1 **Manganese oxide integrated catalytic ceramic membrane for**

2 **degradation of organic pollutants using sulfate radicals**

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Abstract

Membrane separation and advanced oxidation processes (AOPs) have been respectively demonstrated to be effective for a variety of water and/or wastewater treatments. Innovative integration of membrane with catalytic oxidation is thus expected to be more competing for more versatile applications. In this study, ceramic membranes (CMs) integrated with manganese oxide (MnO_2) were designed and fabricated via a simple one-step ball-milling method with a high temperature sintering. Functional membranes with different loadings of MnO_2 (1.67%, 3.33% and 6.67% of the total membrane mass) were then fabricated. The micro-structures and compositions of the catalytic membranes were investigated by a number of advanced characterisations. It was found that the MnO_2 nanocatalysts (10-20 nm) were distributed uniformly around the Al_2O_3 particles (500 nm) of the membrane basal material, and can provide a large amount of active sites for the peroxymonosulfate (PMS) activation which can be facilitated within the pores of the catalytic membrane. The catalytic degradation of 4-hydroxylbenzoic acid (HBA), which is induced by the sulfate radicals via PMS activation, was investigated in a cross-flow membrane unit. The degradation efficiency slightly increased with a higher MnO_2 loading. Moreover, even with the lowest loading of MnO_2 (1.67%), the effectiveness of HBA degradation was still prominent, shown by that a 98.9 % HBA degradation was achieved at the permeated side within 30 min when the initial HBA concentration was 80 ppm. The stability and leaching tests revealed a good stability of the catalytic membrane even after the 6th run. Electron paramagnetic resonance (EPR) and quenching tests were used to investigate the mechanism of PMS activation and HBA degradation. Both sulfate radicals ($SO_4^{\cdot-}$) and hydroxyl radicals ($^{\cdot}OH$) were generated in the catalytic membrane process. Moreover, the contribution from non-radical process was also observed. This study provides a novel strategy for preparing a ceramic membrane with the

45 function of catalytic degradation of organic pollutants, as well as outlining into future

46 integration of separation and AOPs.

47 **Keywords:** Manganese oxides; Catalytic membrane; Sulfate radicals; 4-hydroxylbenzoic acid

48 (HBA); AOPs.

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1. Introduction

51 Aqueous organics pollution is one of the most serious environmental issues, and has drawn

52 increasing public concerns. Organic contaminants, for example, hydrocarbons, detergents,

53 pharmaceutical compounds, pesticides, surfactants and dyes, are recalcitrant to natural

54 degradation, therefore have caused various problems related to water shortage and public health

55 risks (Sun and Wang 2015). This leads to the development of a variety of water treatment

56 technologies, for instance, adsorption, flocculation, biodegradation, and advanced oxidation

57 processes (AOPs) (Duan et al. 2018c). Different from other technologies, AOPs are generally

58 conducted with the presence of strong oxidizing species, for example, hydroxyl ($^{.}OH$), sulfate

59 ($SO_4^{.-}$), and superoxide radicals ($O_2^{.-}$), which are produced *in situ* through photocatalysis,

60 electrochemistry, or activation of superoxides (hydrogen peroxide, ozone, and persulfate, etc.).

61 The reactive radicals can trigger a sequence of reactions that decompose the organic

62 compounds into smaller and less harmful substances (Chan et al. 2011, (Duan et al. 2018c).

63 For example, Fenton reaction is a classical AOP, which relies on the reactions between

64 Fenton's reagents, e.g., hydrogen peroxide (H_2O_2) and ferrous ions, to generate hydroxyl

65 radicals ($^{.}OH$). However, the Fenton's reaction prefers an acidic environment (pH < 3), which

66 requires the extra controls of the solution, including reducing the solution pH value before the

67 treatment, and neutralizing after the reactions. Furthermore, there are associated drawbacks

68 that cannot be ignored, such as the large amount of sludge produced, as well as the difficulties

69 in storing and using H_2O_2 (Neyens and Baeyens 2003, (Sun and Wang 2015).

70 As an alternative to hydroxyl radicals ($\cdot$OH), sulfate radicals ($SO_4^{\cdot-}$) have the merits of a higher

71 oxidative potential (2.5- 3.1 V at neutral pH vs 1.8-2.7 V of hydroxyl radicals), a relative non-

72 selectivity, a longer lifetime, and good activity across a wide range of pH values (Sun and

73 Wang 2015). Because of the advantages of sulfate radicals, the sulfate radical-based advanced

74 oxidation processes (SR-AOPs) have broad applications in removing refractory organic

75 pollutants (Xia et al. 2017, (Yin et al. 2019), microorganisms (Wang et al. 2019) and

76 microplastic (MPs) (Kang et al. 2019b). Sulfate radicals can be generated via the activation of

77 either peroxymonosulfate (HSO_5^-, PMS) or persulfate ($S_2O_8^{2-}$, PS). The asymmetric structure

78 (HO-O-SO_3^-) and longer superoxide O-O bond ($l_{\text{o-o}}$ =1.326 Å) make PMS easier be dissociated

79 than PS, since PS has a symmetric structure (SO_3^--O-O-SO_3^-) and a more compact O-O bond

80 ($l_{\text{o-o}}$=1.322 Å)   (Duan et al. 2018b). Persulfate salts (PMS and PS) are hard to decompose

81 naturally, thus a catalyst is usually required to activate persulfate salts (PMS and PS) to

82 accelerate the process of producing sulfate radicals ($SO_4^{\cdot-}$). Similar to H_2O_2 and O_3 that are

83 commonly used in other AOPs, PMS and PS can be activated either homogeneously with metal

84 ions (Anipsitakis and Dionysiou 2003, (Anipsitakis and Dionysiou 2004a, b) or

85 heterogeneously with metal oxides/metal-free carbons. Compared with homogeneous

86 activation, heterogeneous activation by catalysts can avoid the severe loss of metal ions. Metal

87 based-catalysts such as manganese oxides (Saputra et al. 2013a, (Saputra et al. 2013b, (Saputra

88 et al. 2013c, (Wang et al. 2015a), cobalt oxides (Saputra et al. 2013a, (Wang et al. 2015c) and

89 zero valence iron (Sun et al. 2012, (Wang et al. 2015b), were found to be very effective in the

90 activation of PMS/PS. Although the effectiveness of metal-based catalysts has been verified,

91 the potential leaching of toxic transition metals into water system is a serious issue resulting in

92 secondary contamination to environment. As a promising alternative, metal-free nanocarbons

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93 and carbonaceous catalysts have been proven to be an inexpensive and environmental-friendly

94 choice for SR-AOPs. Great works have been done and a variety of novel metal-free catalysts

95 such as reduced graphene oxide (rGO) (Duan et al. 2015a, (Duan et al. 2016b, (Duan et al.

96 2018c, (Kang et al. 2016), carbon nanotubes (CNTs) (Duan et al. 2018c, (Kang et al. 2019a,

97 (Sun et al. 2014), and cubic mesoporous carbon (CMK) (Duan et al. 2018c, (Duan et al. 2018d)

98 were synthesized for achieving the sulfate radicals ($SO_4^{\cdot-}$) generation. Along with the SR-

99 AOPs, two possible pathways, e.g. radical and nonradical degradation, have been proposed

100 (Duan et al. 2018a, (Duan et al. 2016a, (Duan et al. 2018c).

101 A major problem of SR-AOPs with homogeneous/heterogeneous catalysis is the recovery and

102 reuse of the catalysts. Catalytic membrane is thus a promising solution by combining

103 membrane separation of catalysts, and catalytic decomposition of the organic pollutants via

104 radicals. The studies on photocatalytic membranes (Wang et al. 2017b, (Zhao et al. 2016) and

105 ozonation membranes (Chen et al. 2015, (Guo et al. 2016) revealed the competing

106 performances in the treatments of aqueous organic pollutants. Recently, integrated membrane

107 with sulfate radicals ($SO_4^{\cdot-}$) based-catalytic oxidation has attracted increasing attention. Cheng

108 et al. studied ferrous iron/peroxymonosulfate (Fe (II)/PMS) oxidation process as a pre-

109 treatment method for fouling alleviation on ultrafiltration (UF) ceramic membrane caused by

110 natural organic matters (NOMs). It was found that the sulfate radicals in Fe (II)/PMS oxidation

111 process were very effective both in the removal of atrazine (ATZ) (98.2% ATZ removal with

112 Fe (II)/PMS at 50/50 μM), and the mitigation of membrane fouling caused by humic acid (HA),

113 sodium alginate (SA), bovine serum albumin (BSA), and their mixture (HA-BA-BSA) (Cheng

114 et al. 2017). In another work, the anti-fouling performance for algal extracellular organic

115 matters (EOMs) was investigated, and it was found that UV/Fe(II)/PMS process showed the

116 best anti-fouling performance (Cheng et al. 2018). Bao et al. prepared $CoFe_2O_4$ nanocatalysts

117 impregnated Al_2O_3 ceramic membrane via the urea-assisted one-step combustion method.

118   Nearly 100% sulfamethoxazole (SMX, initial concentration of 10 ppm) was removed within

119   90 s. The effects of Oxone loading, humic acid (HA) concentration and anions (CO_3^{2-}, SO_4^{2-},

120   NO_3^-, and Cl^-) on degradation efficiencies were also investigated (Bao et al. 2018). Luo et al.

121   synthesized a free-standing glass fibre supported hierarchical α-MnO_2@CuO membrane for

122   organic dye removal. Fast degradation of methyl blue (MB) was achieved within 0.23 s of the

123   residence time when the solution flow rate was controlled at 20 mL/min. The mechanistic study

124   was conducted by electron paramagnetic resonance (EPR) and quenching tests. Both sulfate

125   radicals ($SO_4^{·-}$) and hydroxyl radicals ($^·OH$) were produced from the interaction between PMS

126   and α-MnO_2@CuO catalytic membrane (Luo et al. 2018). Zhao el al. fabricated different metal

127   oxides (MnO_2, Fe_2O_3, Co_3O_4, CuO and Mn_3O_4) coated ceramic membranes (CMs) and

128   compared their performances for cleaning foulants with the assistance of PMS. The MnO_2-

129   coated CM showed the best performance of flux recovery after the cleaning using PMS solution

130   (Zhao et al. 2019). In addition, the MnO_2 and Co_3O_4 are the most popular metal-based catalysts

131   for heterogeneous activation of PMS. It was suggested that MnO_2 might be better than cobalt

132   oxides for wider applications in SR-AOPs because of the abundance of MnO_2 in nature and its

133   relatively lower toxicity to water bodies. It was reported that the LC_{50} (metal concentrations in

134   water resulting in 50% mortality in 4 weeks) of cobalt and manganese are 183 and 197,000

135   nmol L^{-1}, respectively (Norwood et al. 2007).

136   Herein, we report a MnO_2 integrated ceramic membrane prepared via a simple one-step ball-

137   milling with high temperature sintering method. To the best of our knowledge, this is the first

138   study on loading MnO_2 nanoparticles uniformly into the pores and surface of a ceramic

139   membrane for AOPs. Compared with other AOPs based-catalytic membranes, our catalytic

140   ceramic membranes showed an outstanding performance in degrading the antibiotic pollutant

141   of 4 hydroxylbenzoic acid (4-HBA), even at a very high initial concentration (80 ppm), because

142   of the dispersive distribution of very fine MnO_2 nanoparticles (10-20 nm) within the pores and

143 on the surface of the membrane. In addition, unlike the polymeric supports, the alumina

144 ceramic membrane support provides a high stability for the catalytic oxidation reactions. The

145 reusability tests showed no significant decrease in the degradation performance of HBA after

146 the 6th run. The one-step ball-milling preparation method in this study makes the catalytic

147 membrane feasible for practical applications at a large scale.

