Supplementary Information for

Selective spectrophotometric determination of trace permanganate based on 2,2-azino-bis(3-ethylbenzothiazoline-6-sulfonate) oxidation with strong resistance to manganese dioxide interference

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Contents

Text S1. Chemicals and reagents

Sodium hydroxide (NaOH, purity ≥98%), sodium carbonate (Na_2CO_3, purity ≥99.8%), sodium bicarbonate ($NaHCO_3$, purity ≥99.5%), sodium phosphate monobasic (Na_2HPO_4, purity ≥99%), disodium hydrogen phosphate (NaH_2PO_4, purity ≥99%), acetate (CH_3CO_2H, ≥99.5%), sodium acetate (CH_3CO_2Na, purity ≥99%), boric acid (H_3BO_3, purity ≥99.5%), sodium tetraborate ($Na_2B_4O_7$, purity ≥99%), sodium chloride (NaCl, purity ≥99%), manganese sulfate ($MnSO_4$, purity ≥99%), chromic chloride ($CdCl_2$, purity ≥99%) and perchloric acid ($HClO_4$) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Diclofenac (DCF, purity >98%), bisphenol A (BPA, purity ≥99%), hydroxylamine (HA, purity ≥99%), 2,4-dichlorophenol (2,4-DCP, purity ≥99%) and humic acid were all purchased from Aladdin Bio-Chem Technology Co., Ltd (Shanghai, China). ascorbic acid (AA, purity >99%) and glutathione (GSH, purity ≥98%) were purchased from Macklin (Shanghai, China). Acetonitrile (HPLC grade) was purchased from ANPEL Laboratory Technologies (Shanghai, China). All of the chemical solutions were prepared with ultrapure water (18.2 MΩ · cm), and were used directly in the experiments without further purification.

Text S2. Filter validation for 0.22 μm polytetrafluoroethylene (PTFE) filter.

To validate whether permanganate (Mn(VII)) could be filtering out by 0.22 μm polytetrafluoroethylene (PTFE) filter, a known permanganate concentration (i.e., 6 μM) was spiked in water and detected with previous ABTS method. It could be found that there was negligible changes for the determination of Mn(VII) before and after filtration. As a result, polytetrafluoroethylene filters were applied to remove the coexistent MnO_2 in water.

Sample	$ABTS^{\bullet+}$ Absorbance (415 nm)	Signal Reduction
No Filter	0.732	N/A
0.22 μm polytetrafluoroethylene filter	0.732	0

Text S3. Kinetic rate constant measurements

(1) The bimolecular reaction rate constants between Mn(VII) and bisphenol A using the modified ABTS method: the apparent second-order rate constants (k_{app}) of Mn(VII) and bisphenol A were measured at pH 5.0 under the pseudo-first-order (i.e., [bisphenol A] > > [Mn(VII)]). Specifically, Mn(VII) consumption in the presence of excess bisphenol A (50−80 μM) was determined by the modified ABTS method. The $\ln([Mn(VII)]_t/[Mn(VII)]_0)$ values and reaction times kept a great linear relationship ($R^2 > 0.98$) on all occasions, where $[Mn(VII)]_t$ and $[Mn(VII)]_0$ represented the Mn(VII) concentrations at different reaction times. The pseudo-first-order rate constant (k_{obs}) concerning time and bisphenol A concentration was obtained from the slope of the fitted line in **Fig. S8a**. Moreover, the k_{obs} values concerning bisphenol A concentration were also first-order ($R^2 > 0.99$, **Fig. 4a**). Thus, the Mn(VII) decomposition as a function of bisphenol A concentration conformed to the second order reaction kinetics, and the k_{app}, calculated by **Eq. S1**, was 16.70 M^{-1} s^{-1} at pH 5.

