Electronic Supplementary Information for

The synthesis of novel Co-Al_2O_3 nanofibrous membranes with efficient activation of peroxymonosulfate for bisphenol A degradation

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Text S1

During the degradation process, the solution pH was real time monitored by a pH meter, and $NaHCO_3$ was dropwise added to the solution to matin the solution pH at 7. Carbonate buffer was usually used in PMS activation process for organic pollutant degradation.[1-3] The $NaHCO_3$ was 3 mM when the solution pH was maintained at 7 during reactions.

Herein, the effect of $NaHCO_3$ concentration on BPA degradation was studied. As shown in Fig. S2, 88%, 100%, 94%, 83% and 80% BPA were removed within 60 min when 0, 3, 5, 7, and 10 mM $NaHCO_3$ were added, respectively. It can be seen that the degradation rate increased when using 3 mM $NaHCO_3$ buffer compared to that without buffer, but decreased when the concentration of $NaHCO_3$ buffer increased from 3 mM to 10 mM, and inhibited at high $NaHCO_3$ buffer concentrations (higher than 7 mM). Fig. S2B present the corresponding pH during reactions, which was at pH3 when without $NaHCO_3$ and were generally neutral (pH7-8) with $NaHCO_3$ (3-10 mM). The reason for the effect of $NaHCO_3$ on BPA degradation was analyzed as follows:

On one hand, it is reported that low pH has negative effect on the degradation due to the scavenge of $\cdot$OH and $SO_4^{-\cdot}$ by excess H^+ (Eqs. (S1)-(S2)).[4-6] Commonly, oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was used as PMS, which was acidity.[2,3] As shown in Fig. S2B, with the addition of PMS, the pH sharply decreased to 3.2 when without buffer, while slightly decreased and kept at ~7.0 when with 3 mM $NaHCO_3$ buffer. Obviously, the buffer could alleviate the acidification that caused by PMS addition. Therefore, the BPA degradation rate increased when with 3 mM $NaHCO_3$ buffer compared to that without buffer.

$$\cdot OH + H^+ + e^- \rightarrow H_2O \qquad (S1)$$

$$SO_4^{-\cdot} + H^+ + e^- \rightarrow HSO_4^{-\cdot} \qquad (S2)$$

On the other hand, HCO_3^- can react with •OH or $SO_4^{\bullet -}$ to generate $CO_3^{\bullet -}$ free radicals at high rate (Eq. (S3)-(S4)).[6-8] It is reported that the steady-state concentration of $CO_3^{\bullet -}$ is 600-fold higher than $SO_4^{\bullet -}$ in the UV/persulfate system.[7] Thus the role of $CO_3^{\bullet -}$ should be taken into consideration in the degradation process. The oxidization potential (E^0) and reaction rate constants between BPA and various free radicals were listed in Table S1.[7,9] It can be seen that E^0 ($SO_4^{\bullet -}$)> E^0 (HO•)> E^0 ($CO_3^{\bullet -}/HCO_3^{\bullet}$), which indicates that $CO_3^{\bullet -}$ process a weaker oxidation ability than $SO_4^{\bullet -}$ and HO•. The reaction rate constants of both $k_{SO4\bullet\text{-}BPA}$ and $k_{HO\bullet BPA}$ were 3-4 orders of magnitude higher than $k_{CO3\bullet\text{-}/HCO3\bullet BPA}$. Hence, excess amount of HCO_3^- usually exhibits inhibition effect on BPA degradation in •OH or $SO_4^{\bullet -}$ based advanced oxidation processes.[6,8,10-14]

$$\bullet OH + HCO_3^- \rightarrow CO_3^{\bullet -} + H_2O \qquad 8.6 \times 10^6\ M^{-1}\ s^{-1} \qquad (S3)$$

$$SO_4^{\bullet -} + HCO_3^- \rightarrow HSO_4^- + CO_3^{\bullet -} \qquad 2.6\text{-}9.1 \times 10^6\ M^{-1}\ s^{-1} \qquad (S4)$$

