 5 kDa 40 layers of Fe ₂ O ₃	C _m = 65 μM C _{O₃} = 2.5 mg/L pH = 8 T = 20 °C TMP = 5 × 10 ⁴ Pa	SOP = 40% (240min) COP > 95% (240 min)	[89]
DEET	PAC/PVDF	S _{BET} = 760 m ² /g Pore diameter = 2.4 nm Pore volume = 0.46 cm ³ /g Thickness = 20 μm (of the coating)	C _m = 200 mg/L C _{O₃} /O ₂ = 120 mg/L	SAP = 83% (10 min) SOP = 45% COP = 39%	[90]
	Fh ⁽²⁾ -AC/PVDF	S _{BET} = 730 m ² /g Pore diameter = 2.7 nm Pore volume = 0.49 cm ³ /g Thickness = 20 μm (of the coating)		SAP = 80% (10 min) SOP = 45% COP = 60%	
KHP	Alumina/ZSM-5	Pore diameter = 6.40 nm Pore volume = 0.63 cm ³ /g S _{BET} = 395 m ² /g IEP = 8.2 (of the coating) Surface area(contactor) = 48 m ²	C _m = 100 mg/L C _{O₃} = 100 mg/L pH = 7 T = 40 °C	COP = 100% High adsorption capacity Better TOC removal	[92]
	Hydrotalcite/ZSM-5	Pore diameter = 6.23 nm Pore volume = 0.07 cm ³ /g S _{BET} = 44 m ² /g IEP = 11.7 (of the coating) Surface area (contactor) = 90 m ²		COP = 100% High adsorption capacity	

⁽¹⁾ng: negligible;⁽²⁾ Fh: Ferrihydrite.

4.3. Removal of Bacteria

Except for the removal of MPs some researchers have used the catalytic ozonation by membrane process also for the removal of bacteria. The relevant studies have shown that the metal oxides, such as iron oxides, can retard the transport of bacteria. The adhesion of bacteria to a metal oxide surface will increase the retention of them at the membrane interface and subsequently, the contact of bacteria with ozone will be prolonged. Ozone reacts with the catalytic surface and HO^\bullet or other radical species would be formed and inactivate the bacteria near them. Therefore, this mechanism enhances the disinfection behavior of the treatment system [68].

Karnik et al. [68] used a catalytic membrane for the removal of *Escherichia coli*. The ceramic membrane was coated with 40 layers of iron oxide nanoparticles and sintered at 900 °C. Ozonation was followed, resulting in the decrease of live *E. coli* numbers. The combination of ozone with the virgin membrane presents only slightly higher efficiency than that observed in the single membrane filtration experiment. With the use of coated membrane, the number of live bacteria in the permeate was further decreased and the concentration of ozonation by-products in it was significantly reduced. Similar results were also observed by Davies et al. [69]; they studied both iron and manganese oxides as appropriate coatings for a TiO_2 -substrate ceramic membrane. The iron oxide coating membrane was proved to be the most efficient catalyst and hence this was used for the removal of *E. coli*, providing an excellent performance. The mortality of bacteria was significantly higher regarding the application of hybrid treatment systems. It appears that the bacteria are concentrated at the membrane surface and the secondary radicals produced by the decomposition of ozone also at the membrane surface can effectively inactivate the bacteria. The survival of the bacteria was less than 1%, which is significantly lower than that with the uncoated membrane (comparison experiments). The adhesion of bacteria onto the iron oxide surface may also result in the more effective inactivation of them, when using the coated membrane.