$$k_{app} = \frac{k_{obs}}{[\text{bisphenol A}]_0} \quad \text{(S1)}$$

(2) The bimolecular reaction rate constants between Mn(VII) and bisphenol A using HPLC method: the apparent second-order rate constants (k_{app}) of Mn(VII) and bisphenol A were measured at pH 5 under the pseudo-first-order (i.e., [Mn(VII)] > > [bisphenol A]). Specifically, bisphenol A degradation in the presence of excess Mn(VII) dosages (50−80 μM) was determined by HPLC. The $\ln([\text{bisphenol A}]_t/[\text{bisphenol A}]_0)$ values and reaction times kept a great linear relationship ($R^2 > 0.96$) on all occasions,

where [bisphenol A]$_t$ and [bisphenol A]$_0$ represented the bisphenol A concentrations at different reaction times. The pseudo-first-order rate constant (k_{obs}) concerning time and Mn(VII) concentration was obtained from the slope of the fitted line in **Fig. S8b**. Moreover, the k_{obs} values concerning Mn(VII) concentration were also first-order (R^2 > 0.99, **Fig. 4b**). Thus, the bisphenol A degradation as a function of Mn(VII) conformed to the second order reaction kinetics, and the k_{app}, calculated by **Eq. S2**, was 14.87 M^{-1} s^{-1} at pH 5.

$$k_{app}=\frac{k_{obs}}{[Mn(VII)]_0} \quad (S2)$$

(3) Potential limitations underlying the pseudo-first-order approximation method:

The validity of the pseudo-first-order approximation is highly dependent on the initial concentration ratio. It is generally accepted that this approximation is reasonable when one reactant's concentration is at least 10–20 times that of the other. In our experiments, the [Bisphenol A]/[Mn(VII)] ratio ranged between 20 and 100 (e.g., [Bisphenol A] = 0.1–0.5 mM, [Mn(VII)] = 5 μM). This ratio falls within conventional standards but is not infinitely large. Consequently, minor errors may arise in the late stages of the reaction when the high-concentration reactant is consumed in trace amounts. We minimized this error by calculating the rate constant using only the initial reaction rate data.

This approach obscures secondary reaction kinetic features. While it efficiently validates the detection method's self-consistency, precisely determining k_{app} itself theoretically requires a series of experiments at multiple different excess concentrations,

confirming a strict linear relationship between k_{app} and $[reactant]_0$. The core objective of our study is to validate the analytical method's accuracy, not to precisely determine the reaction kinetic parameters between Bisphenol A and Mn(VII). Therefore, we selected representative concentration conditions for cross-validation.

Table S1. Details of the eluents and detection wavelengths of HPLC

Contaminants	Flow rate (mL/min)	Mobile phase Acetonitrile : 0.1% acetic acid	Wavelengths (nm)	Retention time (min)
Bisphenol A (BPA)	1.0	70 : 30	275	2.564
Diclofenac (DCF)	1.0	70 : 30	273	3.955

Table S2. Cost analysis comparison of reagent and equipment requirements.

Method	Chromogenic agent	Chromogenic agent cost	Concentration	Volume required each time	Other cost	Total cost
DPD method	DPD	\$3.62 per g	5 mM	0.5 ml	PTFE	\$0.1524
NaI method	NaI	\$0.23 per g	100 mM	4 ml	filter:	\$0.1638
Previous ABTS method	ABTS	\$19.47 per g	1 g L^{-1}	0.1 ml	\$0.15 each	\$0.1519
Modified ABTS method	ABTS	\$19.47 per g	5 mM	0.5 ml	-	\$1.38 × 10^{-3}

Table S2. The standard deviation of blank samples for ultrapure water (n=10)

	Ultrapure water
Blank value	0.001
	0.000
	0.000
	0.000
	0.000
	0.000
	0.000
	0.000
	0.001
	0.000
σ	0.0002

Table S3. Accuracy and precision of the modified ABTS method in three water samples (n = 5)[a]

Water samples	Spiked Mn(VII) concentration (μM)	Measured wavelength (nm)	Measured Mn(VII) concentration (μM)[a]	RSD (%)[b]	recovery rate (%)
Ultrapure water	1	732	0.998 ± 0.013	1.30	98.83
	2	732	2.001 ± 0.002	0.10	100.06
	5	732	4.995 ± 0.002	0.04	99.93
Underground water	1	732	0.986 ± 0.003	0.30	98.65
	2	732	1.993 ± 0.003	0.15	99.68
	5	732	5.020 ± 0.013	0.26	100.42
Surface water in Quanzhou	1	732	0.989 ± 0.016	1.62	98.91
	2	732	1.990 ± 0.002	0.10	99.56
	5	732	4.988 ± 0.005	0.10	97.63
Surface water in Xiamen	1	732	0.992 ± 0.015	1.47	99.17
	2	732	1.955 ± 0.056	2.86	97.73
	5	732	4.917 ± 0.086	1.76	98.35

[a] Measured concentration and ratio represent mean value ± standard deviation.