Moreover, because the reaction rate constants of both $k_{SO4\bullet\text{-}BPA}$ and $k_{HO\bullet BPA}$ were 3-4 orders of magnitude higher than $k_{SO4\bullet\text{-}HCO3\text{-}}$ and $k_{HO\bullet\ HCO3\text{-}}$ (Table S1 and Eq. (S3)-(S4)), the concentration of $CO_3^{\bullet -}$ may be not as high as 600-fold higher than $SO_4^{\bullet -}$ and •OH when at low HCO_3^- concentration in this reaction. Therefore, the contribution of $CO_3^{\bullet -}$ to the degradation of BPA is small when using 3 mM $NaHCO_3$.

In short, the positive effect of $NaHCO_3$ at low concentration was due to its buffer function, while the negative effect of $NaHCO_3$ at high concentration was due to its scavenge of •OH and $SO_4^{\bullet-}$ by HCO_3^-. The results are in accordance with many previous reports.[6,14]

Text S2

The possible byproducts formed from BPA degradation were identified by LCMS. To ensure the veracity, two samples including the solution of 100% BPA removed (initial conc. 20 mg L^{-1}, denoted as Sample A), and the solution of 59% BPA removed (initial conc. 100 mg L^{-1}, denoted as Sample B) were tested. As shown in Fig. S8, only a few peaks were observed in Sample A, while more peaks were observed in Sample B. In the mass spectra (Fig. S8(b-e)), the products at m/z 227, 243, 221, 135, 75 were detected, and they correspond to BPA itself and its byproducts formulated as P1, P2, P3, P4, respectively. As shown in Table S5, only P1 and P3 were detected in Sample A, while BPA itself and P1 to P4 were detected in Sample B. Because the initial concentration of Sample B was high, and BPA was only partially degraded in Sample B, thus BPA itself and some intermediates as well as some small m/z byproducts were detected in Sample B.

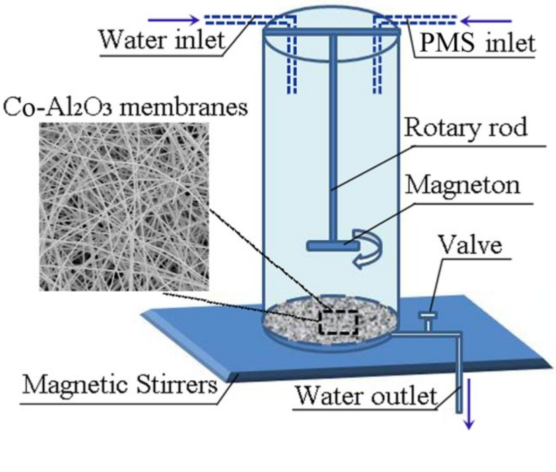


Fig. S1 The membrane reactor that used in the degradation process.

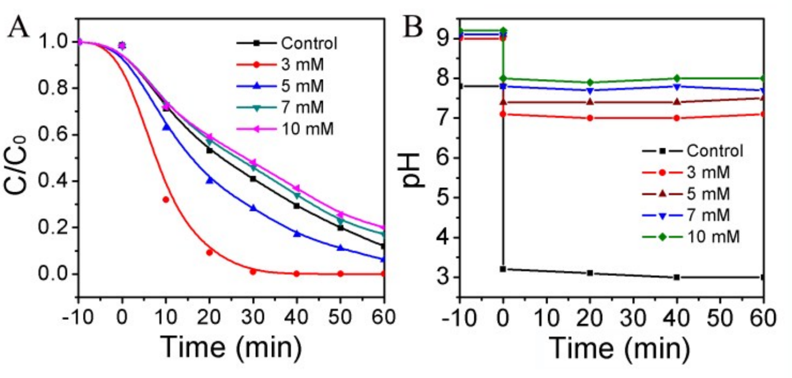


Fig. S2 (A) Effect of $NaHCO_3$ concentration on BPA degradation by 11% Co-Al_2O_3-600 °C membrane, and (B) the corresponding pH during reactions. Conditions: [BPA] = 20 mg L^{-1}, [PMS] = 1 mM.