4.4. Special Applications

Chan et al. [92] prepared an advanced hybrid ozone/membrane reactor that can synergistically combined ozone oxidation, adsorption, and membrane separation. The compact unit used a porous stainless steel membrane as ozone distributor, a porous alumina membrane as contactor and a zeolite membrane as water separator, arranged concentrically (Figure 9). The ozone was fed as fine bubbles along the length of the reactor. The catalytic membrane (contactor) was coated with alumina and hydrotalcite ($\text{Mg}/\text{Al} = 3$). The amount of coating was adjusted accordingly for both alumina and hydrotalcite to adsorb the same amount of Potassium Hydrogen Phthalate (KHP), used as “model” compound. The alumina-coated membrane contactor had about ten times higher surface area than the hydrotalcite (i.e., $S_{\text{BET}} = 45 \text{ m}^2$), but the hydrotalcite had three times greater absorption capacity against the examined pollutant (KHP), when compare to alumina. Therefore, the amount coated in the contactor surface was 0.14 g and 0.04g for the alumina and hydrotalcite, respectively. Although alumina and hydrotalcite had different pH_{pzc} (i.e., at pH 8.2 and pH 11.7, respectively), both were positively charged at neutral pH value. The membrane distributor is designed to generate minute ozone bubbles in water, enhancing the mass-transfer rate and the oxidation of organic pollutants. The membrane contactor increased the interfacial contact area between the gas phase ozone and the dissolved organics and also it can adsorb and trap the organics within the reaction zone, which resulted in more complete remediation/removal. The membrane separator was capable of producing clean water and also concentrated the organics within the reaction zone, resulting in better reaction kinetics and enhanced removal of pollutants. When using the membrane distributor and an uncoated membrane contactor only, a complete conversion of 100 mg/L phthalate and 20% reduction of TOC were obtained, applying residence time 2.4 min and using 100 mg/L ozone. Both hydrotalcite and alumina coatings produce the complete phthalate conversion and 30% increase of TOC removal. Separate studies showed that hydrotalcite and alumina did not act as catalysts in the ozone reaction, but they can strongly adsorb the examined pollutant (phthalate) and its ozonation

by-products. Therefore, this organic compound was trapped in the reaction zone for longer (residence) time, resulting in higher degradation and TOC removal.

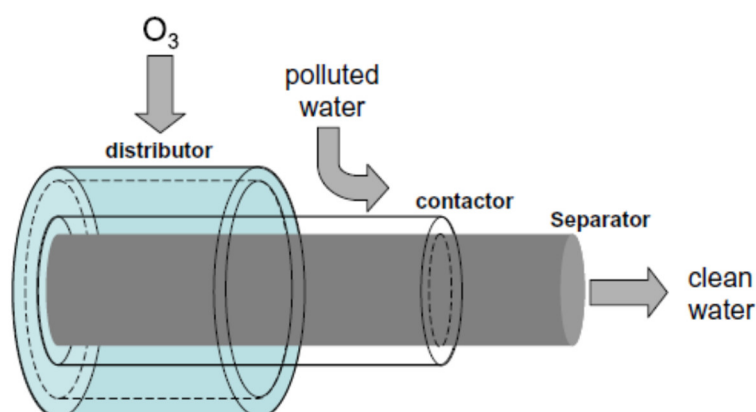


Figure 9. An advanced hybrid ozone membrane distributor/contactor/separator concentrically arranged [92].

Another interesting application of catalytic membranes was proposed by Li et al. [43], designing a novel electro-CMC (Figure 10). A metallic (nickel) foam plate and a hydrophobic PVDF membrane were placed in the contactor device. The Ni foam contacted with the water phase and acted as a cathode in the electro-chemical reactor, while the PVDF membrane was fixed tightly to the Ni foam and contacted with the gas phase. O_2 diffused into the aqueous phase through the hydrophobic membrane and it was electrolytically reduced to H_2O_2 . H_2O_2 was produced on the surface of membrane and reacts with the O_3 molecules, producing hydroxyl radicals. With the electrolytically procedure H_2O_2 is produced on site and the relevant risks during transportation and storage of high concentrated H_2O_2 solutions were avoided. Also, the production of H_2O_2 can be easily controlled by adjusting the respective electro-chemical conditions.