[b] RSD represent relative standard deviations.

Table S4. Determination of Mn(VII) concentration using different method in three water samples (n = 5)[a]

Water samples	Concentration of Mn(VII) (μM)	Measured concentration (μM)		F-value in F-test
		The modified ABTS method at 732 nm	The previous DPD method at 551 nm (filtered sample)	
Ultrapure water	1.0	0.988 ± 0.013	0.995 ± 0.006	4.97
	2.0	2.001 ± 0.002	2.008 ± 0.002	0.62
	5.0	4.995 ± 0.002	5.013 ± 0.003	0.54
Underground water	1.0	0.986 ± 0.003	0.989 ± 0.016	4.85
	2.0	1.993 ± 0.003	1.996 ± 0.006	0.37
	5.0	5.020 ± 0.013	5.001 ± 0.007	2.728
Surface water in Quanzhou	1.0	0.989 ± 0.016	0.986 ± 0.003	0.28
	2.0	1.990 ± 0.002	1.994 ± 0.002	0.66
	5.0	4.988 ± 0.005	4.991 ± 0.003	2.90
Surface water in Xiamen	1.0	0.992 ± 0.015	0.959 ± 0.015	0.95
	2.0	1.955 ± 0.056	1.983 ± 0.034	0.35
	5.0	4.917 ± 0.086	4.989 ± 0.045	0.24

F(5, 5) = 5.05

Table S5. Main indexes of water quality of natural water samples

Indexes	Underground water [1]	Surface water in Quanzhou [1]	Surface water in Xiamen [1]	High TOC water bodies[1, 2]
pH	8.03	8.05	7.57	6.85
TOC (mg L^{-1})	0.755	6.27	1.8	10.81

[1]: Water samples were filtered by 0.22 μm cellulose acetate membrane.

[2]: Water samples were taken from the effluent of the secondary sedimentation tank.

Table S6. Bland-Altman Descriptive Statistics Table

Category	Value
Target	0
Mean	0.19376
Mean + 1.96 * SD	0.8296
Mean - 1.96 * SD	-0.44209
UCL of Mean	0.39988
LCL of Mean	-0.01236
UCL of Mean + 1.96 * SD	1.19225
LCL of Mean + 1.96 * SD	0.46696
UCL of Mean - 1.96 * SD	-0.07944
LCL of Mean - 1.96 * SD	-0.80473

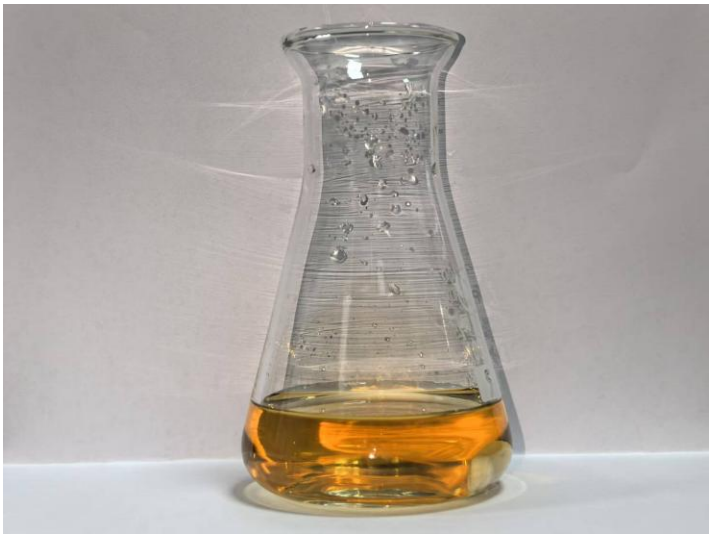


Fig. S1 MnO_2 colloid under pH 8 conditions.

