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COUPLING CATALYTIC OZONATION AND MEMBRANE SEPARATION: A REVIEW

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Abstract

Ozonation is an efficient process for oxidation of organic pollutants. This process is effective but it can sometimes generate byproducts more toxic than the initial micropollutants. For a better oxidation, an enhanced production of hydroxyl radicals can be obtained through to the use of ozonation catalysts. In order to improve the removal of organic compounds in water, a promising solution relies on the coupling of membrane filtration with catalytic ozonation. Indeed, it allows combining advantages of filtration (possible rejection of colloids, molecules and ions) and advantages of catalytic ozonation (degradation of molecules).

Various process configurations were investigated for the ozonation membrane filtration (OMF) and the catalytic ozonation membrane filtration (COMF). Three main types of processes can be defined, with water ozonation occurring before, during or after the membrane filtration, respectively. In the case of simultaneous ozonation and membrane separation, catalysts can be dispersed in the feed or supported on the membrane.

The literature about such coupling is not very abundant but some studies were performed, involving mainly organic or ceramic ultrafiltration membranes. Removal of micropollutants and mitigation of membrane fouling have been evidenced.

Coupling catalytic ozonation and nanofiltration appears as very promising with both organic and ceramic membranes. Nanofiltration would enable a better selectivity and retention of very small molecules as well as a higher efficiency as contactor for catalytic ozonation.

Key-words

Catalytic ozonation, membrane separation, hybrid processes, organic membranes, ceramic membranes

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1. Introduction

Nowadays, water scarcity and quality are big challenges for humanity in many places around the world [1]. Water scarcity affects more than 40 percent of the global population and this matter will get even more important with climate change [2].

The quality of water decreases more and more. Indeed during the last years, a significant number of chemical and oil industries increased leading to an increase in the volume of wastewaters. These industries provide different organic compounds such as dyes, detergents, pharmaceuticals, personal care products, pesticides and hydrocarbons. Moreover, because of human activity, urban and farm wastewaters are increasingly contaminated by organic pollutants such as biocides and environmental persistent pharmaceutical substances [3], [4]. Wastewaters include, among other substances, toxic, carcinogenic, persistent and mutagenic organic compounds. Although their concentrations can be low, their impact in the environment and on human health is significant and can be disastrous. Indeed, their potential persistence in the environment, their possible endocrine disrupting effect and their accumulation in biological bodies represent a global concern. In addition, human and veterinary antibiotics have been found widespread in different environmental compartments due to their persistence and low degradability. Thus, the presence of antibiotics resistance genes is increasing in the environment. All these issues have led to increasing awareness and changes in legislations, for example with Water Utilities (REACH 2006, 2000 and 2012) [5]. These evolutions have driven the wastewater treatment to come up with new and advanced technologies [6]–[9].

Numerous conventional methods used for the removal of organic compounds in aqueous effluents can be quoted such as adsorption [10], coagulation [11], [12], flocculation [13], [14], incineration [15], granular media filtration [16], membrane separation [6], biological oxidation [17], [18], oxidation [19]. The conventional methods can be coupled to enhance this removal process [9], [20]. However, they present some limitations like a lower degradation efficiency and/or a higher energy consumption. These problems have led scientists and industrials to develop new processes in order to completely degrade organic compounds. First of all, a membrane bioreactor can be used to degrade carbon, nitrogen and sometimes phosphorous pollutions thanks to microorganisms. That first step is useful but is not enough to eliminate non-biodegradable and non-adsorbed pharmaceutical compounds. Thus, additional methods are widely used such as the adsorption on activated carbon and oxidative processes. Adsorption on activated carbon is not an expensive method and is effective on a wide range of micropollutants. However, it is not efficient for polar compounds and for the disinfection of water. From this point of view, oxidative processes seem more interesting to be used alone or in coupling.

In oxidative processes, advanced oxidation processes (AOPs) have received increasing interest from the scientific community in the last few years because of their high efficiency in removing organic compounds [19], [21]–[25]. AOPs are based on the production of reactive species, among which OH^\bullet radicals were mainly used but it exists other species like $\text{SO}_4^{\bullet-}$, $\text{O}_2^{\bullet-}$, $^1\text{O}_2$, which have a high oxidizing potential and a non-selective action [26], [27]. Among oxidation processes, ozonation (O_3) [19], [22], [23], use of hydrogen peroxide ($\text{H}_2\text{O}_2/\text{O}_3$) [28], Fenton/photo Fenton processes [29], [30], wet air oxidation (WAO) [31], electrocoagulation [32], photocatalytic oxidation [33], peroxymonosulfate (PMS) activation [27], combined microwave-induced and photocatalytic oxidation [34] are widely investigated.

Ozonation is a common method for disinfecting and removing odours and tastes of drinking waters. Moreover, ozonation is used for oxidizing organic compounds in order to obtain smaller biodegradable molecules. However, ozone efficiency is highly dependent on the organic pollutants, the chemistry of the effluent and the amount of O_3 and OH^\bullet formed. Concerning ozonation of

secondary effluents from urban wastewater plants, many studies have shown promising results with a reduction in chemical oxygen demand (COD) [35]–[37], a drastic decrease in five days of biochemical oxygen demand (BOD₅) [35] and a reduction of total organic carbon (TOC) [38], [39] and suspended solid concentration [40], [41]. O₃ can remove 50 to 90% of anionic and non-anionic detergents [42]–[45]. A complete or partial elimination of aromatic compounds, a reduction of unsaturated fatty acids and a 50% reduction of anionic detergents can be also observed [41]. Sasai et al. reported a 12% reduction of TOC and a 33% reduction of COD after ozonation of a secondary effluent [40].

Ozonation has also the main advantage to be effective for the inactivation of microorganisms [46], which can be a key parameter when the treated wastewater is released into sensitive areas. Ozone is a selective oxidant which reacts with organic compounds and functional groups with high electron density (double bonds, activated aromatic systems, non-protonated secondary and tertiary amines and reduced sulphur species) under a second-order rate constants. At the same time, ozone decomposed into hydroxyl radicals reacts non-selectively with high rate constant (10^9 to 10^{10} M⁻¹ s⁻¹) with organic molecules [47]. Non selective hydroxyl radicals contribute to the oxidation of compounds that present very low reactivity with ozone. Therefore, direct and indirect reactions of ozone allow treating very large panel of pollutants (Fig 1).

However, one concern was raised related to ozonation because of the formation of oxidation by-products from matrix components and micropollutants (bromate, N-nitroso dimethylamine), which can be sometimes toxics[48], [49].

In order to increase the production of hydroxyls radicals, and at the same time increase the removal performance, ozonation can be performed in the presence of solid catalysts (heterogeneous catalysis), namely catalytic ozonation. Many noble metals and metal oxides, immobilised or not on supports, have been used for catalytic ozonation.

Various noble metals supported on Al₂O₃ support have been investigated for the decomposition of ozone in aqueous solution. Al₂O₃ support was chosen because that material stands stable against ozone. Coated on alumina, the order of catalytic activity of various noble metals for the decomposition of ozone is the following one [50], [51]:

Pt > Pd > Ag > Ru, Rh, Ir > Ni > Cd > Mn > Fe > Cu > Zn, Zr >> Co, Y, Mo, Ti, Au

A lot of studies have been done on the activity of heterogeneous catalysts during ozonation for the degradation and mineralisation of organic pollutants in water. The main catalysts quoted in the literature are metal oxides (e.g. MnO₂, Fe₂O₃, Co₃O₄, TiO₂, Al₂O₃, MgO) supported or not [22], [52]. The evaluation of the performance of a catalyst is challenging since numerous parameters have to be taken into account like morphology, crystallography structure, surface properties, pH of the solutions and chemical stability during the oxidation process [19].

Besides oxidation processes, the removal of micropollutants can also be improved using membrane processes like nanofiltration [6], [53]–[63] or reverse osmosis [53]–[63]. However, even if membrane processes are widely used they have only a function of physical separation. They must be coupled with other techniques in order to permit efficient destruction of pollutants and possible disposal of retentates. In this view, coupling of membrane processes and AOP could thus be a promising treatment solution for micropollutants removal and even for the mitigation of membrane fouling. These unit operations can be performed in series, the catalytic ozonation followed by membrane filtration [64]–[71] or the membrane filtration followed by ozonation [72]. Catalysis can be sometimes homogeneous with metal ions [73] or mainly heterogeneous with dispersed [74]–[77] or supported metal oxides particles. In literature, hybrid processes combining catalytic ozonation and membrane filtration have also been reported where membrane plays the role both as catalyst for ozonation and as filter [37], [39], [38], [78]–[80], [75], [81], [73], [82], [83].

A recent review [84], focused on AOP treatment of concentrates, mentions that the main technologies applied for nanofiltration/reverse osmosis concentrates are ozonation, Fenton, photocatalysis and photo oxidation, sonolysis and electrochemical oxidation. However, most of the studies reviewed were based mainly on DOC removal, while results related to pharmaceutical elimination at realistic concentrations through this combined system are still very limited.

Filtration associated with catalytic ozonation present some advantages such as the potentiality to retain micropollutants and by products created during the ozonation process. In addition, several researchers investigated the effect of O_3 on fouling (ultrafiltration membranes) with promising results. They showed that the combination of O_3 pre-oxidation and membrane filtration was effective for the prevention of membrane fouling [38], [64], [67], [70], [71], [76], [83], [85].

The present review is a state of the art about the combination of filtration and ozonation processes which is a field of interest for wastewater treatments. First, basic information on ozonation and catalysts used for catalytic ozonation will be presented. Then, recent advances about coupling catalytic ozonation and membrane separation will be developed.

2. Advanced Oxidation Process by ozonation

Ozone in water can react on an organic compound by two distinct mechanisms and leads to the formation of various oxidative species [86] (Fig. 1): O_3 molecular reaction pathway and OH^\bullet reaction mechanism. The direct reaction is defined as a molecular mechanism with a selective reaction of the molecular ozone on the organic compound (electrophilic substitution, cycloaddition and nucleophile reaction).

The indirect reaction, also called radical reaction corresponds to a non-selective reaction of free radicals produced by ozone decomposition in water. This decomposition is highly dependent on pH, temperature and nature and concentration of organic and inorganic compounds present in aqueous solution.

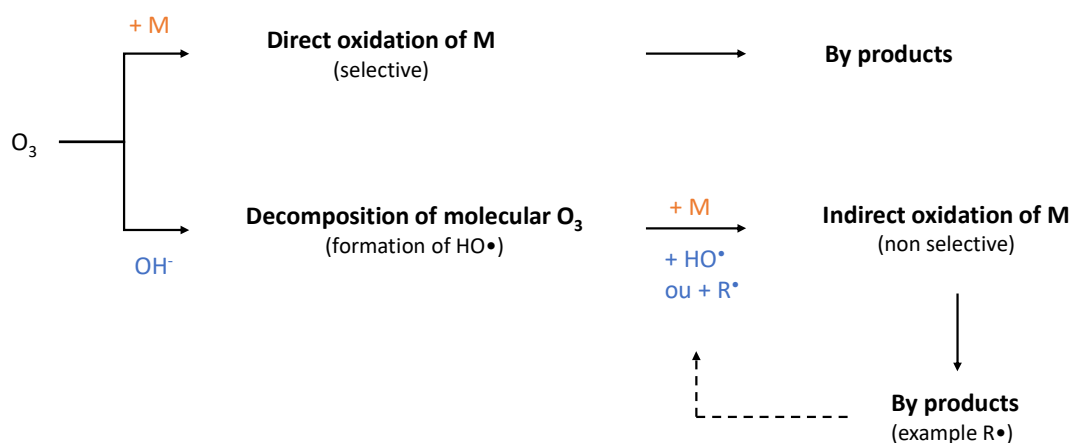


Fig. 1. Ozone reactions: direct and indirect reactions according to Hoigne and Bader [86].

Molecular ozone, with a molar mass of 48 g mol^{-1} , is composed of three oxygen atoms linked with two oxygen-oxygen bounds of 1.278 \AA and an angle of 116.8° . Thanks to the electronic displacement, the ozone molecule has resonance structures and can react as a dipole, an electrophilic or a nucleophile agent. In addition, ozone molecule is highly reactive and unstable in water. This instability leads to its decomposition and to the production of hydroxyl radicals via a chain reaction mechanism [19].

Ozone molecule and hydroxyl radicals (HO^\bullet) have a high oxidative power with high redox potentials, $E^0=2.07$ V and $E^0=2.33$ V, respectively [87]. These oxidative powers are higher than those of chlorine (1.36 V), hypochloric acid (1.49 V) and H_2O_2 (1.77 V) [87], [88]. Ozone decomposition in water is highly influenced by the pH value of the solution. Basic pH causes an increase of ozone decomposition. For acid pH ($\text{pH} < 3$) hydroxyl ions do not influence ozone decomposition. For neutral to basic pH ($7 < \text{pH} < 10$), ozone has a typical life-time of 15 to 25 min [89], [90]. Some species can promote, initiate or inhibit the radical reaction chain process [19], [91], [86]. For example, OH^- , $\text{H}_2\text{O}_2/\text{HO}_2^-$, Fe^{2+} , humic substances and formate can promote the formation of superoxide ion $\text{O}_2^{\bullet-}$ from an ozone molecule. Regeneration of $\text{O}_2^{\bullet-}$ from the hydroxyl radicals can be performed thanks to promoters like $\text{R}_2\text{-CH-OH}$, aryl-(R), formate, humic substances and O_3 . Some compounds can inhibit the reaction, consuming hydroxyl radicals without regeneration of superoxide ion (e.g. $\text{CH}_3\text{-COO}^-$, alkyl-(R), $\text{HCO}_3^-/\text{CO}_3^{2-}$, humic substances).

2.1. Direct oxidation

Ozone can react as a nucleophilic and electrophilic compound thanks to the electronic displacement between the three oxygens.

Following the cycloaddition reaction (Criegee mechanism) [92], [93], ozone can react with an unsaturated double bond. Cycloaddition on unsaturated double bonds of aromatic rings leads to the ring opening. Cycloaddition of ozone on double bond allows the formation of a five-atom ring (molozonide). Then, a molecule of water promotes the opening of the ring to form a ketone or an intermediate which, after rearrangements, turns into ketone as well. Molecular ozone can also react with a α -position C-H bond of an electron-donor function (alcohol, ether and aldehyde).

Ozone also reacts with electron-donor compounds with electrophilic substitution [50]. For instance, ozone reacts with aromatic compounds having an electron-donor function (e.g.: $-\text{OH}$, $-\text{NH}_2$, $-\text{OCH}_3$, amines and mercaptans). These aromatic rings exhibit electron rich areas located on the ortho and para carbons. Ozone reaction forms with these areas hydroxylated compounds in ortho or para positions. After the ring opening, carboxylic and carbonyl functions are then obtained. On the contrary, aromatic compounds with electrophilic functions (e.g.: $-\text{COOH}$, $-\text{NO}_2$) are poorly reactive with ozone. In such a case, ozone reacts with the most electrophilic carbon atom in meta position.

Finally, nucleophilic reactions can exist on electrophilic groups, usually on carbons with electrophilic functions. These reactions are well known and intensely used in the oxidation of micropollutants (acetaminophen, carbamazepine, phenol, etc.).

2.2. Indirect oxidation – radical reaction

The decomposition of the ozone is described according to several models but in this review, only the Staehelin and Hoigne [94] model will be presented because of its applicability with acid and neutral pHs.

First of all, the model without solute is presented according to the Staehelin and Hoigne model [94]. Ozone decomposition is the result of chain reactions with initiation, propagation and ending phases. The initiation corresponds to the reaction between ozone and OH^- ions to form hydroperoxides radicals HO_2^\bullet . During the propagation, HO_2^\bullet is in equilibrium with the superoxide radical ($\text{O}_2^{\bullet-}$). The reaction between ozone and superoxide radical produces ozonide $\text{O}_3^{\bullet-}$ which reacts with H^+ to form HO_3^\bullet . Then HO_3^\bullet is dissociated into OH^\bullet and O_2 . Finally, the cycle is closed with the dissociation of HO_4^\bullet into HO_2^\bullet and O_2 . HO_4^\bullet is formed with the reaction between O_3 and HO^\bullet .

With the presence of organic and inorganic solutes and according to the study of Staehelin and Hoigne [95], ozone decomposition is slightly different. The reaction initiation occurs thanks to the hydroxyl ions OH^\cdot and the solutes which generate the production of HO_2^\cdot , O_2^\cdot and O_3^\cdot . Then the propagation takes place through the decomposition of O_3^\cdot and HO_3^\cdot into HO^\cdot which can then react with a solute. The solute can have inhibitor or promotor effects depending on its chemical nature. The reaction of R^\cdot radicals with oxygen forms new radical species such as ROO^\cdot which is unstable. It decomposes itself to produce oxidation by-products, releasing HO_2^\cdot radicals. The regeneration of O_2^\cdot maintains the cycle. The reaction between hydroxyl radicals and solutes leads to the formation of non-radical species which can stop the radical reaction. The inhibitors have the advantages to stop the reaction and to be poorly reactive with molecular ozone. Thus, they cannot sustain and initiate the decomposition of ozone.

The production of hydroxyl radicals is interesting because these radicals can oxidise organic compounds thanks to their high oxidative power. They can react with numerous organic compounds (ethylenic, aliphatic, aromatic and lipidic) to form shorter compounds (peroxides, aldehydes, acids...).

Several chemical species can be used to initiate the radical reaction: OH^\cdot , H_2O_2 , aromatic compounds such as aryls, some metal cations (Co(II), Fe(II and III), Mn(II), Cu(II)), formate anions (HCOO^-), methanol and aromatic substances (humic substances). These compounds are responsible for the formation of O_2^\cdot ions. Carbonates, bicarbonates, nitrites, phosphates, alkyl species and tertiary alcohol (T-BuOH) are competitor compounds of HO^\cdot and play the role of inhibitors. Thus, a catalyst based on metal oxides can promote the production of hydroxyl radicals which are necessary to the oxidation of organic molecules.

3. Catalysts for catalytic ozonation

An advanced oxidation process is defined as an oxidation process which generates a sufficient quantity of hydroxyl radicals for water treatment. Several agents are essential to realize AOP, such as oxidants (O_3 , H_2O_2), acoustic assistance (ultrasounds), photocatalysis (under UV activation) and catalysts. In this paper, only the combination of catalysts and ozone will be presented.

In order to improve the production of hydroxyl radicals, addition of a catalyst is required. Catalytic ozonation can be homogeneous catalysis with usually metal ions, or heterogeneous catalysis with the presence of metal oxides or metals/metal oxides on supports.

3.1. Mechanism of homogeneous catalysis

The catalyst used for homogeneous catalytic ozonation is usually based on transition metal cations such as Fe(II), Mn(II), Ni(II), Co(II), Cd(II), Cu(II), Ag(I), Cr(III), Zn(II).

Gracia et al. [96], showed that using transition metal during ozonation, mainly Mn(II) and Ag(I), causes important decreases in organic matter content. Mn(II) is responsible for a TOC reduction of 62% and Ag(I) for 61%. In the same study, ozonation in the presence of other transition metals (Fe(II), Cd(II), Fe(III), Cu(II), Zn(II), Co(II) and Cr(II)) was slightly less efficient. The use of catalytic ozonation presents a good alternative to obtain significant humic substances removal as reported by Garcia.

Cortes et al. [97] tested Mn(II) and Fe(II) ions at the concentration of $6 \times 10^{-5} \text{ mol L}^{-1}$ for the ozonation of chlorinated benzene derivatives in neutral condition and at an ozone dose of $1.5 \text{ g}(\text{O}_3) \text{ g}(\text{TOC})^{-1}$. After 20 min of contact time, the chemical oxygen demand (COD) removal was 18% for ozone alone, 12% for catalytic ozonation with Fe(III), 55% for catalytic ozonation with Fe(II), 66% for

catalytic ozonation with Mn(II). The involved mechanism for Fe(II)/O₃, Fe(II)/UV and Fe(II)/O₃/UV is based on the generation of hydroxyl radicals. This latter was investigated by Piera et al. [98] and Sauleda and Brillas [99]. It can be described by the following reactions:



In reaction (2), Fe²⁺ involves the formation of HO[•] with the reaction of ozone. FeO²⁺ can also oxidise Fe²⁺ in Fe³⁺ with the termination of the chain reaction:



Co(II) was also examined as ozonation catalyst for the degradation of the oxalic acid [100], [101]. A hydroxyl radical probe compound, p-chlorobenzoic acid (pCBA), was used to follow the generation of radicals in presence of this catalyst. Co(II) catalyst increases the removal rate of pCBA indicating that hydroxyl radicals are by-products from cobalt(II)-catalysed ozonation of oxalate. Mechanisms involved are not really well understood but authors highlight the formation of a cobalt(II) -oxalate complex. Indeed, during homogeneous catalytic ozonation, complexes can also be formed with organic molecules such as carboxylic acids. Thus, Pines et al. proposed that Co(II) oxalate is then oxidized by ozone to form Co(III) oxalate. The catalytic reaction is completed with the decomposition of Co(III) complex to restore the catalyst Co(II) and an oxalate radical.