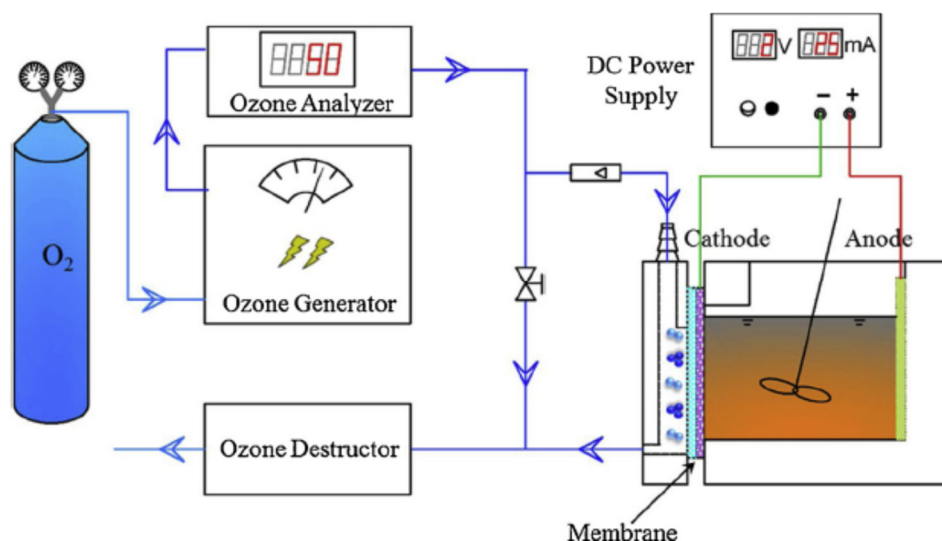


Figure 10. Schematic of the experimental setup [43].

For the evaluation of this process the researchers were used nitrobenzene as “model” compound. The increased ozone concentration in the gas phase and the increase of current density (leading to the increase of H_2O_2 production/accumulation) enhanced the hydroxyl radicals’ production and subsequently, the removal of nitrobenzene. At acidic pH values the production of H_2O_2 increased, but the ozone molecules were more stable and the production of hydroxyl radicals by the ozone self-decomposition decreased. On the contrary, in alkaline conditions the production of

H₂O₂ could be inhibited to some degree, but the ozone self-decomposition is accelerated and consequently, the higher production of hydroxyl radicals is also occurring. The highest removal rate (95.7%) was observed, when the initial pH value of the experiment was 4.5, while the lowest, when the pH value was 7. However, due to the fact that in this study the production of hydroxyl radicals is based both on the action of H₂O₂ and O₃ oxidant agents, this particular treatment system can perform very well in a large range of pH values ($3 \leq \text{pH} \leq 9.5$). These special applications about the removal of MPs are included in Table 4.

4.5. Catalytic Membrane Stability

Metal oxides are commonly used as coatings deposited onto the surface of membranes, acting as catalysts. The stability of catalytic membranes is considered to be a crucial factor for continuous running treatment operations. Except for the membrane material that must be stable enough, when contacting ozone, the used coating also must be stable and not easily leached/removed from the membrane surface. However, in most cases smaller or larger amounts of deposited metals can be potentially leached into the solution during the application of catalytic ozonation.

Guo et al. [18] used a ceramic membrane of $\alpha\text{-Al}_2\text{O}_3$, where MnO₂-Co₃O₄ was deposited. The membrane stability test showed that Al, Mn, and Co ions were leached into the solution to be treated. The leached Mn ion concentrations were found to be lower than the National Standards, considering the respective Intergrated Wastewater Discharge Standards in China (limit concentration $C_{\text{Mn}} < 2 \text{ mg/L}$), while there is no limit, regarding the presence of for Al and Co. As a result, the researchers suggest that the leached ions cannot be considered to be a negative factor for the application of membrane catalytic ozonation. Although there are no regulation limits for certain metals, researchers observed that many of them can be potentially dangerous for the human health. For example, exposure to aluminum higher than the set concentrations limits (e.g., through drinking water consumption) can cause cognitive impairment or dementia [93], whereas cobalt can cause congestive heart failure [94].