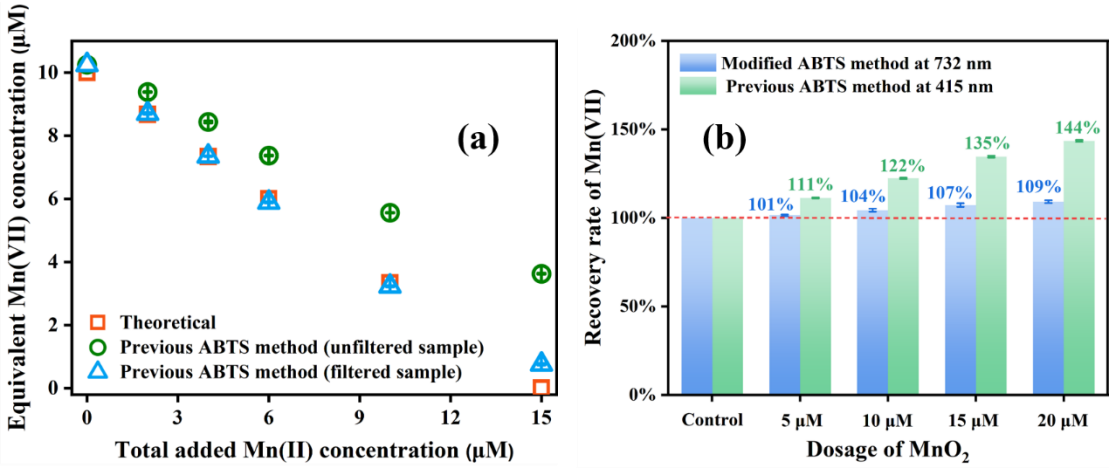


Fig. S2 (a) Impact of coexistent MnO_2 for the determination of Mn(VII) using previous ABTS method before and after filtering out coexisting MnO_2. (b) Influence of MnO_2 on Mn(VII) measurement by the modified ABTS method and the previous ABTS method.

Conditions: $[ABTS]_0$ = 1 mM or 1 g/L, $[Mn(VII)]_0$ = 10 μM for (a) and 6 μM for (b), pH = 7.0 with phosphate buffer for previous ABTS method and room temperature.

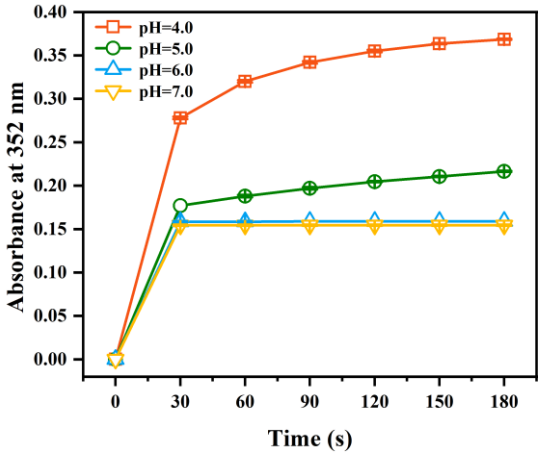


Fig. S3 Effect of pH on the production of I_3^- from the oxidation of NaI by MnO_2. Conditions: $[MnO_2]_0$ = 20 μM, $[NaI]_0$ = 16 mM, pH = 4.0 - 5.0 with 40 mM acetic acid buffer, pH = 6.0 - 7.0 with 40 mM phosphate buffer, and room temperature.

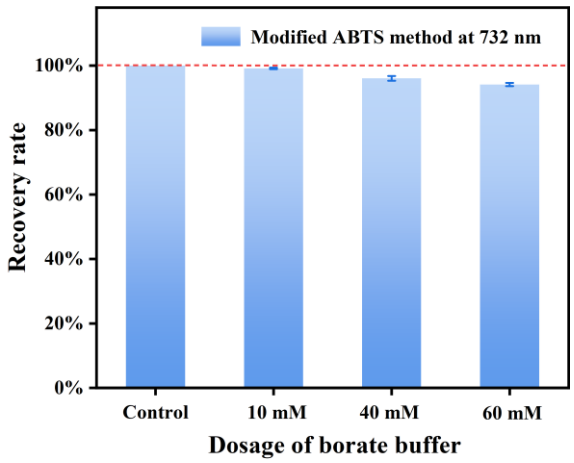
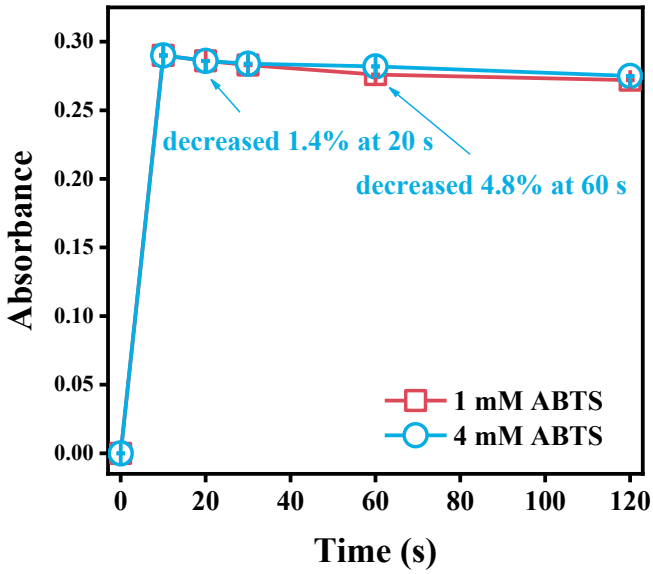