Overall, two main processes can be cited to explain the mechanism of homogeneous catalytic ozonation: ozone decomposition thanks to transition metal species, followed by the generation of free radicals as well as formation of complexes between catalyst and organics. Moreover, it is important to note that the pH of the solution and the reagent concentration can influence the efficiency and the mechanism of homogeneous catalytic ozonation.

3.2. Mechanism of heterogeneous catalysis

The main catalysts found in literature associated with heterogeneous catalytic ozonation are metal oxides (MnO₂, Fe₂O₃, Al₂O₃, TiO₂), metals (Cu, Fe, Mn...) and metal oxides on metal oxides supports (TiO₂/Al₂O₃, Fe₂O₃/Al₂O₃, Mn₂O₃/Al₂O₃...). The catalytic activity is usually evaluated thanks to the catalytic decomposition of ozone and the enhanced generation of hydroxyl radicals. However, the results from different studies suggest different ozonation mechanisms.

Various supported noble metals were reported in literature for the decomposition of the ozone in liquid phase. For example, if the support is alumina, the order of catalytic activity of noble metals for ozone decomposition is the following one, according to Baig and Mouchet [46, 47]:

Pt > Pd > Ag > Ru, Rh, Ir > Ni > Cd > **Mn** > **Fe** > Cu > Zn, Zr >> **Co**, Y, Mo, **Ti**, Au

Noble metals in bold are presented more in details in that review. The advantages of a catalyst in the ozonation process can be explained by three different mechanisms presented in Fig. 2. [50]. The organic matter (OM) and ozone are adsorbed at the surface of the catalyst (Fig. 2.a). The ozone molecule and other oxidizing compounds generated by the catalyst can oxidize directly the organic compound (OM). The liquid/solid interface enables the formation of a layer where the concentration of ozone and organic matter is high, facilitating the oxidation (Fig. 2.b). Moreover, the local pH at the surface can strongly promote the generation of hydroxyl radicals. Fig. 2.c illustrates the adsorption of the organic matter on the catalyst, its oxidation by O₃ and its release into the

solution. Then, the interaction between the catalyst and ozone can promote the formation of hydroxyl radicals which can then react with organic matter OM.

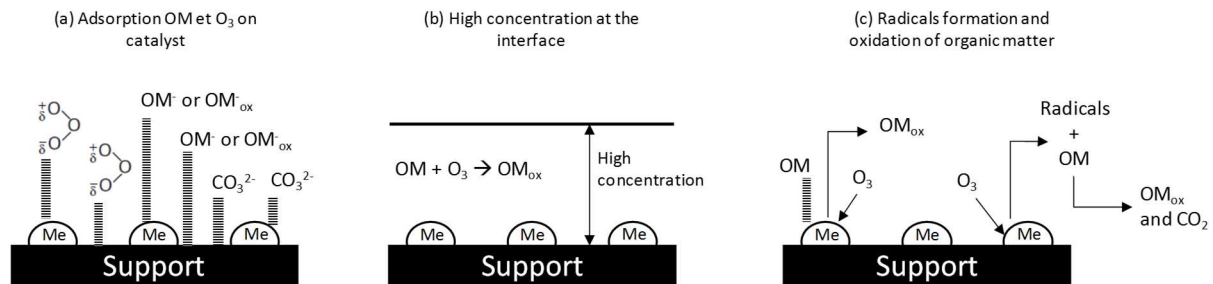


Fig. 2. Interactions between supported noble metal catalysts (heterogeneous catalysis) and organic molecules (MO); adapted from Baig and Mouchet [50].

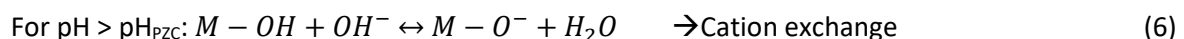
The activity of heterogeneous catalysts for the degradation and the mineralisation of organic pollutant have been evaluated in many studies. Supported or not metal oxides such as MnO₂, Fe₂O₃, Co₃O₄, TiO₂, Al₂O₃ and MgO are also considered in literature for pollutant degradation. The efficiency of a catalyst is not always easy to determine because a lot of parameters are involved in the process as shown for instance in the work of Kasprzyk-Hordern et al. [19]:

- Chemical, crystallographic and morphological nature of the catalyst;
- Surface properties of the catalyst (e.g. point of zero charge (PZC), specific surface area, porosity);
- pH and the nature of the inorganic and organic compounds present in the solution;
- Chemical stability of the catalyst during the ozonation process (to avoid leaching and adsorption without desorption).

3.2.1. Intrinsic physicochemical properties of currently used heterogeneous catalysts

Catalytic properties are closely linked to acid and basic characteristics of the metal oxides. Metal oxides have hydroxyl groups OH at the surface with surface density and acid-base properties changing with the metal nature. OH functions can react as Brönsted acid ($AH \leftrightarrow A^- + H^+$) [19]. Lewis acid part (electron acceptor) and basic part (electron donor) are situated on the metallic cation. Lewis and Brönsted acids are the catalytic centres of the metal oxides.

Metal oxides can behave as acid or basic materials depending on the PZC (Fig. 3.).



The values of PZC can differ according to the studies, probably because they are varying with the synthesis route, the impurities content and the thermal history of the catalyst (Table 1).

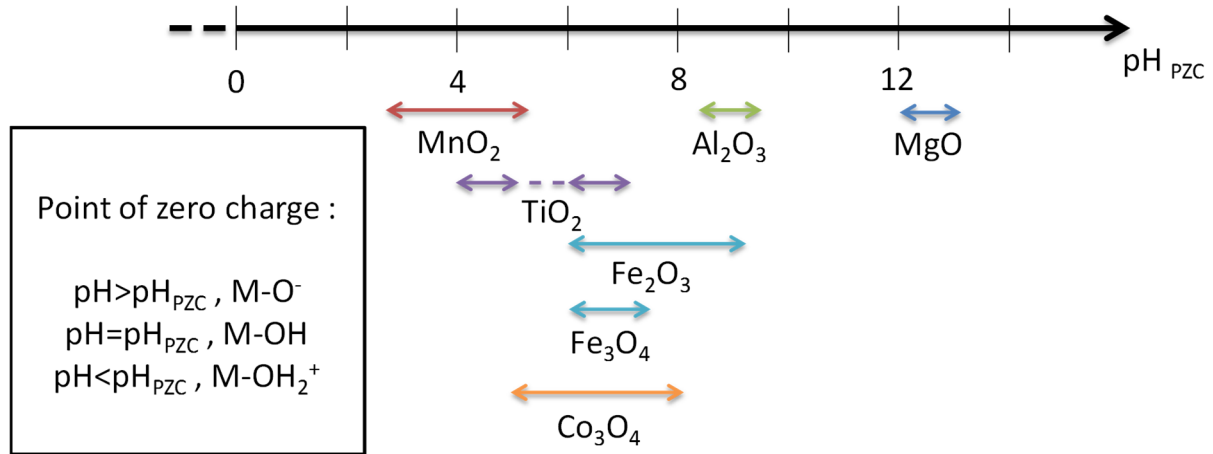


Fig. 3. Mapping of the PZC for different metal oxides.

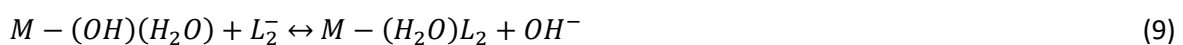
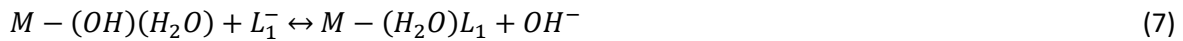
Table 1

Values of PZC for different metal oxides.

Catalysts	ZPC	Ref.
MgO	12-13	(Haussonne et al., 2005) [102]
Al ₂ O ₃	8.5-9.5	(Haussonne et al., 2005) [102]
	6.94 ± 0.37	(G.A. Parks and P.L. de Bryun, 1962)[103]
TiO ₂	6-7 (anatase)	(Haussonne et al., 2005) [102]
	4-5 (rutile)	(Haussonne et al., 2005) [102]
	6.7	(G.A. Parks and P.L. de Bryun, 1962)[103]
Fe ₂ O ₃	6-9	(Haussonne et al., 2005) [102]
	8.5	(G.A. Parks and P.L. de Bryun, 1962)[103]
Fe ₃ O ₄	6-7	(Haussonne et al., 2005) [102]
MnO ₂	3-5	(Boczkaj & Fernandes, 2017) [7]
Co ₃ O ₄	5-8	(Pirovan & Trasatti, 1984) [104]

For water with pH around 7, MnO₂, TiO₂, Co₃O₄ and Fe₃O₄ are negatively charged (M-O⁻). Al₂O₃ and MgO are positively charged (M-OH₂⁺) and Fe₂O₃ is mainly neutral (M-OH).

Metal oxides can also exchange ligands with the presence of Lewis acid sites, water molecules bounded or other ligands linked to surface. Ligands exchange can be written as follows, with L₁ = O₃ and L₂ = anions contained in water (F⁻, PO₄³⁻, SO₄²⁻...) [19]:



At high pH, ligand exchanges can be neglected because of the presence of OH⁻ ions which are powerful Lewis bases. However, OH⁻ ions initiate the radical reaction of ozone to form hydroxyl radicals OH[•] useful as oxidant. Moreover, the exact nature of the organic molecules present in the solution also depends on the pH solution. In order to better understand the interaction between surface and organic molecules, their pKa and the PZC of the catalyst are important to consider in the analysis of the electrostatic interactions.

For pH < pKa, molecules will have an acidic behaviour with a majority of protonated sites.

For pH = pKa, molecules will be globally uncharged with a compensation of protonated and deprotonated sites.

For pH > pKa, molecules will have a basic behaviour with a majority of deprotonated sites.

Thus, catalysts and molecules with the same charges are repulsed while if they have opposed charges, they stick to each other. In the case of coupled catalytic ozonation and filtration, two phenomena can occur:

- The adsorption of the organic molecule on the catalyst to facilitate oxidation;
- The repulsion of the molecule avoiding fouling and improving the separation [105].

It is important to find a compromise between those two opposed phenomena in order to obtain the highest overall efficiency. For example, for the removal of phenol (pKa = 9.95) at pH=7, catalysts are negatively charged except for MgO and Al₂O₃ and phenol which are mostly positively charged. Therefore, the electrostatic attraction is quite high between phenol and MnO₂, TiO₂, Fe₃O₄, Fe₂O₃, Co₃O₄. This is in agreement with the ranking experimentally established in terms of efficiency for phenol removal: MgO [106] > MnO₂ [107] > Fe₃O₄ [108], [109] > TiO₂ [110] > Co₃O₄ [111] > Al₂O₃ [112], [113]. MgO exhibits the best removal efficiency. The authors explained that the hydroxyl radical reaction is not the dominant mechanism of phenol degradation and that other mechanisms like catalyst surfaces and bulk solution are also involved in this process. For example, when catalyst surface is negatively charged, the decomposition of O₃ is favoured because of the presence of OH⁻ [109]. Hydroxyl ions initiate the radical decomposition of O₃ to form the HO[•] which present a high oxidative power, useful in the degradation of organic molecules. Finally, it is important to underline that other features must be considered before concluding on the efficiency of a catalyst, such as its morphology, its porosity or its crystalline structure.

From the literature, the comparison between the different catalysts is difficult because the conditions of ozonation are not identical (e.g. ozone flux, quantity of catalyst, catalyst morphology). In addition, the catalysts presented are not always supported and can be in heterogeneous or homogeneous form. The pollutant degradation is evaluated through several indicators like the degradation percentage for the pollutant or the TOC or the COD percentage reduction. Moreover, some studies showed that the presence of organic substances can improve the degradation from O₃. Ma and Graham [114] studied the ozonation of atrazine using MnO₂ as catalyst in presence of humic substances. They demonstrated the catalytic activity of MnO₂ and highlighted the enhancement of the O₃ decomposition into HO[•] and the degradation of atrazine with humic substances.

3.2.2. *Catalytic activity of metal oxides used for heterogeneous catalytic ozonation*

A short review on the catalytic activity of the main catalysts of metal oxide type is proposed in this section. For their performance assessment, the implemented analytical techniques for

measuring pollutant removal are usually based on liquid chromatography coupled with mass spectrometry or with ultraviolet detection.

3.2.2.1. MgO

As mentioned previously, the phenol removal with MgO catalyst can be quite complete with 96% of removal in 80 min [106]. This fact corresponds to a COD removal around 70% in 80 min.

The work of Moussavi and Mahmoudi [115] highlighted a full COD reduction for pH above 8. Indeed, in these conditions, the hydroxyl ions on the surface and in solution promote the generation of HO[•] radicals highly useful in the oxidation of micropollutants. Yaghmaeian et al. [116] worked on the degradation of the acetaminophen (ACT) with the MgO catalyst. The ACT adsorption on this catalyst was around 3.5% for pH between 2 and 10. That adsorption was low but others studies have shown that MgO has a strong affinity with pharmaceutical compounds such as cephalexin and cefixime [117]. The ozonation process, with a pH=5, enables degradation of about 25% of ACT. With the pH increase, the ACT elimination percentage is higher because of the presence of the OH⁻ ions, which promotes the ozone decomposition into HO[•]. With the addition of MgO as catalyst, the ACT removal percentage achieves 94% with pH=5.4. This value changes a little when the pH increases. Overall, the addition of MgO as catalyst improved the ACT elimination process by promoting the ozone decomposition in radicals rather than by ACT adsorption.

MgO exhibits interesting performance concerning the removal of some organic compounds (phenol, azo dye RR198 and acetaminophen). Table 2 is a summary from literature on the catalytic activity of MgO in presence of O₃.

Table 2

Removal efficiency of MgO as catalyst with ozone (A: developed area of catalyst in the reactor; D: equivalent diameter of the elemental particles or powder particles of catalyst).

Catalysis	Pollutant	Conditions	Catalyst characteristics	Pollutant degradation (%)	TOC or COD removal (%)	Reference
Heterogenous catalysis	Phenol 1100 mg L ⁻¹	O ₃ : 0.25 g h ⁻¹ MgO: 4 g L ⁻¹ pH=7 Salt water [NaCl]= 20-40 g L ⁻¹	MgO A=122 m ² D=1-2 μm	96 (80 min)	70 / COD (80 min)	Moussavi et al., 2010 [106]
Heterogenous catalysis	Azo dye RR198 200 mg L ⁻¹	O ₃ : 0.2 g h ⁻¹ MgO: 5 g L ⁻¹ pH=8	No catalyst MgO A=56 m ² D=65 nm	- -	20 / COD (10 min) 61 / COD (10 min)	Moussavi & Mahmoudi, 2009 [115]
Heterogenous catalysis	Acetaminophen 50 mg L ⁻¹	O ₃ : 0.11 g h ⁻¹ MgO: 2 g L ⁻¹ pH=5.4	No catalyst MgO A=26 m ² D=23.6 nm	25 (10 min) 94 (10 min)	29.7 / TOC (30 min) 94 / TOC (30 min)	Yaghmaeian et al., 2017 [116]

3.2.2.2. Al₂O₃

Al₂O₃ is another metal oxide that has been investigated as a catalyst in the catalytic ozonation of organic pollutants.

Results from published articles are reported in Table 3. The work of Ernst et al. [118] highlighted differences in terms of ozonation efficiency, adsorption and catalytic ozonation considering different organic compounds (oxalic acid, acetic acid, salicylic acid and succinic acid). Ozonation alone is efficient for the removal of the salicylic acid but not really for the other compounds at pH=5. The adsorption of the acetic and succinic acids on the catalyst is naught while it is important with the salicylic acid (41.4% TOC removal) and not negligible with oxalic acid (8.8% TOC removal). The catalytic ozonation seems to improve the TOC removal except in the case of acetic acid. For example, in presence of a catalyst, the TOC removal for salicylic acid is around 83.5%. It is a significant increase compared to ozonation and adsorption alone. For the succinic acid, the TOC removal (62.9%) is better with the catalytic ozonation than ozonation and adsorption alone. The oxalic acid is removed with a value of 19% which is better than with ozonation and adsorption alone. Concerning catalyst with smaller particles, adsorption of succinic acid is important disregarding the pH value (12-19%). The catalytic ozonation leads to a TOC reduction percentage around 35% with pH=5 and 46.5% with pH=7. Therefore, a pH close to the neutrality improves the catalytic oxidative action and decreases the sorption phenomena. However, the reduction of succinic acid with this aluminium oxide is lower than the results obtained with γ -Al₂O₃. The work of Cooper and Burch [119] highlighted the interest of catalytic oxidation compared to oxidation alone for some compounds (e.g. oxalic acid, chloroethanol and chlorophenol). S. Heng [113] pointed out the high adsorption of the potassium hydrogen-phthalate on aluminium oxide (20% of TOC reduction) while it was quite negligible for the phenol.

Table 3

Removal efficiency of Al₂O₃ as catalyst with ozone (A developed area of catalyst in the reactor; D: equivalent diameter of the elemental particles or powder particles of catalyst).

Catalysis	Pollutant	Conditions	Catalyst characteristics	Pollutant degradation (%)	TOC removal (%)	Reference
Heterogenous catalysis	Oxalic acid ^a / acetic acid ^b /salicylic acid ^c / succinic acid ^d [TOC] _m =60 mg L ⁻¹	pH=5 O ₃ : 50 g N ⁻¹ m ⁻³ [Al ₂ O ₃] _m =50 g L ⁻¹	No catalyst	-	0.2 ^a /2.2 ^b /44.9 ^c /0.4 ^d	Ernst et al., 2004 [118]
			γ -Al ₂ O ₃ /O ₃ (Rhône-Poulenc) A=279 m ² D=45 μ m	-	19.0 ^a /0 ^b /83.5 ^c /69.2 ^d	
			Adsorption (without O ₃)	-	8.8 ^a /0 ^b /41.4 ^c /0 ^d	
Heterogenous catalysis	Succinic acid [TOC] _m =60 mg L ⁻¹	pH=5 O ₃ : 50 g N ⁻¹ m ⁻³ [Al ₂ O ₃] _m =50 g L ⁻¹	Aluminium oxide 60G (Merck) A=288 m ² D=30 μ m	-	35.0 (pH=5) 46.5 (pH=7)	Ernst et al., 2004 [118]
			Adsorption (without O ₃)	-	18.8 (pH=5) 12.2 (pH=7)	

Heterogeneous catalysis	Succinic acid 200 mg L ⁻¹	pH=3.6 [O ₃]gas = 51.5 g m ⁻³ O ₃ flow rate: 300 mL min ⁻¹ [Al ₂ O ₃] _m =10 g L ⁻¹	Al ₂ O ₃ D=50-80 μm	38		Peng et al. 2018 [120]
Heterogeneous catalysis	Succinic acid 1.00 mmol L ⁻¹	pH=3.4 [O ₃]gas = 55 mg L ⁻¹ O ₃ flow rate : 300 ml min ⁻¹ [Al ₂ O ₃] _m =1 g L ⁻¹	No catalyst γ-Al ₂ O ₃ A=164 m ² Adsorption (without O ₃)	3 10 5	3 10 5	He et al. 2010 [121]
Heterogeneous catalysis	Oxalic acid ^a Chloroethanol ^b Chlorophenol ^c (1000 ppm each)	Flux O ₃ : 24 mg(O ₃) L ⁻¹ h ⁻¹	Al ₂ O ₃	15 ^a /12 ^b /2 5% 85 ^a /17 ^b /8 4%		Cooper & Burch, 1999 [119]
Heterogeneous catalysis	Potassium hydrogen phthalate ^a (2.6.10 ⁻³ mol L ⁻¹) Phenol ^b (2.7.10 ⁻³ mol L ⁻¹)	[Al ₂ O ₃] _m =2 ^a g L ⁻¹ pH=4.2 ^a I ^a =10.6 mg(O ₃) mg(C) ⁻¹ [Al ₂ O ₃] _m =1 ^b g L ⁻¹ pH=5.3 ^b I ^b =16.6 mg(O ₃) mg(C) ⁻¹ [O ₃] _m =100 mg L ⁻¹	No catalyst With Al ₂ O ₃ A=199 m ² ^a A=99.5 m ² ^b Adsorption (without O ₃)		49 ^a /41 ^b 60 ^a (120 min) 51 ^b (90 min) 20 ^a (120 min) 0 ^b (90 min)	Heng, 2006 [113]

According to the results for ozonation alone and for adsorption on the catalyst, alumina does not seem to have a real catalytic activity except for phenol.

