Supplementary Information

Preparation, Performance and Mechanism of Metal Oxides Modified Catalytic Ceramic Membranes for Wastewater Treatment

Yangbo Huang[a,b*], Zeyu Guan[a], Qiang Li[a], Qian Li[c], Dongsheng Xia[a,b]

a School of Environmental Engineering, Wuhan Textile University, Wuhan, Hubei 430073, China

b Engineering Research Center for Clean Production of Textile Dyeing and Printing, Ministry of Education, Wuhan, Hubei 430073, China

c China Three Gorges Corporation, Wuhan 430014, China

*Corresponding author: ybhuang@wtu.edu.cn

List of Tables and Figures

Text S1 The possible catalytic mechanism for PMS activation in different CM/PMS systems

CuCM activated PMS for phenol removal based on a series of reactions as Eq. (1)~(4). With the addition of PMS, HSO_5^- could replace some surface $-OH$ to bond with the metal sites of the oxides via ligand displacement, giving rise to the formation of $Cu(II)-(HO)OSO_3^-$ [1]. The subsequent decomposition of surface $Cu(II)-(HO)OSO_3^-$ complex leads to the production of $SO_4^{\cdot-}$ and Cu(III). Afterwards, Cu(III) can further react with HSO_5^- to generate more sulfate radicals.

$$\equiv Cu(II)\text{-}OH^- + HSO_5^- \rightarrow \equiv Cu(II)\text{-}(HO)OSO_3^- + OH^- \tag{1}$$

$$\equiv Cu(II)\text{-}(HO)OSO_3^- \rightarrow \equiv Cu(III)\text{-}OH^- + SO_4^{\cdot-} \tag{2}$$

$$\equiv Cu(III)\text{-}OH^- + HSO_5^- \rightarrow \equiv Cu(II)\text{-}OOSO_3^- + H_2O \tag{3}$$

$$2\equiv Cu(II)\text{-}OOSO_3^- + 2H_2O \rightarrow 2\equiv Cu(II)\text{-}OH^- + O_2 + 2SO_4^{\cdot-} + 2H^+ \tag{4}$$
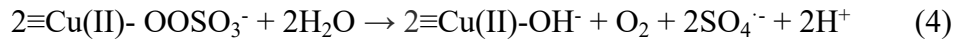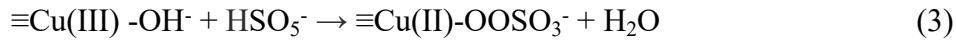
Similarly, the possible mechanism for PMS activation by MnCM was proposed in Eq. (5)~(8) [2].

$$\equiv Mn(III)–OH + HSO_5^- \rightarrow \equiv Mn(III)–OOSO_3^- + H_2O \rightarrow$$

$$\equiv Mn(IV)–OH + O_2^{\cdot-} + 2HSO_4^- \tag{5}$$

$$2O_2^{\cdot-} + 2H_2O \rightarrow {}^1O_2 + H_2O_2 + 2OH^- \tag{6}$$

$$O_2^{\cdot-} + H_2O_2 \rightarrow {}^1O_2 + \bullet OH^- + OH^- \tag{7}$$

$$O_2^{\cdot-} + \bullet OH^- \rightarrow {}^1O_2 + OH^- \tag{8}$$
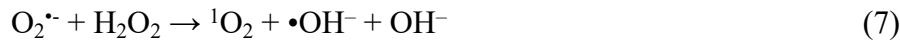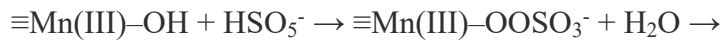
For FeCM, the possible mechanism of PMS activation was as follows [3]:

$$Fe(III) + HSO_5^- \rightarrow Fe(II) + SO_5^{\cdot-} + H^+ \tag{9}$$

$$Fe(II) + HSO_5^- \rightarrow Fe(III) + SO_4^{\cdot-} + OH^- \tag{10}$$

$$SO_4^{\cdot-} + OH^- \rightarrow \cdot OH + SO_4^{2-} \tag{11}$$
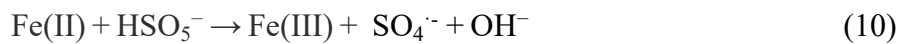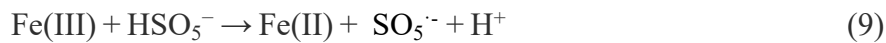
Table S1 Characteristics of the virgin ceramic membrane

