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Dual function filtration and catalytic breakdown of organic pollutants in wastewater using ozonation with titania and alumina membranes

Dual function filtration and catalytic breakdown of organic pollutants in wastewater using ozonation with titania and alumina membranes

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ABSTRACT

Water recycling via treatment from industrial and/or municipal waste sources is one of the key strategies for resolving water shortages worldwide. Polymer membranes are effective at improving the water quality essential for recycling, but depend on regular cleaning and replacement. Pure ceramic membranes can reduce the cleaning need and last significantly longer in the same applications whilst possessing the possibility of operating in more aggressive environments not suitable for polymers. In the current work, filtration using a tubular ceramic membrane (α-Al$_2$O$_3$ or TiO$_2$) was combined with ozonation to remove organic compounds present in a secondary effluent to enhance key quality features of the water (colour and total organic carbon, TOC) for its potential reuse.

'Bare' commercial α-Al$_2$O$_3$ filters (pore size ~0.58 μm) were tested as a microfiltration membrane and compared with the more advanced catalytically active TiO$_2$ layer that was formed by the sol-gel method. The presence of anatase with a 4 nm pore size at the membrane surface was confirmed by X-ray diffraction (XRD) and N$_2$ adsorption. Filtration of the effluent over a 2 hour period led to a reduction in flux to 45% and 60% of the initial values for the α-alumina and TiO$_2$ membrane, respectively. However, a brief dose (2 mins) of ozone at the start of the run resulted in reductions to only 70% of the initial flux for both membranes. It is likely that the oxide's functional property

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facilitated the formation of hydroxyl (OH$^{\bullet}$) or other radicals on the membrane surface from ozone decomposition which targeted the breakdown of organic foulants thus inhibiting their deposition. Interestingly, the porous structure therefore acted in a synergistic, dual function mode to physically separate the particulates whilst also catalytically breaking down organic matter. The system also greatly improved the efficiency of membrane filtration for the reduction of colour, A$_{254}$ (organics absorption at the wavelength of 254 nm) and TOC. The best performance came from combined ozonation (2 min ozonation time with an estimated applied ozone dose of 8 mg L^{-1}) with the TiO$_2$ membrane, which was able to reduce colour by 88%, A$_{254}$ by 75% and TOC by 43%. It is clearly evident that a synergistic effect occurs with the process combination of ozonation and ceramic membrane filtration demonstrating the practical benefit of combining ceramic membrane filtration with conventional water ozonation.

1. Introduction

Water has become a scarce resource in many countries, and the demand for treating and reusing poor quality water sources such as wastewater effluent has greatly increased over the last 10 years. There are significant opportunities to reuse a larger amount of this treated wastewater, and some juristictions have set recycled water targets. Many identified uses of water do not require treatment to drinking water standard, and the use of recycled water for non-drinking purposes is a net benefit to the community and a minimisation of detrimental discharges to the environment. Through the development of improved purification processes, practices of water reuse have also become more technically feasible [1]. However, barriers to the reuse of the treated wastewater exist. While the majority of organic material (measured as Biochemical Oxygen Demand, BOD or Chemical Oxygen Demand, COD) and other contaminants are readily removed by biological treatment in wastewater treatment plants (WWTPs), the treated wastewater still contains contaminants which may adversely affect human or environment health, or be aesthetically unappealing (i.e. odorous or visually unattractive). For example, colour and non-biodegradable trace organics present in the treated wastewater from WWTPs have a negative impact on public acceptance of recycling. Therefore, further treatment is often required for the treated wastewater from WWTPs to make the 'water fit for purpose'.

The application of membrane filtration for the reuse of municipal WWTP effluent has dramatically increased over the past decade. Historically, the use of membrane filtration for water and wastewater treatment has been almost exclusively focused on polymer membranes [2]. One of the major challenges associated with the operation of membrane filtration plants is an increase in the operational costs as a result of the decrease in the specific permeate flux due to membrane fouling caused by the deposition of contaminants such as natural organic matter (NOM) [3, 4]. Commercial polymer filtration membranes also degrade when exposed to extreme acidic or alkaline environments [5], or extreme oxidising conditions created by the presence of chlorine or ozone [6].

Ceramic membranes have the combined advantage of high chemical, mechanical and thermal resistance, making them suitable for high temperature, extreme acidity or alkalinity, and high pressure operations where these conditions preclude the use of existing polymeric membranes. An advantage of ceramic membranes is that the pore size can be easily controlled by the sintering and the sol gel processes used in their manufacture [2]. In addition, ceramic membrane performance can often be enhanced by innovative cleaning methods such as ozonation in tandem with existing ozonation of the water. Ceramic membranes such as titania, zirconia, γ-alumina, and silica/γ-alumina have been studied for separation of ions from aqueous solutions by nanofiltration [7-11]. Titania membranes have also been studied for water treatment by several research groups [12-15]. Recently, a commercial ceramic membrane module from NGK Insulators, Ltd. (Japan) was trialled in water microfiltration [16]. These modules have an active surface area of 25 m^2 for permeation and have been operated in dead-end filtration mode through 2000 channels that have a 0.1 μm separation layer. They have been shown to operate at significantly higher flux than polymeric membranes when combined with the ozone treatment of wastewater [16]. Futhermore, recent advances in module design make them cost competitive with polymeric membranes [17].

Ozone is a strong oxidiser having high reactivity with organic compounds and has been used for various aspects of water treatment. Ozone can oxidize organic matter that is understood to be responsible for the fouling of membranes [18]. Ozonation has been successfully used at full scale and can be combined with other advanced oxidation processes such as photocatalysis for the degradation of organic substances [19-21]. Several studies have investigated the combination of ozonation and membrane processes using polymeric membranes [12], but the poor stability of polymeric membranes when exposed to ozone [6] has made this process unviable. To realise the benefit of combined oxidation processes incorporating membranes and to overcome issues of membrane degradation, some

researchers have investigated the combination of ozonation and ceramic membranes for water or wastewater treatment [12, 13, 16]. Their results have demonstrated a high permeate flux without membrane damage, but further investigation of the improvement in quality to real waters coupled with the use of membranes designed to have catalytically active surfaces is still in need to demonstrate this promising process, as undertaken in this study.

In this study, a TiO_2 membrane was prepared by applying TiO_2 nanoparticles to a tubular α-Al_2O_3 support using a dip-coating method. The prepared membrane was used with ozonation to treat the wastewater from a major WWTP to reduce colour and trace organics, and therefore improve the clarity of water for reuse. The effects of ozone on the permeate flux and efficiency of the process for the improvement to critical features of water quality (colour, A_{254}, TOC) were also investigated.