In the literature, only few examples about alumina used as a supported catalyst are referenced. Alumina presents a certain catalytic activity but the adsorption of organic molecules is often quite high. The efficiency for the removal of salicylic and succinic acids was not the same according to different studies [118], [120], [121]. Alumina is mostly used as catalyst support.

3.2.2.3. TiO₂

Table 4 summarizes different studies dealing with the decomposition of organic molecules using supported or not titanium dioxide as catalyst.

Two crystalline phases of titanium dioxide have been implemented, anatase and rutile. Anatase seems to be the most commonly used form but Yang's work [122] showed that the rutile form has better catalytic performance for the removal of nitrobenzene. These results have to be mitigated in regards to other parameters such as morphology, pollutant nature and ozonation conditions. The adsorption of nitrobenzene on titania is quite important. The work of Beltrán et al. [123] reported the degradation of 78% of oxalic acid after 180 min. When titanium dioxide is supported on Al₂O₃, the degradation of oxalic acid is around 87% but the duration of the experiment is not given. Therefore, the comparison is difficult but the trend is the same. Rosal's work [124] highlighted interesting removal of naproxen and carbamazepine. However, those molecules can

adsorb on the catalyst surface. Naproxen ($pK_a=4.60$) is well adsorbed on TiO_2 ($pH_{pZC}=6.6$) with acid pH for the solution ($pH=3$). Then, higher the pH of solution is and lower the molecules are adsorbed because of charge repulsion. Carbamazepine ($pK_a=14.0$) is protonated when pH is between 3 and 7 and consequently its adsorption is low in this pH range. For these two drugs, the adsorption equilibrium is long to reach but after one hour, adsorption is 5-15%. Even if adsorption is not so important, it cannot be neglected. Heng's study [113] revealed that TiO_2 coated on alumina did not increase the removal of potassium hydrogen phthalate (53%) and phenol (47%) in comparison with alumina alone (60% for potassium hydrogen phthalate and 51% for phenol).

Titanium dioxide adsorbs some organic molecules, then competitive adsorption between organic molecules and O_3 , could limit the decomposition of ozone into hydroxyl radical. Thus, supported titanium dioxide does not present a real advantage for the catalytic ozonation according to the studies presented in Table 4.

Table 4

Removal efficiency of TiO_2 as catalyst (A: developed area of catalyst in the reactor; S: specific surface area of the catalyst; D: equivalent diameter of the elemental particles or powder particles of catalyst).

Catalysis	Pollutant	Conditions	Catalyst characteristics	Pollutant degradation (%)	TOC removal (%)	Reference
Heterogeneous catalysis	Oxalic acid $8 \cdot 10^{-3} \text{ mol L}^{-1}$	O_3 30 mg L^{-1} $[TiO_2]_m=3.75 \text{ g L}^{-1}$ $T=20^\circ\text{C}$ $pH=2.5$	Anatase TiO_2 Powder	78 (180 min)	-	Beltrán et al., 2002 [123]
Heterogeneous catalysis	Nitrobenzene $60 \mu\text{g L}^{-1}$	O_3 0.367 mg L^{-1} $[TiO_2]_m=0.1 \text{ g L}^{-1}$ $T=20^\circ\text{C}$ $pH=7$ Results after 20 min	No catalyst	30	-	Yang et al., 2007 [122]
			Rutile $S=3 \text{ m}^2 \text{ g}^{-1}$ $D=30 \text{ nm}$	52	-	
			Anatase $S=114 \text{ m}^2 \text{ g}^{-1}$ $D=6 \text{ nm}$	15	-	
			65% Rutile/35% Anatase $S=40 \text{ m}^2 \text{ g}^{-1}$ $D=20 \text{ nm}$	57	-	
Heterogeneous catalysis	Naproxen ^a et carbamazepine ^b 15 mg L^{-1}	O_3 $38-40 \text{ g N}^{-1} \text{ m}^{-3}$ $[TiO_2]_m=1 \text{ g L}^{-1}$ $T=25^\circ\text{C}$ $pH=5$ Results after 2h	No catalyst	-	≈ 40 for a and b	Rosal et al., 2008 [124]
			80% Anatase /20% Rutile $S=50 \text{ m}^2 \text{ g}^{-1}$ $D = 20 \text{ nm}$	-	60 ^a 70 ^b	

Heterogenous catalysis	Oxalic acid ^a Chloroethanol ^b Chlorophenol ^c	Flux O ₃ : 24 mg(O ₃) L ⁻¹ h ⁻¹	No catalyst TiO ₂ on Al ₂ O ₃	15 ^a /15 ^b /25 ^c 87 ^a /47 ^b / 100 ^c	- -	Cooper & Burch, 1999 [119]
Heterogenous catalysis	Potassium hydrogen phtalate ^a (2.6.10 ⁻³ mol L ⁻¹) Phenol ^b (2.7.10 ⁻³ mol L ⁻¹)	[Cat] _m =2 ^a g L ⁻¹ pH=4.2 ^a l ^a =10.6 mg(O ₃) mg(C) ⁻¹ [Al ₂ O ₃] _m =1 ^b g L ⁻¹ pH=5.3 ^b l ^b =16.6 mg(O ₃) mg(C) ⁻¹ [O ₃] _m =100 mg L ⁻¹	TiO ₂ on Al ₂ O ₃ A=176 m ² ^a A=88 m ² ^b	-	53 ^a 47 ^b	Heng, 2006 [113]

3.2.2.4. MnO₂

Table 5 gives the degradation percentage of organic molecules using manganese oxide as catalyst.

The study of Zhao et al. [107] highlighted the good performance of MnO₂ catalyst with 95% of the degradation of phenol when ozone was used. Phenol degradation reaches 52.4% with ozonation alone. Moreover, the phenol adsorption on catalyst is low and stable over the time with a value around 2%. The O₃ decomposition rate with MnO₂ catalyst is 67.7% whereas without manganese oxide, it is closed to 23.1%. MnO₂ catalyst improves the decomposition of O₃ and increases the degradation of organic molecules. According to Nawaz et al. [125], crystalline α-MnO₂ exhibited the best performance for the degradation of 4-nitrophenol compared to other phases (β-, γ-, δ-, ε- and λ-MnO₂). Therefore, as stated previously, the catalyst performance for the degradation of micropollutants depends on the used crystalline phases.

In literature, mixed oxides have also been studied with manganese oxides supported by alumina or silica. Studies of Yang [126] highlighted the increase of TOC removal when alumina support is used but possible adsorption is not taken into account. Then, when manganese oxide is present with alumina, the TOC removal is the largest one using mesoporous gamma aluminium oxide. Roshani et al. [127] observed a good removal of benzotriazole and a TOC decrease when Mn/Al₂O₃ is used with slight differences depending on pH. However, the adsorption of benzotriazole on the catalyst is always evidenced whatever the pH value. It can reach 12%. S. Heng [113] underlined that manganese oxide catalysts improved the removal of phenol but not that of potassium hydrogen phthalate. Thus, a same catalyst can have removal efficiency which strongly depends on the organic molecules. The removal of clofibric acid with ozone and MnO_x/SBA-15 (silica) catalyst was better than with ozone alone [128]. Adsorption of clofibric acid exists but is low in comparison with catalytic ozonation.

All these works illustrate the high capability of manganese oxide for the catalytic ozonation of micropollutants.

Table 5

Removal efficiency of MnO₂ as catalyst (A: developed area of catalyst in the reactor).

Catalysis	Pollutant	Conditions	Catalyst characteristics	Pollutant degradation (%)	TOC removal (%)	Reference
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Heterogeneous catalysis	Phenol 300 mg L ⁻¹	[MnO ₂] _m = 1.0 g L ⁻¹ O ₃ : 0.80 mg min ⁻¹ T=25°C pH=6.4 Results after 1h	No catalyst α-MnO ₂ nanotubes (100x30 nm) A=4 m ²	52.4 94.9	- -	Zhao et al., 2014 [107]
Heterogeneous catalysis	4-nitrophenol 25 mg L ⁻¹	[MnO ₂] _m =1.1 g L ⁻¹ O ₃ 2 mg min ⁻¹ T=25°C pH=7 Results after 45 min	No catalyst α-MnO ₂ /O ₃ β-MnO ₂ /O ₃ γ-MnO ₂ /O ₃ δ-MnO ₂ /O ₃ ε-MnO ₂ /O ₃ λ-MnO ₂ /O ₃	60 99.3 86.4 93.3 96.6 89.8 90.0	35 82.4 50.1 64.2 73.5 60.1 61.8	Nawaz et al., 2017 [125]
Heterogeneous catalysis	Pharmaceutic compounds (phenazone) 40 mg L ⁻¹	O ₃ 30 L h ⁻¹ [MnO ₂] _m =1.5 g L ⁻¹ T=20°C pH=7 Results after 60 min	No catalyst non- porous α- Al ₂ O ₃ (NP) commercial mesoporous γ- Al ₂ O ₃ (CM) synthetized mesoporous γ- Al ₂ O ₃ (SM) MnO _x on NP MnO _x on CM MnO _x on SM	- - - - - -	30 40 60 70 54 65 84	Yang et al., 2009 [126]
Heterogeneous catalysis	Benzotriazole 10 mg L ⁻¹ ≈ TOC= 6 mg L ⁻¹	O ₃ 2.6 g h ⁻¹ Catalysts 1 g L ⁻¹ T=25°C pH=2 ^a ; 5.6 ^b ; 7.4 ^c ; 10 ^d	No catalyst Mn(II) (10% wt.) on γ-Al ₂ O ₃ particles (D= 0.2-0.4 mm) A= 171 m ² Adsorption (without O ₃)	60 ^a (5 min) 100 ^a (5 min)	75 ^a (10 min) 78 ^b (30 min) 42 ^c (30 min) 62 ^d (30 min) < 12 (90 min)	Roshani et al., 2014 [127]
Heterogeneous catalysis	Potassium hydrogen phthalate ^a (2.6.10 ⁻³ mol L ⁻¹) Phenol ^b (2.7.10 ⁻³ mol L ⁻¹)	[Cat] _m =2 ^a g L ⁻¹ pH=4.2 ^a I ^a =10.6 mg(O ₃) mg(C) ⁻¹ [Al ₂ O ₃] _m =1 ^b g L ⁻¹ pH=5.3 ^b I ^b =16.6 mg(O ₃) mg(C) ⁻¹ [O ₃] _m =100 mg L ⁻¹	Al ₂ O ₃ Mn(II) on Al ₂ O ₃ (metal loading 5wt.% ^a) (metal loading 10 wt.% ^b)		60 ^a /51 ^b 51 ^a /67 ^b	Heng, 2006 [113]
Heterogeneous catalysis	Clofibrac acid 50 mg L ⁻¹	O ₃ 0.1 g h ⁻¹ [Cat] _m =200 mg L ⁻¹ T=25°C pH=3.85 Results after 1h	No catalyst MnO _x on mesoporous silica SBA-15 Adsorption (without O ₃)	95 95 6	19.5 43.8 -	Sun et al., 2015 [128]

3.2.2.5. Fe₂O₃-Fe₃O₄

There are very few studies about the use of iron oxides for catalytic ozonation but this number increases when considering iron oxides mixed with other active oxides or with supporting phases. Lv et al. [108] studied the adsorption of 2,4-dichlorophenol (2,4-D) on iron oxides catalyst (Fe_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$ and $\text{Fe}_{2.7}\text{Co}_{0.3}\text{O}_4$) which it is low. Fe_3O_4 seems to be a better catalyst than $\alpha\text{-Fe}_2\text{O}_3$ for ozonation of 2,4-D as shown in Table 6. However, Fe_3O_4 coupled with Co is the best catalyst for the degradation of 2,4-D. Zhu et al. [67] investigated the removal of atrazine by Fe_3O_4 . As mesoporous oxide, Fe_3O_4 enables degradation 82% of atrazine with a low adsorption, around 5% while nano- Fe_3O_4 enables degradation of about 25% of atrazine in the same conditions. Thus, the morphology of the catalyst has a real influence on the removal efficiency during the catalytic ozonation.

Concerning mixed oxides or supported iron oxides, iron is often associated with cobalt [108], [129] which induces an improvement of the organic molecule degradation. For example, Tong et al. [129] observed an increase in the removal of 2,4-DP using supported Fe_3O_4 (30.89%) and above all with the mix $\text{Fe}_3\text{O}_4\text{-CoO}$ (34.66%). Shahamat et al. [109] published an interesting study concerning the removal of phenol with iron oxide supported by activated carbon (AC) with a COD removal close to 50% in 240 min. In several studies [119], [129], iron oxides are mixed with alumina with an improvement of the catalytic ozonation compared to alumina alone. With addition of Fe_2O_3 in presence of alumina, the removal of chloroethanol is 45% instead of 17% without iron oxide [119]. Iron oxide can be also mixed with titanium dioxide [130], with an improvement of the catalytic ozonation compared to titanium dioxide alone.

These elements enable to conclude that iron oxides can be good catalysts for the removal of micropollutants by catalytic ozonation. Moreover, iron oxide can be advantageously mixed with other metal oxides like alumina or titania or with activated carbon.

Table 6

Removal efficiency of $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$ catalyst (A: developed area of catalyst in the reactor; D: equivalent diameter of the elemental particles or powder particles of catalyst).

Catalysis	Pollutant	Conditions	Catalyst characteristics	Pollutant degradation (%)	TOC or COD removal (%)	Reference
Heterogenous catalysis	2,4-dichlorophenol (2,4-D) 20 mg L ⁻¹	O ₃ : 30 mg L ⁻¹ [Cat] _m = 1g L ⁻¹ T=20°C, pH=6 (20 min)	Fe ₃ O ₄	-	60 / TOC	Lv et al., 2012 [108]
			$\alpha\text{-Fe}_2\text{O}_3$	-	33 / TOC	
			Fe _{2.7} Co _{0.3} O ₄	-	93 / TOC	
Heterogenous catalysis	Atrazine 5.0 $\mu\text{mol L}^{-1}$	[O ₃]=0.1 mmol L ⁻¹ [Cat] _m =0.2 g L ⁻¹ T=25°C pH=5.5 (10 min)	No catalyst	9.1	24/TOC (10 min)	Zhu et al., 2017 [67]
			Nanoparticles (NPs) Fe ₃ O ₄	25	-	
			Ordered mesoporous Fe ₃ O ₄	82	-	
			Adsorption (without O ₃)	5.1	-	
Heterogenous catalysis	Phenol 500 mg L ⁻¹	[O ₃]=33 mg min ⁻¹ [Fe ₃ O ₄]=2 g L ⁻¹ pH=8 (240 min)	NPs Fe ₃ O ₄ on Activated Carbon (AC) A=407 m ² D = 25-30 nm		50/ COD	Shahamat et al., 2014 [109]

Heterogeneous catalysis	2-(2-4-dichlorophenoxy) propionic acid (2,4-DP) 100 mg L ⁻¹	O ₃ 98.5 mg min ⁻¹ [Cat] _m = 20 g L ⁻¹ pH=3.3 30min	Al ₂ O ₃	-	17.55 / COD	Tong et al., 2011 [129]
			Fe ₃ O ₄ on Al ₂ O ₃	-	30.89 / COD	
			CoO on Al ₂ O ₃	-	22.78 / COD	
			Fe ₃ O ₄ -CoO on Al ₂ O ₃	-	34.66 / COD	
Heterogeneous catalysis	Oxalic acid ^a Chloroethanol ^b Chlorophenol ^c	Flux O ₃ : 24 mg(O ₃) L ⁻¹ h ⁻¹	Al ₂ O ₃	85 ^a /17 ^b /84 ^c	-	Cooper & Burch, 1999 [119]
			Fe ₂ O ₃ on Al ₂ O ₃	88 ^a /45 ^b /100 ^c	-	
Heterogeneous catalysis	Humic acid 10 mg L ⁻¹	[XTiO ₂] _m =0.1 g L ⁻¹ pH=7	TiO ₂ 80% anatase /20% rutile	28.4	-	Yuan et al., 2013 [130]
			Al-Fe (0.25/0.75) 1% co-doped TiO ₂ anatase + UV	79.4	63.2 / TOC	
			Fe 1% doped TiO ₂ + UV	77.7	-	

3.2.2.6. Co₃O₄

Most of the studies presented in Table 7 concerning the catalytic activity of cobalt oxide with ozone are related to supported cobalt oxide and/or mixed with another metal oxide. Dong et al. [111] studied the removal of phenol without or with Co₃O₄ in presence of ozone. Without catalyst the COD removal is around 36% whereas with catalyst it is 53%. Other studies, except for Beltrán [101] (Table 7), do not show a real increase in the micropollutant removal using catalysts based on cobalt oxides. Cobalt oxides are mostly supported on alumina during catalytic ozonation tests with an increase in the molecule removal compared to alumina alone [113], [123], [129], [131]. The work of Beltrán et al. [101] claimed a total mineralization of oxalic acid with Co₂O₃/Al₂O₃ as catalyst.

Table 7

Removal efficiency of Co₃O₄ catalyst (D: equivalent diameter of the elemental particles or powder particles of catalyst).

Catalysis	Pollutants	Conditions	Catalyst characteristics	Degradation of compound (%)	TOC or COD removal (%)	Reference
Heterogeneous catalysis	Phenol 100 mg L ⁻¹	[Cat] _m = 0.83g L ⁻¹ T=20°C (1h)	No catalyst	-	36 / COD	Dong et al., 2007 [111]
			Co ₃ O ₄ D = 3.5 à 20 nm	-	53 /COD	

Heterogeneous catalysis	Oxalic acid 0.008-0.016 mol L ⁻¹	O ₃ : 15-45 mg L ⁻¹ [Cat] _m = 1.25-3.75 mg L ⁻¹ T=10-40°C pH=2.5 (90 min)	No catalyst	2	Total mineralisation of oxalic acid	Beltrán et al., 2003 [101]
			Co ₃ O ₄ on Al ₂ O ₃ (10%wt.) Leaching: 1mg(Co)L ⁻¹	97		
			Adsorption (without O ₃)	10		
Heterogeneous catalysis	Phenol 100 mL 0.0055 mol L ⁻¹	O ₃ 0.6 g h ⁻¹ (4h)	Co(II) on Al ₂ O ₃ (metal loading 1%wt.)	-	55 / TOC	Gruttadauria et al., 2007 [131]
Heterogeneous catalysis	2-(2-4-dichlorophenoxy) propionic acid (2,4-DP) 100 mg L ⁻¹	O ₃ : 98.5 mg min ⁻¹ [Cat] _m = 20g L ⁻¹ pH=3.3 (30min)	Al ₂ O ₃	-	17.55 / COD	Tong et al., 2011 [129]
			CoO on Al ₂ O ₃	-	22.78 / COD	
			Fe ₃ O ₄ -CoO on Al ₂ O ₃	-	34.66 / COD	
Heterogeneous catalysis	Potassium Hydrogen phthalate ^a (2.6.10 ⁻³ mol L ⁻¹) Phenol ^b (2.7.10 ⁻³ mol L ⁻¹)	[Cat] _m =2 ^a g L ⁻¹ pH=4.2 ^a I ^a =10.6 mg(O ₃) mg(C) ⁻¹ [Al ₂ O ₃] _m =1 ^b g L ⁻¹ pH=5.3 ^b I ^b =16.6 mg(O ₃) mg(C) ⁻¹ [O ₃] _m =100 mg L ⁻¹	Al ₂ O ₃	-	60 ^a /51 ^b / TOC	Heng, 2006 [113]
			Co(II) on Al ₂ O ₃ (metal loading 5 wt.% ^a) (metal loading 9 wt.% ^b)	-	59 ^a /52 ^b / TOC	

Hence, catalysts based on cobalt oxides do not seem to have an important catalytic activity with ozone for the degradation of organic molecules in comparison with other metal oxides such as iron oxide or manganese oxide.

