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Combined TiO_2 membrane filtration and ozonation for efficient water treatment to enhance the reuse of wastewater

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Abstract

A mesoporous titania (TiO_2) membrane on an alumina support was successfully fabricated via the sol–gel processing method. The effects of combined ozonation and TiO_2 membrane filtration on the permeate flux and permeate quality were investigated. Ozone injection into the feed water during the filtration resulted in an increase in the permeate flux within the first 0.5 h. Ozonation decreased the fouling on the membrane surface. However, at the end of 2 h filtration, ozonation did not significantly impact on the permeate flux. It is likely that there would be minimal ozone residual remaining in the feed after 2 h filtration, which is why fouling was evident after this time, probably in the form of an organic film on the membrane surface reducing the flux. Under the hybrid ozonation-membrane filtration system, the removal of colour, A_{254} (UV absorbance measured at a wavelength of 254 nm) and total organic carbon (TOC) was found to be 88.5%, 75.4% and 48.7%, respectively. Membrane filtration or ozonation alone did not achieve the degree of reduction obtained with hybrid ozonation-membrane filtration. Increasing the ozonation time from 2 min to 10 min gave no consistent trend in the percent removal of the colour and UV-254 absorbing compounds. Even at low ozonation time, there was a significant decrease in the UV-254 and colour. However, increasing the ozonation time beyond a threshold value (2 min) had a negative effect on reduction of TOC. Ozonation of organic matter is known to result in a decrease in the molecular weight of the organic matter, which would then result in these compounds passing through the membranes giving arise this effect.

Keywords: TiO_2 membrane; Filtration; Ozonation; Wastewater reuse

1. Introduction

The application of membrane filtration processes in wastewater treatment is gaining popularity in the world today as there is an increasing demand for water reclamation. Compared to conventional treatment methods, membrane filtration is an effective method to remove particles, microorganisms and organic matter from real wastewaters, consistently achieving high quality treated water. However, the most critical limitation of current membrane filtration is membrane fouling. Membrane fouling generates considerable attention, because it can result in permeation flux decline and costly clean-up requirements [1]. Although many attempts have been made to improve the membrane surfaces, the result does not satisfactorily prevent membrane fouling. Recently the combination of advanced oxidation technologies (AOTs) and membrane separation technologies has received great attention, due to their synergistic effects, for water and wastewater treatment [2-5].

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Ozone is one of the strongest oxidants and disinfectants used for water and wastewater treatment. The application of ozonation prior to membrane filtration could reduce membrane fouling and enhance permeate flux [2, 3, 5-11]. Purification processes using a combination of ozone reaction with membrane separation offer improved operation over each unit process in isolation and are potentially cost-efficient. The combined ozonation-membrane process has not been extensively investigated, because the concomitant application of ozonation and membrane filtration is limited by the low chemical resistance of most polymeric membrane materials to ozone [12].

Ceramic membranes are ozone resistant, and when these membranes are used in combination with ozone, stable permeate fluxes can be achieved without membrane damage. Titania membranes have been paid more significant attention because of their unique structure and surface properties, exhibiting better chemical stability, good resistance to fouling (and hence high water flux), semiconductivity and photo-catalytic properties [13].

In this study, we have fabricated a nanostructured TiO_2 membrane on a tubular α-Al_2O_3 support using a dip-coating method. Using this TiO_2 membrane we have investigated the permeate flux and quality of water after combined ozonation-TiO_2 membrane filtration. The permeate water was analysed for A_{254}, TOC and colour to determine the treatment efficiency. The effect of ozonation time on the flux and water quality of the permeate was also investigated.