Components	Description
Support layer material	α-Al$_2$O$_3$
Membrane configuration	Flat membrane with circular multichannel
Effective filtration area / cm^2	16
Surface pore size / μm	0.1
Porosity	30% − 40%

Table S2 Surface element compositions of the pristine and modified membranes

Membrane	Element weight percentage* wt%					
	Al	O	Co	Mn	Fe	Cu
Pristine CM	51.81	48.19	-	-	-	-
CoCM	51.74	47.90	0.36	-	-	-
MnCM	52.23	47.23	-	0.55	-	-
FeCM	53.33	46.22	-	-	0.45	-
CuCM	50.02	49.34	-	-	-	0.64

*The values were the average of the EDS results of five measurement points.

Table S3 Cross-section element compositions of the pristine and modified membranes

Membrane	Element weight percentage* wt%					
	Al	O	Co	Mn	Fe	Cu
Pristine CM	50.60	49.40	-	-	-	-
CoCM	50.10	49.06	0.84	-	-	-
MnCM	48.75	50.23	-	1.02	-	-
FeCM	49.80	49.00	-	-	1.20	-
CuCM	49.13	49.56	-	-	-	1.31

*The values were the average of the EDS results of five measurement points.

Table S4 Comparison of the literature with this work on degradation efficiency of phenol by catalytic membranes

