

# Characteristics of ozone decomposition inside ceramic membrane pores as nano-reactors

X. J. Fan and X. H. Zhang

## ABSTRACT

The characteristics of ozone decomposition inside the nano-pores of ceramic membranes were identified according to nano-reactor configuration. Three types of ceramic membranes with a pore size of 50 nm were tested with compositions of  $\text{Al}_2\text{O}_3$ ,  $\text{MnO}_2/\text{Al}_2\text{O}_3$  (4%) and  $\text{CeO}_2/\text{Al}_2\text{O}_3$  (4%) respectively. The results showed that the specific decomposition rate of ozone inside membrane pores was 428 times higher than that in pure water outside the pores. The influences of pH values or  $\text{H}_2\text{O}_2$  dosages on ozone decomposition in bulk water can be explained on the basis of chain reactions or hydroxyl-radical mechanism; however, these did not work for the behaviours inside the nano-pores of membranes. The extents of the influences of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  were even opposite inside to outside the nano-pores of membranes. A unique configuration of nano-reactors within the ceramic membranes tested was proposed based on zeta potentials and water molecule-clusters. Inner charge layer and highly ordered water clusters might play critical roles for the reaction processes inside the nano-reactors.

**Key words** | catalytic, ceramic membrane, membrane pore, nano-reactor, ozone decomposition

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## INTRODUCTION

Low pressure membrane ultrafiltration (UF) has been widely applied to the treatment of drinking water (Gao *et al.* 2011). Compared with the conventional filtration treatment process, UF is more effective in the removal of particles, microorganisms and large molecules of natural organic matter (NOM) with relatively less footprint and lower cost (Shannon *et al.* 2008; Iris *et al.* 2010; Xiao *et al.* 2012). At the same time, it can produce drinking water with better quality and higher efficiency.

Membrane fouling is considered as one of the major challenging issues in the application of UF membranes to water treatment (Howe & Clark 2002). It is mainly caused by the adsorption of organic matter on the membrane surface or inside the membrane pores. Although regular backwashing is efficient in cleaning up reversible fouling, it is hard to sweep out irreversible fouling from membrane pores. Ozone is a powerful oxidant that can oxidise NOM effectively and has been shown to reduce membrane fouling (Hashino *et al.* 2000; Schlichter *et al.* 2003, 2004). However,

ozonation cannot be used simultaneously with the widely used polymeric membranes, because of their low chemical-resistance. So, in most cases, ozone is used prior to membrane UF.

Ceramic membranes have greater resistance to ozonation than common organic membranes do. Some studies reported that the membrane fouling that caused NOM was meaningfully reduced in the hybrid processes of ozonation and ceramic UF membrane (Karnik *et al.* 2005a, b, 2006, 2009). The appropriate process parameters considering ozone dosage and hydrodynamic conditions had been investigated for optical control of ceramic membrane fouling in the hybrid system (Kim *et al.* 2008). When membrane surfaces were fabricated with manganese, iron or titanium oxides as coatings, the control on membrane fouling was improved, furthermore, the formation of disinfection by-products decreased significantly (Byun *et al.* 2011; Corneal *et al.* 2011). Recent research indicated that *in situ* ozonation inside membrane pores may play

an important role in alleviating irreversible fouling (Zhang *et al.* 2013).

The sizes of the ceramic membrane pores are at a magnitude of nanometres, which are much smaller than those of conventional reactors and even some of the micro-reactors. Numbers of studies have been demonstrated that the efficiencies of mass transfer and reactions can be substantially improved in micro-reactors (Mills *et al.* 2007). The concept of nano-reactors has stipulated high anticipation in dramatically enhancing reaction efficiencies (Qiao *et al.* 2008; Monteiro 2010). Thus, the exploration of reaction performance inside the ceramic membrane pores is of great meaning on the basis of the nano-reactor concept. It may provide a way like never before to control the membrane fouling and to enhance the efficiency of drinking water treatment in the nano-era.

The purpose of this study was to investigate the ozone decomposition inside the nano-pores of ceramic membranes. The effects of different catalysts, pH, hydrogen peroxide and typical ions were examined.