148

2. Experimental

150 2.1. Reagents and materials

151 In the study, 4-hydroxylbenzoic acid (4-HBA), Oxone (PMS, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), acetic

152 acid (CH_3COOH), hydrochloric acid (HCl), polyvinyl alcohol (($C_2H_4O)_x$, PVA), methanol

153 (CH_4O), *tert*-buanol (TBA), ethanol (C_2H_5OH) and 5, 5-dimethyl-1-pyrrolidine N-oxide

154 (DMPO) were purchased from Sigma-Aldrich. Potassium permanganate ($KMnO_4$) was

155 supplied by Chem-Supply. Glycerol ($C_3H_8O_3$) was obtained from Rowe-Scientific. Al_2O_3

156 nanoparticles (corundum, 500 nm) were purchased from NanoAmor. Grinding balls

157 (Zirconium, 1, 2, 5, 10 and 20 MM diameters) were supplied by Nikkato. All solutions were

158 prepared using ultrapure water (18.2 MΩ.cm at 25 °C) from a Mill-Q water system. All

159 chemicals were used as received without further purification.

160 2.2. Synthesis of MnO_2 catalysts

161 Spherically structured MnO_2 was prepared by a modified hydrothermal process, via the

162 reduction of $KMnO_4$ reported in our previous studies (Wang et al. 2015a). The amount of HCl

163 was modified in order to obtain uniform MnO_2 of the desired nanostructure. In a typical

164 synthesis, 2.85 mM of $KMnO_4$ was first dissolved in 80 mL of ultrapure water. Then 2 mL of

165 HCl (37 wt%) was added to the solution drop wisely under vigorous magnetic stirring to form

166 the precursor solution. After stirring for about 20 min, the solution was transferred into a 120

167 mL Teflon-lined stainless steel autoclave. The autoclave was then heated in an electric oven to

168 110 ℃ for 12 h. The autoclave was then naturally cooled down to room temperature. The black

169 precipitate was then collected by vacuum filtration, followed by washing with deionized water

170 and ethanol for 3 times and then dried at 60 ℃ overnight.

171 2.3. Preparation of manganese oxide-integrated ceramic membranes

172 MnO_2 integrated CM discs (3.5 g each) were prepared by the following route: a certain amount

173 of MnO_2, PVA (1 %), glycerol (1.5 %) and Al_2O_3 were first mixed together and put into the

174 ZrO_2 ball-milling bowl (500 mL in volume, Fritsch, Germany), where the MnO_2 loading was

175 set to 1.67%, 3.33%, and 6.67% of the total mass of membrane samples which were then

176 denoted to Mn-1/Al, Mn-3/Al, and Mn-6/Al, respectively. A planetary ball-mill (Fritsch,

177 Pulverisette 6, Germany) was utilised to mix the membrane contents, in which the grinding

178 balls were a mixture of Nikkato ZrO_2 balls in the diameters of 1, 2, 5, 10, and 20 mm. The mass

179 ratio of powders to balls was set at 1/10. Then the after-milling powders were transferred to an

180 automatic sieve shaker (Retsch, AS 200 Control, Germany) to obtain uniform fine powder

181 mixture. The sieved powders were then transferred to a disc mould and pressed under the

182 pressure of 5 bar by a hydraulic press (Specac, UK) to produce the green-pressing membranes.

183 After dried at 60 ℃ in the oven overnight, the green-pressing membranes were sintered in a

184 high temperature muffle furnace at 1050 ℃ to obtain the final membranes (28 mm in diameter

185 size and 3.5 mm in thickness). In addition, the pure alumina ceramic membrane supports were

186 made by the same procedure without the addition of any manganese oxides when ball-milling.

187 The photos of the pure alumina ceramic membrane support and Mn-1, Mn-3 and Mn-6

188 membranes are shown in Fig. S1 (a), and the size of membrane disc is displayed in Fig. S1 (b)

189 and (c).

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2.4. Characterization
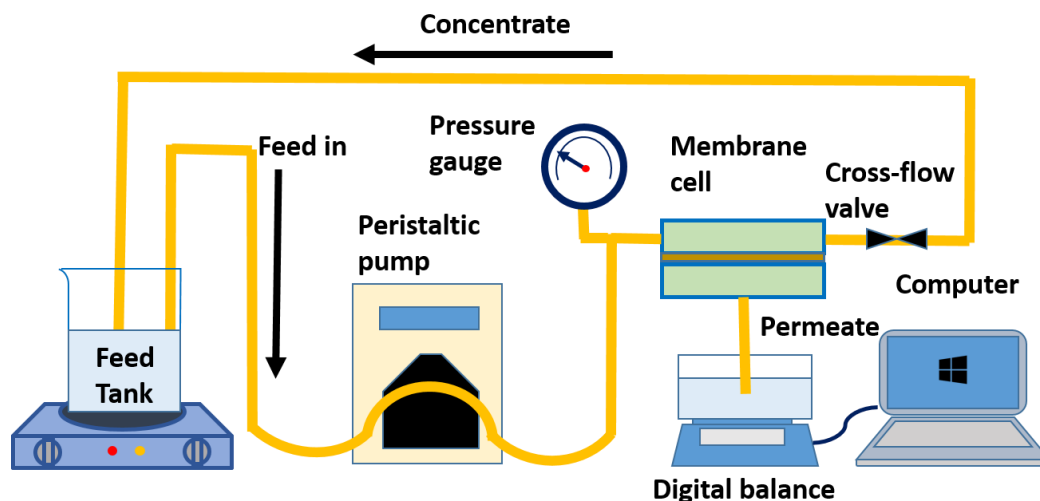
The surface morphologies and energy dispersive spectrometry (EDS) element mappings of the catalytic membranes were characterised by scanning electron microscopy (SEM, Zeiss 1555, Germany). The morphologies and lattice spacing of manganese oxide catalysts within alumina aggregates were investigated by a high resolution transmission electron microscopy (HRTEM, Thermo FEI Titan G2 80-200, US). The components and structures of ceramic membranes were investigated by X-ray diffraction (XRD, Bruker D8 diffractometer, Germany) using filtered Cu Kα radiation ($\lambda = 1.5418$ Å) with an accelerating voltage of 40 kV and a current of 30 mA. X-ray photoelectron spectroscopy (XPS) was used to determine the chemical states of elements on a Thermo Escalab 250 (Thermo Fisher Scientific, US) with Al-Kα X-ray. Electron paramagnetic resonance (EPR) spectra were obtained on a Bruker EMS-plus to detect the free radicals generated during PMS activation. Mn ions were detected by a 4200 MP-AES system (Agilent, US).

2.5. Membrane catalytic oxidation tests

The performance of the MnO_2/Al_2O_3 membrane was tested in a laboratory-scale SR-AOPs catalytic membrane system (Fig. 1). Membrane was fixed in a cross-flow membrane module. A peristaltic pump was used to drive the feed solution and circulate it back to the feed tank. 4-hydroxylbenzoic acid (HBA) was selected as the target pollutant to investigate the ability of antibiotic pollutants removal on the MnO_2/Al_2O_3 via PMS activation. In comparison, different manganese loading of MnO_2/Al_2O_3 (1.67%, 3.33% and 6.67% wt % MnO_2 in Al_2O_3 of Mn-1/Al, Mn-3/Al and Mn-6/Al, respectively) catalytic membranes and pure Al_2O_3 membrane under the same condition were carried out in the same membrane unit. Unless stated otherwise, the flow rate was kept at 0.2 mL/min, and the transmembrane pressure (TMP) was controlled

214   at 2 bar. HBA concentrations of feed and filtrate were monitored by an ultra-high performance

215   liquid chromatography (UHPLC, Shimadzu Prominence, Japan) with a column (Restek Raptor

216   C18, 2.7 μm, 100 × 2.1 mm, France). The solvent used in the UHPLC was water (pH adjusted

217   by acetic acid at 3.5): methanol in the ratio of 90:10, with the flow rate was set at 0.3 mL/min.

218   The column oven was set at 30 ℃ and the detector wavelength was 270 nm. At certain time

219   internals, 1 mL solution was extracted from both permeate side and feed side. Then 1 mL

220   sample solution was transferred into a 1.5 mL HPLC vial which contained pre-injected 0.5 mL

221   methanol as the quenching agent.

222   The intermediates of HBA degradation were identified by a GC-MS (Agilent 7890B/5977B,

223   Agilent, USA). The GC-MS was equipped with a DB-17MS column (30 m × 0.25 mm × 0.25

224   μm) with ultrahigh purity helium (99.999%, BOC, Australia) as the carrier gas at a flow rate

225   of 1.0 mL min^{-1}. The concentrated reaction mixture was initially in the aqueous form, which

226   was mixed with ethyl acetate in order to extract the organic compounds from aqueous to

227   organic phase and further, taken into GC–MS analysis. The sample pretreatment procedures

228   are as follows: at certain time intervals 2 mL solution from permeate side was transferred to a

229   centrifuge tube, then 2 mL extraction organic solvent ethyl acetate was added in the centrifuge

230   tube. Then the solution was mixed in a vortex mixer (VELP Scientifica, US) at 2,000 rpm for

231   60 s and followed by 10 min centrifugation at 9,000 rpm in a lab centrifuge (Sigma, US). The

232   ramp of the analysis was as follows: initial column temperature was held for 1 min at 80 °C,

233   ramped at 5 °C/min to 120 °C and then immediately ramped at 10 °C/min to 240 °C. Then the

234   analysis was immediately ramped at 240 to 280 °C holding for 5 min at the same temperature.

235   The sample was injected in the splitless mode and the MS analysis was carried out with 70 eV

236   as ionization energy, 6 kV accelerated voltage and 1,000 as resolving power with solvent delay

237   (3 min). The inject temperature was set as 280 °C. MS source was set at 230 and MS quad set

238   at 150 °C. Full scan model (m/z= 50-550) was used.

239

Fig. 1. Process flow diagram of catalytic membrane filtration system.

2.6. Membrane fouling control analysis

The flux changes of the pristine alumina (Al_2O_3) ceramic membrane and the manganese oxide (MnO_2) -based catalytic membranes with different Mn loading (Mn-1, Mn-3 and Mn-6) were tested in a dead-end filtration cell. The transmembrane pressure (TMP) was kept at 1 bar through a nitrogen cylinder connected with the filtration cell. During the filtration tests, the permeate flux was monitored by an electronic balance (Kern KB 3600-2N, Germany) connected with computer and the output data were periodically recorded. To measure the pure water permeate flux (J0), ultrapure water was filtered under a pressure of 1 bar during a 30 min filtration period and the average flux was decided as J0. To measure the fouling resistance towards humic acid of the MnO_2 based catalytic membranes (Mn-1, Mn-3 and Mn-6) and the pristine ceramic membrane, a mixture solution (100 mL) of HA (2 g/L) and PMS (4 g/L) was stirred for 30 min at 200 rpm. After that, the pretreated solution samples were immediately used for membrane filtration.
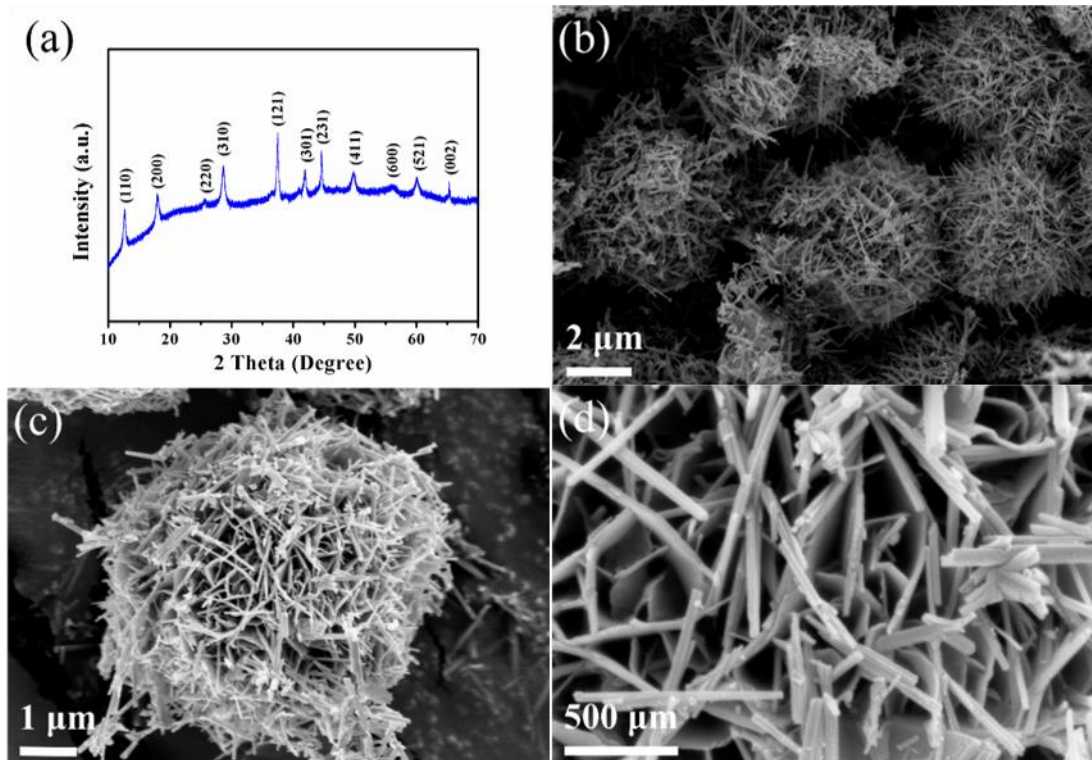
254