Fig. S4 Influence of borate buffer on Mn(VII) measurement by the modified ABTS method. Conditions: $[ABTS]_0$ = 1 mM, $[Mn(VII)]_0$ = 6 μM, pH = 8.0 with 10 - 60 mM borate buffer, reaction time = 10 s, and room temperature.



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18 **Fig. S5** Effect of reaction time and ABTS concentration on Mn(VII) measurement by the modified
19 ABTS method at 732 nm.
20 Conditions: $[Mn(VII)]_0$ = 6 μM, pH = 8.0 with 20 mM borate buffer, and room temperature.

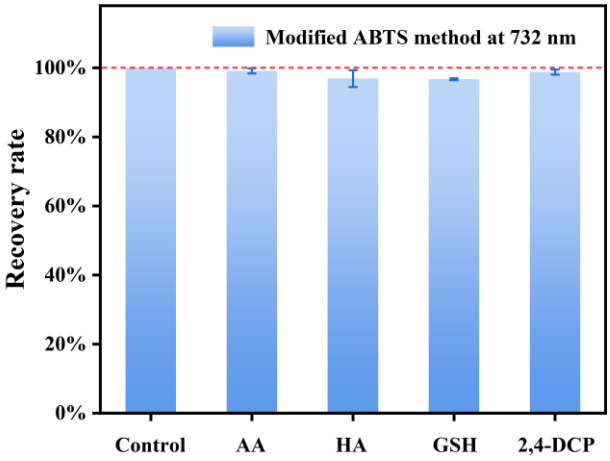

Fig. S6 Influence of reducing substances on Mn(VII) measurement by the modified ABTS method. Conditions: $[ABTS]_0$ = 1 mM, $[Mn(VII)]_0$ = 6 μM, [ascorbic acid]0 = $[hydroxylamine]_0$ = $[glutathione]_0$ = $[2,4\text{-dichlorophenol}]_0$ = 1 μM, pH = 8.0 with 20 mM borate buffer, reaction time = 10 s, and room temperature.

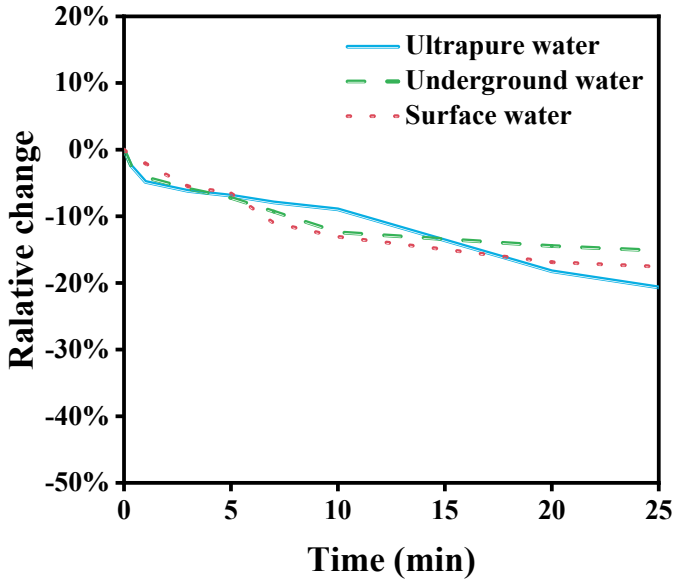

Fig. S7 Stability of generated $ABTS^{\bullet+}$ in three different water samples at 732 nm. Conditions: $[Mn(VII)]_0$ = 6 μM, $[ABTS]_0$ = 1 mM, pH = 8.0 with 20 mM borate buffer, and room temperature.