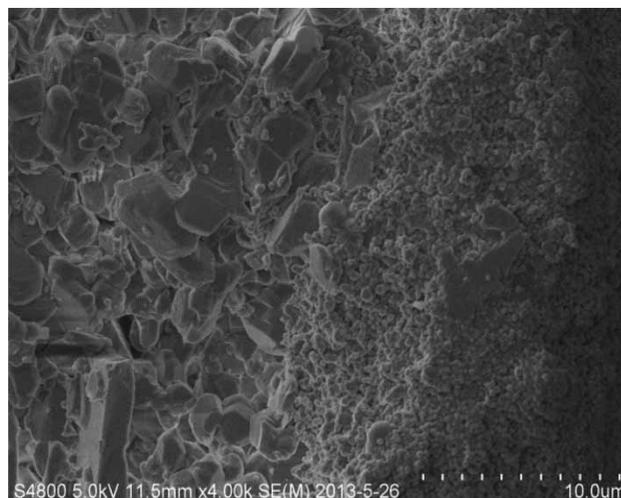
## MATERIALS AND METHODS

### Membranes

In this study we used three kinds of flat ceramic membranes with the compositions of  $\text{Al}_2\text{O}_3$ ,  $\text{MnO}_2/\text{Al}_2\text{O}_3$  (4%) and  $\text{CeO}_2/\text{Al}_2\text{O}_3$  (4%) respectively (Kelin, China). The  $\text{Al}_2\text{O}_3$  membrane was made without catalysts, while the other two membranes were produced by doping  $\text{MnO}_2$  or  $\text{CeO}_2$  precursors into the membrane materials before the sintering of membranes, as shown in Figure 1. The catalyst was equally distributed on the surface and inside the membrane pores. Each membrane had a total filtration area of  $102\text{ cm}^2$ . The pore size is  $50\text{ nm}$  on average, the thickness of the pore layer and support layer are  $12\text{ }\mu\text{m}$  and  $1.5\text{ mm}$  separately.

### Ozone injection and filtration set-up

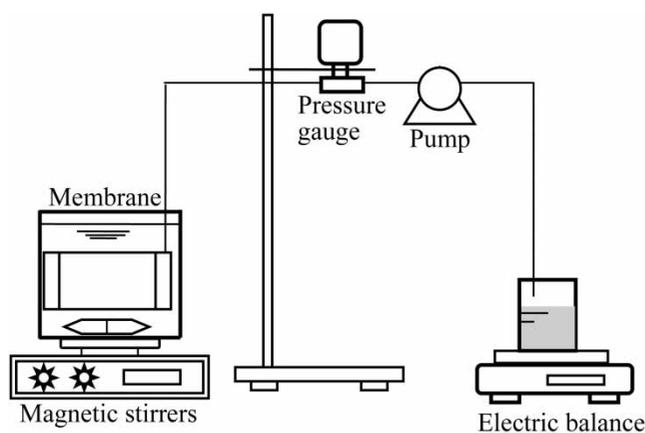
Ozone was generated with a high-pressure ozone generator (Guolin, China). The pure oxygen from a gas cylinder went through a silica gel drier and was fed to the ozone generator. The ozone-containing gas flow was injected directly into a



**Figure 1** | Scanning electron microscope (SEM) image of cross section of  $\text{MnO}_2/\text{Al}_2\text{O}_3$  membrane.

glass container with  $5\text{ L}$  of pure water (Milli-Q, USA). The ozone injection was stopped until the ozone concentration in the pure water was almost  $5\text{ mg/L}$ . Then the ceramic membrane was placed into the glass container and the filtration started immediately. The filtration system was shown in Figure 2. It was operated by controlling the trans-membrane pressure with a peristaltic pump (Longer Pump, China). The permeation mass was measured by an electronic balance (Chengdu PRIS, China) at intervals of  $60\text{ s}$ . The temperature of the pure water was maintained at  $28 \pm 0.5\text{ }^\circ\text{C}$  during the whole experiments.

The ozone concentration of the water samples was analysed by the indigo method as follows. As soon as the water



**Figure 2** | Schematic of the filtration test system.

sample was collected, 9 mL sample was immediately mixed with 1 mL potassium indigo trisulfonate solution of 0.77 g/L (or an appropriate dilution) within 30 s. Then the mixture was detected with an ultraviolet and visible spectrophotometer (Shimadzu, Japan) at 600 nm in 2 hours. Ozone was reacted with potassium indigo trisulfonate at a molar ratio of 1:1.