To sum up about the catalytic activity of metal oxides used for heterogeneous catalytic ozonation, it can be noted that magnesium oxide exhibits good results concerning the removal of organic molecules such as phenol, acetaminophen and azo dye RR198. The literature is rich about the use of alumina as catalyst for ozonation and mostly under the γ -Al₂O₃ phase (70% TOC removal with succinic acid). When alumina is coupled with MnO_x (80% TOC removal with phenazone) or Mn (75% TOC removal with benzotriazole), the ozonation performance is generally improved according to the operating conditions and the structure of the catalyst. Titanium dioxide is often found under the anatase crystalline form, sometimes as rutile form, although an article indicated that the rutile form has better performance in catalysis (50% TOC removal with nitrobenzene [122]). Some papers deal with coupling between Al, Fe or Al-Fe leading to better conversion rates (60-70% TOC removal). MnO₂ catalysts are good candidates for ozonation because the percentage of TOC removal is important (80-90% for 4-nitrophenol). Iron oxides seem to be also interesting with for example, 60% of the TOC removal for Fe₃O₄ with 2,4-dichlorophenol. Cobalt oxides, Co₃O₄, give contrasted results about the degradation of micropollutants. Performances of cobalt oxide are rather low but the study of Beltrán et al. [101] highlighted the complete mineralisation of oxalic acid. All these different catalysts are thus interesting for catalytic ozonation but according to the literature, manganese and iron oxides seem to be the most promising ones.

3.2.3. Catalyst stability towards lixiviation and catalyst inhibition by adsorption

Catalysts have to be stable and active during ozonation. As a consequence, leaching and adsorption inhibiting the catalytic sites have to be prevented. The leaching consists in the solubilisation of the solid catalyst resulting in the release of metal cations into the solution.

Álvarez et al. [132] worked on ozonation of pyruvic acid using γ -Al₂O₃ and Co/Al₂O₃. The alumina-based substrate was impregnated with trihydrate cobalt acetate and, after calcination, CoO, Co₃O₄ and/or CoAl₂O₄ were formed. The leaching of Co was studied during catalytic ozonation operations. The percentage of Co leaching was close to 0.10%, after 2 h of reaction. Thereby, for long term processes, Co leaching was not negligible. Ma and Graham [114] studied the adsorption of atrazine on the MnO₂ catalyst. Organic molecules are poorly adsorbed on manganese dioxide catalyst according to literature [133], [134]. Without ozone, MnO₂ adsorbed poorly the atrazine (< 10%). Moreover, according to the authors the addition of humic substances did not have an impact on the adsorption of atrazine. Qi et al. [135] worked on the catalytic ozonation of phenacetin (PNT) with MnFe₂O₄ and NiFe₂O₄ as catalysts. To evaluate the possible adsorption of PNT, the authors replaced ozone with oxygen and no removal of PNT was observed. With ozone and no catalyst, the phenacetin mineralization was around 29.6% while with a catalyst, it was 60%. These results indicate that adsorption is minor and the addition of a catalyst enhances the ozonation efficiency. Moreover, the measured leaching was non-congruent: 0.034 % for Fe and 0.0018 % for Ni and Mn over 3 hours.

Based on the available data, it seems that the risk of inhibition of the catalytic activity by adsorption phenomena is limited. Regarding the catalyst lixiviation and considering technological requirements, significant risks can be noted about a long-term solubilisation of the catalyst as well as a progressive change of chemical composition in the case of mixed oxides due to incongruent lixiviation.

4. Coupling between catalytic ozonation and membrane separation

An increasing number of studies are emerging combining filtration and (catalytic) ozonation [37]–[39], [136]. The implemented membranes are organic or ceramic membranes and the targeted objectives are the degradation of pollutants and the mitigation of organic fouling [137].

4.1. Process configurations

In literature, various processes were investigated for the ozonation membrane filtration (OMF) and the catalytic ozonation membrane filtration (COMF) [83], [138]. Three types of processes can be defined. They are schematically represented in Fig. 4.

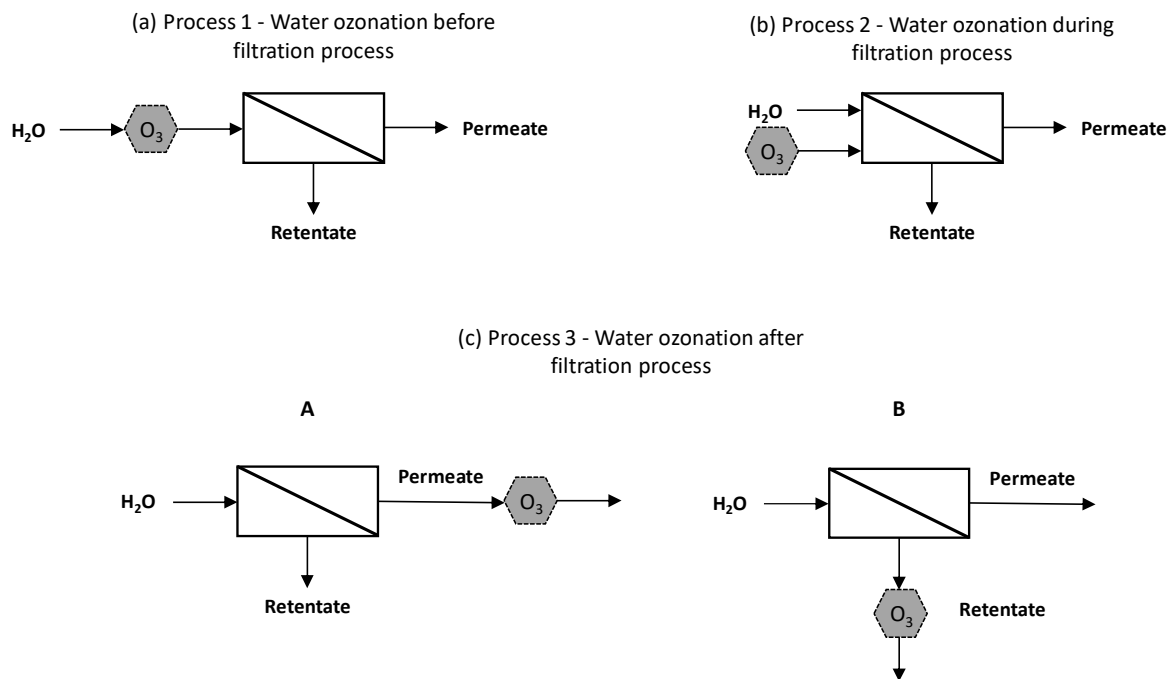


Fig. 4. Three distinct processes coupling ozonation and membrane filtration.

In Fig. 4.a water ozonation occurs before the membrane filtration. In Fig. 4.b, ozonation and membrane filtration are simultaneous. Fig. 4.c corresponds to a unit operation of membrane filtration of water followed by the ozonation of the permeate (Fig. 4.c-A) or the retentate (Fig. 4.c-B).

To improve ozonation, a catalyst can be used dispersed in the liquid phase, which poses the problem of its recovery (Fig. 5.a), or supported on the membrane (Fig. 5.b). For this second figure, the catalyst is deposited on the separative layer of the membrane, i.e. the feed side, which is the most common case even if the deposition of catalyst on the permeate side could be also considered.

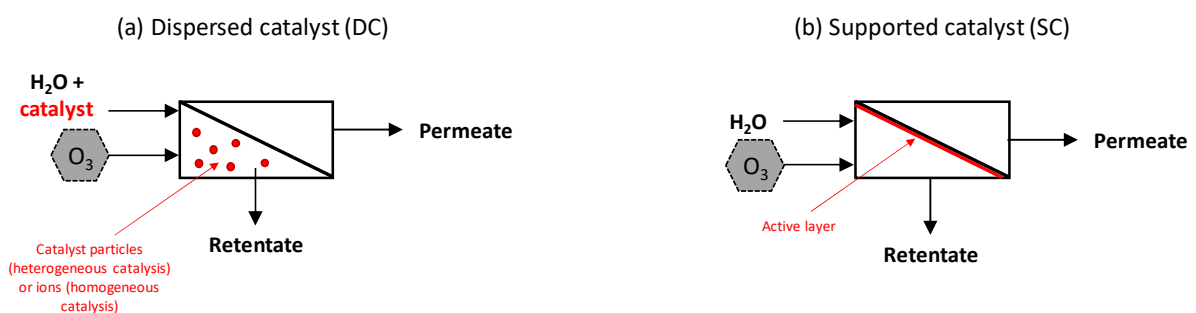


Fig. 5. Homogeneous and heterogeneous catalytic ozonation coupled with membrane filtration.

Several types of processes have been described in literature about organic membranes, which are reported in Tables 8, 9 and 10. Without catalyst, ozonation of water before and after the membrane filtration is often described (Process 1 and 3 on Fig. 4.). By contrast, the use of a catalyst leads to the application of the process 2 in Fig. 4 where ozonation is applied during the membrane process. This choice is motivated by the necessity to put together water, membrane, ozone and catalyst especially if the catalyst is coated on membrane. Ozonation after the filtration process can be used to protect the membrane from oxidation by ozone. Few publications have been found concerning the addition of a catalyst within the organic membrane in order to improve the ozonation process. Z. He et al. [83] and W. Yu [82] used MnO_2 hollow microspheres as catalyst on a PVDF flat

sheet membrane. Another study concerning the use of a homogeneous catalyst with Cu(II) ions [73] can also be referenced. Examples with catalyst fixed on organic membranes for ozonation process are scarce maybe since it is difficult to depose a catalyst on organic membrane because of unfavourable interactions.

Several processes were investigated in literature which involved ceramic membranes. The ozonation can be performed before membrane filtration (Process 1 on Fig. 4.) or it can be done and enhanced by membrane filtration (Process 2 on Fig. 4.). Table 11 summarizes different studies where the main process used is the process 2 (Fig. 4.) and where water and ozone are directly injected in the membrane area. The process 1 (Fig. 4.) for water ozonation is also found in literature but in a less extent way. As explained previously, a catalyst can be deposited at the surface of the ceramic membrane. These catalysts can be alumina, titanium dioxide, iron oxide, manganese oxide, zirconium oxide and mixed oxides. In Table 11, most of the references deal with a layer of catalyst deposited on the membrane surface.

Whatever the type of membrane, ozonation with or without catalysts coupled with membrane filtration has been tested. In contrary to organic membranes sensitive to oxidative conditions, ceramic membranes can be used directly as a catalytic contactor. Moreover, metal oxide coatings are easier to deposit when the support is already a metal oxide-based porous ceramic membrane.

4.2. *Organic membranes*

The organic membranes for coupling with ozonation are usually made from polypropylene (PP) polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE) but polyamide has also been recently used. There are a large number of references with polyimide membranes used for ozonation but without catalyst. It is important that the membrane materials are resistant to ozone which is a strong oxidant. Mori et al. [64] reported that the ozone resistance of the material is the following one: PTFE > PVDF > PE (polyethylene). Bamperng [139] compared PVDF and PTFE hollow fiber membranes. It appears that PVDF membranes provide higher initial ozone flux than PTFE but that PTFE is more stable and gives higher flux than PVDF for long-term operations. PTFE membranes are more hydrophobic than PVDF membranes and more resistant to ozone attack. Most of published papers in the coupling of catalytic ozonation and filtration deal with PVDF because these membranes are the most common ones and a layer of catalyst can be deposited on the surface.

4.2.1. *Removal of micropollutants using ozonation and organic membranes*

In this section, the performances of organic membranes for pollutants removal are investigated without catalyst (Table 8) and with catalyst (Table 9).

Without catalyst, different types of membranes are considered in Table 8: ultrafiltration (UF) membranes (tubular ones: BTU-P1S/02AE, flat sheet modules: PES-10, a polyethersulfone membrane, spiral membranes: GR40PP, GR51PP, GR61PP, GR81PP) and nanofiltration (NF) membranes (polyamide membrane: NF 90, ESNA1-LF-4040; polysulfone-polyamide-polypyperazinamide membrane and polyamine-polyester membrane). Different molecules were investigated: atrazine (ATR) [72], antibiotics and pollutants [36], [140]–[144](norfloxacin (NOR), ofloxacin (OFL), roxithromycin (ROX) and azithromycin (AZI), 1-H-benzotriazole (BZ), nortriptyline HCl (NH), N,N-diethyl-m-toluamide (DEET), chlorophene (CP), 3-methylindole (ML), acetaminophen (ACT), metoprolol (MET), caffeine (CAF), antipyrine (ANT), sulfamethoxazole (SUL), flumequine (FLUM), ketorolac (KET), hydroxybiphenyl (HYD), diclofenac (DCF), carbamazepine (CBZ), atenolol (ATL), diatrizoic acid (DTZ), amoxicillin (AMOX), hydrochlorothiazide (HCT), naproxen (NAP), phenacetin (PHE), indomethacin (IND), prophylphenazone (PRO), paroxetine (PAR), sulfamethazine (SULF), codeine (COD), trimethoprim (TRIM)) and wastewater[35], [70], [145]–[147]. As previously

mentioned, the analytical techniques for measuring pollutant removal are usually based on liquid chromatography coupled with mass spectrometry or with ultraviolet detection.

The processes commonly used with these organic membranes are Process 1 with feed ozonation, Process 3-A with ozonation of the permeate and Process 3-B with ozonation of the retentate (Fig. 4.). Without catalyst, no publication involving Process 2 and organic membranes has been found.

Feed ozonation (Process 1) does not always give rise to an improvement of the compound removal. For example, Vatankhah et al. [70] indicated that the % DOC removal did not increase with the preozonation but that the total fluorescence decreased. Flyborg et al. [145] indicated a decrease of the TOC removal of 14% during feed ozonation and a total TOC removal after nanofiltration around 56%. In comparison, with the same membrane, Flyborg [145] studied ozonation of the permeate after filtration. It appears that, with filtration only, the TOC removal is closed to 64 % and that, after permeate ozonation, the TOC removal reaches 69%. Process 3-A seems to be more efficient than Process 1 in terms of carbon removal. P. Luis and P. Liu [72], [140], studied the performance of Process 3-A, with ozonation of the permeate. The main influence of UF, NF and RO filtrations is on the permeate composition, mainly i) on the molecular weight (MW) of the NOM and ii) on the level of bicarbonate/carbonate content. Luis et al [72] made the assumption that the higher MW compounds act mainly as radical scavengers, while the lower MW compounds may act as radical promoters. The filtration with UF membrane (PES-10 membrane [72]) before ozonation, for a pH=3 of the solution, leads to higher kinetic constant for the degradation of atrazine than the NF and RO filtrations whereas the DOC was higher in the permeate from UF. Indeed, the DOC that goes through the membrane has a lower MW and promotes the O₃ decomposition into hydroxyl radicals. For pH=7, the beneficial effect of ultrafiltration is diminished because, probably, the content of bicarbonate is higher and thus presents a scavenger effect. In the previous pH conditions, reverse osmosis (BTU-P1S/ O2AE) before O₃ gives a higher apparent kinetic constant probably because of simultaneous removal of NOM and bicarbonate ions. Liu [140] evidenced important adsorption of antibiotics on the membrane. The removal of the antibiotics was high with 99% of removal in 10 min for OFL, AZI and ROX and in 20 min for NOR. The coupled process 3-A is able to lead to low concentrated permeate for which ozonation of the organic compounds is easier.

Acero et al. [141] tested the Process 1 and Process 3-B with effluent containing several molecules (BZ, NH, DEET, CP and ML) with a NF polyamide membrane. During ozonation of the feed, the concentrations of pollutants decreased from 30% (DEET) to 88% (NH) according to the pollutants. After filtration, the removal of NH and DEET was total and the removal of BZ was closed to 75 %. The Process 3-B with the ozonation of the retentate after the filtration allows assessing the ozonation efficiency of concentrate effluent. Retentate ozonation led to a decrease of 21 % of the DOC removal with complete removal for CP and ML and an important removal of BZ, NH and DEET. As a conclusion, the authors said that both sequences, Process 1 and 3, provide high levels of elimination for pollutants and as well as for DOC. In Process 3, nanofiltration provides permeate with low amounts of pollutants and ozonation of the retentate demonstrates a good reduction of contaminants. In Process 1, pre-ozonation exerts a positive influence in the NF filtration process. The generated permeate has a good quality and the retentate presents a better quality and a higher biodegradability than without ozonation. Another publication from Acero et al. (2016) [142], described the removal of some micropollutants (ACT, MET, CAF, ANT, SUL, FLUM, KET, ATR, ISOP, HYD and DIC) in municipal wastewater by coupling nanofiltration and retentate ozonation (Process 3-B). It appears that ozone leads to better micropollutant removal efficiency than other oxidants. With a specific ozone dose of 0.5 mg O₃ mg C⁻¹, the removal of fast ozone-reacting compounds is important but the level of mineralisation is not significant.

F. J. Real et al. [144] studied also the removal of some micropollutants (AMOX, HCT, MET, NAP and PHE) with UF and NF organic membrane thanks to Processes 1 and 3. First of all, with Process 3, nanofiltration gives a better rejection than UF. When nanofiltration is coupled with ozonation of the permeate or the retentate, the removal efficiency increases. With permeate ozonation (Process 3-A), AMOX is totally removed, MET and NAP are removed at 95% and HCT and PHE at 55%. In the retentate, the removal levels are less important with 93% of AMOX removal, 91% of NAP removal, 49% of PHE removal, 33% of HCT removal and 19% of MET removal. With feed ozonation (Process 1), the pollutant rejections are better than without (Process 3). This phenomenon was already observed in the paper of Acero et al. [141]. With coupling feed ozonation and nanofiltration (Process 1), the removal of micropollutants increases with 100% of AMOX removal, 98.3% of NAP removal, 75.5% of MET removal, 60.6% of PHE removal and 58.4% of HCT removal. Process 1 seems to provide the best removal for pharmaceutical compounds.

In literature, Process 3-B (retentate ozonation) has been more studied than Process 3-A (permeate ozonation), probably because high micropollutant concentrations in retentate are more problematic. A. Azaïs et al. [143] studied the removal of some micropollutants in the retentate (ACT, CBZ, ATL and DTZ) with the NF90 membrane. That nanofiltration membrane provided high percentage of rejection, between 88 and 90 % according to various volumetric reduction factors (VRF). The retentates are thus highly concentrated. Coupling with ozonation allows to remove 90% of ACT, 80% CBZ, 62% ATL and 48% DTZ. Ozone only is not able to completely remove pollutants but the biodegradability of retentates is improved. D.C. Santos also observed a favourable increase of the biodegradability with ozonation of the retentates for a series of four UF membranes having decreasing MWCO. The COD removal decreases when the MWCO decreases.

A. Justo et al. [36] studied the elimination of pharmaceutical compounds in retentates from UF and RO brines in the case of tertiary treatment (Process 3-B). With an O_3 dose of $1.38 \text{ mg}(O_3) \text{ mg}(C)^{-1}$, the removal of IND, NAP, PRO, PAR, SULF, SUL, COD, TRIM and CBZ was complete. DCF was removed at 96% and ATEN at 78%. The removal of the TOC was weak, 0.6%, but the COD decrease was equal to 11%. Therefore, combining filtration and ozonation enables to eliminate pharmaceutical compounds and to increase the biodegradability of the retentates.

G. R. Pophali et al. [147] studied the elimination of refractory organics from tannery industrial retentates (Process 3-B) thanks to ozonation. With that process, the COD removal reached 78% before 70 min and with an ozone dose equal to $[O_3]_{liq}=0.232 \text{ mg L}^{-1}$.

It is more common in literature to find processes with filtration followed by retentate ozonation (Process 3-B). That coupling is able to provide retentates with lower concentrations and higher biodegradability. However, the increase of dissolved carbon and bicarbonate concentration in retentates for higher VRF values can induce a very important inhibition effect. That leads to huge amounts of O_3 to be transferred in the liquid phase in order to reach high yield of removal of the micropollutants. The permeate ozonation (Process 3-A) is also possible to improve the final quality of the treated water. Some examples with pre-ozonation (Process 1) exist, with an improvement of the permeate quality. To conclude, the use of processes coupling filtration by organic membranes and ozonation, has a positive impact on the removal of pollutants.

Table 8

Coupling of ozonation (without catalyst) with organic membranes - Impact of ozonation on the removal of organic molecules (A: area of membrane in the filtration module; TMP: transmembrane pressure; MWCO: molecular weight cut-off).