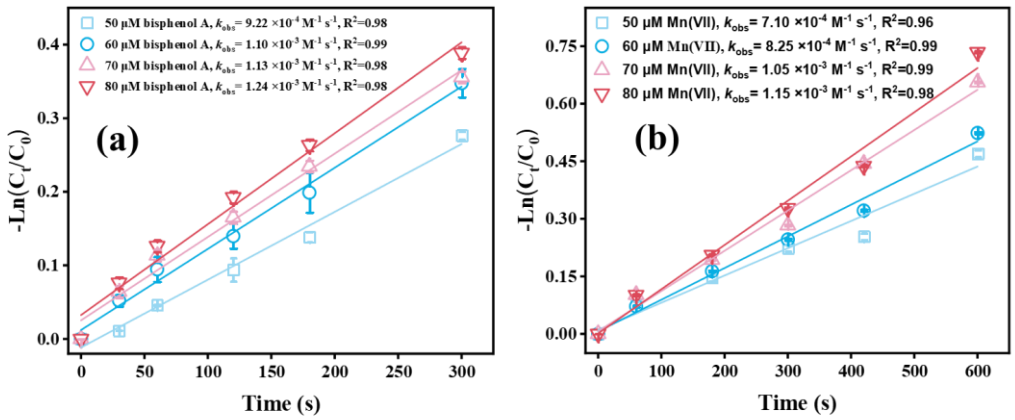

Fig. S8 The kinetic rate constants (k_{obs}) of Mn(VII) decomposition (a) and bisphenol A degradation (b) in the presence of excess bisphenol A and Mn(VII).

Conditions: $[Mn(VII)]_0 = 5$ μM for (a), $[bisphenol\ A]_0 = 5$ μM for (b), pH =5, and room temperature.

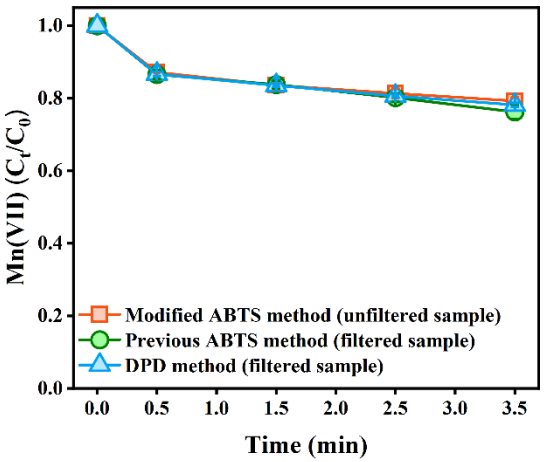

Fig. S9 Changes of Mn(VII) concentration measuring with different methods in water bodies with 10.81 mgC L^{-1} TOC.

Conditions: $[Mn(VII)]_0$ = 10 μM, $[ABTS]_0$ = 1 mM or 1 g/L, $[DPD]_0$ = 1.25 mM and room temperature.