Lee et al. [70] observed that the Ce-CCM modified membrane showed better stability than the Mn-CCM. The leached ion for Ce-CCM were 0.61 mg/L Ce, while in the case of Mn-CCM the leached Mn was almost ten times of magnitude higher and equal to 5.99 mg/L. An increase of Ce loading can increase the Ce leaching and decreases the permeability of modified membrane. This would also increase the operating cost and the energy consumption. Guo et al. [71] evaluated the stability of their membrane coating by using it in a 30 min operation. The leaching of the two active components (in this case copper and manganese ions) was 32 and 230 $\mu\text{g/L}$, respectively; noting that these components did not participate in the oxidation reactions as homogeneous catalysts (i.e., homogeneous catalytic ozonation process).

The coated PVDF membranes were found to be more stable under ozone contacting, because the coating layer can protect the membrane from wetting [90]. Wang et al. [48] studied a cementitious membrane. The ions of that membrane were intensively released from the surface within 1 h. At that time Al and Fe concentrations in the system were 0.13 mg/L and 0.05 mg/L, respectively; i.e., quite significant, but within the respective legislative limits. However, further running of the process for 48 h could effectively reduce the ions release from the membrane surface and minimize the residual ions concentration levels by 77% and 100%, i.e., after 48 h of operation time the effluent was not dangerous, regarding the water safety. Scarati et al. [8] used a ceramic membrane deposited with CuO. The reusability of this catalytic membrane was tested in four subsequent operation cycles. The Cu leaching in every cycle was 0.58 mg/L, which is inside the regulation limits, but only if this membrane was used for 1–2 cycles. Then the Cu leaching will be very high, but also the membrane was de-activated. Table 5 presents the regulation limits of WHO, USEPA and Bureau of Indian Standards (BIS) in drinking water, considering the metals/oxides mostly used in the catalytic ozonation processes.

Table 5. Drinking water standards for the most frequently used metals in catalytic ozonation processes [95–97].

Heavy Metal	Limit (µg/L)		
	WHO, 2017	USEPA, 2015	BIS, 2012
Iron (Fe)	NGV	300	300
Manganese (Mn)	NGV	50	100
Zinc (Zn)	NGV	7400	5000
Copper (Cu)	2000	1300	50
Nickel (Ni)	70	610	20
Aluminum (Al)	NGV *	200	30

* NGV: not given value.

5. Conclusions

Membrane filtration has been widely applied in recent decades for the treatment of water or wastewater, but it presents a critical limitation, i.e., membrane fouling. Membrane fouling reduces the efficiency of treatment systems and increases the operational cost. Membranes are also used for the removal of organic pollutants, but they are just a physical barrier that can only separate/remove them from the feed water and not to degrade them. Coupling filtration with an advanced oxidation process, such as ozonation, can lead to the additional removal of contaminants through the performance of oxidative reactions, whereas membrane fouling can be also simultaneously reduced. Furthermore, by using a membrane as ozone diffuser, the system efficiency can be increased, and the operational cost decreased. The system efficiency can be further enhanced by the addition of an appropriate catalyst.

Catalytic ozonation has been a highly studied treatment process in recent years and it is based on the acceleration of hydroxyl radicals' production to degrade refractory organic compounds, such as MPs (pharmaceuticals etc.). This review is focused on the application of catalytic membranes coupled with the ozonation process. Catalytic membranes can act simultaneously as ozone contactors and catalytic reactors.

Up to now, several metal oxides have been used as coating materials, except for one case, where AC was used. However, AC acts mostly as an absorbent that pre-concentrates the MPs content. The most used catalysts are manganese and iron oxides. The virgin membrane can be either ceramic or polymeric. Ceramics are resistant to ozone, whereas only certain specific polymers are suitable for ozone applications, i.e., PDMS, PVDF, PTFE. Also, the polymeric membranes, due to their intrinsic hydrophobicity, may increase the fouling occurrence. In the membrane catalytic ozonation process, so far mostly PVDF membranes have been used. Ceramic membranes have been studied extensively, because their surface can be quite easily coated with metal oxides, acting as catalysts. These membranes are mostly made from Al_2O_3 . The hydrophilicity of ceramic membranes is associated with lower fouling incidence, but they present higher wettability that obstructs gas transfer (ozone) rate. In most cases the catalytic membranes cannot decrease membrane fouling, when singly applied, i.e., without the help of an oxidant agent, such as ozone.

