Surfactant-free Porous nano-Mn_3O_4 as a Recyclable Fenton-Like Reagent That Can Rapidly Scavenge Phenolics without H_2O_2

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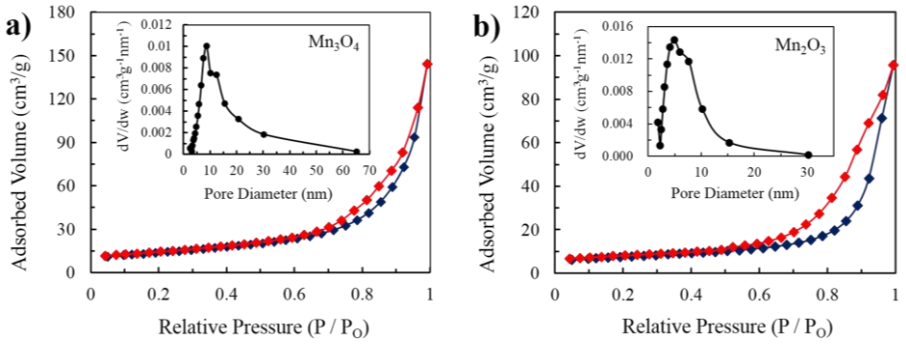

Figure S1. The Brunauer–Emmett–Teller plot of the porous Mn_3O_4 and Mn_2O_3 microspheres.

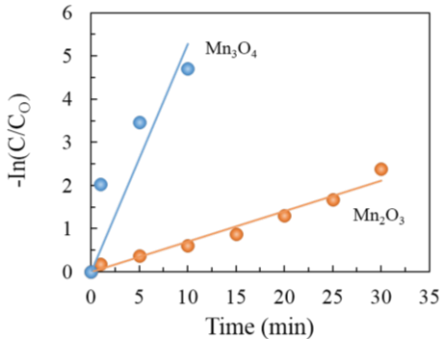

Figure S2. Calculation of the rate constant (k) of phenol removal by Mn_3O_4 and Mn_2O_3.

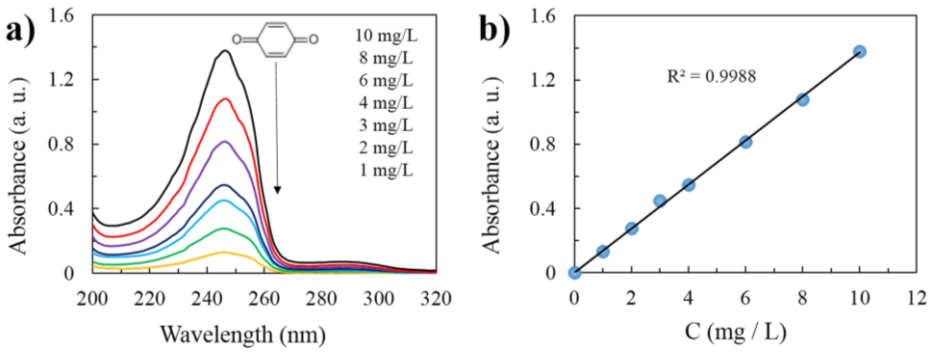

Figure S3. a) The UV-vis spectra of p-benzoquinone with varied concentration from 1 to 10 mg/L; b) the standard curve of UV-vis absorbance vs p-benzoquinone concentration recorded at 246 nm.

Table S1. Percent contribution of Mn^{2+}, $Mn^{3+}$and Mn^{4+} to the Mn $2p_{3/2}$ peak in the XPS spectra.

Sample	Mn^{2+}	Mn^{3+}	Mn^{4+}	Average valence state of Mn
Mn_3O_4	45.0%	55.0%	n.d.	2.6
Mn_3O_4-phenol	n.d.	25.3%	74.7%	3.7
Mn_2O_3	n.d.	59.5%	40.5%	3.4
Mn_2O_3-phenol	n.d.	36.9%	63.1%	3.6

n.d.: not detected.

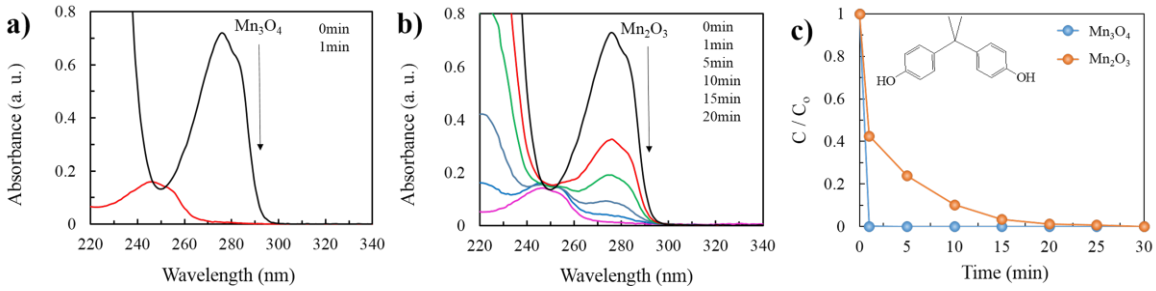

Figure S4. The UV-Vis absorption spectra of bisphenol A solution in the presence of a) Mn_3O_4 and b) Mn_2O_3; and c) the corresponding removal efficiency by Mn_3O_4 and Mn_2O_3 as a function of time.