2. Experimental and methods

2.1 Materials

The water source used for this study was secondary effluent (non-chlorinated), sampled from one of Melbourne's WWTPs by the authorized operator. The effluent characteristics are shown in Table 1. The molecular weights of the colour-causing organic compounds in the effluent sample were in a wide range, i.e. 400–10,000 Daltons [22]. For the membrane preparation, titanium butoxide ($Ti(OC_4H_9)_4$, 97%) was purchased from Aldrich. Ethanol (Ajax Finechem, Australia) and nitric acid (68.5–69.5 wt%, BDH Chemicals, Australia) were also used. All these chemicals were used as received without further purification. Ceramic tubes (α-Al_2O_3, external diameter 14 mm, length 90 mm, ~0.58 μm nominal pore size, ~22.4 vol% apparent porosity) and discs (99.8% Al_2O_3, ~25 mm diameter × 2 mm thick, 0.5–1 μm pore size, ~30 vol% porosity) used for the current work were supplied by Chosun Refractories Co., Ltd. Korea (tubes), and Rojan Advanced Ceramics Pty Ltd (discs), Australia, respectively.

Table 1

Typical characterization of WWTP non-chlorinated effluent sample

Parameter	Value
pH	6.8
True colour, Pt-Co Units	110
A_{254} (UV absorption), cm^{-1}	0.37
TOC (total organic carbon), mg L^{-1}	13.9

2.2 Preparation of TiO$_2$ membrane

The TiO$_2$ membranes used for this study were prepared by depositing polymeric titania sol on the α-Al$_2$O$_3$ tube or Al$_2$O$_3$ disc using a dip-coating method. The titania sol coated α-Al$_2$O$_3$ tube and Al$_2$O$_3$ disc were calcined in air at 400 ºC for 1 h with a temperature increase/decrease rate of 0.1 ºC min^{-1}. To avoid crystallisation of amorphous titania by rapid drying, the coated tube and disc were dried under ambient conditions for a period of 24 h before calcination. Polymeric titania sol was prepared by mixing 34 mL titanium butoxide, 45 mL ethanol, 1.6 mL nitric acid and 2.6 mL deionised water (DI water) whilst vigorously stirring. The size of nanoparticles in the prepared polymeric titania sol was measured at around 4 nm by a Zetasizer (Malvern Instruments-Nano-series with cell type DTS0012 disposable sizing curvette, the dispersant chosen was ethanol with viscosity 1.1 cP and a refractive index of 1.33 at a temperature of 25 °C). The sol was sealed in a 100 mL glass flask and aged at room temperature for at least 24 h prior to deposition. The unsupported TiO$_2$ membrane used for characterisation was prepared by drying the same titania sol in a Petri dish to form a gel layer. The obtained gel layer was then calcined using the same procedures as those used for the supported membrane.

2.3 Characterisation

The prepared unsupported TiO$_2$ membrane was characterised by N$_2$ adsorption and XRD. The TiO$_2$ membrane disc was also characterised by XRD. The N$_2$ adsorption experiments were carried out using a Tri Star 3000 porosity analyser (Micromeritics, USA) at liquid N$_2$ temperature on the unsupported TiO$_2$ membrane sample degassed for 4 h at 150 °C. XRD measurements were performed on a Bruker-AXS D2 Phaser Desktop X-ray Diffractometer (CuKα, λ = 1.5406 Å) with a Lynx-Eye detector from 10 degrees to 60 degrees two theta with a 0.05 degree step and an 91 second per step counting time. Zeta potential measurements were conducted on the same Zetasizer used for the particle size measurements. The powders ground from a new α-Al$_2$O$_3$ tube and the unsupported TiO$_2$ membrane were dispersed in DI water (pH is close to that of the feed water) and the suspensions were treated in an ultrasonic bath (U-lab Instruments, Australia) for 1 h. pH values of the Al$_2$O$_3$ and TiO$_2$ suspensions were measured at 6.16 and 6.20, respectively. Suspension samples were then measured at 25 °C and results were reported as the average of three measurements, each an average of 100 runs.

2.4 Apparatus and procedures

 The bench ozonation-membrane filtration system with a tubular membrane (Al_2O_3 or TiO_2) used in this study is illustrated in Figure 1. For the filtration experiments, a peristaltic pump (Masterflex 77200-62, Cole-Parmer, USA) (number 2 in Fig. 1) was employed to circulate effluent from the feed vessel (number 1 in Fig. 1) through the membrane module (number 6 in Fig. 1) at a flow rate of 50 mL min^{-1}. A magnetic stirrer at the bottom of the vessel was used to mix the water sample. The filtration direction occurred from the inside to outside of the membrane, and a cross flow velocity of 0.01 m s^{-1} was maintained through the experiments. A constant pressure of 50 kPa-g was also maintained through the experiments via the valve (number 5 in Fig. 1). The permeate flowed from the membrane into a beaker (number 7 in Fig. 1) beneath the membrane, and the amount of permeate was monitored by a balance (FX-3000iWP, A&D Mercury Pty. Ltd., Australia). The weight was recorded by a computer with A&D WinCT software. After 4 h filtration, the fouled ceramic tube was backwashed for 10 min. The backwashing was operated by closing the valve (number 5 in Fig. 1), immersing in DI water (number 8 in Fig. 1) and reversing the peristaltic pump to apply a vacuum to the inside of the membrane tube via the open end of the tube. Table 2 summarises the operating conditions used for permeate testing and backwashing.
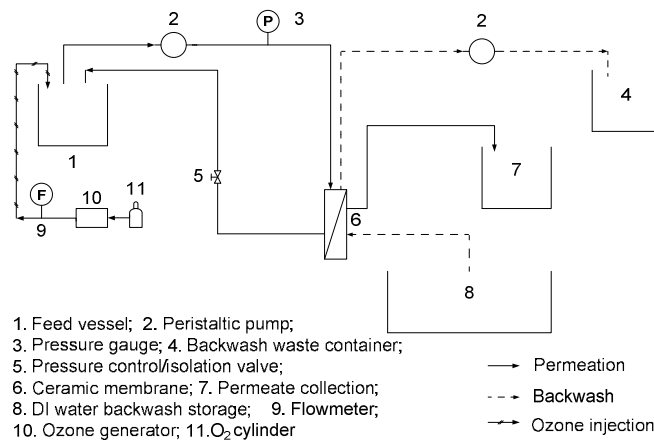

1. Feed vessel; 2. Peristaltic pump;
3. Pressure gauge; 4. Backwash waste container;
5. Pressure control/isolation valve;
6. Ceramic membrane; 7. Permeate collection;
8. DI water backwash storage;   9. Flowmeter;
10. Ozone generator; 11.O_2 cylinder

— Permeation
- - - Backwash
— Ozone injection

Fig. 1. Schematic of the ozonation-membrane filtration system.