2. Experimental

2.1. TiO_2 membrane preparation

A tubular α-Al_2O_3 membrane (Chosun Refractories Co., Ltd. Korea, inside diameter 10 mm, length 90 mm, mean pore size 0.58 μm) was used as a support. TiO_2 membranes were prepared using a polymeric route of the sol-gel technique [14]. The sol was prepared by adding a solution of nitric acid (BDH Chemicals, Australia) in a water/ethanol (Ajax Finechem, Australia) mix dropwise to a solution of titanium butoxide ($Ti(OC_4H_9)_4$, Aldrich, 97%) in ethanol. The molar ratio of titanium butoxide:HNO_3:water used in the experiment to prepare the sol was 1:0.6:0.9. The solution of titanium butoxide was vigorously stirred during the dropwise addition. This stirring continued for 12 h to obtain a stabilised sol. The sol was aged for 24 h in order to increase the viscosity of the dipping solution and to prevent the penetration of the polymeric sol into the pores of the support. The inner surface of the alumina tube was dip-coated with TiO_2 sol and then dried under ambient conditions. The coating and drying steps were repeated four times in order to keep the membrane sufficiently thin and also ensure the membrane integrity. After drying the membrane was calcined in air at 400 ºC for 1 h with a heating and cooling rate of 0.1 ºC/min.

Unsupported membrane was prepared by drying the sol in a Petri dish to form a liquid layer followed by calcination under the same conditions as those used for preparation of the supported membrane.

2.2. Materials characterisation

The particle size distribution of the polymeric sol was determined by a Zetasizer (Malvern Instruments-Nano-series). N_2-sorption measurements were performed on a Tri Star 3000 porosity analyser (Micromeritics, USA) to determine the BET surface area and the pore size of the unsupported TiO_2 membrane. The crystal structure of unsupported TiO_2 membrane was identified by X-ray diffraction (XRD). XRD measurement was performed on a Bruker D2 Phaser Desktop X-ray Diffractometer (CuKα, λ=1.5406 Å) with a 0.05 degree step and a 91 second per step counting time.

2.3. Membrane cleaning

Prior to each experiment, the membrane was thoroughly cleaned by soaking the membrane in a sodium hydroxide solution (15 g/L) at 80 ºC for 30 min. The membrane was then rinsed with deionised water (DIW) and dried. The effectiveness of the cleaning procedure was verified by measuring the permeate flux through the membranes using DIW to ensure that the initial membrane flux was the same in all experiments.

2.4. Water source

Water for the filtration experiments was obtained from one of Melbourne's wastewater treatment plants (WWTP). The molecular weights of the colour-causing organic compounds in the effluent sample were in a wide range, i.e. 400 – 10000 Daltons [15]. The average colour, A_{254} and TOC concentration in the test water were 61 Pt-Co, 0.187 cm^{-1} and 8.824 mg/L, respectively.

2.5. Experimental setup

A schematic representation of the ozonation-membrane system is shown in Figure 1. The tubular TiO_2 membrane described above was used for membrane filtration. The total filtration area was 25.4 cm^2. The apparatus consisted of a membrane module, a recirculation pump, a reservoir, a pressure meter, an ozone injection system and a data acquisition system. A pressure control valve was placed in the retentate line of the membrane system to control the transmembrane pressure to 50 kPa. The retentate was recirculated through the membrane module using a variable speed pump (Masterflex 77200-62, Cole-Parmer, USA). The permeate weight was measured by an electronic balance (FX-3000iWP, A&D Mercury Pty. Ltd., Australia) and recorded continuously using a computer with A&D WinCT software.

