

Supplemental material

Text S1

The RhB, PDS, terbutanol (TBA), 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and phenol used in the experiment were purchased from Shanghai Macklin Biochemical Co., Ltd. The sulfuric acid, sodium hydroxide and methanol (MA) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the above reagents used were analytical reagent grade. During the experiment and related analyses, all solutions were prepared with deionized water.

The MNP and HNP samples used were from mines in Northeast China and Northwest China respectively. Both samples were ground and sieved to <200 mesh, then packed in sealed bags and stored in a vacuum drying oven (DZ-2BCII, Tianjin TAIST Co., Tianjin, China) for subsequent experiments and analysis. In order to simulate natural conditions, our samples were not washed before experiment and analysis.

Text S2

Batch degradation experiments were carried out in 250 mL conical flask containing 100 mL RhB solution at a concentration of 50 mg/L. The solution pH was adjusted by H₂SO₄ or NaOH. The degradation process was carried out in an orbital shaker (ZWY2012C, Shanghai Zhicheng Co., Shanghai, China) with the temperature and rotating speed controlled at 30 °C and 200 r/min, respectively. The system of this study included experimental group (MNP/PDS and HNP/PDS) and blank group (MNP, HNP and PDS). Within the determined time interval, 0.5 mL of the reaction solution was taken out and quenched with excess MA (50 μL) and TBA (50 μL) for subsequent RhB concentration and iron concentration determination. In order to reduce the error during the experiment, each experimental group was carried out in triplicate.

Text S3

The electrochemical tests were performed with a Princeton Model 283 potentiostat (EG & G of Princeton Applied Research) coupled to a personal computer. A conventional three-electrode electrochemical cell was used in this study. The working electrodes were the carbon paste electrodes made of MNP and HNP. Specifically, the working electrode was made from a mixture of 0.7 g of MNP or HNP, 0.2 g of graphite powder and 0.1 g of solid paraffin. The counter electrode used was two wired carbon rods and the reference electrode was an Ag/AgCl (3.0 mol/L KCl) electrode. The electrolyte used was H₂SO₄ or NaOH solution whose pH value matched the batch experiments. The open circuit potential (OCP) was measured prior to the Tafel tests. All the OCP tests were conducted until the potential change within 60 s was no more than 5 mV.

Table S1 Lattice parameters of PDF#89-1954 and PDF#76-2308 cards

| PDF card No. | <i>a</i> /nm | <i>b</i> /nm | <i>c</i> /nm | α /($^{\circ}$) | β /($^{\circ}$) | γ /($^{\circ}$) | Space group |
|--------------|--------------|--------------|--------------|--------------------------|-------------------------|--------------------------|-------------|
| PDF#89-1954 | 1.1902 | 0.6859 | 2.2787 | 90 | 90.43 | 90 | F2/d |
| PDF#76-2308 | 0.6866 | 0.6866 | 1.7088 | 90 | 90.00 | 120 | P3121 |

Table S2 EDS element analysis of selected area of SEM image

| Region | x(Fe)/% | x(S)/% | Chemical formula |
|--------|---------|--------|----------------------|
| M-1 | 45.87 | 54.13 | Fe _{0.85} S |
| M-2 | 44.75 | 55.25 | Fe _{0.81} S |
| M-3 | 46.52 | 53.48 | Fe _{0.87} S |
| M-4 | 46.81 | 53.19 | Fe _{0.88} S |
| H-1 | 48.45 | 51.55 | Fe _{0.94} S |
| H-2 | 48.54 | 51.46 | Fe _{0.94} S |
| H-3 | 46.17 | 53.83 | Fe _{0.86} S |
| H-4 | 49.29 | 50.71 | Fe _{0.97} S |

Table S3 Degradation efficiency of RhB under different reaction systems and different pH conditions

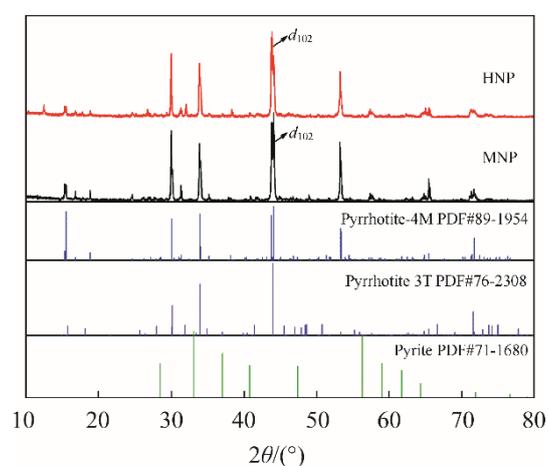
| Reaction system | pH=4 | pH=6 | pH=8 | pH=10 |
|-----------------|--------|--------|--------|--------|
| PDS | 35.05% | 33.48% | 30.19% | 23.38% |
| HNP/PDS | 86.91% | 83.47% | 77.61% | 19.51% |
| MNP/PDS | 97.15% | 95.67% | 89.79% | 29.03% |
| HNP/PDS/TBA | 85.93% | 79.56% | 77.75% | 9.31% |
| HNP/PDS/MA | 33.74% | 23.50% | 20.53% | 9.03% |
| HNP/PDS/phenol | 32.95% | 24.17% | 21.28% | 10.26% |
| MNP/PDS/TBA | 92.23% | 84.22% | 80.73% | 10.54% |
| MNP/PDS/MA | 32.03% | 27.38% | 22.83% | 10.59% |
| MNP/PDS/phenol | 31.01% | 23.78% | 18.36% | 9.98% |