The ozone concentrations were analysed both in the bulk solution and in the membrane effluent. The specific ozone decomposition rates in the bulk solution were quantified according to first-order kinetics, while an ozone decomposition ratio was adopted to characterise the decomposition inside the membrane pores. The ozone decomposition ratio was calculated by the following equation: ozone decomposition ratio (%) =  $[(C_{R(t)} - C_{E(t)}) / C_{R(t)}] \times 100\%$ , where  $C_{R(t)}$  is the ozone concentration in bulk solution,  $C_{E(t)}$  is the ozone concentration in membrane effluent. All the experiments were conducted in duplicate.

## RESULTS AND DISCUSSION

### Ozone decomposition by different membranes

Figure 3 shows the variation of ozone concentrations along with the testing time when contacted with different ceramic membranes. It was found that ozone could naturally

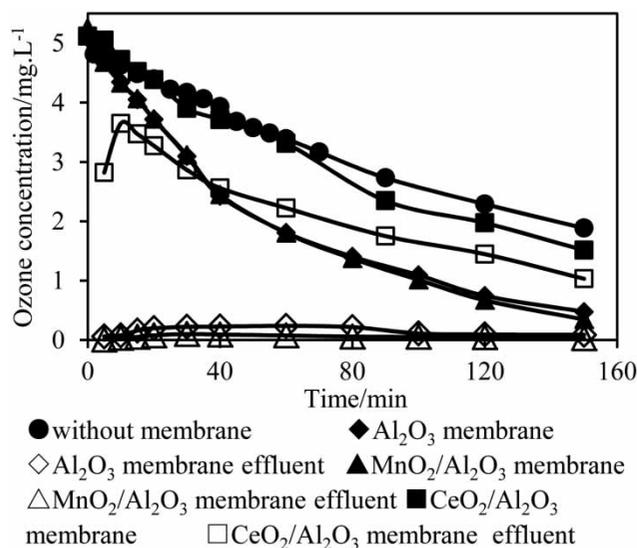


Figure 3 | Ozone decomposition in bulk water and through membrane pores.

decompose in pure water without a ceramic membrane and that the specific decomposition rate was  $1.08 \times 10^{-4} \text{ s}^{-1}$  according to the first-order kinetics.

With the ceramic membranes immersed in the pure water, the ozone decomposition speeded up to different extents. It is considered that the membrane surfaces played substantial roles in catalysing ozone decomposition in the membrane tank. Apparently,  $\text{Al}_2\text{O}_3$  and  $\text{MnO}_2/\text{Al}_2\text{O}_3$  were much better than  $\text{CeO}_2/\text{Al}_2\text{O}_3$  as catalytic materials. The average ozone decomposition rates were  $2.66 \times 10^{-4} \text{ s}^{-1}$  and  $2.68 \times 10^{-4} \text{ s}^{-1}$  for  $\text{Al}_2\text{O}_3$  and  $\text{MnO}_2/\text{Al}_2\text{O}_3$  respectively,  $1.36 \times 10^{-4} \text{ s}^{-1}$  for  $\text{CeO}_2/\text{Al}_2\text{O}_3$ .

Compared with the catalytic reactions in the bulk water, the ozone decomposition through the membrane pores was drastically improved. The ozone concentration of the residual in the effluent of  $\text{MnO}_2/\text{Al}_2\text{O}_3$  membrane was almost zero as compared with its influent concentration of 5 mg/L. The decomposition ratio was over 80% with  $\text{Al}_2\text{O}_3$  membrane and 90% with  $\text{MnO}_2$  doped. However, the ozone decomposition ratio in the pores of  $\text{CeO}_2/\text{Al}_2\text{O}_3$  membrane was only 20–40%. This is consistent with that in bulk water.  $\text{MnO}_2$  and  $\text{Al}_2\text{O}_3$  have better performance in the decomposing ozone than  $\text{CeO}_2$  does.

### Effect of pH value on ozone decomposition

The effects of pH values on ozone decomposition were tested with or without ceramic membranes in pure water, as shown in Figure 4. With the increase of pH values, the ozone decomposition was significantly affected by pH values in the pure water. Higher pH value led to quicker decomposition of ozone. The ozone decomposition rates in pure water without the presence of ceramic membrane increased from  $4.45 \times 10^{-5} \text{ s}^{-1}$  at pH 3.2 to  $3.21 \times 10^{-3} \text{ s}^{-1}$  at pH 9.3.

