

Supporting information

Heterogeneous Fenton-like activity of novel metallosalophen magnetic nanocomposites: Significant anchoring group effect

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Experimental

Remarks

All chemicals were analytical grade reagents and used without further purification. FT-IR spectra were recorded on a Nicolet-Impact 400D spectrometer in the range of 400-4000 cm^{-1} . Thermogravimetric analysis (TGA) of powders carried out on Shimadzu 50 under the air flow at a uniform heating rate of 10 $^{\circ}\text{C min}^{-1}$ in the range of 30-800 $^{\circ}\text{C}$. Transmission electron microscopy (TEM) measurements were obtained by a 906 E instrument (Zeiss, Jena, Germany). The Fe and Mn content of the catalyst was measured by an inductively coupled plasma optical emission spectrometry (ICP-OES), using a VISTA-PRO ICP analyzer. UV-Vis spectra were recorded on a V670 JASCO spectrophotometer. Magnetic properties measurements were performed using vibrating sample magnetometer (VSM, Lake Shore Cryotronics 7407). Powder X-ray diffraction (XRD) was performed on a Bruker D8-advance X-ray diffractometer with Cu Ka ($\lambda = 1.5406 \text{ \AA}$) radiation. EDX elemental analysis performed by Scanning Electron Microscope TESCAN Vega Model with EDX detector. GC-MS analysis was performed by Agilent 5975c.

The Preparation of $\gamma\text{-Fe}_2\text{O}_3$ (MNP)

$\gamma\text{-Fe}_2\text{O}_3$ MNPs were synthesized by a chemical co-precipitation technique reported previously.^{1,2} $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1.99 g) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (3.25 g) were dissolved in deionized water (30 mL) under Ar atmosphere at room temperature. An NH_4OH solution (0.6 M, 200 mL) was then added dropwise (drop rate = 1 mL min^{-1}) to the stirring mixture at room temperature to reach the reaction pH to 11. The resulting black dispersion was continuously stirred for 1 h at room temperature and then heated to reflux for 1 h to yield a brown dispersion. The magnetic nanoparticles were then

separated by an external magnet and washed with deionized water until it was neutralized. The as-synthesized sample was heated at $2\text{ }^{\circ}\text{C min}^{-1}$ up to $250\text{ }^{\circ}\text{C}$ and then kept in the furnace for 3 h to give a reddish-brown powder.

Synthesis of silica-coated maghemite nanoparticles (SMNP)

The silica-coated maghemite nanoparticles were synthesized with minor modifications of literature.³ 1.7 g of synthesized Fe_2O_3 , suspended in 80 mL methanol and 20 mL deionized water and sonicated for 1 h at $40\text{ }^{\circ}\text{C}$. Then aqueous ammonia (25%, 1.8 mL) was added slowly over 10 min and the mixture was heated at $40\text{ }^{\circ}\text{C}$ for 30 min under mechanical stirrer. Then 1 mL of tetraethylorthosilicate (TEOS) was added slowly to the mixture and then stirred mechanically for 24 h at room temperature. The iron oxide nanoparticles with a thin layer of silica ($\text{Fe}_2\text{O}_3@\text{SiO}_2$) were separated by an external magnet and washed two times with ethanol and diethyl ether and dried under vacuum.

Preparation of Fe(III)SalophenCl complex

Fe(III)SalophenCl was prepared as previously described.⁴ In brief, Salophen ligand was synthesized by dropwise adding of two equivalents of 2-hydroxybenzaldehyde (20 mmol) in 25 mL ethanol to one equivalent of 1,2-phenyldiamine (10 mmol) in 25 mL ethanol and refluxing for 1 h that resulted in the yellow precipitate of Salophen. The precipitate cooled down to room temperature and filtered and washed with cold methanol and water. The $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.3 mmol) was mixed with the equivalent amount of Salophen in 10 mL ethanol and heated to $70\text{ }^{\circ}\text{C}$ for 1 h under argon atmosphere. This resulted solution was cooled down to room temperature and filtrated off and washed with cool ethanol and dried under vacuum with P_2O_5 .

Preparation of Mn(III)SalophenCl complex

Mn(III)SalophenCl synthesized according to the method described previously in the literature.⁵ 0.3 mmol of Salophen ligand is in 10 mL hot absolute ethanol. Then Solid $\text{Mn}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.3 mmol) is added in one portion and the solution is refluxed for 1 h. Approximately 1 mmol of solid LiCl are then added and, the mixture is heated to reflux for an additional 0.5 h. Cooling the mixture

to 0 °C affords the Mn(III) complex as dark brown crystals that are washed thoroughly with cool ethanol and H₂O and dried under vacuum.