Proc	Membrane	Catalyst	Conditions	Removal of organics	Reference
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				Membrane	Ozonation	Both	
Process 3-A	Tubular membrane BTU-P1S/02AE (Berghof) MWCO: 5 kDa A=0.0042 m ² TMP=0.4 MPa	No	Atrazine (2 mg L ⁻¹) Natural Organic Matter (NOM) TOC=6.7 mg L ⁻¹ [O ₃] _{in} =20-116 μM Flow: 60L h ⁻¹	18% atrazine removal 34% TOC removal	k _{app} =50.7 ± 4.0 M ⁻¹ s ⁻¹ (pH=7)	k _{app} =64.8 ± 10.3 M ⁻¹ s ⁻¹ (pH=7)	P. Luis et al. 2011 [72]
Process 3-A	Flat Sheet module PES 10 (Nadir) MWCO: 1 kDa A=0.0059 m ² TMP=2 MPa	No	Atrazine (2mg L ⁻¹) Natural Organic Matter (NOM) TOC=6.7 mg L ⁻¹ [O ₃] _{in} =20-116 μM Flow: 60L h ⁻¹	20% atrazine removal 77% TOC removal	k _{app} =50.7 ± 4.0 M ⁻¹ s ⁻¹ (pH=7)	k _{app} =43.2 ± 6.1 M ⁻¹ s ⁻¹ (pH=7) Carbonate /bicarbonate effect	P. Luis et al. 2011 [72]
Process 3-A	Polyamine-polyester membrane MWCO: 150-300 Da A= 75 cm ²	No	Antibiotics (200 μg L ⁻¹) Norfloxacin (NOR) Ofloxacin (OFL) Roxithromycin (ROX) Azithromycin (AZI) v=0.35m s ⁻¹ Flow: 1 L min ⁻¹ 4 mg O ₃ L ⁻¹	No antibiotics in permeate. High adsorption on membrane.	-	99% removal of OFL, AZI and ROX in 10 min 99% removal of NOR in 20 min	P. Liu et al. 2014 [140]
Process 1	NF 90 Polyamide MWCO: 200-300 Da A=0.0139 m ²	No	Influent water DOC=5.7 mg L ⁻¹ COD=17.16 mg L ⁻¹ v=0.4 m s ⁻¹ Flow: 2 L min ⁻¹ J ₀ =30 L m ⁻² h ⁻¹ 0.2 mg(O ₃) mg(DOC) ⁻¹	94% DOC rejection	-	94% DOC (Dissolved Organic Carbon) rejection Pre-ozonation lead to a reduction of the total fluorescence	H. Vatankhah et al. 2018 [70]
Process 3-A	ESNA1-LF-4040, a spiral wound thin film with aromatic composite polyamide A=7.9 m ² MWCO= 150 Da	No	Henriksdal WWTP influent TOC=8.3 mg L ⁻¹	Permeate TOC: 3.0 mg L ⁻¹ 64% TOC	-	Permeate Ozonation TOC: 2.6 mg L ⁻¹ 69 % TOC	L. Flyborg et al. 2010 [145]
Process 1	ESNA1-LF-4040, a spiral wound thin film with aromatic composite polyamide A=7.9 m ² MWCO= 150 Da	No	Henriksdal WWTP influent TOC=9.8 mg L ⁻¹	Permeate TOC: 4.3 mg L ⁻¹ 56% TOC	Feed Ozonation TOC: 8.4 mg L ⁻¹ 14% TOC	-	L. Flyborg et al. 2010 [145]

Process 3-B	NF polyamide membrane MWCO:150 – 300 Da A= 28 cm ² J ₀ =10.2 L h ⁻¹ m ⁻² bar ⁻¹	No	1-H-benzotriazole (BZ: 1 μmol L ⁻¹), Nortriptyline HCl (NH: 1 μmol L ⁻¹) N,N-diethyl-m-toluamide (DEET: 1 μmol L ⁻¹), Chlorophene (CP: 1 μmol L ⁻¹), 3-methylindole (ML: 1 μmol L ⁻¹), DOC: 14 mg L ⁻¹ [O ₃]= 7.5 mg L ⁻¹ Flow: 60 L h ⁻¹ TMP= 20 bar	Retentate DOC: 24 mg L ⁻¹ BZ: 0.91 μmol L ⁻¹ NH: 2.09 μmol L ⁻¹ DEET: 1.6 μmol L ⁻¹ CP: 0.5 μmol L ⁻¹ ML: 0.6 μmol L ⁻¹		Retentate Ozonation DOC: 19 mg L ⁻¹ BZ: 0.18 μmol L ⁻¹ NH: 0.27 μmol L ⁻¹ DEET: 0.36 μmol L ⁻¹ CP: 0 μmol L ⁻¹ ML: 0 μmol L ⁻¹	J. L. Acero et al. 2015 [141]
Process 1	NF polyamide membrane MWCO:150 – 300 Da A= 28 cm ² J ₀ =10.2 L h ⁻¹ m ⁻² bar ⁻¹	No	1-H-benzotriazole (BZ: 1 μmol L ⁻¹), Nortriptyline HCl (NH: 1 μmol L ⁻¹) N,N-diethyl-m-toluamide (DEET: 1 μmol L ⁻¹), DOC: 14 mg L ⁻¹ [O ₃]= 2.25 mg L ⁻¹ Flow: 60 L h ⁻¹ TMP= 20 bar		BZ: 0.4 μmol L ⁻¹ NH: 0.12 μmol L ⁻¹ DEET: 0.7 μmol L ⁻¹	BZ: 0.25 μmol L ⁻¹ NH: 0 μmol L ⁻¹ DEET: 0 μmol L ⁻¹ 90% DOC removal	J. L. Acero et al. 2015 [141]
Process 3-B	Flat Sheet membrane Polysulfone-polyamide-polypiperazine mide MWCO: 150-300 Da TMP=20 bar	No	Acetaminophen (ACT), Metoprolol (MET), Caffeine (CAF), Antipyrine (ANT), Sulfamethoxazole (SUL), Flumequine (FLUM), Ketorolac (KET) Atrazine (ATR) Isoproturon (ISOP) Hydroxybiphenyl (HYD) Diclofenac (DCF) (0.5 mg L ⁻¹) [O ₃] _{in} =5 mg L ⁻¹ Specific O ₃ dose: 0.18 mgO ₃ mgDOC ₁ v= 1 m s ⁻¹	ACT: 0.55 mg L ⁻¹ MET: 0.75 mg L ⁻¹ CAF: 0.65 mg L ⁻¹ ANT: 0.82 mg L ⁻¹ SUL: 0.8 mg L ⁻¹ FLUM: 0.92 mg L ⁻¹ KET: 0.93 mg L ⁻¹ ATR: 0.8 mg L ⁻¹ ISOP: 0.8 mg L ⁻¹ HYD: 0.3 mg L ⁻¹ DCF: 0.8 mg L ⁻¹ In retentate		ACT: 78% MET: 35% CAF: 20% ANT: 48% SUL: 72% FLUM: 20% KET: 68% ATR: 15% ISOP:35% HYD: 80% DCF: 70%	J. L. Acero et al. 2016 [142]

Process 3-B	NF-90 (DOW Filmtec) polyamide membrane MWCO: 100 Da Pore radius: 0.128 nm TMP= 800 kPa $VRF=V_0/(V_0-V_p)$	No	Acetaminophen (ACT) Carbamazepine (CBZ) Atenolol (ATL) Diatrizoic acid (DTZ) (1 g L ⁻¹) WWTP: Wastewater treatment plant $v=0.5 \text{ m s}^{-1}$ Gas flow: 60 L h ⁻¹ [O ₃] _{gas} = 5 g O ₃ m ⁻³	ACT: 87.5% WWTP 90% VRF2 88% VRF5 89% VRF10 %rejection CBZ: 98% WWTP 98.5% VRF2 99% VRF5 97% VRF10 %rejection ATL: 97% WWTP & VRF2 98% VRF5 99% VRF10 %rejection DTZ: 98% WWTP 97.5% VRF2 99% VRF5 98.5% VRF10 %rejection		ACT: 90% WWTP, VRF2 & VRF5 85% VRF10 (10 min) CBZ: 80% WWTP 100% VRF2 58% VRF5 62% VRF10 (10 min) ATL: 62% WWTP 48% VRF2 10% VRF5 22% VRF10 (10 min) DTZ: 48% WWTP 28% VRF2 24% VRF5 15% VRF10 (250 min)	A. Azaïs et al. 2016 [143]
Process 3	UF flat sheet polyethersulfone membrane MWCO: 5000 Da TMP: 5 bar	No	Secondary effluent Amoxicillin (AMOX) Hydrochlorothiazide (HCT) Metoprolol (MET) Naproxen (NAP) Phenacetin (PHE) $v=1 \text{ m s}^{-1}$ O ₃ : 1.5 mg L ⁻¹	Rejection coefficient AMOX: 10.0% HCT: 12.9% MET: 15.2% NAP: 24.9% PHE : 18.9%	AMOX: 38% HCT: 15% MET: 14% NAP: 55% PHE: 11%	Permeate AMOX: 27% HCT: 27% MET: 32% NAP: 58% PHE: 52% Retentate AMOX: 24% HCT: 33% MET: 28% NAP: 40% PHE: 16%	F. J. Real et al. 2012 [144]
Process 3	NF thin film polyamide membrane MWCO: 150-300 Da TMP: 20 bar	No	Secondary effluent Amoxicillin (AMOX) Hydrochlorothiazide (HCT) Metoprolol (MET) Naproxen (NAP) Phenacetin (PHE) $v=1 \text{ m s}^{-1}$ O ₃ : 0.75 mg L ⁻¹ (permeate) O ₃ : 4.5 mg L ⁻¹ (retentate)	Rejection coefficient AMOX: 99.9% HCT: 40.0% MET: 90.2% NAP: 94.5% PHE : 39.9%	AMOX: 38% HCT: 15% MET: 14% NAP: 55% PHE: 11%	Permeate AMOX: 100% HCT: 55% MET: 94% NAP: 95% PHE: 54% Retentate AMOX: 93 % HCT: 33% MET: 19% NAP: 91% PHE: 49%	F. J. Real et al. 2012 [144]

Process 1	NF thin film polyamide membrane MWCO: 150-300 Da TMP: 20 bar	No	Secondary effluent Amoxicillin (AMOX) Hydrochlorothiazide (HCT) Metoprolol (MET) Naproxen (NAP) Phenacetin (PHE) $v=1 \text{ m s}^{-1}$ $\text{O}_3: 2.25 \text{ mg L}^{-1}$	Rejection coefficient AMOX: /% HCT: 48.2% MET: 69.1% NAP: 95.4% PHE : 49.7%	AMOX: 100% HCT: 19.7% MET: 20.6% NAP: 63.5% PHE: 21.7%	AMOX: 100% HCT: 58.4% MET: 75.5% NAP: 98.3% PHE: 60.6%	F. J. Real et al. 2012 [144]
Process 3-B	4 UF spiral membranes (Polypropylene, polysulfone, polyethersulfone) GR40PP, 100 kDa GR51PP, 50 kDa GR61PP, 20 kDa GR81PP, 10 kDa	No	Raw Cork Boiling Wastewater (CBW) $v=0.87 \text{ m s}^{-1}$	GR40PP, COD: 3436 mg L^{-1} GR51PP, COD: 1348 mg L^{-1} GR61PP, COD: 1175 mg L^{-1} GR81PP, COD: 1078 mg L^{-1}		GR40PP, (O_3 appl/COD)=0.38 COD: 69.4% removal GR51PP, (O_3 appl/COD)=0.33 COD: 45.1% removal GR61PP, (O_3 appl/COD)=0.31 COD: 40.9% removal GR81PP, (O_3 appl/COD)=0.41 COD: 40.9% removal	D. C. Santos et al. 2013 [35]
Process 3-B	After ultrafiltration and RO unit RO brines from tertiary treatment	No	Indometacin (IND) Diclofenac (DCF) Naproxen (NAP) Propyphenazone (PRO) Paroxetine (PAR) Sulfamethazine (SULF) Sulfamethoxazol (SUL) Atenolol (ATEN) Codeine (COD) Trimethoprim (TRIM) Carbamazepine (CBZ) O_3 specific dose: 1.38 $\text{mg}(\text{O}_3) \text{ mg}(\text{TOC})^{-1}$		TOC: 27.6 $\text{mg} \text{O}_2 \text{ L}^{-1}$ COD: 77.0 $\text{mg}(\text{O}_2) \text{ L}^{-1}$ BOD ₅ : 2.2 $\text{mg}(\text{O}_2) \text{ L}^{-1}$	IND: 100% DCF: 96% NAP: 100% PRO: 100% PAR: 100% SULF: 100% SUL: 100% ATEN: 78% COD: 100% TRIM: 100% CBZ: 100% TOC: 0.6% COD: 11%	A. Justo et al. 2013 [36]

Process 3-B	FILMTEC NF90-2540 (polyamide thin film composite) a=5.2 m ² TMP: 5 bar	No	Municipal wastewater treatment plant (MWTP) 2.4-2.8 g(O ₃) h ⁻¹ DOC: 53.9 mg L ⁻¹ C ₀ =25.5 ng L ⁻¹ pH 7.9-8.0	C ₀ =76.4 ng L ⁻¹ (retentate)		74 % C ₀ removal (8 min)	S. Miralles-Cuevas et al. 2017 [146]
Process 3-B	No data	No	NF rejects from tannery industry COD: 173 mg L ⁻¹ [O ₃]=50 mg L ⁻¹ [O ₃] _{iq} =0.232 mg L ⁻¹	COD: 178 mg L ⁻¹	1	COD: 38 mg L ⁻¹ 78 % COD reduction (70 min)	G. R. Pophali et al. 2011 [147]

Organic membranes coupled with ozonation give yet contrasted results with, in some cases, limited removal of organic compounds. To improve performances of these membranes, some authors used metal ions (homogeneous catalysis) or metal oxides (heterogeneous catalysis) as catalysts. However, few examples exist concerning the use of organic membranes with a catalyst in order to improve the ozonation efficiency. Table 9 summarizes the publications found in that field. Authors tested mainly PVDF membranes with different catalysts: Cu(II) ions [73], MnO₂ nanoparticles [82] or MnO₂ hollow microspheres [83] and MgO nanoparticles [67] or nanosheets [75].

Y. Zhang et al. [136] studied the impact of the addition of Cu(II) ions as homogeneous catalyst with a PVDF hollow fibre membrane and ozone (Process 2-DC). The authors also tested other metal ions like Pb(II), Cd(II), Ce(II), Zn(II), Ni(II), Fe(III and II), Cr(III) but Cu(II) remained the best. The filtration alone gives rise to a TOC removal of 24.3% and ozone alone to a TOC removal around 50% after 1h. When the PVDF membrane, the Cu(II) ions catalyst and the ozone are implemented together, the TOC removal reaches 98.6%. The effect of the addition of a catalyst cannot be clearly put in evidence. However, the coupled processes have a really positive impact on the TOC removal. The homogeneous catalyst is almost fully recovered by the membrane and the heterogeneous catalyst is supposed to be attached to the surface of the membrane. However, some metal ions pass through the membrane which it is critical if the catalyst is expensive and/or toxic.

The article written by H. Zhu et al. [67], [148] presents the use of dispersed MgO nanoparticles (Process 1-DC, Table 9). Authors observed the increase in the COD removal in presence of ozone compared to filtration alone, 68.1% instead of 52.3% [148]. The COD removal increased even more with additional MgO (92.7% of COD removal).

Concerning the use of a heterogeneous catalyst deposited at the membrane surface (Process 2-SC, Table 9), only MnO₂ coating was reported in literature. W. Yu et al. [82] used MnO₂ nanoparticles, around 25 nm in diameter, on the membrane surface. Ozone alone can remove 15.7% of TOC. With the MnO₂ NPs catalyst, the TOC removal is around 21% indicating that MnO₂ seems to have a measurable catalytic activity. When ozone is applied with the non-functionalized PVDF membrane, the TOC removal is equal to 29.1% so twice higher than ozone alone. Moreover, when the catalyst is added on the membrane surface, the TOC removal reaches 34.8% which is not negligible.

Another study performed by Z. He et al. [83], highlighted an increase of the degradation of the bisphenol A in presence of MnO₂ catalyst, membrane and ozone. With catalyst, the bisphenol A degradation is equal to 81.2% while its degradation is close to 62.0% without catalyst.

Table 9

Coupling of ozonation (using catalyst) with organic membranes - Impact of ozonation on the removal of organic molecules (A: area of membrane in the filtration module; MWCO: molecular weight cut-off

and *: studies where authors compared results from catalytic ozonation and catalytic ozonation with membrane filtration).

Process	Membrane	Catalyst	Conditions	Removal of organics					Reference
				Membrane	Ozonation	Ozonation + Catalyst	Membrane + ozonation	Membrane + ozonation + catalyst	
Process 2-DC Homogeneous catalysis	PVDF hollow fibre membrane A=0.00854 m ² Pore size 168 nm	Homogeneous catalyst ([Cu(II)]=1 mM)	Saline wastewater 1000 mg L ⁻¹ KHP (potassium hydrogen phthalate) v=0.038 m s ⁻¹ O ₃ : 60 mg L ⁻¹ Flow: 30 L h ⁻¹	24.3% TOC (1h) (k=0.00461 min ⁻¹)	50.1% TOC (1h) (k=0.011 61 min ⁻¹)	-	-	98.6% TOC (1h)	Y. Zhang et al. 2016 [136]
Process 1-DC Heterogeneous catalysis	PVDF hollow fiber MBR membrane A=0.2 m ² Pore size: 0.2 μm	Nano MgO ([MgO]=0.2 g L ⁻¹)	Effluent of secondary settling tank COD: 150-180 mg L ⁻¹ pH=7.5-8.5 [O ₃]=4 mg L ⁻¹	52.3% COD removal	-	-	68.1% COD	92.7.1% COD	H. Zhu et al. 2017[148]
* Process 2-SC (+coagulation) Heterogeneous catalysis	PVDF hollow fiber UF membrane MWCO: n.d. A=0.025 m ² Pore size: 0.03 μm	Heterogeneous Catalyst MnO ₂ NPs (ϕ=25 nm)	Tap water + 5 mg L ⁻¹ Suwanee River Humic Acid DOC=3.51 mg L ⁻¹ O ₃ applied dose: 1.0 mg(O ₃) L ⁻¹ Gas flow: 0.5 L min ⁻¹ J ₀ =20 L m ⁻² h ⁻¹	-	15.7% TOC (70 days)	20.8% TOC (70 days)	29.1% TOC (70 days)	34.8 % TOC (70 days)	W. Yu et al. 2016 [82]
Process 2-SC Heterogeneous catalysis	PVDF flat sheet membrane MWCO > 2.5 kDa A=0.1 m ² Pore size: 0.1 μm	Heterogeneous Catalyst 3D MnO ₂ hollow microspheres (0.4 g L ⁻¹)	Bisphenol A ([BPA]=50 mg L ⁻¹) Humic acid ([HA]=10 mg L ⁻¹) pH=7 O ₃ applied dose: 5 mg L ⁻¹	-	-	-	62.0% BPA degradation (2h30)	81.2% BPA degradation (2h30)	Z. He et al. 2018 [83]

All these studies evidenced a positive impact of heterogeneous or homogeneous catalysis associated with membrane and ozone, on the TOC removal and/or on the degradation of organic molecules.

4.2.2. Degraded products and toxicity

During the ozonation process, the degradation of organic molecules leads to the formation of by-products potentially more harmful and carcinogenic. Therefore, it is important to have an evaluation of the properties of the by-products. Among oxidation by-products, bromate (BrO₃⁻) and nitrosamines (e.g. N-nitrosodimethylamine (NDMA) are reported as possible human carcinogens [48], [70]. However, it is often difficult to identify by-products. Researchers most often have not addressed these issues.

Only one publication clearly develops this aspect concerning the degradation of atrazine with the formation of deisopropylatrazine (DIA), deethylatrazine (DEA) and deethyldeisopropylatrazine (DEDIA) [72]. S. Miralles-Cuevas et al. [146] revealed that the removal of microcontaminants by

ozonation is effective but an acute toxicity was reported. However, it was not possible to assess if this toxicity is due to intermediate products of micro contaminants or to other compounds present in water.