In the presence of the ceramic membranes containing  $\text{Al}_2\text{O}_3$ ,  $\text{MnO}_2/\text{Al}_2\text{O}_3$  and  $\text{CeO}_2/\text{Al}_2\text{O}_3$ , the curves of the ozone concentrations varied very similarly to that without membranes, and the related decomposition rate was  $6.07 \times 10^{-5} \text{ s}^{-1}$  at pH 3.2 and  $3.25 \times 10^{-3} \text{ s}^{-1}$  at pH 9.3 for  $\text{MnO}_2/\text{Al}_2\text{O}_3$  membranes. Still, the ozone decomposition rate catalysed by  $\text{CeO}_2/\text{Al}_2\text{O}_3$  membrane was slightly lower than that of the other two membranes in pure water.

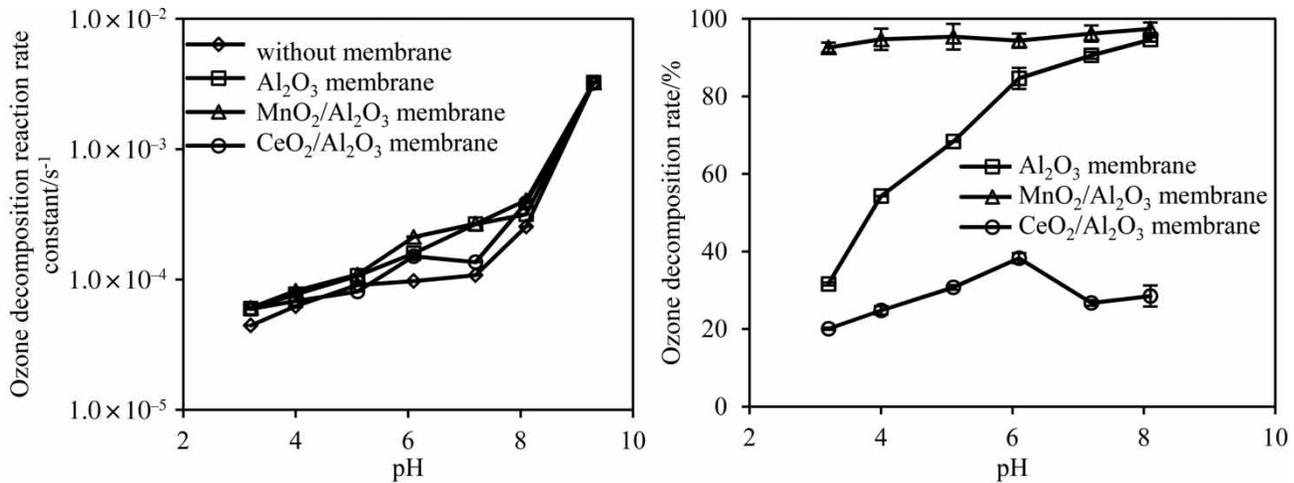


Figure 4 | Effect of pH on ozone decomposition in bulk solution (left) and membrane pores (right).

The ozone decomposition through ceramic membrane pores was quite different when pH ranged from 3.2 to 8.1. The decomposition ratio with Al<sub>2</sub>O<sub>3</sub> membrane increased gradually from 32 to 95%; it was significantly affected by pH. However, when the membranes were doped with MnO<sub>2</sub>, the ozone decomposed almost completely at all the pH values tested, while the ozone decomposition ratio was less than 40%.

### Effect of H<sub>2</sub>O<sub>2</sub> on ozone decomposition

Figure 5 shows the results of ozone decomposition when adding H<sub>2</sub>O<sub>2</sub>. At a molar ratio of m<sub>H<sub>2</sub>O<sub>2</sub></sub>/m<sub>O<sub>3</sub></sub> of 0.1, the

ozone decomposition rate increased to  $8.43 \times 10^{-4} \text{ s}^{-1}$  in pure water without the membrane. The ozone decomposition speeded up in the presence of ceramic membranes and H<sub>2</sub>O<sub>2</sub> together. MnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> membrane gave the highest decomposition rate constant of  $12.6 \times 10^{-4} \text{ s}^{-1}$  at 0.1 m<sub>H<sub>2</sub>O<sub>2</sub></sub>/m<sub>O<sub>3</sub></sub>.