| Catalytic membrane	Pollutant	Degradation efficiency under optimal condition	Reference
N-doped GO membrane	50 mg/L phenol	94% after 180 min	S[4]
Coal-based carbon membrane	10 mg/L phenol	100%	S[5]
rGO-PTFE membrane	50 mg/L phenol	96% after 180 min	S[6]
CoCM	30 mg/L phenol	100% after 30 min	In this work
MnCM	30 mg/L phenol	99% after 30 min	In this work
FeCM	30 mg/L phenol	87% after 30 min	In this work
CuCM	30 mg/L phenol	83% after 30 min	In this work
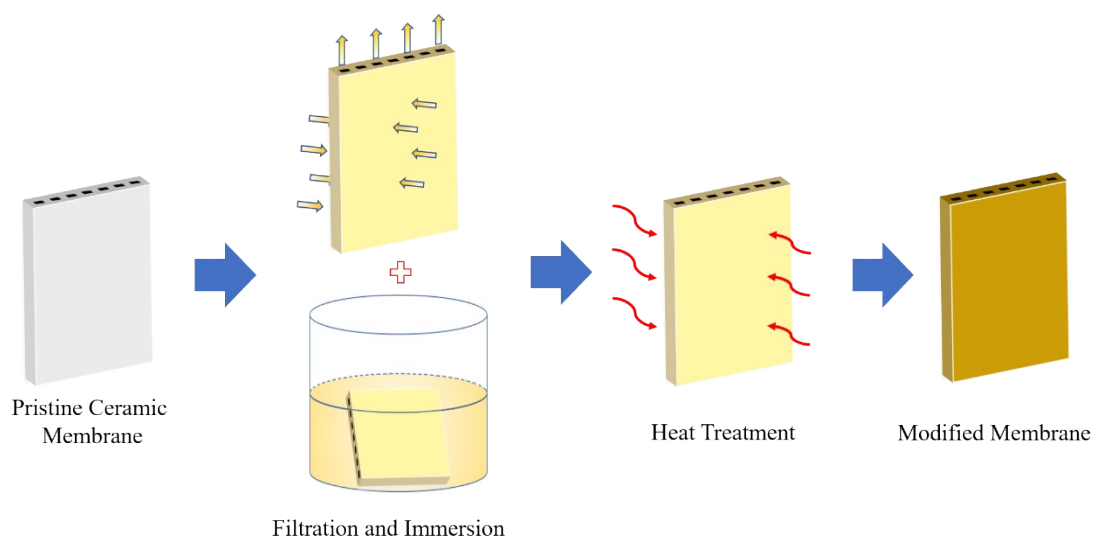
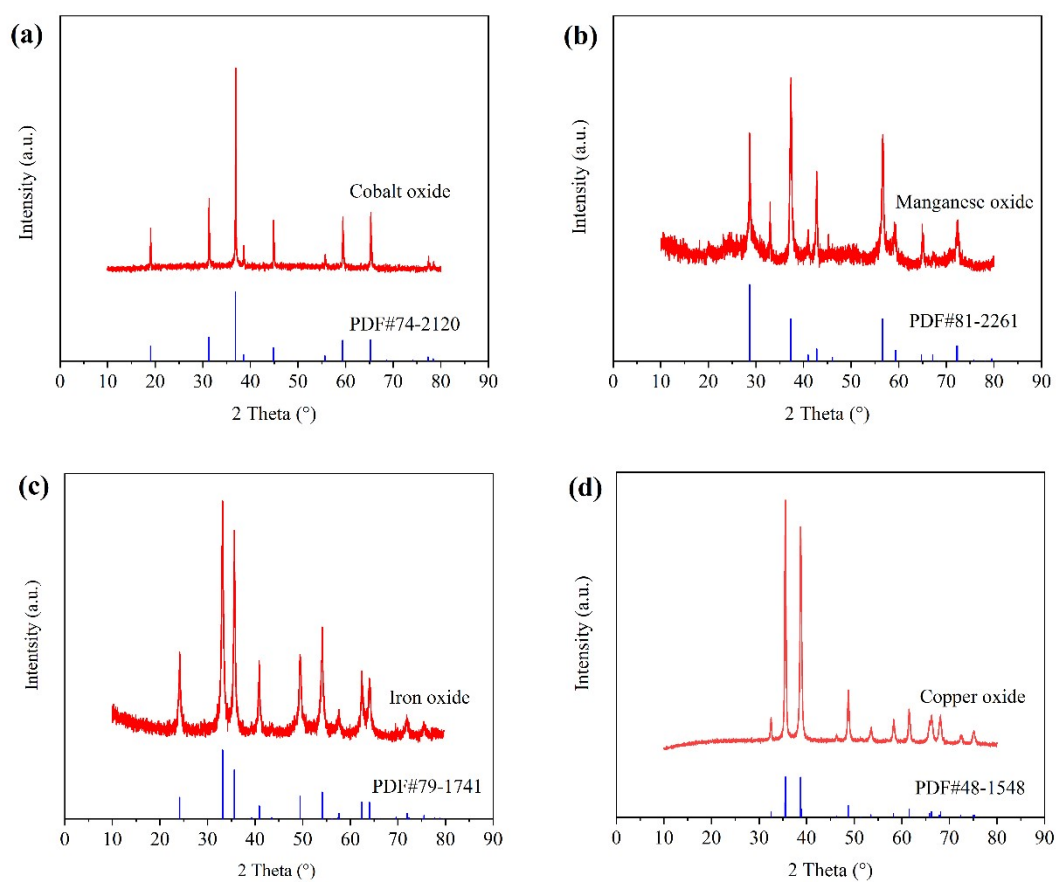Fig. S1 Procedures for the preparation of modified CMs.