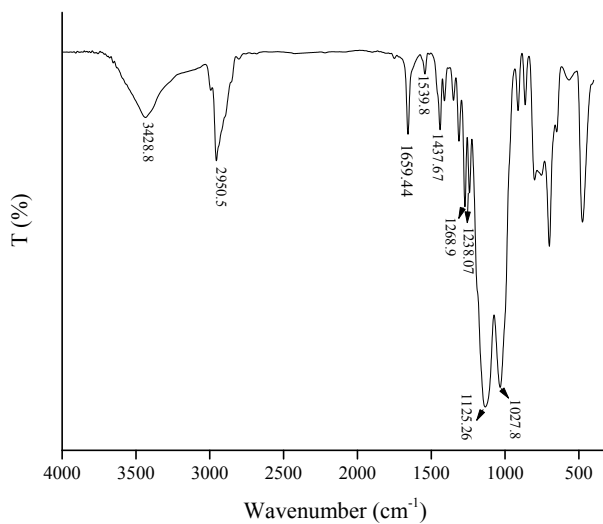


Fig. S1. FT-IR spectra of SAPy

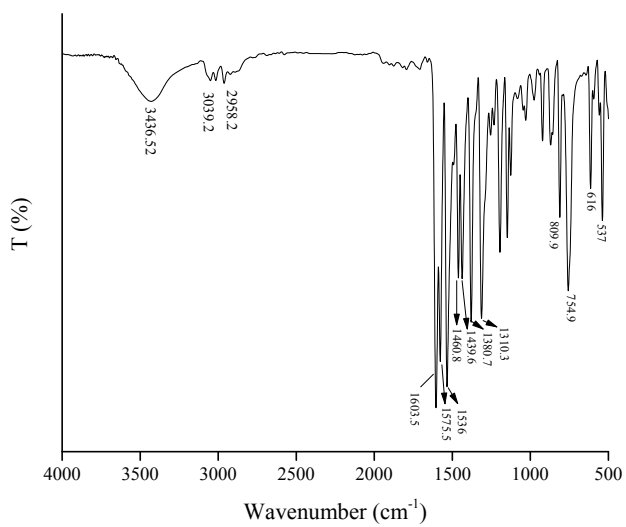


Fig. S2. FT-IR spectra of Fe(III)SalophenCl

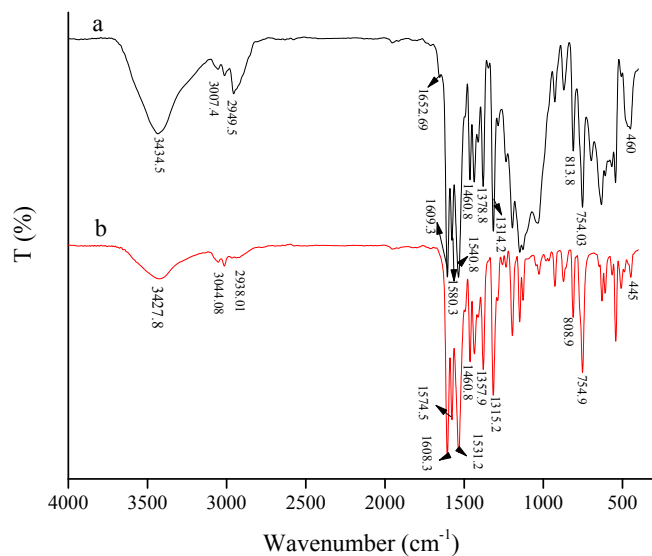


Fig. S3. FT-IR spectra of (a) SMNP@SAPy/MnSal, (b) Mn(III)(Salophen)Cl .