Table 2

Operating conditions used for permeate testing and backwashing

Initial volume of water sample	2 L
Feed circulation flow rate	50 mL min^{-1}
Transmembrane pressure	50 kPa-g
Pressure for backwash	~–100 kPa-g
Ozone input flow rate under normal temperature and pressure (NTP)	0.4 L (NTP) min^{-1}
Ozone injection time	2–10 min (8–40 mg L^{-1})[a]
Backwash time	10 min

[a]Estimated applied ozone doses are in the parenthesis.

Ozone was generated from pure oxygen by an ozone generator (SOZ-6G, A2Z Ozone Systems INC., USA) (number 10 in Fig. 1) with an ozone production capacity of 6 g h^{-1}. The production of ozone used for this study was set at 4.8 g h^{-1} with an oxygen flow rate of 4 L (NTP) min^{-1}. The ozone input flow rate for treatment of effluent samples was 0.4 L (NTP) min^{-1}. During ozonation-filtration treatment, ozone was bubbled into the water sample in the feed vessel upon commencing filtration for a range of times (typically 2, 6 or 10 minutes), through a porous diffuser. Since not all ozone that is injected to the water is transferred into the liquid phase, "applied ozone dose" was used to describe the ozone dosage in this study. The applied ozone dose is the quantity of ozone added but not necessarily transferred to the water, and is calculated as follows [23]:

$$D = O/V \qquad (1)$$

where

D = applied ozone dose (mg L^{-1})
O = quantity of ozone added (mg)
V = volume of water (L)

In the current work, quantity of ozone added (O) can be estimated as follows:

$$O = ((P \times F_o)/F_g) \times T \qquad (2)$$

where

P = production of ozone from the ozone generator = 4.8 g h^{-1}

F_g = gas flow rate of the ozone generator = 4 L (NTP) min^{-1}

F_o = ozone input flow rate = 0.4 L (NTP) min^{-1}

T = ozonation time (min)

The applied ozone doses used in this study were estimated according to equation (2), and the corresponding values for ozonation time of 2 min, 6 min and 10 min were approximately 8 mg L^{-1}, 24 mg L^{-1}, and 40 mg L^{-1}, respectively. All the experiments were carried out at room temperature. The permeate samples were collected for analysis.

2.3 Water sample analysis

True colour and A$_{254}$ were measured by a spectrophotometer (HACH DR5000, USA) using the standard methods provided by HACH. Platinum-Cobalt Standard Method (Method 8025, HACH) was used in the current work for true colour measurements and reported as true colour (Pt-Co units). The presence of organic constituents in the water sample is indicated by measuring the absorption of the sample at a wavelength of 254 nm against organic-free water as blank (A$_{254}$-UV absorbing, Method 10054, HACH). Results are reported in absorbance per centimeter (cm^{-1}). The total organic carbon (TOC) was determined by a TOC-Vcsh TOC analyser (Shimadzu, Japan).

3. Results and discussion

3.1 Properties of TiO$_2$ materials

The surface and bulk properties of titania, such as purity, surface area and porosity are critical to membrane performance. It is known that an anatase crystal phase of high purity, small crystallite size, high surface area and porosity and narrow pore size distribution is very important for its functions of separation and catalytic activity [14]. For example, TiO$_2$ with an active anatase structure generally exhibits higher photocatalytic activity than those with other types of structures such as rutile and brookite [24-26], and crystallite size ranging from 8 to 10 nm is known to be optimum for high catalytic activity [27]. The surface and bulk properties of the TiO$_2$ materials prepared in this study have therefore been investigated in detail using N$_2$ adsorption and XRD.

3.1.1 N₂ adsorption

The N_2 adsorption/desorption isotherms (Fig. 2a inset) for the unsupported TiO_2 membrane appeared to be a typical type-IV, indicating that the sample is mesoporous in nature [28, 29]. A type H2 hysteresis loop that closes at a relative pressure, p/p^0, of around 0.4 is associated with capillary condensation occurring in mesopores and indicated that this mesoporous material consisted of spherical particles with an "ink bottle"-type pore shape [29]. BET specific surface area and pore volume of the unsupported TiO_2 membrane sample were found to be around $46.4 \, m^2 \, g^{-1}$ and $0.057 \, cm^3 \, g^{-1}$, respectively. It has been reported that the surface areas of TiO_2 samples synthesised by sol-gel methods are much higher than that of the ones prepared by the solvothermal method [30, 31]. In general, it is well known that TiO_2 particles with anatase phase prepared via the sol-gel process possess a surface area of about $60 \, m^2 \, g^{-1}$ [32]. The surface area of Degussa P25, which is widely known as a commercial TiO_2 photocatalyst, was reported to be around 50–$75 \, m^2 \, g^{-1}$ [32-34]. The BET surface area measured in this study for the unsupported TiO_2 membrane is close to the range reported in literature.
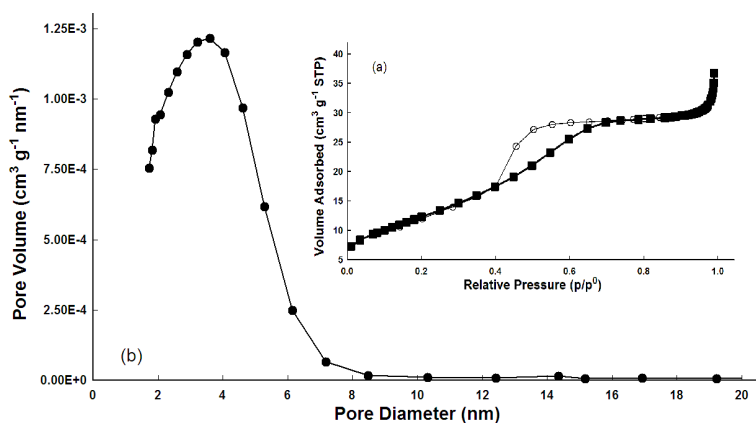

Fig. 2. (a) Adsorption/desorption isotherms and (b) BJH pore size distribution of unsupported TiO_2 membrane.

It is known that the particle size of the starting material has a great impact on the resulting pore size of filtration membranes [35]. Consequently, different preparation routes will result in significant differences in pore size of the filtration layers. In literature, unsupported membranes are commonly characterised by N_2 adsorption to estimate the pore size of the supported membranes [35-37]; a method

also used in this study. Figure 2b shows the BJH pore size distribution curve of the unsupported TiO_2 membrane sample calculated from the adsorption curve. It was found that the unsupported TiO_2 membrane had a relatively narrow pore distribution, ranging from 2 to 8 nm with a maximum at around 4 nm. The average pore size of 4.28 nm, obtained from the adsorption curve, was similar to the desorption curve value of 3.86 nm , indicating a homogeneous pore structure [14].