In other cases, the water toxicity was clearly mitigated thanks to catalytic ozonation and filtration. P. Liu highlighted a reduction of acute toxicity (58%) and an increase of biodegradability (increase of BOD₅/COD ratio of 4.6 times) for water containing antibiotics using nanofiltration and ozonation [140]. During the filtration and ozonation of four compounds (acetaminophen, carbamazepine, atenolol and diatrizoic acid), A. Azaïs et al. observed an improvement of the biodegradability with an increase of the BOD₅/COD ratio from 0.2 to 0.4-0.8 [143]. Another study indicated a decrease of the toxicity (3 times) and an increase of the biodegradability (about 4 times) of the retentate (fraction 10 kDa) during the filtration and ozonation of raw cork boiling wastewater [35]. A. Justo et al. also obtained effluents with a biodegradability ratio (BOD₅/COD) higher than 0.3 when complete removal was achieved using ozonation and filtration process [36]. The rejected water could then undergo conventional water treatment processes.

The combination of ozonation and membrane separation seems thus to lead to high organic removal and sufficiently high effluent quality for an environmentally friendly disposal.

4.2.3. Limitation of organic membrane fouling using ozonation

Membrane fouling is a major limitation for the use of UF and NF for natural water and waste water treatment because it increases the operating costs. Chemical coagulation can be used as pre-treatment to control membrane fouling but that solution remains unsatisfying. On the contrary, when ozone is applied, the experimental results generally indicate a significant reduction of membrane fouling as it is presented in Table 10.

During ozonation, the permeate flux significantly increases with time in comparison with experiments without ozone. For example, PVDF hollow fiber membranes have a permeate flux J equal to $60 \text{ L m}^{-2} \text{ h}^{-1}$ without O_3 whereas with ozone J it is equal to $150 \text{ L m}^{-2} \text{ h}^{-1}$, which is 2.5 times more [64]. In similar conditions, S.-H.You et al. [149] demonstrated that without ozonation the permeate flux decreases by 60% after 1h while with ozone, it could be maintained at 90% during all the experiment. They put on evidence less carbonate calcium precipitation in the fouling layer. The nanofiltration membrane NF 90 leads to the same trend with a drop of 70% without O_3 while the permeate flux is maintained at 90% with O_3 [70]. Ozone can inhibit fouling thanks to the presence of organic carbon which can change the chemical structure and characteristics of filtration cake [149]. Moreover, ozonation can lead to a decrease of calcium carbonate precipitation [149].

The presence of a catalyst can also participate to reduce the fouling phenomena. The addition of MnO_2 nanoparticles with a PVDF hollow fiber membrane lead to apply a transmembrane pressure close to 1 kPa. On the contrary, without the catalyst, 5 kPa was required in order to maintain an equivalent flux [82]. With MnO_2 porous hollow microspheres, the same trend was observed but with the combined effect of ozone and catalyst the required transmembrane pressure was close to 8 kPa. In absence of catalyst and O_3 , the transmembrane pressure increased up to 11 kPa [83]. The homogeneous catalysis was also studied using Cu(II) but in that case, only the addition of ozone can be discussed because the catalyst is always present (with or without O_3). As stated previously, the presence of ozone limits the fouling phenomenon. Finally, the presence of MnO_2 coated on membrane seems to protect the surface from fouling [82]. The coating induces a decrease of bacteria inducing a reduction of the polysaccharide concentration. Moreover, through the generation of OH^\bullet and the ozone decomposition at the surface of the MnO_2 nanoparticles, the concentration of Extracellular Polymeric Substances decreases in the cake. Thus, some flocs are attached to the membrane surface and fouling is inhibited.

When magnesium oxide catalyst is used in addition of ozone, the transmembrane pressure of organic membrane stays low (15 kPa) for 280 days. Without ozone, it has to be increased above 40 kPa in order to maintain a constant flux [148]. H. Zhu et al. 2017 [148] noted the decrease of membrane fouling when MgO catalyst is added with ozone.

Ozonation and catalytic ozonation coupled with membrane filtration are promising solutions to mitigate the fouling of organic membranes.

Table 10

Fouling of different organic membranes with or without ozonation and with or without catalyst (A: area of membrane in the filtration module; TMP: transmembrane pressure; MWCO: molecular weight cut-off).

Process	Membrane	Catalyst	Effluent	Permeate flux			Reference
				without O ₃	with O ₃	with O ₃ + catalyst	
Process 1	PVDF hollow fiber membrane MWCO: n.d. A=6.9 m ² Pore size 0.1 or 0.4 μm (microfiltration)	No	Surface water (COD= 2 mg L ⁻¹) O ₃ : 3 mg L ⁻¹	J=60 L m ⁻² h ⁻¹ (20h)	J=150 L m ⁻² h ⁻¹	-	Y. Mori et al. 1998 [64]
Process 1	PVDF membranes MWCO: 50 kDa A=0.012 m ² Pore size 0.01 μm	No	Tertiary effluent v=0.3 m s ⁻¹ O ₃ : 8.79 mg min ⁻¹	60 J/J ₀ % (1h)	90 J/J ₀ % (1h)	-	S.-H. You et al. 2007 [65]
Process 1	NF 90 (Dow Filmtec) polyamide, TFC MWCO: 200-300 Da Pre ozonation	No	Influent water COD=17.16 mg L ⁻¹ V=0.4 m s ⁻¹ J ₀ =30 L m ⁻² h ⁻¹ 0.4 mg(O ₃) mg(DOC) ⁻¹	70 J _s /J _{0s} % (24h) (J _s =J/ΔP J _{0s} =J ₀ /ΔP)	90 J _s /J _{0s} % (24h)	-	H. Vatankhah et al. 2018 [70]
Process 2-DC Homogeneous catalysis	PVDF hollow fiber membrane MWCO: n.d. A=0.00854 m ² Pore size 168 nm	Homogeneous catalysts ([Cu(II)]=1 mM)	Saline wastewater 1000 mg L ⁻¹ KHP (potassium hydrogen phthalate) v=0.038 m s ⁻¹ O ₃ : 60 mg L ⁻¹	60 J/J ₀ % (60h) NB: Catalyst presence	-	90 J/J ₀ % (60h)	Y. Zhang et al. 2016 [136]
Process 2-SC (+coagulation) Hetero. catalysis	PVDF hollow fiber UF membrane MWCO: n.d. A=0.025 m ² Pore size: 0.03 μm	MnO ₂ NPs (ϕ=25 nm)	Tap water + 5 mg L ⁻¹ Suwanee River Humic Acid DOC=3.51 mg L ⁻¹ O ₃ applied dose: 1.0 mg(O ₃) L ⁻¹ Gas flow: 0.5 L min ⁻¹	-	For J=20 L m ⁻² h ⁻¹ and before 30 days, TMP=5 kPa	For J=20 L m ⁻² h ⁻¹ and before 30 days, TMP=1 kPa	W. Yu et al. 2016 [82]
Process 2-SC Heterogeneous catalysis	PVDF flat sheet membrane MWCO > 2.5 kDa A=0.1 m ² Pore size: 0.1 μm	3D MnO ₂ porous hollow microspheres (0.4 g L ⁻¹)	Bisphenol A 50 mg L ⁻¹ Humic acid 10 mg L ⁻¹ O ₃ applied dose: 5 mg L ⁻¹	For J=15 L m ⁻² h ⁻¹ and before 240 min, TMP=11 kPa	-	For J=15 L m ⁻² h ⁻¹ , TMP=8 kPa	Z. He et al. 2018 [83]
Process 1-DC Heterogeneous catalysis	PVDF hollow fiber MBR membrane A=0.2 m ² Pore size: 0.2 μm	Nano MgO ([MgO]=0.2 g L ⁻¹)	Effluent of secondary settling tank COD: 150-180 mg L ⁻¹ pH=7.5-8.5 [O ₃]=4 mg L ⁻¹	TMP > 40 kPa in 280 days	-	TMP= 15 kPa in 280 days	H. Zhu et al. 2017[148]

4.2.4. Discussion

Organic membranes have been widely investigated for pollutant removal. Different types of membranes can be found in terms of used materials (polyethersulfone, polyamide, polysulfone-polyamide-polypyperazinamide and polyamide-polyester) and of geometries (hollow fibers, tubular, flat sheet and spiral modules). The pollutants tested are numerous such as natural organic matter, organic dyes, chemical additives, agricultural residues and pharmaceutical residues. The processes with feed ozonation (Process 1), with permeate ozonation (Process 3-A) as well as retentate ozonation (Process 3-B) have been widely investigated.

Process 1 without catalyst, with a pre-ozonation of the feed, allows to slightly improve the compound removal in the permeate. Process 3 without catalyst, more studied in literature, leads to better results than Process 1 especially when it corresponds to retentate ozonation (Process 3-B). Indeed, the high concentration of pollutants in retentate is an issue. Thanks to ozonation, it is possible to lower that concentration. However, it was demonstrated that even if the removal is not complete, the biodegradability of the retentates was improved [143]. The increase of dissolved carbon and bicarbonate concentration in retentates can have an inhibition effect. It leads to produce huge amounts of O_3 transferred in the liquid phase for improving the water quality. Permeate ozonation (Process 3-A) is also possible with an improvement of the water quality.

Organic membranes coupled with ozonation give some interesting results but, in order to improve the pollutant removal, some authors add metal ions or oxides as catalysts (Cu^{2+} [136], MgO nanoparticles [148] and MnO_2 nanoparticles [82], [83]). The membranes used are PVDF hollow fibres or flat sheet membranes. All the studies, with homogeneous and heterogeneous catalysis, evidenced a positive impact on the TOC removal and/or on the degradation of organic molecules.

Membrane fouling represents a major limitation for the use of UF and NF for natural water and waste water treatment. However, the use of ozonation and catalytic ozonation enable to mitigate fouling.

All the considered studies highlight the positive impact of a heterogeneous or homogeneous catalyst associated with membrane and ozone, in the TOC removal or in the degradation of organic molecules and in the toxicity decrease. The combination of ozonation and membrane separation seems to lead to high organic removal and sufficiently high effluent quality for an environmentally friendly disposal of the effluents. Moreover, all the considered studies show a mitigation of fouling when ozone is used. The anti-fouling action is also enhanced when catalytic ozonation is activated. All these data confirm the interest of combining catalytic ozonation and membrane filtration in the case of organic membranes.

4.3. Ceramic membranes

The organic membranes are commonly used because of their low prices but the ceramic membranes increasingly interest researchers and industries. Ceramic membranes present several advantages like an excellent resistance against high pressures, high temperatures, aggressive solvents and extreme pHs. Therefore, they have a longer lifetime and a broader field of applications. However, the development of these membranes is longer because of synthesis and shaping difficulties, and more particularly for obtaining nanopore with a controlled pore size. These membranes are mostly made with metal oxides like TiO_2 , ZrO_2 and Al_2O_3 or more recently with silicon carbide. In this review, only UF and NF ceramic membranes will be considered because they exhibit

interesting properties in terms of rejection and also as contactor for catalytic ozonation. Indeed, ceramic membranes are resistant against oxidation contrary to organic membranes. In order to obtain low molecular weight cut off, researchers usually apply a sol-gel route for preparing the nanoporous separative layers. Stacking of several intermediate layers is required between the macroporous support and this separative top layer. These ceramic membranes are convenient for depositing the catalytic layer based on metal oxides on/in the separative top layer also based on metal oxides.

4.3.1. Removal of micropollutants using ozonation and ceramic membranes

There are few studies dealing with ceramic membranes with a catalytically active coating reported in literature. UF membranes have mainly been tested. In Table 11, studies related to UF and NF ceramic membranes and catalytic ozonation are summarized. That table enables to compare the removal performance in terms of membrane filtration, ozonation alone, ozonation in coupling with membrane filtration, and catalytic ozonation coupled with membrane filtration. The selected membranes have molecular weight cut-off from 200 Da (NF) to 5 kDa (UF) when specified. These membranes are formed with alumina, titanium dioxide, mixed titanium- zirconium oxide and mixed alumina-zirconium oxides. The supports are mainly made of titanium dioxide or of alumina. The organic compounds tested are various (e.g. humic substances, natural organic matter (NOM), aniline, trihalomethane (THM), halo acetic acid (HAA), para-chloronitrobenzene (p-CNB), benzophenone-3 (BP-3), benzotriazole (BZA) and 2-phenylbenzimidazole-5-sulfonic acid (PBSA)). The analytical techniques for measuring pollutant removal are mainly based on liquid chromatography coupled with mass spectrometry or with ultraviolet detection. The studied catalysts are iron oxides, manganese oxides, titanium dioxides and mixed oxides ($\text{Ti-Mn}_2\text{O}_3$, CuMn_2O_4 and $\text{MnO}_2\text{-Co}_3\text{O}_4$).

First of all, it appears that the use of an UF membrane slightly improves the removal of the tested organic molecules compared to ozonation alone. With ozone, the COD removal is about 8.3% whereas with the ceramic membranes, it is around 12.5% [148]. X. Cheng et al. [68] presented another example of the membrane impact on ozonation of an organic compound: with ozone alone the p-CNB removal is 41.4% whereas with the addition of a ceramic membrane the removal increases to 48%. However, it is difficult to determine what the best membrane for ozonation due to experimental conditions not being standard across the published works.

In most cases, the catalyst is coated on membrane surface. Y.-H. Wang et al. [76] proposed the implementation of an UF ceramic membrane with TiO_2 nanopowder dispersed in the feed tank and stopped by the membrane. It appears that the TOC removal is increased in presence of catalyst (50%) instead of 35% without catalyst.

Iron oxide catalysts on ceramic membranes (Fe_2O_3) in presence of ozone enable high COD removal efficiencies- around 93-94% instead of 45% without catalyst- [37] and an enhanced DOC removal around 41-44% instead of 12 and 30% without catalyst [78]. Byun and al. [38] compared the performance of Fe_2O_3 and Mn_2O_3 as catalysts for the removal of trihalomethane and haloacetic acid compounds. According to this study, Fe_2O_3 is not a good catalyst for the removal of these compounds. As a matter of fact the TOC removal is equal to 20% whereas it is around 30% without catalyst. However, manganese oxide seems to be a good catalyst with a TOC removal equal to 39%. The catalytic activity of iron oxide in ozonation membrane process is real but the observed performance strongly depends on the operating conditions.

Concerning manganese oxide, several studies highlighted the efficiency of this catalyst for the removal of TOC or organic compounds. Corneal et al. [39] claimed the increasing of the TOC removal with Mn_2O_3 catalyst with a value equal to 56%. Without any catalyst, the TOC removal falls down to 43%. Another study compared different manganese oxides with various particle diameters (14.2 μm , 7.4 μm and 52 nm) [68]. p-CNB removal is better when the particle size is smaller. For

example, for the smallest particles, the p-CNB removal is 68% whereas without catalyst it is 48%. Manganese oxide shows thus interesting properties for the catalytic ozonation filtration but it is difficult to conclude if it is better than iron oxide. Indeed, the addition of a catalyst enhanced the COD removal with maybe better results with iron oxide than manganese oxide. However, these conclusions must be mitigated because they are based on only few publications and it is not always the same type of organic matter which is considered (COD and TOC removal). Furthermore, according to the TOC removal, Mn_2O_3 seems to be a better catalyst than Fe_2O_3 for eliminating trihalomethane and haloacetic acid [38].

Lee et al. [150] studied two types of catalyst, CeO_x and MnO_x , with a hybrid process coupling ozonation and filtration. CeO_x exhibits superior pollutant mineralization capability compared to that MnO_x catalyst, virgin membrane and non-catalysed ozonation.

J. Chen [75] presented the use of dispersed MgO nanoparticles (Process 1-DC, Table 11) and highlighted the high removal of nitrobenzene with coupling catalytic ozonation and filtration.

Researchers also studied mixed oxides as catalyst like $Ti-Mn_2O_3$, $CuMn_2O_4$ and $MnO_2-Co_3O_4$. J. Zhang and Zhu [73], [80] highlighted the increase in COD removal of aniline and dyestuff wastewaters with $Ti-Mn_2O_3$ compared to the system without catalyst. Dyestuff wastewaters COD removal is equal to 46% with O_3 /catalyst and 34% with O_3 alone. For aniline, the COD removal is 37.5% with O_3 /catalyst whereas it is just 12.5% with only O_3 . However, S. Chen [75] published totally different results, with a total ammonia nitrogen (TAN) removal in aquaculture wastewater. Indeed, with and without $Ti-Mn$ catalyst in presence of O_3 and membrane, the TAN removal is 62%. In that condition the addition of the catalyst does not improve the TAN reduction. However, it is important to note that the addition of ozone during membrane filtration improves the TAN removal. Y. Guo [66] presented a study on the removal of organic compounds (benzophenone-3 (BP-3), benzotriazole (BZA) and 2-phenylbenzimidazole-5-sulfonic acid)) by coupling catalytic ozonation and membrane filtration. The use of ozone with a ceramic membrane increases the removal of the organic compounds. For example, BP-3 removal is around 75% with the combined process whereas with ozonation alone it is 68% and with the membrane it is just 10%. That example shows a notable interest for ozone coupling with membrane for the removal of micropollutants. Then, with the addition of a catalyst based on $CuMn_2O_4$, the BP-3 removal is also increased to 90%. The removal of other organic compounds (BZA and PBSA) and the TOC removal are also improved using ozone and catalyst. However, the TOC removal, with and without membrane, in presence or not of ozone, is quite the same ($\approx 20\%$) which means that the combined process does not have an important impact in that case on TOC removal. Guo [66] did the same study for the removal of benzophenone-3 (BP-3) with another catalyst, $MnO_2-Co_3O_4$. The results are a little bit different from $CuMn_2O_4$ catalyst with less good removal of BP-3. Unfortunately, the reaction times are not the same so it is difficult to compare these results. However, the combined process (membrane and ozone) increases the BP-3 removal in comparison with ozone and filtration alone, 52% instead of 47% (O_3) or 12% (membrane). When the catalyst was added at the combined process, the BP-3 removal is increased to 76%.

In conclusion, hybrid processes associating catalytic ozonation and ceramic membrane filtration improve the removal of organic compounds. Several catalysts can be advantageously used like iron oxides, manganese oxides and mixed oxides. These oxides are highly promising with maybe a preference for manganese and iron oxides.

Table 11

Coupling of ozonation (with catalyst) with ceramic membranes - Impact of ozonation on the removal of organic molecules. A: area of membrane in the filtration module; D: equivalent diameter of the elemental particles or powder particles of catalyst; S: specific surface area; TMP: transmembrane

pressure; MWCO: molecular weight cut-off and *: studies where authors compared results from catalytic ozonation and catalytic ozonation with membrane filtration.