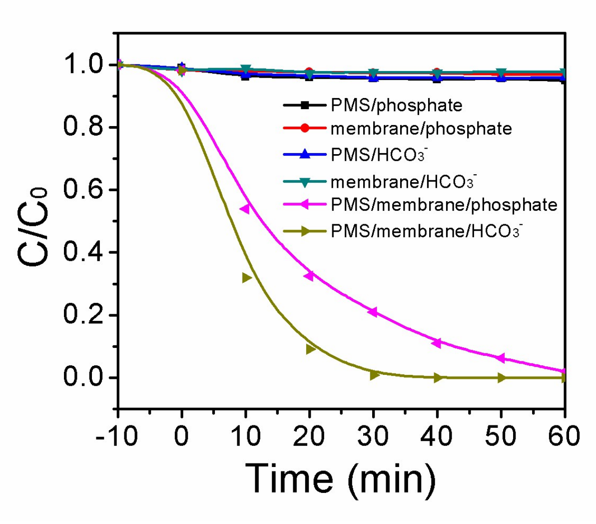


Fig. S3 The comparison of different system on BPA degradation by 11% Co-Al_2O_3-600 °C membrane. Conditions: [BPA] = 20 mg L^{-1}, [PMS] = 1 mM, the pH was adjusted by phosphates at pH7 when HCO_3^- is not added.

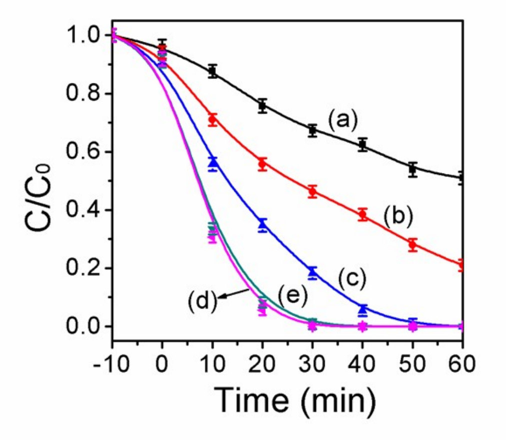


Fig. S4 Effect of membrane dosage on BPA degradation by 11% Co-Al_2O_3-600 ^oC membrane. (a) 0.12 g L^{-1}, (b) 0.25 g L^{-1}, (c) 0.5 g L^{-1}, (d) 1.0 g L^{-1}, (e) 1.25 g L^{-1}. Conditions: [BPA] = 20 mg L^{-1}, [PMS] = 1 mM.

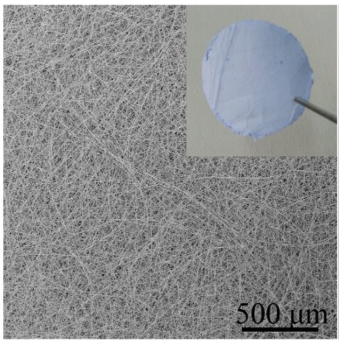


Fig. S5 A SEM image and optical image (the insert) of the membrane after use.

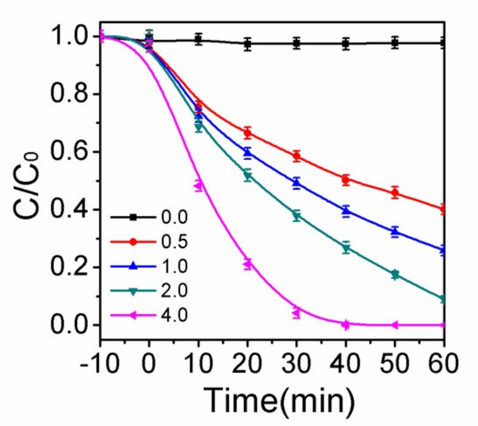


Fig. S6 Effect of PMS dosage on BPA degradation by 5.5% Co-Al_2O_3-600 ^oC membrane. Conditions: [BPA] = 20 mg L^{-1}.