Fig. S2 The XRD analysis of metal oxides. (a) cobalt oxide, (b) manganese oxide, (c) iron oxide and (d) copper oxide.
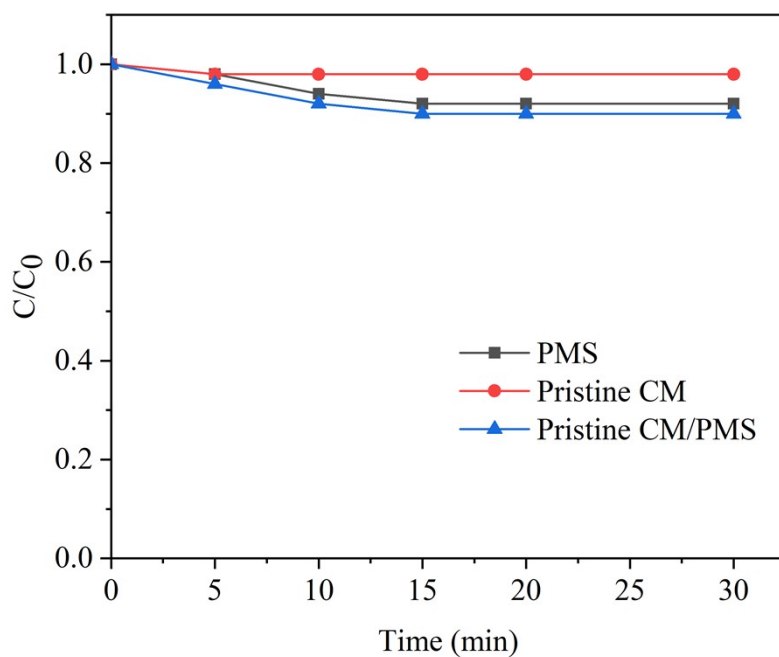
Fig. S3 Phenol removal efficiency by PMS direct oxidation, CM adsorption or a combination of both. Experimental conditions: C_{phenol} = 30 mg/L, C_{PMS} =2 mM, pH=7, T=25℃.
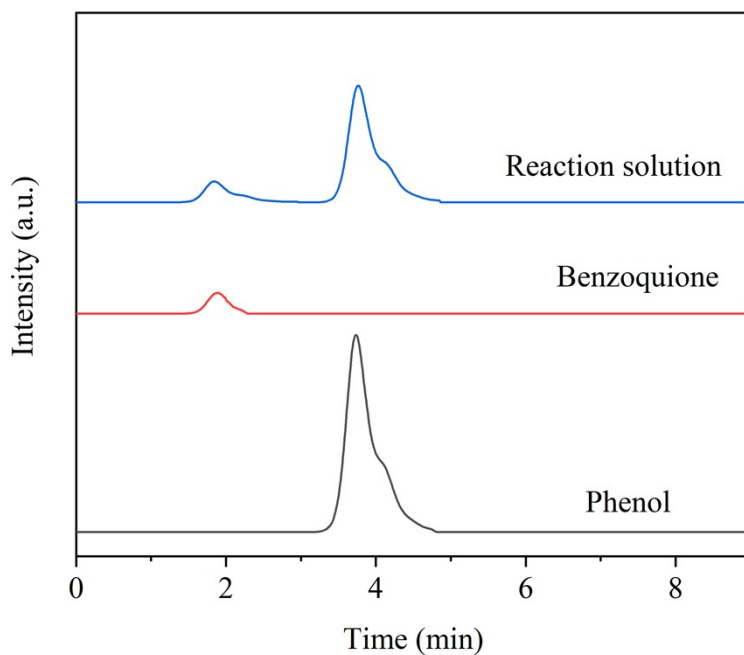