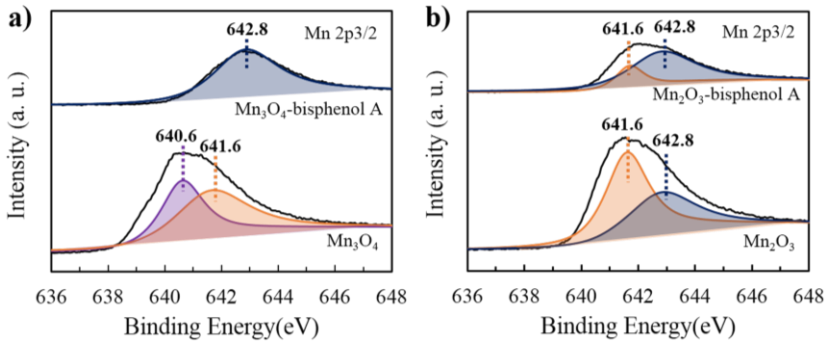

Figure S5. The Mn $2p_{3/2}$ peak in the XPS spectra of a) Mn_3O_4 and b) Mn_2O_3, before and after bisphenol A removal.

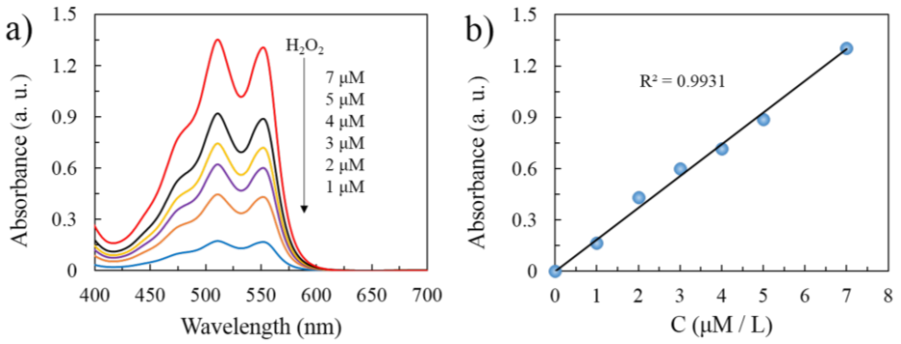

Figure S6. a) The UV-vis spectra and b) the standard curve of absorbance vs H_2O_2 concentration (1 to 7 μM) recorded at 551 nm. The curves were obtained by the addition of DPD (50 μL) and POD (50 μL) to the sampled aliquots and measuring the UV-vis spectra of the resulting solution

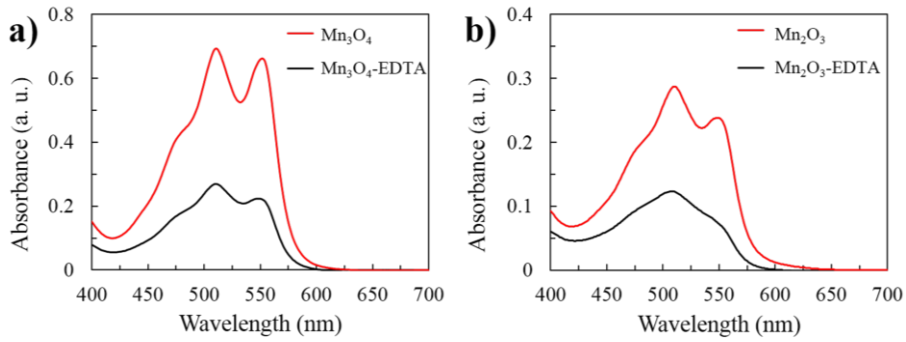

Figure S7. Detection of H_2O_2 in the aqueous dispersions of a) Mn_3O_4 and b) Mn_2O_3 with EDTA addition; The curves were obtained by the addition of DPD (50 μL) and POD (50 μL) to the sampled aliquots (after 30 min of reaction) in the phenol removal experiments and measuring the UV-Vis spectra of the resulting solution.

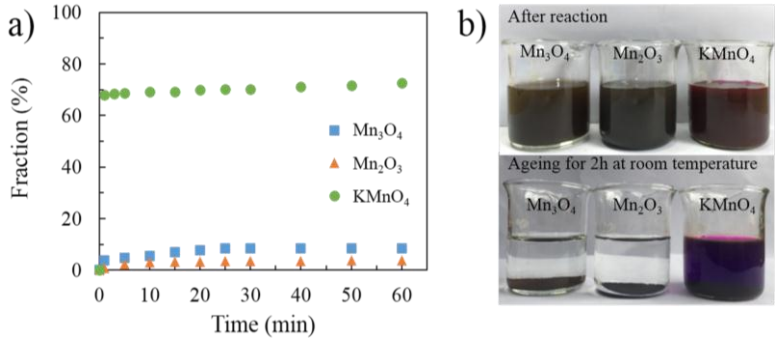

Figure S8. a) The leaching ratio of manganese in solution as time function, during phenol removal with Mn_3O_4, Mn_2O_3 and $KMnO_4$ at acidic condition (pH=2.0), respectively; b) The settleability test of solution after the use of identical-molar manganese of Mn_3O_4, Mn_2O_3 and $KMnO_4$, respectively.