3. Results

3.1. Characterisation of MnO_2 catalysts

The crystalline structure of α-MnO_2 nanostructure was investigated by X-ray diffraction (XRD) (Fig.2a). Diffraction peaks at 2θ of 12.7, 18.0, 25.6, 28.7, 37.6, 42.0, 46.1, 49.9, 56.1, 60.2, and 65.5 ^{o} were observed, corresponding to (110), (200), (220), (310), (121), (301), (231), (411), (600), (521), and (002), respectively. The XRD pattern of manganese oxide was identified to α-MnO_2 (JCPDS No.72-1982, tetragonal, a = b = 9.815 Å, c = 2.847 Å) (Wang et al. 2015a). No other crystalline phase was observed in the pattern, indicating the high purity of the catalyst. The reaction involved in the hydrothermal process for MnO_2 formation can be described in Eq. 1:

$$2\ KMnO_4 + 8\ HCl \xrightarrow{110℃} 2\ MnO_2\ (\alpha\ type) + 3\ Cl_2 + 2\ KCl + 4\ H_2O \qquad \text{Eq. 1}$$

Figs. 2 b-d show the SEM images of the structure and morphology of the synthesised MnO_2 catalysts. After the hydrothermal process at 110 ℃, the hollow sea-urchin shaped MnO_2 catalysts with a diameter of around 5 μm (Figs. 2b-c) were synthesised. The sea-urchin shaped MnO_2 were made of hollow nanorods with a diameter of about 40 nm (Fig. 2d). The supplementary images of MnO_2 catalysts and MnO_2/Al_2O_3 mixture after ball-milling are shown in Fig. S2. From Figs. S2a and b, we can further confirm the uniform, spherical MnO_2 nanoparticles with a diameter of 5 μm. Figs. S2c-f show that after ball-milling, the MnO_2 nanospheres sticked with Al_2O_3, and some MnO_2 catalysts were wrapped by Al_2O_3 nanoparticles. The morphologies of MnO_2 heated at different temperatures are shown in Fig. S3. Figs. S3a and b reveal the SEM images of pristine MnO_2 after the 110 ^{o}C hydrothermal process. It was found that the sea-urchin shaped MnO_2 were made of hollow nanorods. When the MnO_2 catalysts were heated at 300 ^{o}C, the structure and morphology were still maintained.

278 When the heating temperature further rose up to 700 °C, the sea-urchin structure transferred to

279 an irregular structure with a diameter of 2 to 5 μm. The hollow nanorods structure largely

280 disappeared but can be still clearly seen at some part of nanorods. Further increasing the

281 temperature to 1050 °C (equal to the membrane calcination temperature), all particles showed

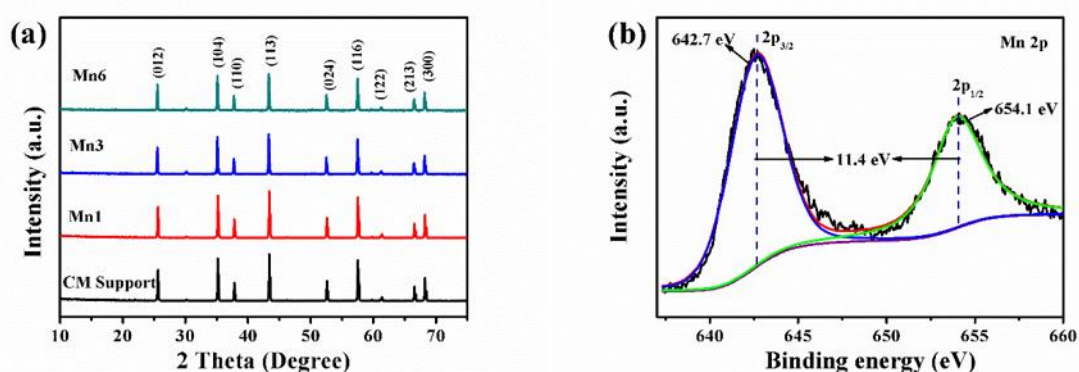282 an irregular structure and the nanorods morphology completely disappeared.

283

284 **Fig. 2.** (a) XRD pattern of MnO$_2$ catalysts; (b-d) SEM images of MnO$_2$ catalysts.

285 3.2. Properties of MnO$_2$ integrated ceramic membranes

286 Fig. 3a shows XRD patterns of Mn-1/Al, Mn-3/Al, Mn-6/Al catalytic membranes and the pure

287 Al$_2$O$_3$ membrane. Diffraction peaks at 25.6, 35.2, 37.9, 43.4, 52.7, 57.6, 61.3, 66.7, and 68.4°

288 were observed, corresponding to (012), (104), (110), (113), (024), (116), (122), (214), and

289 (300), respectively. The XRD patterns of all the membranes were identified to Al$_2$O$_3$ (JCPDS

290 No.71-1125, corundum, a = b = 4.748 Å, c = 12.954 Å, α = β = 90°, γ = 120°). No MnO$_2$

291 diffraction peaks were observed, which may be because that the MnO$_2$ loading is low with a

13

292 high dispersion degree (Guo et al. 2016). XPS analysis of the pristine membrane and MnO_2

293 integrated catalytic membranes was carried out to unveil the chemical states of manganese (Fig.

294 3 b and Figs. S4-7). As shown in Figs. S 4-6, four main elements namely Mn, Al, O, and Zr,

295 were observed in the XPS survey spectrum. Zr was from the zirconium oxide (ZrO_2) grinding

296 bowl and grinding balls. Besides them, C element was due to the ingredients of PVA and

297 glycerol during the membrane preparation. Al, O, and Mn were the target elements in the Mn-

298 1/Al catalytic membrane. The high resolution Mn 2p spectrum (Fig.3b) shows a $Mn2p_{1/2}$ peak

299 at 654.1 eV and a Mn $2p_{3/2}$ peak at 642.7 eV. The binding energies of Mn 2p with a spin-energy

300 separation of 11.4 eV are in accordance with the previous results for MnO_2 (Kim et al. 2013,

301 (Wang et al. 2013, (Xiao et al. 2014).

302

303 **Fig. 3.** (a) XRD patterns of the membranes: uncoated ceramic membrane, Mn-1/Al, Mn-3/Al,

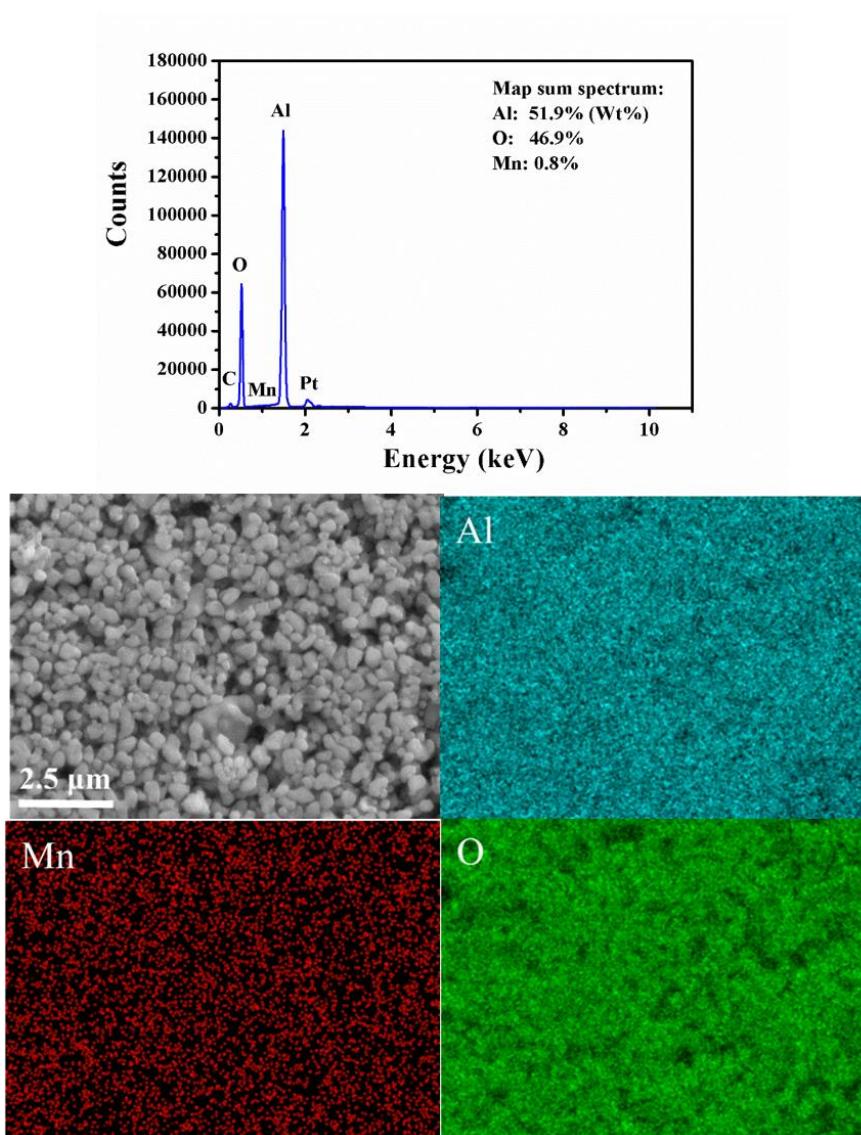304 and Mn-6/Al catalytic membranes; and (b) Mn 2p spectrum of Mn-1/Al catalytic membrane.