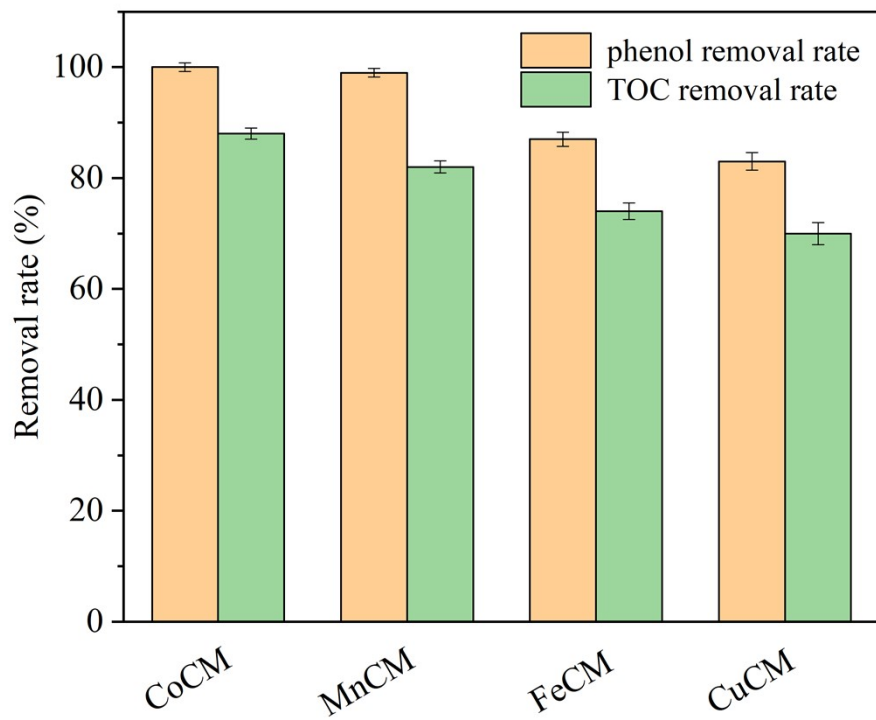Fig. S4 Liquid chromatograms of phenol in the pristine CM/PMS system and the standard samples.

Fig. S5 Comparison of the phenol and TOC removal rate in the four membrane systems
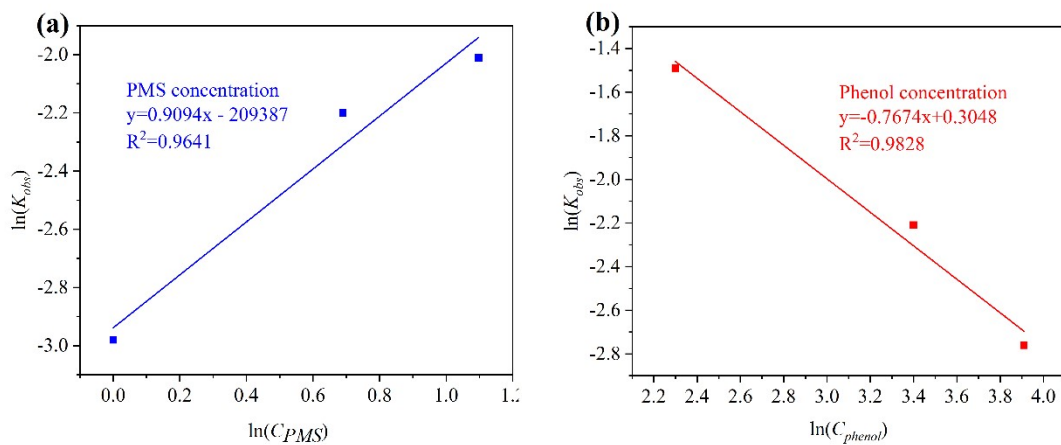