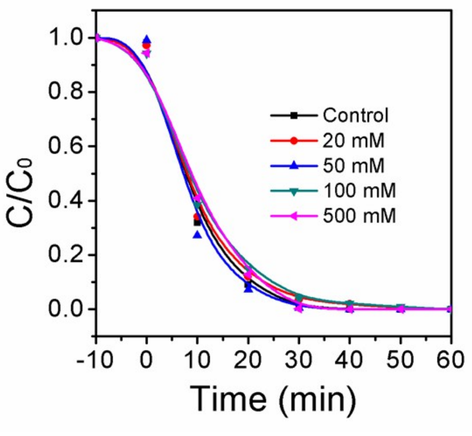


Fig. S7 Effect of ion strength ($NaClO_4$) on BPA degradation by 11% Co-Al_2O_3-600 °C membrane. Conditions: [BPA] = 20 mg L^{-1}, [PMS] = 1 mM.

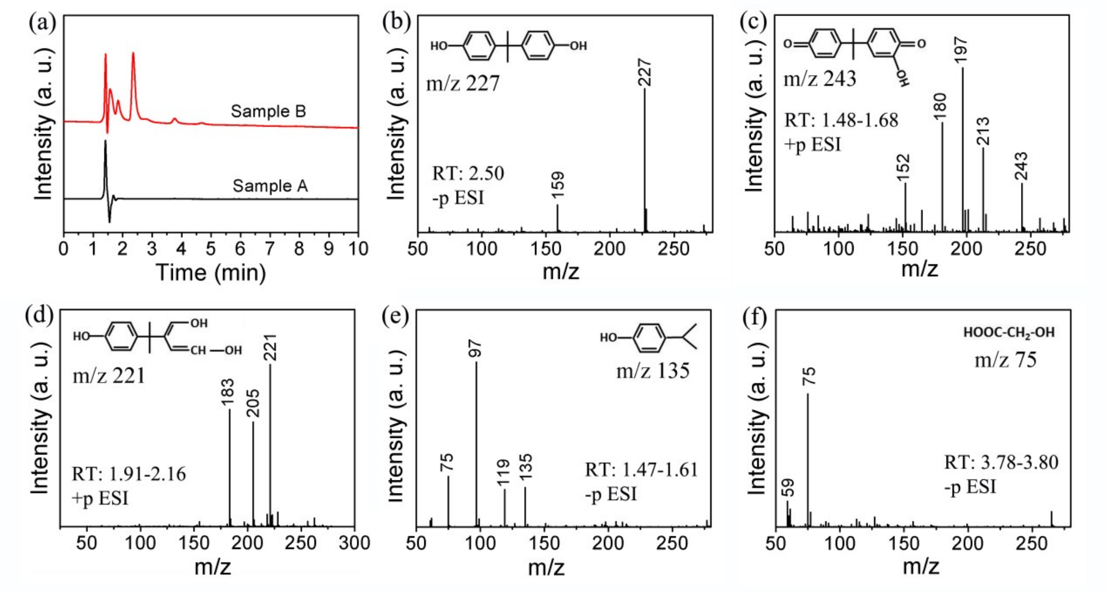


Fig. S8. (a) Chromatogram of the samples, and (b-e) Mass spectra and proposed structures of BPA and byproducts. Note: Sample A corresponds to the solution of 100% BPA removed (initial conc. 20 mg L^{-1}); Sample B corresponds to the solution of 59% BPA removed (initial conc. 100 mg L^{-1}).