In general, when a catalyst is immobilized, its catalytic activity is usually less than when it is used as free aqueous suspension. However, with the application of catalytic membranes the used catalyst does not need to be recovered to be available for reuse. The catalytic membranes coupled with ozone can efficiently reduce the fouling event, as well as the formation of cake layer, deposited in the surface of the membrane and interfering with the membrane operation. Simultaneously, this hybrid process can remove/effectively degrade the MPs content. Pore size, smoothness, hydrophobicity, and surface charge can highly influence the fouling degree of a membrane, while there are four main factors that affect the catalytic performance of the system, i.e., coating times, pore size, preparation method of the metal oxide, and adsorption capacity. Except for the removal of MPs, some researchers have used the membrane catalytic ozonation process also for the effective removal of bacteria. Metal oxides agglutinate bacteria and the presence of oxidizing radicals can efficiently inactivate them.

Although coupling catalytic membranes with ozonation seems to be a promising technology, the stability of the coatings constitutes a quite important issue of concern. In most cases the amounts of initially deposited metals leached may back into the aqueous solutions during the operation and can lead to a secondary pollution. Even for the metals without established regulation limits, their potential occurrence in drinking water sources can raise health issues. Moreover, studies about the formation of ozonation by-products and their acute potential toxicity will be considered to be essential, because they can be an additional pollution source. Finally, the coating techniques must be further developed, especially regarding the application of more ozone-resistant polymeric materials, and new solid materials can be examined for deposition onto the membranes surface, acting as potential catalysts, leading to the increase of catalyst range/options.

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Abbreviations

AC	Activated Carbon
AOPs	Advanced Oxidation Processes
BP-3	Benzophenone-3
BPA	Bisphenol-A
CA	Cellulose Acetate
CCM	Ceramic Catalytic Membrane
CMC	Catalytic Membrane Contactor
C_m	Micropollutant concentration
Co_3	Ozone concentration
COD	Chemical Oxygen Demand
COP	Catalytic Ozonation Process
DBPs	Disinfection by-products
DEET	N,N-Diethyl-meta-toluamide
EffOM	Effluent Organic Matter
GAC	Granular Activated Carbon
GO	Graphene Oxide
IEP	Isoelectric Point
KHP	Potassium Hydrogen Phthalate
MIEX	Magnetic Ion Exchange Resins
MF	Microfiltration
MPs	Micropollutants
MTBE	Methyl Tert-Butyl Ether
MWCO	Molecular Weight Cut-Off
NF	Nanofiltration
NOM	Natural Organic Matter
$O_2^{\bullet-}$	Superoxide ions
HO^{\bullet}	Hydroxyl radicals
PAC	Powder Activated Carbon
PAN	Poly-acrylonitrile
p-CNB	p-chloronitrobenzene
PDMS	Poly-dimethyl-siloxane
PEI	Polyether-imide
PES	Polyether-sulfone
pH_{pzc}	Point of zero charge
PI	Polyimide
PP	Polypropylene

PTFE	Polytetrafluoroethylene
PVA	Polyvinyl-alcohol
PVDF	Polyvinylidene fluoride
RO	Reverse Osmosis
ROS	Reactive Oxygen Species
SA	Salicylic Acid
SAP	Single Adsorption Process
S _{BET}	Surface Area
SOP	Single Ozonation Process
T	Temperature
TMP	Trans- Membrane Pressure
TOC	Total Organic Carbon
UF	Ultrafiltration
%wt	Weight percent
WWTP	Wastewater Treatment Plant

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