Table S4 Fitting results of Fe 2P_{3/2} spectra of HNP and MNP samples

| HNP | Binding energy/eV | Reference/eV | Fe species |
|--------------------|-------------------|--------------|------------|
| Original HNP | 707.1 | 707.0 [1] | Fe(II) |
| | 710.9 | 710.8 [2] | Fe(II) |
| | 713.2 | 713.5 [3] | Fe(III) |
| HNP after reaction | 706.8 | 707.0 [1] | Fe(II) |
| | 710.6 | 710.8 [2] | Fe(II) |
| | 712.7 | 712.6 [2] | Fe(III) |
| Original MNP | 710.5 | 710.8 [2] | Fe(II) |
| | 711.8 | 711.4 [2] | Fe(III) |
| | 714.2 | 714.3 [3] | Fe(III) |
| MNP after reaction | 707.1 | 707.0 [1] | Fe(II) |
| | 710.6 | 710.8 [2] | Fe(II) |
| | 712.1 | 712.4 [1] | Fe(III) |

Table S5 Fitting results of S 2P_{3/2} spectra of HNP and MNP samples

| HNP | Binding energy/eV | S species |
|--------------------|-------------------|--|
| Original HNP | 161.5 | S ²⁻ |
| | 162.5 | S ₂ ²⁻ |
| | 163.7 | S _n ²⁻ /S ⁰ |
| | 168.6 | SO ₄ ²⁻ |
| HNP after reaction | 160.9 | S ²⁻ |
| | 162.7 | S ₂ ²⁻ |
| | 168.4 | SO ₄ ²⁻ |
| Original MNP | 159.3 | S ²⁻ |
| | 162.3 | S ₂ ²⁻ |
| | 164.3 | S ⁰ |
| | 168.7 | SO ₄ ²⁻ |
| MNP after reaction | 161.1 | S ²⁻ |
| | 162.8 | S ₂ ²⁻ |
| | 166.6 | SO ₃ ²⁻ |
| | 168.5 | SO ₄ ²⁻ |