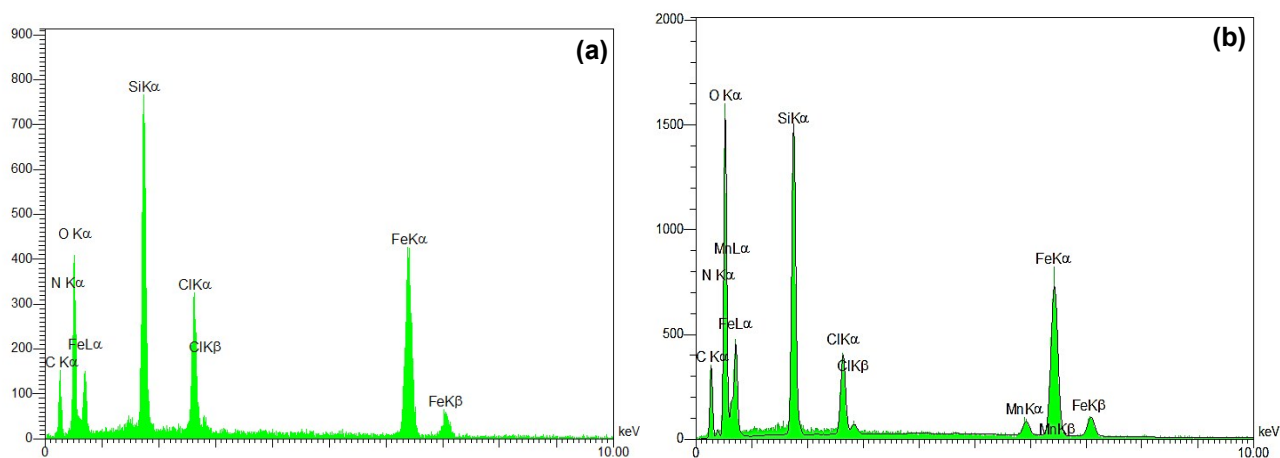


Fig. S4. EDS Spectrum of the as-prepared (a) SMNP@SAPy/FeSal, (b) SMNP@SAPy/MnSal .

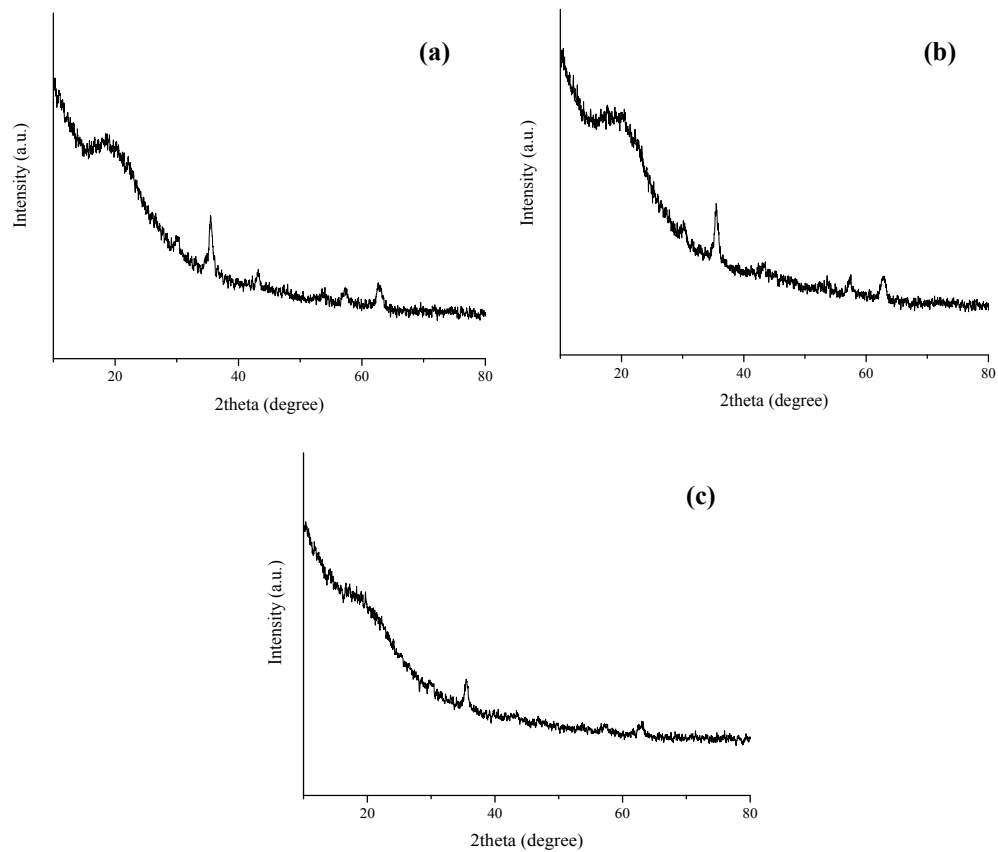


Fig. S5. XRD pattern of (a) SMNP@SAPy, (b) SMNP@SAPy/FeSal and (c) SMNP@SAPy/MnSal .