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306 The morphologies of the prepared membranes are presented in Fig.4. In Figs. 4a and b, the

307 Al_2O_3 membrane support shows the particle size ranging from 300 to 500 nm. The surface

308 morphologies of Mn-1/Al, Mn-3/Al, and Mn-6/Al membrane are displayed in Figs. 4c and d,
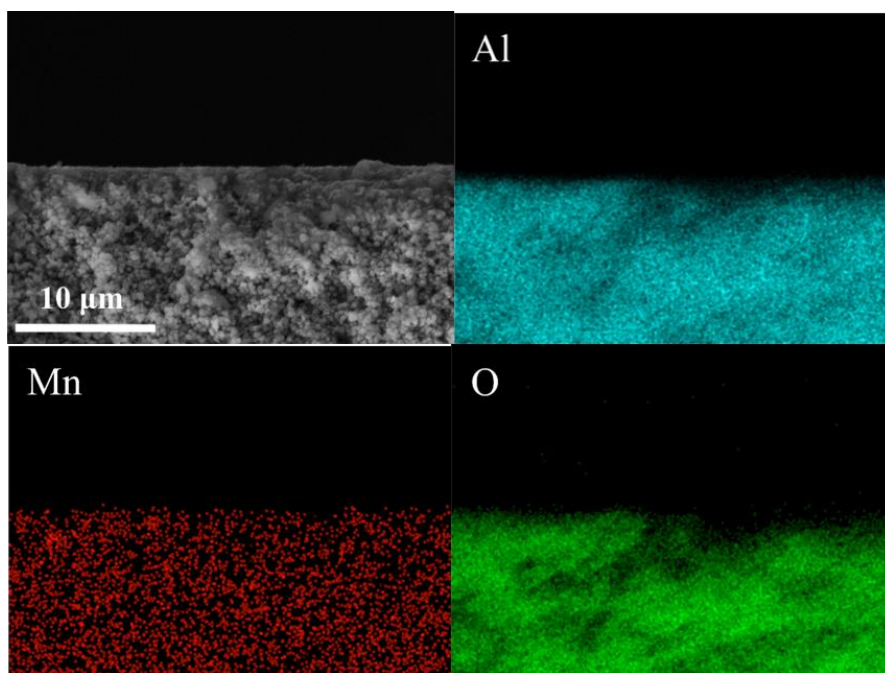
309 e and f, and g and h, respectively.

14

Fig. 4. SEM images of the ceramic membranes (surface): (a), (b) pristine ceramic membrane, (c), (d) Mn-1/Al catalytic membrane, (e), (f) Mn-3/Al catalytic membrane, and (g), (h) Mn-6/Al catalytic membrane.

314   Microanalysis of EDS surface mapping was performed on the Al_2O_3 membrane and the

315   modified Mn-1/Al, Mn-3/Al and Mn-6/Al membranes. The EDS mapping of the uncoated (Fig.

316   S8) and different loaded catalytic membranes (Fig. 5, Fig. S8, and Fig. S9) indicate that the

317   uniformly-distributed MnO_2 fine particles are integrated by the membrane. This can be further

318   confirmed by the cross-sectional SEM-EDS mapping (Fig. 6). The element spectra of uncoated

319   catalytic membranes with different loading are also shown in Fig.5, and Figs. S 8-10, wherein

320   manganese can be confirmed. And from the quantitative analysis of area EDS spectrum results,

321   the content of manganese increased with a higher Mn loading in membranes.

322

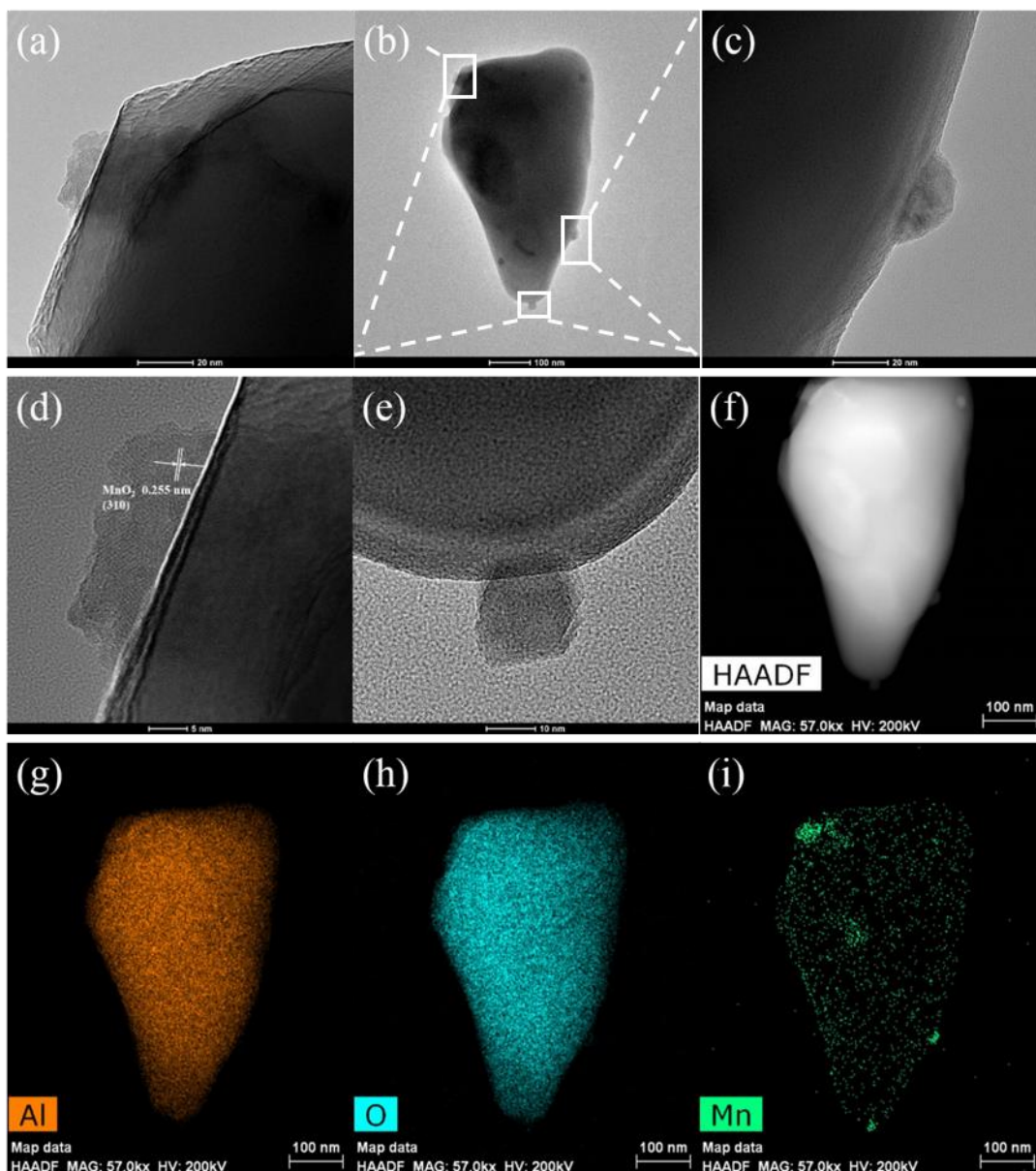323   **Fig. 5.** EDS mapping image and spectrum of Mn-1/Al catalytic membrane (surface).

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Fig. 6. EDS mapping image of Mn-3/Al catalytic membrane (cross-sectional).

Fig. 7 shows the HRTEM images and EDS mapping of a single $MnO_2@Al_2O_3$ particle from a crushed powder of Mn-6/Al catalytic membrane. Fig.7b reveals three small MnO_2 nanoparticles (10 - 20 nm) distributed dispersively on a Al_2O_3 particle at the left top corner, the right bottom corner, and the bottom corner, respectively. The zoom-in HRTEM images of the three fine MnO_2 particles are shown on Figs. 7 a, c and d. The 10-20 nm sized-MnO_2 particles half embedded into the 200-500 nm Al_2O_3 particle. The fine dispersive MnO_2 particles on Al_2O_3 can provide active sites for the catalytic oxidation process. In addition, the uniform dispersion will enable evenly distributed flow of the fluid across the membrane, and efficient interaction between MnO_2 with PMS, which will lead to the high degradation rate of HBA. Fig. 7d reveals a lattice fringe with a distance of 2.55 Å, which is derived from the (310) crystal plane of MnO_2 (Ramsdellite, PDF# 72-1983).

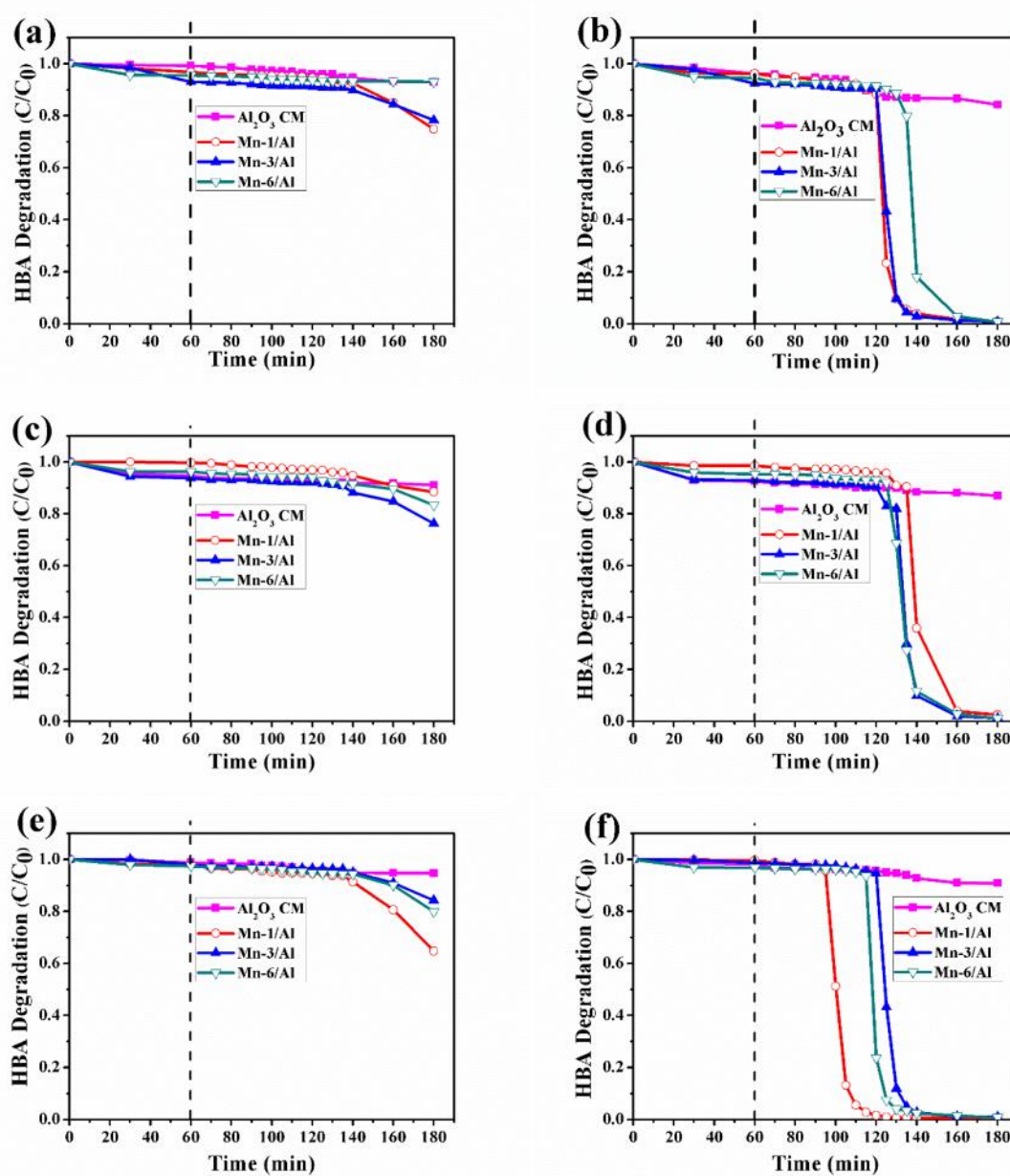**Fig. 7.** (a-e) HRTEM images, (f) HADFF, (g-i) elemental mapping of single MnO$_2$@Al$_2$O$_3$ nanoparticles from membrane Mn-6/Al.