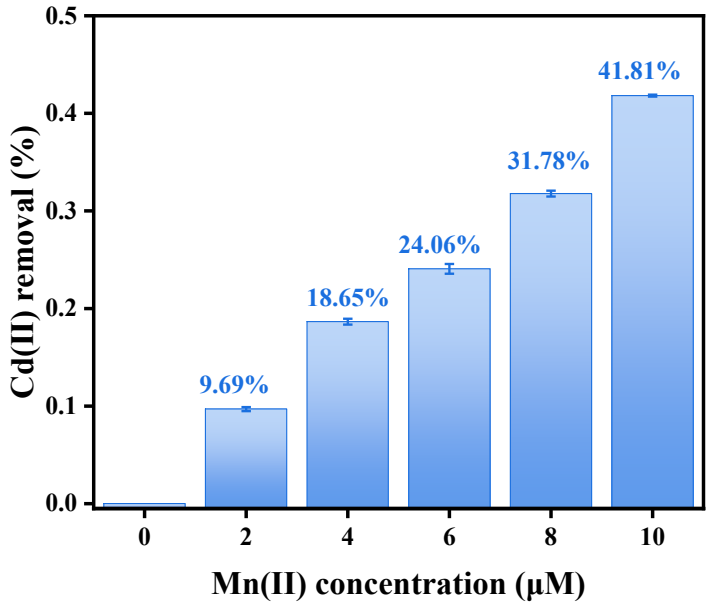

Fig. S10 Effect of Mn(II) concentration on Cd(II) removal in Mn(II)/Mn(VII) system. Conditions: $[Mn(VII)]_0$ = 10 μM, $[Cd(II)]_0$ = 0.6 mg/L, pH = 5.8, and room temperature.

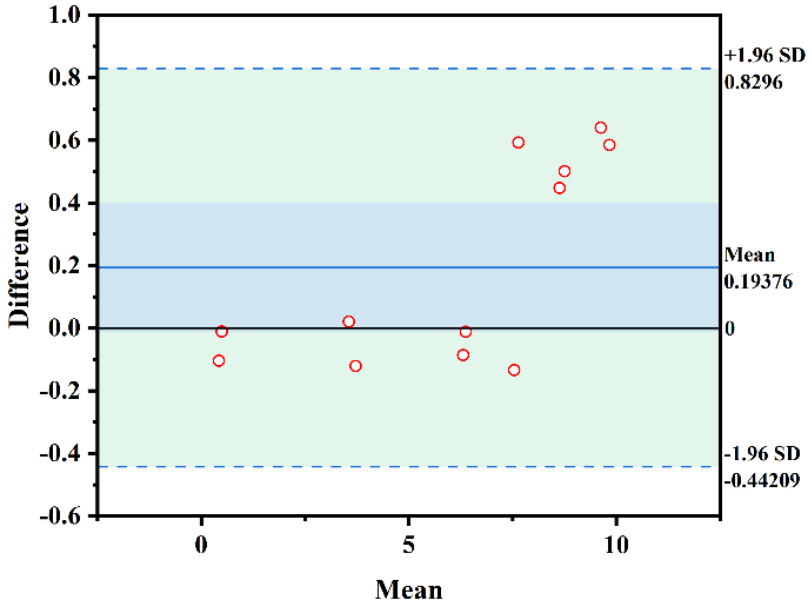

Fig. S11 Bland-Altman plots for the previous method and the modified method

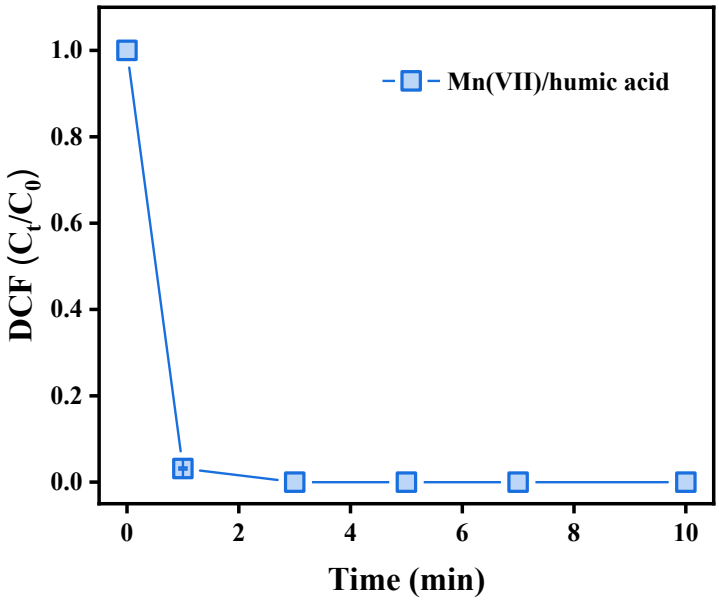

Fig. S12 DCF degradation in humic acid-enhanced Mn(VII) process.

Conditions: $[Mn(VII)]_0$ = 50 μM, $[humic\ acid]_0$ = 10 mg/L, $[DCF]_0$ = 5 μM, pH = 4.5, $[acetic\ acid]_0$ = 10 mM, and T = room temperatue.