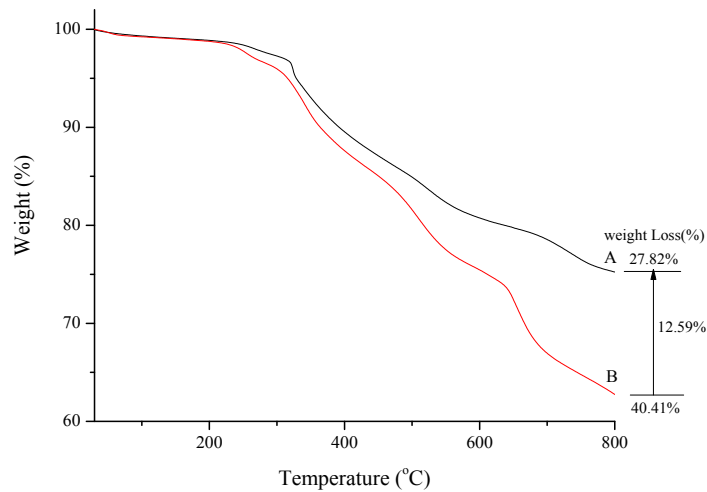


Fig. S6. TGA thermograms of SMNP@SAPy/MnSal (B) in comparison with SMNP@SAPy (A) .

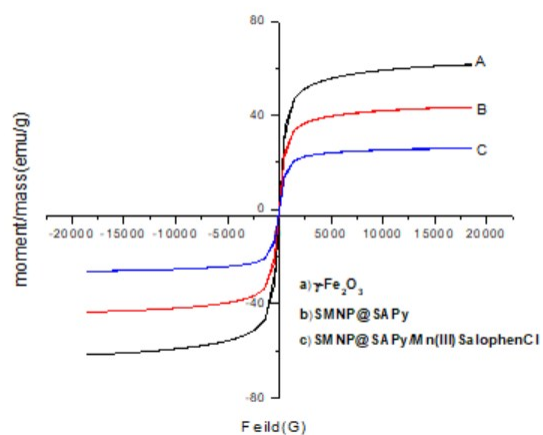


Fig. S7. Hysteresis loops of the as-synthesized (a) bare $\gamma\text{-Fe}_2\text{O}_3$, (b) SMNP@SAPy, and (c) SMNP@SAPy/MnSal, at 298 K.

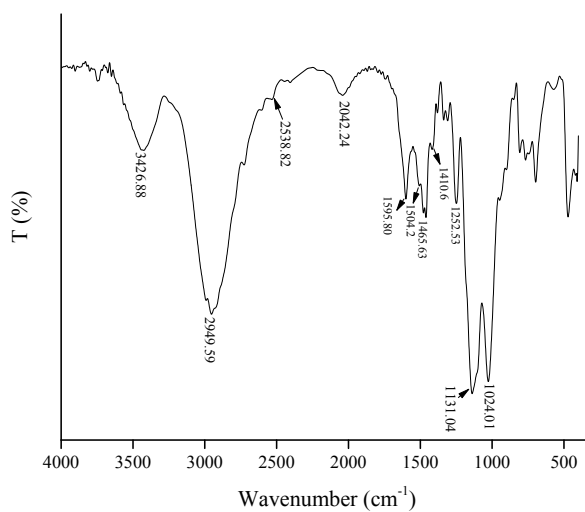


Fig. S8. FT-IR spectra of SAET

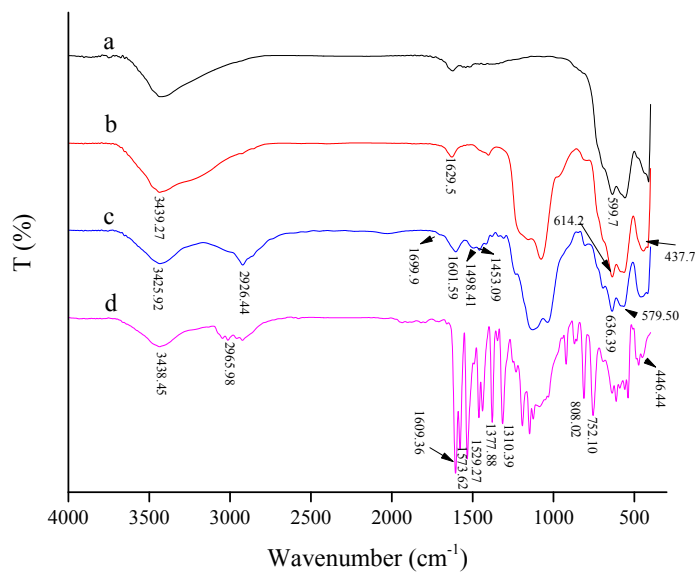


Fig. S9. FT-IR spectra of MNP (a), SMNP (b), SMNP@SAET (c) and SMNP@SAET/FeSal (d).