3.1.2 XRD

To determine the crystal structure of the tubular TiO_2 membrane, unsupported TiO_2 membrane and disc shape TiO_2 membrane samples prepared using the same procedures as those used for preparation of the tubular TiO_2 membrane, were analysed by XRD. The XRD pattern obtained for the disc shape TiO_2 membrane sample is shown in Figure 3. The XRD pattern of the unsupported TiO_2 membrane sample is also included in Figure 3 for comparison. The powder diffractograms revealed that the unsupported TiO_2 membrane sample used in the current work appeared to be anatase in nature (major peaks at around 25.2°, 37.8°, 47.9°, and 54.5° 2θ). While no reference samples were run to assist in a crystallite size determination, the somewhat broad nature of the peak was suggestive of a small crystallite size. The diffractogram for the disc sample showed predominantly α-Al_2O_3 peaks (major peaks at around 25.6°, 35.1°, 37.8°, 43.4°, 52.6°, and 57.5° 2θ). There was however evidence of a broad peak at 25.2° (2θ) seen as a shoulder to the peak at 25.6° (2θ), the position of the strongest anatase peak. There was also a possibility of an overlay between α-Al_2O_3 and TiO_2 peaks at a 2θ of 37.8°. Choi and co-workers [38] have reported that at least seven coatings (~0.7 μm) were needed for the anatase crystal peak (101) to be clearly identified by XRD. The coating method (four coatings) used here should provide only a very thin coverage of titania that would not be easily detected with XRD due to the small amount of TiO_2 material on the substrate. However, the appearance of the broad peak at 25.2° (2θ) seemed to confirm the presence of a very thin film of the crystalline anatase on the α-Al_2O_3 surface.
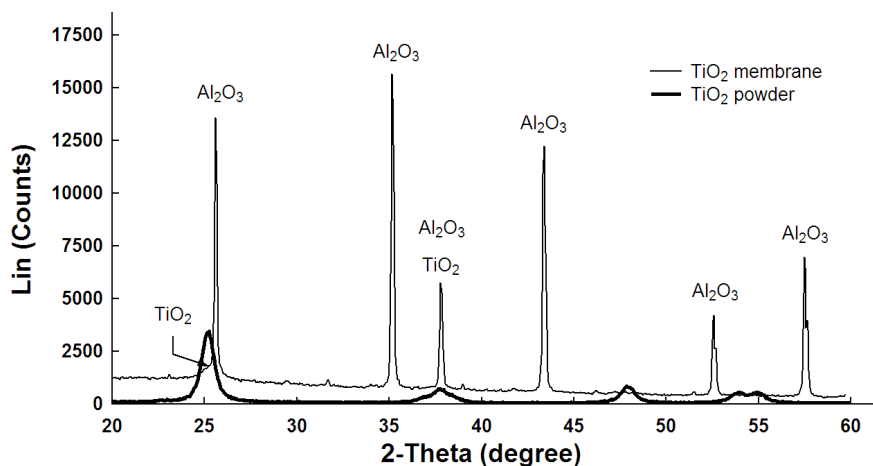
Fig. 3. XRD patterns of TiO_2 coated Al_2O_3 disc and unsupported TiO_2 membrane samples.

Successful use of ceramic membranes in practical applications strongly depends on the preparation of good quality membranes with the desired pore size and pore structure. The sol-gel process is one of the techniques most commonly used to produce high quality and tailor-made ceramic membranes. Particle size is one of the most important aspects of sol-gels [39]. The pore size of membranes is dictated by the size of the particles in the sol used for membrane fabrication [40]. To obtain a titania membrane with optimum properties, the titania sol should have narrow particle size distribution [41]. In the current work, a titania sol with small nanometer-sized particles (measured at 4 nm by a Zetasizer) was synthesised through a controlled hydrolysis reaction. The results obtained from N_2 adsorption and XRD confirmed that the prepared polymeric titania sol has good potential for its application in fabricating TiO_2 membranes.

3.2 Membrane filtration water treatment

The filtration experiments were carried out under permeate testing and backwashing conditions as listed in Table 2. Fresh feed water was used for each permeate test. A cross flow velocity of 0.01 m s^{-1} was maintained through the experiments which was practically very slow compared to those (0.1–7 m s^{-1}) reported in literature for a variety of applications [42-44]. It is well known that using a higher cross flow velocity can reduce membrane fouling, thus maintaining a higher flux, but the influence of cross flow velocity varies with membrane types and the filtration unit used [42, 44]. A low cross flow velocity was used in this study to achieve maximum membrane fouling so as to explore the effects of DI water backwash and ozonation on permeate flux. Prior to the filtration experiments on wastewater,

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the membranes were tested using DI water and the permeate flux of DI water for Al_2O_3 (79 L m^{-2} h^{-1}) and TiO_2 (90 L m^{-2} h^{-1}) obtained from the testing was used as a benchmark for non-fouling filtration. The results showed that the TiO_2 membrane had a slightly higher pure water flux than the Al_2O_3 membrane. There is no clear explanation for this at this stage as intuitively the coated membrane having a smaller pore size should have a lower flux. However, this indicated that both membranes could treat a similar amount of water in the same time, which allowed for better comparability of the results obtained from the filtration experiments. Flux of pure water for both Al_2O_3 and TiO_2 membranes was relatively constant for 2 hours, but upon the introduction of wastewater it was found that there was a decrease in the permeate flux during filtration for both Al_2O_3 and TiO_2 membranes (Fig. 4). This indicated that significant membrane fouling occurred during filtration. Both membranes showed a sharp decrease to 70% of initial flux within 20 min of filtration. The permeate flux for Al_2O_3 membrane decreased continuously to about 38% of its initial value within 4 h of operation, while the flux for TiO_2 membrane decreased gradually to around 53% of its initial value over the same testing time (0–4 h in Fig. 4), suggesting that the TiO_2 membrane had better anti-fouling ability than the Al_2O_3 membrane under normal filtration.
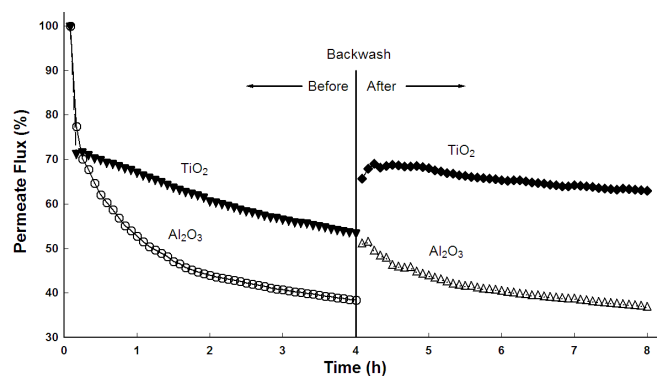

Fig. 4. Permeate flux recovery with DI water backwash (Operating conditions provided in Table 2).