Process	Membrane	Catalyst	Conditions	Removal of organics				Reference
				Membrane	Ozonation	Membrane + ozonation	Membrane + ozonation + catalyst	
Process 2	Tubular ceramic UF membrane (α -Al ₂ O ₃ & TiO ₂) (Attaxx, USA) MWCO : 5 kDa J ₀ = 143 L m ⁻² h ⁻¹ bar ⁻¹	No	Lake Lansing TOC : 11.8 mg L ⁻¹ TMP: 0.68 bar O ₃ dose: 5.5 g m ⁻³ v=0.88 m s ⁻¹			TOC: 10.8 mg L ⁻¹		J. Kim et al. 2008[151]
Process 2-DC Heterogeneous catalysis	UF ceramic membrane MWCO: 5 kDa Substrate: TiO ₂ Membrane: TiO ₂	TiO ₂ (rutile and anatase) (Degussa P-25) D < 100 nm	Humic substances (NOM) 8 mg L ⁻¹ TriHaloMethane (THM) [O ₃] _{gas} =2.5 mg L ⁻¹ Gas flow rate: 50 mL min ⁻¹ [Catalyst]=3 g L ⁻¹	-	-	35% TOC 25% THMs	50% TOC 86% THMs	Y.-H. Wang et al. 2013 [76]
Process 1-DC Heterogeneous catalysis	UF ceramic membrane (Tami Industries) MWCO: 5 kDa A=0.0132 m ²	TiO ₂ (Degussa P-25)	DOC=8 mg L ⁻¹ pH=8 [O ₃] _{gas} =2.5 mg L ⁻¹ Gas flow rate: 50 mL min ⁻¹ [Catalyst]= 3 g L ⁻¹	93% DOC	-	-	97% DOC	C.-J. Chen et al. 2017[77]
Process 2-SC Airlift reactor Hetero. catal.	Ultrafiltration membrane Pore size: 5.5 nm	TiO ₂ membrane	Humic acids (HAs)	61% COD 36.5% TOC (conventional airlift reactor)	-	-	91.0% COD 70.0% TOC	H. Mei et al. 2015 [81]
Process 2-SC Heterogeneous catalysis	MWCO: 15kDa Substrate + Membrane: α -Al ₂ O ₃ -ZrO ₂ -TiO ₂	Fe ₂ O ₃	Trihalomethane 0.08 mg L ⁻¹ Haloacetic Acid 0.06 mg L ⁻¹ TOC 8.6-11.6 mg L ⁻¹ [O ₃] _{gas} =2.5 mg L ⁻¹ Lp ₀ = 60 L m ⁻² h ⁻¹ bar ⁻¹	-	-	45% COD	93% COD	B. Karnik et al. 2005 [37]
Process 2-SC Heterogeneous catalysis	MWCO: 5kDa Substrate + Membrane: α -Al ₂ O ₃ -ZrO ₂ -TiO ₂	Fe ₂ O ₃	Trihalomethane 0.08 mg L ⁻¹ Haloacetic Acid 0.06 mg L ⁻¹ [O ₃] _{gas} =2.5 mg L ⁻¹ TOC 8.6-11.6 mg L ⁻¹ Lp ₀ = 60 L/m ² hbar	-	-	45% COD	94% COD	B. Karnik et al. 2005 [37]

Process 2-SC Heterogeneous catalysis	UF ceramic membrane MWCO:7.5 kDa Substrate/membrane: γ -Al ₂ O ₃ (Inopor)	Iron oxide NPs (IONS) α -Fe ₂ O ₃ (50-100 nm) 0.56 mg(ions) cm ⁻² membrane	Suwanee River natural organic matter (SRNOM): DOC=3.4 mg(C) L ⁻¹ Youngsan River natural organic matter (YRNOM): DOC=2.3 mg(C) L ⁻¹ TMP: 0.8 bar Flow: 0.02 L min ⁻¹ [O ₃] _{gas} =10 mg L ⁻¹ Lp ₀ = 55.3 L m ⁻² h ⁻¹ bar ⁻¹	SRNOM 27% DOC YRNOM 26% DOC	- -	SRNOM 12% DOC YRNOM 30% DOC	SRNOM 41% DOC YRNOM 44% DOC	H. Park et al. 2012 [78]
Process 2-SC Heterogeneous catalysis	MWCO: 5kDa Substrate: TiO ₂ Membrane: TiO ₂ -ZrO ₂	Fe ₂ O ₃ or Mn ₂ O ₃	TOC 10-12 mg(C) L ⁻¹ Trihalomethane & haloacetic acid compounds O ₃ applied dose: 1.67 μ g (O ₃) s ⁻¹ J ₀ =115 +/- L m ⁻² h ⁻¹ between 1.9 and 2.2 bars	-	-	30% TOC	Fe ₂ O ₃ 20% TOC Mn ₂ O ₃ 39% TOC	S. Byun et al. 2011 [38]
Process 2-SC Heterogeneous catalysis	MWCO: 5kDa Substrate: TiO ₂ Membrane: TiO ₂ -ZrO ₂	α -Mn ₂ O ₃ NPs	TOC 10 mg(C) L ⁻¹ [O ₃] _{gas} =9.5 mg L ⁻¹	-	-	43% TOC	56% TOC	L. Corneal et al. 2010[39]
* Process 1-SC Heterogeneous catalysis	MWCO: 50 kDa Substrate: TiO ₂ Membrane: TiO ₂ -ZrO ₂	a) commercial MnO ₂ NPs D=14.16 μ m b) M-MnO ₂ D =7.38 μ m c) S-MnO ₂ D=51.59 nm	Na alginate (1.0 g L ⁻¹) p-chloronitrobenzene (p-CNB: 100 μ g L ⁻¹) [O ₃] _{liq} =0.5 mg L ⁻¹ TMP: 100 kPa Ozone stock solution in contact with the membrane	6% p-CNB without catalyst Up to 15% p-CNB with catalysts	41.4% p-CNB	48% p-CNB	a)52% b)60% c)68% p-CNB	X. Cheng et al. 2017 [68]
* Process 2-SC Heterogeneous catalysis	MWCO: Tubular membrane Substrate: α -Al ₂ O ₃ Membrane: α -Al ₂ O ₃ Pore size: 600 nm	a) MnO _x (Mn ₂ O ₃) 4.2 mg g ⁻¹ Al ₂ O ₃ b) CeO _x (CeO ₂) 10.1 mg g ⁻¹ Al ₂ O ₃	Bisphenol A ([BPA] ₀ = 3 mg L ⁻¹) Benzotriazole ([BTZ] ₀ =3 mg L ⁻¹) Clofibric Acid ([CA] ₀ =3 mg L ⁻¹) [TOC] ₀ = 6 mg L ⁻¹ Feed flow: 20 mL min ⁻¹ O ₃ gas flow: 500 mL min ⁻¹ [O ₃] _{(aq)0} = 4 mg L ⁻¹	Low adsorption <5% without catalyst a) 55% BPA by adsorption 11% TOC b) Low adsorption <5%	84% BPA 57% BTZ 49% CA	0% TOC	a) 11% TOC (1h) b) 38% TOC (1h)	W. J. Lee et al. 2019 [150]

Process 2-SC Heterogeneous catalysis	MWCO: Substrate: α - Al_2O_3 Membrane: TiO_2 (rutile)	Ti-Mn ₂ O ₃	Dyestuff wastewater treatment plant COD=100 mg L ⁻¹ [O ₃] _{liq} =1 mg L ⁻¹ v=0.4 m s ⁻¹ P=0.15 MPa	27% COD	-	34% COD	46% COD	J. Zhang et al. 2016[73]
* Process 2-SC Heterogeneous catalysis	MWCO: 200 kDa Substrate: α - Al_2O_3 Membrane: TiO_2 (rutile)	Ti-Mn ₂ O ₃	Aniline (50 mg L ⁻¹) Red-3BS (10 mg L ⁻¹) COD= 322 mg L ⁻¹ [O ₃] _{liq} =2.5 mg L ⁻¹ Lp ₀ = 1081 L m ⁻² h ⁻¹ bar ⁻¹	-	8.3% COD removal	12.5% COD removal	Ti-Mn ₂ O ₃ 37.5% COD removal	Y. Zhu et al. 2013 [80]
Process 2-SC Heterogeneous catalysis	MWCO: Substrate: α - Al_2O_3 Membrane: rutile TiO_2 \varnothing pore: 2 μm	Ti-Mn	Aquaculture wastewater COD _{Mn} =2.1-4.1 mg L ⁻¹ Total Ammonia Nitrogen (TAN):0.2-0.4 mg L ⁻¹ O ₃ applied dose: 52 mg(O ₃) min ⁻¹ Gas flow: 0.6 L min ⁻¹	8% TAN removal	-	62% TAN removal	62% TAN removal	S. Chen et al. 2015 [75]
Process 1-DC Heterogeneous catalysis	Ceramic hollow cylinder membrane (micro filtration)	Catalyst particles, MgO nanosheet (111) 25.0 mmol L ⁻¹	Nitrobenzene ([NB]=50 mg L ⁻¹) pH: 6.7 Constant flux 3.92 L m ⁻² min ⁻¹ O ₃ : 5.0 mg L ⁻¹ Flow : 33.3 mL min ⁻¹	-	-	NB : 50% (30 min) 30.8 % TOC (90 min)	NB : 90% (30min) 50.8 % TOC (90 min)	J. Chen et al. 2015[152]
Process 2-SC Heterogeneous catalysis	Ceramic membrane Thickness 1.5 μm (mean pore size 9 nm) MWCO: 80 kDa	CeO ₂ -TiO ₂	Tetracycline and humic acids Lp ₀ = 83L m ⁻² h ⁻¹ bar ⁻¹ [O ₃] _{liq} =5 mg L ⁻¹ Catalyst: 1 g L ⁻¹	-	-	-	Increase of the removal of the tetracycline and humic acids	Y. Zhu et al. 2012 [79]

* Process 1-SC Heterogeneous catalysis	MWCO: Substrate: α - Al_2O_3 Membrane: ZrO_2	Catalyst: CuMn_2O_4 Ø_{pore} : 8.9 nm $S=3.2 \text{ m}^2 \text{ g}^{-1}$	Flow: $3.0 \text{ m}^3 \text{ h}^{-1}$ TMP: 0.1 kPa Benzophenone- 3 [BP-3]= 0.5 mg L^{-1} Benzotriazole [BZA]= 0.5 mg L^{-1} 2-phenyl benzimidazole- 5-sulfonic acid [PBSA]= 0.5 mg L^{-1} [O_3] _{liq} = 2 mg L^{-1} 2 hours	10% BP-3, BZA and PBSA (adsorption) 18% TOC	BP-3: 68% BZA: 60% PBSA: 55% 20% TOC	BP-3: 75% BZA: 70% PBSA: 60% 19% TOC	BP-3: 90% BZA: 100% PBSA: 100% 32% TOC	Y. Guo et al. 2018 [71]
* Process 1-SC Heterogeneous catalysis	MWCO: Substrate: α - Al_2O_3 Membrane: Al_2O_3 - ZrO_2	Catalyst: MnO_2 - Co_3O_4 NPs (D=7 nm, S=90 $\text{m}^2 \text{ g}^{-1}$)	Flow: $3 \text{ m}^3 \text{ h}^{-1}$ TMP: 0.11 KPa Benzophenone- 3 ([BP-3]= 2 mg L^{-1}) pH=7.12 [O_3] _{liq} = 1 mg L^{-1} [catalyst]=100 mg L^{-1} 30 min	12% (adsorption)	47%	52%	76%	Y. Guo et al. 2016 [71]

4.3.2. Degraded products and toxicity

Concerning organic matter, humic acids were often used in model effluents [76], [78]. The formation of disinfectant by-products, such as trihalomethane (THMs), after chlorination was also studied [37], [76]. Among THMs compounds, chloroform (CHCl_3), bromodichloromethane (CHBrCl_2), dibromochloromethane (CHBr_2Cl) and bromoform (CHBr_3) were monitored [76]. When a catalyst is added, TiO_2 in the work of Y.H. Wang [76] or Fe_2O_3 in the work of B. Karnik [37], the concentration of ozonation by-products can be reduced. B. Karnik [37] presented that the reactions occurring during ozonation give rise to different by-products including aldehydes (formaldehyde, glyoxal, and methylglyoxal), ketones, glyoxylic acid and pyruvic acid. Some of these by-products are of particular concern because of their possible mutagenicity and carcinogenicity. However, these molecules are easily biodegradable and can be removed by biofiltration [153]–[155].

The work of H. Park et al. [78] highlighted that the by-products formed by degradation of the hydrophobic fraction pass through the membrane and are thus present in the permeate. Thus, the question of the permeate quality must be addressed. The catalytic oxidation of p-CNB (p-chloronitrobenzene) [68], ten oxygenated compounds can be detected among by-products formed. Aldehydes, ketones, carboxylic acids and alcohols are less toxic than p-CNB. p-CNB can also be removed and the water toxicity seems to be reduced [156]. During ozonation of Red-3BS, authors explain that Red-3BS is oxidised to intermediate substances with sufficient groups of SO_3H and NH_3 [80]. The by-products formed during the catalytic ozonation and membrane filtration of bisphenol A (BPA), benzotriazole (BTZ) and clofibric acid (CA) using a CeO_x coated membrane are identified as

dicarboxylic acids ($C_4H_3O_4N_3$, $C_{15}H_{16}O_5$, $C_{13}H_{14}O_5$ and $C_{10}H_{11}O_7Cl$) due to the oxidation and ring cleavage of the initial compounds [150].

The toxicity of the effluents is not completely studied in the literature. J. Zhang et al. [136] however emphasised that effluent genotoxicity was eliminated thanks to the catalytic ozonation and filtration process. Moreover, Y. Guo et al. [71] evidenced that a coating with $CuMn_2O_4$ and catalytic ozonation coupled with filtration significantly reduced the toxicity for microorganisms of water containing initially benzophenone-3 (BP-3). The same conclusion was presented in another study carried out by the same scientists [66] using $MnO_2-CO_3O_4$ catalyst and BP-3.

By-products generated during ozonation are not always considered. These by-products can be harmful. However, they are surprisingly more biodegradable than the starting molecules. Moreover, the effluent toxicity is lowered using catalytic ozonation coupled with membrane filtration. The catalyst seems to have a positive impact on the toxicity.

4.3.3. Limitations of ceramic membrane fouling using ozonation

Coupling ozonation and ceramic membrane filtration seems to have a positive impact on membrane fouling compared to membrane filtration alone. Indeed, with a tubular ceramic UF membrane in alumina and titanium dioxide, the relative permeate flux (J/J_0) increases in presence of ozone, 85% instead of 40% [85]. Moreover, a study of an alumina flat sheet membrane showed a weaker increase of the transmembrane pressure at constant flux in presence of ozone [157]. Thus, ozone delays the membrane fouling.

Other examples are reported in Table 12. They illustrate the positive impact of adding a catalyst on membrane fouling. Ceramic membranes without catalyst exhibit an increase in the relative permeate flux (J/J_0) when ozone is added.

When catalyst is coated on the membrane surface, or dispersed in the feed tank [76], an increase of the relative permeate flux is not always observed. The effect depends on the nature of the catalyst. For example, Byun et al. [38] tested an iron oxide catalyst (Fe_2O_3) on a TiO_2-ZrO_2 membrane. The relative permeate flux was quite the same with or without catalyst in presence of ozone (58 and 60 J/J_0 % respectively). Another study with iron oxide ($\alpha-Fe_2O_3$) on $\gamma-Al_2O_3$ membrane in presence of ozone showed better results with an increase of the permeate flux, 85 J/J_0 % instead of 75 J/J_0 % without catalyst.

With TiO_2 as catalyst, an increase in the relative permeate flux is also observed. TiO_2 on UF ceramic membrane leads to a relative permeate flux with ozone equal to 84% whereas without catalyst it is 77% and without ozone and catalyst it is 60% [76]. X. Wang et al. [158] observed a relative permeate flux around 78% with ozone and TiO_2 catalyst on an Inside CeRAM, brand name of a seven channels tubular ceramic membrane (TAMI North-America, Saint-Laurent, Quebec, Canada). Without ozone, it is around 56%. Thus, TiO_2 as catalyst seems to limit membrane fouling.

Studies were also carried out with manganese oxide catalysts. Wang et al. [158] observed an increase in the relative permeate flux with Mn_2O_3 and ozone (65%) whereas without ozone it was around 36%. Byun et al. [38] noted also an increase in the relative permeate flux (84%) with ozone and Mn_2O_3 compared to tests with O_3 /without catalyst (60%), with catalyst/without O_3 (55%) and without catalyst/without O_3 (50%). The catalyst improves anti-fouling in the same way as ozone. Moreover, when catalyst and ozone are combined, anti-fouling effect is stronger. The authors explained that manganese oxide with the lowest point of zero charge, has more hydroxyl groups at $pH=8$ and so repulses more the negatively-charged organics. The repulsive electrostatic forces reduce adsorption of organics and limit pore blocking and associated fouling. X. Cheng et al. [68] compared different forms of manganese oxides, commercial MnO_2 particles with a diameter of particles equal to 14.2 μm , MnO_2 particles with 7.4 μm in diameter and MnO_2 nanoparticles with 52 nm in diameter.

It appears that the relative permeate flux depends on the state of division of the catalyst. It increases with the reduction of the particle size.

Some mixed oxides were also tested in COMF processes. In Table 12, studies with mixed titanium manganese oxide and copper manganese oxide are presented. CuMn_2O_4 in presence of O_3 leads to a higher relative permeate flux, 90% compared to Ti-Mn (56, 47 and 46%).

Fouling of ceramic membranes can be thus reduced with ozonation. Moreover, when a heterogeneous (or homogeneous) catalyst is added, the anti-fouling effect of the ozonation process is improved. The composition and the shape of the used catalysts affect the anti-fouling effect. In the literature, the main tested catalysts with ceramic membranes are iron oxides, titanium dioxides, manganese oxides and mixed oxides (CuMn_2O_4 and $\text{Ti-Mn}_2\text{O}_3$). From the literature it is difficult to conclude what is the best catalyst for COMF processes because operating conditions are not the same. Despite this, coupling catalytic ozonation and ceramic membrane separation seems to open a promising way for intensifying the membrane processes.

Table 12

Fouling of different ceramic membranes with or without ozonation and with or without catalyst (A: area of membrane in the filtration module; S: specific surface area; TMP: transmembrane pressure; MWCO: molecular weight cut-off).

Process	Membrane	Catalyst	Effluent	Permeate flux			Reference
				without O_3	with O_3	with O_3 + catalyst	
Process 2	Tubular ceramic UF membrane (Attax, USA) $\alpha\text{-Al}_2\text{O}_3$ and TiO_2 MWCO : 5 kDa	No	Lake Lansing TOC=11.8 mg L ⁻¹ $L_{p0}=143 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ $v=0.88 \text{ m s}^{-1}$ TMP: 0.68 bar O_3 : 9.6 g m ⁻³ Flow: 0.2 L min ⁻¹	40 J/J ₀ % ($V_{\text{filtered}}=1.5 \text{ L}$)	85 J/J ₀ % ($V_{\text{filtered}}=2 \text{ L}$)	-	J. Kim et al., 2009 [85]
Process 2	Alumina flat sheet ceramic membrane (Meidensha Corporation, Japan) Pore size: 60 nm	No	Dongjiang River & Hanxi River TOC= 4.0 mg L ⁻¹ TMP: 0.018 bar $v=0.1 \text{ m h}^{-1}$ O_3 : 2.0-2.5 mg L ⁻¹	Increase of the TMP in 7 days from 18 kPa to 36 kPa	Increase of the TMP in 13 days from 18 kPa to 36 kPa	-	X. Zhang et al., 2013 [157]
Process 2-SC Heterogeneous catalysis	UF ceramic membrane MWCO:7500 Da Substrate/membrane: $\gamma\text{-Al}_2\text{O}_3$ (Inopor)	Iron oxide NPs $\alpha\text{-Fe}_2\text{O}_3$ (D=50-100 nm) 0.56 mg(ions) cm ⁻² membrane	Suwanee River natural organic matter (SRNOM): DOC=3.4 mg(C) L ⁻¹ Youngsan River natural organic matter (YRNOM): DOC=2.3 mg(C) L ⁻¹ TMP: 0.8 bar Flow: 0.02 L min ⁻¹ O_3 : 10 g m ⁻³ $L_{p0}= 55.3 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$	70 J/J ₀ % (6h)	75 J/J ₀ % (6h)	85 J/J ₀ % (6h)	H. Park et al. 2012 [78]
Process 2-SC Heterogeneous catalysis	MWCO: 5kDa Substrate: TiO_2 Membrane: $\text{TiO}_2\text{-ZrO}_2$	Fe_2O_3 or Mn_2O_3	TOC 10-12 mg(C) L ⁻¹ Trihalomethane & haloacetic acid compounds $J_0=115 \text{ +/- } \text{L m}^{-2} \text{ h}^{-1}$ between 1.9 and 2.2 bars	50 J/J ₀ % (12h) 40 J/J ₀ % (*with Fe_2O_3) (12h)	60 J/J ₀ % (7h)	58 J/J ₀ % (7h)	S. Byun et al. 2011 [38]