3.3. Catalytic oxidation of HBA

The catalytic activity of the ceramic, catalytic membranes for PMS activation was investigated through the degradation of a typical antibiotics pollutant of 4-hydroxylbenzoic acid (HBA) (Criquet and Leitner 2015, (Tian et al. 2018). Compared to the catalytic oxidation using suspended catalysts, the MnO$_2$-incorporated catalytic membranes would avoid the recovery of

18

347   catalysts from the solution. Fig. 8 shows the effect of MnO_2 loading on catalytic oxidation of

348   HBA by the catalytic membranes. In all tests PMS was added at the time of 60 min. It was

349   noticed that even at the permeate side, the catalytic oxidation reaction did not occur

350   immediately. It normally experienced a concentration platform. This is because when the PMS

351   was just added in the feed-in solution (Fig. 1), PMS needs time to be transported to the surface

352   of membrane through tubing, because of the slow setting rate of peristaltic pump (around 0.2

353   mL/min). The purpose of using a low feeding rate is to maintain the transmembrane pressure

354   (TMP) at around 2 bar throughout the tests. The platform was not unanimous in every test that

355   involves different catalytic membranes. This is because the actual pore size of different

356   membranes changes with the loading of MnO_2, leading to the varied permeation resistance and

357   subsequently varied velocity when the solution permeates through the membrane and flows in

358   the system. However, the tendencies of HBA degradation were still very clear for each test. In

359   this study, the catalyst loading amounts were 0.0167, 0.033, and 0.067 g of per gram Al_2O_3 on

360   Mn-1/Al, Mn-3/Al and Mn-6/Al, respectively. The weight of one ceramic membrane is 3.5 g.

361   Taking Mn-1/Al catalytic membrane for example, there was 0.058 g MnO_2 catalyst in the

362   membrane. The solution used for catalytic oxidation was 500 mL, so the MnO_2 catalysts

363   loading in solution system can be equivalent to 0.1, 0.2 and 0.6 g/L, respectively. The former

364   two catalysts loadings are common in SR-AOPs with suspended catalysts (Kang et al. 2016,

365   (Tian et al. 2018, (Wang et al. 2015a, (Yin et al. 2018). Figs. 8 a, c, and e show the HBA

366   degradation at the feed-in side when initial HBA concentrations were at 20, 40, and 80 ppm,

367   respectively. While Figs. 8 b, d, and f show the HBA concentrations on the permeate side. The

368   pristine Al_2O_3 ceramic membrane has minor performance on HBA degradation. A similar low

369   performance was found on Mn-6 membrane without PMS on HBA degradation (Fig. S11).

370   This is because that the HBA adsorption on membrane surface and within the membrane pores

371   is negligible and the HBA degradation was caused by PMS itself (direct oxidation). With the

19

372 increase of MnO$_2$ loading amount, more catalytically active sites were provided for SO$_4^{•-}$

373 generation from PMS activation. In a previous study, the organic pollutants degradation did

374 not show a big difference with increasing catalysts amount in catalytic membrane, which was

375 explained by mass transfer instead of radical generation (Bao et al. 2018). When compared

376 with the degradation results in other works (Wang et al. 2018, (Zhu et al. 2018), our

377 membranes showed a very good performance even at a high HBA initial concentration (80
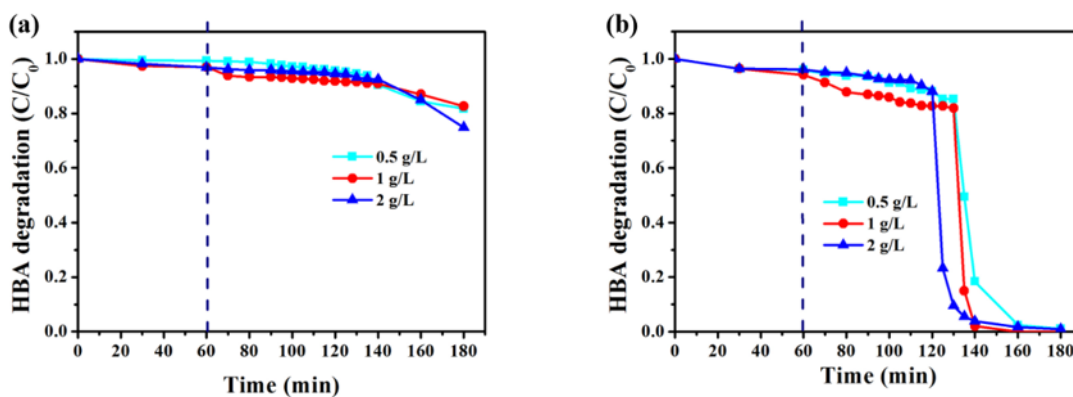
378 ppm).

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Fig. 8. Effect of initial HBA concentration on HBA degradation by different Mn loaded catalytic membranes and unmodified membrane. (a) 20 ppm, feed-in side; (b) 20 ppm, permeate side; (c) 40 ppm, feed-in side; (d) 40 ppm, permeate side, (e) 80 ppm, feed-in side, and (f) 80 ppm, permeate side. PMS loading: 2 g/L; TMP: 2 bar; and temperature: 25 °C. PMS was added at the time 60 min.

Figs. 9 (a) and (b) display the influence of PMS loading on HBA removal efficiency in the range of 0.5 to 2 g/L. The HBA degradation at the permeate side (Fig. 9b) shows that the oxidation reaction efficiency increased with the increase of PMS loading from 0.5 to 1 g/L. However, a further increase of PMS loading to 2 g/L slightly reduced the overall oxidation efficiency because of the self-quenching reaction with excess PMS. The effect of SR-AOPs pretreatment was investigated and the results are shown in Fig. S12. In the pretreatment process, PMS (2 g/L) and MnO_2 powders (0.2 g/L) were added in 100 mL HBA solution (20 ppm) and stirred (200 rpm) for 10 min. Then the pretreatment solution was immediately added in the dead-end filtration cell and the TMP was kept by nitrogen cylinder at 2 bar. At certain time interval, 1 mL HBA solution was collected and the concentration was tested by HPLC. It was found that the pretreatment process by MnO_2/PMS cannot significantly degrade the HBA in a 120 min run. The 40 % degradation at the 5 min is due to the HBA degradation happened outside the membrane cell (10 min stirring process). The 10 min equilibrium process can be seen as a heterogeneous activation process by MnO_2 which leads to the most HBA degradation.
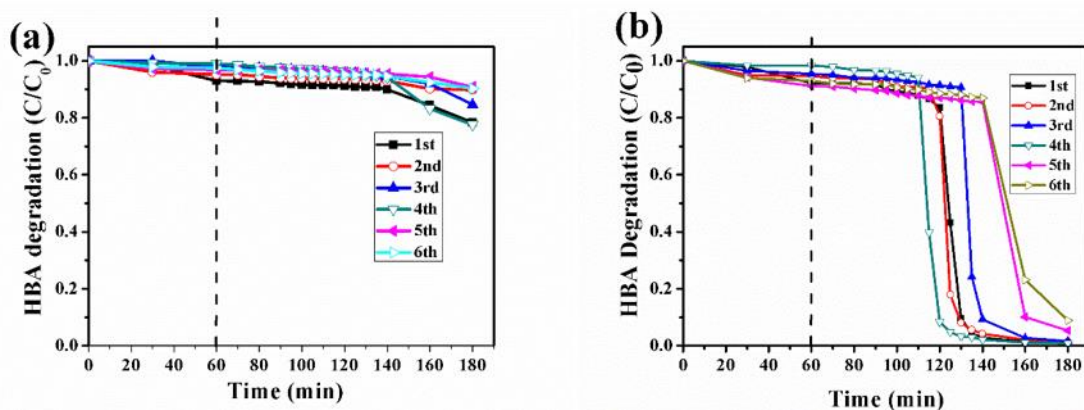
401   **Fig. 9.** Effect of initial PMS concentration on HBA degradation on Mn-1 membrane: (a) feed-

402   in side; (b) permeate side. Initial HBA concentration: 20 ppm; TMP: 2 bar; and temperature:

403   25 ℃. PMS was added at the time 60 min.

404

405   The effect of SR-AOPs pretreatment was investigated and the results are shown in Fig. S12. In

406   the pretreatment process, PMS (2 g/L) and MnO_2 powders (0.2 g/L) were added in 100 mL

407   HBA solution (20 ppm) and stirred (200 rpm) for 10 min. Then the pretreatment solution was

408   immediately added in the dead-end filtration cell and the TMP was kept by nitrogen cylinder

409   at 1 bar. It was found that the pretreatment process by MnO_2/PMS cannot significantly degrade

410   the HBA in a 120 min run. The 40 % degradation at the 5 min is owing to the HBA degradation

411   happened outside the membrane cell (10 min stirring process). The 10 min equilibrium process

412   can be seen as a heterogeneous activation process by MnO_2 leading to the most HBA

413   degradation.

414   The reusability tests of catalytic membrane were also investigated on Mn-3/Al membrane to

415   treat 80 ppm HBA concentration in six runs (Fig. 10). The Mn-3/Al membrane was used

416   directly without any post regeneration treatment but only being washed by ultrapure water and

417   then dried in an oven overnight. The effectiveness of MnO_2 membrane did not decrease till the

418   4th run. The degradation rate of 80 ppm HBA was still 100% at 180 min. At the 5th run and 6th

419   run, the degradation rates decreased slightly for direct use, which were 95% and 91%,

420   respectively. The robust and uniform structure of the ball-milling catalytic membrane provides

421   a better stability than the other membranes reported recently (Wang et al. 2017a, (Wang et al.
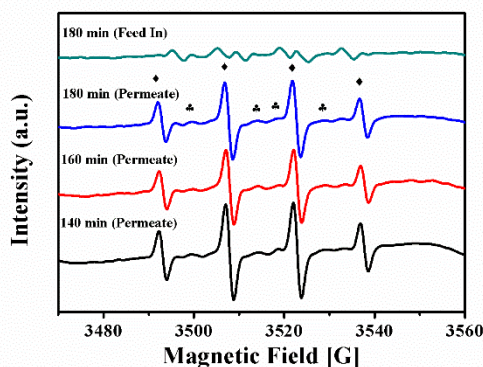
422   2018).

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Fig. 10. Reusability tests of HBA degradation on Mn-3/Al catalytic membrane. (a) Feed-in side; (b) Permeate side. HBA initial concentration: 80 ppm; PMS loading: 2 g/L; TMP: 2 bar; and temperature: 25 ℃. PMS was added at the 60 min.

