Catalytic Ozonation and Membrane Contactors

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Membrane filtration has been widely used in water and wastewater treatment. However, this process is not very effective for the removal of refractory organic compounds (e.g., of pharmaceutical origin). Alongside, ozonation is an efficient oxidative process, although ozone is considered to be a rather selective oxidant agent and sometimes it presents quite low mineralization rates. An improvement of this oxidation process is catalytic ozonation, which can degrade organic compounds via the acceleration of hydroxyl radicals' production. The hydroxyl radicals are unselective oxidative species, presenting high reaction constants with organic compounds. An efficient way to couple membrane filtration with catalytic ozonation is the deposition of an appropriate solid catalyst onto the membrane surface. Catalytic membrane ozonation can enhance the degradation of these compounds and, subsequently, the incidence of membrane fouling (i.e., the major problem of membrane uses).

catalytic membranes ozonation hybrid process fouling control micropollutant removal

1. Definition

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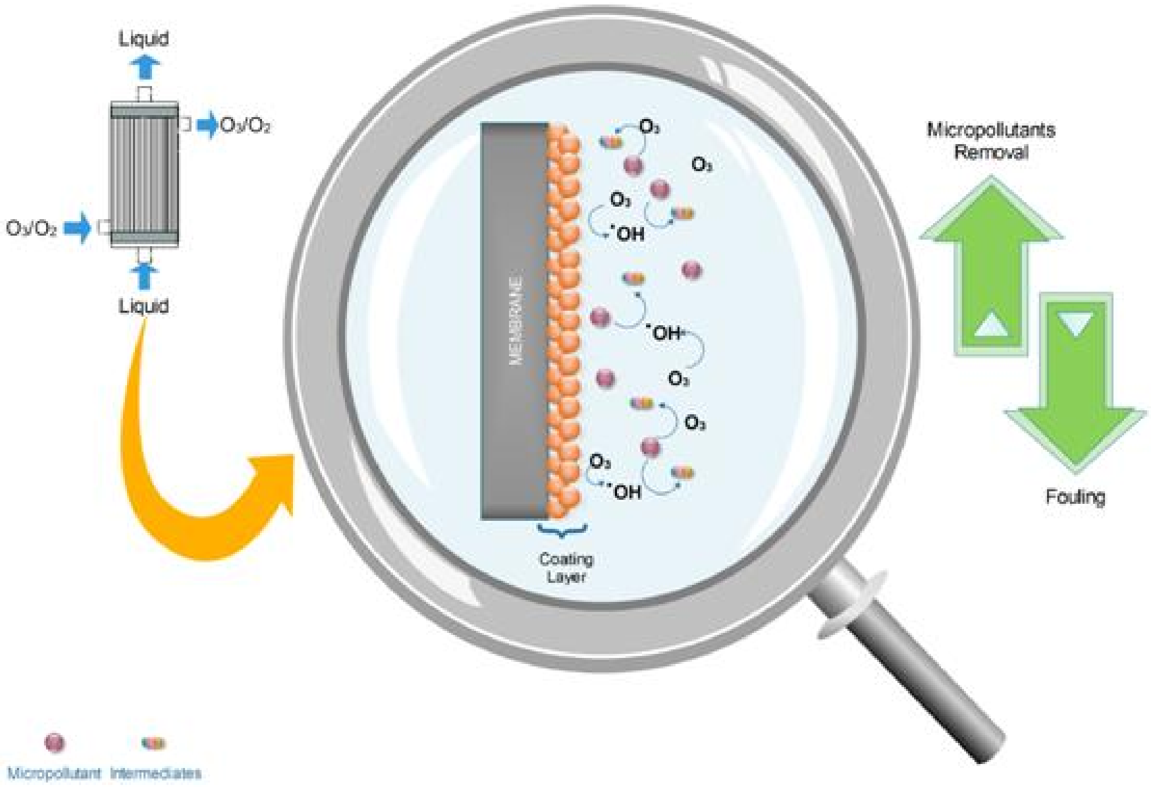

Figure 1. Basic operating mechanism of a catalytic membrane contactor [1].