Process 2-DC Heterogeneous catalysis	UF ceramic membrane MWCO: 5 kDa Substrate: TiO ₂ Membrane: TiO ₂	Catalyst: TiO ₂ (rutile and anatase) (Degussa P-25) D < 100 nm	Humic substances (NOM) 8 mg L ⁻¹ TriHaloMethane (THM) O ₃ : 2.5 mg L ⁻¹ Gas flow rate: 50 mL min ⁻¹ Catalyst: 3 g L ⁻¹	60 J/J ₀ % (4h)	77 J/J ₀ % (6h)	84 J/J ₀ % (6h)	Y.-H. Wang et al. 2013 [76]
Process 1-SC Heterogeneous catalysis	MWCO: 5kDa Inside CeRAM (Tami North America)	Mn ₂ O ₃ and TiO ₂ A=131.9 cm ²	Lake Lansing TOC: 12.1 mg(C) L ⁻¹ J=81.2 L m ⁻² h ⁻¹ v=0.5 m s ⁻¹ O ₃ flow: 10 mL min ⁻¹ O ₃ : 10 µg s ⁻¹	TiO ₂ 56 J/J ₀ % (*with catalyst) (4h)	-	TiO ₂ 78 J/J ₀ % (4h)	X. Wang et al. 2017 [158]
Process 1-DC Heterogeneous catalysis	UF ceramic membrane (Tami Industries) MWCO: 5 kDa A=0.0132 m ²	TiO ₂ (Degussa P-25)	DOC=8 mg L ⁻¹ pH=8 [O ₃] _{gas} =2.5 mg L ⁻¹ Gas flow rate: 50 mL min ⁻¹ [Catalyst]= 3 g L ⁻¹	50 J/J ₀ % two hours after J/J ₀ = 60% without O ₃ and catalyst	77.5 J/J ₀ % two hours after J/J ₀ = 60% without O ₃ and catalyst	82.9 J/J ₀ % two hours after J/J ₀ = 60% without O ₃ and catalyst	C.-J. Chen et al. 2017 [77]
Process 1-SC Heterogeneous catalysis	MWCO: 5kDa Inside CeRAM (Tami North America)	Mn ₂ O ₃ and TiO ₂ A=131.9 cm ²	Lake Lansing TOC: 12.1 mg(C) L ⁻¹ J=81.2 L m ⁻² h ⁻¹ v=0.5 m s ⁻¹ O ₃ flow: 10 mL min ⁻¹ O ₃ : 10 µg/s	Mn ₂ O ₃ 36 J/J ₀ % (*with catalyst)	-	Mn ₂ O ₃ 65 J/J ₀ %	X. Wang et al. 2017 [158]
Process 1-SC Heterogeneous catalysis	MWCO: 50 kDa Substrate: TiO ₂ Membrane: TiO ₂ -ZrO ₂	a) commercial MnO ₂ NPs (D=14.2 µm) b) M-MnO ₂ (D=7.4 µm) c) S-MnO ₂ (D=51.6 nm)	Na alginate (1.0 g L ⁻¹) p-chloronitrobenzene (p-CNB: 100 µg L ⁻¹) O ₃ : 0.5 mg L ⁻¹ TMP: 1 bar Ozone stock in contact with the membrane	37 J/J ₀ %	55 J/J ₀ %	a)57 J/J ₀ % b)61 J/J ₀ % c)69 J/J ₀ %	X. Cheng et al. 2017 [68]
Process 2-SC Heterogeneous catalysis	MWCO: 5kDa Substrate: TiO ₂ Membrane: TiO ₂ -ZrO ₂	Fe ₂ O ₃ or Mn ₂ O ₃	TOC 10-12 mg(C) L ⁻¹ Trihalomethane & haloacetic acid compounds J ₀ =115 +/- L m ⁻² h ⁻¹ between 1.9 and 2.2 bars	50 J/J ₀ % (12h) 55 J/J ₀ % (*with Mn ₂ O ₃) (12h)	60 J/J ₀ % (7h)	84 J/J ₀ % (7h)	S. Byun et al. 2011 [38]
Process 1-SC Heterogeneous catalysis	MWCO: Substrate: α-Al ₂ O ₃ Membrane: Al ₂ O ₃ -ZrO ₂	Catalyst: CuMn ₂ O ₄ Øpore: 8.9 nm S=3.2 m ² g ⁻¹	Flow: 3.0 m ³ L ⁻¹ TMP: 0.1 kPa [BP-3]=0.5 mg L ⁻¹ [BZA]=0.5 mg L ⁻¹ [PBSA]=0.5 mg L ⁻¹ O ₃ : 2 mg L ⁻¹	30 J/J ₀ % (2h)	62 J/J ₀ % (2h)	90 J/J ₀ % (2h)	Y. Guo et al. 2018 [71]
Process 2-SC Heterogeneous catalysis	MWCO: Substrate: α-Al ₂ O ₃ Membrane: rutile TiO ₂ Øpore: 2 µm	Ti-Mn	Aquaculture wastewater COD _{Mn} =2.1-4.1 mg L ⁻¹ O ₃ : 52 mgO ₃ min ⁻¹ (applied dose) Gas flow: 0.6 L min ⁻¹	30 J/J ₀ % (4h)	40 J/J ₀ % (4h)	56 J/J ₀ % (4h)	S. Chen et al. 2015 [75]
Process 2-SC Heterogeneous catalysis	MWCO: Substrate: α-Al ₂ O ₃ (GuangZhou JieXi LiShun Co.) pore size: 2 µm Membrane: TiO ₂ (rutile)	Ti-Mn ₂ O ₃ pore size: 100 nm	Dyestuff wastewater treatment plant COD=100 mg L ⁻¹ O ₃ : 1 mg L ⁻¹ v=0.4 m s ⁻¹ P=0.15 MPa	36 J/J ₀ % (4h)	40 J/J ₀ % (4h)	47 J/J ₀ % (4h)	J. Zhang et al. 2016 [73]
Process 2-SC Heterogeneous catalysis	MWCO: Substrate: α-Al ₂ O ₃ (disk membrane) pore size: 2 µm Membrane: TiO ₂ (rutile, pore size: 200 nm)	Ti-Mn pore size: 26nm	Red-3BS (10 mg L ⁻¹) Aniline (COD _{Cr} =310.3 mg L ⁻¹) TMP: 2 bars v=0.05 m s ⁻¹ O ₃ : 2.5 mg L ⁻¹	30 J/J ₀ % (*with catalyst) (5h)	10 J/J ₀ % (5h)	46 J/J ₀ % (5h)	Y. Zhu et al. 2013 [80]

4.3.4. Long-term stability of the coated membrane

The catalytic layer deposited on the membrane surface has to be mechanically and chemically stable enough to limit catalyst release. Some works provide results about catalyst leaching (Table 13). Karnik et al. [37] underlined the importance to have a good adhesion between coating and membrane surface. Guo [71] highlighted a high leaching rate of Cu ($32.0 \mu\text{g L}^{-1}$) and Mn ($2300 \mu\text{g L}^{-1}$) from the catalyst but also a low leaching rate of alumina ($12.0 \mu\text{g L}^{-1}$) from the ceramic membrane. In another study [66], the leaching of alumina was also observed, equal to $7.7 \mu\text{g L}^{-1}$. However, leaching from the catalyst is very low in comparison with that observed in the previously mentioned publication. Mn leaching rate is $7.1 \mu\text{g L}^{-1}$ and Co leaching rate is $2.9 \mu\text{g L}^{-1}$. In another study the leaching rate of Ce is very low (0.3%) compared to the leaching rate of Mn (3.5%) whereas the method of preparation is the same [150].

Adsorption of organic compounds on the catalyst surface can also be a problem because the whole catalyst surface is no longer accessible and fouling can develop. In the examples cited in Table 13, adsorption can be limited [37], negligible [75], close to 10% [71] or very important (55%) [150]. Byun et al. [38] indicated that the repulsive electrostatic forces between NOM (Natural Organic Matter) and membrane surface depend on the nature of the metal oxide with the following order Mn oxide > TiO_2 > Fe_2O_3 . That order is the opposite to the degree of fouling observed. Thus, the repulsive electrostatic forces reduce the adsorption of organics and limit the fouling.

Table 13

Leaching and adsorption of organic compounds on coated ceramic membranes (A: area of membrane in the filtration module; D: equivalent diameter of the elemental particles or powder particles of catalyst; S: specific surface area; TMP: transmembrane pressure; MWCO: molecular weight cut-off).

Process	Membrane	Catalyst	Conditions	Adsorption	Leaching	Reference
Process 2-SC Heterogeneous catalysis	MWCO: 15kDa/ 5 kDa Substrate + Membrane: $\alpha\text{-Al}_2\text{O}_3\text{-ZrO}_2\text{-TiO}_2$	Fe_2O_3	Trihalomethane 0.08 mg L^{-1} Haloacetic Acid 0.06 mg L^{-1} TOC $8.6\text{-}11.6 \text{ mg L}^{-1}$ $[\text{O}_3]_{\text{gas}}=2.5 \text{ mg L}^{-1}$ $L_{p0}= 60 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$	Sorption of natural organic material on iron oxide coating is expected to be very low, since the iron oxide coatings are extremely thin.	Not mentioned but authors tried "to improve the adhesion of the coating on the membrane".	B. Karnik et al. 2005 [37]
Process 1-SC Heterogeneous catalysis	MWCO: n.d. Substrate: $\alpha\text{-Al}_2\text{O}_3$ Membrane: ZrO_2	CuMn_2O_4 $\varnothing_{\text{pore}}: 8.9 \text{ nm}$ $S=3.232 \text{ m}^2 \text{ g}^{-1}$	Flow: $3.0 \text{ m}^3 \text{ h}^{-1}$ TMP: 0.1 kPa Benzophenone-3 [BP-3]= 0.5 mg L^{-1} Benzotriazole [BZA]= 0.5 mg L^{-1} 2-phenyl benzimidazole-5-sulfonic acid [PBSA]= 0.5 mg L^{-1} $[\text{O}_3]_{\text{liq}}=2 \text{ mg L}^{-1}$	BP-3 membrane adsorption: 10%	Low leaching of alumina ions ($11.0\text{-}12.0 \mu\text{g L}^{-1}$) High leaching of copper ($32.0 \mu\text{g L}^{-1}$) and manganese ($230.0 \mu\text{g L}^{-1}$)	Y. Guo et al. 2018 [71]

Process 1-SC Heterogeneous catalysis	MWCO: n.d. Substrate: α -Al ₂ O ₃ Membrane: Al ₂ O ₃ -ZrO ₂	MnO ₂ -Co ₃ O ₄ NPs (D=7 nm, S=90 m ² g ⁻¹)	Flow: 3 m ³ h ⁻¹ TMP: 0.11 KPa Benzophenone-3 ([BP-3]=2 mg L ⁻¹) pH=7.12 [O ₃] _{liq} =1 mg L ⁻¹ [catalyst]=100 mg L ⁻¹	BP-3 membrane adsorption: 12%	Al ion leaching: 7.7 μ g L ⁻¹ Mn ion leaching: 7.1 μ g L ⁻¹ Co ion leaching: 2.9 μ g L ⁻¹	Y. Guo et al. 2016 [66]
Process 2-SC Heterogeneous catalysis	MWCO: Substrate: α -Al ₂ O ₃ Membrane: rutile TiO ₂ \varnothing pore: 2 μ m	Ti-Mn	Aquaculture wastewater COD _{Mn} =2.1-4.1 mg L ⁻¹ Total Ammonia Nitrogen (TAN): 0.2-0.4 mg L ⁻¹ O ₃ applied dose: 52 mg(O ₃) min ⁻¹ Gas flow: 0.6 L min ⁻¹	Adsorption membrane negligible	-	S. Chen et al. 2015 [75]
Process 2-SC Heterogeneous catalysis	MWCO: 5kDa Substrate: TiO ₂ Membrane: TiO ₂ -ZrO ₂	Fe ₂ O ₃ or Mn ₂ O ₃	TOC 10-12 mg(C)/L Trihalomethane & haloacetic acid compounds J ₀ =115 +/- L m ⁻² h ⁻¹ between 1.9 and 2.2 bars	Adsorption of organics is limited. Repulsive forces between NOM and oxides: MnO _x > TiO ₂ > Fe ₂ O ₃	-	S. Byun et al. 2011 [38]
Process 2-SC Heterogeneous catalysis	MWCO: Tubular membrane Substrate: α -Al ₂ O ₃ Membrane: α -Al ₂ O ₃ Pore size: 600 nm	a) MnO _x (Mn ₂ O ₃) 4.2 mg g ⁻¹ Al ₂ O ₃ b) CeO _x (CeO ₂) 10.1 mg g ⁻¹ Al ₂ O ₃	Bisphenol A ([BPA] ₀ =3 mg L ⁻¹) Benzotriazole ([BTZ] ₀ =3 mg L ⁻¹) Clofibrac Acid ([CA] ₀ =3 mg L ⁻¹) [TOC] ₀ =6 mg L ⁻¹ Feed flow: 20 mL min ⁻¹ O ₃ gas flow: 500 mL min ⁻¹ [O ₃] _{(aq)0} =4 mg L ⁻¹	Low adsorption <5% without catalyst a) 55% BPA by adsorption 11% TOC b) Low adsorption <5%	a) Mn leaching: 5.99 mg L ⁻¹ (3.5%) b) Ce leaching: 0.61 mg L ⁻¹ (0.3%)	W. J. Lee et al. 2019 [150]

Adsorption of organic compounds on catalyst and catalyst leaching are key issues for further development of hybrid processes coupling catalytic ozonation and ceramic membrane filtration.

4.3.5. Discussion

In the literature, the ceramic membranes have molecular weight cut-off ranging from 5 kDa to 200 kDa (UF). These membranes are formed with alumina, titanium dioxide, mixed titanium-zirconium oxide or mixed alumina-zirconium oxides. The main advantage of ceramic membranes compared to organic membranes is their high ozone and corrosion resistance. Thus, the Process 2 with water ozonation during filtration process is the most used and studied in the literature. The organic compounds tested are various, from natural organic matter to synthetic compounds. The study of NOM (Natural Organic Matter) can be difficult because it can play the role of radical promoter or scavenger depending on its nature [47], [95]. In some types of wastewaters, bicarbonate and organic impurities may significantly scavenge the OH^{*} radicals. This represents a drawback for the use of ozone for water treatment. However, the literature concerning ozonation of wastewater or natural water is abundant [78], [81], [85], [157], [158]. Even if NOM can inhibit OH^{*}, ozonation proves its efficiency in the removal of organic compounds, in the decrease of the overall toxicity and in the increase of the biodegradability of retentates and permeates.

It appears that UF membranes alone slightly improve the removal of the organic molecules compared to ozonation alone. In order to improve the degradation of organic molecules a catalyst can be added as dispersed particles or as supported particles on ceramic membranes. In most cases, the catalyst added (iron oxides, manganese oxides, titanium dioxides and mixed oxides) is in the form of a coating on the ceramic membrane. However some authors also studied TiO₂ nanopowder

dispersed in the feed tank (heterogeneous catalysis) with an increase of TOC removal of 15% compared to experiment without catalyst [76]. Iron oxide catalysts on ceramic membrane present a good catalytic activity in ozonation membrane process but the performance depends on the operating conditions [37], [38], [78]. Manganese oxide, show also interesting properties for catalytic ozonation filtration but it is difficult to conclude what is the better catalyst between iron and manganese because the operating conditions are not identical [38], [39], [68]. Researchers also studied mixed oxides as catalyst like $\text{Ti-Mn}_2\text{O}_3$ [73], CuMn_2O_4 [71] and $\text{MnO}_2\text{-Co}_3\text{O}_4$ [71] with quite good organic molecules removal.

The by-products generated during ozonation are not always explained but those coming from humic acids are well-known. The by-products can be harmful but, the final effluents appear to be more biodegradable than the initial effluent. Moreover, the toxicity is lowered using catalytic ozonation coupled with filtration. The catalyst seems to have a positive impact on the decrease of the toxicity.

Coupling ozonation and ceramic membrane filtration seems to have a positive impact on membrane fouling compared to membrane filtration alone. When a catalyst is added, the anti-fouling effect of the ozonation process is improved. However, the chemical composition and the shape of the used catalyst affect the anti-fouling effect.

The long-term stability of the coated membranes is a key issue for further development and use of catalytic ceramic membranes. Adsorption of organic compounds at the catalyst surface can be a problem because the whole catalyst is no more accessible and the fouling can become important. The catalyst leaching is also a key point for the sustainability of the functionalized membranes. Literature was not very abundant on this topic and the results are very different between the different publications.

5. Conclusions

Advanced Oxidation Process was highly studied over the past few years for the treatment of wastewater and natural water. AOP is based on an enhancement of the production of hydroxyl radicals in order to degrade a majority of organic compounds. Water treatment also involved membrane filtration process (UF, NF, RO...) to retain organic pollution. In this review we focused on the coupling of these two processes: catalytic ozonation as AOP process and membrane filtration.

The catalysts, usually metal cations (homogeneous catalysis) or metal and metal oxides (heterogeneous catalysis), exhibit variable performances depending on the nature of the pollutants. It is thus difficult to rank the catalysts because the operating conditions are never the same. Phenol removal with different catalysts was in particular carried out through several publications. It appears that phenol elimination is promoted when catalysts like MgO , MnO_2 and Fe_3O_4 are used. Until now, the mechanisms of hydroxyl radical production by the catalyst are not very well understood.

Ultrafiltration and nanofiltration organic membranes have been combined with ozonation. In order to resist to strong oxidation, only few organic materials can be used such as polypropylene (PP), polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE) and polyamide (PA). PVDF is widely used for catalytic ozonation. However polyamide membranes are mainly implemented in the literature without catalysts. When ozone is coupled with organic membrane filtration, it appears that fouling is mitigated. Ozonation of concentrated retentate was widely studied with sometimes a significant organic removal, TOC decrease and enhanced biodegradability. If catalyst is added in the process, anti-fouling is more important and organic removal is also promoted.

In literature, there are more papers involving ceramic membranes coupled with catalytic ozonation. These membranes are made of oxides such as TiO_2 , ZrO_2 and Al_2O_3 which are not sensitive to oxidation. Ozonation can be performed directly in the membrane module and not in a pre-ozonation reactor. Only papers dealing with ultrafiltration ceramic membranes coupled with catalytic ozonation were found. As for organic membranes, fouling is reduced when ozone is applied. This phenomenon is also observed when a catalyst is added in suspension. The observed effect depends on the nature of the catalyst (iron oxides, titanium dioxides, manganese oxides or mixed oxides like CuMn_2O_4 and $\text{Ti-Mn}_2\text{O}_3$). The chemical composition and the microstructure of the catalyst influence the final anti-fouling performances. It is not possible to define the best catalyst for the catalytic ozonation filtration process as it strongly depends on the operating conditions. In regards to organic compound degradation, coupling catalytic ozonation and ceramic membrane filtration is anyway promising. The advantage of ceramic membranes is that the catalyst can be easily coated and fixed at the membrane surface. Among the available catalysts, iron oxides and manganese oxides have been mainly studied giving promising results. According to some studies, iron oxide catalysts can double the COD removal while some authors did not notice any improvement about the TOC removal using Fe_2O_3 . Manganese oxides exhibit also interesting performance for the TOC removal but in less extent compared to iron oxides. Mixed oxides show also attractive results but their synthesis is more complex for a functional gain which is not always significant. On the other hand, it is crucial to be sure that the catalyst is weakly lixiviated in water and that the adsorption of the pollutants on catalyst remains low enough.

6. Prospects

Coupling of catalytic ozonation and membrane filtration is very promising because it allows combining the advantages of filtration with the possible rejection of small molecules and the advantages of catalytic ozonation with the degradation of molecules. The literature about such a coupling is not very abundant but few papers exist, involving organic or ceramic membranes.

There is clearly a lack of studies concerning catalytic ozonation coupled with organic membranes due to the difficulty of adding a catalyst at the membrane surface and the chemical resistance towards ozone. However, it has been shown that coupling always a positive impact on TOC removal and on the degradation of organic molecules.

Ceramic membranes are more widely studied for catalytic ozonation because they are strongly resistant to ozone and a catalytic layer can be easily deposited on the membrane surface. However, ceramic membranes are more expensive and only few are commercially available especially ceramic nanofilters. Recently, ceramic membrane manufacturers have done technical advances to reach lower molecular weight cut-offs and prepared nanofiltration membranes. So, it would be interesting to implement such ceramic nanofilters coupled with catalytic ozonation. Nanofiltration would enable a better selectivity and retention of very small molecules (like ozonation by-products) and a higher efficiency as contactors for catalytic ozonation.

During membrane filtration, concentrated retentates are produced. Thanks to ozonation, retentates may have better quality and biodegradability. Some researches should be conducted to examine more in depth this aspect. Permeates present usually a quality which is enough to be reused. It is a strong advantage of this hybrid process.

It is important to notice that the by-products generated during ozonation are not enough studied as well as their toxicity. Mechanistic studies are needed about identification of degradation pathway during such coupling, fate of by-products, and toxicity of the effluent.

In the literature, the long-term stability of the membrane is not always mentioned whereas it is a key issue for future uses in industry and in water treatment plants. The irreversible fouling and the possible release of catalyst should be investigated in further studies about catalytic membranes.

Finally, the mechanisms of OH^\bullet production by catalyst stay not well understood and deserve to be better clarified.

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