3.4. Mechanistic studies of HBA degradation in the MnO_2 CM/PMS system

It was reported that various reactive radicals such as $SO_4^{\bullet-}$, $^{\bullet}OH$, and $O_2^{\bullet-}$ will be produced in SR-AOPs system (Wang et al. 2017c).To identify the generation of reactive radicals as well as the dominant radicals in the SR-AOPs facilitated by the catalytic membrane system, EPR tests with DMPO as the spin trapping agent, were first performed. DMPO can react with hydroxyl radicals and sulfate radicals, which can be revealed as the signals of DMPO- $^{\bullet}OH$ and DMPO- $SO_4^{\bullet-}$ in Fig. 11. The EPR tests were performed in the membrane catalytic oxidation of 20 ppm HBA by the Mn-3/Al membrane. Both $SO_4^{\bullet-}$ and $^{\bullet}OH$ were produced during the PMS activation (Luo et al. 2018, (Ma et al. 2019). The signals from Feed-in side are much weaker than that of permeate side, because the main reactions of radicals generation occur when PMS interacts with MnO_2 in the pores of catalytic membrane.
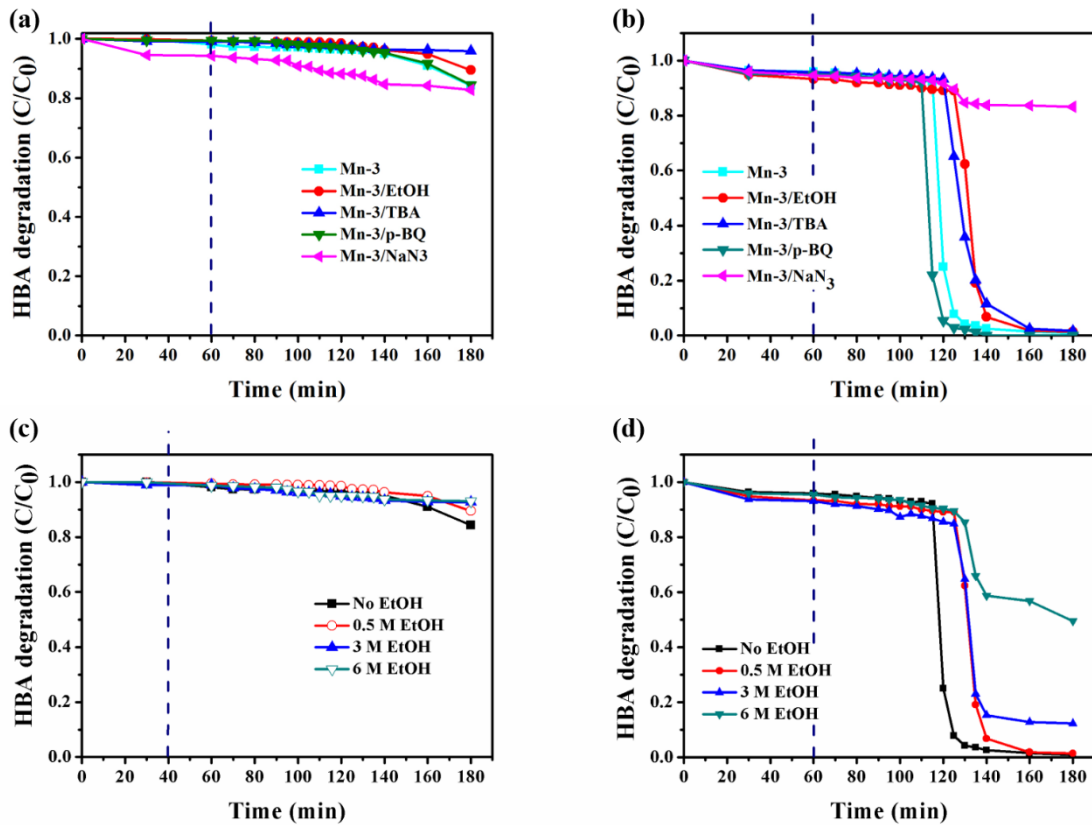
439

Fig. 11. EPR spectra for the Mn-3/Al sample. ((HBA)$_0$: 20 ppm, PMS: 2 g/L, [T]: 25 ℃; TMP: 2 bar; and pump rate: 0.2 mL/min. DMPO – ˙OH ◆;   DMPO – SO$_4$˙$^-$ ♣.

To probe the major radicals involved in the catalytic membrane system, ethanol (EtOH), tert-butanol (TBA) and benzoquinone (p-BQ) were employed as the radical scavengers. EtOH is effective to quench both hydroxyl radicals (rate constant of 1.6 - 7.7 $\times$ 10^7 M^{-1}s^{-1}) and sulfate radicals (rate constant of 1.2-2.8 $\times$ 10^9 M^{-1}s^{-1}). TBA particularly works for the identification of sulfate radicals because of the much larger rate constant with SO$_4$$^{•-}$ (3.8 - 7.6 $\times$ 10^9 M^{-1}s^{-1}) compared with that of ˙OH (4.0 - 9.1$\times$ 10^5 M^{-1}s^{-1}) (Kang et al. 2019a). And p-BQ can be used to identify superoxide radicals (O$_2$$^{•-}$) (rate constant = 0.9 - 1$\times$ 10^9 M^{-1}s^{-1}). Fig. 12 shows the quenching results on Mn-3/Al membrane. It was shown that SO$_4$$^{•-}$ was the dominant radicals in SR-AOPs using the catalytic membrane. Fig. 12 b shows that adding p-BQ has no significant effect on HBA degradation, suggesting the absence of superoxide radicals. Both hydroxyl radicals and sulfate radicals were proven to exist in this SR-AOPs catalytic membrane system, owing to the decline of HBA oxidation efficiency at the permeate side.

Besides the reactive radicals oxidation pathway, non-radical oxidation pathway which relies on singlet oxygen (^{1}O$_2$) was also an important reaction mechanism in SR-AOPs systems (Duan et al. 2018c). It was found that with the addition of 40 mM NaN$_3$, the HBA degradation at the permeate side almost completely stopped. This finding is also consistent with a previous study

459   using metal oxides-coated ceramic membrane (CM) in Alcian Blue 8 GX dye removal (Zhao

460   et al. 2019). However, as a strong reducing agent, sodium azide (NaN_3) can react with not only

461   singlet oxygen ($^1O_2$) but hydroxyl and sulfate radicals (Duan et al. 2018c). The role of free

462   radical pathway is then needed to be further investigated. Figs. 12c-d show the effect of ethanol

463   concentration on HBA catalytic oxidation. At the permeate side (Fig. 12d), the 20 ppm HBA

464   solution can be completely degraded in 180 min. The addition of 0.5 M ethanol can slightly

465   suppress the generation of $SO_4^{\bullet-}$ and $^{\bullet}OH$, and still a HBA degradation efficiency of 98.6% can

466   be achieved. When further increasing the ethanol concentration to 3 and 6 M, only 87.8 % and

467   50.6% of HBA were decomposed in 180 min. In a previous study, ethanol was used as a radical

468   scavenger in a Co_3O_4 / PMS system. It was found when the ethanol to PMS ratio are 500:1

469   (3.25 M of PMS) and 1000:1 (6.5 M of PMS), only around 40% and 20% of HBA degradation

470   efficiency were achieved, respectively. And when the water was completely replaced by

471   ethanol, no phenol degradation was observed (Duan et al. 2015b). Zhu et al. studied the

472   mechanism of β-MnO_2/PS system and found that the sulfate and hydroxyl radicals were not

473   produced. The singlet oxygen was generated and accounted for the phenol oxidation (Zhu et al.

474   2019). Zhou et al. analysed the radical generation in α-MnO_2/PMS and δ-MnO_2/PMS systems.

475   The results suggested that $^1O_2$ and $O_2^{\bullet-}$ have a little effect on the 4-NP (4-nitrophenol)

476   degradation (Zhou et al. 2019). In conclusion, sulfate radicals ($SO_4^{\bullet-}$), hydroxyl radicals ($^{\bullet}OH$)

477   and the non-radical degradation pathway exist in the Mn-catalytic membrane/PMS system, and

478   no superoxide radicals ($O_2^{\bullet-}$) produced. Free radical pathway dominated the reaction and $SO_4^{\bullet}$

479     $^-$ plays a much more important role than $^{\bullet}OH$ in HBA degradation.

Fig. 12. Quenching tests for the Mn-3/Al sample. (a) Different quenching agent (feed-in side); (b) Different quenching agent (permeate side) (TBA: 0.5 M, EtOH: 0.5 M, p-BQ: 2 mM, and NaN$_3$: 40 mM); (c) Different EtOH concentration quenching (feed-in side); and (d) Different EtOH concentration quenching (Permeate side). (HBA)$_0$: 20 PPM; PMS: 2 g/L; [T]: 25 ℃; TMP: 2 bar; and pump rate: 0.2 mL/min.
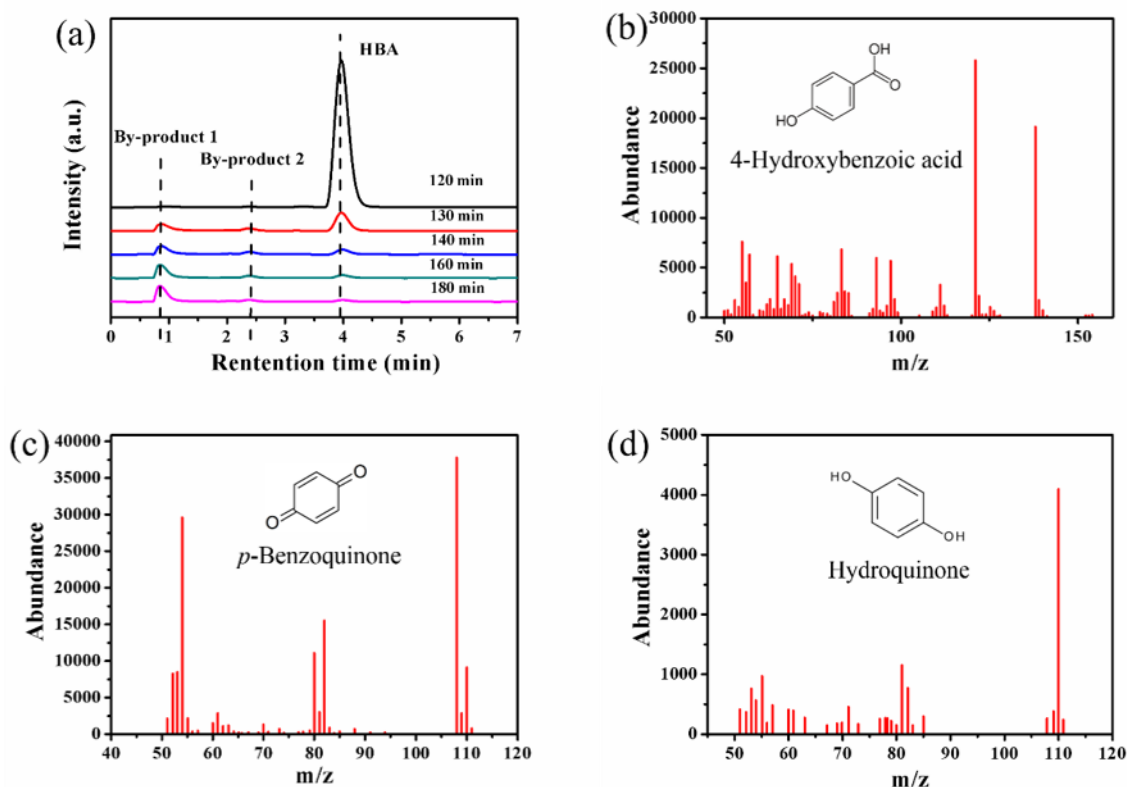
The manganese ions content was tested on ICP to verify Mn ion leaching. Samples from feed-in tank of Mn-3/Al after the 1st, 4th, 5th, and 6th run of 20 ppm HBA degradation (the condition is identical with Fig. 9 stability tests) are shown in Fig. S13. The Mn leaching of all the runs were very low and the Mn ions in solution slightly increased with the test times. The Mn ions content were in the order of 1st (1.16 mg/L) < 4th (1.69 mg/L) < 5th (1.99 mg/L) < 6th (2.82 mg/L).

3.5. HBA degradation pathways

In order to clarrify the reaction pathway of the degradation of HBA over MnO_2 catalytic membrane in the presence of PMS, GC-MS analysis of the intermediates was carried out for the samples collected from permeate side on certain time interval (120, 130, 140, 160 and 180 min). First, those solutions (1 mL solution without GC-MS extraction pretreatment steps) were injected into 1.5 mL UHPLC vials which pre-injected with 0.5 mL methanol as the quenching agent. The decay of HBA during the oxidation process monitored by UHPLC is illustrated in Fig. 13a.
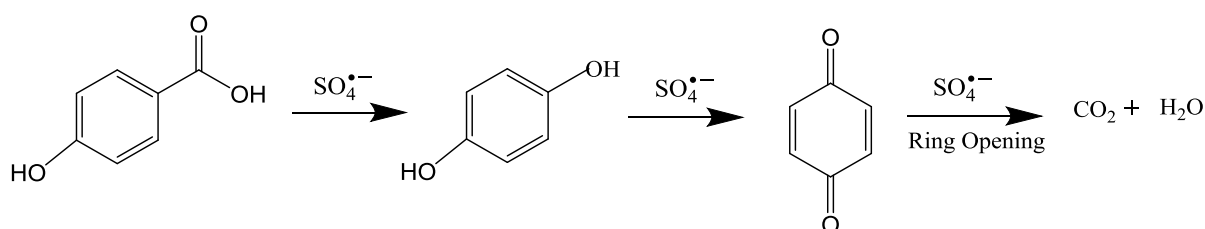

Fig. 13. (a) HPLC spectra of HBA degradation in a 180 min experiment. (Initial HBA concentration: 20 ppm, Mn-1/Al catalytic membrane, PMS concentration: 2 g/L, TMP: 2 bar); Mass spectra of (b) HBA, (c) p-Benzoquinone, and (d) Hydroquinone. (Initial HBA concentration: 20 ppm, Mn-3/Al catalytic membrane, PMS concentration: 2 g/L, and TMP set at 2 bar).