It is understood that many factors affect membrane fouling. The main parameters studied include membrane structure parameters (surface roughness, porosity, size and shape of pores and pore size distribution) and membrane/effluent coupling parameters (membrane material, hydrophobicity and surface charge, etc.) [45]. Differences in fouling behaviour between Al_2O_3 and TiO_2 membranes observed in this study may be largely attributed to their different pore size, surface roughness, surface chemistry and microstructure.

Larger pore-sized and smaller pore-sized membranes are suggested to have different fouling mechanisms [46]. Larger pore-sized membranes have higher fouling potential [46-48] and are more difficult to clean after fouling than smaller pore-sized ones [47]. The pore size of the prepared unsupported TiO_2 membrane (~0.004 μm) was much smaller than that of the Al_2O_3 membrane (~0.58 μm). The supported membrane could have an even smaller effective pore size due to the capillary forces from the ceramic tube acting on the sol during drying [49]. The polymeric sol-gel route used in this study has demonstrated the ability to produce filtration layers with less than 2 nm pores which have a molecular cut-off < 1,000 Dalton [35]. The water sample use for this study was secondary effluent from one of Melbourne's WWTPs, which contains not only the organic compounds with a molecular weight range of 400–10,000 Daltons as mentioned previously, but also visible particulate contamination. These particulates and the organic compounds with relatively large molecular weights caused the significant fouling on both Al_2O_3 and TiO_2 membranes, thus resulting in a reduction in permeate flux. For the filtration process with the TiO_2 membrane, it is most likely that these particulates and organic compounds predominantly deposit on the membrane surface due to the small pore size of the membrane and the relative ease of removal during cross-flow operation. Some particulates did however accumulate, forming a fouling layer on the membrane surface (i.e. cake filtration), and caused a gradually decrease in permeate flux during the filtration process. During filtration with the Al_2O_3 membrane, the particulates and large organic compounds present in the effluent sample not only accumulated on the membrane surface, but also have the potential to enter larger membrane pores (~0.58 μm) (i.e. pore constriction) and could not be easily removed by the cross-flow operation, thus resulting in a more significant reduction in permeate flux compared to that with the TiO_2 membrane (~0.004 μm on the dry material) over the same operation time.

The relatively smooth surface of the TiO_2 membrane is also likely to have improved its fouling-resistant ability. The influence of surface roughness on membrane fouling has been studied, and it is well understood that membranes with smoother surfaces have higher anti-fouling ability [46, 50-52]. Vrijenhoek and co-workers [50] found that more particles were deposited on the membranes with rough surfaces than on those having smooth surfaces at the initial stages of fouling. The preferential accumulation of particles in the "valleys" of rough membranes resulted in "valley clogging", which caused a more significant decline in flux than smooth membranes. They also considered that surface roughness was the most effective parameter on the anti-fouling ability of membranes independent of

operating conditions. It is known that coating with TiO_2 could significantly reduce the surface roughness of the membrane [53, 54], thus improving membrane anti-fouling capability.

Apart from pore size and surface roughness of the membrane, other parameters such as surface charge and hydrophilicity of the materials would also affect the fouling tendency of the membranes. Hydrophilic membranes are known to be more fouling tolerant due to the presence of electrostatically charged surface groups. Surface charge properties of the membranes have also attracted great attention as electrostatic interactions during filtration of charged particles are very important for understanding the separation properties of membranes [35]. The zeta potential of the membranes showed that the surface of the Al_2O_3 membrane (zeta potential +6.4 mV at pH = 6.16) was positively charged and would attract negatively charged groups associated with the organics. However, the surface of the TiO_2 membrane was negatively charged (zeta potential –31.3 mV at pH = 6.20), which could attract positively charged groups associated with the organics. Work by Jucker and Clark has suggested that most NOM is negatively charged [55] and negatively-charged surface tend to result in lesser adsorption of these compounds. If this were the case then in this work the negative surface charge of TiO_2 would lead to a surface that is less likely to foul than the positively charged Al_2O_3. This was ultimately seen during the experiment.

After the filtration experiments, the fouled ceramic membranes were backwashed with DI water for 10 min, followed by another 4 h filtration of fresh effluent sample (4–8 h in Fig. 4). It was found that the permeate flux for the Al_2O_3 membrane recovered to approximately 50% of its initial flux value after DI water backwash, and decreased to a similar value to that before backwashing after 4 h operation on fresh effluent sample. The TiO_2 membrane recovered its permeate flux to around 70% of the initial flux value after 10 min DI water backwash, and only showed a small decrease (around 7%) over another 4 h filtration of fresh effluent sample (4–8 h in Fig. 4). The results obtained indicate that backwashing the fouled ceramic membranes with DI water resulted in some improvement to performance of the membranes. Both membranes achieved a similar recovery (around 30%-points gained) in permeate flux from DI water backwash.

3.3 Combined membrane filtration and ozonation water treatment

3.3.1 Effect of ozone injection on permeate flux

Permeate testing with ozonation was conducted under the same conditions as those used above (Table 2). To explore the effects of residual ozone, a "single dose" was used in this work to apply ozone into the system at the beginning of the filtration instead of continuous ozonation during the whole period of filtration. At the beginning of the filtration, ozone was injected into the feed for 2 min at an input gas flow rate of 0.4 L (NTP) min^{-1}. The corresponding applied dose at the end of the ozone period was estimated to be approximately 8 mg L^{-1} which is within the range applied in ozonation pilot plants for disinfection of secondary and tertiary domestic effluents [56]. As mentioned previously in Section 2.4, the applied ozone is not necessarily fully transferred into the liquid phase. It is also well known that the solubility of ozone depends on the water temperature and the ozone concentration in the gas phase. The dissolved ozone concentration in DI water was measured at an applied dose of 8 mg L^{-1} by a HACH DR5000 spectrophotometer (Method 8025, HACH, USA), and the value was around 1.2 mg L^{-1}. This result was indicative only as the dissolved ozone concentration in DI water would change during sampling and analysis due to the short half-life time (the order of 500 s) of ozone [57, 58]. After each experiment, the ceramic membranes were cleaned with NaOH and HNO$_3$ solutions following the procedures used by Karnik et al. [12] prior to starting the experiment again. After cleaning, the permeate flux of DI water for each membrane was measured to ensure that the initial flux was the same in all experiments. During filtration, the feed was slowly concentrated and the remaining volume of the feed after 2 h filtration ranging from around 85% to 92% of the original volume depending on the process.