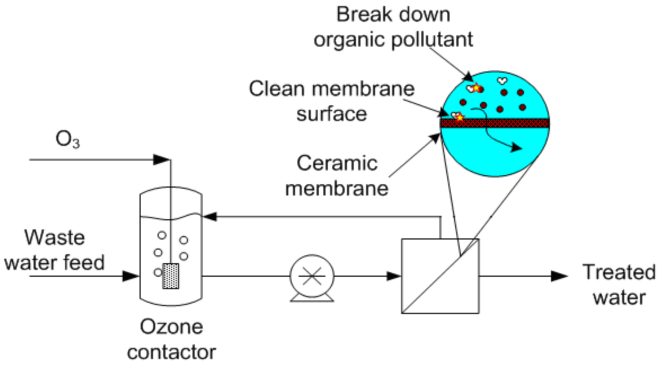

Figure 1. Schematic of the ozone-membrane filtration system

To generate ozone, pure oxygen gas from a pressurized cylinder was fed to an ozone generator (SOZ-6G, A2Z Ozone Systems INC., USA). The production of ozone used for this study was set at 4.8 g/h. At the beginning of the filtration, ozone was injected into the 2 L of feed through a porous diffuser for 2 min, 6 min and 10 min. The corresponding injection ozone doses were estimated to be 8 mg/L, 24 mg/L and 40 mg/L, respectively.

The detailed operating conditions are shown in Table 1. The operating conditions were determined based on previous experiments [16].

Table 1 Operating conditions for ozone-membrane filtration system

Initial volume of feed	2 L
Feed recirculation flow rate	50 mL/min
Feed temperature	Room temperature
Transmembrane pressure	50 kPa
Ozone gas flow rate under normal temperature and pressure (NTP)	0.4 l (NTP)/min
Ozone dose	8 – 40 mg/L
Cross-flow velocity	0.01 m/s

2.6 Analytical method

The UV absorbance (A_{254}) of the water samples was measured at a wavelength of 254 nm with a spectrophotometer (HACH DR5000, USA). Platinum-Cobalt Standard Method (Method 8025, HACH) was used in the current work for true colour measurements by the same spectrophotometer and reported as true colour (Pt-Co units). The TOC was analysed by a TOC-Vcsh TOC analyser (Shimadzu, Japan). To ensure method reliability, a standard having TOC concentration of 20 mg/L was run with every set of samples.

3. Results and discussion

3.1. Properties of TiO_2 materials

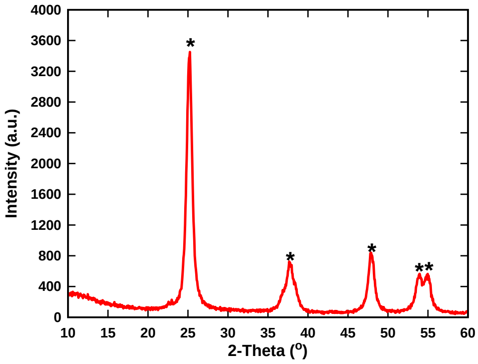

Figure 2. XRD pattern of unsupported TiO_2 membrane, * anatase peak.

During the TiO_2 synthesis process, the concentration of water was kept at an optimum ratio to have a controlled hydrolysis reaction so as to obtain small nanometer-sized particles (measured at 4 nm by a Zetasizer). The sol's particle size distribution needs to be narrow to give a titania membrane with optimum properties [17].

The crystalline phase of the unsupported TiO_2 membrane was characterised by XRD. The result, shown in Figure 2, suggests the unsupported TiO_2 membrane was pure anatase after being sintered at 400 ºC for 1 h. Among three different crystal structures of TiO_2, rutile, anatase and brookite, the anatase structure has attracted much attention in recent years for its technological applications [18]. The titania membrane prepared in this work could also be used as a photocatalyst coating and/or titania-supported catalysts in later research.

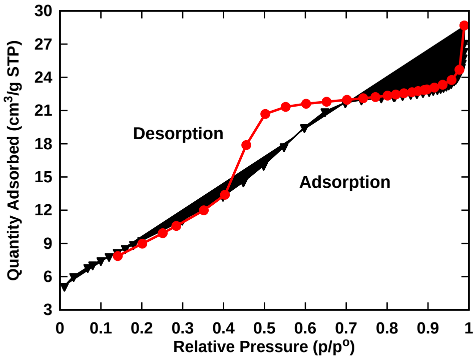

Figure 3. N_2-sorption hysteresis of the unsupported TiO_2 membrane

The prepared unsupported TiO_2 membrane was mesoporous according to the nitrogen adsorption–desorption isotherms (Figure 3), which was a typical type IV with a hysteresis [19]. The specific surface area and the pore size were measured as 35.5 m^2/g and 5.0 nm, respectively.