508

509   It can be seen that a well-defined HBA peak appeared at retention time (t_R) = 3.98 min and the

510   peak intensity gradually decreased while two major by-products were emerged during the

511   oxidation process. GC-MS tests were carried out on the Agilent 7890B/5977B GC-MS system.

512   The extract ion chromatography (EIC) signals of the HBA degradation intermediates were

513   recorded with retention time between 0 − 28 min. When in the presence of $SO_4^{\bullet-}$, two by-

514   products were confirmed: *p*-benzoquinone (m/z = 108.1) and hydroquinone (m/z = 110.1),

515   during the HBA (m/z = 138.1) oxidation process. The retention of *p*-benzoquinone (4.380 min)

516   and hydroquinone (12.017 min) were shorter than that of HBA (15.618). The mass spectra of

517   HBA, *p*-benzoquinone, and hydroquinone are shown in Figs. 13 b-d, respectively. Unlike $^{\bullet}OH$,

518    $SO_4^{\bullet-}$ does not add to aromatic ring of HBA but directly reacts with HBA via electron transfer

519   from the ring leading to the formation of a radical cation. The decarboxylation of the radical

520   cation to HBA results in the formation of hydroquinone. Because the hydroquinone is easily to

521   be oxidised, when in presence of $SO_4^{\bullet-}$, it will be further oxidised to *p*-benzoquinone.

522   Subsequently, the $SO_4^{\bullet-}$ can attack the C=C and C-C bond of *p*-benzoquinone, leading to the

523   ring opening and formation of inorganic ions, carbon dioxide and water (Criquet and Leitner

524   2015). The $SO_4^{\bullet-}$ based HBA degradation pathway is shown in Fig. 14.
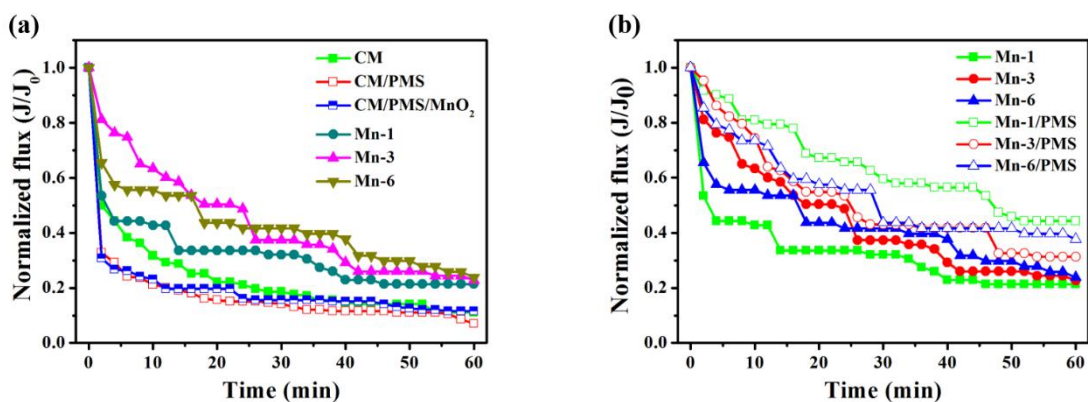
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526

527   **Fig. 14.** Proposed degradation pathway of 4-hydroxylbenzoic acid by MnO_2 integrated catalytic

528   membrane at the presence of PMS.

529   3.6. Membrane filtration performance

530   Fig. 15 shows the flux decline curves during the filtration of humic acids (HAs) by different

531   membranes (CM, Mn-1, Mn-3, and Mn-6) under same parameters. For the CM, Mn-1, Mn-3,

532   and Mn-6 samples, 100 mL HAs solution (2 g/L) was stirred for 30 min and then filtered

533   through the dead-end filtration cell installed with the respective membrane (CM, Mn-1, Mn-3

534   and Mn-6) under a pressure of 1 bar kept by the nitrogen cylinder. For the CM/PMS, Mn-1,

535   Mn-3 and Mn-6 samples, the same amount HAs solution (2 g/L) mixed with PMS (4 g/L) was

536   stirred for 1 h to reach a uniform dispersion of PMS within HAs solution, then filtered through

537   the dead-end membrane cell. For the CM/PMS/MnO_2 system, the HAs solution (2 g/L) mixed

538   with PMS (4 g/L) and MnO_2 (0.2 g/L) catalysts was stirred for 1 h to reach a uniform dispersion

539   of PMS and MnO_2 within HAs solution, then filtered through the membrane cell which

540   installed with the pure ceramic membrane (CM) under 1 bar pressure. The results showed that

541   the flux decline of the pure ceramic membrane support (CM) is higher than that of Mn-1, Mn-

542   3, and Mn-6 membrane, suggesting that the MnO_2 integrated ceramic membranes have a better

543   fouling resistance compared with the pure alumina membrane support (Fig. 15a). When

544   comparing with the permeate flux of CM, CM/PMS and CM/PMS/MnO_2, it can be found that

545   adding PMS or PMS and MnO_2 catalysts in HAs has no function in fouling alleviation when

546   using pure ceramic membrane support (CM). The addition of PMS and MnO_2 even worsened

547   the fouling condition. This can be ascribed to the fouling caused by MnO_2 nanoparticles and

548   PMS (Fig. 15a). Fig. 15b shows the fouling alleviation performance of MnO_2 based catalytic

549   membrane using PMS (4 g/L), The flux recovery happened in the MnO_2 based catalytic

550   membranes with all loading (Mn-1, Mn-3 and Mn-6). It was found that the Mn-1/PMS sample

551   has the best fouling recovery rate because of the relatively low flux resistance of the Mn-1

552   membrane without PMS. A further increase of flux recovery rate from Mn-3/PMS to Mn-

29

553 6/PMS is because that the great increase of Mn loading leads to an improvement of anti-fouling

554 performance.

555

556 **Fig. 15.** Specific flux of different coated and uncoated membranes for filtration of humic acids

557 (2 g/L). (a) pure ceramic supports and Mn catalytic membranes without PMS; (b) the

558 comparative study of Mn catalytic membranes in flux change with or without PMS.

559

4. Conclusions

561 In summary, catalytic ceramic membranes consisting of nano-structured MnO_2 dispersed

562 uniformly inside the pores were prepared via a simple one-step ball-milling method for the first

563 time. The ball-milling process not only contributes to the stable ceramic membrane formation,

564 but helps the well-dispersive arrangement of fine MnO_2 catalysts on the surface of Al_2O_3

565 particles. Different loading of MnO_2 catalytic membranes (1.67%, 3.33% and 6.67% of total

566 membrane mass) were fabricated and the performance on HBA degradation were tested and

567 compared. The uniform distribution of MnO_2 nanoparticles within the membrane pores and on

568 the membrane surface provided sufficient active sites for PMS activation to generate $SO_4^{\bullet-}$,

569 endowing the MnO_2 catalytic membrane with an excellent performance towards HBA catalytic

570 oxidation even at a high initial HBA concentration (80 ppm) in a continuous cross-flow

571 membrane device. It was found that the degradation efficiency slightly increased on a higher

572 loading, but even with the lowest loading (1.67% of MnO_2) the effectiveness of HBA

573 degradation was still high. This indicates the importance of membrane micro-structures for

574 efficient utilisation of the MnO_2 catalyst. The stability and leaching tests revealed a good

575 stability of the catalytic membrane even after the 6th run. EPR and quenching tests were applied

576 to investigate the mechanism of PMS activation and HBA degradation. Both sulfate radicals

577 ($SO_4^{\bullet-}$) and hydroxyl radicals ($^{\bullet}OH$) were generated in the catalytic membrane process. In

578 addition, the non-radical pathway was also confirmed by NaN_3 and varying amount of ethanol

579 quenching tests, but was not dominant for the degradation. Free radical pathway dominated the

580 reaction and $SO_4^{\bullet-}$ plays a much more important role than $^{\bullet}OH$ in HBA degradation. HBA

581 degradation intermediates were investigated by GC-MS, suggesting that hydroquinone and p-

582 benzoquinone are the main intermediates. A possible HBA degradation route under the

583 presence of $SO_4^{\bullet-}$ was also proposed. This study provides a novel way for integrating

584 membrane technology and AOPs towards practical water/wastewater treatments.

Acknowledgements

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593 **References**

594 Anipsitakis, G.P. and Dionysiou, D.D., 2003. Degradation of organic contaminants in water
595 with sulfate radicals generated by the conjunction of peroxymonosulfate with cobalt. Environ.
596 Sci. Technol. 37(20), 4790-4797.

597 Anipsitakis, G.P. and Dionysiou, D.D., 2004a. Radical Generation by the Interaction of
598 Transition Metals with Common Oxidants. Environ. Sci. Technol. 38(13), 3705-3712.

599 Anipsitakis, G.P. and Dionysiou, D.D., 2004b. Transition metal/UV-based advanced oxidation
600 technologies for water decontamination. Appl. Catal., B 54(3), 155-163.

601 Bao, Y., Lim, T.-T., Wang, R., Webster, R.D. and Hu, X., 2018. Urea-assisted one-step
602 synthesis of cobalt ferrite impregnated ceramic membrane for sulfamethoxazole degradation
603 via peroxymonosulfate activation. Chem. Eng. J. 343, 737-747.

604 Chan, S.H.S., Yeong Wu, T., Juan, J.C. and Teh, C.Y., 2011. Recent developments of metal
605 oxide semiconductors as photocatalysts in advanced oxidation processes (AOPs) for treatment
606 of dye waste-water. Journal of Chemical Technology & Biotechnology 86(9), 1130-1158.

607 Chen, S., Yu, J., Wang, H., Yu, H. and Quan, X., 2015. A pilot-scale coupling catalytic
608 ozonation–membrane filtration system for recirculating aquaculture wastewater treatment.
609 Desalination 363(Supplement C), 37-43.

610 Cheng, X., Liang, H., Ding, A., Tang, X., Liu, B., Zhu, X., Gan, Z., Wu, D. and Li, G., 2017.
611 Ferrous iron/peroxymonosulfate oxidation as a pretreatment for ceramic ultrafiltration
612 membrane: Control of natural organic matter fouling and degradation of atrazine. Water Res.
613 113, 32-41.

614 Cheng, X., Wu, D., Liang, H., Zhu, X., Tang, X., Gan, Z., Xing, J., Luo, X. and Li, G., 2018.
615 Effect of sulfate radical-based oxidation pretreatments for mitigating ceramic UF membrane
616 fouling caused by algal extracellular organic matter. Water Res. 145, 39-49.

617 Criquet, J. and Leitner, N.K.V., 2015. Reaction pathway of the degradation of the p-
618 hydroxybenzoic acid by sulfate radical generated by ionizing radiations. Radiat. Phys. Chem.
619 106, 307-314.

620 Duan, X., Ao, Z., Zhang, H., Saunders, M., Sun, H., Shao, Z. and Wang, S., 2018a.
621 Nanodiamonds in sp2/sp3 configuration for radical to nonradical oxidation: Core-shell layer
622 dependence. Appl. Catal., B 222, 176-181.

623 Duan, X., Ao, Z., Zhou, L., Sun, H., Wang, G. and Wang, S., 2016a. Occurrence of radical and

624 nonradical pathways from carbocatalysts for aqueous and nonaqueous catalytic oxidation. Appl.