The trends in the permeate flux for Al$_2$O$_3$ and TiO$_2$ membranes under ozone injection conditions are shown in Figure 5. The permeate fluxes obtained without ozone injection for both membranes (Fig. 4 data) were overlayed in Figure 5 for comparison. As discussed above, it can be seen that as a result of fouling the permeate flux decreased significantly within 20 min of operation without ozone injection for both Al$_2$O$_3$ and TiO$_2$ (both decreased to 70% of initial flux) membranes. When ozone was applied however, the permeate flux for both ceramic membranes remained at a higher level during filtration, dropping to only 70% and 66% of the initial flux after 2 hours for the Al$_2$O$_3$ and TiO$_2$ membranes respectively. These results demonstrated that ozone injection at the beginning of filtration can substantially reduce the initial fouling, thus maintaining the permeate flux at a higher level. This is

mainly attributed to the oxidative degradation of organic pollutants in the water sample by direct attack of ozone [59] and/or OH$^\bullet$ or other radicals produced from the decomposition of ozone [12]. It is also known that the metal oxides commonly used for preparation of ceramic membranes such as alumina, titania and zirconia, have the ability to promote ozone decomposition and the formation of OH$^\bullet$ radicals [60, 61]. Also, ozonation has been shown to result in microflocculation of particles that can assist with filtration and sedimentation [62]. Large particulates would also reduce the occurrence of particles in the pores and increase their occurrence on the surface. This would lead to easier removal during cross-flow operation. Both membranes achieved a similar level of permeate flux under ozonation conditions. However, it was found that the addition of ozone was more beneficial for the Al$_2$O$_3$ membrane than the TiO$_2$ membrane to improve the permeate flux when compared to membrane filtration only. With the assistance of ozonation, the Al$_2$O$_3$ membrane achieved a 25–30%-point difference toward higher flux than that of membrane filtration only over 2 h filtration. The permeate flux of the TiO$_2$ membrane exhibited a 15–30%-point difference toward improved flux in the first 1 h in the presence of ozone, but only remained slightly higher than that of filtration only for the rest of the operation. From this it is likely that from the perspective of flux, that ozonation has a greater benefit to Al$_2$O$_3$ membrane performance, but it is important to keep in mind that the TiO$_2$ layer was inherently more tolerant to fouling due to surface charge and smoothness when exposed to this water and can be cleaned simply by backwash. Further investigation from here is therefore focused on the effect of ozone dose and the quality of the water in the permeate.
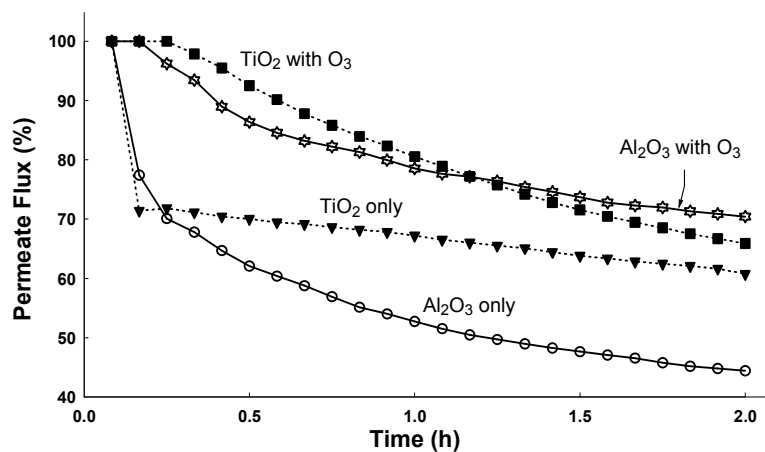

Fig. 5. Membrane permeate flux as a function of time and filtration processing conditions. Estimated applied ozone dose = 8 mg L^{-1}.

It was found that for the Al_2O_3 membrane, the permeate flux over 2 h filtration was higher when the applied ozone dose was increased (Fig. 6a). However, the TiO_2 membrane presented similar trends in permeate flux (Fig. 6b) at different applied ozone doses at the beginning of testing. There were no differences in the permeate flux between the estimated applied ozone doses of 8 mg L^{-1} and 24 mg L^{-1}. Only a slight increase in flux was observed when increasing the estimated applied ozone doses to 40 mg L^{-1}.
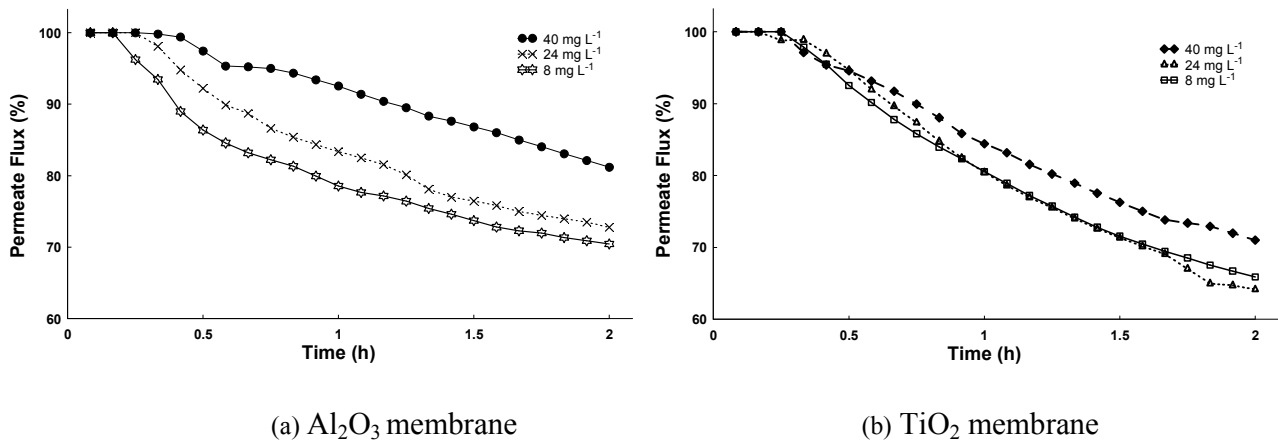

(a) Al_2O_3 membrane   (b) TiO_2 membrane

Fig. 6. Effect of ozonation on permeate flux of Al_2O_3 (a) and TiO_2 (b) membranes.