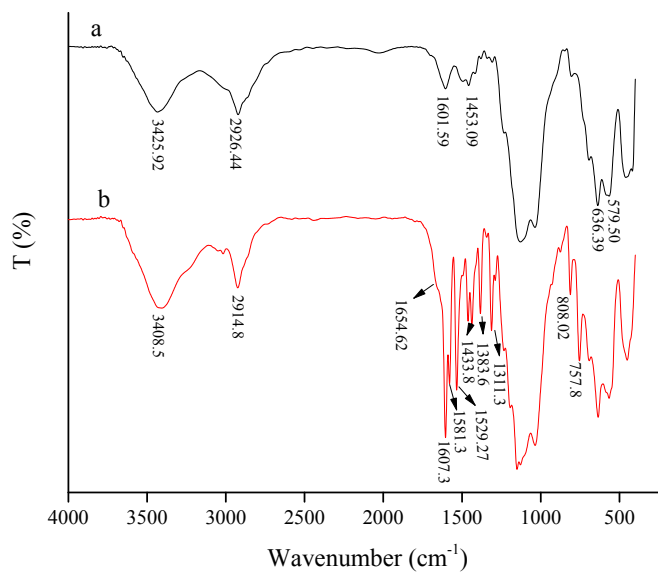


Fig. S10. FT-IR spectra of SMNP@SAET/MnSal

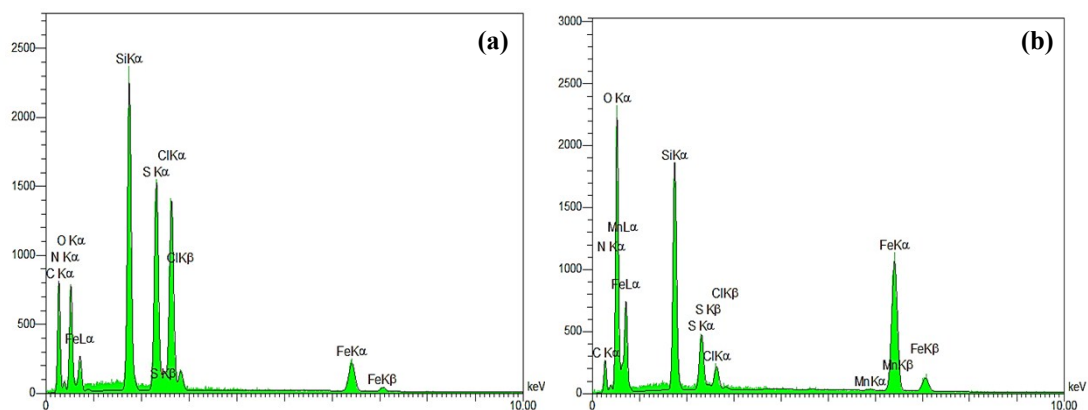


Fig. S11. EDS Spectrum of the as-prepared (a) SMNP@SAET/FeSal, (b) SMNP@SAET/MnSal.