Ozone decomposition catalysed by the matter inside the membrane pores was also improved by the H<sub>2</sub>O<sub>2</sub> present. When m<sub>H<sub>2</sub>O<sub>2</sub></sub>/m<sub>O<sub>3</sub></sub> was 0.1, the decomposition ratios were 95 and 99% respectively for Al<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> membrane pores; 38.5% for CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> membrane.

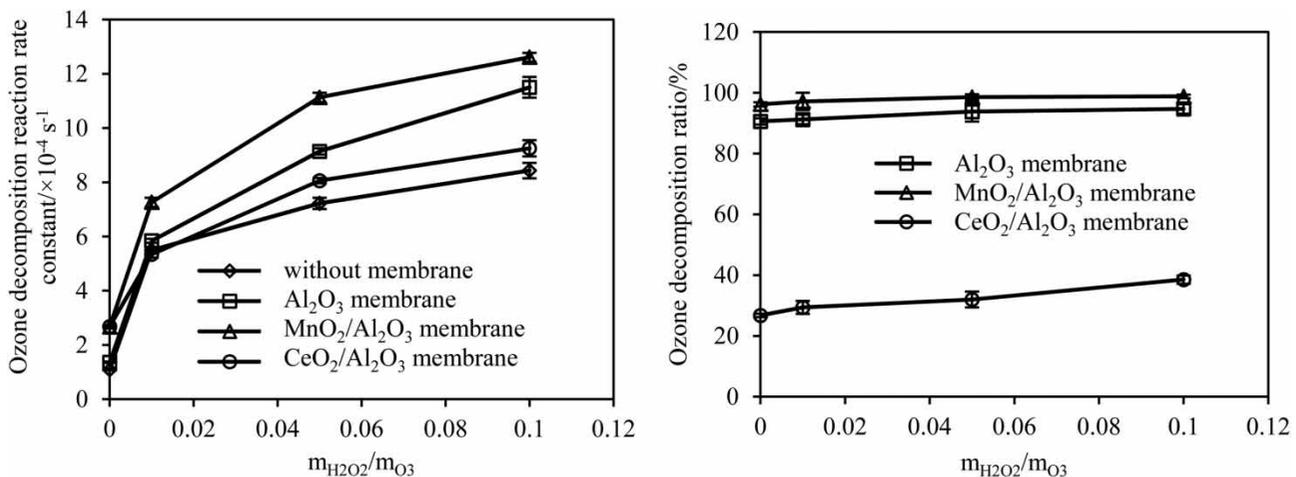


Figure 5 | Effect of H<sub>2</sub>O<sub>2</sub> dosage on ozone decomposition catalysed by membrane surface (left) and membrane pore (right).

## Effects of ions on ozone decomposition

Figure 6 shows the results of ozone decomposition affected by inorganic ions such as  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  in the testing system. For  $\text{Al}_2\text{O}_3$  or  $\text{MnO}_2/\text{Al}_2\text{O}_3$  membranes in the pure water tank, it was found that the ozone decomposition got improved significantly with the addition of  $\text{Ca}^{2+}$  compared with the situation of  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$ , almost two times higher. Relatively, the influence of ions on  $\text{CeO}_2/\text{Al}_2\text{O}_3$  membrane was very limited.

When monitoring the influences of these ions on the ozone decomposition inside the membrane pores, it was surprising that the effect of  $\text{Ca}^{2+}$  became a little bit lower than  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$ . For the case of  $\text{CeO}_2/\text{Al}_2\text{O}_3$  membrane, the addition of  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$  can help improve the ozone decomposition inside the pores of ceramic membrane.