Fig. S6 The linear correlation between ln(kobs) and ln(concentration) in the kinetic study. (a) PMS concentration, (b) Phenol concentration.
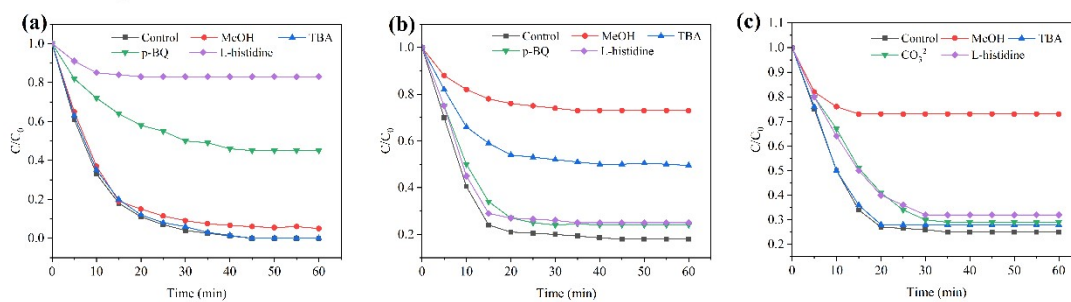
Fig. S7 Quenching experiments of (a) MnCM, (b) FeCM and (d) CuCM. Experimental conditions: C_{PMS} =2 mM, C_{PMS} =30 mg/L, pH=7.0, C_{MeOH} =500 mM, C_{TBA}=500 mM, C_{p-BQ}=10 mM, $C_{L-histidine}$=20 mM, C_{DMPO}=100 mM, C_{TEMP}=100 mM.
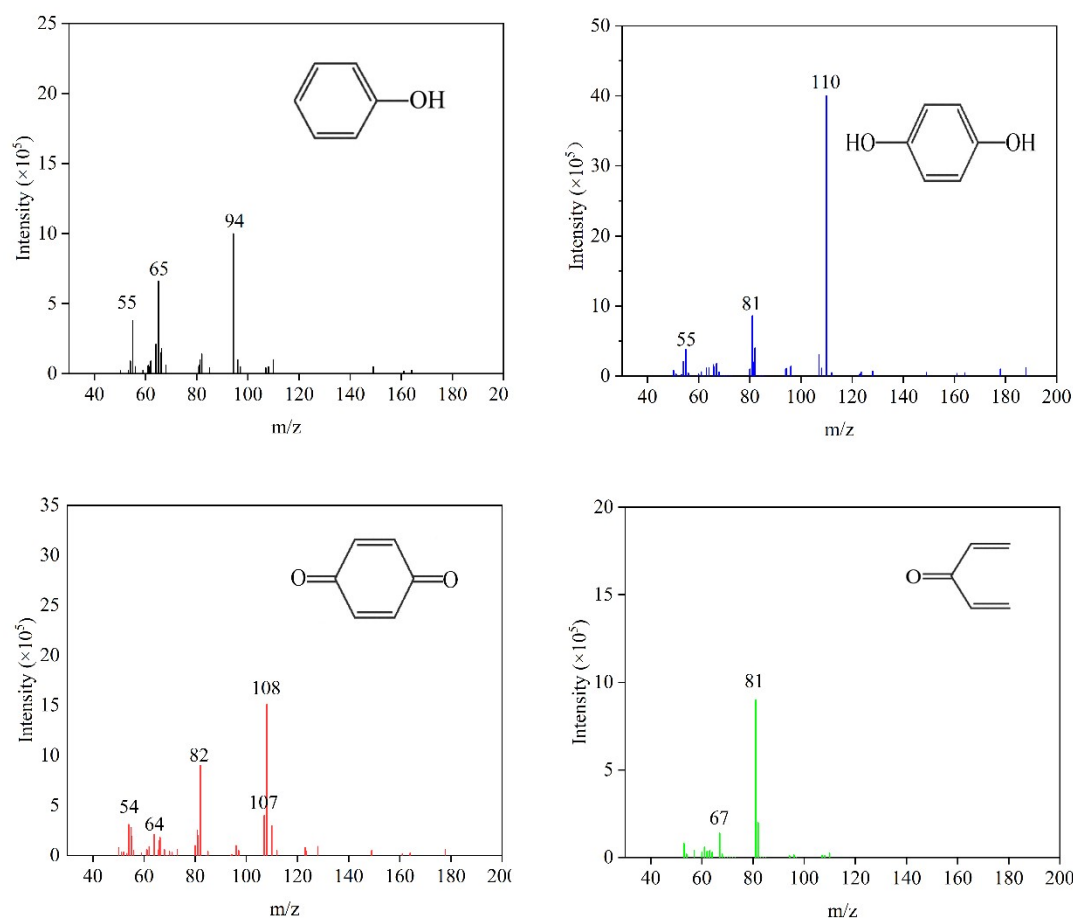

Fig. S8 Mass spectrograms of phenol degradation at 5 min. Experimental conditions: C_{PMS} =2 mM, C_{PMS} =30 mg/L, pH=7.0.

References

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