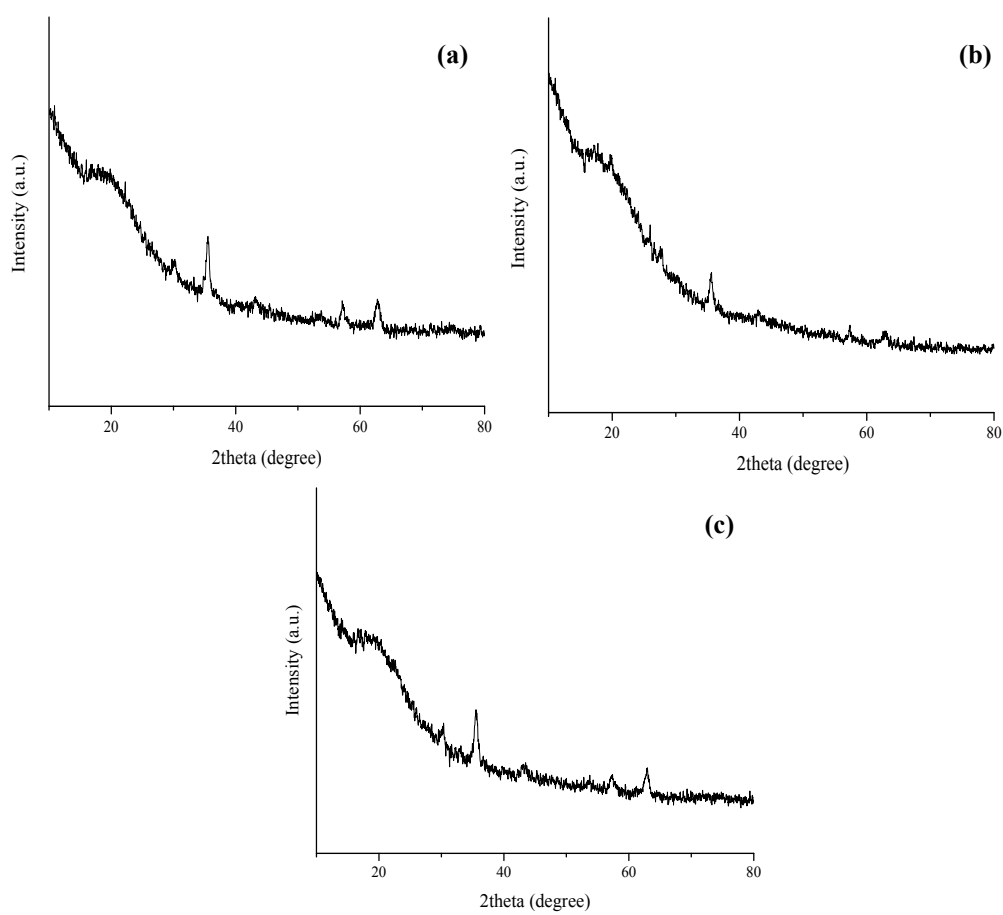


Fig. S12. XRD pattern of (a) SMNP@SAET, (b) SMNP@SAET/FeSal, and (c) SMNP@SAET/MnSal .

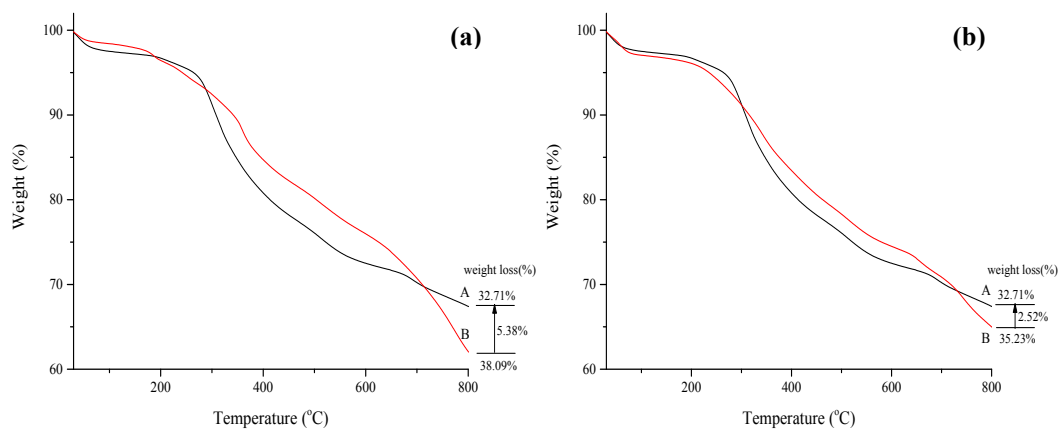


Fig. S13. TGA thermograms of (a,B) SMNP@SAET/FeSal and (b,B) SMNP@SAET/MnSal in comparison with SMNP@SAET (A in a,b).