## Discussions based on nano-reactors

The experimental results indicated that the ozone decomposition proceeded much faster inside the membrane pores, where the membrane porous interface played a major catalytic role, than in the membrane tank. The volume of water occupying the membrane pores was 6 ml. The time of water through the membrane pores was 35.29 s at permeate flux of  $60 \text{ L/m}^2 \cdot \text{hour}$ . As in the results mentioned above, ozone concentration in the  $\text{MnO}_2/\text{Al}_2\text{O}_3$  membrane effluent was only  $0.079 \text{ mg/L}$  while it was  $4.877 \text{ mg/L}$  in the bulk solution. The ozone decomposition reaction rate constant was as high

as  $0.1148 \text{ s}^{-1}$  catalysed by the matter inside the membrane pores and only  $2.68 \times 10^{-4} \text{ s}^{-1}$  in the bulk solution catalysed by the matter on the membrane surface. The diameter of the porous channel is  $50 \text{ nm}$  in the membrane layer with a thickness of  $12 \mu\text{m}$ , and the correspondent specific surface area in the porous channel was  $8 \times 10^7 \text{ m}^2/\text{m}^3$  water. The diameter of the membrane pores in the support layer is  $200 \text{ nm}$  to  $6 \mu\text{m}$  with a thickness of  $1.5 \text{ mm}$ , while the related specific surface area is  $3 \times 10^5$  to  $2 \times 10^7 \text{ m}^2/\text{m}^3$  water. Comparatively, the specific surface area of membrane modules in the bulk water is less than  $100 \text{ m}^2/\text{m}^3$  water in this study. Therefore, the ceramic membranes tested in this paper provide a tens of thousands times larger interface inside pores than an outside flat surface for ozone decomposition.

Ozone decomposition in pure water involves a chain of reactions as the following (Masschelein 1992).

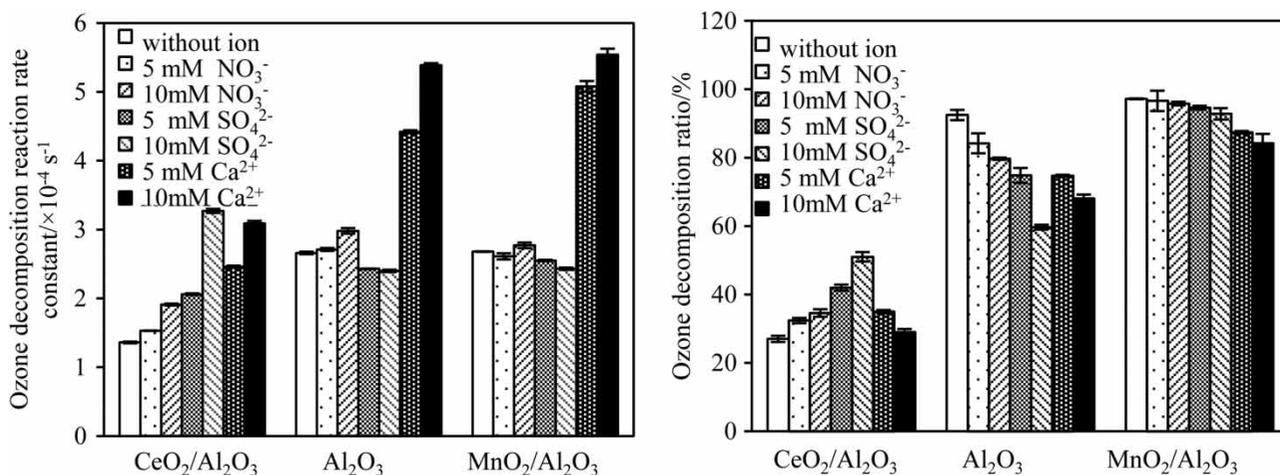
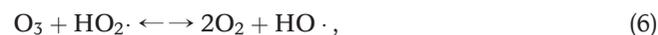
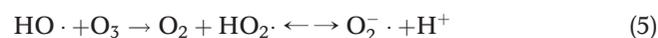


Figure 6 | Effects of typical ions on ozone decomposition on the membrane surface (left) or inside the membrane pores (right).

where reactions (1) and (2) are the ignition steps of the chain reactions. It is reported that the specific reaction rate of reaction (1) is  $1.1 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$ , which is 636 thousand times slower than that of reaction (2) as  $70 \text{ mol}^{-1} \text{ L s}^{-1}$ . Thus, ozone reacting with  $\text{OH}^-$  would be the major route for ozone decomposition. This is helpful in understanding the data shown in Figure 4; that is, enhancing the pH values will provide more  $\text{OH}^-$ , thus directly driving ozone decomposition in water.