2. Ozonation

Ozone is a strong oxidant agent that can be used in water and wastewater treatment operations for the removal/oxidation of organic/inorganic pollutants, as well as of microorganisms. Ozone can participate into the respective oxidation reactions via two major routes, i.e., (1) it can directly react with the pollutants, or (2) it can be decomposed into hydroxyl radicals and these (more) reactive species can then react with the contaminants[2]. Ozone decomposes into hydroxyl radicals ($HO^\bullet$) by a 3-step mechanism, which involves initiation reactions, radical chain reactions, and a termination step. The overall reaction of ozone decomposition into $HO^\bullet$ is:

$$3O_3 + HO^- + H^+ \rightarrow 2HO^\bullet + 4O_2 \tag{1}$$

More specific information about the complex ozone reaction mechanisms can be found in the reference of Gottschalk et al.[3]. The main disadvantages of the ozonation process are considered to be the relatively slow oxidation/reaction time and the high energy requirements[4]. Although ozone is used frequently, especially in water treatment applications (mainly for disinfection purposes), its production cost is still quite high. The high cost is mainly a function of pure mass-transfer operation and its production process[5]. Overall, the efficiency of the ozonation process is considered rather low and several ways to improve it have been proposed[6].

The conventional ozone contactors are based on bubble diffusers, injectors and static mixers[6]. These types of reactors present rather small mass-transfer rates, because they are producing bubbles with quite small contact area (interface)[7]. Due to the low use efficiency, an excess amount of ozone is necessary to be produced/added in order to be able to achieve the required ozone dosefor the respective reactions to be effectively taking place[8]. A more eco-friendly approach is considered the use of membranes as efficient ozone diffusers/contactors, improving the respective mass transfer operation[7].

3. Membrane Contactors

Membrane contactors are appropriate modules that can help the transfer of a constituent between a gas and a liquid phase and they are quite frequently used in ozone-based oxidation processes. The membrane is the interface that allows the two phases to flow separately. The introduction of this technology increases substantially the capital cost of ozonation process, but as counter-balance it can decrease also the operational cost (due to limited ozone losses) and eventually to increase the overall process efficiency[9]. The membranes that are used as contactors in the ozonation processes must have three important attributes, i.e., (1) long-term stability to ozone exposure, (2) surface hydrophobicity, and (3) porosity[10]. The material used for the construction of most membrane contactors is polymeric, but the use of these materials in ozone-based processes is rather limited, due to the oxidation reactivity of ozone and the potential quick destruction of these organic-based membranes. Therefore, ceramic membranes are more frequently selected. These membranes are mostly tubular, while the polymeric membranes can be also available as flat-sheet, or hollow-fiber configurations[8]. In terms of micropollutants' removal the NF membranes are more suitable for their separation, since they can operate at rather low pressures and their pore sizes are around the size of such compounds[4]. The most investigated membrane contactors for ozone diffusion are based on the application of direct ozonation. According to the this concept, ozone alone is considered to be incapable of mineralizing the refractory organic compounds; however, their degradation can be significantly improved by the combination of a membrane contactor with a proper catalyst, leading to the catalytic ozonation process[8].

4. Catalytic Ozonation

Catalytic ozonation has been a highly studied treatment process during recent years and it is based on the acceleration of $HO^{\bullet}$ production to degrade the refractory organic compounds, such as most micropollutants are. Catalytic ozonation can be divided in two main categories, based on the type of catalyst that will be applied, i.e.,*homogeneous* catalytic ozonation (using mainly dissolved transition metals) and *heterogeneous* catalytic ozonation (using mainly specific solid materials). Regardless of the type of catalytic ozonation the main goal of this process is the higher efficiency of oxidation system, or the use of reduced ozone amount to reach the same efficiency, when compare to the application of single ozonation. That requires the acceleration of $HO^{\bullet}$ production, which present an electro-chemical potential of 2.7 V, i.e., they are considered as more powerful oxidant agents, than the application of single ozone (2.07 V) and also, they can participate unselectively in the oxidation reactions taking place[3].

Catalytic ozonation has been studied extensively; however, there is a lack of understanding, concerning the detailed reaction mechanism taking place. In general, catalytic ozonation can occur only when ozone or organic molecules or both are being adsorbed in the catalyst surface[11]. A hybrid process of ozonation and membrane filtration can be performed by following the three subsequent modes, i.e., (1) membrane filtration followed by ozonation, (2) ozonation followed by membrane filtration, and (3) ozonation and membrane filtration taking place simultaneously. The use of catalytic ozonation process before or after the membrane filtration is rather seldom applied. Only very few research studies have been found to investigate such systems[12][13][14]. Usually, the hybrid catalytic ozonation—membrane filtration system is applied by the 3rd mode, in which the oxidation and filtration processes are carried out quite simultaneously[15]. By that point the heterogeneous catalytic ozonation can be sub-classified in two groups, i.e., the *single heterogeneous catalytic ozonation*, when the solid material is added to the oxidation system usually in powdered form (i.e., as suspension)[16], and the *membrane catalytic ozonation*, when the solid catalyst is preliminary deposited onto a membrane surface[1]. Then the Catalytic Membrane Contactor (CMC) is transformed into a unit that acts simultaneously as a contactor (improving the ozone diffusion/transfer) and as a reactor (for the oxidation of organic compounds)[17].