These results indicated that ozonation was more helpful for the improvement in the permeate flux of Al_2O_3 membrane. As discussed in Section 3.2, significant fouling occurred on the membrane during filtration without ozone mainly due to the deposition of the particulates and large organic compounds on the membrane surface as well as the pores of the membrane. Ozonation not only cleaned the Al_2O_3 membrane surface, but also reduced the accumulation of the particulates and large organic compounds in the pores of the membrane, thus greatly increasing the permeate flux. Increasing the applied ozone dose resulted in the formation of more OH$^{\bullet}$ or other radicals, which enhanced its efficiency in removal of organic foulants, and therefore significantly reduced membrane fouling. The TiO_2 membrane, however, had less accumulation of the particulates and large organic compounds on its surface. Only a small dose of ozone was needed to clean the membrane surface and increase the permeate flux. Increases of applied ozone dose, therefore, did not necessarily have a higher impact on the degree of the improvement in the permeate flux. Although the testing demonstrated a unique opportunity for ozone coupled filtration, testing the membranes with continuous ozone dosing and on-line monitoring is needed. This is the subject of our continued work in this area.

3.3.2 Effect of ozone injection on colour, A_{254} and TOC removal

In this study, the permeate was characterised by key water quality parameters including colour, A_{254} and TOC to assess the efficiency of the process. The influence of ozone injection on the efficiency of membrane filtration for colour, A_{254} and TOC removal was also studied. Colour is a useful index of dissolved humic substances in water, and is sometimes a concern because of aesthetic impacts on public acceptance of water recycling. The specific ultraviolet light absorption is a parameter indicating the quantity of unsaturated bonds contained in organic matter, the higher the quantity of unsaturated bonds, the higher the A_{254} absorbance [63].

The reductions of colour, A_{254} and TOC for the permeate samples obtained from different processes are compared in Figure 7. Ozonation conditions were the same as those used above for the permeate flux tests. Water samples used for analysis were withdrawn from the permeate collection tank after 2 h filtration (average permeate sample). As shown in Figure 7a, ozonation alone had a positive effect on colour removal. Around 39% of colour was removed from the feed water sample after 2 min of ozonation (estimated applied ozone dose of 8 mg L^{-1}). It should be noted that the effect of ozone on colour is highly dependent in the water source and the source of the colour in the water and this would be expected to vary from site to site. For example, in ozonation for drinking water treatment, an ozone dose of 4 to 5 mg L^{-1} can be used which reduces colour from 32–57 colour units to 1–4 colour units [23]. It was reported that ozonation removed more than 50% colour from the secondary effluent under UV radiation [19]. The combined membrane filtration with ozonation processes achieved much higher colour removal compared to the filtration treatments without ozone injection. For the Al_2O_3 membrane filtration without ozone injection, the colour removal was the lowest, with only about 10% colour removal after 2 h filtration. However, for the permeate test using the Al_2O_3 membrane with an assistance of 2 min ozonation (estimated applied ozone dose of 8 mg L^{-1}), approximately 68% of colour was removed after 2 h operation. Similar to the Al_2O_3 membrane, the TiO_2 membrane filtration in combination with ozonation achieved a very high level (around 88%) of colour reduction. These results indicated that filtration through a ceramic membrane with the assistance of ozonation has a potential for application in colour removal from treated effluent for water reuse.

Similar to the results of colour removal (Fig. 7a), A_{254} absorbance reduced significantly (nearly 22% reduction) within 2 min ozone injection (estimated applied ozone dose of 8 mg L^{-1}) (Fig. 7b). The value

of A_{254} reduction for the combined 2 min ozonation and 2 h filtration was twice that of the TiO_2 membrane and 4-fold higher for the Al_2O_3 membrane compared to filtration alone. Significant reductions of both colour (Fig. 7a) and A_{254} absorbance (Fig. 7b) values within 2 h filtration with the assistance of ozonation indicated the progress in reduction of TOC during the operation. A decrease in TOC is indicative of organic matter mineralisation. This progress was determined at the end of the filtration period and results are shown in Figure 7c.
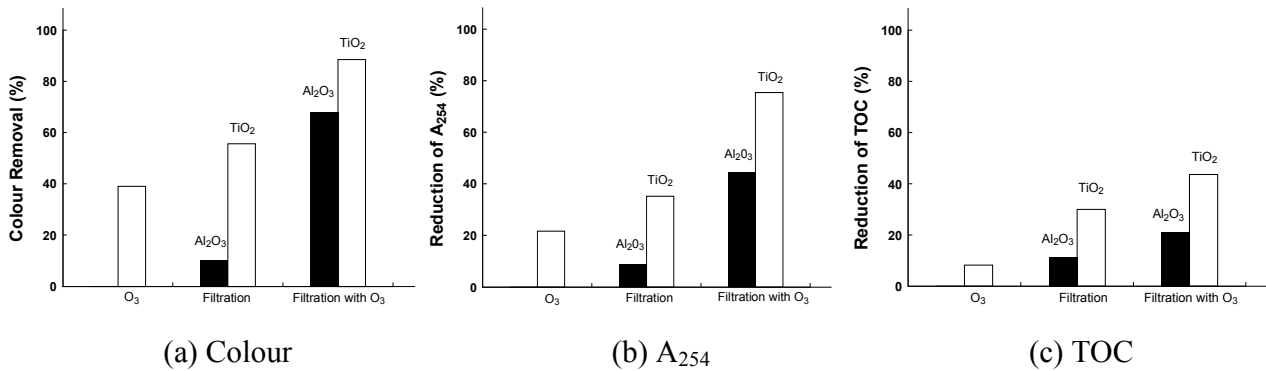

| (a) Colour | (b) A_{254} | (c) TOC |

Fig. 7. Variation of colour (a), A_{254} (b) and TOC (c) removal with different processes. Filtration time = 2 h. Estimated applied ozone dose = 8 mg L^{-1}.

As seen from Figure 7c, ozonation greatly enhanced the membrane filtration in the reduction of TOC. The combined Al_2O_3 membrane filtration and ozonation reduced TOC by almost twice that for filtration only, with around 21% of TOC being removed after 2 h treatment. It was also found that TOC removal obtained for the combined Al_2O_3 membrane filtration and ozonation process was 2.5 times higher than that for the operation with ozonation only. When ozone was applied to the filtration with the TiO_2 membrane for 2 min (estimated applied ozone dose of 8 mg L^{-1}), a reduction of around 43% in TOC was achieved at the end of 2 h operation, which was almost 1.5 times higher than that of filtration only and 5-fold more than ozonation alone.

The results presented in Figure 7 also showed that without ozone, filtration through the Al_2O_3 membrane showed only a 10% reduction in colour, A_{254} and TOC after 2 h. Meanwhile the permeate from the TiO_2 membrane achieved much higher reductions in colour (~55%), A_{254} (~35%) and TOC (~30%). This is mainly attributed to the small size of pores of the TiO_2 membrane compared to Al_2O_3 (0.004 μm vs. 0.58 μm respectively on the dry material), which only allowed the small organic

compounds through its pores and rejected coloured organic compounds with relatively large molecular weights during the filtration.