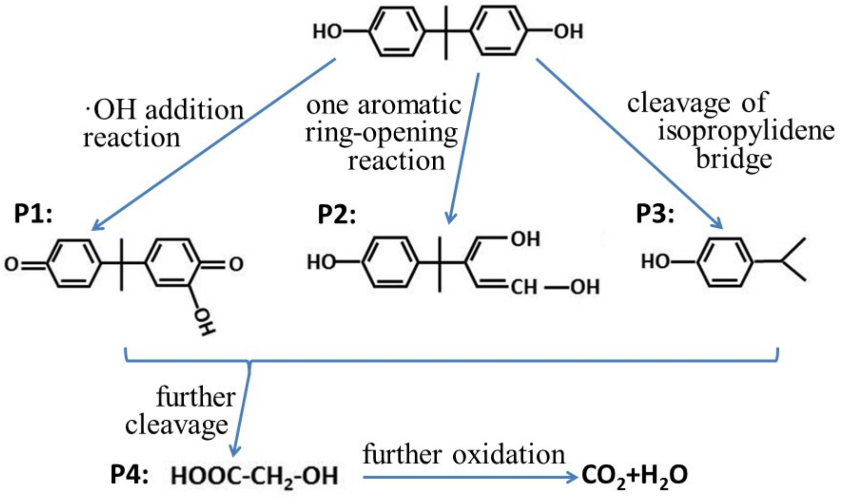


Fig. S9 The degradation pathway for BPA in this reaction.

Table S1 The property and relative constants of various free radicals

Free radicals	E^0	k (between the radicals and BPA)
HO•	1.9-2.7 V	$1.70 \pm 0.21 \times 10^{10}$ M^{-1} s^{-1}
SO_4•$^-$	2.5-3.1 V	$1.37 \pm 0.15 \times 10^{9}$ M^{-1} s^{-1}
CO_3•$^-$/HCO_3•	1.78 V	$3.89 \pm 0.09 \times 10^{6}$ M^{-1} s^{-1}

Table S2 Properties of final solutions for the samples with various initial pH.

Initial pH	Final pH	Co leaching (mg L^{-1})	Al leaching (mg L^{-1})
3.0	2.5	0.12	0.66
5.0	2.7	0.13	0.60
7.0	6.7	0.10	0.19
9.0	7.2	0.11	0.20
11.0	10.1	0.13	0.27

Table S3 Properties of final solutions for various membranes

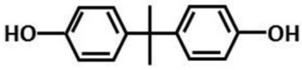
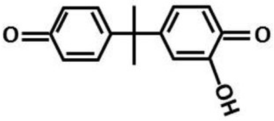
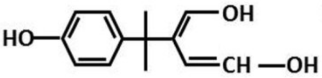
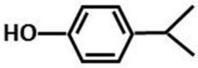
membrane	Final pH	Co leaching (mg L^{-1})	Al leaching (mg L^{-1})
1.1%-Co-Al_2O_3-600 °C	7.1	0.06	0.18
5.5%-Co-Al_2O_3-600 °C	7.0	0.09	0.20
11%-Co-Al_2O_3-600 °C	7.1	0.13	0.17
5.5%-Co-Al_2O_3-700 °C	7.0	0.10	0.11
5.5%-Co-Al_2O_3-800 °C	7.2	0.11	0.00

Table S4 Results of BPA degradation by activation of PMS via various catalysts

Catalysts	morphology	BPA initial conc. (ppm)	PMS initial concentration (mM)	Removal ability	Ref.
$CuFe_2O_4$	nanoparticles	50	1.00	95.2% in 60 min	[15]
$Mn_{1.8}Fe_{1.2}O_4$	Nanospheres	10	0.65	95% in 30 min	[16]
CoMnAl mixed metal oxides	powders	10	0.50	100% in 90 min	[17]
sulfur-doped carbon nitride with visible light irradiation	powders	50	1.00	50% in 120 min	[18]
Ag/mpg-C_3N_4 with visible light irradiation	powders	20	1.00	100% in 60 min	[19]
11% Co-Al_2O_3-600 °C	membranes	20	1.00	100% in 40 min	This work

Reaction conditions: Intial pH 7, at 20-30 °C.

Table S5 Possible byproducts identified by LCMS.

Products	Structure	m/z	Sample A	Sample B
BPA		227	not detected	detected
P1		243	detected	detected
P2		221	not detected	detected
P3		135	detected	detected
P4	$HOOC\text{-}CH_2\text{-}OH$	75	not detected	detected

Note: Sample A corresponds to the solution of 100% BPA removed (initial conc. 20 mg L^{-1}); Sample B corresponds to the solution of 59% BPA removed (initial conc. 100 mg L^{-1}).

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