5. Catalytic Membrane Contactors

Membranes modified with metal oxide particles, proved to prevent fouling and to present higher efficiencies, regarding the removal/degradation of organic pollutants. However, some membranes are prepared from materials with inherent catalytic activity and therefore, can enhance the production of hydroxyl radicals without any further modification. The most commonly applied relevant materials are Al_2O_3, TiO_2, and ZrO_2[18][19]. There are five main factors that can influence the catalytic performance of a membrane[4][20][21][22]:

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

The most convenient used oxides, applied as coatings in catalytic membranes, are iron and manganese oxides. Park et al.[22] coated a γ-Al_2O_3 membrane with iron oxide nanoparticles. From the flux experiments it was obvious that the combination of ozone with the catalytic membrane can decompose/mineralize and alter the characteristics of NOM and as a consequence, membrane fouling was also significantly reduced. Guo et al.[23] used a ceramic membrane modified/deposited with $CuMn_2O_4$ particles to enhance the removal of benzophenone-3, as compared to the respective virgin membrane and to the application of single ozonation. In the ozonation process superoxide ions ($O_2^{\bullet-}$) and H_2O_2 were produced, promoting the molecular ozone decomposition into $HO^{\bullet}$, and that generation was enhanced during the application of catalytic ozonation process. Consequently, the larger molecular weight organic molecules were able to degrade to smaller molecules, or to be transformed to hydrophilic ones.

In most cases ceramic membranes have been used in catalytic ozonation systems, because the substrate material is simpler to be coated. However, Yu et al.[24] coated a PVDF (polymeric) membrane with MnO_2 nanoparticles. They observed that the presence of MnO_2 surface layer lowered the fouling rate. For the initial 10 days of operation the increase of Trans-Membrane Pressure (TMP) was very small, partly as a consequence of ozone presence, limiting the development of biological activity and the bio-accumulation of several components onto the membranes' surface. Furthermore, Sun et al.[25] doped such a membrane with nano-TiO_2 to examine the removal of nitrobenzene. Under acidic conditions the removal rate of the pollutant was rather low, but that was increased with the increase of pH values. At alkaline pH values the decomposition of ozone is accelerated, but when the pH value was higher than 10, the nitrobenzene removal rate was (again) reduced, because under the influence of highly alkaline conditions the produced $HO^{\bullet}$ radicals can be quickly decomposed into O^{-} and H^{+}. Therefore, higher efficiency was obtained at the max. pH value 10.

Almost all the researchers have observed that the catalytic membrane ozonation follows a mechanism based on radicals. The predominant radical species in most cases were the $HO^{\bullet}$. In some cases both $HO^{\bullet}$ and $O_2^{\bullet-}$ radicals were found to participate in the catalytic reaction[20]. However, Scarati et al.[21] noticed that when they used a CuO-coated membrane for the 1,4-dioxane oxidation/removal, then the primarily oxidative species were the $O_2^{\bullet-}$. Although the production of $O_2^{\bullet-}$ is a part of ozone decomposition mechanism for the formation of $HO^{\bullet}$ (e.g.,[3][26]), it seems that in this case the decomposition pathways were different. The obtained results were not very promising and this membrane maybe not suitable for catalytic reactions.

Except for the removal of micropollutants some researchers have used the catalytic ozonation induced by membrane contacting process also for the removal of bacteria. The relevant studies have shown that the metal oxides, such as iron oxides, can retard the transport of bacteria. The adhesion of bacteria to a metal oxide surface will increase the retention of them at the membrane interface and subsequently, the contact of bacteria with ozone will be prolonged. Ozone reacts with the catalytic surface and $HO^{\bullet}$ or other radical species would be formed and inactivate the bacteria near them. Therefore, this mechanism enhances the disinfection behavior of the treatment system[27][28].

Although coupling catalytic membranes with ozonation seems to be a promising technology, the stability of applied coatings constitutes a quite important issue of concern. In most cases the amounts of initially deposited metals leached into the aqueous solutions during the operation and can lead to a secondary pollution problem. Even for the metals without established regulation limits (e.g., Sn), their potential occurrence in drinking water sources can raise some health issues. Moreover, the relevant studies about the formation of ozonation by-products and their acute potential toxicity will be still considered to be essential, because they can be an additional pollution source[29][30]. Finally, the coating techniques must be further developed, especially regarding the application of more ozone-resistant polymeric materials, and new solid materials can be examined for deposition onto the membranes surface, acting as potential catalysts, leading to the increase of catalyst range/options.

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