The mechanisms of  $\text{MnO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{CeO}_2$  catalysing ozone decomposition in water might be indirectly related with hydroxyl ion (Kasprzyk-Hordern *et al.* 2003). As reported by Andreozzi *et al.* (1996), the pH value of point of zero charge for  $\text{MnO}_2$  is 2.8–4.5 or 5.6.  $\text{MnO}_2$  exhibits a negative surface charge that can provide potential  $\text{OH}^-$  ions on its surface within pH range from 5 to 11 (Ma & Graham Nigel 1999). Many studies have proved that ozone decomposition takes place on the surface of  $\text{Al}_2\text{O}_3$  particles through hydroxyl interaction, which leads to increased efficiency for the removal of organic matter (Cooper & Burch 1999; Qi *et al.* 2008). For cerium oxide, it was reported that anions such as  $\text{O}_2^-$  and  $\text{HO}_2^-$  are easy to be adsorbed on cerium oxide. Thus, ozone decomposition was slowing down (Zhang *et al.* 2006; Pinheiro da Silva *et al.* 2010; Orge *et al.* 2011).

The influence of  $\text{H}_2\text{O}_2$  might be related to hydroxyl radical instead of hydroxyl ion, according to the following reactions (Neta *et al.* 1988).



$\text{HO}\cdot$  or derived  $\text{O}_2^- \cdot$  in the presence of  $\text{H}_2\text{O}_2$  would transform more  $\text{O}_3$  molecules into  $\text{O}_2$  directly.

Inside the porous channels of the ceramic membranes tested in this paper, the ozone decomposition behaved quite differently from that in bulk water. Space limit or specific surface enlargement can partially explain the speeding up of ozone decomposition, as shown in Figure 3. Chain reaction mechanisms with  $\text{O}_3$  alone or with  $\text{H}_2\text{O}_2$  together

can partially explain the influence of pH and  $\text{H}_2\text{O}_2$  on ozone decomposition, but not all. Finally, the unusual impact of inorganic ions such as  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  cannot be explained even reluctantly.

These phenomena may be attributed to the special configurations of membrane pores as nano-reactors. Some researches revealed that double layers of zeta potentials and molecular clusters of water phase in the porous channels are substantially different from the bulk water in the membrane tank. Due to the diameter of porous channels being on the scale of nano-meters, the double layers of zeta potentials on the interface of pores wall may have overlapped (Skulzacek *et al.* 2007; Bruni & Bandini 2009), thus any ions that enter into the membrane pores may insert into inner Helmholtz layers or even Stern layers, therefore, their behaviour may change totally differently to that in the bulk water.

In nano-scale channels, highly ordered clusters of water molecules will be very important in the transferring of reactionary electrons (Mulvaney *et al.* 1990; Fricke & Huttenrauch 1991; Meisel *et al.* 1991; Karmazina *et al.* 2005). It can be reasonably imagined that any hydrated ions such as  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  may change the structures of water clusters, and then result in unusual process behaviours.

It is believed that the influences of pH (hydroxyl ion),  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$  as well as  $\text{H}_2\text{O}_2$  on ozone decomposition are closely related with the configuration of nano-pores, including zeta-potential double layers and water molecule-clusters. The configuration of nano-reactors might be critical to the *in situ* control of membrane fouling and the oxidative degradation of organic pollutants. Further mechanisms or kinetics need to be explored in the future.

## CONCLUSIONS

Ozone decomposition in pure water is improved with submerged ceramic membranes. Mixed  $\text{MnO}_2/\text{Al}_2\text{O}_3$  ceramic membrane has better performance of ozone decomposition than  $\text{Al}_2\text{O}_3$  or  $\text{CeO}_2/\text{Al}_2\text{O}_3$ . pH value is a dominant factor that influences the ozone decomposition in the pure water with the ceramic membranes tested. Ozone decomposition is improved by hydrogen peroxide, but is inhibited by anions such as  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . The ozone decomposition

rate is enhanced drastically inside the membrane pores compared with that in the bulk phase, about 428 times faster in the case of  $\text{MnO}_2/\text{Al}_2\text{O}_3$  membranes. Specific configurations inside membrane pores as nano-reactors were proposed based on water clusters and double layers of zeta potentials. It is believed that the catalytic ozonation inside the membrane pores would be critical for the alleviation of membrane fouling and the more efficient degradation of organic pollutants inside the membrane pores. Further studies are needed on the reactions of ozone with organic matter inside the membrane pores.

## ACKNOWLEDGEMENTS

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