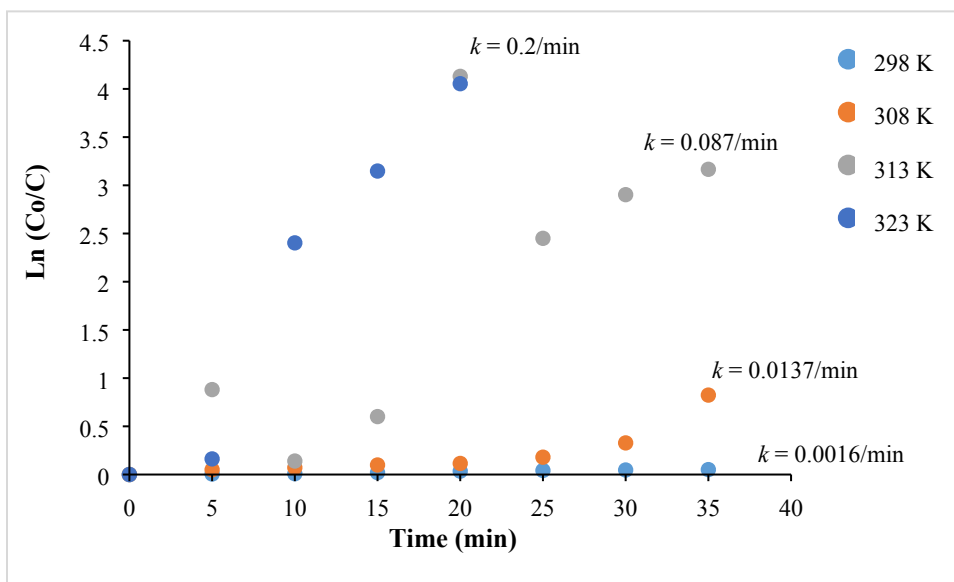


Fig. S14. $\ln[\text{RhB}]_o/[\text{RhB}]_i$ as a function of reaction time for $T = 298, 308, 313, 323 \text{ K}$.

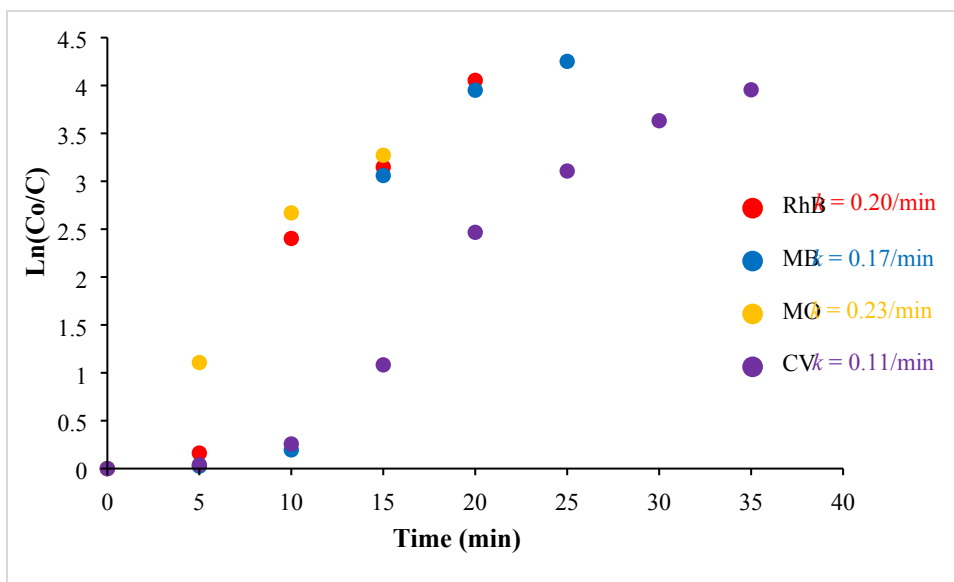
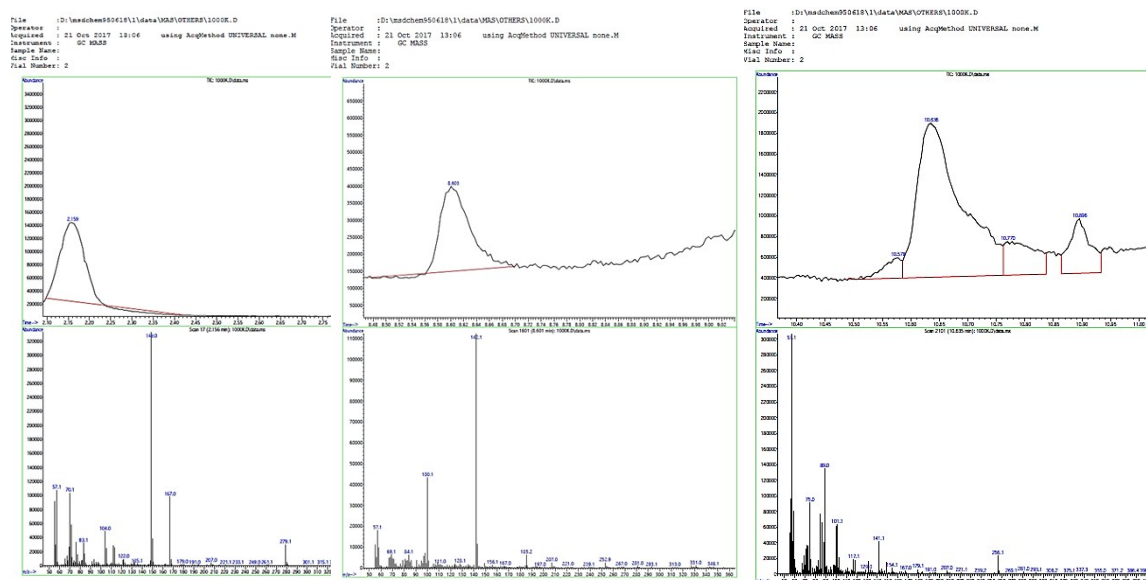