3.2. Effect of ozonation on permeate of flux

Figure 4 compares the observed permeate flux for membrane filtration only and hybrid ozonation-TiO_2 membrane filtration for different ozone injection times. For filtration using membrane only, the permeate flux declined more significantly than that observed during the ozonation-membrane filtration. Without ozonation, after 0.5 h of operation, the permeate flux was only 70% of the initial value (Figure 4). However, when ozonation (2 min) was applied to the system, after 0.5 h of operation, the permeate flux remained at 92.5% of the initial value. Ozone decomposition, resulting in the formation of ·OH or other radicals at the membrane surface, is thought to result in the decomposition of organic foulants at the membrane surface and reduce the extent of membrane fouling [8]. However, at the end of 2 h filtration, ozonation did not significantly impact on the permeate flux. In this work, it was chosen to apply a single dose of ozone at the beginning of the filtration as opposed to continuous ozonation primarily to explore the effects of residual ozone. Since the half-life for ozone in water is of the order of 500 s [20, 21], at the end of the 2 h test period, it is likely that there would be minimal ozone residual remaining in the feed. This would explain why fouling, likely in the form of an organic film on the membrane surface, was evident after this time. This film would have the added effect of reducing the accessibility of any residual ozone to the membrane surface, where the catalytic reaction occurs, thereby diminishing the catalytic performance of the TiO_2 membrane.

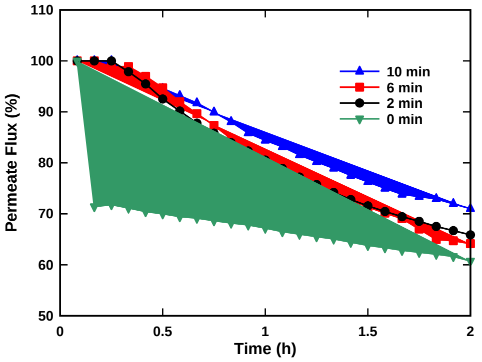

Figure 4. Permeate flux decline at filtration only and hybrid ozonation-membrane filtration (ozonation time at 2 min, 6 min and 10 min). Initial flux is 71.6 L/m^{2}h.

3.3 Effect of ozonation on permeate water quality

Figure 5 compares the permeate water quality from different processes: ozonation only (ozonation time 2 min), membrane filtration only, and hybrid ozonation-membrane filtration (ozonation time 2 min). As shown in Figure 5, under the ozonation-membrane filtration system, the removal of colour, A_{254} and TOC were found to be 88.5%, 75.4% and 48.7%, respectively. Using membrane filtration or ozonation alone did not achieve the levels of treatment obtained with combined ozonation-membrane filtration.

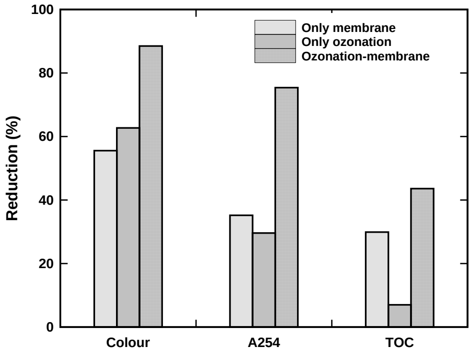

Figure 5. Effect of ozonation, membrane filtration and ozonation-membrane filtration on water quality. Filtration time = 2 h.

3.4. Effect of ozonation time on water quality during membrane filtration

Figure 6a shows the reduction of colour versus ozonation time. There was little difference between the different ozonation times and the extent to which the absorbance was reduced. Thus a minimum threshold ozonation time (2 min) was required to obtain a reduction of colour. However, beyond a certain ozonation time (2 – 6 min), further increases in ozonation did not affect the reduction of colour. Figure 6b shows the effect of ozonation time on A_{254} removal. Increasing the ozonation time from 2 to 10 min revealed no consistent trend regarding the effect of ozonation time on the percent removal of the UV-254 absorbing compounds. Even at low ozonation time (< 2 min), there was a significant decrease in the UV-254 and colour. These results are consistent with previous research on the ozonation of water [3].