625 Catal., B 188, 98-105.

626 Duan, X., O'Donnell, K., Sun, H., Wang, Y. and Wang, S., 2015a. Sulfur and nitrogen co-

627 doped graphene for metal-free catalytic oxidation reactions. Small 11(25), 3036-3044.

628 Duan, X., Su, C., Miao, J., Zhong, Y., Shao, Z., Wang, S. and Sun, H., 2018b. Insights into

629 perovskite-catalyzed peroxymonosulfate activation: Maneuverable cobalt sites for promoted

630 evolution of sulfate radicals. Appl. Catal., B 220, 626-634.

631 Duan, X., Sun, H., Ao, Z., Zhou, L., Wang, G. and Wang, S., 2016b. Unveiling the active sites

632 of graphene-catalyzed peroxymonosulfate activation. Carbon 107, 371-378.

633 Duan, X., Sun, H., Shao, Z. and Wang, S., 2018c. Nonradical reactions in environmental

634 remediation processes: Uncertainty and challenges. Appl. Catal., B 224, 973-982.

635 Duan, X., Sun, H., Tade, M. and Wang, S., 2018d. Metal-free activation of persulfate by cubic

636 mesoporous carbons for catalytic oxidation via radical and nonradical processes. Catal. Today

637 307, 140-146.

638 Duan, X., Sun, H., Wang, Y., Kang, J. and Wang, S., 2015b. N-Doping-induced nonradical

639 reaction on single-walled carbon nanotubes for catalytic phenol oxidation. ACS Catal. 5(2),

640 553-559.

641 Guo, Y., Xu, B. and Qi, F., 2016. A novel ceramic membrane coated with MnO_2–Co_3O_4

642 nanoparticles catalytic ozonation for benzophenone-3 degradation in aqueous solution:

643 Fabrication, characterization and performance. Chem. Eng. J. 287(Supplement C), 381-389.

644 Kang, J., Duan, X., Zhou, L., Sun, H., Tadé, M.O. and Wang, S., 2016. Carbocatalytic

645 activation of persulfate for removal of antibiotics in water solutions. Chem. Eng. J. 288, 399-

646 405.

647 Kang, J., Zhang, H., Duan, X., Sun, H., Tan, X., Liu, S. and Wang, S., 2019a. Magnetic Ni-Co

648 alloy encapsulated N-doped carbon nanotubes for catalytic membrane degradation of emerging

649 contaminants. Chem. Eng. J. 362, 251-261.

650 Kang, J., Zhou, L., Duan, X., Sun, H., Ao, Z. and Wang, S., 2019b. Degradation of cosmetic

651 microplastics via functionalized carbon nanosprings. Matter 1, 745-758.

652 Kim, M., Hwang, Y. and Kim, J., 2013. Graphene/MnO_2-based composites reduced via

653 different chemical agents for supercapacitors. J. Power Sources 239, 225-233.

654 Luo, X., Liang, H., Qu, F., Ding, A., Cheng, X., Tang, C.Y. and Li, G., 2018. Free-standing

655 hierarchical α-MnO_2@CuO membrane for catalytic filtration degradation of organic pollutants.

656 Chemosphere 200, 237-247.

657   Ma, T., Liu, L., Meng, B., Gao, J., Wang, S. and Liu, S., 2019. Heterogeneous activation of

658   peroxymonosulfate via a Ag-La$_{0.8}$Ca$_{0.2}$Fe$_{0.94}$O$_{3-\delta}$ perovskite hollow fibre membrane reactor for

659   dye degradation. Sep. Purif. Technol. 211, 298-302.

660   Neyens, E. and Baeyens, J., 2003. A review of classic Fenton's peroxidation as an advanced

661   oxidation technique. J. Hazard. Mater. 98(1–3), 33-50.

662   Norwood, W.P., Borgmann, U. and Dixon, D.G., 2007. Chronic toxicity of arsenic, cobalt,

663   chromium and manganese to Hyalella azteca in relation to exposure and bioaccumulation.

664   Environ. Pollut. 147(1), 262-272.

665   Saputra, E., Muhammad, S., Sun, H., Ang, H.-M., Tadé, M.O. and Wang, S., 2013a. A

666   comparative study of spinel structured Mn$_3$O$_4$, Co$_3$O$_4$ and Fe$_3$O$_4$ nanoparticles in catalytic

667   oxidation of phenolic contaminants in aqueous solutions. J. Colloid Interface Sci. 407, 467-

668   473.

669   Saputra, E., Muhammad, S., Sun, H., Ang, H.-M., Tadé, M.O. and Wang, S., 2013b.

670   Manganese oxides at different oxidation states for heterogeneous activation of

671   peroxymonosulfate for phenol degradation in aqueous solutions. Appl. Catal., B 142, 729-735.

672   Saputra, E., Muhammad, S., Sun, H., Ang, H.M., Tade, M. and Wang, S., 2013c. Different

673   crystallographic one-dimensional MnO$_2$ nanomaterials and their superior performance in

674   catalytic phenol degradation. Environ. Sci. Technol. 47(11), 5882-5887.

675   Sun, H., Kwan, C., Suvorova, A., Ang, H.M., Tadé, M.O. and Wang, S., 2014. Catalytic

676   oxidation of organic pollutants on pristine and surface nitrogen-modified carbon nanotubes

677   with sulfate radicals. Appl. Catal., B 154–155, 134-141.

678   Sun, H. and Wang, S., 2015. Catalytic oxidation of organic pollutants in aqueous solution using

679   sulfate radicals. Catalysis 27, 209-247.

680   Sun, H., Zhou, G., Liu, S., Ang, H.M., Tadé, M.O. and Wang, S., 2012. Nano-Fe^0 encapsulated

681   in microcarbon spheres: Synthesis, characterization, and environmental applications. ACS

682   Appl. Mater. Interfaces 4(11), 6235-6241.

683   Tian, W., Zhang, H., Qian, Z., Ouyang, T., Sun, H., Qin, J., Tadé, M.O. and Wang, S., 2018.

684   Bread-making synthesis of hierarchically Co@C nanoarchitecture in heteroatom doped porous

685   carbons for oxidative degradation of emerging contaminants. Appl. Catal., B 225, 76-83.

686   Wang, G., Wang, D., Dong, X., Zhang, X. and Ma, H., 2017a. Sodium persulfate based PVDF

687   membrane for concurrent advanced oxidation and ultrafiltration of ofloxacin in water. Chem.

688   Eng. J. 315, 509-515.

689   Wang, J.-G., Yang, Y., Huang, Z.-H. and Kang, F., 2013. A high-performance asymmetric

690   supercapacitor based on carbon and carbon–MnO$_2$ nanofiber electrodes. Carbon 61, 190-199.

691 Wang, W., Wang, H., Li, G., An, T., Zhao, H. and Wong, P.K., 2019. Catalyst-free activation
692 of persulfate by visible light for water disinfection: Efficiency and mechanisms. Water Res.
693 157, 106-118.

694 Wang, X., Wang, G., Chen, S., Fan, X., Quan, X. and Yu, H., 2017b. Integration of membrane
695 filtration and photoelectrocatalysis on g-C_3N_4/CNTs/Al_2O_3 membrane with visible-light
696 response for enhanced water treatment. J. Membr. Sci. 541(Supplement C), 153-161.

697 Wang, Y., Cao, D., Liu, M. and Zhao, X., 2017c. Insights into heterogeneous catalytic
698 activation of peroxymonosulfate by Pd/g-C_3N_4: The role of superoxide radical and singlet
699 oxygen. Catal. Commun. 102, 85-88.

700 Wang, Y., Sun, H., Ang, H.M., Tadé, M.O. and Wang, S., 2015a. 3D-hierarchically structured
701 MnO_2 for catalytic oxidation of phenol solutions by activation of peroxymonosulfate: Structure
702 dependence and mechanism. Appl. Catal., B 164, 159-167.

703 Wang, Y., Sun, H., Duan, X., Ang, H.M., Tadé, M.O. and Wang, S., 2015b. A new magnetic
704 nano zero-valent iron encapsulated in carbon spheres for oxidative degradation of phenol. Appl.
705 Catal., B 172–173, 73-81.

706 Wang, Y., Zhao, S., Fan, W., Tian, Y. and Zhao, X., 2018. The synthesis of novel Co–Al_2O_3
707 nanofibrous membranes with efficient activation of peroxymonosulfate for bisphenol A
708 degradation. Environ. Sci.: Nano 5(8), 1933-1942.

709 Wang, Y., Zhou, L., Duan, X., Sun, H., Tin, E.L., Jin, W. and Wang, S., 2015c. Photochemical
710 degradation of phenol solutions on Co_3O_4 nanorods with sulfate radicals. Catal. Today 258(Part
711 2), 576-584.

712 Xia, D., Yin, R., Sun, J., An, T., Li, G., Wang, W., Zhao, H. and Wong, P.K., 2017. Natural
713 magnetic pyrrhotite as a high-Efficient persulfate activator for micropollutants degradation:
714 Radicals identification and toxicity evaluation. J. Hazard. Mater. 340, 435-444.

715 Xiao, K., Li, J.-W., Chen, G.-F., Liu, Z.-Q., Li, N. and Su, Y.-Z., 2014. Amorphous MnO_2
716 supported on 3D-Ni nanodendrites for large areal capacitance supercapacitors. Electrochim.
717 Acta 149, 341-348.

718 Yin, Y., Shi, L., Li, W., Li, X., Wu, H., Ao, Z., Tian, W., Liu, S., Wang, S. and Sun, H., 2019.
719 Boosting Fenton-like reactions via single atom Fe catalysis. Environ. Sci. Technol. in press
720 (DOI: 10.1021/acs.est.9b03342).

721 Yin, Y., Wu, H., Shi, L., Zhang, J., Xu, X., Zhang, H., Wang, S., Sillanpd, M. and Sun, H.,
722 2018. Quasi single cobalt sites in nanopores for superior catalytic oxidation of organic
723 pollutants. Environ. Sci.: Nano 5(12), 2842-2852.

724 Zhao, H., Chen, S., Quan, X., Yu, H. and Zhao, H., 2016. Integration of microfiltration and

725 visible-light-driven photocatalysis on g-C_3N_4 nanosheet/reduced graphene oxide membrane for

726 enhanced water treatment. Appl. Catal., B 194, 134-140.

727 Zhao, Q., Lu, D., Jiang, H., Zhao, Y., Sun, Y., Li, Z., Yang, M., Wang, P. and Ma, J., 2019.

728 Peroxymonosulfate-based cleaning technology for metal oxide-coated ceramic ultrafiltration

729 membrane polluted by Alcian Blue 8GX dye: Radical and non-radical oxidation cleaning

730 mechanism. J. Membr. Sci. 573, 210-217.

731 Zhou, Z.-G., Du, H.-M., Dai, Z., Mu, Y., Tong, L.-L., Xing, Q.-J., Liu, S.-S., Ao, Z. and Zou,

732 J.-P., 2019. Degradation of organic pollutants by peroxymonosulfate activated by MnO_2 with

733 different crystalline structures: Catalytic performances and mechanisms. Chem. Eng. J. 374,

734 170-180.

735 Zhu, S., Li, X., Kang, J., Duan, X. and Wang, S., 2019. Persulfate activation on crystallographic

736 manganese oxides: Mechanism of singlet oxygen evolution for nonradical selective

737 degradation of aqueous contaminants. Environ. Sci. Technol. 53, 307-315.

738 Zhu, Z.-S., Qu, J., Hao, S.-M., Han, S., Jia, K.-L. and Yu, Z.-Z., 2018. α-Fe_2O_3

739 Nanodisk/bacterial cellulose hybrid membranes as high-performance sulfate-radical-based

740 visible light photocatalysts under stirring/flowing states. ACS Appl. Mater. Interfaces 10,

741 30670-30679.

742