It was also interesting to note that the reductions of colour, A_{254} and TOC for the combined filtration and ozonation process for both Al_2O_3 and TiO_2 membranes (except colour removal for TiO_2 membrane) were considerably higher than the sum of that using filtration and ozone alone (Fig. 8). This implied a possible synergistic effect between ceramic membranes and ozonation, which is supported by the literature [60, 61] that reported that ceramic materials such as alumina, titania and zirconia can promote ozone decomposition to form $OH^{\bullet}$ radicals. In this case the formation of radicals conveniently occurs at the same place that membrane fouling occurs: on the membrane surface.

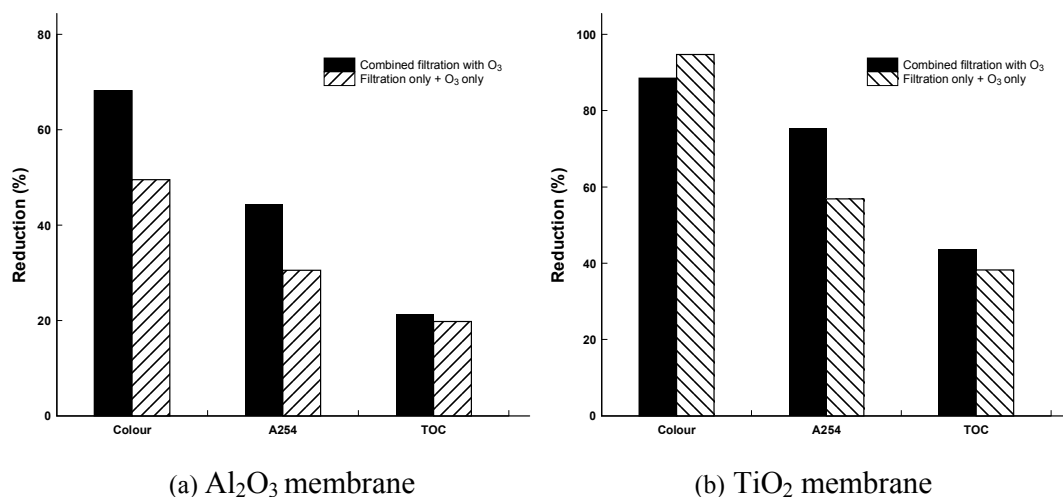(a) Al_2O_3 membrane   (b) TiO_2 membrane

Fig. 8. Comparison of colour, A_{254} and TOC removal by ozonation and filtration displayed as combined or separate processes to demonstrate synergistic effects for bare Al_2O_3 (a) and TiO_2 (b) membranes. Filtration time = 2 h. Estimated applied ozone dose = 8 mg L^{-1}.

The synergistic effect of the membrane coupled with ozonation could be explained in terms of how the membrane operates as shown in Figure 9. Normally during pressure driven filtration, there is a concentration polarization effect which leads to a higher than normal concentration of non-permeable components (i.e. the organic pollutants) near the surface. Also, the nature of these components can lead to a force of attraction making them 'adhere' to the surface. As discussed previously, hydrophilicity and surface charge property of the membrane could have an impact on its performance. Hydrophilic membranes are more fouling tolerant. Our zeta potential results showed that Al_2O_3 had a positively

charged surface, while the surface of TiO_2 was negatively charged. As noted previously NOM tends to be negatively charged [55] and would be more strongly attracted to the Al_2O_3 surface. This would in turn lead to greater fouling to be observed on this surface and an apparently greater fouling resistance on the TiO_2 membrane. In any case, increased organic concentration either from electrostatic attraction, concentration polarisation or general deposition result in fouling which reduces performance, but the species which are also desired to be broken down by the ozone are now more concentrated at the oxide surface. Conveniently this surface breaks down ozone molecules in water to form OH radicals which will in turn create a highly reactive boundary at the pore entrance of the membrane that oxidise the attracted organic molecules. This seems a likely explanation whereby we utilise the tendency for fouling in our favour to enhance the oxidation ability of ozone for breakdown of these organic molecules.
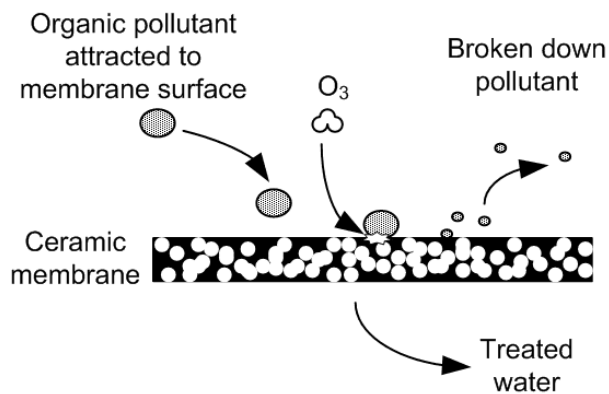

Fig. 9. Mechanism of the synergistic ability for ceramic membranes to enhance ozonation.

The key finding of this work has therefore been in demonstrating the dual functional capacity (physical separation and catalytic breakdown of organics) of inorganic materials for treatment of wastewaters. Of particular significance is the ability for the process to be adopted into a conventional ozonation system in a water treatment plant to substantially enhance the water quality by simply placing the membrane filtration system immediately after the ozone contactor. As part of our ongoing work in this area, there are still areas in need of exploration such as continuous ozone dosing, longer term performance and the ability to directly measure the ozone in the water. This will allow us to explore the performance over the longer term and also assess the quality of the reject (membrane retentatate) stream which although contains concentrated organics, will have been broken down by the ozonation process and may also be more effectively treated at this concentration by further ozonation,

or simply recycled back to the WWTP feed so that only permeate is disposed or recycled. For this, more practical understanding of the performance such as maximum recovery of the membrane stage is needed. Here, we have demonstrated that ozonation treatment coupled with filtration with two common ceramic membrane materials, α-Al_2O_3 and TiO_2, is worth considering for further demonstration toward cost effective water treatment. Further to this, although we developed one type of functional TiO_2, there are many opportunities to pursue in enhancing the functionality of this layer to improve its porous and catalytic properties. Further work is underway to optimise the membrane materials and surface to reduce fouling and also optimise the ozonation conditions for further long-term performance evaluation.

4. Conclusion

The present study investigated the effect of ozonation on the permeate flux, and colour and organics removal during filtration processes through a tubular ceramic membrane (α-Al_2O_3 or TiO_2) under a range of operating conditions. The results indicated that ozonation can greatly reduce membrane fouling and thus improve the permeate flux during filtration. Ozone also significantly enhanced the process efficiency by reducing colour, A_{254} absorbance and TOC. The colour of the treated water was almost colourless, making this treated water more likely to be accepted as non-potable recycled water. A synergistic effect was observed when using a ceramic membrane filtration process in combination with ozonation.

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