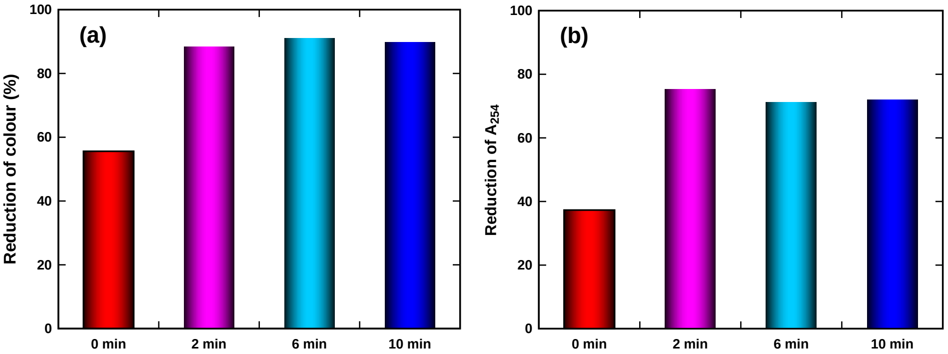

Figure 6. Effect of ozonation time on colour (a) and A_{254} (b) removal. 0 min corresponds to filtration only. Filtration time = 2 h.

Figure 7 shows the effect of ozonation time on the reduction of TOC. The decrease in TOC was in large part due to membrane filtration (see Figure 5). However, increasing the ozonation time beyond 2 min had a negative effect on reduction of TOC. With an ozonation time of 10 min, the reduction of TOC was lower than that without ozonation. Extended ozonation is known to result in the degradation of large molecular weight organic matter and to ultimately reduce the molecular weight of compounds in water [9]. In this case, the increased ozone dose resulted in an increased concentration of highly reactive radicals at the membrane surface that then decompose the organic foulants present at the surface from high molecular weight to low molecular weight [9]. This lower molecular weight material would more easily pass through the membrane resulting in lower rejections which has also be found by other work on ozonation of wastewater followed by filtration with ceramic membranes [8].

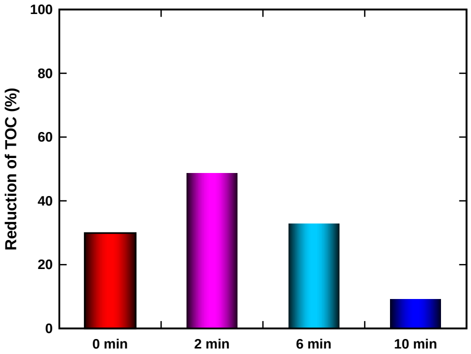

Figure 7. Effect of ozonation time on TOC removal. 0 min corresponds to filtration only. Filtration time = 2 h.

4. Conclusion

This study demonstrated that under appropriate operating conditions, the hybrid ozonation–TiO_2 tubular membrane filtration system can significantly reduce membrane fouling and improve the permeate quality during the treatment of wastewater. With respect to permeate flux and permeate quality, ozonation-TiO_2 membrane filtration showed better performance than only ozonation or only membrane filtration. The other key finding of this work was in demonstrating the effect of ozonation time on permeate flux and water quality in an ozonation-titania membrane filtration system. The removal of colour and A_{254} in the permeate increased with ozonation, suggesting that the quality of the water was improved through hybrid ozonation-membrane filtration. However, beyond a particular ozonation time (2 min), further increases in ozonation time had no benefit on the level of permeate flux and permeate water quality. The percent removal of TOC observed in these experiments tended to decrease with increasing ozonation time, suggesting partial degradation of organic matter to form smaller molecular weight molecules that can pass through the membrane.

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