Fig. S15. $\ln[C]_0/[C]_t$ as a function of reaction time for RhB, methylene blue (MB), methyl orange (MO) and crystal violet (CV) at $T = 323$ K.



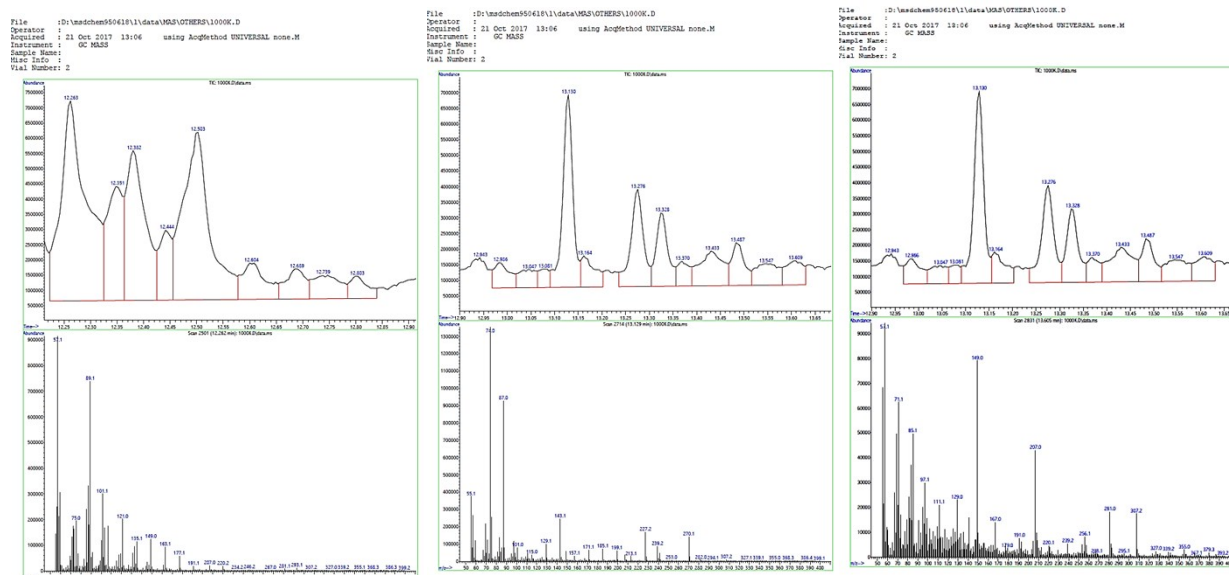


Fig. S16. GC trace and MS spectra of intermediates of RhB degradation in the present system.

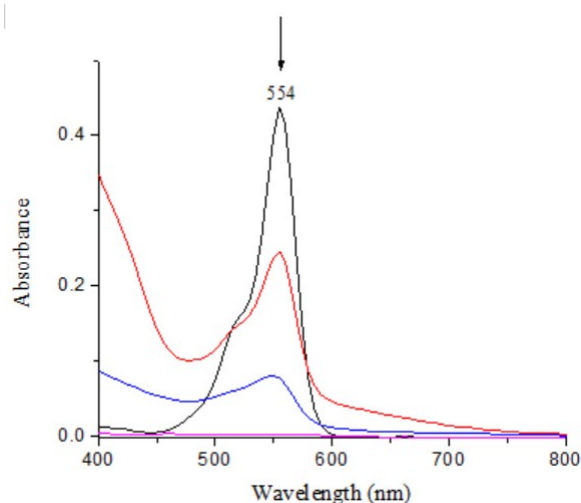


Fig. S17. UV-Vis spectral changes of RhB in the present system.

References

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