**Figure S1** XRD patterns of MNP and HNP samples and associated PDF cards

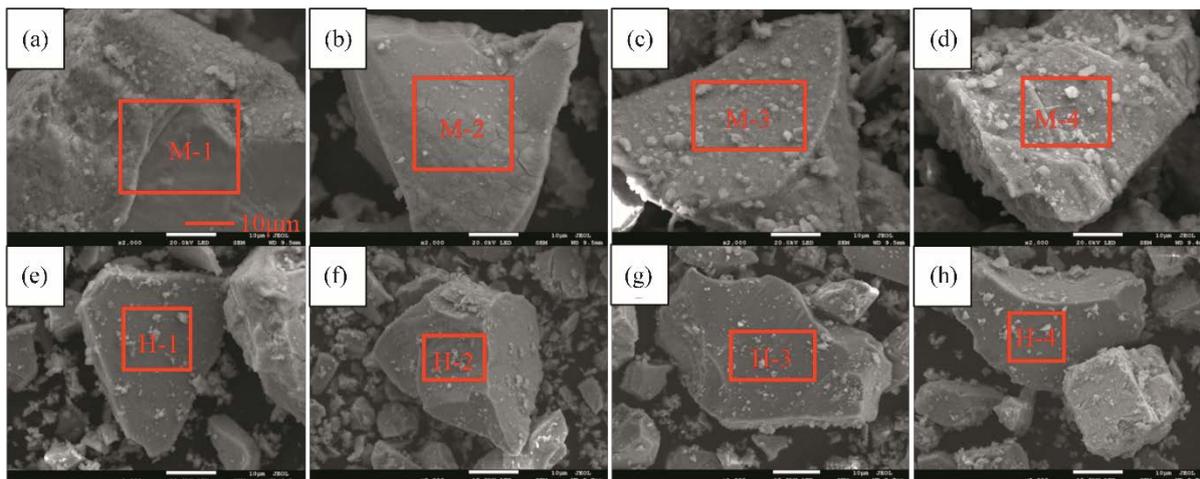


Figure S2 SEM images of MNP (a–d) and HNP (e–h) samples

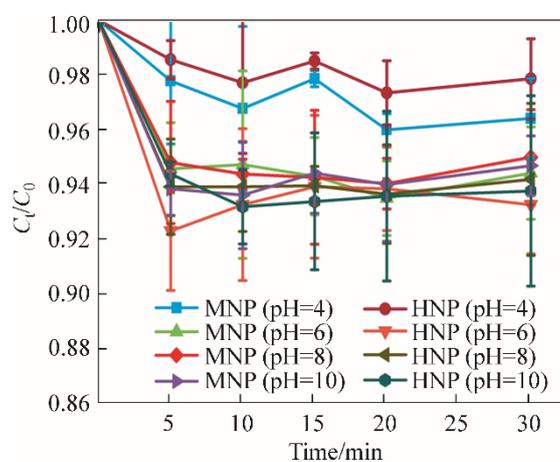


Figure S3 Adsorption curves of RhB by HNP and MNP samples under different pH conditions ($C_{0,RhB}=50$ mg/L, $C_{0,HNP}=C_{0,MNP}=0.2$ g/L, $T=30$ °C)

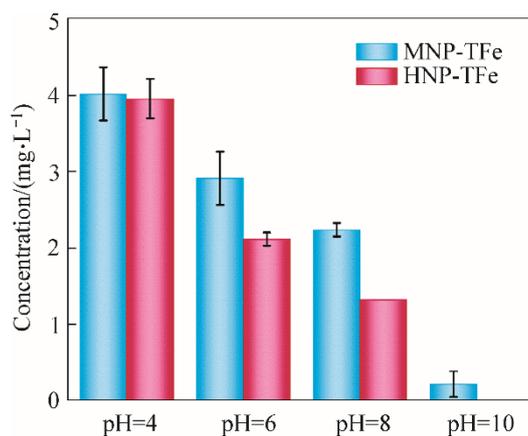


Figure S4 Dissolved concentrations of total iron in each reaction system under different pH conditions ($C_{0,RhB}=50$ mg/L, $C_{0,HNP}=C_{0,MNP}=0.2$ g/L, $C_{0,PDS}=2$ mmol/L, $T=30$ °C, $t=30$ min)

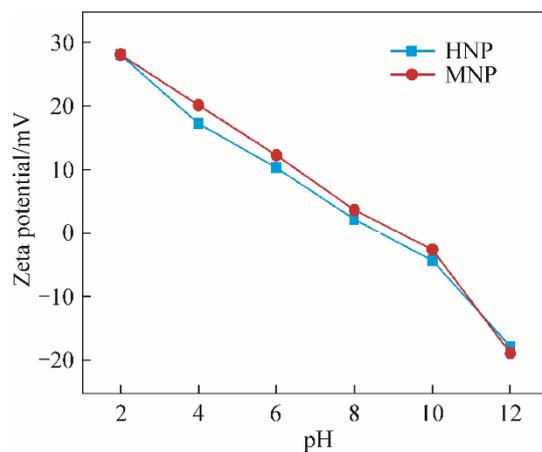


Figure S5 Zeta potential of HNP and MNP under different pH conditions

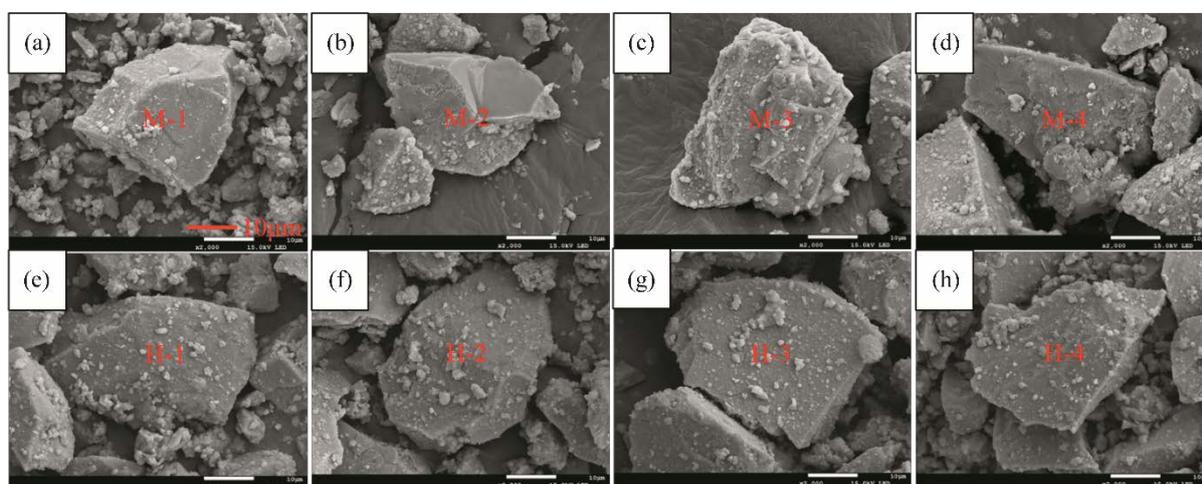


Figure S6 SEM images of MNP (a–d) and HNP (e–h) samples after degradation reaction